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Oxidation of some Main Group elements and their low oxidation state compounds by substituted o-benzoquinones.

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OXIDATION OF SOME MAIN GROUP ELEMENTS AND THEIR LOW OXIDATION STATE COMPOUNDS BY SUBSTITUTED *O*-BENZOQUINONES

by

ZHIGANG TIAN

A DISSERTATION

submitted to the Faculty of Graduate Studies and Research through the
Department of Chemistry and Biochemistry in
partial fulfillment of the requirements for the
degree of Doctor of Philosophy at the
University of Windsor

Windsor, Ontario, Canada

1993

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ABSTRACT

OXIDATION OF SOME MAIN GROUP ELEMENTS AND THEIR LOW OXIDATION STATES COMPOUNDS BY SUBSTITUTED *O*-BENZOQUINONES

by

ZHIGANG TIAN

This work was undertaken to further develop work carried out in this laboratory in recent years on the oxidation of Main Group 3A and 4A elements, and of compounds of these elements in low oxidation states, by focusing on the oxidation of the Main Group 5A and 6A elements phosphorus, tellurium and antimony, and of their low oxidation states compounds.

The phosphorus compounds $P(O_2C_6R)_2Br$ ($R = Cl_4$, Br_4 or $Bu^t_2H_2$) have been prepared by the reaction of P_4, Br_2 and the substituted *o*-benzoquinone *o*-O_2C_6R. There is no reaction between *o*-$O_2C_6Bu^t_2H_2$ (dbbq), P_4 and Ph_2Se_2, but in the presence of catalytic quantities of Br_2 the product is $P(dbc)_2(SePh)$ (dbc = 3,5-di-Bu^tcatecholate). Electron spin resonance (ESR) spectra identify the presence of the corresponding *o*-semiquinone species in these reactions. The ^{13}C and ^{31}P NMR spectra of these phosphoranes are studied and compared with those of $P(O_2C_6R)X_3$ ($X_3 = Ph_3$, Ph_2Cl, Br_3 or Cl_3) prepared by the reaction of PX_3 and *o*-O_2C_6R.

The oxidation of elemental tellurium by three *o*-benzoquinones *o*-O_2C_6R ($R = Cl_4$, Br_4 or $Bu^t_2H_2$) is a direct route to the corresponding tellurium(IV) catecholates $Te(O_2C_6R)_2$. The analogous reaction with organotellurium(II) TeR'_2 [$R'_2 = Et_2$, Me_2, Ph(Et) or Ph(Br)] gives the products $Te(O_2C_6R)R'_2$. The reactions proceed in each case by one-electron transfer, since the presence of the semiquinone radical O_2C_6R in the reaction mixture has been demonstrated by ESR spectroscopy. The $Te(O_2C_6R)_2$ species resist further oxidation, and also show weak donor and acceptor properties. The structure of the compounds $Te(dbc)_2(bipy)$ **3.1** and $Te(O_2C_6Cl_4)_2$(18-

crown-6) **3.2** have been determined by X-ray crystallography. In both structures, the average Te-O distances (2.012 and 2.015 Å respectively) are typical of tellurium(IV) compounds, and the average C-O distances (1.370 and 1.34 Å respectively) confirm that the ligands are aromatic diolates.

The oxidation of elemental antimony by the tetrahalogeno-*o*-benzoquinones *o*-O_2C_6R (R = Cl_4 or Br_4) in diethyl ether gives the unusual antimony(v) products $Sb(O_2C_6R)_{2.5} \cdot nEt_2O$ (R = Cl_4, n = 1.5; R = Br_4, n = 1). The same *o*-benzoquinones, and dbbq, upon treatment with Sb + $1/2X_2$ (X = Br or I) in diethyl ether, give the antimony(III) derivatives $Sb(O_2C_6R)X$ (R = Cl_4, Br_4 or $Bu^t_2H_2$). The oxidations are shown by ESR spectroscopy to proceed via the *o*-semiquinone intermediates. Adducts of $Sb(O_2C_6R)I$ with bidentate neutral donors have been prepared. The structure of Sb(dbc)I(bipy) **4.1** has been shown to be that of a pseudo-octahedral molecule with a stereochemically active lone pair of electrons. In this structure, the average Sb-O distance (2.014 Å) is well within the range of distances reported for a wide variety of antimony(III)-oxygen complexes, the average C-O distance (1.366 Å) is typical of that for catecholato complexes, as required by the formulation of this complex.

The reactions between diphenyl ditelluride and tetrahalogeno-*o*-benzoquinones *o*-$O_2C_6X_4$ (X = Cl or Br) give $[(X_4C_6O_2)TeC_6H_5]_2O$. The structure of $[(Cl_4C_6O_2)TeC_6H_5]_2O$ **5.1** has been established crystallographically. The reactions between Ph_2Te_2 and other oxidants have also been studied. The reaction mechanism is complicated in these processes, and the only certain feature is the observation of a paramagnetic species.

Preliminary results are also presented on the reaction between *o*-quinones with tin, and with tin dichloride, as well as the preparation of a novel Schiff-base biquinone lead(II) complex $Pb(Cat\text{-}N\text{-}BQ)_2$ [Cat-N-Bq = 3,5-di-Bu^t-1,2-quinone 1-(2-hydroxy-3,5-di-Bu^tphenyl] **7.1**. The structure of **7.1** has been determined by X-ray crystallography. It shows significantly different features in comparison with the known structures of transition metal elements with the same ligand.

ACKNOWLEDGEMENTS

First of all, I would like to express my sincere gratitude to Professor D.G. Tuck for his valuable and enthusiastic guidance throughout all the different stages of this work. His patience and encouragement are duly acknowledged.

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A special mention of gratitude to Drs. B.R. McGarvey and A. Ozarowski for their enthusiastic help on the ESR-related work. Dr. D.W. Stephan is sincerely thanked for his help in solving X-ray crystallographic structures. Drs. S. Wang and S. Loeb are also thanked in this regard.

Many thanks to past and present members of laboratory 362 Essex Hall for their help and contributions in different ways to the outcome of this research project. A special mention is due to (the late) Dr. T.A. Annan for his enthusiastic help in the beginning of my study in Windsor and for conducting part of the experiments in Chapters 2 and 3.

I am also indebted to the faculty members of the Department of Chemistry and Biochemistry, the members of the technical and secretarial staff, and many graduate students for their friendship and help throughout my study in Windsor. Those of special mention are Mr. M. Fuerth for his help in the NMR-related work, Mr. D. Hill for his earnest help, and Dr. J.M. McIntosh and Mr. M.K. McKay for their help in preparing graphs and Ms. Maeve Doyle-Catomeris for her patience and help in the preparation of this dissertation.

Finally, I would like to thank my family, especially my wife Li Sheng for being so understanding and supportive, and for the confidence she placed in me.

DEDICATION

To Li Sheng,

My wife

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LIST OF ABBREVIATIONS

bipy	2,2′-bipyridine
BQ	*o*-Benzoquinone
br	broad
Bu^t	tert-butyl
cat	catecholato anion
calc	calculated
18-crown-6	1,4,7,10,13,16-hexaoxacyclooctadecane
d	doublet
dd	double doublet
dbc	3,5-di-tert-butyl-1,2-catecholato anion
dbbq	3,5-di-tert-butyl-1,2-benzoquinone
dbsq	3,5-di-tert-butyl-1,2-benzosemiquinone
DMF	N,N′-dimethylformamide
DMSO	dimethylsulphoxide
DPPH	diphenyl picrylhydrazyl
Et	ethyl
ESR	electron spin resonance
G	gauss
IR	infrared
m	medium, multiplet
Me	methyl
M.W.	molecular weight
NMR	nuclear magenetic resonance

Ph	phenyl
phen	1,10-phenanthroline
phen-5,6-dione	1,10-phenanthroline-5,6-dione
phen-5,6-cat	1,10-phenanthroline-5,6-catecholate
ppm	parts per million
py	pyridine
Q	Quinone
q	quartet
s	strong, singlet
SQ	semiquinone
thf	tetrahydrofuran
tmed	N,N,N',N'-tetramethylethylenediamine
TMS	tetramethylsilane
Tol	toluene
UV	ultra-violet
vs	very strong
w	weak

CHAPTER 1

INTRODUCTION

The renaissance of inorganic chemistry which began in the 1950's was based primarily on transition metal chemistry. Although interest in the coordination chemistry of Main Group metallic elements has grown in parallel with the development of transition metal chemistry, progress was relatively slow in comparison with the latter area, due in part to the lack of theoretical developments and experimental techniques analogous to those provided by ligand field theory, magnetochemistry, and electronic spectroscopy which are primarily related to properties of the incomplete d-shell, and generally much less useful for the closed d-shell Main Group compounds. As a result, structural studies of colourless diamagnetic Main Group compounds depended for many years on vibrational and NMR spectroscopy, before the availability of computerized X-ray crystallographic methods.

We are now seeing a growth in Main Group chemistry, driven in part by the potential applications of important compounds in material sciences, by recent progress in those areas closely related to organic chemistry and transition metal chemistry, and by the growing availability of new techniques which can probe the structures of these species. It will be clear from reviews[1] of the recent progress in Main Group chemistry, that Main Group chemistry is actually an active area full of promise and challenge, both in the scope of the reactions which can be studied, and the related theoretical aspects which need to be understood.

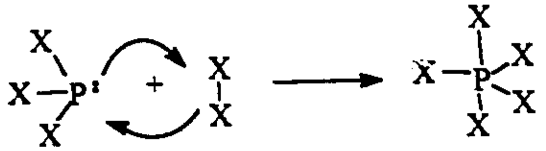
From the point of view of pure science, it would be a great advantage not only to discover new reactions and phenomena but also to unravel the mechanistic details behind them. There are many topics in this aspect of Main Group chemistry which need to be explored. Since this thesis deals mainly with the oxidation of Main Group elements or their low oxidation state compounds by substituted *o*-benzoquinones, a brief review of the related earlier work will be presented. It is beyond the scope of this introduction to discuss many other current interests in Main Group chemistry, many of which have been reviewed elsewhere.[1]

1.1 Studies on the Oxidation Processes of Main Group Substances

1.1.1 Previous Knowledge

The previous consideration of redox processes involving Main Group elements is often conditioned by our knowledge of the series of oxidation states of the stable p-block compounds, which generally differ by two electrons.[2] For example, +1, +3 for indium, +2, +4 for tin, +3, +5 for phosphorus and +2, +4, +6 for sulfur are the most common oxidation states of these elements in their compounds.

Theoretically, there will be two possible pathways accounted for these redox reactions, either a two-electron transfer or two successive one-electron transfer steps. For a variety of practical reasons, such as the generally high reaction rate and the oxidants used in these processes, such redox reactions have not been the subject of mechanistic studies in the past. Most convenient oxidants are two-electron oxidants, which usually react so rapidly that the spectroscopic identification of any one-electron transfer intermediate is impossible by the available techniques. In the absence of evidence related to a one-electron transfer, it has been assumed that redox processes involving Main Group compounds will be two electrons transfer in a concerted fashion. For example:



This simple model of a two-electron redox reaction seems to have been based on the stoichiometry alone. Even though it is in keeping with the stoichiometry of oxidative process, it does not offer any insight to the real mechanism involved.

1.1.2 Intermediate Oxidation States of Main Group Elements

In comparison with the coordination chemistry of the Main Group elements in their higher oxidation states, the coordination chemistry of their lower oxidation states (especially the intermediate oxidation states) is largely unexplored. Here we use the term of intermediate oxidation states referring the oxidation states with an odd-electron configuration, and therefore different from those commonly encountered as we mentioned in the last section.

The remarkably low stability of the Main Group elements in their intermediate oxidation states is one of the main reasons responsible for the lack of investigation in this area. An unpaired electron in transition metal compounds occupies a low-lying non-bonding d-orbital, and there is no difficulty in preparing many transition metal compounds with a series of oxidation states differing by one unit, and in studying electron transfer processes in such systems. In contrast, an unpaired electron of a Main Group element compound in any odd-electron oxidation state will likely occupy a high frontier orbital and has a high energy which will result a variety of further reactions. For example, despite several reports of seemingly +II aluminum and gallium species in the past years, the only such compounds stable at ambient temperature are diamagnetic and involve M-M bonds.[3-8]

There has been a simplistic argument[9] which shows that, for Group 3A elements, the M-X bonds in a mononuclear MX_2 molecule should be reasonably strong and the M^{2+} ions are certainly accessible energetically, so that the non-existence of such species must be ascribed to kinetic reactivity of the unpaired electron rather than to any thermodynamic instability. Based on this argument, it has been suggested that possible stabilisation of Main Group metal species in their odd-electron states could be achieved by applying appropriate electronic (strong Lewis basicity and weak leaving ability) and steric (bulky in space) effects. Indeed, experimental results in this field are consistent with this idea.

1.1.3 Studies Involving Main Group Elements in Their Intermediate Oxidation States

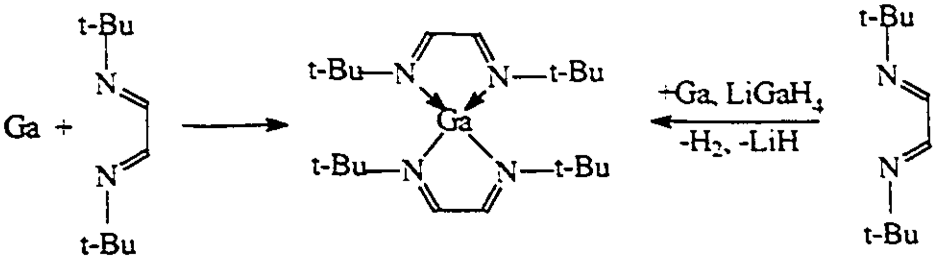
In this largely unexplored research field, the mechanistic studies on the reaction of stable stannylenes with organic halides performed[10-11] by M.F. Lappert *et al.* are an important and exceptional example. Based on the ESR spectra and optical activity data, they proposed a radical pathway for these reactions. Initially, one electron of the stannylene is transferred to the organic halide, the halogen of which is then added on the tin atom according to the following equation:

$$RY + SnX_2 \rightarrow RY^{\bullet -} + \cdot SnX_2^+ \rightarrow R\cdot + \cdot SnX_2Y$$

(X = bulky organic groups, Y = halogens)

They also reported[12-13] the high stability of other Group 4A and Group 5A metal monomeric radical species which include MR_3 (M = Ge, Sn, Si; R = bulky ligands) and MR_2 (M = P, As; R = bulky ligands).

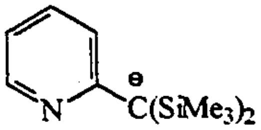
We are now seeing an increasing interest in this field along with the rapid growth of Main Group chemistry. The report of stable aluminum and gallium(II) species appeared only in recent years. The condensation of gallium vapour with 1,4-di-t-butyl-1,4-diazabuta-1,3-diene (dbdab) was reported[14] by Cloke and co-workers to afford bis(1,4-di-t-butyl-1,4-diazabuta-1,3-diene)gallium as the first apparent example of a monomeric Main Group diazadiene complex; X-ray crystallography shows the molecule possesses distorted tetrahedral geometry, which, with ESR and magnetic data, suggests that it might be a gallium (II) compound in which one of the diazadiene ligands has been doubly reduced to the diamino form. They also reported[15] that the reaction of $LiGaH_4$ and gallium metal with 1,4-di-t-butyl-1,4-diazabuta-1,3-diene in diethyl ether at room temperature produces the same compound in a higher yield.



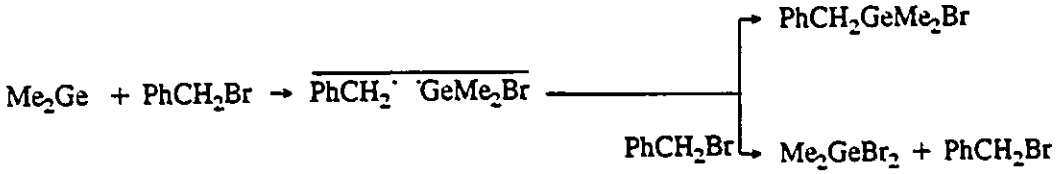
Raston and co-workers also reported[16] the reduction of MR_2Cl, (M = Al or Ga, R = very bulky N-functionalized ligand $2\text{-}C(SiMe_3)_2C_5H_4N^-$) by Na/K alloy in THF produced the paramagnetic dialkyl metal species, $[MR_2]^\bullet$.

$MR_2Cl + Na/K \rightarrow [MR_2]^\bullet_{solv}$

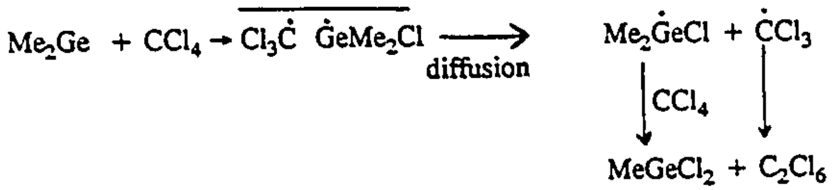
R=



Based on CIDNP measurements, the insertion of Me_2Ge into benzyl bromide has been proposed[17,18] by Neumann and co-workers as a two-step radical abstraction-recombination process. The ^1H NMR-CIDNP pattern is in accordance only with a caged singlet radical pair.



An identical mechanism involving a caged singlet radical pair is given when starting from Cl_3CX (X = Cl, Br) or $PhCH_2X$ (X = Cl, I):



Very recently the synthesis and structure determination of the first Te(III) radical cation has been reported by Roesky and co-workers.[19]

$Te[N(SiMe_3)_2]_2 + AgAsF_6 \rightarrow \{Te[N(SiMe_3)_2]_2\}^{\bullet +}AsF_6^-$

1.2 Metal *o*-Quinone Complexes

I have mentioned in the previous section that the kinetic activity of the Main Group reaction intermediates in odd-electron states, and the usage of two-electron oxidants were the main factors which caused some difficulty in the mechanistic study. There would be a much better opportunity of identifying the odd-electron Main Group species if one-electron oxidants were used in this purpose. This has already been shown in the examples in the previous section; for example, silver(I) was applied in the preparation of the Te(III) radical cation.

Quinones and related molecules occupy a special position in the areas of organic and biochemistry. In comparison with diimines or chelating sulfur donor ligands,[20,21] the coordination chemistry of these potential ligands was relatively neglected until the middle of the 1970's, even though preparative procedures for catecholate and quinone complexes date back to the early part of this century.[22] With the rapid development of this area in the last twenty years, *o*-quinones have been established as a significant class of one-electron oxidants which can be used efficiently and conveniently in the mechanistic investigations of oxidative processes.

1.2.1 Transition Metal *o*-Quinone Complexes

The number of quinoid transition metal complexes[23,24] is very large because of the very facile reduction of *o*-quinones (E_{red} = -0.5 v *vs* SCE), the high stability constants, and the advantageous five-membered chelate rings which are formed. Complexes with all groups of transition metal elements have been studied and reviewed in recent years.[5,23-26] Much of the recent interest in these ligands has been related to bioinorganic chemistry. Of more fundamental interest perhaps is the exceptionally wide variety of electronic structures which can arise in such complexes. For instance, the use of catecholate-containing sequestering agents by various organisms to concentrate V^{3+} and Fe^{3+} ions has been established and successfully modeled in recent years.[27-29] Manganese and iron plastoquinone complexes and catechol dioxygenase enzymes containing copper or iron have also been studied in biological electron-transport chains and organic oxidation processes, respectively.[30-31] The charge distribution for transition-metal complexes containing catecholate or semiquinone ligands have been studied by C.G. Pierpont *et al.*, and other workers.[32-34] The magnetic and optical properties as well as the ESR spectra of a variety of complexes containing paramagnetic metal ions bound to polyoxolene radical anions have been studied by D. Gatteschi and co-workers in recent years.[35-38] In the last ten years the crystallographic information on metal-quinone complexes has grown impressively, and more than 80 structures of such complexes have been determined by this method.[24,39]

(i) Synthetic methods

There are two main methods for the preparation of transition metal *o*-quinone complexes. The first method is a ligand-exchange reaction between a metal salt (*e.g.*, $RuCl_3$, $Fe(SO_4)_2$, $Mn(acac)_3$) with a salt (or basic solution) of catechol or semiquinone. A comprehensive survey of the syntheses of metal catecholate complexes was conducted by Weinland and co-workers during the period from 1910 to 1930, in which a variety of compounds with complex anions such as $Sn(cat)_3^{2-}$, $Co(cat)_2^{2-}$, $Ni(cat)_2^{2-}$, etc. were prepared.[40]

The preparation and characterization of bis(catecholate) complexes $M(cat)_2$ was reported by Holm and co-workers in the mid-1960's.[41]

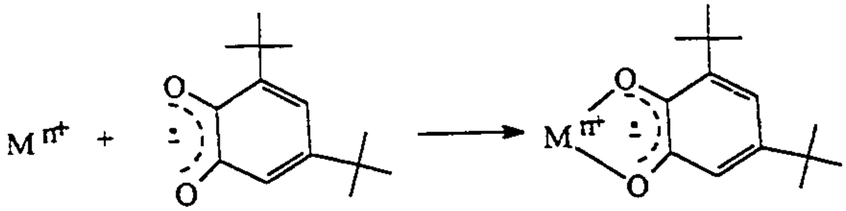
$MX_2 + H_2cat\text{-}R_n + R'_4Y^+X^- \xrightarrow{OH^-} [R_4Y^+]_2[M(cat\text{-}R_n)_2]^{2-}$

$R'_4Y^+ = Pr^n_4N^+, Ph_4As^+, X^- = Cl^-, OH^-$

$X_2 = SO_4^{2-}, 2NO_3^-, 2Cl^-$, etc.

$M = Co, Ni, Cu$ and Zn

Razuvaev and co-workers have also prepared[42-45] a large number of relatively simple compounds consisting of a single semiquinone bonded to a diamagnetic metal ion by treating a metal halide or an organometallic halide directly with a 3,5-di-tert-butyl-semiquinone salt. The metal cations involved in this system include Lu^{3+}, Y^{3+}, Cr^{3+}, V^{3+}, In^{3+}, Al^{3+}, Ga^{3+}, Pd^{2+}, Hg^{2+}, Sn^{4+}, Cu^{1+} and Tl^{1+}.



The preparation of a series of interesting metal catecholate clusters from metal amides has also been very recently reported[46] by Shoner and Power.

$M[N(SiMe_3)_2]_2 + dbcH_2 \rightarrow (1/n)[M(dbc)_2]_n + 2HN(SiMe_3)_2$

M = Mn, Fe; n = 2, 4.

M = Co, n = 4

The second method usually starts with *o*-quinones. For example, Balch has synthesized catecholate adducts of platinum group metals by the oxidative addition of *o*-benzoquinones. The coordinated catechol can then be oxidized to the semiquinone with silver ion.[47]

$$ML_n + BQ\text{-}R_n \rightarrow LnM(cat\text{-}R_n) \xrightarrow{Ag^+} LnM(SQ\text{-}R_n)$$

$MLn = M(PPh_3)_2(CO)Cl$, M = Rh, Ir

$M(PPh_3)_4$, M = Pd, Pt

$Ru(PPh_3)_2(CO)_2$

R = Cl, Br; n = 4

The preparation of transition metal semiquinone complexes starting with a metal carbonyl and substituted ortho-benzoquinone has been found to be very convenient in terms of product isolation and purification. This method was first used by Holm *et al.*[41] and later also employed by both Calderazzo and Pierpont.[48,49]

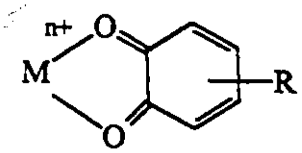
$$M(CO)_n + o\text{-}Q \rightarrow M(SQ)_{2,3}$$

M = V, Cr, Mn, Fe, Co, Ni;

o-Q = dbbq, pq, o-$O_2C_6Cl_4$

(ii) Electronic structure

From the point of view of the inorganic chemist, *o*-quinones exhibit two fundamental properties in common with transition metal ions. They show redox behaviour at easily accessible (and chemically useful) potentials, and they are able to fix substrate molecules by donor-acceptor complexation. The chemical characteristics of transition metal complexes of *o*-quinones include their ability to undergo multistage oxidation and reduction with retention of their structure. It was established that these complexes undergo a number of well-defined, one-electron transfer reactions. The formal examination of the electronic structure of metal complexes of *o*-quinones is usually carried out within the framework of the redox triad of the *o*-quinone. As a result of the characteristic feature of the electronic structure of *o*-quinones, these ligands can give rise, depending on the conditions, to the following types of complexes:



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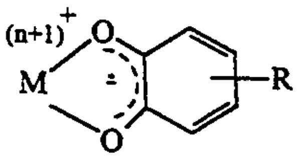
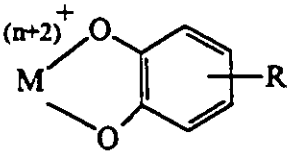


(2)



(3)

Structure (1) corresponds to the coordination of the neutral *o*-quinone via the unshared electron pairs of the oxygen atoms. Structure (2) corresponds to the coordination of the semi-reduced form of the quinone - the semiquinone radical anion. Structure (3) reflects the coordination of the fully reduced quinone - the catecholate dianion. Thus, in contrast to the traditional task of coordination chemistry involving primarily the description of the electronic structure of the central metal ion, an additional task involving the determination of the degree of reduction of the ligand also arises.

The localized quinonoid (quinone, semiquinone, or catechol) electronic levels in metal complexes are close in energy to the metal electronic levels. The ordering of these levels affects the oxidation state of the metal and the quinone via the intramolecular transport scheme. The various bonding descriptions shown above can be induced either chemically or electrochemically by the addition or removal of charge from ligand localized electronic levels by interaction with some external species (*i.e.*, chemical agent, electrode surface). For example, $Cr(SQ)_3$ shows[50] a seven membered redox series corresponding to stepwise oxidation to a cationic $Cr(BQ)_3^{3+}$ or reduction to a $Cr(cat)_3^{3+}$.

$$Cr(BQ)_3^{3+} \xleftarrow{-3e} Cr(SQ)_3 \xrightarrow{+3e} Cr(Cat)_3^{3-}$$

Studies have shown that this type of intramolecular charge distribution can be modified by several factors:

(i) the periodic dependence of metal valence orbital energies, as seen in the complexes of Cr, Mo, W and Mn, Tc, Re triads, in which the complexes of first row transition metal Cr and Mn have $Cr(dbsq)_3$ and $Mn(dbsq)_2$ charge distribution while the complexes of the 4d and 5d members Mo, W, Tc and Re show a shift to higher metal oxidation state and reduced catecholate ligand for $M^{IV}(dbc)_3$ as the metal orbital energy increases.[51-56] The periodic effect is also seen[52,57] in the comparison of the superficially isostructural isoelectronic (d^5) metal complexes $Fe^{III}(dbsq)_4(dbc)_4$ and $Mn^{II}(dbsq)_8$,[62,63] which were made from dbbq and the respective metal carbonyls.

(ii) the donor ability of the counterligand, as in the compounds $Cu(dbc)(py)_2$ and $Cu(dbsq)(Ph_3P)_2$,[58] when the replacement of soft phosphorus donor ligands by hard nitrogen donors cause the charge transfer from Cu cation to dbsq ligand.

(iii) the net charge on the complex, as in the $Mn(dbsq)_2/[Mn(dbc)_2]^-$ and $V(dbsq)_3/[V(dbc)_3]^-$ system,[59,60] since the electronic form of the ligand depends on the preparative route and the overall charge of the final product.

(iv) variations in temperature, as in the $Mn(dbsq)_2(py)_2/Mn(dbc)_2(py)_2$ equilibrium,[61] which exist over the range of temperatures between 240 and 340 K, while at higher temperatures this equilibrium shifts to the bis(semiquinone)Mn(II) form of the complex.

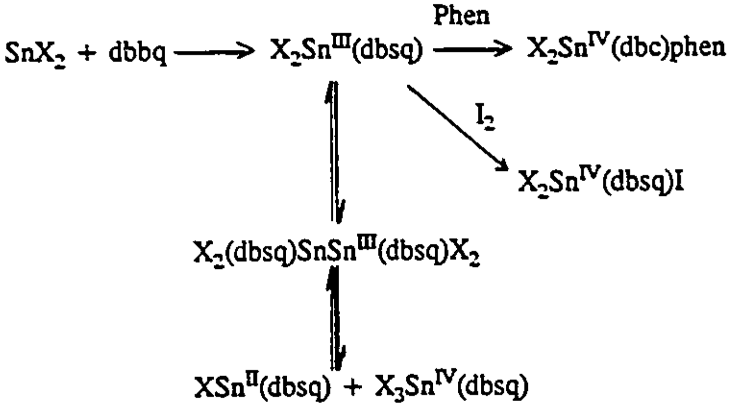
1.2.2 Main Group Element-*o*-Quinone Complexes

To date, most of the studies of metal *o*-quinone complexes have been on the transition metals. There was significant research activity in the Main Group metal quinone coordination chemistry prior to the middle of the 1980's, but most of that work was based only on spectroscopic data for solutions. Electron spin resonance (ESR) and electronic absorption spectroscopy have been used as the main procedures for investigation of the electronic structure of the *o*-quinone complexes.

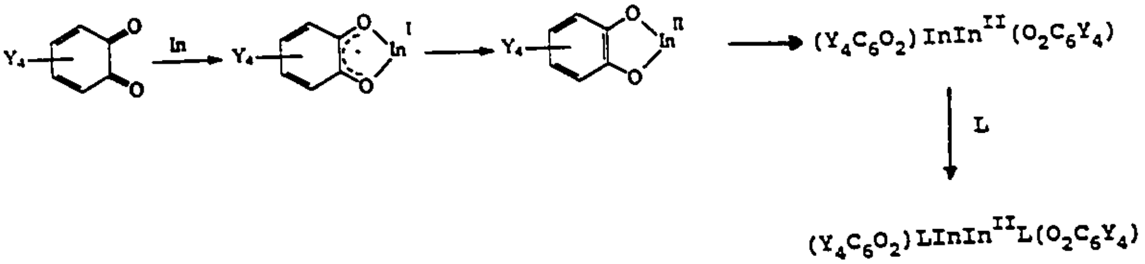
It has been reported[62,63] that 3,6-tert-butyl-1,2-*o*-benzoquinone (dtbq), which can be reduced to the corresponding semiquinone (dtbsq) and catecholate (dtbc), will react with Zn, Cd, and Sn amalgams to give the biradical compounds $M(dtbsq)_2$. The identification was based entirely on the solution ESR spectra of the reaction products, and of the species obtained by further reduction with Na or K mirrors. No isolation of any products or other characterization was reported. For Sn and Si, the biradical species $M(dtbsq)_2(dtbc)$ has been proposed[64] to explain the solution ESR results. The similar reaction between tin amalgam and dtbq has been reported[62] to produce $Sn(dtbsq)_2(dtbq)$, but again no isolation of the compound or independent characterization was done. Solution ESR results were also used to identify the formation of compounds with $S > 1$ in the reaction of dtbq with amalgams of Al, Ga, and In.[65]

Much research on Main Group quinone compounds in the past has applied the reaction between an inorganic or organometallic metal halide with a semiquinone or catecholate salt.[66] Even though it is convenient from the point of view of preparative and structural chemistry to synthesize Main Group metal catecholate or semiquinone compound from the metal halide, this route has no direct relationship to the mechanistic study of the oxidation process of the Main Group elements in their low oxidative states.

A systematic investigation on the reactions between *o*-quinones and Main Group elements or their low oxidation state compounds is being pursued in this laboratory, prompted by an interest in the mechanistic aspect of Main Group metal redox process. Early results from this research have shown[67,68] typical reaction scheme as following:



Scheme 1.1

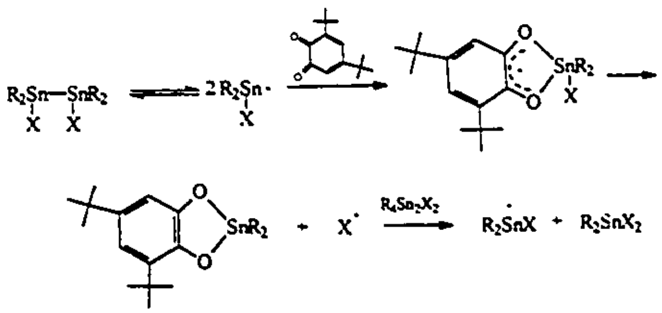


Scheme 1.2

In Scheme (1.1), the dimerization of the presumed Sn(III) mononuclear intermediate gives a dimer which can then disproportionate by halide transfer, and in the absence of other reagents the final solution contains both Sn^{2+} and Sn^{4+} species. The ESR of a frozen solution confirmed the presence of the dimerized diradical. If I_2 is present in the solution, the tin(III) intermediate goes to the trihalogeno-semiquinone tin(IV) derivative, whose ESR parameters are in agreement with those reported for analogous compounds prepared directly. Finally, the effect of a strong bidentate donor such as 1,10-phenanthroline brings about intramolecular electron transfer.

The results point to the involvement of the odd-electron state In^{2+} or Sn^{3+} derivatives as thermodynamically stable intermediates, and hence imply that a process such as $Sn^{2+} \rightarrow Sn^{4+}$ takes place by two successive one-electron transfers.

Recently Newmenn *et al.* also observed[69] a one-electron transfer process in the following reaction:



The intermediate five-coordinate tin-containing radical can be detected by ESR, and sometimes over relatively long time periods.

Another feature of the investigations in our laboratory has been the study of the preparative, spectroscopic and structural chemistry of the oxidation of Main Group elements by *o*-benzoquinones. The products of these reactions are either metal semiquinone or catecholate depending on the metal-*o*-quinone combination. Again ESR studies of the reaction intermediates and products were critical in elucidating the reaction mechanism and the nature of the products. The metals magnesium and barium react[70] with dbbq in refluxing toluene to give $M(dbsq)_2$.

$$M + 2dbbq \rightarrow M(dbsq)_2 \rightarrow M(dbsq)_2L_2$$

$$M = Ba,\ Mg,\ L_2 = \text{bipy or tmed}$$

The reaction of metal tin, gallium and indium with tetrahalogeno-*o*-benzoquinones *o*-$O_2C_6X_4$ (X = Cl or Br) in refluxing toluene produces[71] the catecholate compounds $Sn(O_2C_6X_4)_2$, $[M(O_2C_6X_4)]_2$ or $MX'(O_2C_6X_4)L_2$ (M = In or Ga, X' = I, L_2 = bipy or tmed), while metallic indium reacts[72] with dbbq in refluxing toluene to give semiquinone products (dbsq)InL or $(dbsq)InX_2$ (X = I, SPh and SePh, or $X_2 = O_2C_6Cl_4$ catecholate, L = phen or dbbq). Among these, the reactions between indium metal with *o*-benzoquinones were the most thoroughly studied, and the proposed mechanism based on the ESR spectra of the reaction intermediate is the following:

$$\begin{tikzcd}
\text{In} + \text{dbbq} \arrow[r] & \text{In}^{I}(\text{dbsq}) \arrow[r, "X_2"] \arrow[d, "\text{phen}"'] & X_2\text{In}(\text{dbsq}) \\
 & \text{In}(\text{dbsq})(\text{phen}) \arrow[r, "\text{Ph}_4\text{PCl}"] & \text{Ph}_4\text{P}[\text{In}(\text{dbsq})(\text{phen})\text{Cl}]
\end{tikzcd}$$

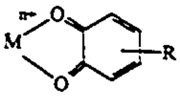
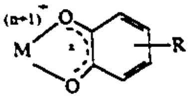
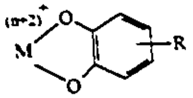
$X_2 = Ph_2S_2$ or I_2

1.2.3 Analysis of the Metal-Quinone Complexes

The study of quinone complexes is also strongly aided by the presence of well-established characterisation methods. Based on the many studies in this area, a combination of convenient and efficient analytical probes has been summarized[5] and used in this research.

TABLE 1.1

Analytical Methods for Metal *o*-Quinone Complexes

			
Ring electrons	18	19	20
Metal electrons	n	n-1	n-2
^{13}C (ppm)	180	-	150
ν(C-O) (cm^{-1})	1670	-	1300
g ESR	-	2.000	-
γ(C-O) (Å)	1.23	1.29	1.35

Firstly, infrared spectroscopy readily identifies the presence or absence of the ν(C=O) vibration of *o*-quinones. For diamagnetic metal complexes, ^{1}H and especially ^{13}C NMR can also serve to demonstrate the change from *o*-quinones to catecholates, and of course, ESR spectroscopy is paramount in characterizing semiquinone species. X-ray crystallography is an extremely valuable tool in evaluating charge distribution in metal quinone complexes. Early structural determinations on complexes containing semiquinone or catecholate ligand indicated that the C-O bond lengths of the ligands are particulary sensitive to the ligand charge, and can be used to provide information on the degree of reduction of the ligand.

1.3 Present Work

This study was undertaken to further develop work carried out in this laboratory in recent years on the oxidation of Main Group 3A and 4A elements, and of compounds of these elements in low oxidation states. The oxidation of elemental phosphorus, tellurium and antimony, and of their low oxidation states compounds are presented in Chapters 2, 3 and 4 respectively. The oxidants used in these reactions are substituted *o*-benzoquinones which are clearly a favourable case for the mechanistic studies of these systems due to the thermodynamic stability of the *o*-semiquinones and the their ready spectroscopic identification. With the aid of ESR spectroscopy it has been established that, contrary to the normal assumption, the mechanism involves a one-electron process as the first step in these systems. The results of the Main Group 5A and 6A elements and their low oxidation state compounds are consistent with those of the Main Group 3A and 4A substances. The reactions involved elemental phosphorus, tellurium and antimony provide convenient one-pot syntheses of useful substances such as phosphoranes. The similarity and differences of these systems will also be presented in the following chapters. The oxidation of a Te-Te bonded compound Ph_2Te_2 is described in Chapter 5. Chapter 6 presents preliminary results of the oxidation of metallic tin with 3,5-di-t-butyl-*o*-benzoquinone. This chapter is in part an extension of the published work of the reaction of this element with tetrahalogeno-*o*-benzoquinones. The oxidation of tin dichloride with a novel *o*-quinone 1,10-phenanthroline-5,6-dione will also be presented in this chapter. The preparation and structure of interesting lead schiff-base quinone complex are presented in Chapter 7.

1.4 Characterization of Products

1.4.1 Elemental Analysis

Halide: the Volhard method was used for halide analysis. Samples (50-100 mg) were added to a known excess of standard silver nitrate. The excess silver nitrate was then back-titrated with standard potassium thiocyanate in the presence of small amounts (2 cm^3) of nitrobenzene, using ferric ammonium sulfate as the indicator.

Antimony, tellurium and tin: antimony, tellurium and tin analyses were by atomic absorption using a IL 251 Atomic Absorption Spectrophotometer. Samples (50-100 mg) were destroyed in HNO_3 and diluted appropriately in order to give concentration of 5-25 mg dm^{-3} (20-80 mg dm^{-3} for tin) for analysis. Standard solutions were prepared by dissolving 1 g of the pure metal in 20 cm^3 of HNO_3 and diluting it to 1000 cm^3 with distilled water; subsequent appropriate dilutions were used for the actual measurement.

Carbon, hydrogen, nitrogen and phosphorus analyses were conducted by Canadian Microanalysis Corporation, Vancouver, BC.

1.4.2 Spectroscopic

1.4.2.1 NMR Spectra

^1H NMR spectra and ^{13}C NMR spectra were recorded on a Bruker AC 300 instrument. ^{31}P, ^{11}B, ^{119}Sn and ^{125}Te NMR spectra were recorded on a Bruker AC 200 instrument.

1.4.2.2 IR Spectra

Infrared spectra in the 4000-400 cm^{-1} region were obtained on the Nicolet 5DX instrument with emulsions of the solid sample as KBr discs.

1.4.2.3 Electronic Spectra

The electronic spectra were taken on a Shimadzu UV-240 spectrophotometer.

1.4.2.4 ESR Spectra

All ESR samples were run in degassed solvents in 2 mm quartz tubes on a Varian E-12 ESR spectrometer operating in the X-band frequency range. The field sweeps were calibrated using a proton NMR magnetometer. The Klystron frequency was calculated from the position of the diphenypicrylhydrazyl signal measured with proton NMR. Low-temperature spectra were taken with the use of a liquid nitrogen dewar insert in the cavity.

CHAPTER 2

STUDIES OF THE OXIDATION OF ELEMENTAL PHOSPHORUS AND PHOSPHORUS(III) COMPOUNDS BY SUBSTITUTED *O*-BENZOQUINONES

2.1 Introduction

The oxidation of Main Group elements, such as gallium,[71] indium,[71,72] magnesium[70] and barium[70] by *o*-benzoquinones has been shown to yield either semiquinonate or catecholate compounds, depending on the metal *o*-quinone combination. The oxidation of indium(I) and tin(II) halides by *o*-quinones offered a more convenient entry for the mechanistic studies of the oxidation process of the Main Group compounds. It has been shown[73,74] that the oxidation of these halides by tetrahalogeno-*o*-benzoquinones yield the corresponding $\mathrm{In(cat)X}$ and $\mathrm{Sn(cat)X_2}$ species as the final product, generally isolated as adducts with neutral or anionic donors, and similar reactions were observed with $\mathrm{Sn(O_2C_6R)_2}$ compounds ($R = H_4$, etc).[75] With other milder substituted *o*-quinones, and especially 3,5-di-tert-butyl-1,2-benzoquinone (dbbq), ESR spectroscopy demonstrated that the oxidation proceeds by successive one-electron transfers, and the presence of the dbsq$^-$ semiquinone radical anion in such reaction mixtures was detected with both indium and tin halides.[67,68]

In view of these results, and our interest in the oxidation processes involving Main Group species, it seemed reasonable to carry out analogous investigations with non-metals and their lower oxidation state compounds. The chemistry of the stable compounds with phosphorus in different oxidation states is well established, and offers a good reference for further studies. However, mechanistic investigations of the oxidation of phosphorus compounds, or elemental phosphorus, are still relatively rare. Phosphorus and its lower oxidation state compounds, therefore, seem to be good candidates for the continuation of the research project in our laboratory. (The late) Dr. T.A. Annan, a postdoctoral fellow in our laboratory at that time, started this part of research in 1988. When I came to Windsor, I joined this project and worked together with him. It is my honour to summarize here the experimental results on this work in order to provide a complete picture of our studies in phosphorus chemistry. In this work the phosphorus compounds $P(O_2C_6R)_mX_n$ (R = Cl_4, Br_4 or $Bu^t_2H_2$; m = 2, n = 1, X = Br; m = 1, n = 3, X_3 = Ph_3, Br_3, Cl_3 and Ph_2Cl) have been prepared by the reaction of the substituted *o*-benzoquinone *o*-O_2C_6R with P_4 and Br_2, or with PX_3. ESR spectra indicate that one-electron transfer takes place in the first stage of these reactions. Methylation of $P(O_2C_6R)_2Br$ yields the corresponding $P(O_2C_6R)_2Me$. There is no reaction between dbbq, P_4, and Ph_2Se_2, but in the presence of catalytic quantities of Br_2 the product is $P(dbc)_2SePh$.

2.2 Experimental

2.2.1 General

Red phosphorus was purified by treating with boiling water.[76] Phosphorus tribromide was prepared by treating phosphorus with bromine.[77] Triphenylphosphine (Aldrich) was recrystallized from diethyl ether, and chlorodiphenylphosphine was distilled *in vacuo* before use. Solvents were dried by conventional methods and stored over drying agents. All other compounds were used as supplied. Reactions were carried out in an atmosphere of dry nitrogen unless otherwise stated.

The instruments and procedures for elemental analysis and spectroscopic studies in this work were described in Chapter 1.

2.2.2 The Reaction of Phosphorus + Bromine + *o*-Quinones

(i) *Tetrahalogeno-o-quinones*

Red phosphorus (0.198 g, 6.4 mmol calculated as P) was suspended in a solution of *o*-$O_2C_6X_4$ (X = Cl, 3.14 g, 12.8 mmol; X = Br, 5.42 g, 12.8 mmol) in hexane (50 cm^3), and a solution of bromine in slight excess (0.20 cm^3, 0.59 g, 3.66 mmol, expressed as Br_2) in the same solvent added dropwise over 30 min. When the reaction mixture was refluxed, signs of reaction were immediately apparent as the red colour of the phosphorus began to change to a light green. The reaction was stopped when red phosphorus was no longer visible in the reaction flask (*ca.* 6 h). The resultant pale green solid was collected by filtration and washed twice with portions (20 cm^3) of light petroleum ether (b.p. 35-60 °C) to remove any unreacted Br_2; the final off-white product was dried *in vacuo* for 24 h. The yields were almost quantitative. The elemental analysis results, given in Table 2.1, agreed very well with the proposed molecular formulae $P(O_2C_6X_4)_2Br$ for the products. This analysis also implied the presence of hexane in each product, and this was confirmed by the ^1H and ^{13}C NMR spectra. The ^1H NMR spectra showed resonances at 0.73-0.74 and 1.10 ppm. The ^{13}C NMR spectra showed resonances at 13.80, 22.04 and 30.96 ppm, corresponding to $C^{1,6}$, $C^{2,5}$ and $C^{3,4}$ respectively. These signals diminished after repeatedly washing the product with light petroleum ether.

(ii) *dbbq*

Red phosphorus (0.198 g, 6.4 mmol calculated as P) was refluxed with 3,5-di-tert-butyl-*o*-quinone (2.28 g, 12.8 mmol) under conditions identical to those described above. The initially red suspension became yellow upon addition of the bromine; refluxing was continued for 2 h, after which the resultant solution was filtered, and the solvent removed under vacuum to give a white flaky product, whose ^{31}P NMR spectrum ($CDCl_3$) showed three signals at -2.4, -2.0 and -0.37 ppm (relative to external 85% H_3PO_4), the intensities of the last two being *ca.* 25% of that of the first. The product was purified by sublimation to yield a waxy solid, which showed a single ^{31}P NMR resonance (in tetrahydrofuran) at -2.37 ppm, and was identified as $P(dbc)_2Br$ by its elemental analysis. This was obtained in almost quantitative yield.

TABLE 2.1

Analytical Results of Phosporane Derivatives(%),

with Calculated Values in Parentheses

Compound	C	H	P
$P(O_2C_6Cl_4)_2Br0.25C_6H_{14}$	25.4 (26.0)		4.40 (4.95)
$P(O_2C_6Br_4)_2Br0.25C_6H_{14}$	16.6 (16.6)		3.45 (3.15)
$P(dbc)_2Br^a$	73.2 (72.5)	3.20 (3.65)	5.40 (5.60)
$P(dbc)_2Me$	71.2 (71.6)	8.75 (8.90)	6.65 (6.35)
$P(O_2C_6Cl_4)Ph_3$	56.1 (56.7)	3.00 (3.00)	5.80 (6.10)
$P(O_2C_6Br_4)Ph_3$	41.6 (42.0)	2.25 (2.20)	4.90 (4.50)
$P(dbc)Ph_3$	78.8 (79.6)	6.90 (7.30)	6.60 (6.40)
$P(O_2C_6Cl_4)ClPh_2$	46.9 (46.3)	2.35 (2.15)	6.60 (6.65)
$P(dbc)ClPh_2^b$			
$P(O_2C_6Cl_4)_2(SePh)$ $0.25C_6H_{14}$	33.2(33.4)	1.30 (1.20)	4.35 (4.40)

a Br 14.6 (14.5%)

b Cl 7.40 (8.05%).

2.2.3 Methylation Reactions

A solution of LiMe (2 cm^3 of a 1.7 mol dm^{-3} solution in Et_2O, 3.4 mmol) was added to a stirred solution containing an equimolar quantity of $P(dbc)_2Br$ (1.88 g, 3.4 mmol) in diethyl ether (50 cm^3) at room temperature. The colourless precipitate which resulted was washed, weighed and identified as LiBr, formed in quantitative yield (Found: Br, 91.5. Calc.: Br, 92.0%). The filtrate was concentrated by removing some of the ether *in vacuo*, and after a day at 0°C acicular crystals were obtained and identified as $P(dbc)_2Me$ by the analytical results. The yield was 70% based on the quantities of the reactants added. In the case of the analogous experiments with $P(O_2C_6Y_4)Br_2$ the yield of LiBr was again quantitative, and the products were identified only by their NMR spectra. These $P(O_2C_6R_2)Me$ products show the ^1H resonances of the PCH_3 group for $P(O_2C_6Cl_4)_2Me$ at 2.20 (d) (J_{PH} 20 Hz), for $P(O_2C_6Br_4)_2Me$ at 2.38 (d) (J_{PH} 22 Hz) and for $P(dbc)_2Me$ at 2.24 (d) (J_{PH} 22 Hz). The presence of coordinated catecholates in these compounds was confirmed by their ^{13}C NMR spectra (see table 2.3 in page 28).

2.2.4 The Reaction of *o*-Quinones with Organophosphorus Compounds

In each case, PPh_3 or PPh_2Cl (1.0 mmol) in toluene (10 cm^3) was added dropwise to an equimolar solution of *o*-quinone in the same solvent (20 cm^3) cooled in an acetone-solid CO_2 bath (-78°C). The reaction caused progressive colour changes from dark red through pale yellow to colourless. The mixture was stirred mechanically for 6 h, after which the mixture was allowed to reach room temperature. The volume of the solution was reduced by *ca.* 80% *in vacuo*; subsequent addition of light petroleum ether (20 cm^3) caused the precipitation of a solid product, which was collected and dried *in vacuo*. The yields of the phosphorus(V) compounds were almost quantitative. These products were identified by their elemental analysis (see Table 2.1), IR and NMR spectra.

2.2.5 The Reaction of Phosphorus + Diphenyl Diselenide + *o*-Quinones

Red phosphorus (0.10 g, 3.23 mmol calculated as P) was suspended in a solution of *o*-$O_2C_6Cl_4$ (0.59 g, 6.64 mmol) and Ph_2Se_2 (0.50 g, 1.62 mmol) in hexane (50 cm^3), and the mixture refluxed for 24 h. There was no evidence of any reaction at this point. One drop of Br_2 was then added, and refluxing continued for 6 h at which point a brown compound began to precipitate. This solid was collected by filtration, washed with light petroleum ether (3 x 20 cm^3) and dried overnight *in vacuo*. The product was identified as $P(O_2C_6Cl_4)_2(SePh)$-$0.25C_7H_8$ by its elemental analysis, IR and NMR spectra (see Tables 2.2 to 2.5). The yield is almost quantitative. The ^1H NMR spectrum revealed the presence of hexane in the final product [0.72 (t) and 1.07 (br)].

2.3 Results and Discussion

2.3.1 Preparations

The reaction between red phosphorus, bromine and substituted *o*-quinone is a simple direct route to the bromobis(catecholate) phosphorane compounds. The formulation of the products was established by the analytical data, and by spectroscopy (see below). This quantitative yield direct 'one-pot' synthesis may have some advantages over the previous route[77] which involves the reaction of phosphorus pentahalide with a 1,2-diol. In addition, the $P(O_2C_6R)_2Br$ products are themselves useful intermediates to such compounds as $P(O_2C_6R)_2Me$, otherwise obtained from the reaction of $PMeCl_2$ with the appropriate catechol.[78] There is no reaction between phosphorus and *o*-quinones in the presence of an agent such as Ph_2Se_2, but catalytic quantities of Br_2 are sufficient to promote reaction under these conditions to produce the $P(O_2C_6R)_2(SePh)$ derivative. The family of compounds $P(O_2C_6R)_2R'$ are important substances because they lend themselves very well to the study of problems of structure and stereochemistry associated with pentavalent state of phosphorus. Based on the above discussion, similar compounds in this family could no doubt be prepared by analogous routes. The significance of the presence of Br_2 is shown by the fact that the reactions reported here involve red phosphorus; when more reactive white phosphorus was used in the synthesis of $[NHEt_3][P(O_2C_6R)_3]$ salts, UV irradiation was necessary to achieve reaction.[79]

It has been reported[80,81] that the reaction of phosphinite ester, phosphonite or trialkyl phosphite $[(RO)PR_2$, $(RO)_2PR$ or $(RO)_3P]$ with *o*-quinones results in the formation of members of the cyclic $(RO)_{5-n}PR_n$ series, where n = 0-2. The use of phosphines in this reaction is more limited, but some cyclic dioxyphosphoranes can be made in the similar route. Our work shows that trivalent phosphorus compounds $Ar_{3-n}PX_n$ (n = 1 or 3) reacted with *o*-benzoquinones under mild conditions and gave corresponding phosphorus(V) catecholate in high yield. The NMR spectra of these products, reported below, were also helpful in confirming the identity of the $P(O_2C_6R)_2Br$ species.

In the course of developing a new method of making oxyphosphoranes, Denney *et al.*, introduced[82,83] the oxidation of trialkyl phosphite by dialkyl peroxides. For example, they have reported the preparation of $(EtO)_5P$ by this method. Beside *o*-benzoquinones, we also tried the reaction of other oxidants (dibenzoxy- and di-t-butyl peroxides) with phosphorus species in this work, but we are unable to detect any paramagnetic intermediate in these reactions. For example, when $Bu^t_2O_2$ (1 mmol) in 10 cm^3 pentane was added to the toluene solution (15 cm^3) of Ph_3P (1 mmol), there was no obvious change after the mixture was stirred for 4 h at room temperature. Removal of the pentane and *ca.* 50% toluene by evaporation, followed by the addition of pentane (30 cm^3) at this point, resulted in a white precipitate after several seconds of stirring. The ^{31}P NMR of this product gave a singlet at 29.2 ppm, which is very close to the literature value of 27.0 ppm for Ph_3PO.[84] The formation of this product is perhaps the result of β-scision of the initial radical adduct of Ph_3P. There have been many reports[85,86] in the literature of this kind of reaction. The reaction rate may be too high for mechanistic study under our experimental conditions.

2.3.2 Spectroscopic results

The characterization of the products as phosphoranes depended on both IR and NMR spectra. Since the subject of this work is the oxidation of phosphorus species *o*-benzoquinones, the changes in the ν(C=O) IR absorption modes associated with the reduction of the carbonyl functional groups will be most important for the study of the IR spectra of these products. In each case of this work the strong ν(C=O) vibration of the original *o*-quinones at *ca.* 1675 cm^{-1} is absent in the products, being replaced by ν(C-O) modes seen as a pair of absorptions at *ca.* 1430 + 1230 cm^{-1}. These bands are usually broader than other bands in their spectra, with the one in *ca.* 1430 being very strong, and is the strongest band in many cases. Fig. 2.1 compares the IR spectrum of a typical phosphorus catecholate complex with the spectrum of the *o*-quinone from which it was derived. The important IR absorptions of the reaction products and their tentative assignments are presented in Table 2.2.

The assignment of the C-O stretching modes in the metal catecholate complexes has been a matter of some discussion. For a series of indium and tin complexes,[73,74] an intense band near 1240 cm^{-1} and a strong broad band near 1430 cm^{-1} have been identified as the C-O stretching vibrations of the catecholate ligand. Similar bands have also been assigned as the C-O stretching modes in a variety of vanadium and cobalt catecholate complexes.[87,88] Based on this discussion, the observation of the ν(C=O) absorption changes in this work provides good evidence for the presence of the coordinated catecholate in the products.

The ^{13}C and ^{31}P NMR spectra of the phosphorane derivatives are summarized in Tables 2.3 and 2.4 respectively. Fig. 2.2 compares ^{13}C NMR spectra of a typical phosphorus catecholate complex with the spectra of the *o*-quinone and Ph_2PCl from which it was derived,

FIGURE 2.1

Infrared Spectra of (A) dbbq and (B) $P(dbc)_2Br$

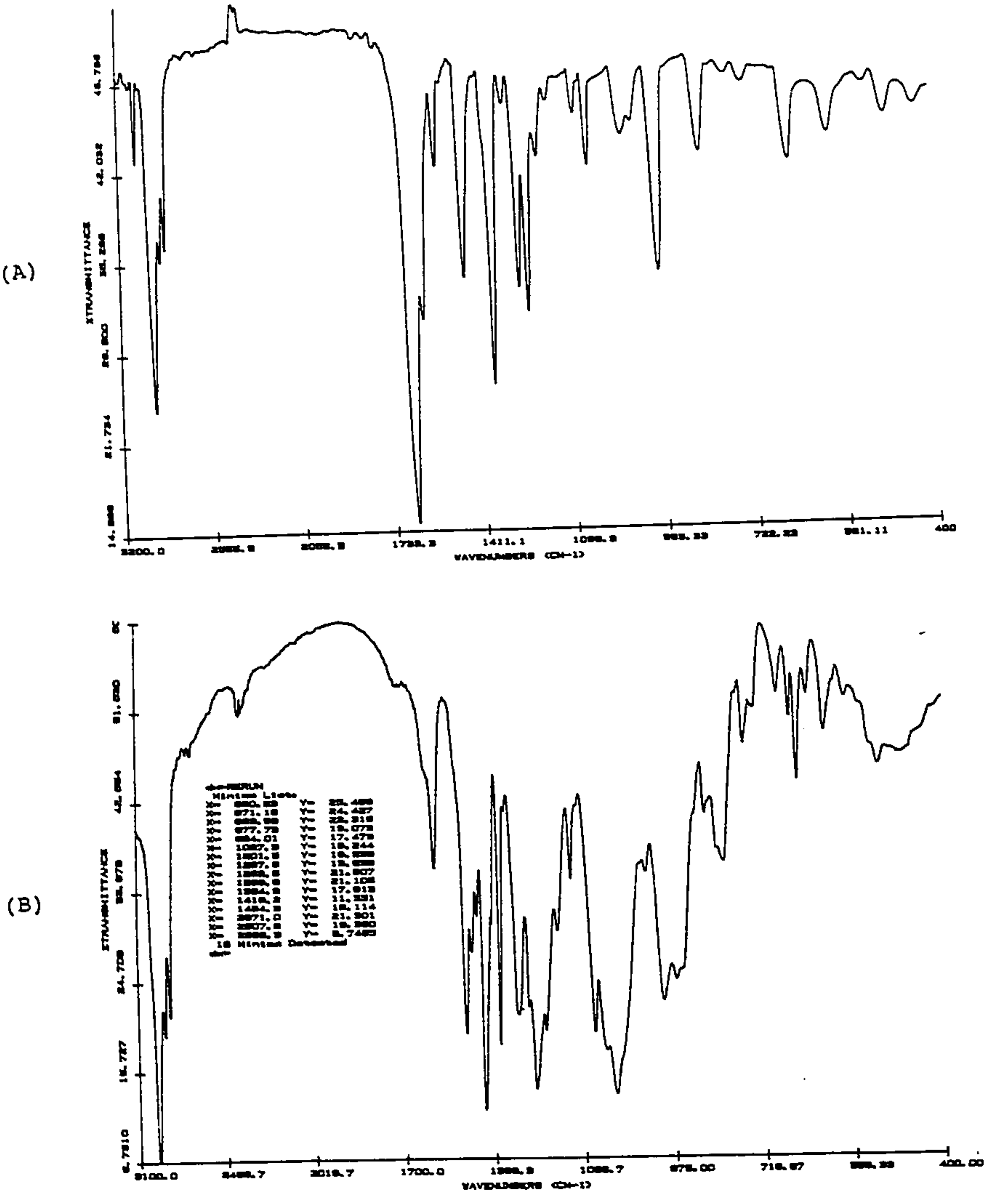


TABLE 2.2

Diagnostic IR Absorptions of Phosphorane Derivatives

Compound	Absorptions	Assignment
o-$O_2C_6X_4$	1675(s)	C=O
$P(O_2C_6X_4)_2Br$	1410(s), 1287(s, br), 1181(s, br)	C-O
$PCl(O_2C_6X_4)Ph_2$	1430(s, br), 1230(m)	C-O
	3060(w)	C-H (Ph)
$P(O_2C_6X_4)Ph_3$	3060(w)	C-H (Ph)
	1436(s), 1230(m)	C-O
$P(O_2C_6Cl_4)_2(SePh)$	3070(w)	C-H (Ph)
	1472(s, br), 1236(m)	C-O
$P(dbc)_2Br$	2962(s), 2907(m), 2871(m)	C-H (Bu^t)
	1419(s, br), 1237(s, br)	C-O
$P(dbc)ClPh_2$	3081(w), 3060(w)	C-H (Ph)
	2957(s), 2905(s), 2867(m)	C-H (Bu^t)
	1440(s, br), 1210(s, br)	C-O
$P(dbc)Ph_3$	2951(s), 2903(s), 2864(m)	C-H (Bu^t)
	1429(s, br), 1260(m)	C-O

X = Cl, Br

TABLE 2.3

^{13}C NMR Spectra of Phosphorane Derivatives;

Values in ppm Relative to TMS ($\delta = 0$)

(a) Tetrahalogenoquinone derivatives

		Diolato			PPh	
Compound	Solvent	$C^{1,2}$	$C^{3,6}$	$C^{4,5}$	$C^{1'}$	Others
$P(O_2C_6Cl_4)_2Br$	$(CD_3)_2SO$	141.3	122.0	113.0		
$P(O_2C_6Br_4)_2Br$	$(CD_3)_2SO$	146.5	120.6	109.1		
$P(O_2C_6Cl_4)_2Me$	$(CD_3)_2SO$	142.4	124.3	113.4		28.2(PMe)
$P(O_2C_6Br_4)_2Me$	$(CD_3)_2SO$	148.0	121.3	108.5		27.8(PMe)
$P(O_2C_6Cl_4)Cl_3$	CH_2Cl_2	138.8	127.1	115.3		
$P(O_2C_6Br_4)Cl_3$	CH_2Cl_2	140.7	122.0	106.5		
$P(O_2C_6Cl_4)Br_3$	Et_2O	142.3	121.1	114.1		
$P(O_2C_6Br_4)Br_3$	Et_2O	146.2	119.7	109.0		
$P(O_2C_6Cl_4)Ph_2$	$CDCl_3$	145.8	123.2	115.5	135.8	129.0-134.0
$PCl(O_2C_6Br_4)Ph_2$	$CDCl_3$	147.1	119.4	106.9	136.8	128.9-134.0
$P(O_2C_6Cl_4)Ph_3$	$CDCl_3$	142.4	122.5	115.3	137.8	128.3-132.3
$P(O_2C_6Br_4)Ph_3$	$(CD_3)_2SO$	144.7	116.7	113.8	133.4	128.6-132.0
$P(O_2C_6Cl_4)(SePh)$	$(CD_3)_2SO$	141.2	122.1	113.2		127.8-130.8

(b) dbbq derivatives

Compound	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}
$P(dbc)_2Br$[a]	141.4	144.3	139.9	110.2	134.5	113.1	34.7	33.9	31.5	29.5

P(dbc)$_2$Me[b]	142.2	145.3	140.1	110.8	135.3	113.4	34.4	33.8	31.4	29.9
P(dbc)Cl_3[c]	142.6	144.6	141.7	109.5	136.4	116.8	34.7	34.1	31.1	29.1
P(dbc)Br_3[c]	142.3	144.6	140.5	109.4	136.5	116.9	34.7	34.5	31.3	29.0
P(dbc)ClPh$_2$[d]	142.0	144.5	139.1	117.1	130.1	120.3	35.5	34.2	31.4	29.7
P(dbc)Ph$_3$[e]	144.1	145.1	140.3	105.8	132.4	114.0	34.8	34.1	31.9	29.7

a solvent = $(CD_3)_2SO$

b solvent = $(CD_3)_2SO$, $\delta = 29.2$ (PMe)

c solvent = CH_2Cl_2

d solvent = $CDCl_3$, $\delta = 139.4$ ($C^{1'}$), $\delta = 128.6$-133.0 (PPh)

e solvent = $CDCl_3$, $\delta = 142.5$ ($C^{1'}$), $\delta = 127.6$-132.4 (PPh)

TABLE 2.4

Phosphorus-31-{H} NMR of Phosphorane Derivatives; Values in ppm Relative to 85% H_3PO_4

Compound	Solvent	Chemical shift
$P(O_2C_6Cl_4)_2Br$	thf	-3.02
$P(O_2C_6Br_4)_2Br$	thf	-1.93
$P(O_2C_6Cl_4)_2Me$	thf	-5.82
$P(O_2C_6Br_4)_2Me$	thf	-4.45
$P(O_2C_6Cl_4)Cl_3$	CH_2Cl_2	-21.75
$P(O_2C_6Br_4)Cl_3$	CH_2Cl_2	-23.96
$P(O_2C_6Cl_4)Br_3$	thf	10.95
$P(O_2C_6Br_4)Br_3$	thf	9.55
$PCl(O_2C_6Cl_4)Ph_2$	$CDCl_3$	-1.54
$PCl(O_2C_6Br_4)Ph_2$	$CDCl_3$	-4.51
$P(O_2C_6Cl_4)Ph_3$	$CDCl_3$	-3.55
$P(O_2C_6Br_4)Ph_3$	$CDCl_3$	-6.94
$P(O_2C_6Cl_4)(SePh)$	$(CD_3)_2SO$	27.28
$P(dbc)_2Br$	toluene	-2.37
$P(dbc)_2Me$	thf	-22.61
$P(dbc)Cl_3$	CH_2Cl_2	-10.34
$P(dbc)Br_3$	CH_2Cl_2	-28.16
$P(dbc)ClPh_2$	thf	-3.60
$P(dbc)Ph_3$	toluene	-22.58

FIGURE 2.2

^{13}C NMR Spectra of (A) dbbq, (B) P(dbc)Cl Ph_2 and (C) dbc

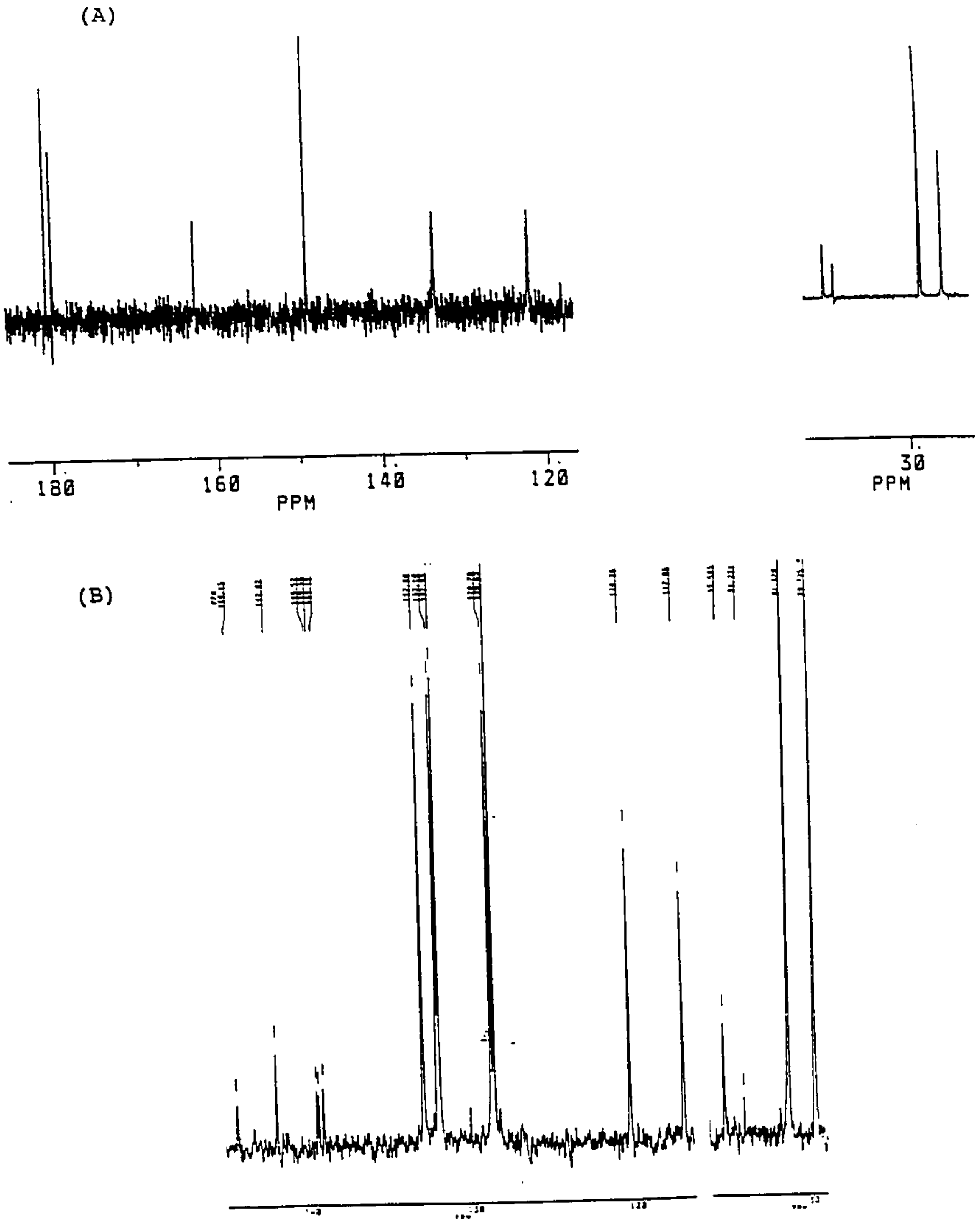
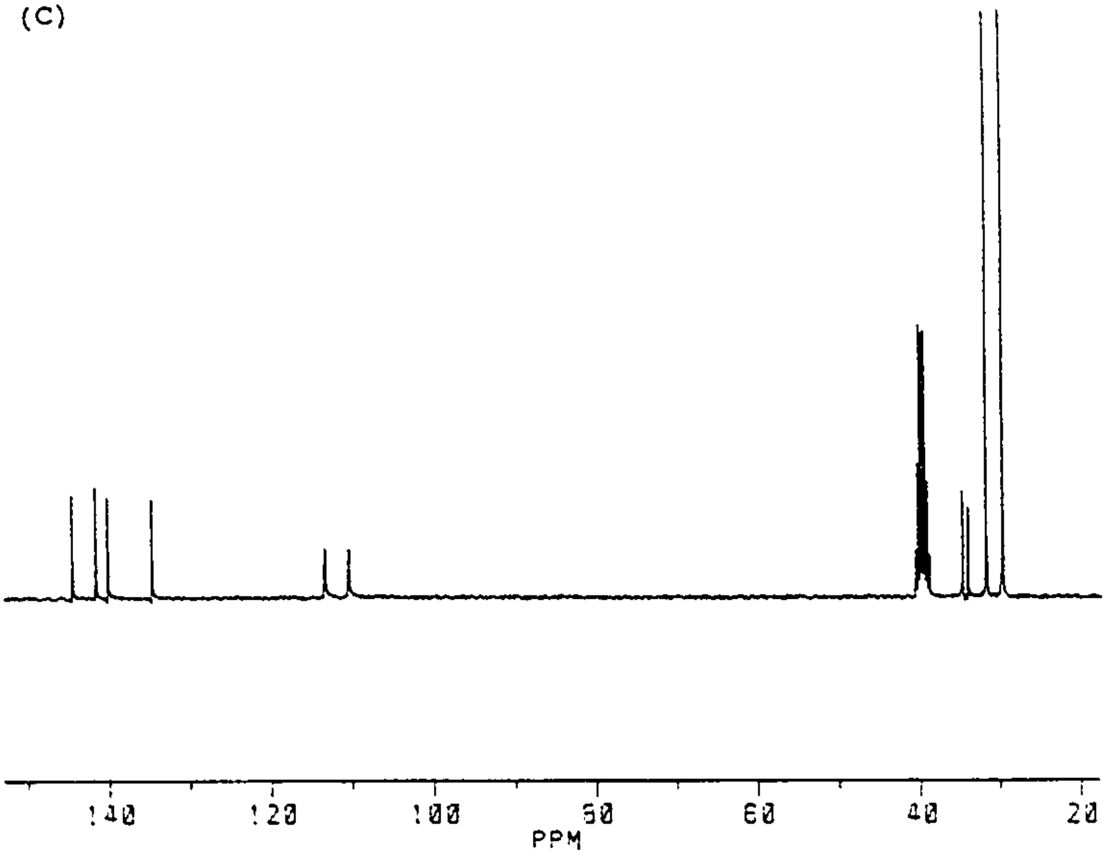


FIGURE 2.2 *cont'd*

^{13}C NMR Spectra of (A) dbbq, (B) P(dbc)Cl Ph$_2$ and (C) dbc



as well as the spectrum of the corresponding catechol. We should note that the ^{1}H NMR spectra of the reaction products (presented in Table 2.5) confirm the presence of Ph groups in the appropriate systems, with typical multiplets in the 7.3 - 7.9 ppm region. The aromatic hydrogens in the catecholate ligands are observed further upfield, in the 6.4 - 6.9 ppm region. In addition, Bu^t resonances are observed as singlets at 1.20 + 1.40 ppm for dbc derivatives, with small variations from one compound to another. These results agree well with those reported for other Main Group metal-dbc complexes by this laboratory.[67] The assignments for the catecholate ligands are based on these previous results and also by comparison with the relevant quinone and diol. In the starting material dbbq, the Bu^t groups give resonances at 1.19 + 1.23 ppm. For 3,5-di-Bu^t-catechol in $(CD_3)_2SO$ solution, we found ^{1}H resonances at 6.71(d), 6.65(d), 2H (H4, H6); 1.35(s), 1.22(s), 18H (Bu^t at C3, C5) and 8.00(br), 2H (OH). Since all the starting materials and reaction products in this work gave relatively simple ^{1}H NMR resonance features which are comparable to other known metal compounds with similar ligands, the coupling constants in these spectra are not included in this and the following chapters.

The ^{13}C NMR resonances are in good agreement with those reported previously for substituted catecholate derivatives of indium and tin.[67,68, 73,74] There are significant changes in the ^{13}C NMR spectra of o-$O_2C_6X_4$ (X_4 = Cl_4, Br_4 and $Bu^t_2H_2$-) following reduction from the quinone to the catechol form (for example, o-$O_2C_6Cl_4$ in $(CD_3)_2SO$, 132.6 for C^4, C^5; 138.7 for C^3, C^6; 167.9 for C^1, C^2. o-$(OH)_2C_6Cl_4$ in $(CD_3)_2CO$,[89] 119.5 for C^4, C^5; 122.5 for C^3, C^6; 143.0 for C^1, C^2), and these same large changes are apparent in the spectra of this work, as in the previous work, confirming the presence of the reduced form in the products. The assignments of these resonances are based on the known compounds with similar ligands and the empirical equations for the effect of substituents on the ^{13}C chemical shifts in substituted benzenes.[90a] There appears to have been no previous report of ^{13}C NMR spectra for $P(O_2C_6R)_2X$ or $P(O_2C_6R)X_3$ compounds,

TABLE 2.5

^1H NMR of Phosphorane Derivatives;

Values in ppm Relative to TMS ($\delta = 0$)

Compound	Solvent	Chemical Shift	Assignment
dbbq	$(CD_3)_2SO$	1.18(s), 1.21(s), 18H	Bu^t
		6.13(d), 6.96(d), 2H	dbc ring
$P(dbc)_2Br$	$(CD_3)_2SO$	1.20(s), 1.39(S), 18H	Bu^t
		6.65(m), 2H	dbc ring
$PClPh_2$	$CDCl_3$	7.40(m), 3H, 7.60(m), 2H	Ph
$PCl(O_2C_6Cl_4)Ph_2$	$CDCl_3$	7.50(m), 3H, 7.92(m), 2H	Ph
$PCl(O_2C_6Br_4)Ph_2$	$CDCl_3$	7.51(m), 3H, 7.92(m), 2H	Ph
$PCl(dbc)Ph_2$	$CDCl_3$	7.53(m), 3H, 7.88(m), 2H	Ph
		1.10(s), 1.40(s), 18H	Bu^t
		6.61(m), 7.00(m), 2H	dbc
$P(O_2C_6Cl_4)Ph_3$	$CDCl_3$	7.45(m), 3H, 7.59(m), 2H	Ph
$P(O_2C_6Br_4)Ph_3$	$CDCl_3$	7.47(m), 3H, 7.65(m), 2H	Ph
$P(dbc)Ph_3$	$CDCl_3$	7.55(m), 3H, 7.70(m), 2H	Ph
		1.20(s), 1.40(s), 18H	Bu^t
		6.72(m), 6.82(m), 2H	dbc
$P(O_2C_6Cl_4)(SePh)$	$(CD_3)_2SO$	7.30(d), 3H, 7.60(d), 2H	Ph

and some interesting correlations can be seen in these results. In the $O_2C_6X_4$ derivatives (X = Cl or Br), $C^{3,6}$ and $C^{4,5}$ are consistently more deshielded for X = Cl, but this effect is reversed at $C^{1,2}$. For the $P(O_2C_6X_4)Y_3$ compounds, the sequence at $C^{1,2}$ is $Cl_3 < Ph_3 < Br_3 < ClPh_2$, suggests that both electronegativity and inductive effects influence the deshielding of these carbon nuclei.

The ^{31}P NMR chemical shifts are in the range reported for phosphorus(V) compounds (for example, -9.7 ppm for $P(cat)_2Cl$ and -26 ppm for $P(cat)Cl_3$ [91a,91b]). The changes in resonance requency are readily identified. For the three $P(cat)_2X$ compounds, replacement of Br by Me produces an upfield shift, most markedly so for the dbc derivative. In the $P(O_2C_6X_4)Y_3$ series, the downfield shifts are in the sequence $Br_3 > ClPh_2 > Ph_3 > Cl_3$, and in this group phosphorus is less shielded in $O_2C_6Cl_4$ derivatives than in $O_2C_6Br_4$ compounds, but this effect is reversed in $P(O_2C_6X_4)_2Br$ and $P(O_2C_6X_4)_2Me$. No detailed analysis of these results can be attempted here, since it is known that ^{31}P NMR frequencies are dependent on both ligand electronegativity and molecular geometry, and Holmes[81,92,93] has shown in an extensive series of structural determinations of phosphoranes and related compounds that a change of ligand almost invariably produces a significant change in the detailed stereochemistry at the phosphorus atom.

2.3.3 Reaction Pathway

The ESR measurements in this work are summarized in Table 2.6. These results point to the overall mechanism of oxidation of P_4 or PX_3 by *o*-quinones. When P_4 was stirred with a solution of *o*-$O_2C_6Cl_4$ and Br_2 in toluene (mole ratio $P_4 : O_2C_6Cl_4 : Br_2 = 0.5 : 4 : 1$) at 0°C the resultant solution showed a resonance centred at $g = 2.003$, with $A_P = 3.0$ G. On warming to room temperature (*ca.* 20°C) over a period of 5 min this signal disappeared. Similar experiments involving equimolar quantities of PCl_3 and *o*-$O_2C_6Cl_4$, *o*-$O_2C_6Br_4$, or dbbq mixed in toluene-methylene chloride solution (1:1, v/v) at -60°C gave ESR spectra similar to those reported by

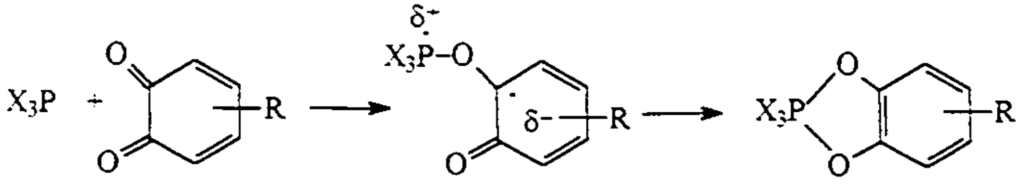
TABLE 2.6

ESR Parameters of *o*-Quinones-Phosphorus Reactions

System	Solvent	Temperature	A_P	$A_H{}^4$
$\frac{1}{4}P_4 + 2O_2C_6Cl_4 + \frac{1}{2}Br_2$	toluene	0°C	3.0G	
$PCl_3 + O_2C_6Cl_4$	toluene - CH_2Cl_2 (1:1, v/v)	-60°C	3.17G	
$PCl_3 + O_2C_6Br_4$	toluene - CH_2Cl_2 (1:1, v/v)	-60°C	3.10G	
PCl_3 + dbbq	toluene - CH_2Cl_2 (1:1, v/v)	-60°C	3.77G	3.77G

Klimov *et al.* for two of these systems in toluene (*o*-$O_2C_6Cl_4$, dbbq). The A_P values deduced from these spectra were 3.17 (*o*-$O_2C_6Cl_4$), 3.10 (*o*-$O_2C_6Br_4$) and 3.77 G (dbbq), and in this last system, A_H^4 = 3.77 G (the coupling due to H^4 can be understood by the different electron densities at C^4 and C^6 of the dbsq ring (ca. 0.117 vs 0.012), which were calculated by B.R. McGarvey, et.al[70]); these results are very similar to those reported by Klimov *et al.*,[94] (A_P = 3.2 G for *o*-$O_2C_6Cl_4$, $A_H^4 = A_P$ = 3.9 G for dbbq). The signals appear to be infinitely stable at -60°C, but disappear as the solution warms to *ca.* 20°C.

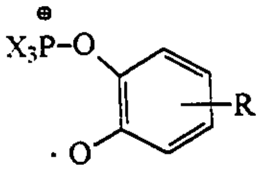
For organophosphorus compounds information on the mechanism of reactions with quinones has been fairly contradictory. Ogata *et al.*, proposed[95-97] an ionic mechanism for this type of reaction based on their kinetic studies of the reactions of substituted α-diketones with alkyl phosphites, but Boekestein *et al.* unequivocally proved[98] the formation of P(III) radical cations in the reaction of 9,10-phenanthroquinone with hexamethylphosphorous triamide. They presented a mechanism involving a number of stages of one-electron transfer based on their ESR measurements. In addition to these and other studies[98,99] of *o*-quinone systems, there have been investigations of the corresponding reactions with p-quinones by a variety of techniques again including ESR and UV-VIS spectroscopy.[100,101] The absence of clear evidence for the presence of $PX_3^{\cdot+}$ species was taken to exclude the possibility of one-electron-transfer processes in these P-quinone studies, although the ESR evidence points to semiquinone radicals being formed. The present and earlier *o*-quinone studies clearly indicate that one-electron transfer does indeed take place in the first stages of the reaction between an *o*-quinone and PX_3. Therefore, the following reaction mechanism for the reactions between phosphorus(III) compounds and *o*-benzoquinones is proposed in Scheme 2.1.



2.1

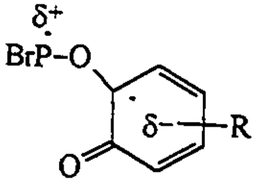
Scheme 2.1

The identifiable coupling between the semiquinone and phosphorus, and the ligand dependence of A_P, favours the formation of an intermediate **2.1** stabilized by the solvent cage, and by the low temperature. There seems to be no reason to invoke the radical cation **2.2** proposed by Klimov *et al.*, since there is no obvious oxidant to explain the electron-removal process postulated by these authors. On warming, **2.1** would easily and rapidly yield the phosphorane product by internal electron transfer and ring closure.



2.2

In the experiment involving elemental phosphorus there is again ESR evidence for a semi-*o*-quinone species coupled to phosphorus. Since the reaction only proceeds in the presence of Br_2 it is likely that this is either **2.3** or **2.1**, involving the intermediate formation of either PBr or PBr_3 which then reacts with the *o*-quinone. We do not have any evidence at this point to allow these possibilities to be distinguished.



2.3

CHAPTER 3

THE REACTION OF SOME SUBSTITUTED *O*-BENZOQUINONES WITH ELEMENTAL TELLURIUM AND WITH TELLURIUM(II) COMPOUNDS

3.1 Introduction

Tellurium is a group 6A element, atomic number 52, with the outer electronic configuration $5s^25p^4$, and has most common formal oxidation states -2, +2 and +4 (as in Na_2Te, R_2Te and R_4Te respectively). It may also complete the noble gas configuration by the formation of formally +6 TeY_6 ($Y = F^-$ or ^-OR) or +1 Te-Te bonded compounds. The chemistry of tellurium, long neglected in favour of the lighter chalcogenide elements, has been the subject of increasing recent interest. Much of the chemistry of tellurium has focused on its organic chemistry,[102] on simple inorganic species[103] (especially its polyatomic ions, as well as halogeno complex anions) and the ligand property[104] of R_2Te, but the coordination chemistry of tellurium itself has received much less attention. Organotellurium compounds are of biological interest[105], and also find increasing use in organic synthesis, semiconductor-MOCVD (metal-organic chemical vapour deposition) preparation,[106] organic superconductors and photographic imaging.[107,108] The two lone pairs of electrons in the R_2Te structure make them useful donor molecules, and a variety of transition metal complexes with tellurium ligands has been reported in recent years.[104,109]

Even though the direct oxidative insertion of elemental tellurium into organic molecules has been known for many years,[110] and the redox process has often been applied in the synthesis of tellurium compounds, especially organotellurium compounds,[111] such reactions have not been the subject of any the mechanistic studies, partly due to the usually high reaction rate or the unfavourable reaction conditions.

It has been established that the oxidation of indium(I) or tin(II) halides by substituted *o*-quinones gives rise to the corresponding halide-catecholate derivatives (See Introduction). The transitory presence of the semiquinone in the reaction mixture, as demonstrated by ESR spectroscopy, implies that two successive one-electron transfers are involved in the formation of these indium(III) and tin(IV) products.[67,68] It has also been shown that *o*-quinones oxidize a number of metallic (In, Ga, Sn, Zn, Cd, Mg and Ba)[70-72] and non-metallic (P, Sb)[112,113] elements, and here again stable catecholate or semiquinone derivatives have been characterized.

In this chapter we will present the results of the reactions between either elemental tellurium or tellurium(II) compounds and *o*-benzoquinones. The products from these reactions are identified as being of the type $Te(O_2C_6R)_2$ or $Te(O_2C_6R)R'_2$ ($R = Cl_4$, Br_4 and $Bu^t_2H_2$; R' = Me, Et or Ph). The pathway for these reactions will be discussed based on the spectroscopic studies of these system. We have also investigated the donor-acceptor chemistry of $Te(O_2C_6R)_2$. The structures of two novel derivatives of these tellurium(IV) species $Te(dbc)_2(bipy)\cdot 0.5C_7H_8$ 3.1 and $Te(O_2C_6Cl_4)_2(18\text{-crown-}6)\cdot C_7H_8$ 3.2 determined by X-ray crystallography during the course of this work will also be discussed in this chapter.

3.2 Experimental

3.2.1 General

Tellurium (Aldrich) and dialkyl tellurides (Alfa) were used as supplied, as were donor ligands 2,2'-bipyridine, N,N-N',N'-tetramethylethane-1,2-diamine, and 1,4,7,10,13,16-hexaoxacyclooctadecane and *o*-quinones. Solvents were dried by standard methods, and stored over appropriate drying agents. All experiments were carried out in an atmosphere of dry nitrogen, using the conventional methods for handling air-sensitive or poisonous substances.

The spectroscopic and elemental analyses were performed by the procedures described in Chapter 1; ^1H and ^{13}C spectra were recorded on a Bruker AC 300 spectrometer at 300 and 75

MHz, respectively. ^{125}Te NMR spectra were recorded on a Bruker AC 200 spectrometer at 63 MHz. The temperature depandence NMR experiments were run on Varian EM 360 spectrometer with a Bruker B-VT1000 variable temperature unit.

3.2.2 Reaction of Tellurium with *o*-Quinones

(i) Tetrahalogeno-o-benzoquinones

Tellurium powder (0.128 g, 1 mmol) was suspended in a solution of *o*-$O_2C_6X_4$ (X = Cl, 0.504 g, 2.05 mmol; X = Br, 0.869 g, 2.05 mmol) in toluene (20 cm^3), and the mixture stirred mechanically at room temperature. After *ca.* 12 h the solution became pale yellow, and the solid phase was perceptibly yellow. When the tellurium had reacted completely (*ca.* 24 h), as shown by its dissolution, the volume of the solution was reduced by *ca.* 80% *in vacuo*, and light petroleum ether (b.p. 35-60°C) (30 cm^3) was added. After further stirring (30 min) the pale yellow final product was collected, washed carefully with n-hexane, and dried *in vacuo*. The yields of $Te(O_2C_6X_4)_2$ were almost quantitative. Analytical results for all products are given in Table 3.1.

(ii) dbbq

The analogous reaction between tellurium (1 mmol) and 3,5-di-tert-1,2-benzoquinone (0.441 g, 2 mmol) in toluene (20 cm^3) required reflux condition in order to achieve a reasonable rate of reaction. After 24 h, the initially dark red solution was dark brown. The mixture was filtered hot, and the filtrate evaporated *in vacuo* to give a residue which was recrystallized from petroleum ether as an orange solid. This product was identified as $Te(dbc)_2$ by analytical results. The yield was 85%.

TABLE 3.1

Analytical Results of Tellurium(IV) Catecholate Compounds (%), with Calculated Values in Parentheses

	Te	C	H
$Te(O_2C_6Cl_4)_2$	21.0 (20.5)	23.9 (23.6)	-
$Te(O_2C_6Br_4)_2$	13.0 (13.0)	-	-
$Te(dbc)_2$	22.5 (22.5)	59.3 (59.2)	6.56 (7.10)
$Te(O_2C_6Br_4)Me_2$	22.0 (22.0)	-	-
$Te(dbc)Me_2$	34.5 (34.0)	-	-
$Te(O_2C_6Cl_4)Et_2$	30.0 (29.5)	27.6 (27.8)	2.45 (2.35)
$Te(O_2C_6Br_4)Et_2$	20.0 (21.0)	20.6 (19.7)	2.12 (1.65)
$Te(dbc)Et_2$	31.0 (31.5)	-	-
$Te(O_2C_6Cl_4)Ph(Et)$	27.0 (26.5)	-	-
$Te(O_2C_6Br_4)Ph(Et)$	19.0 (19.5)	25.4 (25.6)	1.55 (1.53)
Te(dbc)Ph(Et)	28.0 (28.0)	-	-
$Te(O_2C_6Cl_4)Ph(Br)$	23.0 (24.0)	-	-
$Te(O_2C_6Br_4)Ph(Br)$	18.0 (18.0)	20.2 (20.4)	0.90 (0.70)
Te(dbc)Ph(Br)[a]	25.0 (25.5)	-	-
$Te(dbc)_2\cdot(bipy)$ $0.5C_7H_8$[b]	-	64.5 (64.7)	6.90 (6.80)
$Te(dbc)_2(tmed)$	18.5 (18.5)	-	-
$Te(O_2C_6Cl_4)_2\cdot$ 18-crown-6$\cdot(C_7H_8)$	13.0 (13.0)	39.0 (38.2)	3.50 (3.30)
$Te(O_2C_6Cl_4)_2\cdot BCl_3$	17.4 (17.3)		

a Br 15.3 (15.8)%

b N 3.65 (3.60)%.

3.2.3 Dialkyl Tellurides + *o*-Quinones

In each experiment, a solution of 1 mmol of TeR_2 (R = Me or Et) in toluene (15 cm^3) was added dropwise to an equimolar quantity of *o*-quinone in the same solvent (15 cm^3) cooled to -78°C in an acetone-solid CO_2 bath. The mixture was stirred for 2 h and then allowed to warm to room temperature. The resultant solution was pale yellow (o-$O_2C_6X_4$) or pale green (dbbq). In the case of o-$O_2C_6X_4$, the volume of the solution was reduced by *ca.* 90% *in vacuo*, after which light petroleum ether (30 cm^3) was added to precipitate a pale yellow solid which was collected, washed carefully with light petroleum ether and dried *in vacuo*. For the dbbq experiments, the solution was taken to dryness *in vacuo*, and the product recrystallized from light petroleum ether. The analytical results of the reaction products agree with the formulae $Te(O_2C_6R)R'_2$ (R = Cl_4, Br_4 and $Bu^t_2H_2$). The yield was almost quantitative.

3.2.4 Phenyl Ethyl Telluride + *o*-Quinones

(i) Preparation of Phenyl Ethyl Telluride

This tellurium(II) compound was prepared according to the literature method.[114] Diphenyl ditelluride was prepared by the method of Haller and Irgolic,[115] in which phenylmagnesium bromide was treated with an equimolar quantity of tellurium powder in tetrahydrofuran. The final orange-red product was recrystallized from 95% ethanol. A portion of this material (4.09 g, 10 mmol) in absolute ethanol (40 cm^3) was treated with successive quantities of $NaBH_4$ to a total of 0.85 g (22.4 mmol). When the reduction of NaTePh was complete, as judged by the evolution of hydrogen and the formation of a homogeneous mixture, EtBr (2.07 g, 19 mmol) was slowly added. The mixture was stirred at room temperature for 4 h, followed by 30 min at reflux, and then cooled, mixed with water (100 cm^3), and the product extracted into Et_2O (3 x 25 cm^3). Diethyl ether was removed *in vacuo* and the product, PhTeEt, purified by column chromatography on silica gel [hexane, then 9:1 hexane/Et_2O (3 x 25 cm^3)]. This compound was identified by its NMR spectrum (^{13}C NMR in $(CD_3)_2SO$: -0.16, 17.05 (Et), 137.3, 129.1, 127.1 and 111.8 (Ph). ^{1}H NMR in $(CD_3)_2SO$: 1.47 (t, 6H), 2.71 (q, 4H) for Et and 7.10-7.60 (m) for Ph).

(ii) Reaction of PhTeEt with o-Benzoquinones

Treatment of PhTeEt with o-$O_2C_6X_4$ following the methods described above (3.2.2 - 3.2.3) gave $Te(O_2C_6X_4)Ph(Et)$ identified by their analytical results. Similar reactions led to Te(dbc)Ph(Et), and in both cases the yields, based on PhTeEt, were almost quantitative.

3.2.5 Phenyltellurium Bromide + o-Quinones

A solution of PhTeBr was prepared by treating Te_2Ph_2 (0.21 g, 0.5 mmol) in Et_2O (10 cm^3), cooled to -78°C, with Br_2 (0.08 g, 0.5 mmol as Br_2) in the same solvent (10 cm^3).[116] The solution was stirred for *ca.* 15 min, after which o-$O_2C_6Cl_4$ (0.24 g, 1.0 mmol) in toluene (10 cm^3) was added dropwise, and the resultant mixture allowed to reach room temperature with stirring over 1 h. Evaporation *in vacuo* removed Et_2O, and the addition of light petroleum ether (30 cm^3) to the residual mixture precipitated $Te(O_2C_6Cl_4)Ph(Br)$ as a yellow solid. The procedure with dbbq was essentially identical except that n-hexane was used in the final precipitation. The products were identified by the analytical results.

3.2.6 Adducts of Tellurium(IV) Derivatives

(i) a solution of $Te(dbc)_2$ (0.57 g, 1 mmol) and either 2,2′-bipyridine (0.155 g, 1 mmol) or N,N,N′,N′-tetramethylethane-1,2-diamine (0.155 g, 1 mmol) in toluene (30 cm^3) was refluxed for 4 h, during which time the colour changed from orange to pale yellow; toluene was then removed by evaporation *in vacuo*, and the residue treated with light petroleum (5 cm^3). The resultant solution deposited crystals of $Te(dbc)_2(bipy)0.5C_7H_8$, or $Te(dbc)_2(tmed)$, in almost quantitative yield after 12 h at 0°C.

(ii) Tellurium powder (0.13 g, 1 mmol) was suspended in a solution of o-$O_2C_6Cl_4$ (0.49

g, 2 mmol), and 18-crown-6 (0.26 g, 1 mmol) in toluene (50 cm^3) added. This mixture was refluxed for 24 h, filtered hot, and the volume of the filtrate reduced *in vacuo*. The resultant solid was recrystallized from toluene, and identified as $Te(O_2C_6Cl_4)_2(18\text{-crown-}6)\cdot C_7H_8$ from the analytical results. The yield is almost quantitative. In another separate experiment, this compound was also prepared from the reaction between $Te(O_2C_6Cl_4)_2$ and 18-crown-6 (1:1 mole ratio) in toluene under refluxing condition.

3.2.7 Reaction Between $Te(O_2C_6Cl_4)_2$ and BCl_3

When a suspension of $Te(O_2C_6Cl_4)_2$ (0.31 g, 0.5 mmol) in toluene (20 cm^3) was treated dropwise with a solution of BCl_3 in n-hexane (0.5 cm^3 of a 1 mol dm^{-1} solution) the initially yellow mixture became green-yellow. Over a period of 24 h, during which the reaction mixture was stirred at room temperature, the solid dissolved almost completely to give an orange-yellow solution. Small traces of residual solid were removed by filtration, and the volume reduced *in vacuo*; addition of light petroleum ether (*ca.* 20 cm^3) produced a pale yellow precipitate which was collected and dried *in vacuo*. The composition and properties of this material corresponded to those predicted for $Cl_3B\cdot Te(O_2C_6Cl_4)_2$, but re-analysis after a period of 15 days showed that BCl_3 had been lost to give a residue of $Te(O_2C_6Cl_4)_2$.

3.2.8 Attempted Oxidation of $Te(O_2C_6Cl_4)_2$ by Br_2

When $Te(O_2C_6Cl_4)_2$ (0.31 g, 0.5 mmol) in toluene (20 cm^3) was treated with Br_2 (0.08 g, 0.5 mmol as Br_2) the reaction mixture became orange. The mixture was stirred at room temperature for 12 h, and separated by filtration into a pale yellow solid (A) and a dark orange solution, which on evaporation of solvent yielded a dark brown solid (B). The solid A contained Te (26.9%), while B was almost free of this element (Te 2.7%). For comparison, note that $Te(O_2C_6Cl_4)_2Br_2$ has 10.4% Te (calc.), and $Te(O_2C_6Cl_4)Br_2$ has 23.9% Te; $Te(O_2C_6Cl_4)_2$ does not decolorize a solution of I_2 in toluene.

3.3 Results and Discussion

3.3.1 Preparative

The reaction between tellurium and three representative *o*-benzoquinones provides a direct one-pot high-yield synthesis of the corresponding bis(catecholato)-tellurium(IV) compounds. The preparative route used in earlier work on $Te(O_2R)_2$ or $Te(OR)_4$ species involved the treatment of $TeCl_4$ with $R(OH)_2$ or ROH in the presence of base,[117] and other reported methods for alkoxides are based on the reaction between $TeCl_4$ and NaOR,[118-121] so that the use of elemental tellurium offers advantages both in simplicity and in avoiding the use of the moisture-sensitive tetrachloride. Similarly, the preparation of $R_2Te(OR)_2$ described in this work offers advantages in the same aspects in comparison with the preceding work in which these compounds were obtained from R_2TeX_2 and $R(OH)_2$ and base. For example, the preparation of the *o*-diaryltellurium(IV) oximates and mixed chloro-oximates have been reported[122] by the reaction of Ar_2TeCl_2 with an oxime in the presence of trimethylamine:

$$Ar_2TeCl_2 + HONCRR' \rightarrow Ar_2TeCl(ONCRR') + Et_3NHCl$$

$$Ar_2TeCl_2 + 2NaONCRR' \rightarrow Ar_2Te(ONCRR')_2 + 2NaCl$$

Ar = Ph, p-tolyl; R, R′ = Me, Me; Me, Ph; Ph, Ph; $-CH_2(CH_2)_4-$.

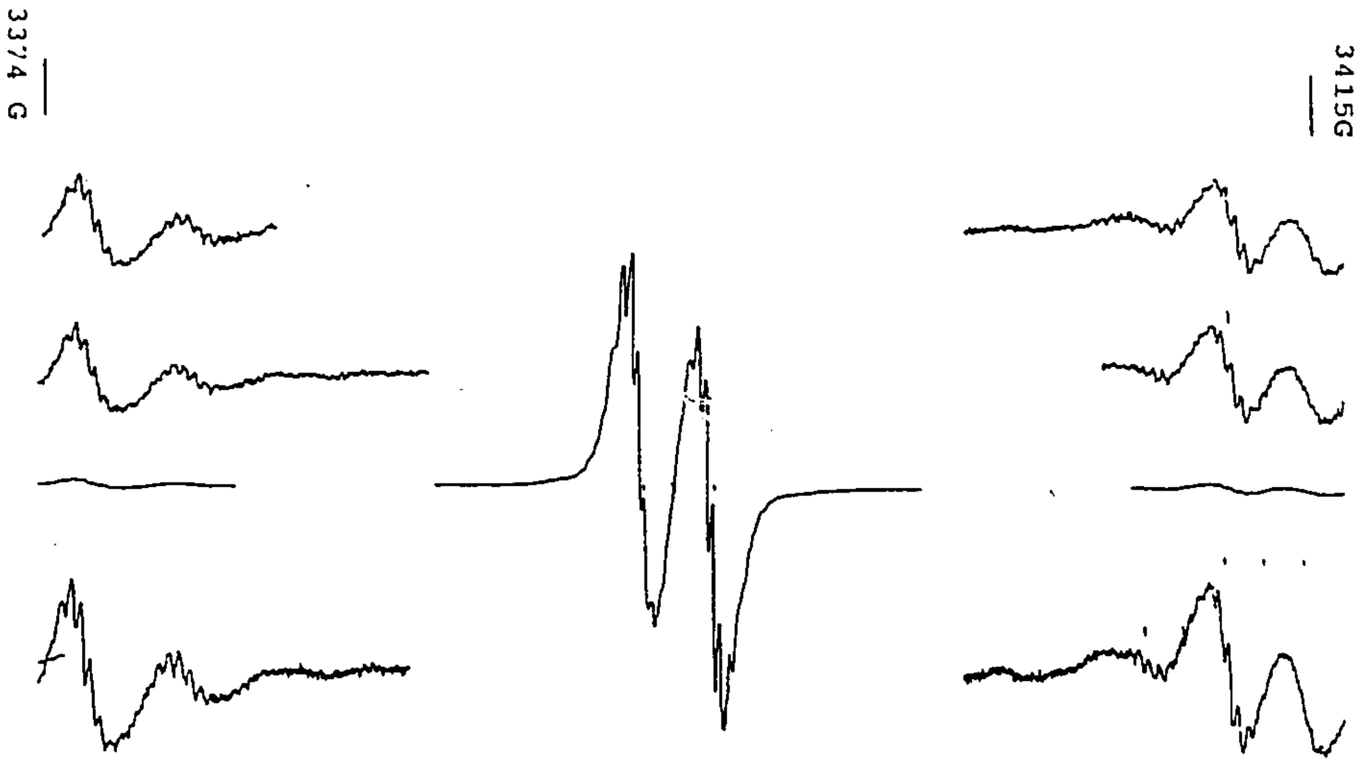
There is an important difference between the present results and those for elemental phosphorus,[112] in that the reaction product is not in the highest oxidation state of the element. Moreover, the $Te(O_2C_6R)_2$ compounds obtained in this way are stable against oxidation by excess *o*-quinone or iodine, and while some reaction occurs on prolonged treatment with bromine, the tellurium analysis shows the product is clearly not $Te(O_2C_6R)_2Br_2$. Since this analysis indicates the tellurium content of the product is higher than it is in $Te(O_2C_6R)Br_2$, bromine is presumably not strong enough to oxidize $Te(O_2C_6R)_2$ and it is more likely that the ligand exchange takes place to some extent in this reaction. Similarly, oxidation reactions between dialkyl tellurides or phenyltellurium bromide and *o*-quinones again produce the appropriate tellurium(IV) species $Te(O_2C_6R)R'_2$. These results are consistent with our knowledge of the oxidation state of tellurium compounds. In contrast to the most common tellurium(IV) compounds, tellurium(VI) species can only be prepared under extremely strong oxidising conditions such as fluoridation or potassium permanganate.[123] No attempt was made to study further the oxidation of these compounds. Similar results have been obtained with antimony, in that $Q + Sb + 1/2Br_2 \rightarrow Sb^{III}(cat)Br$, but $Q + SbPh_3 \rightarrow SbPh_3(cat)$; the comparison of the behaviour of these elements will be discussed in Chapter 4.

3.3.2 The Reaction Mechanism

In earlier discussions of the oxidation of Main Group elements, or their low-oxidation state complexes, by *o*-quinones, the importance of the semiquinone intermediate was stressed, and the identification of these radical anion ligands bonded to the element in question has been a crucial part of the mechanistic evidence.[67,68,71-74] It has now been shown by ESR spectroscopy that the oxidation of $TeEt_2$ by dbbq in toluene at room temperature involves the formation of Te-dbsq species. The spectrum (Fig. 3.1) of a freshly prepared mixture consists of central resonance, which leads to a hyperfine coupling constant $A_H^4 = 2.63$ G ($G = 10^{-4}$ T), and additional fine structure due to interaction with the Bu^t group at C^5 of the ring. This constant is significantly lower than those found for various indium-(I) and -(III) derivatives of this ligand.[67,68] The spectrum also shows a pair of resonances due to coupling with tellurium, with hyperfine constants of 33.2(^{123}Te) and 38.5 G (^{125}Te); the ratio of 0.86 can be compared with that of 0.829 calculated from the ratio of their nuclear magnetic moments (-0.7319/-0.8824), and the agreement seems reasonable in view of the low intensity of these features. The spin density at the tellurium S orbital is 0.2% of the total calculated by employing Morton and Preston's method[124] in which the atomic parameter $\Psi^2(0)$ and the isotropic hyperfine interaction A for unit

FIGURE 3.1

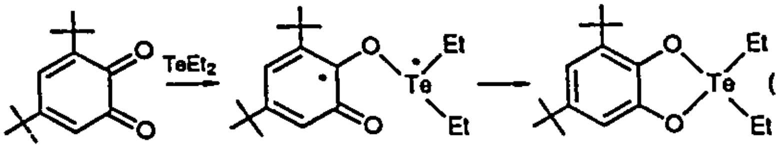
ESR Spectrum of Et_2Te + dbbq



spin density in the corresponding S-orbital are calculated for the most abundant nuclei of the elements from the Hartree-Fock-Slater atomic orbitals of Herman-Skillman wave function. (A = 55590 MHz was used in our calculation.) We also observed ESR-active species in the heterogeneous reaction between tellurium and dbbq indicating the presence of $\text{dbsq}^{\cdot -}$, but no detailed information could be obtained from this experiment.

In no case was it possible to see a resonance from a tellurium centred radical. This was not surprising in view of other work on tellurium compounds reported in the literature.[125-127] This may be a consequence of the increasing large spin-orbital coupling constant as the series S, Se, Te is traversed.

In a subsequent experiment, dilute (*ca.* 10^{-6} mol dm^{-3}) solutions of $TeEt_2$ and dbbq in diethyl ether were mixed at room temperature. After 1 h, the mixture gave an ESR spectrum with the features noted above, indicating the presence of dbsq bonded to tellurium. The intensity was still detectable after 45 h. The existence of a tellurium-semiquinonate species in the reaction mixture identifies an important step in the mechanism as given by equation 3.1. As in other systems



(1)

3.1

studied, the oxidation $Te^{II} \rightarrow Te^{IV}$ by *o*-benzoquinones involves two successive one-electron transfer processes rather than the two-electron process implied by the stoichiometry of the reaction. It seems reasonable to conclude that successive one-electron transfers are a feature of all the redox reactions studied in this work.

It should be noted that there has been an increase in the knowledge of radical pathways redox processes involving tellurium species in recent years. For example, the charge transfer usually occurred in a limit degree in R_2TeTCNQ complexes,[128,129] but the final products may have an ionic structure. The free-radical pathway was also suggested for the reactive decomposition of R_4Te from a study of the decomposition products.[130] The oxidation of R_2Te by silver salt, which was mentioned in Chapter 1, is another such process.[19]

3.3.3 Spectroscopic Results

As in the previous chapter, we have confirmed the formation of the catecholate complexes by both infrared and NMR spectroscopic methods. The infrared spectra (Table 3.2) demonstrated the loss of ν(C=O) of the *o*-quinone, typically at 1600-1700 cm^{-1}, and its replacement by absorptions in the 1200-1400 cm^{-1} region. Similarly, the ^{13}C NMR spectra (Table 3.3) showed changes almost identical to those reported previously,[112] and in particular the reduction in resonance frequency at C^1 and C^2 from *ca.* 180 to *ca.* 150, and a lowering of *ca.* 20 ppm at the other ring carbon atoms of dbbq. The frequency changes for *o*-$O_2C_6X_4$ species (as seen in the example of Figure 3.2) were also close to those found earlier, as were those in the ^{1}H NMR spectra of the compounds prepared. The assignments for bipy and phen are based on the previous work of this laboratory and other groups.[68, 90b, 90c]

In addition, we recorded the ^{125}Te NMR spectra of several of the products, with the results given in Table 3.5. The values are similar to those for other $Te(O_2C_6R)_2$ and $Te(OR)_4$ compounds, for which chemical shifts between 1355 and 1601 ppm have been reported.[21] Other compilations[131-133] of ^{125}Te NMR results demonstrate that the substitution of halogen in TeX_4 (X = Cl or Br) by alkyl or aryl groups causes large changes ($\approx$ 200 ppm) in $\delta(^{125}Te)$, and this is in general agreement with the present results. On the other hand, significant concentration and solvent effects have also been reported, and any detailed analysis of substitution effects in

TABLE 3.2

Diagnostic IR Absorptions of Tellurium(IV) Catecholate Derivatives (cm^{-1})

Compound	Absorptions	Assignment
$Te(O_2C_6Cl_4)_2$	1410(vs, br) 1227(s)	C-O
$Te(O_2C_6Br_4)_2$	1410(vs, br) 1227(s)	C-O
$Te(O_2C_6Cl_4)_2 \cdot BCl_3$	1416(vs, br) 1249(m)	C-O
$PhTeEt(O_2C_6Br_4)$	1419(vs, br), 1229(m)	C-O
	2960, 2928(w)	C-H (Et)
	3058(w)	C-H (Ph)
$PhTeEt(O_2C_6Cl_4)$	1429(vs, br), 1246(s)	C-O
	2973, 2935(w)	C-H (Et)
	3063(w)	C-H (Ph)
$PhTeBr(O_2C_6Cl_4)$	1421(vs, br), 1247(s)	C-O
	3062(w)	C-H (Ph)
$PhTeBr(O_2C_6Br_4)$	1406(vs, br), 1226(s)	C-O
	3058(w)	C-H (Ph)
PhTeEt(dbc)	1413(vs), 1232(m)	C-O
	2959(s), 2908(m), 2869(w)	C-H (Et, Bu^t)
$Et_2Te(O_2C_6Cl_4)$	1403(vs, br), 1227(s, br)	C-O
	2971, 2933(w)	C-H (Et)
$Et_2Te(O_2C_6Br_4)$	1410(vs, br), 1227(s)	C-O
	2969, 2933, 2875(w)	C-H (Et)

$Et_2Te(dbc)$	1414(vs), 1238(s)	C-O
	2959(s), 2909(m), 2872(w)	C-H (Et, Bu^t)
$Me_2Te(O_2C_6Br_4)$	2924(w)	C-H (Me)
	1417(s), 1230 (m)	C-O
$Me_2Te(dbc)$	2962(s), 2935(m), 2916(m)	C-H (Me, Bu^t)
	1416(s), 1240(m)	C-O
$Te(dbc)_2$	1411(vs), 1228(s)	C-O
	2963(s), 2868(m)	C-H (Bu^t)
	3060(w)	C-H (dbc ring)
$Te(dbc)_2 \cdot tmed$	2962(s), 2952(m), 2904(m)	C-H (tmed, Bu^t)
	1411(s), 1229(m)	C-O
$Te(dbc) \cdot bipy \cdot 0.5 (C_7H_8)$	1415(vs), 1235(s)	C-O
	2961(s), 2909(m), 2869(w)	C-H (tol, Bu^t)
	3064(w)	C-H (bipy, dbc ring)
$PhTeEt(O_2C_6Br_4)$	1406 (vs,br), 1226 (s)	C-O
	3058(w)	C-H (Ph)

TABLE 3.3

^{13}C NMR Spectra of Tellurium(IV) Catecholate Derivatives,

Calues in ppm Relative to TMS ($\delta = 0$)

(a) Tetrahalogenoquinone derivatives

		Diolato			Ph and Others	
Compound	Solvent	$C^{1,2}$	$C^{3,6}$	$C^{4,5}$		
o-$O_2C_6Cl_4$	$(CD_3)_2SO$	167.9	138.7	132.6		
o-$(HO)_2C_6Cl_4$[a]	$(CD_3)_2CO$	143.0	122.5	119.5		
$Te(O_2C_6Cl_4)_2$	$(CD_3)_2SO$	146.5	120.7	117.1		
$Te(O_2C_6Br_4)_2$	$(CD_3)_2SO$	147.6	116.0	110.4		
$Me_2Te(O_2C_6Br_4)$	$(CD_3)_2SO$	149.2	111.1	110.7	23.15 (Me)	
$PhTeBr(O_2C_6Br_4)$	$(CD_3)_2SO$	148.4	115.3	110.4	129.1-131.5	
$PhTeEt(O_2C_6Br_4)$	$(CD_3)_2SO$	148.9	111.2 (br)		128.8-132.7	
					8.92, 21.03 (Et)	
$Et_2Te(O_2C_6Cl_4)$	$(CD_3)_2SO$	146.3	124.2	120.4	9.37, 33.07 (Et)	
$Et_2Te(O_2C_6Br_4)$	$(CD_3)_2SO$	151.2	114.4	113.8	9.49, 32.57 (Et)	
$Te(O_2C_6Cl_4)$	$(CD_3)_2SO$	146.5	120.7	117.1	125.2, 128.1, 128.3, 137.3	toluene
					69.81	18-crown-6
					21.0	Me of toluene

a: results from ref. 89

(b) dbbq derivatives

Compound	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}
dbbq[a]	179.7	180.5	162.5	133.4	148.8	121.6	35.7	34.9	29.0	27.5
dbc[b]	141.7	144.3	139.9	113.1	134.5	110.2	34.5	33.8	31.5	29.5
$Te(dbc)_2$[c]	142.6	144.6	141.7	109.5	136.4	116.8	34.7	34.1	31.1	29.1
Te(dbc)·bipy	148.6	143.8	143.3	115.0	136.4	110.2	34.7	34.6	31.8	29.5
$\cdot(C_7H_8)_{0.5}$	155.6	149.4	137.3	123.9	121.4 for bipy					
	125.4-129.2 for toluene									

a solvent = $(CD_3)_2SO$

b solvent = $(CD_3)_2SO$

d solvent=$CDCl_3$

FIGURE 3.2

^{13}C NMR Spectra of (A) $Te(O_2C_6Cl_4)_2 \cdot (18\text{-crown-6}) \cdot 0.5C_7H_8$

(resonances at 69.8 and 21.0 ppm for this compound not shown in this spectrum),

and (B) $o\text{-}O_2C_6Cl_4$

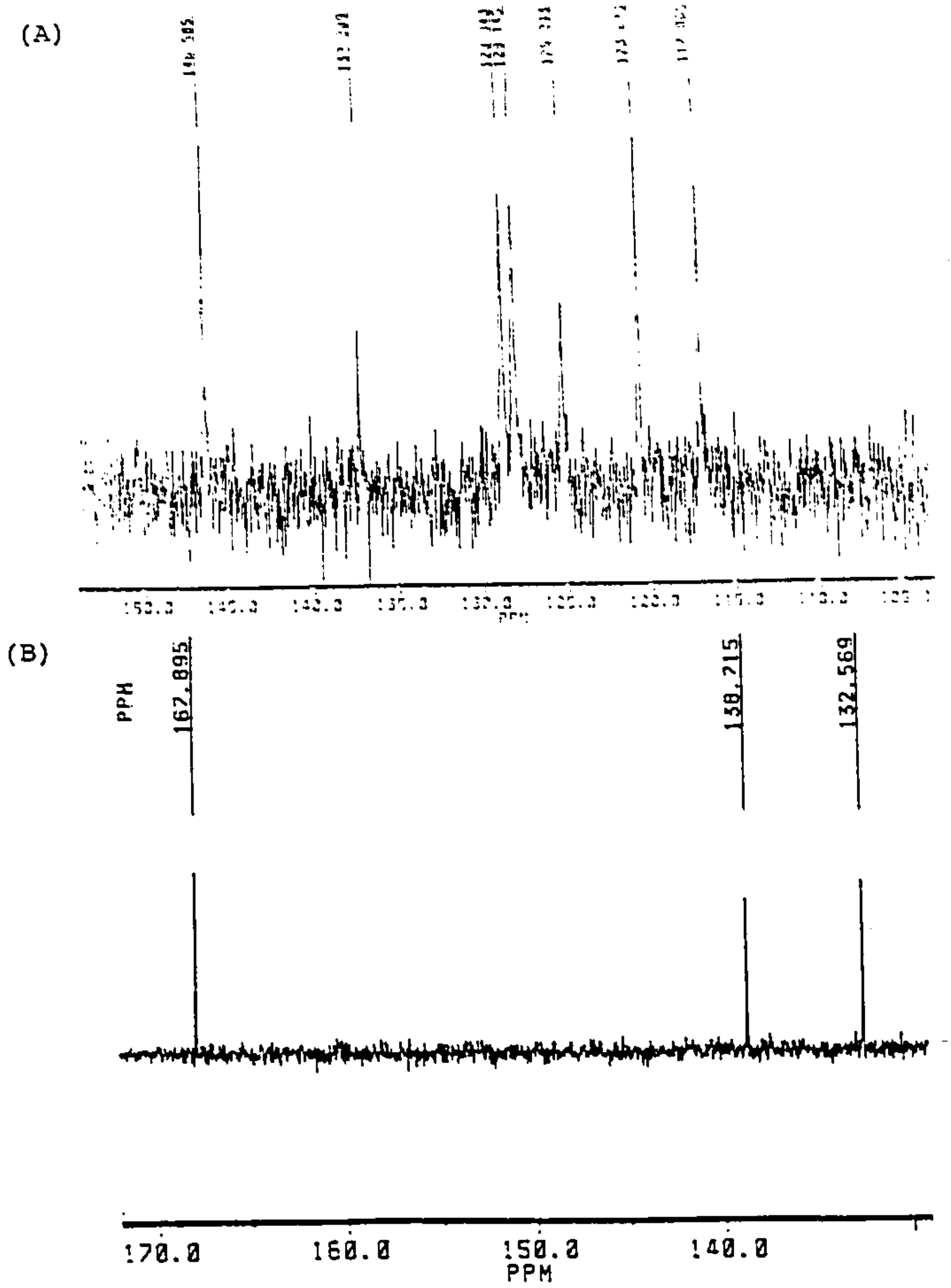


TABLE 3.4

^{1}H NMR of Tellurium Catecholate Derivatives;

Values in ppm Relative to TMS ($\delta = 0$)

Compound	Solvent	Chemical shift	Assignment
dbbq	$(CD_3)_2SO$	1.18(s), 1.21(s), 18H	Bu^t
		6.13(d), 6.96(d), 2H	dbc ring
Te(dbc)$_2$	$(CD_3)_2SO$	1.24(s), 1.31(s), 36H	Bu^t
		6.79(m), 6.88(m), 4H	dbc ring
Te(dbc)$_2$·bipy·$(C_7H_8)_{0.5}$	$(CD_3)_2SO$	1.23(s), 36H	Bu^t
		2.40(s), 1.5H	Me (toluene)
		6.72(m), 6.85(m), 4H	dbc ring
		7.15-7.34(m), 4.5H	bipy/toluene
		7.80(m), 2H	
		8.20(m), 2H	bipy
		8.85(m), 2H	
$Te(O_2C_6Cl_4)_2$·18-crown-6	$(CD_3)_2SO$	2.29(s), 3H	toluene
·$0.5C_7H_8$		7.19(m), 5H	
		3.51(s), 24H	18-crown-6
Et$_2$Te(dbc)	$CDCl_3$	1.25(s), 1.35(s), 18H	Bu^t
		6.64(br), 2H	dbc
		1.62(br), 12H	
		2.48(br), 8H	Et

Et$_2$Te(O$_2$C$_6$Cl$_4$)	(CD$_3$)$_2$SO	1.60(t), 12H	
		3.08(br), 8H	Et
Et$_2$Te(O$_2$C$_6$Br$_4$)	(CD$_3$)$_2$SO	1.60(t), 12H	
		3.07(q), 8H	Et
Me$_2$Te(O$_2$C$_6$Br$_4$)	(CD$_3$)$_2$SO	2.24(s)	Me
PhTeEt(O$_2$C$_6$Br$_4$)	(CD$_3$)$_2$SO	1.41(t, 6H)	
		3.04(q, 4H)	Et
		7.53 (m)	Ph
PhTeEt(O$_2$C$_6$Cl$_4$)	(CD$_3$)$_2$SO	1.37(t, 6H)	
		3.04(q, 4H)	Et
		7.56(m)	Ph
PhTeBr(O$_2$C$_6$Br$_4$)	(CD$_3$)$_2$SO	7.52(m, 3H), 8.05(d, 2H)	Ph

TABLE 3.5

Tellurium-125-{H} NMR of Tellurium Catecholate Derivatives;

Values in ppm Relative to Neat Me_2Te ($\delta = 0$)

Compound	Solvent	Chemical shift
$Te(O_2C_6Cl_4)_2$	$(CD_3)_2SO$	1609.4
$Te(O_2C_6Br_4)_2$	$(CD_3)_2SO$	1591.5
$Te(dbc)_2$	$CDCl_3$	see text
$Te(O_2C_6Br_4)Me_2$	$(CD_3)_2SO$	1369.4
$Et_2Te(O_2C_6Cl_4)$	$(CD_3)_2SO$	1622.6
$Te(dbc)Et_2$	$CDCl_3$	1438.5
$Te(O_2C_6Cl_4)Ph(Et)$	$(CD_3)_2SO$	1470.9
$Te(O_2C_6Br_4)Ph(Et)$	$(CD_3)_2SO$	1480.6
$Te(dbc)_2\cdot bipy$	$CDCl_3$	1650.9
$Te(O_2C_6Cl_4)_2\cdot 18$-crown-6	$(CD_3)_2SO$	1599.4
$Te(O_2C_6Cl_4)_2BCl_3$	$(CD_3)_2SO$	1640.2

$Te(O_2C_6R)_2$ compounds is not justified for the relatively small number of values recorded in this work.

The spectrum of $Te(dbc)_2$ in $CDCl_3$ shows two resonances at room temperature, and there is an interesting temperature dependence, which is illustrated in Fig. 3.3, along with the comparable results for $Te(O_2C_6Cl_4)_2$ and $Te(O_2C_6Br_4)_2$. The chemical shift clearly increases with temperature over the range 300-400 K for all three molecules. In the case of $Te(dbc)_2$, the resonance at 1621.5 ppm is the more intense at 300 K (peak height ratio ca. 2:1); as the temperature increases, the intensity rises (3:1 at 315 K, 4:1 at 330 K) until only one signal is seen, and the almost linear temperature dependence implies that the species responsible for this resonance is present over the whole temperature range studied. The slow exchange process indicated by the presence of two relatively sharp resonances would seem to rule out any explanation based on the presence of both trigonal bipyramidal (TBPY) and square pyramidal (SPY) isomers of $Te(dbc)_2$; exchange between these species can occur without bond breaking and would therefore be expected to be rapid at the temperatures involved. As further support of this argument, we note that only one signal is observed for $Te(O_2C_6X_4)_2$ (X = Cl or Br), and it therefore seems resonable to seek an explanation based on the asymmetry of the dbc ligand (=O-O'), which in the case of a TBPY structure gives rise to three isomers as Fig. 3.4 while contrast two stereoisomers (Fig. 3.5) are possible if the molecule is in the SPY form in solution. We therefore conclude either that $Te(dbc)_2$ in solution has square-pyramidal stereochemistry, or that only two of the three possible trigonal pyramidal forms are present below 330 K in the concentrations detectable by ^{125}Te NMR spectroscopy. For the present, the results are most simply explained in terms of a mixture of IIA and IIB below 330 K. Molecular models do not identify either of the two possible stereoisomers as being obviously more sterically hindered than the other, and so it is not possible to identify the more stable structure which is uniquely present

FIGURE 3.3

Temperature Dependence of ^{125}Te NMR Resonances of $Te(O_2C_6R)_2$ Species in $(CD_3)_2SO$, Relative to $TeMe_2$ ($\delta = 0$) (cf. Table 3.5); $Te(dbc)_2$ (A), $Te(O_2C_6Cl_4)_2$ (B) and $Te(O_2C_6Br_4)_2$ (C)

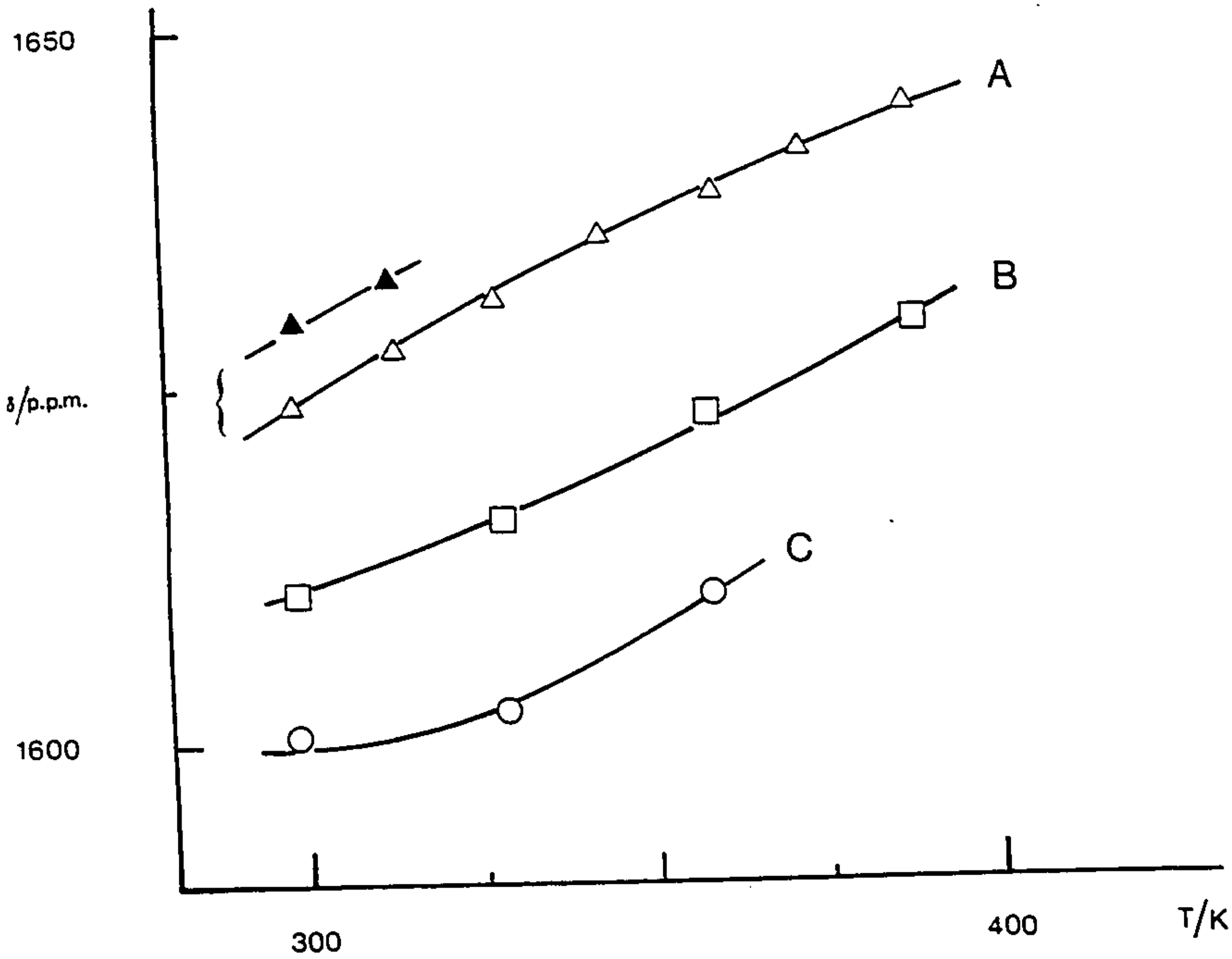
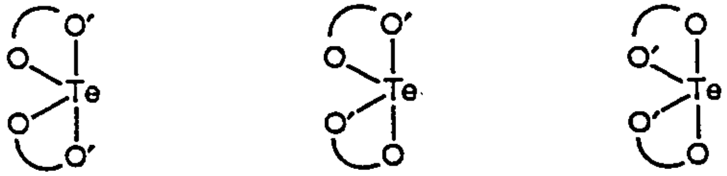


FIGURE 3.4

Possible Trigonal Bipyramidal (TBP) Isomers of Te(dbc)$_2$



IA IB IC

FIGURE 3.5

Possible Square Pyramidal (SP) Isomers of Te(dbc)$_2$

IIA IIB

above 350 K. The crystal structure[121] of $Te(O_2C_6H_4)_2$ shows significant intermolecular interactions between TBPY species in the solid state, so that the presence of the alternative SPY isomer in solution may simply reflect differing stabilizing factors in the two phases.

The ^{13}C NMR spectra of these compounds show only small changes with temperature over the range of these experiments. This result is not unexpected, since the postulated molecular rearrangements only involve changes in the shielding of the tellurium atom. Neither the C_6 rings nor the tert-C_4H_9 groups undergo reorganization as the result of these fluxional processes.

3.3.4 Donor and Acceptor Properties of $Te(O_2C_6R)_2$

It has been reported that both Te(II) and Te(IV) compounds form adducts with both Lewis acids and bases, and TeX_4 form halogeno complex ions with halide ions; there is also a distinct tendency for tellurium to form cationic species such as Te_4^{2+}.[134-136] The donor property of R_2Te has also been found a rich chemistry in recent studies.[104]

3.3.4.1 Donor Properties of $Te(O_2C_6Cl_4)_2$

Valence-shell electron-pair repulsion theory predicts that a TeX_4 species will be of AX_4E type with a lone pair of electrons in an equatorial (TBPY) or apical (SPY) position. Such simple stereochemistry is in fact found only rarely in the tetrahalides, since halide cross-linking leads to oligomerization in the solid state,[137] but in β-TeO_2, and more importantly in $Te(O_2C_6H_4)_2$, the TeO_4 kernel does indeed conform to the predicted TBPY form. On the other hand, the presumed lone pair of electrons is difficult, if not impossible, to remove by oxidation with I_2 or Br_2 (see below), and it therefore seemed useful to investigate the possible donor properties of one of the $Te(O_2C_6R)_2$ compounds synthesised in the present study.

The reaction between $Te(O_2C_6Cl_4)_2$ and BCl_3 gave a product whose tellurium indicated the formation of a 1:1 adduct. The ^{125}Te NMR spectrum in $(CD_3)_2SO$ showed a chemical shift of 1640.2 ppm [cf. 1609.4 ppm for $Te(O_2C_6Cl_4)_2$], and the ^{11}B resonance in the same solvent was at 14.63 ppm (relative to BF_3 in Et_2O, $\delta = 0$), a value which is in the range found for adducts with sulfur or selenium donors (for example, Cl_3B-tetrahydrothiophene in tetrahydrothiophene: 8.1 ppm, Cl_3B-$SeMe_2$ in CH_2Cl_2: 4.5 ppm and Cl_3B-SMe_2 in CH_2Cl_2: 7.1 ppm), and lower than the chemical shift of BCl_3 in non-donor solvents, which is in the range 42-47 ppm (in CH_2Cl_2 or methylcyclohexane, relative to BF_3 in Et_2O).[138] The ^{13}C NMR spectrum of the catecholato ligand showed little or no change from that in $Te(O_2C_6Cl_4)_2$. All this evidence indicates the formation of the adduct, but this compound is apparently unstable, since re-analysis after 2 weeks showed that BCl_3 had been lost, so that $Te(O_2C_6Cl_4)_2$ is apparently only a weak Lewis base.

3.3.4.2 Acceptor Properties of $Te(O_2C_6R)_2$

One of the interesting properties of TeX_4 species is that in addition to any donor property they are also acceptors, and both neutral [*e.g.*, TeF_4L, L = mono- or bi-dentate nitrogen donors,[139] and $TeCl_4$pyo (pyo = pyridine-N-oxide)[140]] and anionic (*e.g.*, TeX_5[137-141]) derivatives have been reported. We have now prepared adducts of $Te(O_2C_6R)_2$ with bidentate nitrogen donors and a crown ether, either by reaction between $Te(O_2C_6R)_2$ and donor, or in the latter case by direct oxidation of elemental tellurium by *o*-$O_2C_6Cl_4$ in the presence of 18-crown-6. The molecular structures of two of these compounds have been established by X-ray crystallography, and we note immediately that in each case the average C-O bond distances in the anionic ligands are indeed typical of C-O single bonds [1.37(1) for 1, and 1.34(1) for 2], confirming that substituted catecholates have been formed by the reduction of the appropriate *o*-quinone. The TeO_2C_2 rings are essentially planar in both molecules.

3.4 Crystallographic Studies

3.4.1 Data Collection and Structure Solution

In the crystallographic study of $Te(dbc)_2(bpy)0.5$ bipy **3.1** the crystal was sealed in a glass capillary and mounted along its longest dimension on a four-circle Syntex $P2_1$ automated diffractometer, equipped with graphite-monochromatized MoKα radiation ($\lambda = 0.71069$ Å). The initial orientation matrices and the crystal system were obtained from 15 machine-centred reflections chosen from a rotation photograph. The cell parameters were measured, checked for dimensions and symmetry from axial photographs, and refined from data from 45 strong reflections in the range $15 < 2\theta < 25°$. Intensity data were then collected[142] via a θ (crystal) - 2θ (counter) scan in 96 steps using bisecting geometry with the scan from $[2\theta <(\mathrm{MoK}\alpha_1) - 1.0]°$ to $[2\theta(\mathrm{MoK}\alpha_2) + 1.0]°$. Backgrounds ($B_1$ and B_2) were measured at the beginning and the end of the scan, each for 25% of the time of the scan. The stability of the system and the crystal was monitored by measuring three strong reflections every 147 data. The intensities of these monitor reflections did not change significantly during the time required for data collection. The appropriate corrections were made for Lorentz and polarization effects; no absorption corrections were used due to the low absorption coefficient. Computation was carried out using the SHELX 76 program package;[143] refinement involved blocked-matrix least-squares techniques, minimizing the function $\Sigma w(|F_o| - |F_c|)^2$ and in the final cycles the weighting scheme $1/[\Sigma\sigma^2(F) + \rho F]^2$ was employed, with $\rho = 0.00001$. Atomic scattering factors and anomalous dispersion[144] were taken from the standard sources. Hydrogen atoms were fixed at idealized positions [r(C-H) = 0.95 Å] and assigned isotropic thermal parameters 10% higher than those of the bonding carbon atoms. Pertinent crystal and experimental data are given in Table 3.6. The density was measured by the flotation method using mixtures of carbon tetrachloride and benzene.

No symmetry or extinctions were observed and the crystal was assigned the centrosymmetric space group $P\bar{1}$, which was subsequently taken to be correct in view of the successful refinement. The tellurium atom site was determined from a three-dimensional Patterson map, and the phases derived from the refinement of this atom were used to locate all the nonhydrogen atoms of the structure. Anisotropic thermal parameters were assigned, first to

TABLE 3.6

Summary of Crystal Data, Intensity Collection and Structure Refinement for Te(dbc)$_2$·bipy (3.1) and Te(O$_2$C$_6$Cl$_4$)$_2$·18-crown-6 (3.2)

Compound	3.1	3.2
Chemical formula	$C_{38}H_{48}N_2O_4Te \cdot 0.5C_7H_8$	$C_{24}H_{24}Cl_8O_{10}Te \cdot C_7H_8$
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
M	770.46	975.83
a/Å	10.388(2)	10.809(4)
b/Å	14.478(3)	18.571(7)
c/Å	15.820(3)	19.287(9)
α/°	106.00(1)	–
β/°	115.98(2)	91.53(4)
γ/°	94.98(2)	–
U/Å	1994(1)	3870(3)
Z	2	4
F(000)	798	1944
d_c/g cm^{-3}	1.28	1.63
d_m/g cm^{-3}	1.30	1.67
Crystal dimensions/mm	0.2 x 0.2 x 0.4	0.4 x 0.3 x 0.3
μ/cm^{-1}	7.11	13.8
2θ/° (max)	45	50
Total reflections measured	4010	7437
Unique data used [$I \geq 3\sigma(I)$]	3424	3768
T/°C	24	23
No. of parameters	435	407
R	0.0424	0.057
R′	0.0439	0.066

the tellurium atom and then to all non-hydrogen atoms, and after several least-squares refinement convergence was achieved with R = 0.053, R' = 0.063. At this stage, the Fourier difference map revealed the presence of toluene in the crystal lattice about an inversion centre, in keeping with the analytical results which indicated the presence of half molecule of toluene. Several attempts were made to establish a disordered model for the toluene, but none led to convergence, and the structure was finally refined with half occupancy for all the atoms of this molecule. The entire structure refined to R = 0.0424, and R' = 0.0439; the largest peak in the final Fourier difference map was 0.76 $eÅ^{-3}$. The final positional parameters are given in Table 3.7, and selected bond lengths and angles in Table 3.8; Fig. 3.6 shows the molecular structure of 3.1.

In the case of $Te(O_2C_6Cl_4)_2$·18-crown-6, 3.2 a suitable crystal on a glass fibre was mounted in a Rigaku AFC6S diffractometer, equipped with MoKα radiation. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using 25 centred reflections in the range $28.1 < 2\theta < 34.5°$. From the systematic absences h0l: h + l $\neq$ 2n; 0k0: k $\neq$ 2n, the space group was identified as $P2_1/n$ (No. 14), and this was confirmed by the subsequent solution and refinement of the structure. Details of the data intensity collection are given in Table 3.6. The density was measured with carbon tetrachloride-ethyl iodide mixtures. The intensities of three representative reflections declined by 2.0%, and a linear correction factor was applied in the calculations. The data were also corrected for Lorentz, polarization and absorption effects.

The structure was solved by a combination of Paterson and direct methods, with non-hydrogen atoms being refined anisotropically. The exceptions to this were C(21) and C(22) of the 18-crown-6 ring; these atoms exhibited unusually high thermal vibrations, and the resultant C-C bond length [1.33(2) Å] is anomalously small. A similar result emerged for C(15)-C(16), although these atoms did refine anisotropically. Such behaviour has been reported previously for

TABLE 3.7

Final Positional Coordinates for Non-hydrogen Atoms of Te(dbc)$_2$·bipy (3.1), with Standard Deviations in Parentheses

	x	y	z
Te	0.57626(4)	0.45325(3)	0.12389(3)
O(1)	0.5661(4)	0.3848(3)	-0.0121(3)
O(2)	0.3605(4)	0.3938(3)	0.0374(3)
O(3)	0.6344(4)	0.3357(3)	0.1502(3)
O(4)	0.5132(4)	0.4552(3)	0.2306(3)
N(1)	0.1254(6)	0.5213(4)	0.8428(5)
N(2)	0.1692(6)	0.4584(4)	0.6819(4)
C(2)	0.0097(7)	0.5034(4)	0.7518(5)
C(3)	-0.1230(8)	0.5215(6)	0.7444(6)
C(4)	-0.1413(9)	0.5548(6)	0.8266(6)
C(5)	-0.0233(8)	0.5713(6)	0.9191(6)
C(6)	0.1061(7)	0.5529(6)	0.9223(5)
C(2′)	0.0322(7)	0.4603(5)	0.6651(5)
C(3′)	-0.0854(8)	0.4205(6)	0.5672(6)
C(4′)	-0.0595(10)	0.3762(7)	0.4901(6)
C(5′)	0.0785(10)	0.3721(6)	0.5083(6)
C(6′)	0.1915(8)	0.4156(6)	0.6053(6)
C(11)	0.3198(7)	0.3295(4)	-0.0568(5)
C(12)	0.4319(7)	0.3206(4)	-0.0829(4)
C(13)	0.4019(7)	0.2540(5)	-0.1755(5)
C(14)	0.2544(7)	0.2006(5)	-0.2401(5)
C(15)	0.1411(7)	0.2105(5)	-0.2167(5)
C(16)	0.1758(7)	0.2760(5)	-0.1232(5)
C(17)	0.5230(7)	0.2375(5)	-0.2050(5)
C(18A)	0.5903(7)	0.3337(5)	-0.2089(5)

C(18B)	0.6422(7)	0.2052(6)	-0.1282(6)
C(18C)	0.4648(8)	0.1569(5)	-0.3080(5)
C(19)	-0.0189(7)	0.1508(6)	-0.2920(6)
C(20A)	-0.0424(10)	0.0941(12)	-0.3860(8)
C(20B)	-0.0662(13)	0.0819(9)	-0.2487(10)
C(20C)	-0.1214(10)	0.2165(8)	-0.3009(8)
C(21)	0.5286(6)	0.3736(5)	0.2566(4)
C(22)	0.5957(6)	0.3092(4)	0.2153(4)
C(23)	0.6198(6)	0.2231(4)	0.2362(4)
C(24)	0.5685(7)	0.2042(5)	0.2999(5)
C(25)	0.4996(6)	0.2643(5)	0.3416(4)
C(26)	0.4815(6)	0.3512(5)	0.3202(4)
C(27)	0.6945(8)	0.1543(5)	0.1896(5)
C(28A)	0.6058(10)	0.1211(5)	0.0747(6)
C(28B)	0.8497(8)	0.2065(6)	0.2243(6)
C(28C)	0.6945(13)	0.0589(7)	0.2140(8)
C(29)	0.4371(8)	0.2366(6)	0.4051(5)
C(30A)	0.2703(9)	0.2154(7)	0.3483(7)
C(30B)	0.4720(11)	0.1423(8)	0.4250(8)
C(30C)	0.4917(13)	0.3175(8)	0.5027(7)

TABLE 3.8

Bond Lengths (Å) and Angles (°) for Te(dbc)$_2$bpy (3.1), with Standard Deviations in Parentheses

Te-O(1)	2.057(5)	O(1)-C(12)	1.374(6)
Te-O(2)	1.992(3)	O(2)-C(11)	1.371(7)
Te-O(3)	1.945(4)	O(3)-C(22)	1.385(9)
Te-O(4)	2.055(5)	O(4)-C(21)	1.353(9)
Te-N(1)	2.877(6)	N(1)-C(2)	1.344(8)
Te-N(2)	2.858(4)	N(1)-C(6)	1.334(12)
		N(2)-C(2')	1.332(10)
		N(2)-C(6')	1.342(12)

O(1)	Te	O(2)	79.1(2)	C(12)	O(1)	Te	113.4(5)
O(3)	Te	O(1)	83.5(2)	C(11)	O(2)	Te	115.0(4)
O(3)	Te	O(2)	97.6(2)	C(22)	O(3)	Te	114.7(4)
O(3)	Te	O(4)	81.0(2)	C(21)	O(4)	Te	111.8(4)
O(4)	Te	O(1)	151.3(2)	C(12)	C(11)	O(2)	116.4(5)
O(4)	Te	O(2)	79.2(2)	C(11)	C(12)	O(1)	114.3(5)
N(1)	Te	N(2)	56.1(2)	C(21)	C(22)	O(3)	115.6(6)
N(1)	Te	O(1)	72.8(2)	C(22)	C(21)	O(4)	116.4(7)
N(1)	Te	O(2)	151.6(2)	C(2)	C(2')	N(2)	118.3(3)
N(1)	Te	O(3)	75.4(2)	C(2')	C(2)	N(1)	116.2(7)
N(1)	Te	O(4)	125.4(2)				
N(2)	Te	O(1)	128.7(2)				
N(2)	Te	O(2)	150.8(2)				

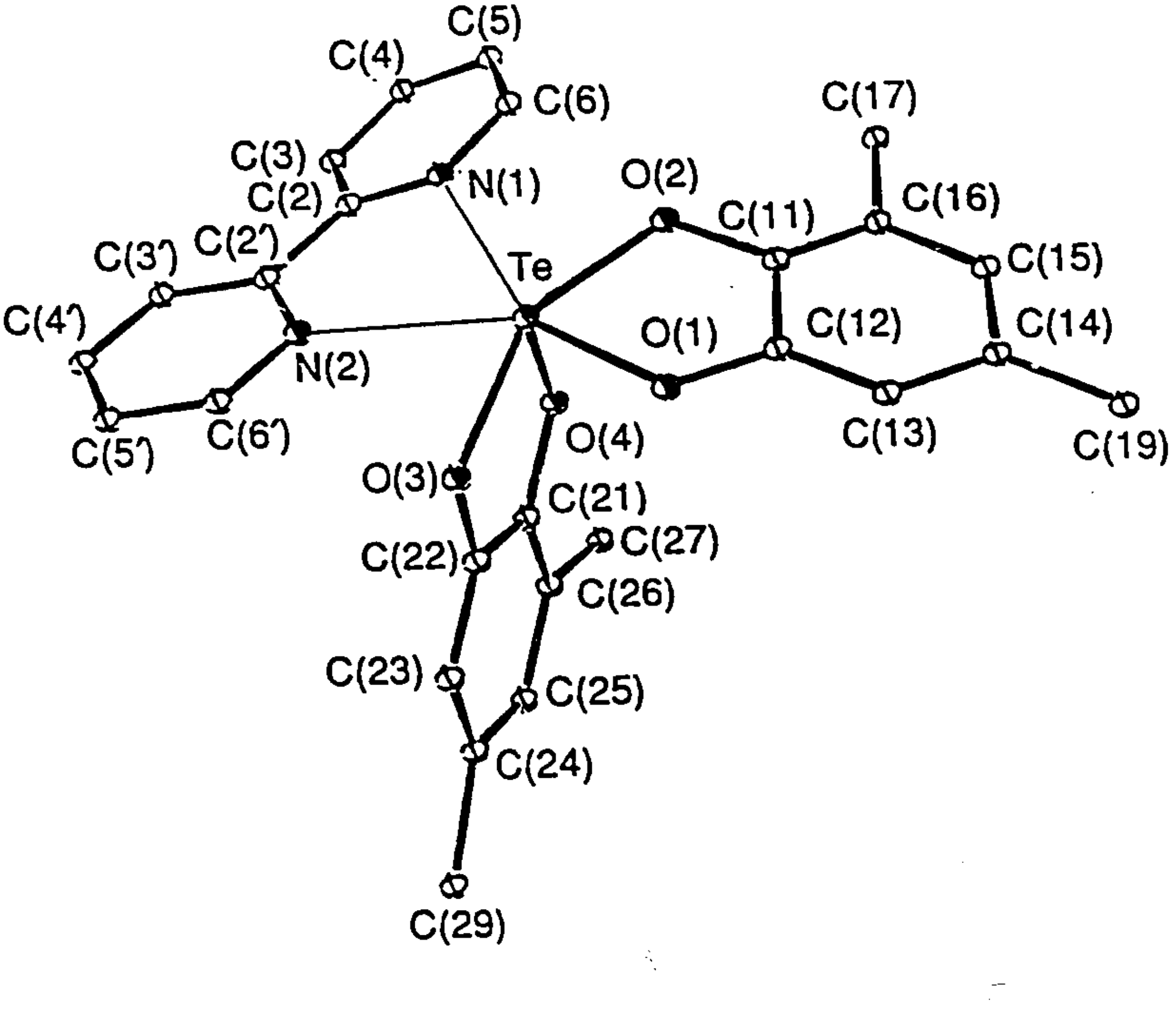
TABLE 3.8 *cont'd*

N(2)	Te	O(3)	79.4(1)
N(2)	Te	O(4)	71.6(2)

Rings,2,2'-bipyridyl		t-Butyl group C(17)-C(18)	
mean C-C	1.37(2)	mean C-C	1.53(1)
mean C-C-C/N-C-C	120(3)	mean C-C-C	108(1)
Ring C(11)-C(16)		t-Butyl group C(19)-C(20)	
mean C-C	1.39(1)	mean C-C	1.46(2)
mean C-C-C	120(3)	mean C-C-C	107(4)
Ring C(21)-C(26)		t-Butyl group C(27)-C(28)	
mean C-C	1.39(1)	mean C-C	1.52(2)
mean C-C-C	120(3)	mean C-C-C	108(2)
		t-Butyl group C(29)-C(30)	
		mean C-C	1.51(2)
		mean C-C-C	108(3)

FIGURE 3.6

An ORTEP Diagram of the Te(dbc)$_2$(bipy) adduct 2.1, with Atoms Shown as 30% Probability Ellipsoids. Hydrogen Atoms and the Methyl Groups of Bu^t have been Omitted for Clarity; C(18A) - C(18C) ride on C(17), C(20a) - C(20C) on C(19), C(28A) - C(28C) on C(27) and C(30A) - C(30C) on C(29)



some crown ether complexes,[145,146] and various locations were tested in an unsuccessful bid to model this disorder. Problems were also encountered with the toluene molecule which is situated in the lattice. This is disordered, but we were unable to model the molecule satisfactorily (cf. refs. 147 and 148). The resultant bond lengths etc. are unsatisfactory, but the effect of this on the overall structure refinement is small.

After several cycles of refinement, the structure converged to R = 0.057 and R′ = 0.066. The maximum shift/estimated standard deviation on any of the parameters in the final cycles in each structure was 0.01. A final Fourier difference map calculation showed no peak of chemical significance; the maximum and minimum peaks correspond to 1.61 and -0.80 eÅ^{-3} respectively. In these calculations, neutral-atom scattering factors were taken from Cromer and Waber.[149] Anomalous dispersion effects were included in the calculation;[150] the value for Δf′ and Δf″ were those published by Cromer.[151] The TEXSAN[152] crystallographic software package was used in the refinement of 3.2. Table 3.9 gives the positional parameters, Table 3.10 the interatomic distances and angles, and the structure of the molecule and its cell packing diagram are shown in Figs. 3.6 and 3.7 respectively.

3.4.2 Description and Discussion of the Structures

The reaction between Te(dbc)$_2$ and 2,2′-bipyridine gives Te(dbc)$_2$(bpy)0.5C$_7$H$_8$ **3.1** in high yield, and the structure of this molecule is based on a TeO$_4$N$_2$ kernel. The Te-O bond distances (Table 3.8) are slightly larger in the apical direction [O(1),O(4), average value 2.056 Å] than in the equatorial (average value 1.969 Å), and in this respect the structure is similar to that of Te(O$_2$C$_6$H$_4$)$_2$ reported by Lindqvist[121] [comparable values 2.06(2), 1.98(2) Å]. The O-Te-O bite angles in the latter [average 81.2(1.0)°] are also close to those in **3.1**, as are the other O-Te-O angles, so that coordination of bipy has not apparently caused any great distortion from the solid-state structure of Te(O$_2$C$_6$H$_4$)$_2$. Of the reported Te-N bonds, those in 2,6-diacetyl

TABLE 3.9

Final Positional Parameters for Non-hydrogen atoms of $Te(O_2C_6Cl_4)_2\cdot(18\text{-crown-}6)$(3.2),

with Standard Deviations in Parentheses

atom	x	y	z
Te(1)	0.26114(7)	0.10613(4)	0.14758(4)
Cl(1)	-0.0869(3)	0.2442(2)	0.0420(2)
Cl(2)	-0.0230(3)	0.4075(2)	0.0218(2)
Cl(3)	0.2387(3)	0.4645(2)	0.0680(2)
Cl(4)	0.4242(3)	0.3570(2)	0.1335(2)
Cl(5)	-0.1029(3)	-0.0345(2)	0.2302(2)
Cl(6)	-0.1600(3)	0.0025(2)	0.3848(2)
Cl(7)	0.0126(3)	0.1094(2)	0.4672(1)
Cl(8)	0.2280(3)	0.1875(2)	0.3904(2)
O(1)	0.3410(6)	0.2059(4)	0.1388(4)
O(2)	0.1199(6)	0.1602(4)	0.1054(4)
O(3)	0.2445(7)	0.1433(4)	0.2426(4)
O(4)	0.1152(6)	0.0446(4)	0.1786(3)
O(5)	0.5519(8)	0.122(5)	0.0714(5)
O(6)	0.331(1)	0.1232(5)	-0.0120(5)
O(7)	0.1604(7)	0.0189(5)	0.0293(4)
O(8)	0.2800(8)	-0.0737(5)	0.1290(4)
O(9)	0.369(1)	-0.0068(7)	0.2513(5)
O(10)	0.525(1)	0.1053(6)	0.2168(5)
C(1)	0.262(1)	0.2548(6)	0.1131(5)
C(2)	0.143(1)	0.2315(5)	0.0944(5)
C(3)	0.0568(9)	0.2773(5)	0.0661(5)
C(4)	0.086(1)	0.3511(6)	0.0572(6)
C(5)	0.202(1)	0.3753(5)	0.0783(5)
C(6)	0.290(1)	0.3287(6)	0.1067(5)

C(7)	0.155(1)	0.1108(6)	0.2793(5)
C(8)	0.083(1)	0.0595(5)	0.2431(5)
C(9)	-0.014(1)	0.0270(6)	0.2761(5)
C(10)	-0.039(1)	0.0426(6)	0.3445(6)
C(11)	0.038(1)	0.0909(6)	0.3815(5)
C(12)	0.134(1)	0.1264(6)	0.3478(6)
C(13)	0.530(1)	0.1682(8)	0.0138(9)
C(14)	0.453(2)	0.130(1)	-0.0377(8)
C(15)	0.257(2)	0.082(1)	-0.059(1)
C(16)	0.150(1)	0.061(1)	-0.0347(7)
C(17)	0.180(1)	-0.0557(8)	0.0201(7)
C(18)	0.176(1)	-0.0928(6)	0.0881(8)
C(19)	0.277(1)	-0.1053(8)	0.1958(8)
C(20)	0.382(2)	-0.080(1)	0.2371(8)
C(21)	0.468(2)	0.023(1)	0.296(1)
C(22)	0.567(1)	0.0508(6)	0.2668(6)
C(23)	0.640(1)	0.1090(9)	0.182(1)
C(24)	0.640(1)	0.1090(9)	0.182(1)
C(25)	0.305(3)	0.242(2)	0.787(2)
C(26)	0.319(2)	0.272(1)	0.846(1)
C(27)	0.214(3)	0.283(1)	0.884(1)
C(28)	0.092(2)	0.267(1)	0.870(1)
C(29)	0.092(2)	0.230(1)	0.803(1)
C(30)	0.185(2)	0.2176(9)	0.7658(9)
C(31)	0.386(2)	0.228(1)	0.741(1)

TABLE 3.10

Bond Lengths (Å) and Angles (°) for $Te(O_2C_6Cl_4)_2\cdot(18\text{-crown-}6)$ (3.2),

with Standard Deviations in Parentheses

Te(1)	O(1)	2.054(7)	O(10)	C(22)	1.46(1)
Te(1)	O(2)	1.983(6)	O(10)	C(23)	1.43(2)
Te(1)	O(3)	1.972(7)	C(1)	C(2)	1.39(1)
Te(1)	O(4)	2.050(6)	C(1)	C(6)	1.41(1)
Cl(1)	C(3)	1.72(1)	C(2)	C(3)	1.37(1)
Cl(2)	C(4)	1.71(1)	C(3)	C(4)	1.42(1)
Cl(3)	C(5)	1.72(1)	C(4)	C(5)	1.38(1)
Cl(4)	C(6)	1.72(1)	C(5)	C(6)	1.39(1)
Cl(5)	C(9)	1.72(1)	C(7)	C(8)	1.41(1)
Cl(6)	C(10)	1.71(1)	C(7)	C(12)	1.38(1)
Cl(7)	C(11)	1.72(1)	C(8)	C(9)	1.38(1)
Cl(8)	C(12)	1.72(1)	C(9)	C(10)	1.39(1)
O(1)	C(1)	1.33(1)	C(10)	C(11)	1.40(1)
O(2)	C(2)	1.36(1)	C(11)	C(12)	1.40(1)
O(3)	C(7)	1.35(1)	C(13)	C(14)	1.46(2)
O(4)	C(8)	1.33(1)	C(15)	C(16)	1.32(2)
O(5)	C(13)	1.42(2)	C(17)	C(18)	1.48(2)
O(5)	C(24)	1.40(1)	C(19)	C(20)	1.45(2)
O(6)	C(14)	1.43(2)	C(21)	C(22)	1.33(2)
O(6)	C(15)	1.43(2)	C(23)	C(24)	1.48(2)
O(7)	C(16)	1.47(2)	C(25)	C(26)	1.27(3)
O(7)	C(17)	1.41(1)	C(25)	C(30)	1.43(3)
O(8)	C(18)	1.40(1)	C(25)	C(31)	1.30(3)
O(8)	C(19)	1.42(1)	C(26)	C(27)	1.38(2)
O(9)	C(20)	1.40(2)	C(27)	C(28)	1.37(3)
O(9)	C(21)	1.46(2)	C(28)	C(29)	1.45(3)
			C(29)	C(30)	1.27(2)

O(1)	Te(1)	O(2)	80.2(3)	Cl(2)	C(4)	C(5)	122.0(8)
O(1)	Te(1)	O(3)	79.1(3)	C(3)	C(4)	C(5)	119.0(9)
O(1)	Te(1)	O(4)	148.8(3)	Cl(3)	C(5)	C(4)	119.6(8)
O(2)	Te(1)	O(3)	96.6(3)	Cl(3)	C(5)	C(6)	119.2(8)
O(2)	Te(1)	O(4)	79.2(3)	C(4)	C(5)	C(6)	121.2(9)
O(3)	Te(1)	O(4)	80.4(3)	Cl(4)	C(6)	C(1)	117.6(8)
Te(1)	O(1)	C(1)	112.3(6)	Cl(4)	C(6)	C(5)	122.4(8)
Te(1)	O(2)	C(2)	114.3(6)	C(1)	C(6)	C(5)	119.9(9)
Te(1)	O(3)	C(7)	114.5(6)	O(3)	C(7)	C(8)	115.9(9)
Te(1)	O(4)	C(8)	112.3(6)	O(3)	C(7)	C(12)	123(1)
C(13)	O(5)	C(24)	110(1)	C(8)	C(7)	C(12)	121(1)
C(14)	O(6)	C(15)	109(1)	O(4)	C(8)	C(7)	116.6(9)
C(16)	O(7)	C(17)	115(1)	O(4)	C(8)	C(9)	124(1)
C(18)	O(8)	C(19)	112(1)	C(7)	C(8)	C(9)	119(1)
C(20)	O(9)	C(21)	114(1)	Cl(5)	C(9)	C(8)	118.2(8)
C(22)	O(10)	C(23)	95(1)	Cl(5)	C(9)	C(10)	120.6(9)
O(1)	C(1)	C(2)	117.4(9)	C(8)	C(9)	C(10)	121(1)
O(1)	C(1)	C(6)	124.2(9)	Cl(6)	C(10)	C(9)	121(1)
C(2)	C(1)	C(6)	118.3(9)	Cl(6)	C(10)	C(11)	119.8(9)
O(2)	C(2)	C(1)	115.7(9)	C(9)	C(10)	C(11)	119(1)
O(2)	C(2)	C(3)	122.5(9)	Cl(7)	C(11)	C(10)	120.7(9)
C(1)	C(2)	C(3)	121.7(9)	Cl(7)	C(11)	C(12)	119.4(9)
Cl(1)	C(3)	C(2)	119.2(8)	C(10)	C(11)	C(12)	119.9(9)
Cl(1)	C(3)	C(4)	121.1(8)	Cl(8)	C(12)	C(7)	118.7(9)
C(2)	C(3)	C(4)	119.7(9)	Cl(8)	C(12)	C(11)	121.7(9)
Cl(2)	C(4)	C(3)	119.0(8)	C(7)	C(12)	C(11)	120(1)
O(5)	C(13)	C(14)	109(1)				
O(6)	C(14)	C(13)	109(1)				
O(6)	C(15)	C(16)	114(2)				
O(7)	C(16)	C(15)	114(1)				
O(7)	C(17)	C(18)	110(1)				
O(8)	C(18)	C(17)	110(1)				

O(8)	C(19)	C(20)	109(1)
O(9)	C(20)	C(19)	110(1)
O(9)	C(21)	C(22)	119(2)
O(10)	C(22)	C(21)	108(1)
O(10)	C(23)	C(24)	109(1)
O(5)	C(24)	C(23)	108(1)
C(26)	C(25)	C(30)	119(3)
C(30)	C(25)	C(31)	111(3)
C(25)	C(26)	C(27)	117(2)
C(26)	C(27)	C(28)	131(2)
C(27)	C(28)	C(29)	105(2)
C(28)	C(29)	C(30)	127(2)
C(25)	C(30)	C(29)	120(2)

FIGURE 3.7

An PLUTO Diagram of the $Te(O_2C_6Cl_4)_2$ ·18-crown-6 Adducts (3.2).

Hydrogen Atoms have been Omitted for Clarity

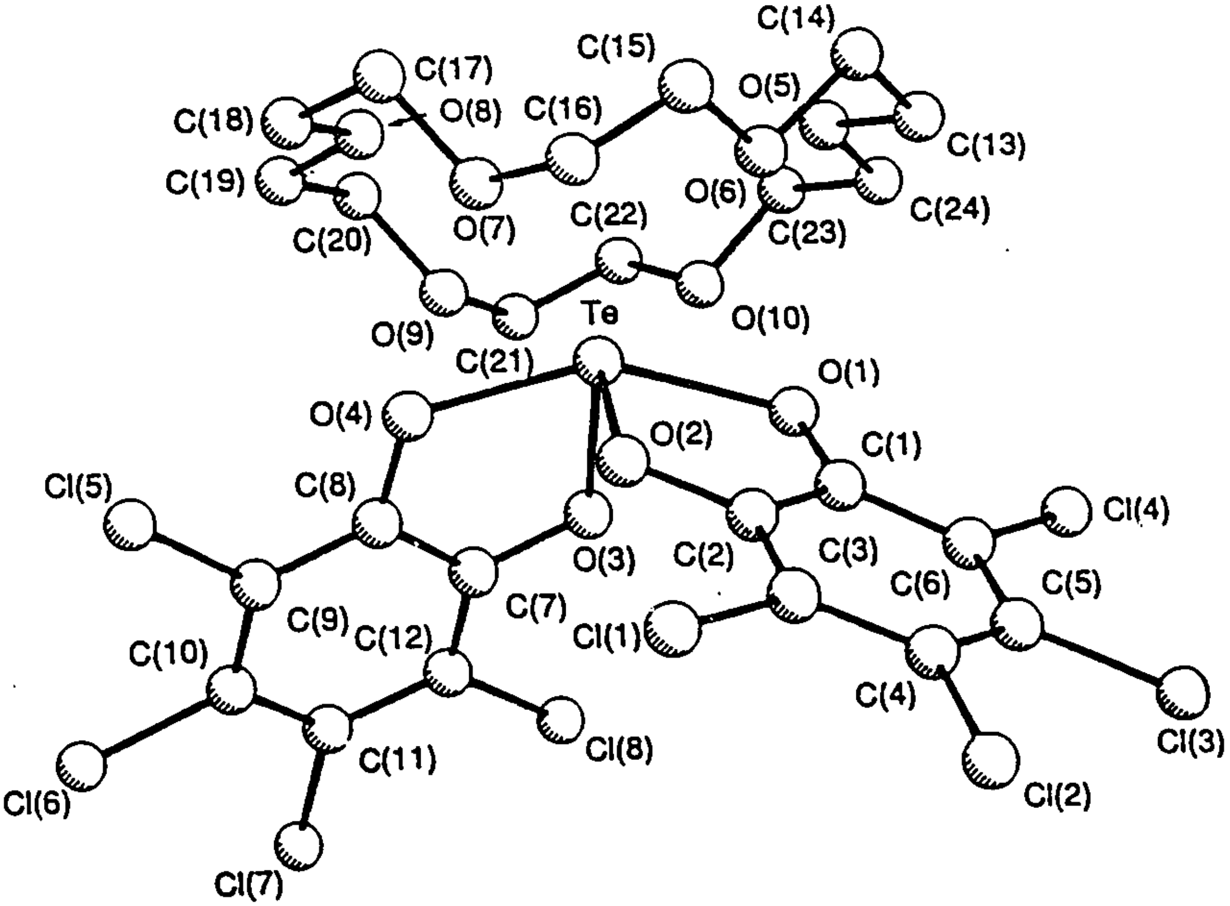
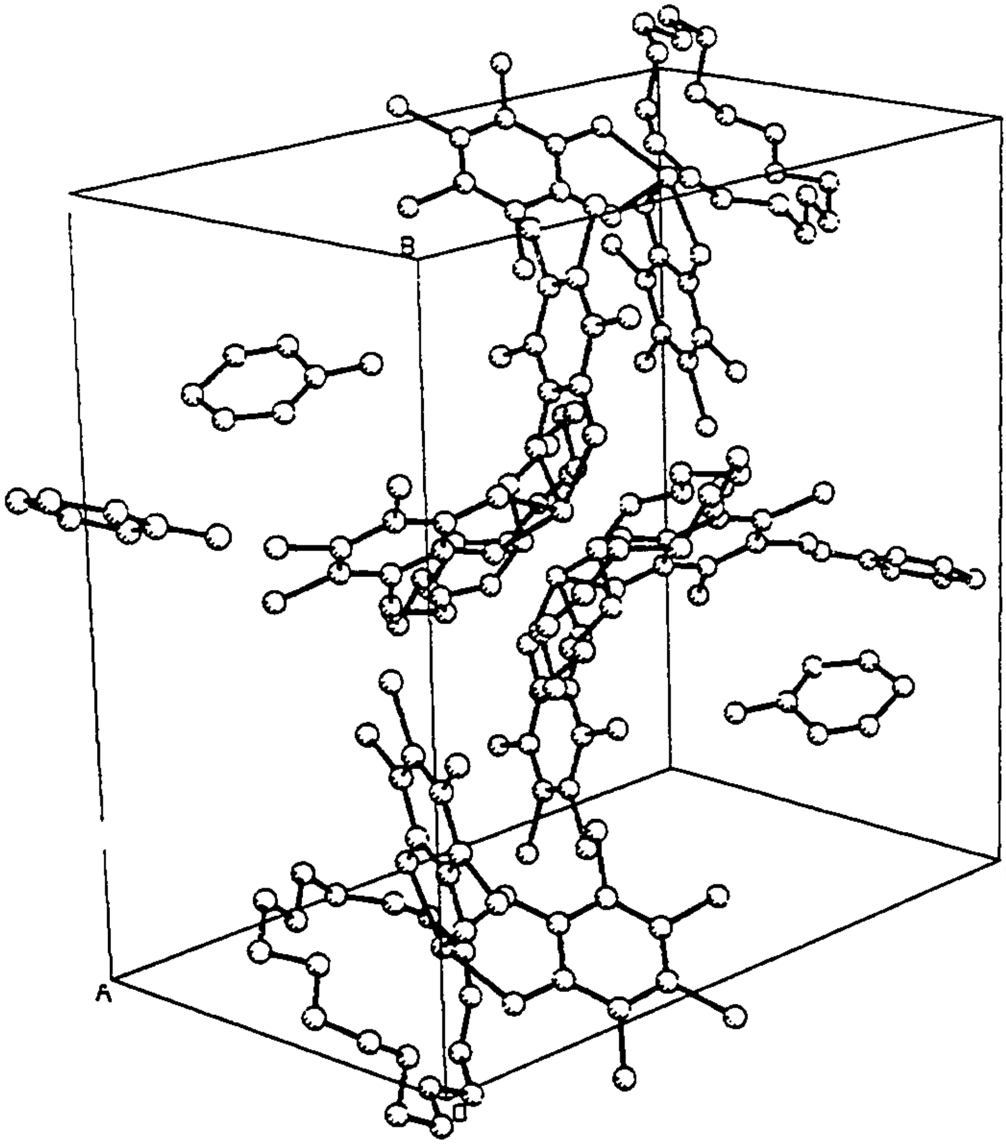


FIGURE 3.8

Cell Packing Diagram of the $Te(O_2C_6Cl_4)_2 \cdot$18-crown-6 Adducts (3.2), Hydrogen Atoms have been Omitted for Clarity



pyridine(C,N,O)tellurium trichloride[153] and 2-(2-pyridyl)phenyltellurium tribromide[154] both involve donation from a nitrogen heterocycle to a tellurium(IV) centre, but in each case the bond distances [2.402(3) and 2.244(14) Å respectively] are considerably smaller than the average value of 2.868 Å in **3.1**. This comparison clearly implies a weak ligand-metal interaction, and the other unusual feature, the small N-Te-N bite angle of 56.1(2)°, which is considerably lower than the values of *ca.* 78° found in the conventional complexes of this ligand, is in keeping with this conclusion. The Te-N(2)-C(2')-C(2)-N(2) ring is planar (mean deviation from planarity of 0.1 Å). The dihedral angles between the three five-membered rings at tellurium are [TeO(1)O(2)]-[TeO(3)O(4)] 91.1, [TeO(1)O(2)]-[TeN(1)N(2)] 163.9 and [TeO(3)O(4)]-[TeN(1)N(2)] 75.2°. The overall effect is that the structure has a large and apparently unoccupied volume above the rough plane defined by Te, O(1), O(2), N(1), N(2) and O(3), and it seems resonable to accept this as evidence of the presence of a stereochemically active lone pair of electrons implied by the AX_4E formulation. The stereochemistry of the interaction between this kernel and 2,2-bipyridine does not correspond to any obvious coordination mode, and it may well be that this is a weak electrostatic interaction between the bipyridine nitrogen and the central tellurium atom.

In the case of $Te(O_2C_6Cl_4)_2$·18-crown-6, **3.2**, the stereochemistry of the tellurium-catecholate interaction is similar to that in **3.1**, and in $Te(O_2C_6H_4)_2$, with two Te-O bonds [O(1),O(4)] in the apical sites being significantly longer (av. 2.052 Å) than those in the equatorial plane (average 1.97 Å). The various O-Te-O angles are also close in value to those in the two previous structures, and the TeO_2C_2 rings are planar, with a dihedral angle of 86.4° between them.

The most striking feature of the stereochemistry of **3.2** is the very large distances between Te and the oxygen atoms of the cyclic polyether, ranging from 2.980(7) to 3.517(8) Å. It is therefore of interest to compare the present structure with other complexes of large metal atoms with 18-crown-6. Complexes formed from macrocyclic polyethers (crown ethers) and p-block elements have been little studied relative to those containing other elements or organic acceptor molecules. The question of M-O distances in complexes with 18-crown-6 has been discussed by Drew and Nicholson[155-157] in terms of a newly developed molecular mechanics method; they have calculated that for cationic heavy-element species the D_{3d} conformation of the ligand is at an energy minimum for M-O bond distances of 2.85 Å, as seen the mean M-O distances 2.80, 2.75, 2.85 and 2.75 Å for K^+, Cd(II), Hg(II) and Pb(II) complexes respectively. These mono- or divalent metal ions are solely bound to the macrocycle in a molecular cation; distortion will then arise if the ions are either too small or too large, as seen in the structures of either Na^+ or Ce^+ and Rb^+ complexes, or if the polyether is forming a molecular adduct, as is the case with $BiCl_3$,[157] or with $SbCl_3$ and 15-crown-5 (1,4,7,10,13-pentaoxacyclopentadecane) in which the crown ether molecules are irregular. These complexes have been described in terms of the metal atoms being sandwiched between three chlorines on one side and the crown ether oxygen atoms on the other.[157] They have proposed the major factor governing the choice of the neutral discrete $SbCl_3$·15-crown-5 adduct and ionic (15-crown-5)$_2$$Sn^{2+}$- $(SnCl_3^-)_2$ is the difference in their ionisation energy, since the Sn^{2+} and Sb^{3+} cations are isoelectronic. The compound 3.2 is clearly an adduct, with considerable distortion of the cryptand ring, and a distribution of Sb-O bond distances, which is not very different from that in $BiCl_3$·18-crown-6, in which the bismuth is sandwiched between three chlorines and six oxygens, is evidence that the stereochemical activity of the lone pair is retained, and a parallel argument can clearly be made for $Te(O_2C_6Cl_4)_2$·18-crown-6. The even larger ionisation energy for Te^{4+} than Sb^{3+} should contribute significantly in precluding complex ionic species. This approach is strengthened by the orientation of the cryptand. A plane defined by the oxygen atoms O(6), O(7), O(9) and O(10) makes dihedral angles of 45.9° with the TeO(1)O(2) ring, and 40.8° with TeO(3)O(4), implying that a vector through the presumed lone pair is almost normal to this O(6)-O(10) plane. Nevertheless, the large Te-O distance to these oxygen atoms brings into question the nature of the bonding interaction, as this is normally understood. Perhaps the only reasonable conclusion is that in this molecule, as in Te(dbc)$_2$(bipy), the structure provides evidence of the stereochemical features expected from a molecule with a lone pair of electrons.

CHAPTER 4

THE OXIDATION OF ELEMENTAL ANTIMONY BY SUBSTITUTED *O*-BENZOQUINONES

4.1 Introduction

In Chapters 2 and 3, we examined the oxidation reaction between substituted *o*-benzoquinones with elemental phosphorus and tellurium as well as their low oxidation state species. The reaction products have been identified as corresponding catecholato derivatives in both systems. Although elemental phosphorus or phosphorus(III) compounds are readily oxidised to the highest oxidation state P(V) compounds, tellurium and tellurium(II) compounds can only be oxidised to Te(IV) compound. This may result from the inert $5s^2$ electron pairs on the tellurium atom.

The oxidation of low-oxidation state compounds of Main Group elements, and of the elements themselves, by substituted *o*-benzoquinones has been of research interest in this laboratory over recent years. Among these studies, the fourth row elements Cd, In, Sn and Te, and their low oxidation compounds have been the most widely studied set in the Periodic Table. In each case, the mechanism involves a one-electron process as the first step in the reaction. The *o*-quinones clearly are a favourable case for the identification of such processes, due to the thermodynamic stability of the *o*-semiquinones and the ready spectroscopic identification in these investigations.

Considering all these facts it therefore seemed logical to investigate the reaction between *o*-quinones and elemental antimony, or antimony(III) compounds. Antimony is a fourth row group 5A element, atomic number 51, with the outer electronic configuration $5s^25p^3$. It is a neighbour of tellurium and a congener of phosphorus in the Periodic Table. Antimony compounds containing bidentate oxygen, nitrogen and especially sulfur donor ligands have been of some interest over the years, particularly because of the information they provide on the coordination chemistry of antimony. The reactive antimony trichloride or organoantimony halides were usually used as the starting material in these reactions which involve either bases or an alkali salt of the corresponding ligand in many cases.[159,160] For example, acetylacetone, 8-hydroquinoline, salicylaldehyde, o-hydroxy-acetophenone and 2-hydroxynaphthaldehyde HL have been employed by Jha and co-workers.[161]

$$R_3SbBr_2 + NaL \rightarrow R_3Sb(OMe)L + 2NaBr$$

The interesting series of $Sb(S_2CNR_2)_3$, $Sb[S_2P(OR)_2]_3$ and bis(quinolin-8-olato)Sb(O-ethylxanthato) complexes were also prepared in similar routes.[162-164] The well-characterized $[Ph_3Sb(O_2C_6H_4)]_2H_2O$ and $[Ph_3Sb(Cl)(O_2C_{10}H_6)]^-[Et_3NH]^+$ are good examples of antimony catecholate compounds.[165]

In this chapter we will present our results on the oxidation of elemental antimony and triphenyl antimony by substituted *o*-benzoquinones. In the event, we find some aspects of these systems which are similar to those involving phosphorus, but equally others in which the better analogy is to tellurium. The structure of an interesting five-coordinated antimony(III) compound Sb(dbc)(bipy)•0.5bipy which we solved during this work will also be presented.

4.2 Experimental

4.2.1 General

All reagents, including elemental antimony (Aldrich) and triphenyl antimony (Aldrich) were reagent grade or better, and used as supplied. Solvents were purified and dried by standard procedures. Reactions were carried out in an atmosphere of dry nitrogen, using conventional techniques for handling potentially air-sensitive materials.

The instruments and procedures for elemental analysis and spectroscopic studies were described in chapter one. The analytical results are present in Table 4.1.

4.2.2 Reaction of Antimony with *o*-Quinones

When antimony powder (0.061 g, 0.5 mmol) was added to a stirred solution of *o*-$O_2C_6X_4$ (X = Cl, 0.369 g, 1.5 mmol; X = Br, 0.636 g, 1.5 mmol) in Et_2O (25 cm^3), a slow reaction ensued. After *ca.* 10 h, the antimony was consumed, and the solid product remaining (colourless for X = Cl, yellow for X = Br) was collected by filtration, washed carefully with n-hexane (2 x 10 cm^3), and dried *in vacuo*. The products were identified by elemental analysis as $Sb(O_2C_5Cl_4)_{2.5}\cdot 1.5Et_2O$ and $Sb(O_2C_6Br_4)_{2.5}\cdot Et_2O$. The yields are *ca.* 90% based on these formulae. In each case, the infrared spectrum showed the absence of ν(C=0) of the parent *o*-quinone. The ^1H NMR spectra in $(CD_3)_2SO$ confirmed the presence of Et_2O (1.07, t, 3H; 3.36, q, 2H, relative to TMS, $\delta = 0$), as did the ^{13}C spectra (δ = 64.85, 15.0 ppm, relative to TMS, $\delta = 0$). In addition, the ^{13}C spectra had features found in other tetrahalogenocatecholate complexes.[73,74]

When toluene or hexane was used as solvent, these reactions did not work well, there were usually still a quite large percentage grey antimony metal powder left (compared to the amount of antimony added) after 24 h reactions.

There were no identifiable reactions when a suspension of the antimony powder either in toluene or in diethyl ether were treated with dbbq at room temperature.

4.2.3 Attempted Reaction of Antimony Trichloride with *o*-Quinones

The reaction between antimony trichloride (1 mmol, 0.228 g) with tetrachloro-*o*-benzoquinone (1 mmol, 0.246 g) in thf (30 cm^3) gave a very viscous syrupy material, due probably to the chain structure of the product. This system was not studied further.

TABLE 4.1

Analytical Results of Antimony Catecholate Compounds (%), with Calculated Values in Parentheses

	Sb	C	H
$Sb(O_2C_6Cl_4)_{2.5}\cdot 1.5Et_2O$	13.9 (14.4)	30.0 (29.8)	2.12 (1.78)
$Sb(O_2C_6Br_4)_{2.5}\cdot Et_2O$	10.0 (9.70)	17.9 (18.2)	1.14 (0.80)
$Sb(O_2C_6Cl_4)Br$	26.7 (27.2)	-	-
$Sb(O_2C_6Br_4)Br$	18.8 (19.5)	-	-
$Sb(O_2C_6Cl_4)I$	25.6 (24.6)	15.0 (14.6)	-
$Sb(O_2C_6Br_4)I\cdot 0.5Et_2O$	16.8 (17.2)	13.4 (13.5)	0.72 (0.71)
Sb(dbc)I	26.2 (26.0)	-	-
Sb(dbc)I(bipy)	19.7 (19.5)	-	-
Sb(dbc)I(phen)	18.0 (18.8)	-	-
Ph_3Sb(dbc)	21.8 (21.2)	66.4 (67.0)	6.43 (6.15)
$Ph_3Sb(O_2C_6Cl_4)$	21.3 (20.3)	-	-
$Ph_3Sb(O_2C_6Br_4)$	16.4 (15.9)	-	-

4.2.4 Reaction of Antimony + Bromine + *o*-Quinones

(i) Bromine (0.240 g, 1.5 mmol Br_2) was weighed into a Schlenk flask containing diethyl ether (30 cm^3), the contents cooled to -78°C, and antimony powder (0.365 g, 3 mmol) and *o*-O2C-$_6$Cl$_4$ g, 3 mmol) added under nitrogen. The mixture was stirred at this temperature; after *ca.* 5 min, the formation of a white solid was apparent, and after 6 h, all the antimony had been consumed. The mixture was allowed to reach ambient temperature, and the product collected by filtration, washed carefully with diethyl ether (2 x 10 cm^3), and dried *in vacuo*. The analytical results identified the product as $Sb(O_2C_6Cl_4)Br$. The yield was quantitative, as was that of $Sb(O_2C_6Br_4)Br$ in an identical experiment. The ^{13}C NMR resonances and the infrared spectra of these products confirmed the presence of the substituted catecholate ligand.

4.2.5 Reaction of Antimony + Iodine + *o*-Quinones

4.2.5.1 Tetrahalogeno-*o*-Quinones

Antimony powder (0.121 g, 1 mmol) was suspended in a solution of *o*-$O_2C_6X_4$ (X = Cl, 0.246g, 1 mmol; X = Br, 0.424 g, 1 mmol) in diethyl ether (30 cm^3), and solid iodine (0.127 g, 0.5 mmol as I_2) added. After about 5 min, the colour of the solution changed to light red, and the suspension turned pale yellow. After 10 h at room temp, with mechanical agitation, the antimony had dissolved; the volume of the now pale yellow solution was then reduced to *ca.* 10 cm^3 *in vacuo*, and the resultant pale yellow precipitate collected by filtration and washed carefully with n-hexane (2 x 5 cm^3). The analytical results of the products agreed with the formulas $Sb(O_2C_6X_4)I.nEt_2O$ (X = Cl, n = 0; X = Br, n = 0.5). These products were obtained in yields of 83% (X = Cl) and 92% (X = Br). The ^{13}C NMR spectrum of the latter also had the characteristic features of Et_2O (resonances at 64.9 and 15.2 ppm).

4.2.5.2 3,5-Di-tert-butyl-*o*-quinone (dbbq)

The procedure was essentially identical to that just described, except that the period to the detectable onset of the reaction (30 min) and the total time required (24 h) indicate a more sluggish reaction. It was necessary to reduce the volume of the final solution to *ca*. 5 cm^3 and to add n-hexane (30 cm^3) in order to precipitate the product completely. The pale yellow solid was dried *in vacuo* for 2 days, and identified as Sb(dbc)I. Yield 80%. In this compound, the ^1H and ^{13}C NMR spectra identified each of the benzenoid carbon atoms and those of the t-butyl groups as well as their corresponding hydrogen atoms.

4.2.6 Adducts of Sb(dbc)I

A solution of Sb(dbc)I in diethyl ether was prepared by the method just described in the previous section (1 mmol product in 30 cm^3 diethyl ether), and an equimolar quantity of solid 2,2′-bipyridine (bipy, 1 mmol) was added. The mixture was stirred for 8 h at room temperature, during which time a yellow precipitate formed. This was collected by filtration and dried *in vacuo*, and identified as Sb(dbc)I(bipy) by its analytical result. The yield was quantitative. The structure of this compound was subsequently the subject of an X-ray crystallographic study. An analogous adduct with 1,10-phenanthroline was also prepared by the same method and was identified as Sb(dbc)I(phen) by the analytical results.

4.2.7 Reaction of Triphenylantimony with *o*-Quinones

(i) In each experiment, Ph_3Sb (0.353 g, 1 mmol) in toluene (20 cm^3) was added dropwise to an equimolar solution of the *o*-quinone (*o*-$O_2C_6X_4$, X = Cl or Br; dbbq) in the same solvent (20 cm^3). A colour change was apparent within a few seconds for *o*-$O_2C_6X_4$, and a few minutes for dbbq. After 4 h of mechanical stirring, the volume was reduced to *ca*. 5 cm^3 *in vacuo* and light petroleum ether (30 cm^3) added to precipitate a colourless solid which was collected and dried *in vacuo*. The analytical results of these compounds are consistent with the formulae $Ph_3Sb(cat)$ (cat = $O_2C_6X_4$ catecholate, X = Cl or Br; and cat = dbc). The yields of these $Ph_3Sb(cat)$ compounds were essentially quantitative.

(ii) Other experiments were not as successful as those just described. When equimolar quantities of Ph_3Sb and anthraquinone were mixed in toluene at room temperature, a pale yellow solution resulted; this quickly became dark green and then yellow over a period of 12 h. The mixture was refluxed for 30 min, toluene removed *in vacuo* (90%), and n-hexane added. The resultant yellow precipitate could not be identified; the infrared spectrum showed the presence of C=0 groups. For the reaction between Ph_3Sb and benzil, the material isolated after refluxing in toluene included unreacted di-ketone as shown in its IR spectrum. None of these systems was investigated further.

4.2.8 Reaction of Ph_3Sb with 1,2-Naphthaquinone

When Ph_3Sb and 1,2-naphthaquinone were mixed in toluene, there was no sign of reaction in room temperature. After the solution was refluxed, its colour changed from yellow-brown to purple-blue and a dark-blue precipitate yield shortly (*ca.* 20 minutes). After being refluxed overnight, the reaction mixture was cooled to room temperature. The dark-blue solid was collected by filtration and dried *in vacuo*. The yield is almost quantitative. This product was confirmed as paramagnetic compound by its ESR spectrum. The elemental analysis is close to that required for $Ph_3Sb(O_2C_{10}H_6)$, Sb 22.5(23.4), C 64.6(65.8) and H 3.92(4.14).

4.3 Results and Discussion

4.3.1 Synthetic Methods

There are a large number of antimony(III) compounds based on bidentate oxygen, nitrogen and especially sulfur donor ligands. As we mentioned in the Introduction, the reactive antimony trichloride or organoantimony halides were usually used as the starting material in these reaction and often involved either bases or an alkali salt of the corresponding ligand in many cases.[166] On the contrary, the synthetic methods in this work are high yield one-pot reactions involving commercially available stable chemicals. The Sb(dbc)I prepared in this work might be a very good precursor for further investigations on antimony(III) compounds due to its high solubility in diethyl ether and the presence of the reactive Sb-I bond.

The interaction of elemental antimony with substituted *o*-quinones makes an interesting contrast with the case of phosphorus, which reacts only in the presence of bromine to give $P(cat)_2Br$.[112] Although the reactions between antimony element with *o*-$O_2C_6Cl_4$ in toluene or n-hexane are very limited, there is a slow reaction with *o*-$O_2C_6X_4$ in diethyl ether at room temperature (*ca.* 23 °C). The cause of this marked solvent effect is not clear, but may be due to a slight solubility of the element in diethyl ether.[167] The easy initiation of these reactions perhaps also reflects the higher metallic property of antimony compared with phosphorus. The products of the reaction are antimony(V) compounds whose structure has not been determined, but which can be written tentatively as the ionic species $[Sb(O_2C_6X_4)_2L_n]^+[Sb(O_2C_6X_4)_3]^-$ which is favourable in solid state by lattice energy consideration, ($L = Et_2O$; $X = Cl$, $n = 2$, $X = Br$, $n = 1$). This formulation is in keeping with earlier work by Hall and Sowerby[165] on the compound $[Ph_3Sb(O_2C_6H_4\text{-}o)(H_2O)][Ph_3Sb(O_2C_6H_4\text{-}o)]$, which demonstrated that antimony(V) species of differing coordination numbers can co-exist in a crystalline lattice. Another possibility would be a polymer linked by bridging $O_2C_6X_4^{2-}$ groups. Even though this coordination mode of catecholate ligands is only a proposed structure feature for some Main Group compounds,[168] it has been identified in the structures of many transition metal complexes[169] by X-ray crystallographic method.

In the presence of bromine, the reaction products are the antimony(III) compounds Sb(cat)X (X = Br or I), different again from the corresponding phosphorus reaction which yielded $P(O_2C_6R)_2Br$ ($R = Cl_4$, Br_4 and $Bu^t_2H_2$) for each of the *o*-quinones in question.[112] The +5 state of antimony is generally stable and accessible, and the isolation of these lower oxidation species may be due to the precipitation of a stable oligomeric species which resists further oxidation; such species are an important feature of antimony(III) chemistry.[170] For example, the oxyfluoride SbOF has a trigonal bipyramidal structure about antimony with three oxygens, one fluorines and one lone pair. This compound may exist in either a ladder or a layered structures. The oxychloride SbOCl and oxyiodides $Sb_lO_mI_n$ (l = 3, m = 4 and n = 1; l = 8, m = 11 and n = 2) also exist in the layered structures.[171] It has also been reported that $Sb_4O_5Cl_2$ has sheets of Sb-O layers, with one half of the Sb in SbO_3 coordination and another half in SbO_4.[172] Finally we note that the oxidation of Ph_3Sb by *o*-quinones leads to the antimony(V) analogues of Ph_3P(cat) species reported earlier,[81,93,112] and the mechanism of this reaction is discussed below.

It is perhaps not surprising that dbbq did not react with elemental antimony under the same conditions, since it is a weaker oxidant than the tetrahalogeno-*o*-benzoquinones. The failure of reactions between triphenyl antimony with other α-diketones may also have resulted from the lower oxidation ability of these oxidants. It seems there are some differences between the antimony chemistry and the phosphorus chemistry in this aspect. While weak oxidative reagents such as benzil can easily oxidise phosphorus(III) compounds,[173] such oxidants failed in our experiments. Holmes *et al.* also reported[174] similar results. In their experiments phenyl(2,2′-diphenylene)stibine could be oxidized by tetrachloro-o-benzoquinone, but the reaction with benzil yielded only the starting materials. They suggest that the presence of electronegative groups on the α-diketone is necessary for such reactions to proceed.

4.3.2 Spectroscopic Results

The formulas of the products based on their elemental analyses are further supported by their ^1H and ^{13}C NMR resonances as well as the integrations in their ^1H NMR spectra. Details of the ^1H and ^{13}C NMR resonances of these products are summarized in Tables 4.2 and 4.3 respectively. The IR spectra of these products are summarized in Table 4.4. Figs. 4.1 and 4.2 show the NMR and IR spectra of a typical antimony catecholate compound prepared in this work.

The ^{13}C NMR spectra of each of the compounds prepared confirm that all of these are based on substituted catecholate ligands, by comparison with the results for compounds with other elements. Equally important is that the ν(C-O) infrared frequencies are in the range 1200-1400 cm^{-1}, substantially lower than ν(C=O) in the original *o*-quinones. The numerical values are close to those reported in previous chapters. The ^{1}H NMR spectra confirm the presence of the Ph-groups in the appropriate systems, with typical multiplets in the 7.4-7.8 ppm region. For the phen or bipy adducts, the existence of to these ligands are easily confirmed by their characteristic downfield resonances in the ^{1}H NMR spectra. Their ^{13}C NMR spectra also show clear similarity to other metal bipy or phen complexes.

As observed in Chapter 2, there are also some interesting correlations that can be seen in the ^{13}C NMR spectra of the antimony $O_2C_6X_4$ catecholate derivatives (X = Cl or Br). $C^{3,6}$ and $C^{4,5}$ are consistently more deshielded for X = Cl, but this effect is reversed at $C^{1,2}$. Another interesting feature is the sequence at $C^{1,2}$ for different groups of antimony compounds. For Sb(III) compounds, this sequence is $Sb(O_2C_6X_4)Br < Sb(O_2C_6X_4)I$, while it is $Sb(O_2C_6X_4)_{2.5} < Ph_3Sb(O_2C_6X_4)$ for Sb(V) compounds. These results may suggest the effect of electro-negativity on the deshielding of these carbon nuclei.

4.3.3 The Lewis Acidity of Antimony(III) Compounds

It is interesting that Sb(III) compounds are weak acceptors, as well as being electron pair donors, and this dichotomy is presumably responsible for the oligomerisation which often occurs in antimony(III) compounds. It has been reported that antimony(III) halides form complexes with Lewis bases as well as aromatic hydrocarbons such as naphthalene or p-xylene.[175] They are

TABLE 4.2

^{1}H NMR of Antimony Catecholate derivatives;

Values in ppm Relative to TMS$_4$ ($\delta = 0$)

Compound	Solvent	Chemical shift	Assignment
dbbq	$(CD_3)_2SO$	1.18(s), 1.21(s) 18H	Bu^t
		6.13(d), 6.96(d) 2H	H^{4,6} of dbc
Sb(dbc)I	$(CD_3)_2SO$	1.21 (s), 1.41 (s), 18H	Bu^t
		6.53-6.73 (m) 2H	H^{4,6} of dbc
Sb(dbc)I(bipy)	$(CD_3)_2SO$	9.20 (dd, 2H), 8.75 (dd, 2H)	
		8.16 (s, 2H), 7.98 (dd, 2H)	bipy
		6.56-6.66 (m), 2H	H^{4,6} of dbc
		1.30 (s), 1.20 (s), 18H	Bu^t
Sb(dbc)I(phen)	$(CD_3)_2SO$	9.20 (dd, 2H), 8.73 (dd, 2H)	
		8.14 (s, 2H), 7.97 (dd, 2H)	phen
		6.57 (d), 6.67 (d), 2H	H^{4,6} of dbc
		1.32 (s), 1.21 (s), 18H	Bu^t
$Ph_3Sb(O_2C_6Cl_4)$	$(CD_3)_2SO$	7.58 (m, 2H), 7.46 (m, 3H)	Ph
$Ph_3Sb(O_2C_6Br_4)$	$(CD_3)_2SO$	7.59 (m, 2H), 7.46 (m, 3H)	Ph
Ph_3Sb(dbc)	$CDCl_3$	7.77 (m), 7.45 (m), 15H	Ph
		6.98 (s), 6.72 (s), 2H	H^{4,6} of dbc
		1.30 (s), 1.44(s), 18H	Bu^t

TABLE 4.3

^{13}C NMR Spectra of Antimony Catecholate Derivatives

Values in ppm Relative to TMS ($\delta = 0$)

(a) Tetrahalogenoquinone derivatives

		Diolato			Ph and Others
Compound	Solvent	$C^{1,2}$	$C^{3,6}$	$C^{4,5}$	
o-$O_2C_6Cl_4$	$(CD_3)_2SO$	168.8	143.7	131.9	
o-$(HO)_2C_6Cl_4^*$	$(CD_3)_2CO$	143.0	122.5	119.5	
$Sb(O_2C_6Cl_4)_{2.5}$	$(CD_3)_2SO$	142.4	121.8	116.9	
$Sb(O_2C_6Br_4)_{2.5}$	$(CD_3)_2SO$	144.1	117.4	110.1	
$Sb(O_2C_6Cl_4)Br$	$(CD_3)_2SO$	143.0	122.4	117.4	
$Sb(O_2C_6Br_4)Br$	$(CD_3)_2SO$	145.9	117.7	110.9	
$Sb(O_2C_6Cl_4)I$	$(CD_3)_2SO$	150.2	118.5	116.8	
$Sb(O_2C_6Cl_4)I$	$(CD_3)_2SO$	151.0	114.2	110.6	
$Ph_3Sb(O_2C_6Cl_4)$	$(CD_3)_2SO$	146.2	117.7	115.2	142.5, 128.9-133.9 (Ph)
$Ph_3Sb(O_2C_6Br_4)$	$(CD_3)_2SO$	147.5	112.7	108.6	142.5, 128.8-133.9 (Ph)

(b) dbbq derivatives

Compound	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}
dbbq^a	179.7	180.5	162.5	133.4	148.9	121.7	35.7	35.0	29.0	27.5
dbc^a	141.4	144.3	140.0	113.1	134.5	110.2	34.4	33.8	31.5	29.5

$Ph_3Sb(dbc)^{b}$	146.7	139.6	138.0	112.5	133.2	107.8	34.7	34.4	31.8	29.7
	143.0 129.2-135.1 (Ph)									
$Sb(dbc)I^{a}$	151.4	147.9	140.5	112.6	135.1	110.5	34.5	34.2	32.0	29.8
$Sb(dbc)I(bipy)^{a}$	151.8	148.2	139.3	111.6	134.4	110.1	34.2	33.8	31.8	29.7
	155.1, 149.1, 137.4, 124.2 and 120.5 (bipy)									
$Sb(dbc)I(phen)^{a}$	151.8	148.2	139.3	111.6	134.4	110.1	34.2	33.8	31.8	29.7
	148.8, 142.1, 138.7, 129.0, 127.1 and 124.4 (phen)									

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a solvent = $(CD_3)_2SO$

b solvent = $CDCl_3$

* results from ref. 89

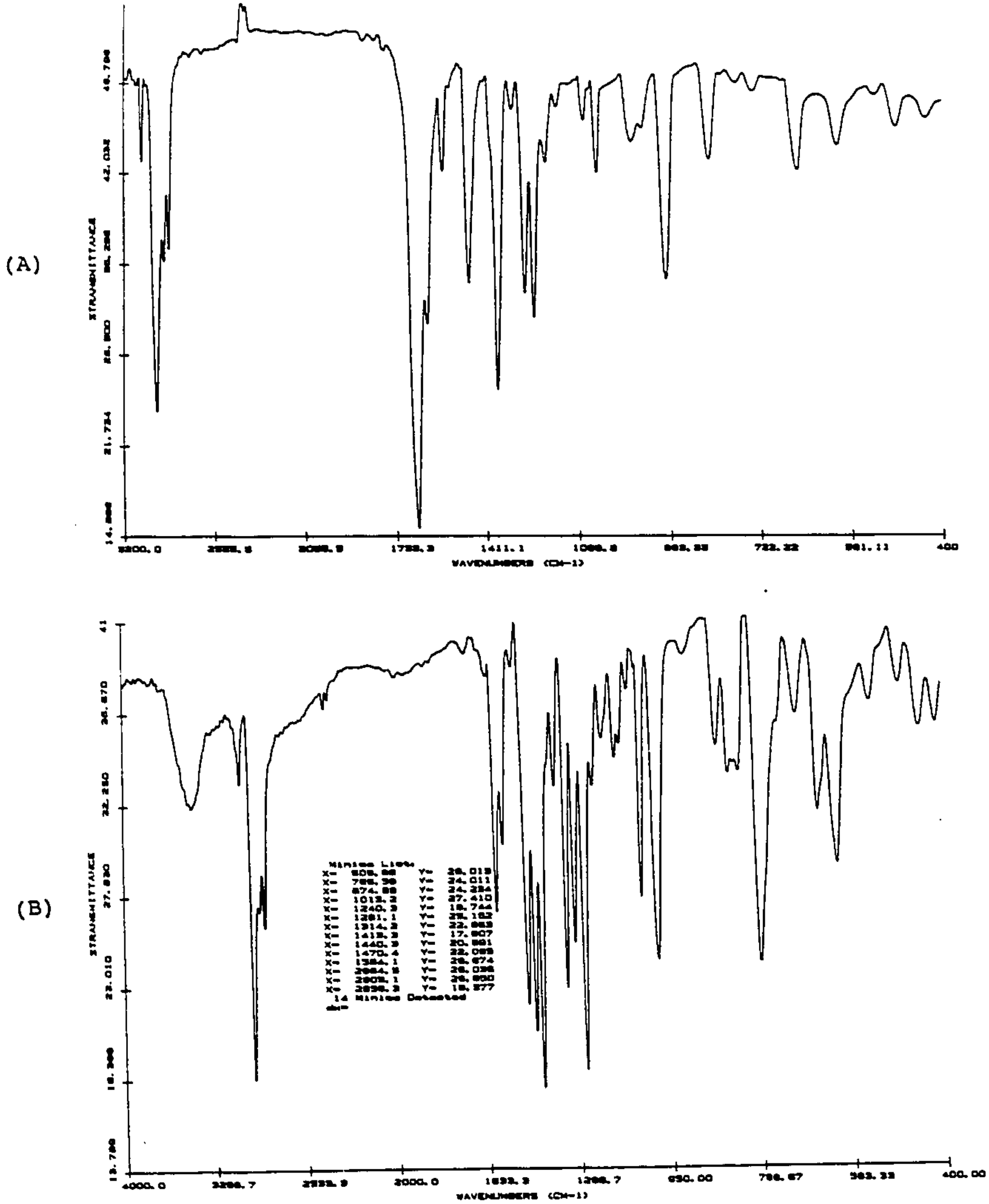
TABLE 4.4

Diagnostic IR Absorptions of Antimony Catecholate Derivatives

Compound	Absorptions ν_{max} (cm^{-1})	Assignment
o-$O_2C_6Cl_4$	1673(s)	C=O
$Sb(O_2C_6Cl_4)_{2.5}\cdot(Et_2O)_{1.5}$	1417(vs, br), 1240(m)	C-O
	2924(w)	C-H (Et)
$Sb(O_2C_6Br_4)_{2.5}\cdot(Et_2O)$	1408(vs, br), 1228(m)	C-O
	2925(w)	C-H (Et)
$Ph_3Sb(dbc)$	1418(vs), 1244(s)	C-O
	3058(w)	C-H (Ph)
	2960, 2932, 2906, 2867(w)	C-H (Bu^t)
Sb(dbc)I	1412(vs), 1237(s)	C-O
	3029(w)	C-H (Ph)
	2964, 2933, 2906, 2873(w)	C-H (Bu^t)
Sb(dbc)I(bipy)	1413(s), 1240(s)	C-O
	2956, 2905, 2865(w)	C-H (Bu^t)
Sb(dbc)I(phen)	3044 (w)	C-H (aromatic)
	2956 (s), 2906 (m), 2967 (m)	C-H (Bu^t)
	1418 (s,br), 1241 (m)	
$Sb(O_2C_6Cl_4)I$	1422 (vs,br), 1245 (m)	C-O
	2973 (w), 2882 (w)	C-H (Et)
$Sb(O_2C_6Br_4)I\cdot0.5Et_2O$	1406 (vs,br), 1226 (m)	C-O
$Sb(O_2C_6Br_4)Br$	1406 (vs,br), 1224 (s)	C-O
$Sb(O_2C_6Cl_4)Br$	1417 (vs,br), 1240 (s)	C-O
$Ph_3Sb(O_2C_6Cl_4)$	3051 (w)	C-H (Ph)
	1436 (s), 1248 (m)	C-O

FIGURE 4.1

Infrared Spectra of (A) dbbq, (B)Sb(dbc)I(bipy) and (C) dbc



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 Minima List:
X=  505.86    Y=  29.015
X=  768.38    Y=  24.011
X=  874.88    Y=  24.224
X=  1012.2    Y=  27.410
X=  1240.3    Y=  18.744
X=  1281.1    Y=  25.162
X=  1314.2    Y=  22.863
X=  1413.3    Y=  17.807
X=  1440.3    Y=  20.881
X=  1470.4    Y=  22.085
X=  1584.1    Y=  28.674
X=  2864.8    Y=  28.036
X=  2902.1    Y=  28.800
X=  2956.3    Y=  18.577
  14 Minima Detected
dx=
```

FIGURE 4.1 *cont'd*

(C)

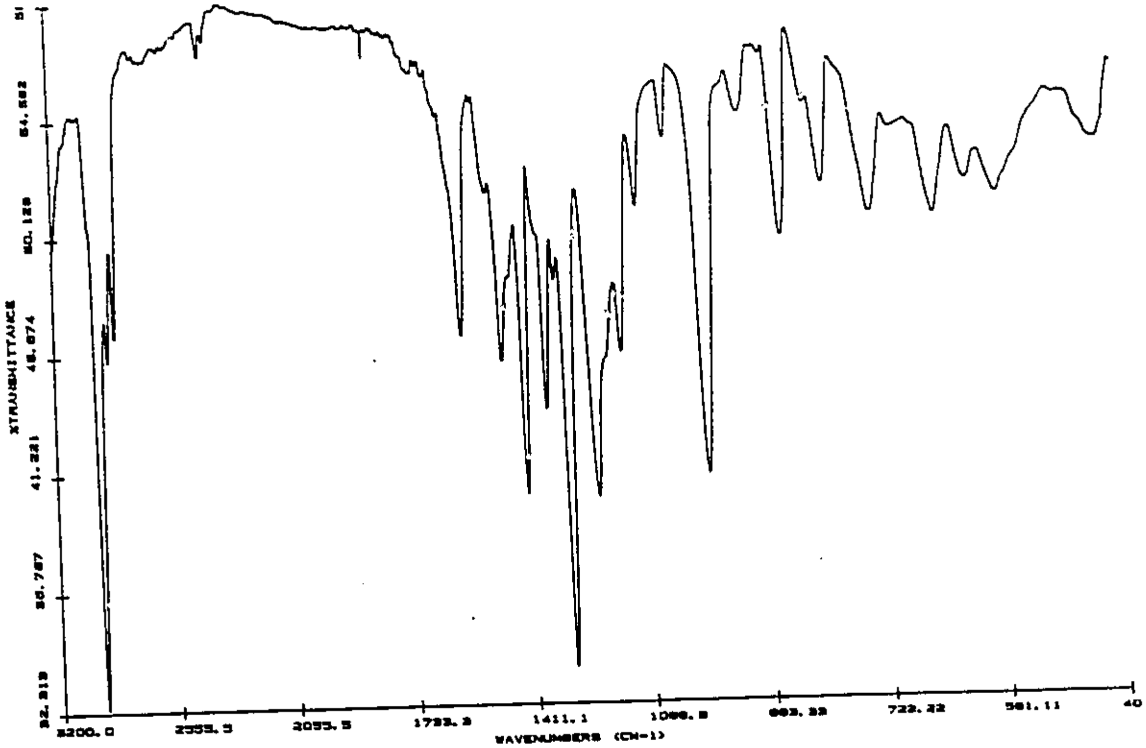
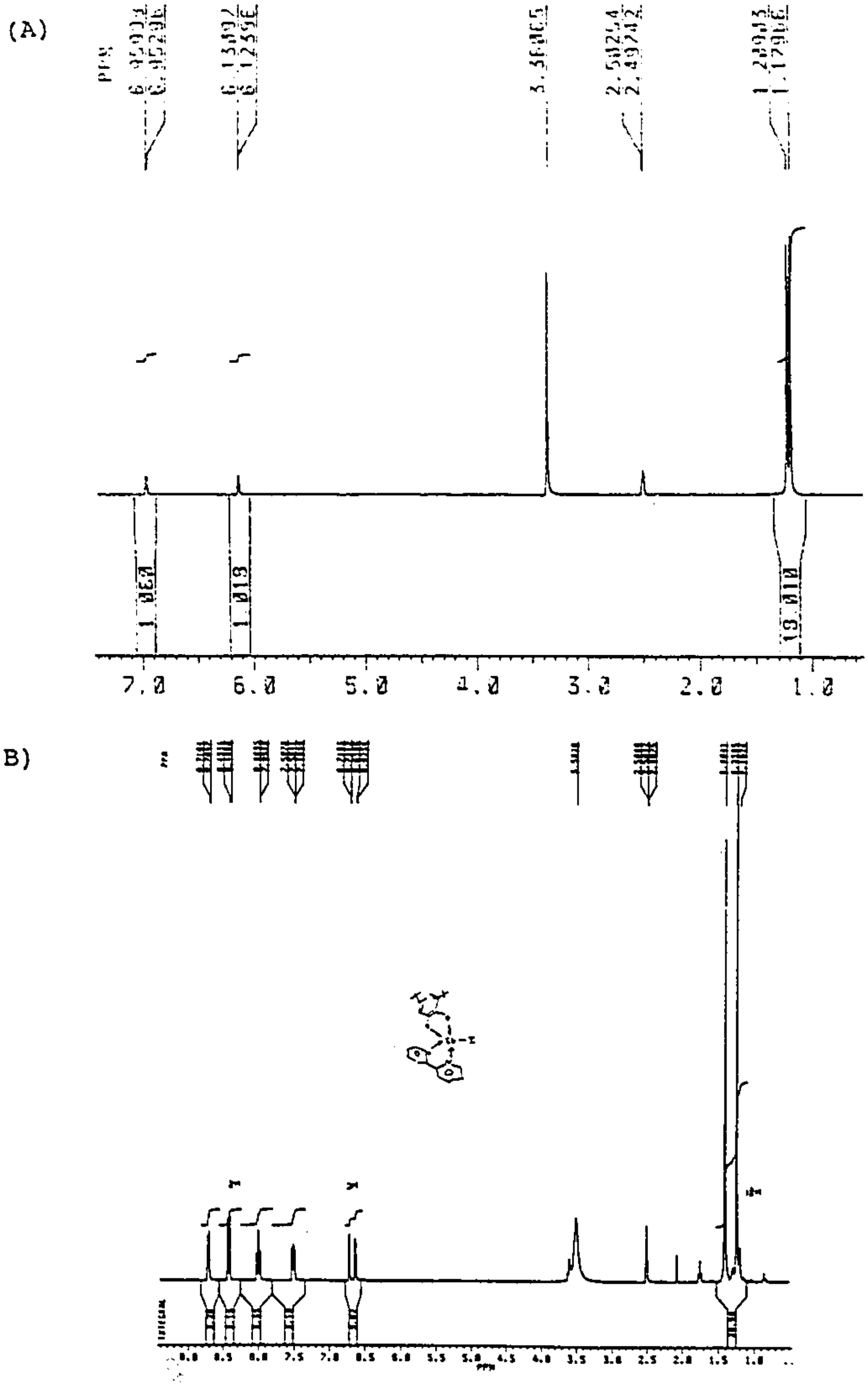


FIGURE 4.2

^{1}H NMR Spectra of (A) dbbq, and (B) Sb(dbc)I(bipy)



also powerful halide acceptors and form complexes with monovalent halides to give a variety of interesting structures. For example, $SbBr_6^{3-}$ and $Sb_2Cl_9^{3-}$ have been reported to have octahedral and confacial bisoctahedral structures, respectively.[176,177] The structure of $Sb_4F_{16}^{+}$ has also been reported. In this work, the reactions of Sb(dbc)I with the neutral bidentate donors 2,2′-bipyridine and 1,10-phenanthroline give 1:1 adducts, and the structure of Sb(dbc)I(bipy), discussed below, is clearly that of a monomer. On the other hand, the processes which give rise to crystals of this compound require more than mere dissolution and recrystallisation from DMF, since the overall change is, at the simplest,

$$2Sb(dbc)I(bipy) \rightarrow Sb(dbc)I(bipy)\cdot 0.5bipy\ (\mathbf{4.1}) + 0.5\ bipy + [Sb(dbc)I]_n \qquad (1)$$

We also observed the precipitation of a non-crystalline material, in addition to the crystals of **4.1**, and presume this to be the oligomer of the uncomplexed Sb(dbc)I, similar to that formed in the reaction between Sb + *o*-quinones + X_2. Thus it seems that the reaction products from such reactions are defined in some measure by the solid state chemistry of antimony(III), rather than by any simple consideration of ionisation energies.

4.3.4 Reaction Mechanism

There have been many studies on the organometallic and inorganic chemistry of antimony with formal valence +3 or +5, especially in the past two decades.[178,179] A great portion of these studies has been focused on the structural chemistry of the antimony complexes with different coordination numbers. Even though ligand substitution has been used extensively in the previous preparative chemistry of antimony compounds, almost no attention has been paid to the mechanistic aspects of the redox chemistry of this element. To extend our interests on the systematic studies of the Main Group metal redox chemistry, we used ESR spectroscopy to investigate the reactions of antimony element or its low oxidation state compounds with *o*-benzoquinones.

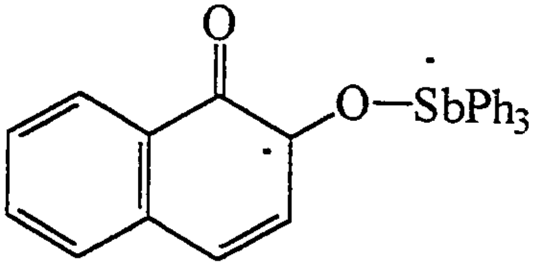
The ESR spectrum of the heterogeneous reaction mixture Sb + 2 dbbq + 1/2 Br_2 in toluene at room temperature gave a clear ESR signal, with the classical features of the dbsq$^{\bullet -}$ semi-quinone, with g = 2.0019. No fine structure was detected, and hence no coupling constants are available. Similar results emerged from the system Sb + *o*-$O_2C_6Cl_4$ in diethyl ether at room temperature. Frozen samples (77 K) showed some fine structure, with g = 2.0067, but the quality of the spectra did not allow more detailed analysis.

The reaction between Ph_3Sb and *o*-benzoquinones in toluene at room temperature is too rapid for study, but we were able to detect a weak ESR signal when solutions of the individual reactants were mixed at 77 K and allowed to warm slowly. For Ph_3Sb + *o*-$O_2C_6Cl_4$, this resonance yielded g = 2.0043. From these results we conclude that semiquinone species are involved in these reactions, and by extension generally in the oxidation of antimony, or Ph_3Sb, by *o*-benzoquinones.

The reaction between Ph_3Sb with 1,2-naphthaquinone(NQ) in toluene under refluxing condition gave a paramagnetic product with a formal composition of $Ph_3Sb(C_{10}H_6O_2$-*o*). The proposed structure of this product needs some crystallographic confirmation. Considering the features of the reactions between M(III) compounds (M = P or Sb) with *o*-quinones, one possibility of this product would be a radical structure after the first one-electron transfer occurred between Ph_3Sb and NQ as shown in Fig. 4.3.

FIGURE 4.3

Possible Structure of the Reaction Product of Ph_3Sb + NQ



4.4 Crystallographic Studies

4.4.1 Data Collection and Structure Solution

A sample of Sb(dbc)I(bipy) was dissolved in N,N-dimethylformamide, and allowed to recrystallise by slow evaporation of the solvent in air. The subsequent structure determination showed that the product of this procedure was in fact Sb(dbc)I(bipy)·0.5bipy (**4.1**), with one molecule of 2,2′-bipyridine and two molecules of Sb(dbc)I(bipy) in the unit cell.

An orange crystal of **4.1** was mounted on a glass fibre in a Rigaku AFC6S diffractometer, using MoKα radiation ($\lambda = 0.71069$ Å) and a rotating anode. Cell constants, and an orientation matrix, were obtained using 25 strong reflections in the range $30.67 < 2\theta < 34.27$. Based on packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be $P\bar{1}$. No decay corrections were needed, since the intensity of three representative reflections remained constant throughout the data collection, but analytical absorption corrections were applied and the data were also corrected for Lorentz and polarization effects. The relevant experimental details are given in Table 4.5. The structure was solved by direct methods. Non-hydrogen atoms were refined anisotropically; hydrogen atoms on carbon were initially included in ideal positions, and subsequently refined isotropically. The programmes and other data used are listed in refs. 144, 149-152, 181, 182. The convergence minimised the function $\Sigma \underline{w}(|F_o| - |F_c|)^2$, and a weighting scheme with $p = 0.003$ was used in the final cycles. The atomic coordinates are presented in Table 4.6, and the important interatomic distances and angles for the (dbc)SbI(bipy) molecule are in Table 4.7. Figure 4.4 shows the structure of this unit, and Fig. 4.5 the arrangement of Sb(dbc)I(bipy) and bipy in the unit cell.

4.4.2 Description and Discussion of the Structure of Sb($O_2C_6Cl_4$)I(bipy)

Of the compounds reported in the Experimental section, the only one which readily

TABLE 4.5

Summary of Crystal Data, Intensity Collection and

Structure Refinement for Sb(dbc)I(bipy)·0.5bipy (4.1)

Formula	$C_{29}H_{32}IN_3O_2Sb$
M	703.25
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
a/Å	9.779(4)
b/Å	18.554(7)
c/Å	8.944(3)
α/°	100.94(3)
β/°	115.11(3)
γ/°	86.82(4)
U/Å	1442(2)
Z	2
D_c/g cm^{-3}	1.62
Crystal dimensions/mm	0.3 x 0.3 x 0.1
μ/cm^{-1}	20.49
2θ/° (max)	50
Total reflections measured	5402
Unique data used [$I \geq 3\sigma(I)$]	3307
Number of parameters	325
F(000)	694
T/°C	23
R	0.044
R'	0.053
Maximum shift/error in final cycle	0.03
Maximum, minimum peaks in final difference map/e Å^{-3}	1.22, -0.91

TABLE 4.6

Final Positional Coordinates for the Non-hydrogen Atoms of (dbc)SbI(bipy)·0.5 bipy (4.1), with Estimated Standard Deviations (esd's) in Parentheses

Atom	x	y	z
I	1.14 350(8)	0.01 355(4)	0.31 448(9)
Sb	0.86 132(6)	0.08 336(3)	0.36 389(7)
O(1)	1.0 016(6)	0.1 477(3)	0.5 817(6)
O(2)	0.8 891(6)	0.1 675(3)	0.2 692(6)
N(1)	0.6 625(7)	0.1 439(4)	0.4 114(8)
N(2)	0.6 261(7)	0.0 876(4)	0.0 997(8)
N(3)	0.685(1)	0.4 901(7)	0.657(2)
C(1)	0.520(1)	0.1 436(5)	0.288(1)
C(2)	0.684(1)	0.1 699(5)	0.571(1)
C(3)	0.569(1)	0.1 958(5)	0.615(1)
C(4)	0.426(1)	0.1 943(6)	0.491(2)
C(5)	0.402(1)	0.1 664(6)	0.328(1)
C(6)	0.504(1)	0.1 174(4)	0.115(1)
C(7)	0.621(1)	0.0 621(6)	-0.051(1)
C(8)	0.491(1)	0.0 666(6)	-0.197(1)
C(9)	0.367(1)	0.0 967(6)	-0.183(1)
C(10)	0.370(1)	0.1 219(5)	-0.025(1)
C(11)	1.0 452(8)	0.2 108(5)	0.553(1)

C(12)	0.9 869(8)	0.2 207(4)	0.387(1)
C(13)	1.0 270(9)	0.2 834(5)	0.349(1)
C(14)	1.127(1)	0.3 341(5)	0.485(1)
C(15)	1.1 840(9)	0.3 241(5)	0.651(1)
C(16)	1.1 416(9)	0.2 609(5)	0.683(1)
C(17)	0.961(1)	0.2 957(5)	0.166(1)
C(18)	1.292(1)	0.3 830(6)	0.791(1)
C(19)	1.017(1)	0.3 698(7)	0.157(1)
C(20)	1.431(2)	0.392(1)	0.771(2)
C(21)	1.338(3)	0.367(2)	0.957(2)
C(22)	1.227(2)	0.455(1)	0.791(4)
C(23)	1.005(1)	0.2 371(7)	0.057(1)
C(24)	0.789(1)	0.2 992(7)	0.097(1)
C(25)	0.558(1)	0.4 716(6)	0.516(1)
C(26)	0.780(2)	0.376(1)	0.595(3)
C(27)	0.792(2)	0.442(1)	0.691(3)
C(28)	0.534(1)	0.4 056(7)	0.411(1)
C(29)	0.650(2)	0.3 539(8)	0.452(2)

TABLE 4.7

Bond Lengths (Å) and Angles (°) for Sb(dbc)I(bipy) and Uncoordinated bipy in (4.1), in esd's in Parentheses[*]

I-Sb	3.148(2)	C(7)-C(8)	1.40(1)
Sb-O(1)	2.033(6)	C(8)-C(9)	1.35(1)
Sb-O(2)	1.994(6)	C(9)-C(10)	1.38(1)
Sb-N(1)	2.345(6)	C(11)-C(12)	1.39(1)
Sb-N(2)	2.513(6)	C(11)-C(16)	1.36(1)
O(1)-C(11)	1.37(1)	C(12)-C(13)	1.39(1)
O(2)-C(12)	1.362(9)	C(13)-C(14)	1.40(1)
N(1)-C(1)	1.36(1)	C(13)-C(17)	1.55(1)
N(1)-C(2)	1.34(1)	C(14)-C(15)	1.39(1)
N(2)-C(6)	1.34(1)	C(15)-C(16)	1.38(1)
N(2)-C(7)	1.32(1)	C(15)-C(18)	1.54(1)
C(1)-C(5)	1.38(1)	C(17)-C(19)	1.54(1)
C(1)-C(6)	1.46(1)	C(17)-C(23)	1.49(1)
C(2)-C(3)	1.38(1)	C(17)-C(24)	1.53(1)
C(3)-C(4)	1.37(1)	C(18)-C(20)	1.46(2)
C(4)-C(5)	1.37(1)	C(18)-C(21)	1.44(2)
C(6)-C(10)	1.39(1)	C(18)-C(22)	1.44(2)
I-Sb-O(1)	89.8(2)	C(7)-C(8)-C(9)	118.6(9)
I-Sb-O(2)	87.4(2)	C(8)-C(9)-C(10)	120.1(9)
I-Sb-N(1)	175.5(2)	C(6)-C(10)-C(9)	118.6(9)
I-Sb-N(2)	116.0(2)	O(1)-C(11)-C(12)	116.9(7)
O(1)-Sb-O(2)	81.4(2)	O(1)-C(11)-C(16)	121.0(7)
O(1)-Sb-N(1)	86.3(2)	C(12)-C(11)-C(16)	122.1(8)
O(1)-Sb-N(2)	142.0(2)	O(2)-C(12)-C(11)	116.7(7)
O(2)-Sb-N(1)	89.7(2)	O(2)-C(12)-C(13)	123.3(7)
O(2)-Sb-N(2)	73.1(2)	C(11)-C(12)-C(13)	120.0(8)
N(1)-Sb-N(2)	66.3(2)	C(12)-C(13)-C(14)	116.7(7)

Sb-O(1)-C(11)	111.6(4)	C(12)-C(13)-C(17)	120.4(7)
Sb-O(2)-C(12)	113.3(5)	C(14)-C(13)-C(17)	122.9(8)
Sb-N(1)-C(1)	122.5(6)	C(13)-C(14)-C(15)	123.1(8)
Sb-N(1)-C(2)	118.3(5)	C(14)-C(15)-C(16)	118.2(8)
C(1)-N(1)-C(2)	118.4(7)	C(14)-C(15)-C(18)	119.4(9)
Sb-N(2)-C(6)	117.8(5)	C(16)-C(15)-C(18)	122.5(8)
Sb-N(2)-C(7)	122.0(6)	C(11)-C(16)-C(15)	119.9(7)
C(6)-N(2)-C(7)	120.2(7)	C(13)-C(17)-C(19)	110.6(8)
N91)-C(1)-C(5)	119.8(8)	C(13)-C(17)-C(23)	111.5(7)
N(1)-C(1)-C(6)	116.2(7)	C(13)-C(17)-C(24)	109.8(8)
C(5)-C(1)-C(6)	124.0(8)	C(19)-C(17)-C(23)	107.8(9)
N(1)-C(2)-C(3)	123.3(8)	C(19)-C(17)-C(24)	106.5(8)
C(2)-C(3)-C(4)	118.4(9)	C(23)-C(17)-C(24)	110.5(8)
C(3)-C(4)-C(5)	118.7(9)	C(15)-C(18)-C(20)	111.6(9)
C(1)-C(5)-C(4)	121.3(9)	C(15)-C(18)-C(21)	113(1)
N(2)-C(6)-C(1)	116.0(7)	C(15)-C(18)-C(22)	112(1)
N(2)-C(6)-C(10)	120.9(8)	C(20)-C(18)-C(21)	107(2)
C(1)-C(6)-C(10)	123.1(8)	C(20)-C(18)-C(22)	105(2)
N(2)-C(7)-C(8)	121.5(9)	C(21)-C(18)-C(22)	108(2)
2,2′-bipyridine			
N(3)-C(25)	1.34(1)	C(25)-N(3)-C(27)	117(1)
N(3)-C(27)	1.30(2)	N(30)-C(25)-C(25′)	115(1)
C(25)-C(25′)	1.48(2)	N(3)-C(25)-C(28)	124(1)
C(25)-C(28)	1.36(1)	C(25′)-C(25)-C(28)	121(1)
C(26)-C(27)	1.35(2)	C(27)-C(26)-C(29)	120(2)
C(26)-C(29)	1.38(2)	N(3)-C(27)-C(26)	124(2)
C(28)-C(29)	1.41(2)	C(26)-C(29)-C(28)	117(1)

---

* Prime indicates atoms related by the symmetry operation 1 - x, 1 - y, 1 - z.

FIGURE 4.4

An ORTEP Diagram of the Sb(dbc)I(bipy) adduct 4.1,

with Atoms Shown as 30% Probability Ellipsoids.

Hydrogen Atoms and the Methyl Groups of Bu^t have been omitted for clarity;

C(19), C(23) and C(24) ride on C(17) and C(20) - C(22) on C(18)

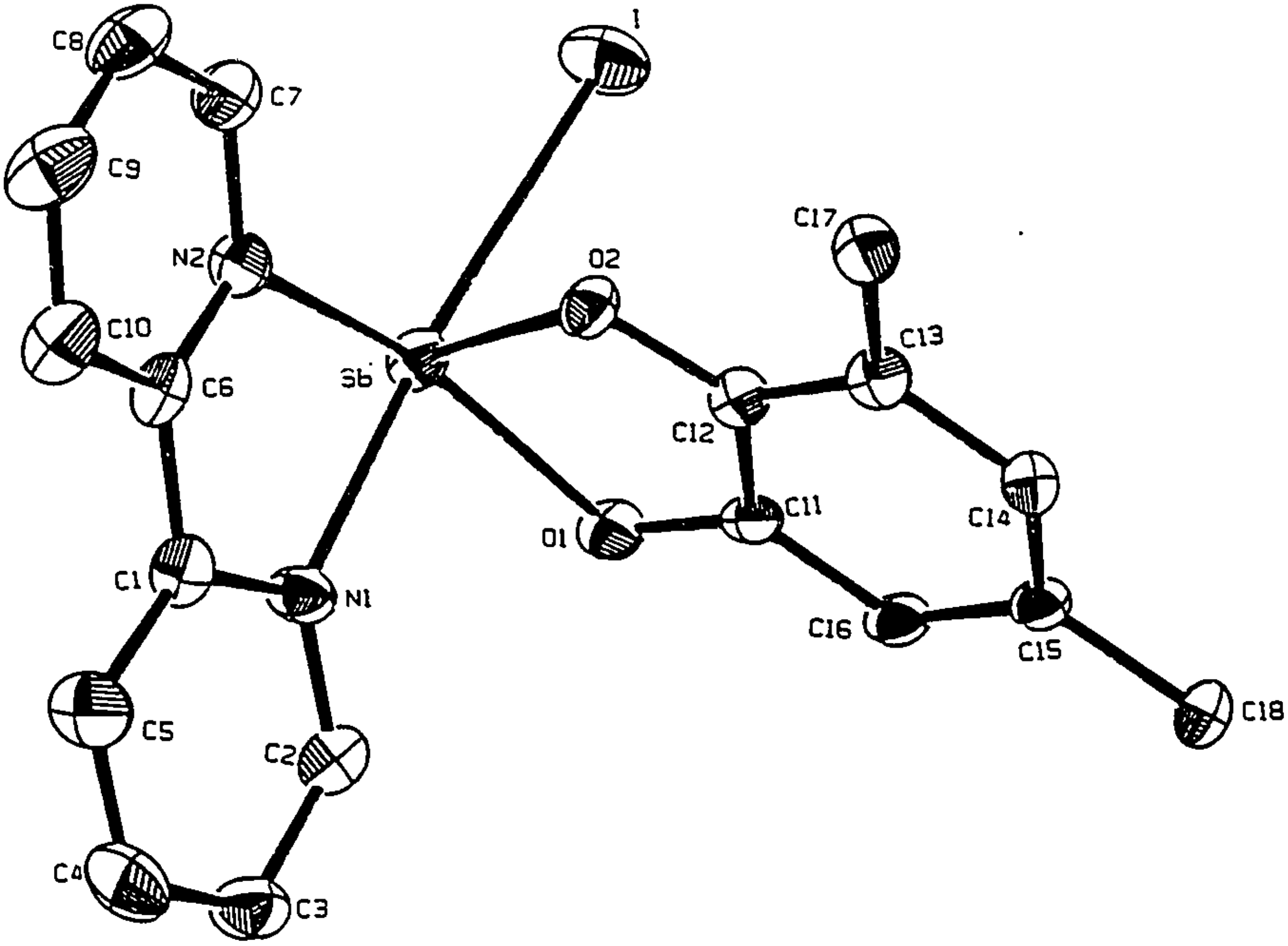
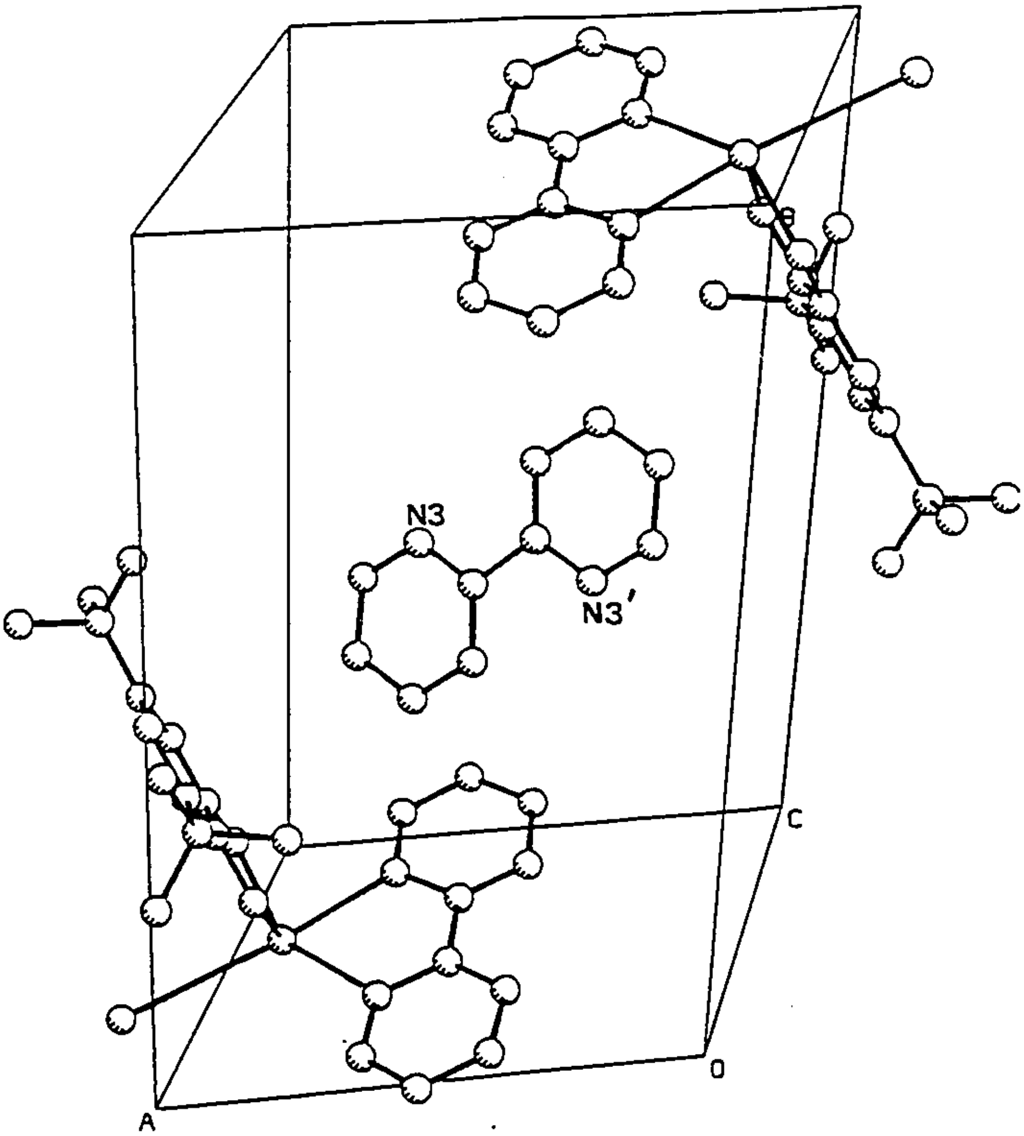


FIGURE 4.5

Cell Packing Diagram of Sb(dbc)I(bipy)·0.5 bipy adduct 4.1.

Hydrogen Atoms have been Omitted for Clarity. Carbon Atoms of

Uncoordinated bipy are C(25) - C(29)



yielded crystalline material was Sb(dbc)I(bipy)·0.5bipy (4.1), which can be viewed as the mononuclear 2,2′-bipyridine adduct of Sb(dbc)I in a lattice also containing uncomplexed 2,2′-bipyridine.

Compared to phosphorus[93,94] and arsenic[93.,183-185] in the five-coordinated states, antimony has not received a great deal of attention.[93,186] For group 5A compounds with formal valence five, it has been found as a general rule that square pyramidal structures are favoured by the presence of two unsatured five-membered rings with like atoms in any one ring attracted directly to the central atom. This has been shown in an extensive series of structural determinations of phosphorus and related compounds by Holmes and coworkers.[93]

A direct comparison with our compound is difficult since consideration should be given to the effect of the lone pair of electrons of the Sb(III) compound. Electron pair repulsion theory predicts that a molecule with an SbO_2N_2I kernel and a lone pair of electrons will have a pseudo-octahedral AX_5E stereochemistry if the lone pair is sterically active, and distorted trigonal bipyramidal or square-based pyramidal structures if it is not. This point has been discussed in terms of the atomic weight of the ligand involved for halide derivatives.[187] The present structure is most conveniently described as AX_5E, but with substantial distortion caused by the steric restrictions of the bidentate ligands. It is of interest to note that a few structures of five-coordinate antimony(III) complexes (for example, Sb(cat)I(phen)[188] and $[(Cl_4C_6O_2)SbCl_2]^-$ $[PyH]^+$[189]) have been reported in which the coordination polyhedron about antimony are distorted octahedrons.

In our compound, the Sb-I bond distance of 3.148(2) Å is slightly larger than the average value for such bonds in crystalline SbI_3 (2.686, 3.313 Å)[190] and r(Sb-O) (av. value = 2.014(6) Å) is well within the range of distances reported for a wide variety of antimony(III)-oxygen complexes.[191] The Sb-N bonds, in contrast, are substantially longer than would be predicted from the covalent radii, or by comparison with r(Sb-O), and this, together with the small N-Sb-N angle of 66.3(2)°, implies a weak donation from 2,2′-bipyridine to the antimony(III) centre. This is similar to the results[190] for Te(dbc)$_2$·bipy, in which the bite angle is only 56.1(2)°, and both are lower than the value of *ca.* 78° usually found in complexes of this ligand. The remaining bond distances call for no comment, except to note that r(C-O) of the dbc^{2-} ligand (av. value 1.366(9) Å) is typical of that for catecholato complexes,[5] as required by the formulation of this complex.

It is generally accepted that a significant unoccupied gap in the coordination sphere usually implies the existence of a stereochemically active lone pair of electrons which compete with the bonding pairs for a position in the coordination sphere. For purposes of discussion of our compound, the I-Sb-N(1) axis (angle 175.5(2)°) can be regarded as passing through a rough plane defined by Sb, N(2), O(1) and O(2); the I-Sb-O(1) and I-Sb-O(2) angles (89.8(2), 87.4(2)°) are compatible with this description, but I-Sb-N(2) (116.0(2)°) shows that N(2) is well below this plane, in keeping with the small N(1)-Sb-N(2) bite angle. The large O(1)-Sb-N(2) angle, and the other features of the structure, indicate that a stereochemically active lone pair indeed occupies the vacant sixth position of the AX_5E kernel.

It has been reported[192,193] that a series of $SbCl_3$ complexes $SbCl_3$·L (L=1/2PhPh, 1/2Ph$_2$NH, PhNH$_2$$^+Cl^-$, and 2PhNH$_2$) gave different kinds of structures in which L coordinated to Sb(III) through nitrogen atoms or aromatic rings or only functioned as a bridging position between chlorine atoms of the antimony-chlorine-bridged tubular chains. The variation of the structures of these complexes has been proposed due to the balance between the factors of the Lewis basicity of the amine versus that of the aromatic system, together with the crystal packing energies in these systems. In Sb($O_2C_6Cl_4$)I(bipy)·0.5bipy (**4.1**), the coordination of bipy toward Sb(III) through nitrogen atoms is certainly due to the chelate effect; the existence of uncoordinated 2,2′-bipyridine, however, more likely result from the crystal packing energy requirement only. The features of the uncoordinated 2,2′-bipyridine in the lattice in which the nitrogen atoms are in the anti-configuration are not significantly different from those previously reported.

CHAPTER 5

THE OXIDATION OF DIPHENYL DITELLURIDE BY SUBSTITUTED *O*-BENZOQUINONES, AND THE MOLECULAR STRUCTURE OF $[(Cl_4C_6O_2)TeC_6H_5]_2O$

5.1 Introduction

In the preceding chapters, we have described the results of preparative and spectroscopic investigations of the reaction between substituted *o*-benzoquinones and different Main Group elements, or the low oxidation state compounds of such elements. Beside these oxidation states which differ by an even number of electrons from their elemental electronic structures, there is a group of relatively simple neutral or ionic compounds which have formal intermediate oxidation states, such as E_2X_4, $E_2X_6^{2-}$, $E_2X_4L_2$ for E = Group 3A elements, E_2X_6 for E = Group 4A elements, and E_2R_4 for E = Group 5A elements. All these imply oxidation states of +2 for Group 3A or 5A elements, or +3 for the group 4A elements. This set of compounds has in common the presence of M-M bonds, and has a rich chemistry to give mono-metal compounds either by self-disproportionation or by oxidation reactions with other reactants.[194] In view of our interest in the oxidation processes of Group 5A and 6A elements and their lower oxidation state compounds, we extended our investigations to the oxidation of diphenyl ditelluride, in which tellurium is formally in the +1 oxidation state.

Various methods have been established for the synthetic applications of diaryl ditellurides. These compounds can be converted to organic tellurium (II) or (IV) compounds by three ways:[195-199]

(1) extrusion of one tellurium from the ditellurides

$$ArTeTeAr \rightarrow ArTeAr + Te$$

$$ArTeTeAr \rightarrow Ar_2Te$$

(2) reaction with diorganyl mercury compounds or Grignard reagents

$$\mathrm{ArTeTeAr + Ar'MgX \rightarrow ArTeAr' + ArTeMgX}$$

$$\mathrm{ArTeTeAr + R_2Hg \rightarrow 2ArTeR + Hg}$$

(3) controlled or completed halogenolysis

$$\mathrm{ArTeTeAr \rightarrow 2ArTeBr \xrightarrow{XY} 2ArTeX}$$

$\mathrm{XY = RMgX, KSeCN, Ph_4M^+X^-}$, etc.

$$\mathrm{ArTeTeAr \xrightarrow{3X_2} 2ArTeX_3}$$

In the present work, a reaction is shown to occur between diphenyl ditelluride and tetrahalogeno-*o*-benzoquinones (*o*-$O_2C_6X_4$; X = Cl, Br) to give $[(X_4C_6O_2)TeC_6H_5]_2O$, and the structure of the tetrachlorocatecholate derivative is established crystallographically. The reaction between Ph_2Te_2 and dbbq gives an apparently related product, but in each case the reaction mechanism is clearly complicated, and the only certain feature is that paramagnetic species are observed, implying the involvement of free radicals in the electron transfer process. The reaction between diphenyl ditelluride and oxidant mixtures Q + Y_2 (Q = dbbq, Y_2 = $Ph_2C_2O_4$) give tellurium(IV) derivatives PhTe(dbc)Y.

5.2 Experimental

5.2.1 General

All reagents, including elemental tellurium (Aldrich), were reagent grade, or better, and were used as supplied. Solvents were dried by conventional methods, and stored over drying agents. All reactions were carried out under dry nitrogen, using conventional techniques for handling potentially air-sensitive materials.

All the instruments and procedures for elemental analysis and spectroscopic studies were those described in Chapter 1.

5.2.2 Preparation of Diphenyl Ditelluride

The preparation followed the method of Irgolic,[112,200] in which phenylmagnesium bromide is treated with tellurium, to give a product presumed to be $C_6H_5TeMgBr$, which on reaction with gaseous oxygen forms $(C_6H_5)_2Te_2$ in 70% yield. Gram quantities of the product were prepared by this route. Fig. 5.1 present the mass spectrum of this compound. It shows significant clusters of peaks centred at m/e = 410 ($Ph_2Te_2^+$), 284 (Ph_2Te^+), 207 ($PhTe^+$), 154 (Ph_2^+) and 77 (Ph^+); in each case, the isotopic distribution agreed with the calculated values within experimental error. ^1H NMR spectrum (in $(CD_3)_2SO$) 7.8, 2H, 7.2, m, 3H; (in $CDCl_3$), 7.78, 7.81, 2H, 7.2 m, 3H (all in ppm; TMS $\delta = 0$). ^{13}C NMR spectrum (in $CDCl_3$) 137.6, 129.3, 128.1, 107.9 ppm (TMS $\delta = 0$). ^{125}Te NMR spectrum (in $CDCl_3$) 421.8 ppm (neat Me_2Te $\delta = 0$).

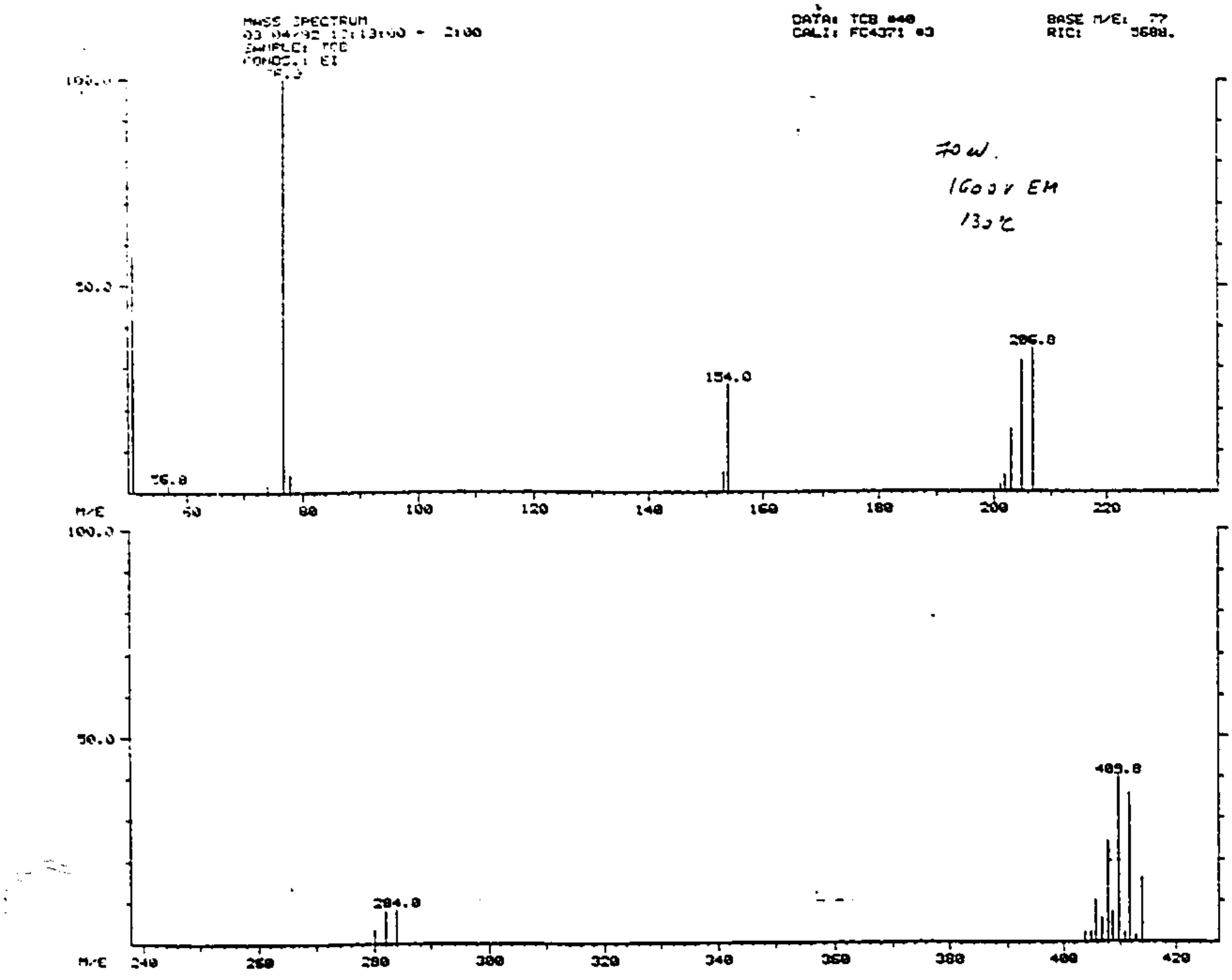
5.2.3 Reaction of Diphenyl Ditelluride with *o*-Quinones

(i) Tetrahalogeno-o-benzoquinones

Diphenyl ditelluride (0.205 g, 0.5 mmol) was dissolved in toluene (15 cm^3), and a solution of *o*-$O_2C_6X_4$ (X = Cl, 0.37 g, 1.5 mmol; X = Br, 0.64 g, 1.5 mmol) in the same solvent (15 cm^3) added dropwise at 0°C over 10 min. Reaction began as soon as the reactants were in contact, as shown by the discharge of the red-orange colour of the initial mixture. The resultant yellow solution was allowed to reach room temperature (*ca.* 20°C) over 1 hour, with stirring. The volume of the solution was reduced by about 80% *in vacuo*; addition of mixed hexanes (20 cm^3) caused the precipitation of a pale yellow solid, which was collected by filtration, washed with hexanes (2 x 5 cm^3) and dried *in vacuo* for 24 hours. The analytical results agreed very well with molecular formulae $[(X_4C_6O_2)TeC_6H_5]_2O$. For $[(Cl_4C_6O_2)TeC_6H_5]_2O$; found C 31.6; H 1.18; Te 27.5%; calculated for $C_{24}H_{10}O_5Cl_8Te_2$ C 31.4; H 1.10; Te 27.8%. For $[(Br_4C_6O_2)TeC_6H_5]_2O$; found C 23.0; H 0.90; Te 20.0%; calculated for $C_{24}H_{10}O_5Br_8Te_2$ C 22.6; H 0.79; Te 20.1%. The yields were almost quantitative, based on the

FIGURE 5.1

Mass Spectrum of Ph_2Te_2



quantity of $(C_6H_5)_2Te_2$ used.

These compounds are air-stable, pale yellow solids, soluble in dimethylformamide, dimethylsulphoxide, tetrahydrofuran, diethyl ether, and toluene.

A sample of $[(Cl_4C_6O_2)TeC_6H_5]_2O$ was recrystallized from tetrahydrofuran for X-ray analysis (see below); the resultant crystals proved to be $[Cl_4C_6O_2)TeC_6H_5]_2O.2thf$. Found C 36.2%; H 2.20%; calculated for $C_{32}H_{20}O_7Cl_4Te_2$ C 36.2%; H 2.47%. The presence of the thf molecules in the lattice was also confirmed by ^1H NMR spectrum and X-ray crystallography.

(ii) dbbq

As in the above experiments, a solution of dbbq (0.33 g, 1.5 mmol) in toluene (15 cm^3) was added dropwise over 10 min to a solution of $(C_6H_5)_2Te_2$ (0.205 g, 0.5 mmol, 15 cm^3 toluene). The work-up of the solution followed the procedures outlined above, except that the reaction solution was taken to dryness, and the residue recrystallised from light petroleum. The ^{125}Te NMR resonance at 1620.8 ppm confirms that the tellurium has been oxidized to the +IV state. Microanalysis identifies the compound as $[(C_{14}H_{20}O_2)TeC_6H_5]_2O.\frac{1}{2}C_7H_8$ (Found C 57.6%; H 6.30%. Calculated for $C_{43.5}H_{54}O_5Te$ C 57.3%; H 5.97%). No further structural studies of this compound were performed. The yield is 0.44 g, 82%, based on initial quantities taken.

5.2.4 Reaction of Diphenyl Ditelluride with dbbq and $Ph_2C_2O_4$

A solution of dbbq (0.220 g, 1 mmol) and $Ph_2C_2O_4$ (0.121 g, 0.5 mmol) in toluene (20 mL) was added dropwise to a toluene solution (10 cm^3) of diphenyl ditelluride (0.205 g, 0.5 mmol) at -78°C. The resulting light yellow solution was stirred as the temperature rose to room temperature. After evaporating off most of the solvent, petroleum ether (20 cm^3) was added to it. The light yellow solid was isolated from the liquid phase by filtration and dried *in vacuo*. The analytical results of this product agree with a formula (dbc)Te(Ph)$(PhCO_2)$. Found: Te 24.0%; Calculated Te 23.5%. The yield is 90% based on this formula. The ^{125}Te NMR resonance of this product in $CDCl_3$ is 1441.7 ppm.

5.3 Results and Discussion

5.3.1 Spectroscopic Studies

(i) NMR

The ^1H and ^{13}C NMR spectra of the products in this work and one of the reactant (Ph_2Te_2) are summarized in Tables 5.1 and 5.2. The spectra of both $[(X_4C_6O_2)TeC_6H_5]_2O$ (X = Cl or Br) compounds are essentially identical, the only significant differences being the ^{13}C NMR resonances of the $X_4C_6O_2$ ring, and the frequencies in these two cases are similar to those found in previous studies of related tellurium catecholate compounds by this laboratory.[190] The ^1H NMR resonances of the phenyl in these products as well as in the thf solvate of $[(Cl_4C_6O_2)TeC_6H_5]_2O$ are more downfield (*ca.* 7.6 and 8.2 ppm) than those in Ph_2Te_2 (7.2 and 7.8 ppm). This is presumably because the change of the oxidation state of tellurium and the electron-withdrawing effect of the catecholate ligands.

The ^{125}Te NMR resonance of $(C_6H_5)_2Te_2$ in $CDCl_3$ is very close to that reported for this compound in CH_2Cl_2 (422 ppm from Me_2Te $\delta = 0$). We see a large change of the ^{125}Te resonance values after the completion of the reaction, and the values for the products in this work ($[(X_4C_6O_2)TeC_6H_5]_2O$ in $(CD_3)_2SO$; X = Cl, 1620.30 ppm; X = Br, 1546.6 ppm. PhTe(dbc)($PhCO_2$) in $CDCl_3$, 1441.7 ppm) are in the range for tellurium(IV) species.[132,190]

(ii) Infrared

The infrared spectra of $[(X_4C_6O_2)TeC_6H_5]_2O$ are also identical except for the C-X regions; the most important feature of the IR spectra is that in each case the strong $\nu(C=O)$ vibrations of the initial *o*-quinone at *ca.* 1675 cm^{-1} region are completely absent in the final products, being replaced by $\nu(C-O)$ modes seen as a pair of absorption at *ca.* 1420 + 1228 cm^{-1}.

(1421.5 + 1227.6 cm^{-1} for $[(Br_4C_6O_2)TeC_6H_5]_2O$ and 1418.3 + 1227.9 cm^{-1} for

^{1}H NMR of the Reactant and Products in this Work;

Values in ppm Relative to TMS ($\delta = 0$)

Compound	Solvent	Chemical shift	Assignment
Ph_2Te_2	$(CD_3)_2SO$	7.8(m), 2H, 7.2(m), 3H	C_6H_5-
$[(Cl_4C_6O_2)TeC_6H_5]_2O$	$(CD_3)_2SO$	7.7(m), 3H, 8.4(m), 2H	C_6H_5-
$[(Br_4C_6O_2)TeC_6H_5]_2O$	$(CD_3)_2SO$	7.6(m), 3H, 8.2(m), 2H	C_6H_5-
$[(Cl_4C_6O_2)TeC_6H_5]_2O$-2thf	$(CD_3)_2SO$	7.6(m), 3H, 8.2(m), 2H	C_6H_5-
		3.60, 4H, 1.75, 4H	thf
PhTe(dbc)($PhCO_2$)	$(CD_3)_2SO$	7.5(m), 10H	Ph- and $PhCO_2$-
		6.70 and 6.58, 2H	$H^{4,6}$ dbc
		1.20 and 1.40, 18H	Bu^t dbc

TABLE 5.2

^{13}C NMR Spectra of the Reactant and Products in this Work; Values in ppm Relative to TMS ($\delta = 0$)

		Diolato			TePh
Compound	Solvent	$C^{1,2}$	$C^{3,6}$	$C^{4,5}$	
Ph_2Te_2	$CDCl_3$				137.6, 129.3, 128.1, 107.9
$[(Cl_4C_6O_2)TeC_6H_5]_2O$	$(CD_3)_2SO$	144.8	116.8	113.9	131.5, 129.2, 109.8
$[(Br_4C_6O_2)TeC_6H_5]_2O$	$(CD_3)_2SO$	149.0	116.3	109.8	131.5, 129.2, 109.8

$[(Cl_4C_6O_2)TeC_6H_5]_2O)$.

(iii) ESR

Dilute toluene solutions of $(C_6H_5)_2Te_2$ and *o*-$O_2C_6Cl_4$ *were mixed in an ESR tube at room temperature and the spectrum recorded immediately. The only feature was a weak broad signal, with* $g = 2.006$. *A similar experiment with* $(C_6H_5)_2Te_2$ *and dbbq* gave a sharper and more intense resonance with no hyperfine structure ($g = 2.005$), and with a poorly resolved doublet, ascribed to coupling between the semiquinone radical and tellurium, with a coupling constant of 43 G. This implies a slightly higher spin density at the tellurium S orbital of the total in this case compared with the value in Et_2Te/dbbq system [the value found for A_{Te} in the reaction between Et_2Te and this *o*-quinone is 38.5 G (for ^{125}Te) (Chapter 3 of this work)].

5.3.2 Reaction Pathway

The overall reaction has three important features: the reduction of *o*-quinone to catecholate, the oxidation of tellurium from +I to +IV with the retention of the Te - C_6H_5 linkage, and the cleavage of the Te - Te bond of $(C_6H_5)_2Te_2$. It is well known that the diorganyl ditellurides generate the corresponding telluro radical by photolysis. As a starting point to a discussion of the reaction mechanism, we note that the lability of the Te-Te bond in diorganyl ditellurides have been applied in the following synthetic reactions, with the assistance of external energy sources:[207,208]

$$\mathrm{PhTeTePh} \xrightarrow{\mathrm{RC{\equiv}CR'}} \mathrm{PhTeCR{=}CR'TePh}$$

$$\mathrm{RTeTeR} \xrightarrow{\mathrm{E}} \mathrm{RTeETeR}$$

R = Ph, $(Me_3Si)_3C$. E = S or Se.

The insertion of carbenes, cadmium or mercury into Te-Te bond have also been reported.[209-211] Such compounds have been proposed as single source precursors to semiconductor compounds such as CdTe and HgTe. The dissociation of Ar_2Te_2 to ArTe was first proposed about 30 years ago.[212] The ^{125}Te NMR studies[213] of the exchange equilibrium between diorganyl ditelluride with Group 5A and 6A alkyl and aryls as shown in the following equation support this idea. Even though the room temperature exchange between two tellurides are very slow, it is still measurable in which ^{125}Te resonance signals due to this exchange process were recorded. This later result is important to the current discussion, since both occurred in similar conditions.

$$\mathrm{RTeTeR} + \mathrm{R_2'E^5E^5R_2'} \rightleftarrows \mathrm{2RTeE^5R_2'}$$

$$\mathrm{RTeTeR} + \mathrm{R'E^6E^6R'} \rightleftarrows \mathrm{2RTeE^6R'}$$

$$\mathrm{E^5 = P, As, Sb, Bi;\ E^6 = S, Se, Te}$$

On the other hand, I note that the reaction between tetraorganylditin dihalides with *o*-quinone has been proposed[17] to proceed through a free radical pathway based on the ESR measurements. In this case, the intermediate five-coordinate tin-containing radical can generally be detected by ESR.

$$\mathrm{XR_2Sn\text{-}SnR_2X} \rightleftarrows \mathrm{2XR_2Sn^{\bullet}} \rightarrow \mathrm{(dbsq)SnR_2X} \rightarrow \mathrm{(dbc)SnR_2}$$

The preparative work described above was carried out in the temperature range 273-295 K, and reaction with $o\text{-}O_2C_6X_4$ was essentially instantaneous under these conditions. Based on the above discussion, we suggest that the reaction pathway in these experiments involves the sequence shown in scheme 5.1:

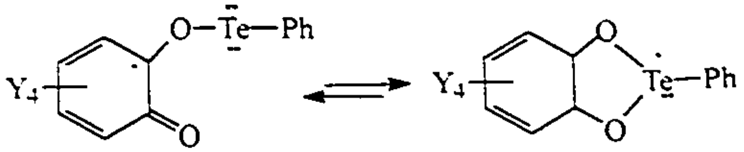
$$\mathrm{Ph_2Te_2} \leftrightarrows \mathrm{PhTe^{\bullet}} \tag{1}$$

$$\mathrm{PhTe^{\bullet}} + o\text{-}\mathrm{Q} \rightarrow \mathrm{(SQ^{\bullet-})\ TePh} \tag{2}$$

$$\mathrm{(SQ^{\bullet-})TePh} \rightarrow \mathrm{(cat)Te^{\bullet-}Ph} \tag{3}$$

Scheme 5.1

The intramolecular electron transfer process in (eq. (3)) is:



so that a tellurium(III) radical complex is formed. Internal rearrangements of this type are common in Q/SQ/cat ligand systems for both transition metal and main group metal complexes. For example:[58,73]

$Cu(SQ)(Ph_3P)_2 \rightarrow Cu(cat)(py)_2$

$Sn(SQ)X_2 \rightarrow X_2Sn(cat)Phen$

Such processes reasonably account for the formation of the $(X_4C_6O_2)(C_6H_5)Te$- groups which are present in the final product, and to this point the mechanism is compatible with the ESR results, which confirm the presence of molecules in which the dbbq radical is bonded to tellurium. The reaction between $(C_6H_5)_2Te_2$ and *o*-$O_2C_6Cl_4$ is much faster than with dbbq, and the weaker ESR signal observed is presumably a consequence of this rate difference, which is itself in keeping with the known stronger oxidising power of the tetrahalogenoquinones. The existence of quinone in these reactions presumably will shift the initial equilibria to the right, as the formation of the final chelated Te(IV) compound served as the driving force. The general conclusion that one-electron transfer processes are involved in the reaction between $(C_6H_5)_2Te_2$ and *o*-quinones is in keeping with similar findings for other reactions of main group compounds.

The source of the oxygen atom in the final product can only be in the excess *o*-quinone in the reaction mixture, since the high yields preclude oxygen or moisture impurity from providing this element in such quantities under the experimental conditions used. This is partially supported by the mass spectroscopic analysis of the residue from the reaction of dbbq with Ph_2Te_2; peaks at 207 (M) and 412 (2M) agree with a molecular formula $C_{14}H_{22}O$ (M.W. 206) in comparison with the original dbbq $C_{14}H_{20}O_2$ (M.W. 220). The composition of the final product may be the result of the space demanding effect of the final Te(IV) compound. In contrast to well-known secondary bonding in Te(IV) compound, $[(Cl_4C_6O_2)TeC_6H_5]_2O$ has a tetracoordinated tellurium even though higher coordination numbers are very common for Te(IV) compound.

For the reaction involving $Ph_2C_2O_4$, two possible pathways exist as shown in the following Schemes 5.3 and 5.4:

$\mathrm{Ph_2Te_2 \rightleftarrows PhTe^{\bullet}}$

$\mathrm{PhTe^{\bullet} + dbbq \rightarrow (dbsq^{\overset{\bullet}{-}})Te^{II}Ph}$

$\mathrm{(dbsq^{\overset{\bullet}{-}})Te^{II}Ph \rightarrow (dbc)Te^{\overset{\bullet}{-}III}Ph}$

$\mathrm{(dbc)Te^{\bullet III}Ph + Ph_2C_2O_4 \rightarrow (dbc)Te^{IV}(Ph)(PhCO_2)}$

Scheme 5.3

$\mathrm{Ph_2Te_2 \rightleftarrows PhTe^{\bullet}}$

$\mathrm{PhTe^{\bullet} + Ph_2C_2O_4 \rightarrow (PhCO_2)Te^{II}Ph}$

$\mathrm{(PhCO_2)Te^{II} + dbbq \rightarrow (dbsq^{\overset{\bullet}{-}})Te^{III}(Ph)(O_2CPh) \rightarrow (dbc)Te^{IV}(Ph)(O_2CPh)}$

Scheme 5.4

Both may involve tellurium and semiquinone radicals in different stages. Scheme 5.3 is very similar to Scheme 5.2 except for the employment of $Ph_2C_2O_4$ as the combining oxidant to produce a tellurium(IV) compound with $\mathrm{(dbc)Te^{\bullet III}Ph}$ in the final stage of reaction processes. The third step of Scheme 5.4 is similar to the previous reactions discussed in Chapter 3 in which a tellurium(II) compound such as Et_2Te reacted with *o*-quinones producing tellurium(IV) compounds. It has been established that semiquinone species are involved as intermediates in those reactions. The lability of Te-Te and O-O bonds in Ph_2Te_2 and $Ph_2C_2O_4$ is an important factor to favour the radical processes in this reaction, but their presence in the same reaction system will certainly increase the difficulty for mechanistic studies. We did not investigate the detail of this rapid reaction in this work.

5.4 Crystallographic Studies

5.4.1 Data Collection and Structure Solution

A yellow block crystal of recrystallized $[(Cl_4C_6O_2)TeC_6H_5]_2O.2thf$ **5.1** was mounted in a glass capillary in the beam of a Rigaku AFC6S diffractometer, using MoKα radiation (λ = 0.71069 Å) at 23°C. Cell constants, and an orientation matrix, were obtained from 12 strong reflections in the range $25.18 < 2\theta < 28.47°$. The systematic absences h0l: $h+l \neq 2n$, 0k0, $k \neq 2n$ indicated the space group $P2_1/n$ (#14), and this was confirmed by the subsequent successful solution and refinement. Details of the data intensity collection are given in Table 5.3. The intensities of three representative reflections measured after every 150 reflections declined by 0.30%, and a linear correction factor was therefore applied in the calculations. An empirical absorption correction (DIFABS[201]) was applied in view of the significant absorption coefficient (21.6 cm^{-1}). The data were also corrected for Lorentz and polarization effects.

The structure was solved by direct methods,[181,182] with non-hydrogen atoms being refined anisotropically. The refinement converged on the values R = 0.055 and R' = 0.068. The programs and other data used in this solution are listed in references.[142,149-152]

The structure of the molecule and its cell packing diagram are shown in Figs. 5.2 and 5.3, the positional parameters in Table 5.4, and the important bond distances and angles in Table 5.5.

5.4.2 Description and Discussion of the Structure of $[(Cl_4C_6O_2)TeC_6H_5]_2O$ (5.1)

The product of the reaction between $(C_6H_5)_2Te_2$ and o-$O_2C_6Cl_4$ is the compound **5.1**,

TABLE 5.3

Summary of Crystal Data, Intensity Collection and

Structural Refinement and $[(Cl_4C_6O_2)TeC_6H_5]_2O.2THF$ (5.1)

Cell constants	$\underline{a}$ 10.88(1) Å, $\underline{b}$ 22.69(3) Å, $\underline{c}$ 15.724(6) Å, ß 103.43(6)°
Cell volume (Å^3)	3777(8)
Space Group	$P2_1/n$(No.14)
Z	4
F(000)	2056
ρ(calc.) (g cm^{-3})	1.866
Abs. coeff. (cm^{-1})	21.63
Min./max. abs. correction	0.82/1.09
Crystal dimensions (mm)	0.3 x 0.3 x 0.2
Total reflections measured	7211
Unique data used [$I \geq 3\sigma(I)$]	3497
Number of parameters	442
2θ/° (max)	50
h, k, l (min/max)	0/12, 0/26, -18/-17
$R = (\Sigma \| F_0 \| - \| F_c \| / \Sigma \| F_0 \|)$	0.055
$R_w = (\Sigma_w(\| F_0 \| - \| F_c \|)^2/\Sigma_w F_0^2)^{1/2}$	0.068
Max. shift/error in final cycle	0.14
$\Delta\rho$(max, min)(e Å^{-3})	0.77, -0.93

FIGURE 5.2

The Molecular Structure of $[(Cl_4C_6O_2)Te(C_6H_5)]_2O$,

Shown as an ORTEP Diagram, with 30% Probability of Ellipsoids.

Hydrogen Atoms have been Omitted for Clarity.

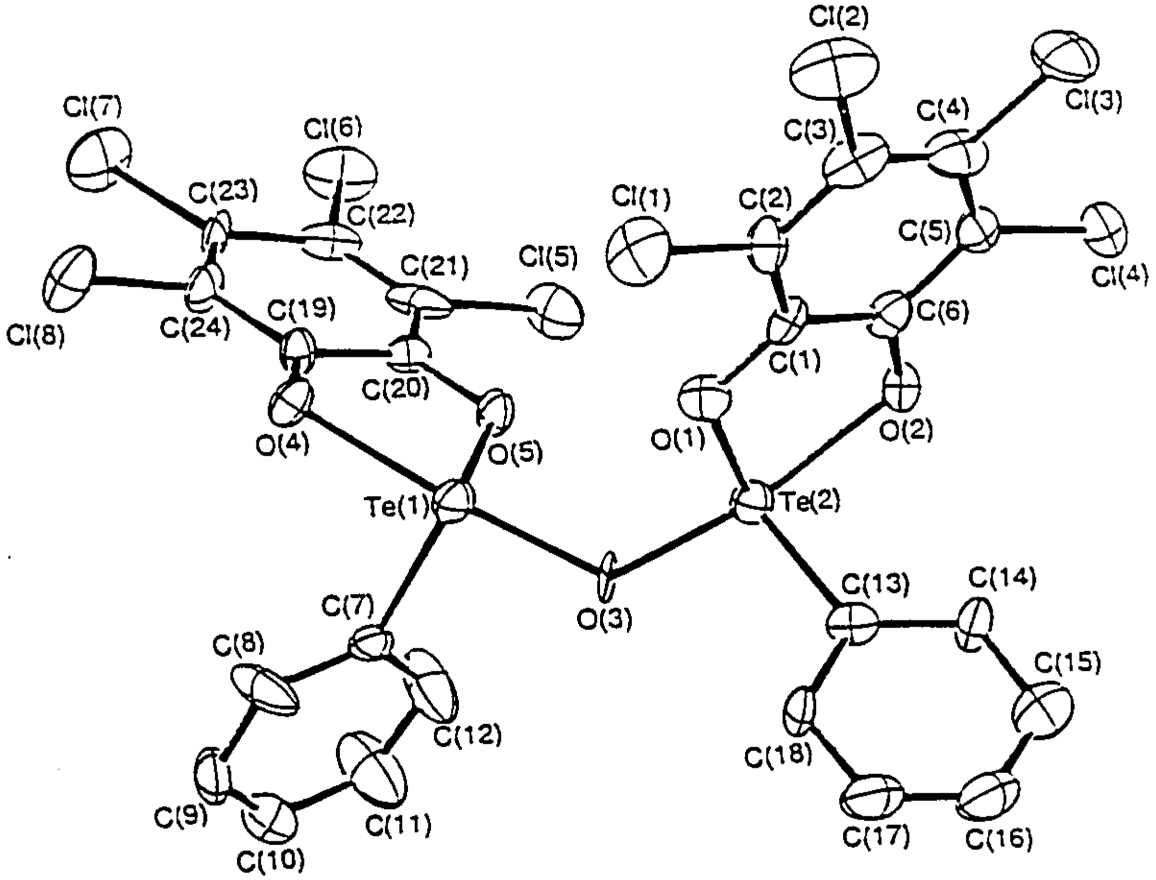


FIGURE 5.3

Cell Packing Diagram of $[(Cl_4C_6O_2)TeC_6H_5]_2O{\cdot}2THF$

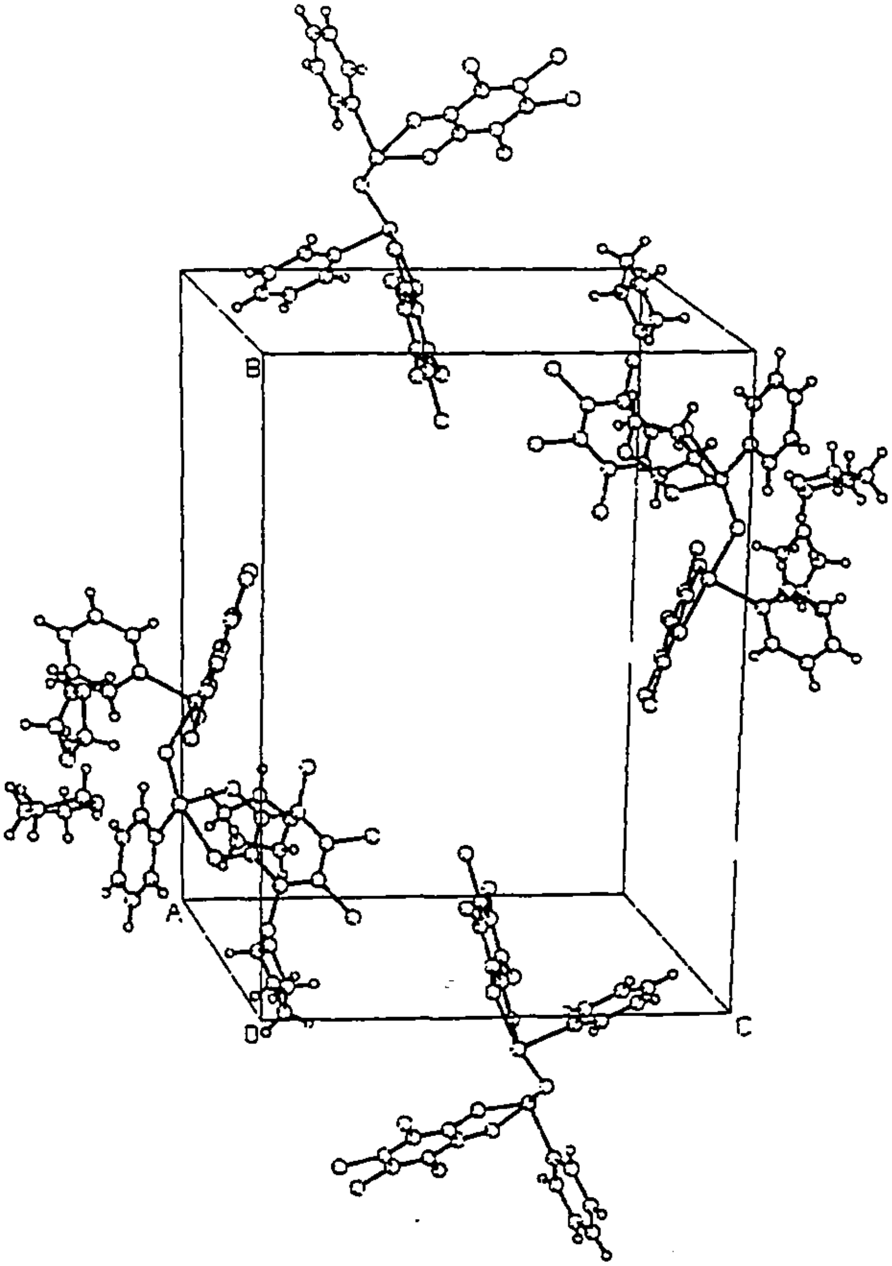


TABLE 5.4

Atomic Coordinates and Thermal Parameters for Non-hydrogen Atoms of $[(Cl_4C_6O_2)TeC_6H_5]_2O$

atom	x	y	z	B(eq)
Te(1)	0.6083(1)	0.57375(4)	1.07195(7)	3.27(4)
Te(2)	0.7895(1)	0.70102(4)	1.13556(7)	3.32(4)
Cl(1)	0.5765(5)	0.6841(2)	0.8229(3)	6.9(3)
Cl(2)	0.6723(5)	0.7755(3)	0.7023(3)	8.4(3)
Cl(3)	0.8936(6)	0.8602(2)	0.7844(3)	7.9(3)
Cl(4)	1.0079(5)	0.8570(2)	0.9876(3)	6.1(2)
Cl(5)	1.0701(4)	0.5515(2)	1.1579(3)	5.3(2)
Cl(6)	1.1656(4)	0.4241(2)	1.1219(3)	6.1(2)
Cl(7)	0.9700(4)	0.3308(2)	1.0287(4)	6.7(3)
Cl(8)	0.6846(4)	0.3630(2)	0.9716(3)	6.0(2)
O(1)	0.7064(9)	0.6932(4)	1.0086(6)	3.8(5)
O(2)	0.8873(8)	0.7659(4)	1.0779(7)	3.6(5)
O(3)	0.6526(9)	0.6456(4)	1.1417(7)	3.9(5)
O(4)	0.6310(8)	0.4858(4)	1.0196(6)	3.5(5)
O(5)	0.7946(8)	0.5651(4)	1.0974(6)	3.6(5)
O(6)	0.565(2)	0.160(1)	0.142(1)	14(2)
O(7)	0.414(3)	0.024(2)	0.066(3)	21(3)
C(1)	0.744(1)	0.7326(6)	0.954(1)	2.9(6)
C(2)	0.694(1)	0.7330(6)	0.866(1)	3.8(7)
C(3)	0.741(2)	0.7735(8)	0.812(1)	4.7(8)
C(4)	0.836(2)	0.8114(7)	0.850(1)	4.8(9)
C(5)	0.889(1)	0.8094(6)	0.939(1)	3.7(7)
C(6)	0.840(1)	0.7692(6)	0.992(1)	3.4(7)
C(7)	0.587(1)	0.5309(6)	1.186(1)	3.3(7)
C(8)	0.498(2)	0.490(1)	1.189(1)	7(1)

C(9)	0.492(2)	0.4593(7)	1.263(1)	6(1)
C(10)	0.576(2)	0.474(1)	1.339(1)	6(1)
C(11)	0.668(2)	0.513(1)	1.338(1)	9(1)
C(12)	0.670(2)	0.5456(9)	1.262(1)	7(1)
C(13)	0.682(1)	0.7701(6)	1.170(1)	3.3(7)
C(14)	0.736(1)	0.8250(7)	1.186(1)	4.3(8)
C(15)	0.670(2)	0.8694(9)	1.216(1)	8(1)
C(16)	0.551(2)	0.860(1)	1.227(1)	7(1)
C(17)	0.496(2)	0.808(1)	1.209(1)	6(1)
C(18)	0.561(2)	0.7612(7)	1.180(1)	4.5(8)
C(19)	0.750(1)	0.4697(6)	1.043(1)	3.1(6)
C(20)	0.838(1)	0.5127(6)	1.0827(9)	2.9(6)
C(21)	0.966(1)	0.4977(8)	1.109(1)	4.3(8)
C(22)	1.008(1)	0.4435(7)	1.091(1)	3.8(7)
C(23)	0.922(1)	0.3994(6)	1.051(1)	4.0(7)
C(24)	0.793(1)	0.4141(6)	1.025(1)	3.6(7)
C(25)	0.553(3)	0.175(2)	0.045(2)	12(2)
C(26)	0.668(3)	0.201(1)	0.039(2)	12(2)
C(27)	0.736(2)	0.214(1)	0.129(2)	10(2)
C(28)	0.672(1)	0.1899(7)	0.1847(8)	2.6(6)
C(29)	0.283(4)	-0.047(1)	0.104(3)	16(3)
C(30)	0.398(6)	-0.026(2)	0.094(4)	22(5)
C(31)	0.218(3)	0.010(1)	0.095(2)	12(2)
C(32)	0.304(3)	0.055(1)	0.074(2)	10(2)

TABLE 5.5

Interatomic Distances (Å) and Angles (°) for $[(Cl_4C_6O_2)TeC_6H_5]_2O\text{-}2THF$,

with esd's in Parentheses

atom	atom	distance	atom	atom	distance
Te(1)	O(3)	1.961(9)	C(2)	C(3)	1.42(2)
Te(1)	O(4)	2.195(9)	C(3)	C(4)	1.37(2)
Te(1)	O(5)	1.983(9)	C(4)	C(5)	1.39(2)
Te(1)	C(7)	2.10(1)	C(5)	C(6)	1.42(2)
Te(2)	O(1)	1.999(9)	C(7)	C(8)	1.35(2)
Te(2)	O(2)	2.138(9)	C(7)	C(12)	1.36(2)
Te(2)	O(3)	1.969(9)	C(8)	C(9)	1.37(2)
Te(2)	C(13)	2.10(1)	C(9)	C(10)	1.37(2)
Cl(1)	C(2)	1.71(2)	C(10)	C(11)	1.34(2)
Cl(2)	C(3)	1.72(2)	C(11)	C(12)	1.41(3)
Cl(3)	C(4)	1.72(2)	C(13)	C(14)	1.38(2)
Cl(4)	C(5)	1.72(2)	C(13)	C(18)	1.38(2)
Cl(5)	C(21)	1.72(2)	C(14)	C(15)	1.38(2)
Cl(6)	C(22)	1.73(1)	C(15)	C(16)	1.36(2)
Cl(7)	C(23)	1.71(1)	C(16)	C(17)	1.33(2)
Cl(8)	C(24)	1.73(2)	C(17)	C(18)	1.40(2)
O(1)	C(1)	1.37(2)	C(19)	C(20)	1.41(2)
O(2)	C(6)	1.33(2)	C(19)	C(24)	1.40(2)
O(4)	C(19)	1.32(1)	C(20)	C(21)	1.40(2)
O(5)	C(20)	1.32(1)	C(21)	C(22)	1.36(2)
O(6)	C(25)	1.54(3)	C(22)	C(23)	1.41(2)
O(6)	C(28)	1.38(2)	C(23)	C(24)	1.40(2)
O(7)	C(30)	1.24(5)	C(25)	C(26)	1.40(3)
O(7)	C(32)	1.42(3)	C(26)	C(27)	1.46(3)
C(1)	C(2)	1.37(2)	C(27)	C(28)	1.36(3)

C(1)	C(6)	1.36(2)	C(29)	C(30)	1.38(6)
			C(29)	C(31)	1.46(4)
			C(31)	C(32)	1.46(3)

atom	atom	atom	angle	atom	atom	atom	angle
O(3)	Te(1)	O(4)	158.6(4)	Cl(2)	C(3)	C(4)	122(2)
O(3)	Te(1)	O(5)	82.1(4)	C(2)	C(3)	C(4)	120(2)
O(3)	Te(1)	C(7)	88.2(5)	Cl(3)	C(4)	C(3)	119(1)
O(4)	Te(1)	O(5)	77.7(3)	Cl(3)	C(4)	C(5)	120(1)
O(4)	Te(1)	C(7)	86.8(4)	C(3)	C(4)	C(5)	120(2)
O(5)	Te(1)	C(7)	86.8(4)	C(3)	C(4)	C(5)	120(2)
O(1)	Te(2)	O(2)	78.0(4)	Cl(4)	C(5)	C(6)	119(1)
O(1)	Te(2)	O(3)	79.7(4)	C(4)	C(5)	C(6)	120(1)
O(1)	Te(2)	C(13)	100.0(5)	O(2)	C(6)	C(1)	119(1)
O(2)	Te(2)	O(3)	156.6(4)	O(2)	C(6)	C(5)	122(1)
O(2)	Te(2)	C(13)	87.5(5)	C(1)	C(6)	C(5)	119(2)
O(3)	Te(2)	C(13)	89.6(5)	Te(1)	C(7)	C(8)	125(1)
Te(2)	O(1)	C(1)	116.0(8)	Te(1)	C(7)	C(12)	117(1)
Te(2)	O(2)	C(6)	111.0(9)	C(8)	C(7)	C(12)	119(2)
Te(1)	O(3)	Te(2)	126.5(5)	C(7)	C(8)	C(9)	124(2)
Te(1)	O(4)	C(19)	109.8(8)	C(8)	C(9)	C(10)	118(2)
Te(1)	O(5)	C(20)	116.5(8)	C(9)	C(10)	C(11)	119(2)
C(25)	O(6)	C(28)	104(2)	C(10)	C(11)	C(12)	122(2)
C(30)	O(7)	C(32)	104(4)	C(7)	C(12)	C(11)	118(2)
O(1)	C(1)	C(2)	122(1)	Te(2)	C(13)	C(14)	119(1)
O(1)	C(1)	C(6)	116(1)	Te(2)	C(13)	C(18)	122(1)
C(2)	C(1)	C(6)	122(1)	C(14)	C(13)	C(18)	119(1)
Cl(1)	C(2)	C(1)	119(1)	C(13)	C(14)	C(15)	120(2)
Cl(1)	C(2)	C(3)	122(1)	C(14)	C(15)	C(16)	121(2)
C(1)	C(2)	C(3)	119(1)	C(15)	C(16)	C(17)	121(2)
Cl(2)	C(3)	C(2)	119(1)	C(16)	C(17)	C(18)	120(2)

C(13)	C(18)	C(17)	120(1)	O(7)	C(32)	C(31)	105(2)
O(4)	C(19)	C(20)	117(1)	Cl(7)	C(23)	C(22)	122(1)
O(4)	C(19)	C(24)	123(1)	Cl(7)	C(23)	C(24)	119(1)
C(20)	C(19)	C(24)	120(1)	C(22)	C(23)	C(24)	119(1)
O(5)	C(20)	C(19)	118(1)	Cl(8)	C(24)	C(19)	119(1)
O(5)	C(20)	C(21)	123(1)	Cl(8)	C(24)	C(23)	121(1)
C(19)	C(20)	C(21)	119(1)	C(19)	C(24)	C(23)	121(1)
Cl(5)	C(21)	C(20)	118(1)	O(6)	C(25)	C(26)	107(2)
Cl(5)	C(21)	C(22)	121(1)	C(25)	C(26)	C(27)	106(2)
C(20)	C(21)	C(22)	121(1)	C(26)	C(27)	C(28)	109(2)
Cl(6)	C(22)	C(21)	122(1)	O(6)	C(28)	C(27)	112(2)
Cl(6)	C(22)	C(23)	117(1)	C(30)	C(29)	C(31)	97(3)
C(21)	C(22)	C(23)	121(1)	O(7)	C(30)	C(29)	124(5)
				C(29)	C(31)	C(32)	109(3)

whose structure reveals a number of interesting features. The presumed pseudo-trigonal bipyramidal stereochemistry at the $TeCO_2O'$ kernel can be regarded as identifying the tellurium(IV) MX_3YE unit predicted by valence shell electron pair repulsion theory, and the vertical axis of this structure is then O(3)-Te(1)-O(4) in the left-hand moiety of the molecule as portrayed in Figure 5.2, (angle = 158.6(4)°), with the equatorial plane being occupied by Te-C(7) and Te-O(5) bonds, and the presumed lone pair of electrons. The smaller O(5)-Te(1)-C(7) angle in the trigonal plane perhaps reflects the spatial demands of the lone pair of electrons in this plane. This is typical geometry for four bond group 14 element (IV) compounds, as in the example of Me_2TeCl_2.[202] It is interesting to note that four bond Group 16 compounds with elements in the valence states (II) or (VI) would have a different geometries; for example, $Te[SC(NH_2)_2]_2Cl_2$ and SeO_2Cl_2 have square and tetrahedral geometry respectively.[203]

This compound is an oxide, in which the oxygen atom bridges two tellurium(IV) atoms with r(Te-O) = 1.965(9) Å (av.) and Te-O-Te = 126.5(5)°; very similar values were reported for the related molecule $[(C_6H_5)_2TeNCS]_2O$,[204] for which r(Te-O) = 1.985(4) A, and Te-O-Te = 121.7(4)°. The Te-O bond length is greater than the sum of their covalent radii. A more significant difference (*ca.* 0.19 Å) emerges if we compare this value to those for other axial Te-O bonds in the same molecule. The large bond angle also needs some comment. A large number of oxygen compounds contain two-coordinate oxygen, in which the atom forms two single bonds and has two unshared pairs of electrons in its valence shell. In the simple systems without significant π-bonding, the X-O-X group is bent with bond angles close to sp^3 tetrahedral angle, as for example, 104.5° in H_2O and 111° in Me_2O. In many substances, where the X atoms of X-O-X group have orbitals (usually d-orbitals) capable of interacting with the lone-pair orbitals of the oxygen atom, the X-O bonds are believed to acquire some π-character. Such interaction causes shortening of the X-O bonds and usually increases the X-O-X bond angles. For example, in silicates the Si-O-Si unit show Si-O distances that were considered to be "too short" for a single bond; the bond angles in Ph_2O (124°) and the Si-O-Si in quartz (142°) are apparently larger than normal tetrahedral angles.[205] Therefore, the Te(1)-O(3)-Te(2) feature in this compound is understandable based on this discussion.

(i) Te-phenyl Interaction

The average Te-C bond length is 2.10(1) Å, which is clearly similar to that in other organotellurium(IV) molecules; in $[\underline{p}\text{ - }PhOC_6H_4TeCl_3]_2$,[206] for example, r(Te-C) = 2.110(6) Å [12]. The C(7)-Te(1) bond is approximately orthogonal to a plane defined by O(3), O(4), O(5) and Te(1), with angles of 88.2(5)° (C(7)-Te(1)-O(3)), 95.4(5)° (C(7)-Te(1)-O(5)) and 86.8(4)° (C(7)-Te(1)-O(4).

(ii) Te-$Cl_4C_6O_2$-o Interaction

The $Te(O_2C_6Cl_4)$ part of the molecule is structurally very similar to the same unit in $Te(O_2C_6Cl_4)_2$-(18-crown-6) in which the average Te-O bond distance at the tetrachlorocatecholate ligand is 2.014(7) Å, and the r(C-O) value is 1.34(1) Å. Here, as in the present compound, for which the average r(Te-O) and r(C-O) values are 2.075(1) and 1.34(2) Å respectively, the C-O bond length confirms the formulation of the ligand as being a catecholate derived from the *o*-quinone by reduction at the initial tellurium(I) centre. The other feature of interest is that the equatorial Te(1)-O(5) bond (1.983(9) Å) is substantially shorter than the apical Te(1)-O(4) bond (2.195(9) Å) of the catecholate ligand.

Allowing for the distortion from idealized AX_4E stereochemistry caused by the presence of the bidentate ligand(s), the structures of this molecule, of $Te(O_2C_6H_4)_2$,[121] and of $Te(O_2C_6Cl_4)_2\cdot$(18-crown-6) (see Chapter 3 in this work), are all in reasonable agreement.

There remains the matter of the orientation of the two $(Cl_4C_6O_2)TeC_6H_5$ units with respect to each other, and to the bridging oxygen atom. The arrangement can be viewed as a balance between (i) the repulsive interactions between the presumed lone pair of one tellurium and the catecholate oxygens of the other, and (ii) the attraction of each formally positive tellurium atom to the lone pair of its neighbour. The Te(1)-Te(2) distance in the molecule is 3.509(4) Å, which argues against the presence of any Te-Te bonding interaction. The Te(1)-O(1) and Te(1)-O(2) distances are 3.16(1) and 5.30(1) Å respectively.

The crystal lattice contains two molecules of tetrahydrofuran per molecule of $[(Cl_4C_6O_2)TeC_6H_5]_2O$. These molecules are disordered, and show high thermal vibrational motion, which results in anomalous C-O distances (See Tables 5.4 and 5.5; C(30)-O(7) = 1.24(5), C(32)-O(7) = 1.42(3) Å). It was not possible to model the disorder, but fortunately the effect of this on the overall structure refinement is small. There is no interaction between tellurium atom of the title molecule; the closest approach is at a distance of 3.6 Å.

CHAPTER 6

REACTION OF *o*-QUINONES WITH ELEMENTAL TIN, AND TIN(II) CHLORIDE

6.1 Introduction

Previous works[68,73] in this laboratory have described the results of preparative and spectroscopic investigations of the reactions between substituted *o*-quinones with tin(II) halides. Reactions involving 3,5-di-Bu^t-*o*-benzoquinone (dbbq) or 9,10-phenanthroquinone were found suitable for study by ESR spectroscopy, which showed that tin-semiquinone derivatives are intermediates in these processes. A satisfactory mechanism was proposed for these reactions to explain both preparative and ESR results in terms of two successive one-electron transfer processes.

In a related study, it was also reported[71] that elemental tin reacted with tetrahalogenated orthobenzoquinones *o*-$O_2C_6X_4$ (X = Cl or Br) in refluxing toluene, to give tin(IV) catecholato species $Sn(O_2C_6X_4)_2$, from which neutral and anionic derivatives could be obtained. The reaction of Sn + *o*-$O_2C_6X_4$ + I_2 + 1,10-phenanthroline was reported to produce $Sn(O_2C_6X_4)I_2phen$.

In this chapter we will present some preliminary results on the preparative and spectroscopic investigation of the reaction between elemental tin and dbbq, and that between tin(II) chloride and the unusual *o*-quinone 1,10-phenanthroline-5,6-dione.

6.2 Experimental

6.2.1 General

All chemicals were reagent grade or better, and were used as supplied. Solvents were dried by conventional methods, and stored over drying agents. All reactions were carried out in an atmosphere of dry nitrogen unless otherwise noted.

The instruments and procedures for spectroscopic and elemental analysis in this work have been described in Chapter 1 of this dissertation.

6.2.2 Reaction of Tin Metal with dbbq

Finely divided tin metal (0.119 g, 1 mmol) was added to a toluene (20 cm^3) solution of dbbq (0.441 g, 2 mmol). The mixture showed no sign of reaction at room temperature, but after it was heated to reflux conditions, the red-green colour of the solution darkened. After *ca.* 6 h refluxing, all the tin metal disappeared and a dark green homogeneous solution was obtained. This solution was kept under reflux overnight and then cooled to room temperature. A sample of this greenish solution gave a strong ESR spectrum which is characteristic for a multiple radical substance. The final product seems very soluble in toluene or hexanes, since efforts at isolation failed for both of these solvents. When acetonitrile instead of toluene was used as reaction solvent, a similar colour change was observed, but the reaction is very limited in this medium as shown by the large amount of tin metal left after 24 h refluxing. A filtered solution of the product in toluene was usually used directly as starting material for the further reactions. A solid sample of this product was obtained by completely evaporating the solvent, and dried *in vacuo*. This solid product analysed as $Sn(dbsq)_2$ by elemental analysis, but with significant errors. Found: C 57.6, H 6.66 and Sn 20.3%. Calculated for $C_{28}H_{40}O_4Sn$: C 60.1, H 7.21, Sn 21.2%. The yield of this green product is almost quantitative based on the reactants added.

6.2.3 Reaction of $Sn(dbsq)_2$ with Lewis Bases

(i) There was no precipitate when hexanes (20 cm^3) were added to the filtered toluene solution (20 cm^3) from the reaction of tin metal with dbbq in 1:2 mole ratio (0.5 mmol tin and 1 mmol dbbq). When 0.5 mmol 2,2'-bipyridine was added to the above mixture, a yellow-brown solid came out of solution immediately, and the colour of the solution changed to pale yellow. The resultant mixture was stirred at room temperature for 2 h, after which the precipitate was collected by filtration, washed carefully with hexanes (2 x 10 cm^3), and dried *in vacuo*. The weight of this product was 0.403 g, yield 92% based on the quantities of the reactants added. In the later analysis, 0.5 molecule toluene was found for each molecule of $Sn(dbc)_2$.bipy. Found: C 65.4, H 6.79, N 3.46 and Sn 16.1%. Calculated for $(C_{28}H_{40}O_4)Sn(C_{10}H_8N_2)0.5(C_7H_8)$: C 65.5, H 6.88, N 3.68 and Sn 15.6%. The ^{119}Sn NMR of this product in $(CD_3)_2SO$ shows a resonance at -513.22 ppm.

(ii) 4-Bu^t-pyridine (0.270 g, 2 mmol) was added to the filtered toluene solution (20 cm^3) from the reaction of tin metal (0.119 g, 1 mmol) with dbbq (2 mmol) through a dropping funnel at room temperature. During this addition, the original dark green colour of the solution discharged, and a pale yellow clear solution was eventually obtained. When hexanes (15 cm^3) were added to this solution, no precipitation occurred, but when the mixture was placed in the refrigerator, a 60% yield (based on the quantity of tin metal used) of a pale yellow crystalline product resulted after 24 h. This product was identified as $(C_{28}H_{40}O_4)Sn(4\text{-t-butyl-}C_5H_4N)\text{-}C_7H_8$. Found: Sn 14.5%, Calculated: Sn 14.3%.

6.2.4 Reaction of $Sn(dbsq)_2$ with Ph_4PCl

A solution of Ph_4PCl (0.5 mmol, 0.187 g) in acetonitrile (10 cm^3) was added to a filtered toluene solution (20 cm^3) from the reaction of dbbq with tin metal in 2:1 ratio (1 mmol dbbq, and 0.5 mmol tin) at room temperature. The resultant solution was stirred at room temperature for 4 h. No precipitate appeared either in these processes or in the subsequent evaporation of the solvent under vacuum. After all solvent was removed, diethyl ether (20 cm^3) was added to the residue. The resultant pale green solid was collected by filtration, washed carefully with diethyl ether (2 x 5 cm^3), and dried *in vacuo*. The weight of this product was 0.65 g, yield 70% based on the quantities of the reactants used. Found: C 65.2, H 6.07 and Sn 12.2%. Calculated for $(Ph_4P)^+[Sn(dbc)_2Cl]^-$: C 66.9, H 6.47 and Sn 12.7%. ^1H NMR resonances are listed in Table 6.1.

TABLE 6.1

^{1}H-NMR of Sn(dbc)$_2$L$_2$nC$_7$H$_8$ in (CD$_3$)$_2$SO;

Values in ppm Relative to TMS (δ=0)

Compound	Chemical Shifts	Assignment
Sn(dbc)$_2$(4-Bu^t-Py)$_2$	1.22(m), 1.46(s), 54H	Bu^t-, dbc and 4-Bu^t-Py
(C$_7$H$_8$)	2.34(s), 3H	Me-, Toluene
	6.54(d), 6.6(d), 2H	H^4 and H^6, dbc
	7.20-7.32(m), 5H	aromatic H, Toluene
	7.33(d), 4H	H^3 and H^5, 4-Bu^t-Py
	8.52(d), 4H	H^2 and H^6, 4-Bu^t-Py
Sn(dbc)$_2$(bipy)	1.22(s), 1.39(s), 36H	Bu^t-, dbc
0.5(C$_7$H$_8$)	2.30(s), 1.5H	Me-, toluene
	6.48(s), 6.61(b), 4H	H^4 and H^6, dbc
	7.16-7.25(m), 2.5H	aromatic H, toluene
	7.45(t), 2H	H^6 and H$^{6'}$,
	7.93(t), 2H	H^5 and H$^{5'}$,
	8.40(d), 2H	H^4 and H$^{4'}$, dipy
	8.70(d), 2H	H^3 and H$^{3'}$
(Ph$_4$P)$^+$	6.31-6.81(m, br), 4H	H^4 and H^6, dbc
[Sn(dbc)$_2$Cl]$^-$	1.19(s), 1.34(s), 36H	Bu^t-, dbc
	7.79-7.97(m), 20H	Ph, Ph$_4$P$^+$

6.2.5 Reaction of Sn(dbsq)$_2$ with Tetrahalogeno-*o*-benzoquinone

Tetrachloro-*o*-benzoquinone (0.1230 g, 0.5 mmol) was added to a filtered toluene solution (20 cm^3) from the reaction of dbbq with tin metal in 2:1 ratio (1 mmol dbbq, 0.5 mmol tin) at room temperature. The resultant solution was then stirred at room temperature for 24 h, refluxed for 1 h and then cooled to room temperature. A sample of this resultant solution showed characteristic multiple radical feature in its ESR spectrum when measured in both room temperature and 77 K. All solvents were removed under vacuum, after which acetonitrile (20 cm^3) was added to the reaction residue. The resultant grey-green precipitate was collected by filtration and dried *in vacuo*. The weight of this product was 0.49 g, yield 61%, based on the quantities of the reactants used. Found: Sn 14.0%. Calculated for Sn(dbsq)$_2$(O$_2$C$_6$Cl$_4$): Sn 14.7%. A similar reaction conducted by using tetrabromo-*o*-benzoquinone gave a similar result. Found: Sn 11.3 %. Calculated for Sn(dbsq)$_2$(O$_2$C$_6$Br$_4$): Sn 12.1%.

6.2.6 Preparation of 1,10-Phenanthroline-5,6-dione (phen-5,6-dione)

This *o*-quinone ligand was prepared in the fumehood by slight modification of a published procedure.[214] 1,10-Phenanthroline (11.35 g, 63 mmol) in 20% oleum (62.5 cm^3) was heated to 110-115°C and concentrated nitric acid (16.5 cm^3) added. The reaction mixture was then heated to *ca.* 145°C and more concentrated nitric acid (33 cm^3) added over 30 min. At the end of the addition the temperature had dropped to *ca.* 115°C. After stirring for 1.5 h the reaction mixture was cooled to room temperature, poured onto ice, and neutralized with 30% aqueous NaOH solution. The beige precipitate was removed by filtration and thoroughly washed with water. After drying the yield of this solid, which is crude 5-nitro-1,10-phenanthroline, was 9.2 g. The filtrate containing the desired product, was extracted with dichloromethane (3 x 40 cm^3). The crude extract (3.6 g) was recrystallized from methanol and yield pure phen-5,6-dione (2.45 g, 18% yield based on quantity of phenanthroline used), m.p. 254°C. (lit., m.p. 251°C and

258°C);[214,215] ^{1}H NMR in $CDCl_3$: 8.98-9.00 ppm (dd, J_{HH} 1.65, 4.61 Hz, 2H), 8.37-8.41 ppm (dd, J_{HH} 1.71, 7.80 Hz, 2H) and 7.65-7.69 ppm (dd, J_{HH} 4.65, 7.83 Hz, 2H).

6.2.7 Reaction of Phen-5,6-dione with $SnCl_2$ and $CdCl_2$

$CdCl_2$ (0.183 g, 1 mmol) and $SnCl_2$ (0.190 g, 1 mmol) were mixed in a 100 mL Schlenk flask and acetonitrile (20 cm^3) added to the mixture. When phen-5,6-dione ligand (0.210 g, 1 mmol) was added to the above system, a brown-red precipitate was thrown out of the solution immediately and the colour of the solution changed to light brown-yellow. The solid product was collected by filtration and dried *in vacuo*. The yield was quantitative based on the quantities of the reactants added. The elemental analysis of this product agreed with the proposed formula $(CdCl_2)(SnCl_2)$(phen-5,6-cat)•CH_3CN. Found: C 26.8, H 1.62 and N 5.23%; Calculated for $C_{13}H_9O_2N_3SnCdCl_4$: C 26.9, H 1.45 and N 6.73%.

6.3 Results and Discussion

6.3.1 Reaction of Metallic Tin with dbbq

The formation of $Sn(dbsq)_2$ in the reaction between metallic tin with dbbq in refluxing toluene was identified by the elemental and spectroscopic (IR and ESR) analysis as well as by the results of its further reactions with other chemicals. The poor agreement in the elemental analysis of this compound and of $\{(Ph_4P)^+[Sn(dbc)_2Cl]^-\}$ shows that further work is needed to confirm the tentative results. The presence of dbsq radical anions in the products is evidenced by the ESR spectrum, the colour and the infrared spectrum. The very strong broad IR band centred at 1654 cm^{-1} in free dbbq, identified as $\nu(C=O)$, is completely absent in the product, being replaced by strong $\nu(C\text{-}O)$ modes seen as a pair of absorptions at *ca.* 1440 + 1250 cm^{-1}, confirming the reduction of the quinone. The room temperature ESR spectrum of the toluene solution of $Sn(dbsq)_2$ shows a doublet, which might result from the coupling between the unpaired electrons and a proton in the dbsq ring, and the further coupling of spin active isotopes of tin was very weak but observable. The spin-triplet spectra were observed in frozen solution at 77K and the signal for half-resonant-field transition was also observed in this case. Qualitatively, the addition of a small amount of bipy [much less than the quantity of $Sn(dbsq)_2$] to this solution at room temperature caused additional coupling, and a decrease in the intensity of the spectrum. In another experiment, we investigated the toluene solution that resulted from the reaction of metallic tin with dbbq in 1:4 molar ratio. We were able to obtain an interesting spectrum from this system. Fig. 6.1 shows the experimental and simulated ESR spectra of this system. The computer simulation and calculation gave the important parameters as following: $g_x = g_y = 2.003$, $g_z = 2.000$, $D = 209$ G (195×10^{-4} cm^{-1}), $E = 44$ G. (The spin-spin parameters D and E are determined by the dipole-dipole interaction between spins on the two semiquinone radical anions and are useful for the conformation information of the metal complexes). It is interesting to note in an earlier paper,[70] Dr. B.R. McGarvey *et al*. calculated a value of $D = -210 \times 10^{-4}$ cm^{-1} for $Sn(IV)(dbsq)_2(dbc)$. (dbbq = 3,6-di-Bu^t-1,2-*o*-benzoquinone) based on previous results[63b], while they calculated $D = -162 \times 10^{-4}$ cm^{-1} and -109×10^{-4} cm^{-1} for the cis and trans forms of $Sn(dbsq)_2$. Our experimental product in this system (Sn + dbbq, 1:4 molar ratio), therefore, would be more likely $Sn(IV)(dbsq)_2(dbc)$.

The reaction of metallic tin with dbbq can be understood in terms of reactions already reported in other papers from our laboratory and other groups.[71,72] The analogous reaction between indium metal and dbbq has been shown[72] to give rise to a stable $(dbsq)In^I$: species in solution. The reaction of metallic tin with tetrahalogeno-*o*-benzoquinone was also proposed to involve two successive one-electron transfer processes, giving a tin(II) species as the primary result. The spectroscopic investigation of 3,6-di-Bu^t-1,2-*o*-benzoquinone with amalgamated tin was also reported by Kabachnik *et al*[62,64]. Based on their ESR spectra they proposed either the four-coordinate tin(II) complex $Sn(dbsq)_2$ or six-coordinate tin(IV) complex $Sn(dbsq)_2(dbc)$ as the

FIGURE 6.1

ESR Spectra of Sn + dbbq (1:4 mole ratio)

(A) Experimental and (B) Simulated Result

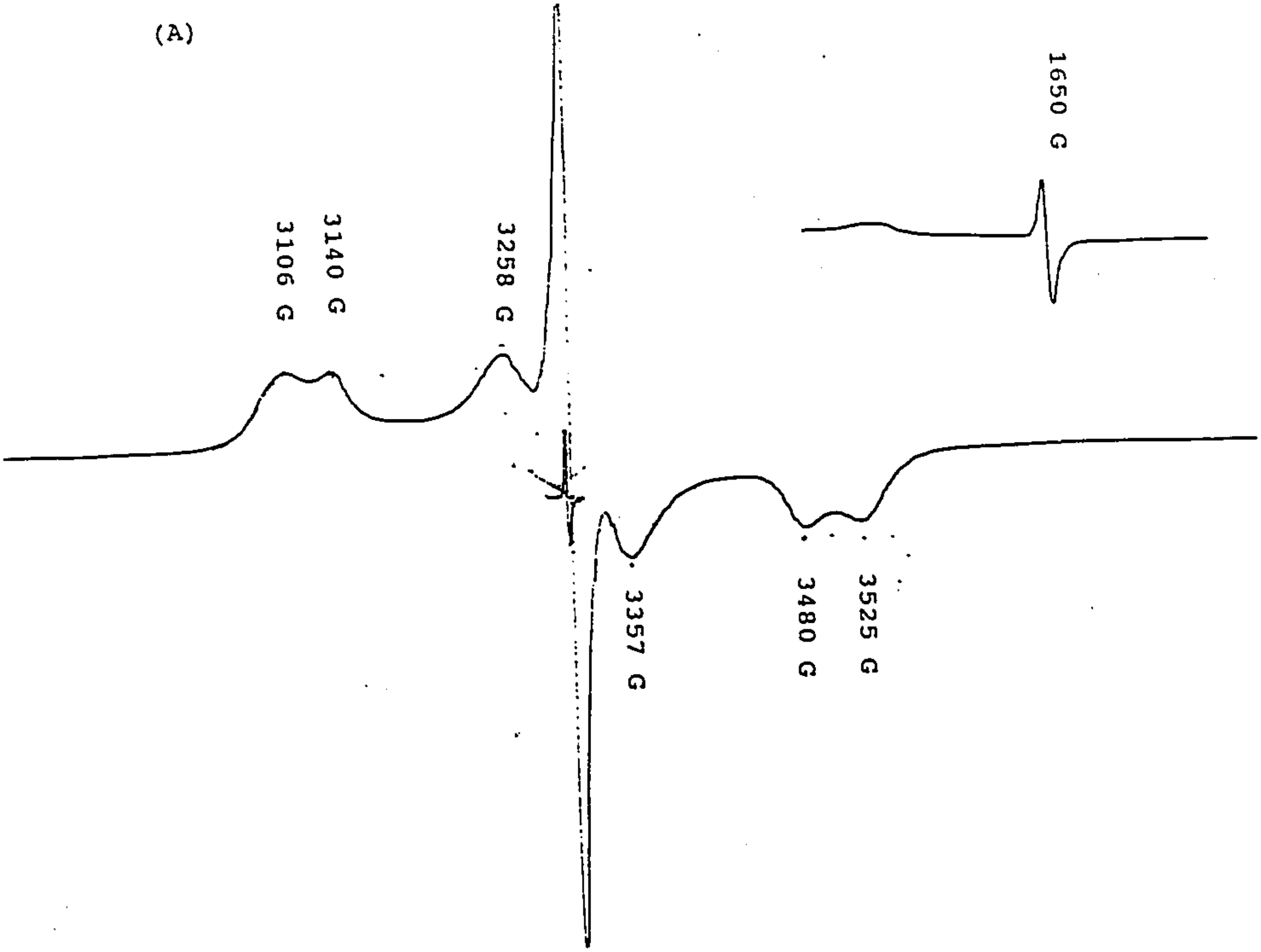
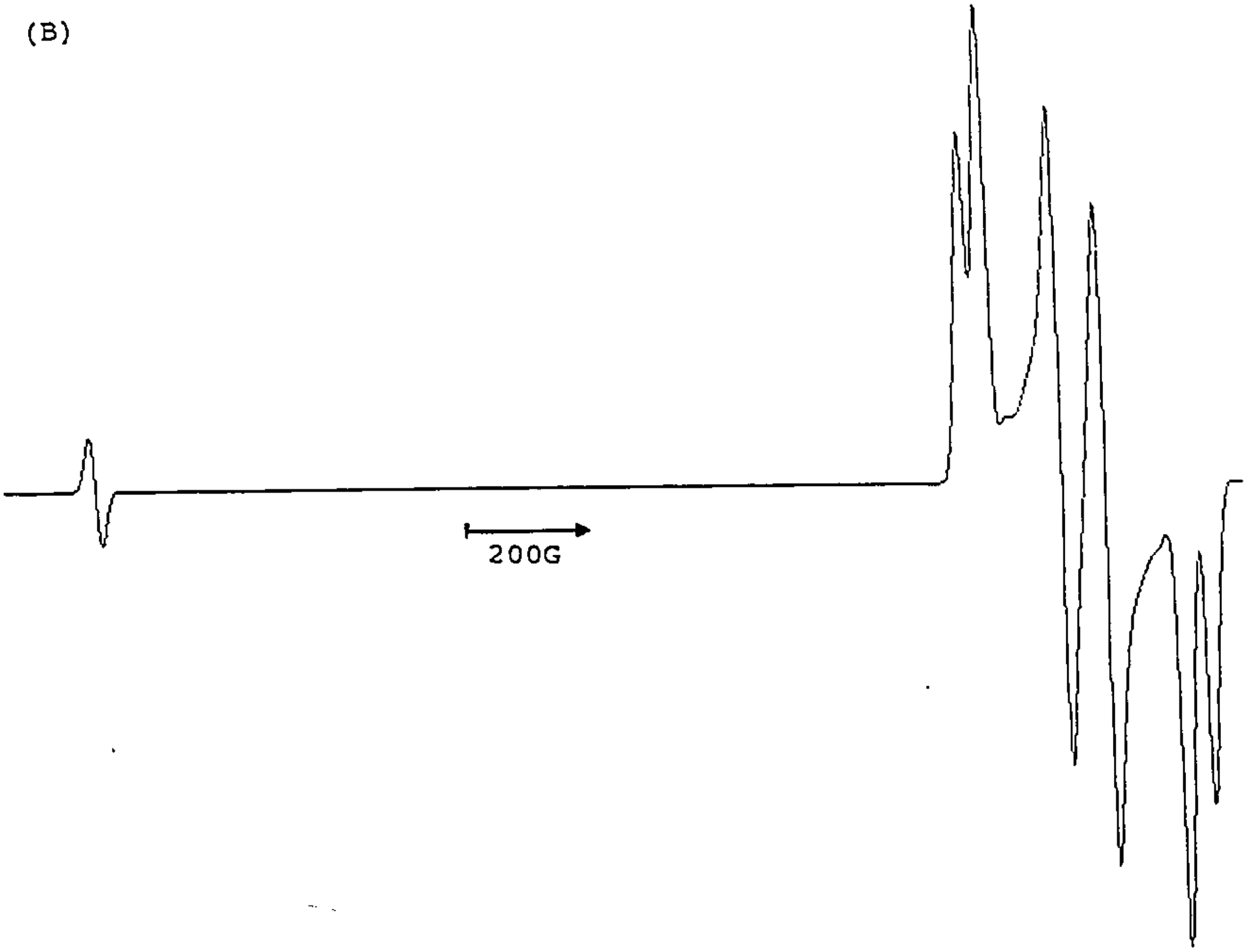


FIGURE 6.1 *cont'd*



reaction products, depending on the quantities of tin and quinone used in the reactions. Another report[70] which is relevant to our current study has shown the direct reaction of metals with dbbq was an effective method of preparing biradical complexes M(dbsq)$_2$ (M = Zn, Cd, Mg and Ba). Based on this information, and on our own results on tin-quinone system, we propose that the initial step is a one-electron transfer process; the resultant Sn^I(dbsq) then undergoes a second one-electron transfer reaction to give the stable Sn(dbsq)$_2$ product (see below). By comparison with the reactions of other main group metal systems described in recent papers[71,72] from this laboratory, the further reactions of Sn(dbsq)$_2$ are also understandable (see below). The stability of Sn(dbsq)$_2$ compared to the product of the reaction of tin with tetrahalogeno-*o*-benzoquinones, which yielded Sn(O$_2$C$_6$X$_4$)$_2$ catecholate compounds, might depend on the fact that dbbq has a weaker oxidizing power than tetrahalogeno-*o*-benzoquinones. In the existence of excess dbbq, the six-coordinate Sn(dbsq)$_2$(dbc) was produced by further oxidation of the initial product.

6.3.2 Reactions of Sn(dbsq)$_2$

The investigation of the tin-*o*-quinone reaction systems has proved very interesting, and an important part of our knowledge of this area. Even though the work discussed here is only at its beginning, we already see some promising results and more effort is required in this area. At this point, the processes which we have already investigated can be tentatively summarised in Scheme 6.1.

$$\begin{tikzcd}
 & & {[(dbc)_2Sn^{IV}Cl]^-(Ph_4P)^+} & \\
dbbq + Sn \arrow[r] & (dbsq^{\dot{-}})Sn^{I} \arrow[r] & (dbsq^{\dot{-}})Sn^{II}(dbsq^{\dot{-}}) \arrow[u, "Ph_4PCl"'] \arrow[r, "2L"] \arrow[d, "o\text{-}Q"] & L_2Sn^{IV}(dbc)_2 \\
 & & (dbsq^{\dot{-}})_2Sn^{IV}(R_n\text{-cat}) &
\end{tikzcd}$$

L_2 = bipy, 2 (4-Bu^t-py). *o*-Q = dbbq; *o*-$O_2C_6X_4$, X = Cl or Br.

R_n-cat = dbc and X_4-catecholate.

Scheme 6.1

The reaction of $Sn(dbsq)_2$ with Lewis donors may induce intramolecular electron transfer between Sn(II) and dbsq radical anions to produce the stable diamagnetic six-coordinate Sn(IV) complexes $Sn(dbc)_2L_2$ (L_2 = bipy or 2 x 4-Bu^t-py). Strong ESR signals were absent in these adducts. This type of electron transfer process has been found in a variety of examples for both transition metal and main group metal complexes.[58,68] Using chlorides from Ph_4PCl as the donor would cause a similar electron transfer to produce a five-coordinate Sn(IV) complex. The ^1H and ^{13}C NMR spectra of the products from these reactions are summarised in Tables 6.1 and 6.2 respectively. The characteristic aromatic resonances for the bidentate nitrogen donor ligands and the integrations in the ^1H NMR support the proposed formulae for these compounds. These and the ^{13}C NMR results are consistent with the reported results for similar metal adduct compounds, and are assigned according to these reported results[68] and the NMR empirical equations for substituted pyridine[90a].

TABLE 6.2

^{13}C NMR of Sn(dbc)$_2$L$_2$nC$_7$H$_8$ in (CD$_3$)$_2$SO;

Values in ppm Relative to TMS (δ = 0)

(a) Sn(dbc)$_2$(bipy)·0.5(C$_7$H$_8$)

dbc

C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}
145.8	149.2	137.1	109.2	132.6	110.2	34.4	33.7	31.8	29.8

2,2'-dipyridine

$C^{1,1'}$	$C^{3,3'}$	$C^{4,4'}$	$C^{5,5'}$	$C^{6,6'}$
149.2	155.2	137.3	120.4	124.2

0.5(C$_7$H$_8$)

C^α	Others
21.0	125.3-137.8

(b) Sn(dbc)$_2$(4-Bu^t-Py)$_2$·C$_7$H$_8$

dbc

C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}
146.7	146.7	139.1	110.6	134.6	112.0	35.0	34.3	30.1	29.8

4-Bu^t-pyridine

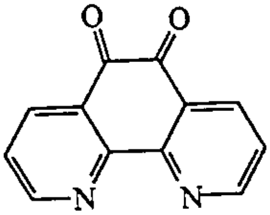
$C^{2,2'}$	$C^{3,3'}$	C^4	C^α	C^β
149.1	122.6	165.4	35.4	31.7

C$_7$H$_8$

C^α	Others
21.5	128.2-129.0

The reduction of tetrahalogeno-*o*-benzoquinone by $Sn(dbsq)_2$ was demonstrated by the absence of $\nu(C=O)$ in the infrared spectra of the reaction products. The room temperature ESR spectra of these systems were broad singlets. The spin-triplet spectra of these systems were observed in frozen solution at 77 K, a signal of half-resonance-field transition, typical for biradical system, were also observed. Considering the stronger oxidizing power of tetrahalogeno-*o*-benzoquinones relative to dbbq, it is reasonable to propose that the dbsq radical anion would be more stable than the corresponding X_4-semiquinones. We therefore propose the final products are $Sn(dbsq)_2(X_4\text{-cat})$.

6.3.3 Reaction of Phen-5,6-dione ligand with $SnCl_2$ and $CdCl_2$



1,10-Phenanthroline-5,6-dione(phen-5,6-dione)[216] has a unique bifunctional structure and therefore introduces new dimensions and interest to the study of *o*-quinone-metal complexes. In addition to the structural character, this ligand may also be used to adjust electrochemical potentials and it may serve as a bridging ligand in the construction of multinuclear complexes. When coordinated through either its oxygen atoms or nitrogen atoms, the entire complex resembles either a "bipyridine-equivalent" or a "*o*-benzoquinone-equivalent" ligand in the synthesis of a binuclear complex. Complexes of the forms $(Ph_3P)_2Pt(O,O'\text{-phen-5,6-cat})$, $Cl_2Pd(N,N'\text{-phen-5,6-dione})$ as well as $(Ph_3P)_2Pt(O,O'\text{-phen-5,6-cat-}N,N')PdCl_2$ have been prepared in recent years.[240-243] During these studies it has been proved that the phen-5,6-dione bridge has a redox activity at potentials near the redox potentials of electroactive transition metal ions. The electrochemical behaviour of this ligand and its N,N'-coordinated metal complexes has been examined by Abruna and Goss[244] using cyclovoltametry. In acetonitrile, the free ligand shows two reversible one-electron reduction waves. The formal potential for these processes are -0.445 and -1.251 v, which represent the formation of the anion radical and dianion of the ligand. The quinone-based redox properties of this ligand are retained after coordination to a metal ion, while the reduction potentials corresponding to these properties are changed by this coordination. For example, these reductive potentials are -0.112 and -0.425 v in [Co(phen-5,6-dione)], and -0.067 and -0.655 v in $[Os(bipy)(phen\text{-}5,6\text{-}dione)_2]^{2+}$. The electronic and cyclovoltametry spectra indicate it has stronger πacidity than phen.

In this work we studied the reaction of phen-5,6-dione with a redox inert metal halide $CdCl_2$ and a redox active metal halide $SnCl_2$. The elemental analysis identified the final product as $(CdCl_2)(SnCl_2)$(phen-5,6-cat)CH_3CN. The existence of CH_3CN in the final product was also confirmed by NMR spectroscopic results, which showed a singlet at 2.08 ppm (3H) in ^1H and resonance at 1.17 ppm in ^{13}C NMR. The reduction of phen-5,6-dione ligand was demonstrated by the absence of the characteristic strong $\nu(C=O)$ vibration of the original phen-5,6-dione at 1682 cm^{-1} in the infrared spectrum of the product, replacing by a pair of strong absorptions at *ca.* 1376 and 1071 cm^{-1}. Based the different redox properties of the metal halides used in this work, we propose that the $CdCl_2$ coordinated to the nitrogen atoms of phen-5,6-dione, and that $SnCl_2$ was oxidized to Sn(IV) and bonded to the catecholate of phen-5,6-dione to form Cl_2Cd(N,N'-phen-5,6-cat-O,O')$SnCl_2 \cdot CH_3CN$. Table 6.3 presents the ^1H NMR resonances of this product compared with those of phen-5,6-dione ligand. The ^{13}C NMR of the product shows the resonances at 118.1, 123.6, 132.2, 133.3, 140.2 and 144.5 ppm respectively. Presumably this is due to the phen-5,6-cat ligand carbons in six different environments. The symmetric nature of the resonances shows that this catecholate ligands is symmetrically bonded to the metal atoms, and this symmetry is also confirmed by its ^1H NMR data.

TABLE 6.3

^{1}H-NMR of PHD Ligand and Its Metal Complexes

Values in ppm Relative to TMS ($\delta = 0$)

Compound	Chemical Shifts	Assignment
Phen-5,6-dione[a]	8.98-9.00(dd), 2H	
	8.37-8.41(dd), 2H	
	7.65-7.69(dd), 2H	
(Phen-5,6-cat)SnCdCl$_4$[b,c]	8.89-8.95(br), 2H*	
·CH_3CN	8.70-8.73(br), 2H*	
	7.92-7.95(br), 2H*	
	2.08(s), 3H	CH_3CN

a in $CDCl_3$

b (Phen-5,6-cat)SnCdCl$_4$ = Cl_2Cd(N,N'-phen-5,6-cat-O,O')$SnCl_2$·CH_3CN

c in $(CD_3)_2SO$

* poor resolved double doublet

In view of the promising results of the transition metal phen-5,6-dione complexes and the well developed main group metal o-quinone coordination chemistry, it would be interesting to extend this work to other main group substances in the future. Based on the fact that this ligand and its N,N'-coordinated metal complexes offer a variety chemically useful oxidative strengths, it would be interesting to try the reactions between main group elements such as indium, gallium, tin, etc. or their low oxidation state compounds such as InX, SnX_2, TeR_2, AR_3 (A = P or Sb), R_6Sn_2, Ar_2Te_2, etc. with either this ligand or its N,N'-coordinated metal complexes. These alternative routes may provide important results of the interesting products in terms of their electrochemical properties, spectroscopic characteristics and structural features. Another advantage for such studies is the improved preparation method for phen-5,6-dione ligand and the availability of its derivatives. For example, a high yield one-pot preparation of this ligand and its 2,9-dichloro derivatives has been reported[245] by Yamada and co-workers very recently. The preparation of the corresponding quinoneimines has also been described[246] by Thomas and co-workers.

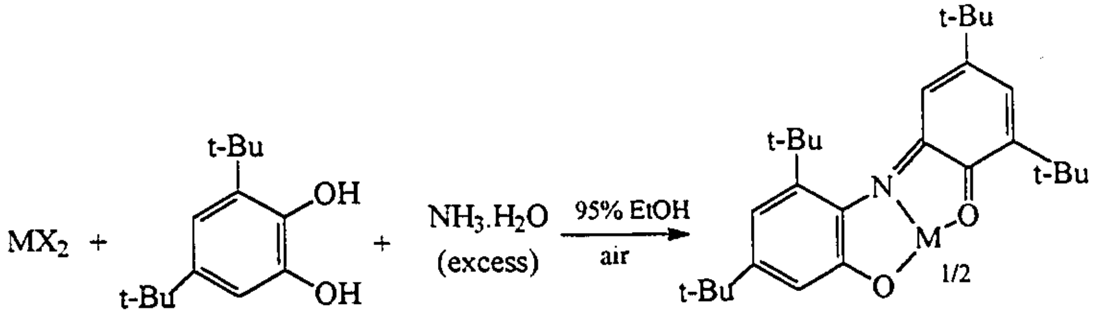
CHAPTER 7

PREPARATION, SPECTROSCOPIC AND STRUCTURAL STUDIES OF A NOVEL SCHIFF-BASE BIQUINONE LEAD(II) COMPLEX

7.1 Introduction

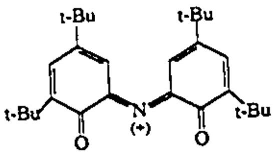
In the previous chapters, we discussed the formation of the Main Group catecholate or semiquinonate complexes from substituted ortho-quinones and a variety of main group elements and their low oxidation state compounds. The reaction of a metal halide complex with a catechol in the presence of base offers an alternate method for the same result. Although this latter method usually does not involve any redox process, it possible to produce compounds with interesting structures which would be difficult to prepare by other routes.

In the mid-70's, Girgis and Balch found[222] that on treating a 95% ethanol solution containing 3,5-di-tert-butylcatechol and a divalent metal ion with concentrated ammonium hydroxide in the presence of air, complexes of the 3,5-di-tert-butyl-1,2-quinone 1-(2-hydroxy-3,5-di-tert-butylphenyl) imine (Cat-N-BQ) anion could be formed:

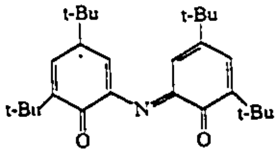


M = Mg, Zn, Fe, Ni, Cu, Cd

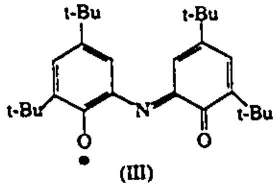
In principle, this ligand may exist in forms ranging in charge from +1 to -3



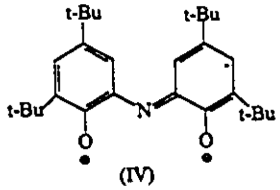
(I)



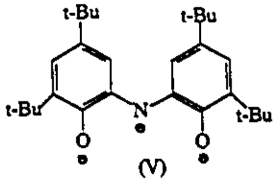
(II)



(III)



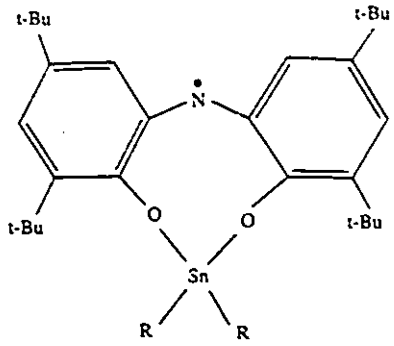
(IV)



(V)

All these forms, especially III-V, may potentially contribute to the coordination properties of this interesting ligand system. Many Cat-N-BQ monoanion or Cat-N-SQ dianion transition metal complexes in which metal cations are in different oxidation states (*e.g.*, M^{2+}, M = Ni, Cu, Zn and Cd; M^{3+}, M = Fe and Co; M^{4+}, M = Ti and Mn) have been prepared and studied by spectroscopic, electrochemical and X-ray crystallographic methods.[222-226] These results are comparable to those on the complexes of simple quinone ligands. On the other hand, additional chemical and physical features have also been found due to the structure and the large number of accessible redox states of this special ligand. For example, a large intramolecular ferromagnetic interaction (coupling constant 56 cm^{-1}) was observed in the titanium(IV) complex.[226]

The research of the main group metal complexes of this ligand is relatively scarce. Beside the preparative work on magnesium complex by Girgis and Balch, Stegmann and Scheffler reported[227,228] that a series of tin(IV) Cat-N-SQ complexes can be produced from the reaction of 2-amino-4,6-di-tert-butylphenoxyl with aryltin (IV) halides. Although they proposed a structure (see below),



based on the spectroscopic results, in which the ligand acts as a bidentate ligand utilizing two oxygen donors. It has been argued[222] from the inspection of space-filling molecular models (Corey-Pauling-Koltum) of this ligand that this type of coordination is impossible. Our interests in main group metal quinone complexes lead us to investigate the reaction of 3,5-di-tert-butylcatechol with lead difluoride under the similar conditions in the transition metal systems. The microanalysis, IR, UV-Visible, ^1H and ^{13}C NMR spectra prove that the reaction product is the lead(II) Cat-N-BQ complex. The X-ray crystallographic studies of this product show that the structure of this complex is remarkably different from those reported for transition metal complexes.

7.2 Experiment

All the chemicals in this work are reagent grade or better and are used as supplied. The instruments and procedures for analysis of this compound were those described in Chapter 1.

7.2.1 Preparation

(i) Lead difluoride (0.294 g, 1.20 mmol) was suspended in a solution of 3,5-di-tert-butylcatechol (1.060 g, 4.82 mmol) in 95% ethanol (50 cm^3). After addition of concentrated aqueous ammonia solution (5 cm^3), a stream of air was gently bubbled through this mixture. The colour of the solution turned dark olive green at this point. After about 30 minutes of stirring, the formation of a dark black-green solid became apparent. After overnight stirring, the olive green solution was filtered and the dark green solid product was washed carefully with 95%

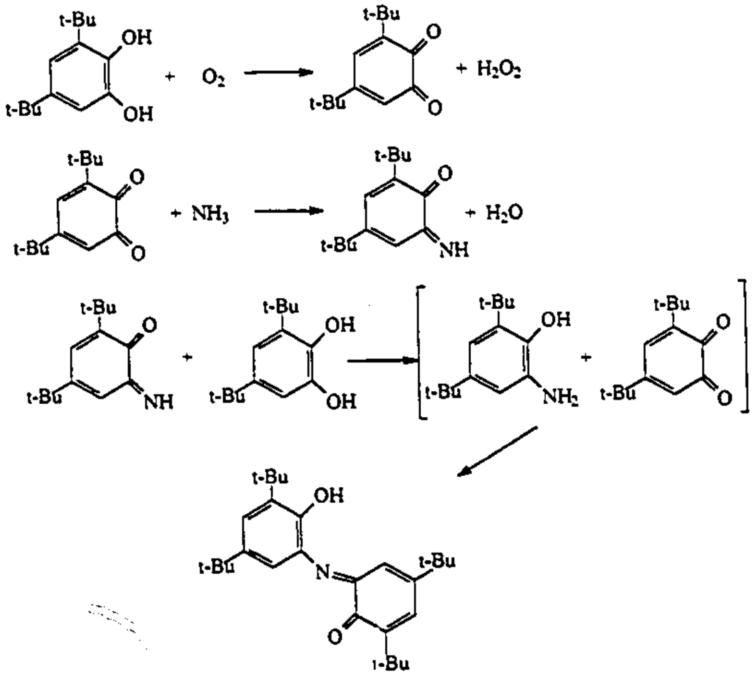
ethanol (2 x 5 cm^3). The vacuum dried product weighed 1.010 g, yield was 80% based on the proposed molecular formula $C_{56}H_{80}N_2O_4Pb$. This formula has been confirmed by the elemental analysis. Found: C 63.9, H 7.57 and N 2.70%. Calculated for $C_{56}H_{80}N_2O_4Pb$: C 63.9, H 7.66 and N 2.66%.

(ii) In another experiment, 3,5-di-tert-butyl-o-benzoquinone (0.530 g, 2.41 mmol) and 3,5-di-tert-butylcatechol (0.530 g, 2.41 mmol) were used to react with lead difluoride (0.294 g, 1.20 mmol). The same procedure in (i) was used in this case except for the employment of air stream. The product in this case gave the same IR and ^{1}H NMR spectra as in (i).

7.3 Discussion

7.3.1 Preparation

The complex $Pb(Cat\text{-}N\text{-}BQ)_2$ was synthesized using procedures similar to those published for transition metal complexes of the same ligand. Girgis and Balch have proposed[222] a reaction pathway for the facile formation of this unusual tridentate ligand in which two redox steps and two Schiff base condensations occur in alkaline solution.



They also reported that the same complexes were formed by the reaction of the metal ion with 3,5-di-tert-butylcatechol, 3,5-di-tert-butyl-1,2-quinone, and ammonia in the absence of air. In this work we find that both routes produce the same lead(II) complex. This complex exhibited moderate solubility in chloroform, acetone and dichloromethane. The colour of its solution is deep green; the solid appears dark black-green. It is interesting to note that the complexes with the metal atoms in their highest oxidation state were reported to be the reaction products when redox active metal halides such as $TiCl_3$, $CoCl_2$ or $MnCl_2$ were used in this type of reactions. In this work the formation of lead(II) complex instead lead(IV) presumably is related to the well known inert electron pair effect of lead $6s^2$ electrons.

7.3.2 Spectroscopic Results

The infrared spectrum of this complex shows similar features with other M(Cat-N-BQ)$_2$ complexes in the region between 700 and 1200 cm^{-1} which are relatively insensitive to ligand charge. For example, the strong bands which appear at 1100, 1000, 900, 860 and 794 cm^{-1} for Zn(Cat-N-BQ)$_2$ complex were found at 1096, 996, 897, 864 and 794 cm^{-1} for this complex. The region from 1200 to 1600 cm^{-1} should contain the C-O and C-N stretching vibrations mixed with aromatic ring vibrational modes and be most sensitive to charge distribution in the complexes. The different band positions in this complex compared with those reported values [eg. absorption bands at 1588, 1472, 1448, 1384, 1359, 1277 and 1246 cm^{-1} for our complex vs 1522, 1375, 1362, 1304, 1291, 1260 and 1244 cm^{-1} for Ni(Cat-N-BQ)$_2$] might indicate different structural features in different complexes. This is consistent with the different geometries of these complexes (see below). The lack of absorptions in the regions associated with N-H and O-H stretching and bending vibrations is consistent with the absence of these units in the complex.

The far-infrared spectrum of this complex shows absorptions at 432, 419, 348 and 286 cm^{-1}; these bands could be due to Pb-X (X = N and O) bonds in this complex. It has been reported[229] that lead oxides show absorptions in the similar region, *e.g.*, 337 and 300 for PbO, 445, 380 and 320 for Pb_3O_4.

All reported complexes of the Cat-N-BQ ligand are highly coloured, with intense absorptions in the visible region of the UV-visible spectra. We observed a very broad strong absorption centred at 778 nm which is comparable to the reported values of 793 and 736 nm for the Zn(cat-N-BQ)$_2$ complex. The spectra of these two complexes in the UV region are also very similar with absorptions at 232, 293 sh, 352 and 467 nm for our complex, against 241, 300 sh, 365 and 430 nm for the Zn complex. This similarity in the spectra of different complexes seems to strengthen the previous argument that the observed transitions are ligand based, and prevent any use of the spectra for probing the electronic structure of the metal ions.

^1H and ^{13}C NMR resonances of this complex were presented in Tables 7.1 and 7.2. Its ^1H and ^{13}C NMR spectra indicate a diamagnetic species. It has been reported that the paramagnetic Cu, Fe and Ni complexes either gave quite different spectra or no spectrum at all. The hydrogens from different aromatic rings and t-butyl groups cannot be clearly distinguished in the ^1H NMR spectrum, but the integration of the spectrum is consistent with the composition of this compound. The ^{13}C NMR spectrum shows the existence of two sets of different C_6 rings in this complex which is quite different from the completely delocalized forms in other M(Cat-N-BQ)$_2$ complexes.

7.4 X-Ray Crystallographic Study

7.4.1 Data Collection and Structure Solution

A dark black green block crystal of $PbO_4N_2C_{56}H_{80}$ **7.1** was mounted on a glass fibre. All measurements were made on a Rigaku AFC6S diffractometer with graphite monochromated MoKα radiation (λ = 0.71069 Å) and a rotating anode generator. Cell constants, and an orientation matrix for data collection, were obtained from a least-squares refinement using the

TABLE 7.1

^{1}H NMR Spectrum of Pb(Cat-N-BQ)$_2$ in Comparison with Other Metal Diquinone Complexes*; Values in ppm Relative to TMS

	Chemical Shifts	
Compound	Ring Protons	Bu^t Protons
$ZnC_{56}H_{80}N_2O_4$	7.28, 7.12	1.23, 1.13
$CdC_{56}H_{80}N_2O_4$	7.14	1.22, 1.19
$FeC_{56}H_{80}N_2O_4$	83.13, 15.13	3.20, -2.11
$NiC_{56}H_{80}N_2O_4$	29.45, 8.17	1.76, 0.21
$CuC_{56}H_{80}N_2O_4$	cannot be observed	
$PbC_{56}H_{80}N_2O_4$	7.10, 6.90	1.40, 1.20
dbbq	6.96, 6.13	1.21, 1.18
dbc	6.71, 6.66	1.35, 1.22

* results from ref. 222

TABLE 7.2

^{13}C NMR Spectrum of Pb(Cat-N-BQ)$_2$ in CDCl$_3$ (PPM) Relative to TMS

Chemical shift	Assignment
29.2 29.9	primary carbons of Bu^t
30.5 31.3	C25-C27; C29-C31; C33-C35; C54-C56; C38-C41; C42-C44;
	C46-C48; C50-C52
34.1 34.7	quarternary carbons
35.0 35.2	of Bu^t
	C28, C32, C36, C37, C41, C45, C49, C53
121.2 127.9	carbons of the
129.1 133.8	four C$_6$ rings
136.1 137.5	C1-C6, C7-C12, C13-C18, C19-C24
139.4 140.5	
142.4 147.0	
170.8 179.9	

setting angles of 25 carefully centred reflections in the range $25.12 < 2\theta < 29.06°$. Based on the systematic absences h0l: $h + l \neq 2n$; 0k0: $k \neq 2n$, the space group was identified as: $P2_1/n$ (no. 14), and this was confirmed by subsequent solution and refinement of the structure. Details of the intensity collection are given in Table 7.3.

No decay correction was applied, since the intensities of three representative reflections which were measured after every 150 reflections remained constant throughout the data collection, indicating crystal and electronic stability. The linear absorption coefficient for MoKα is 30.6 cm^{-1}. An empirical absorption correction, using the program DEFABS, was applied which resulted in transmission factors ranging from 0.92 to 1.01. The data were also corrected for Lorentz and polarization effects.

The structure was solved by direct methods. The non-hydrogen atoms were refined either anisotropically or isotropically [those carbon atoms which were refined isotropically are C(7)-C(13), C(17), C(38), C(41) and C(44)]; hydrogen atoms on carbon were initially included in ideal positions, and subsequently refined isotropically. After several cycles of refinement, the structure converged to $R = 0.068$ and $R' = 0.083$. A final Fourier difference map calculation showed no peaks of chemical significance; the maximum and minimum peaks corresponded to 1.20 and -1.90 eÅ^{-3} respectively. In these calculations, neutral-atom scattering factors were taken from Cromer and Waber.[149] Anomalous dispersion effects were included in the calculations;[150] the values for $\Delta f'$ and $\Delta f''$ were those published by Cromer.[151] All calculations were performed using the TEXSAN[152] crystallographic software package. The structure of the molecule and the cell packing diagram are shown in Figs. 7.1 and 7.2, the positional parameters in Table 7.4, and the important bond distances and angles in Table 7.5.

7.4.2 Description and Discussion of the Structure

Even though the transition metal complexes of this ligand exist in different electronic

Table 7.3

Summary of Crystal Intensity Data, Collection, and Structural Refinement for Pb(Cat-N-BQ)$_2$

Chemical formula	$PbC_{56}H_{80}N_2O_4$
M	1052.46
Crystal system	Monoclinic
Space group	$P2_1/n$ (no. 14)
a/Å	14.525(9)
b/Å	26.048(1)
c/Å	15.118(5)
$\alpha/°$	90.00
$\beta/°$	99.87(4)
$\gamma/°$	90.00
U/Å^3	5635(5)
Z	4
F(000)	2176
D_c/g cm^{-3}	1.240
Crystal dimensions/mm	0.4 x 0.4 x 0.3
μ/cm^{-1}	30.6 cm^{-1}
$2\theta/°$ (max)	50
Total reflections measured	10628
Unique data used [$I \geq 3\sigma$ (I)]	4451
T/°C	23
No. of parameters	513
R	0.068
R'	0.083
Maximum shift/error in final cycle	0.00
Maximum, minimum peaks in final difference map/eÅ^{-3}	1.20, -1.90

FIGURE 7.1

An ORTEP Diagram of Pb(cat-N-BQ)$_2$ 7.1, with Atoms Shown as 30% Probability Ellipsoids. Hydrogen Atoms and the Methyl Groups of Bu^t have been Omitted for Clarity; C(29)-C(31) RIDE ON C(28), C(33)-C(35) on C(32), C(25)-C(27) on C(36), C(38)-C(40) on C(37), C(42)-C(44) on C(41), C(46)-C(48) on C(45), C(50)-C(52) on C(49) and C(54)-C(56) on C(53)

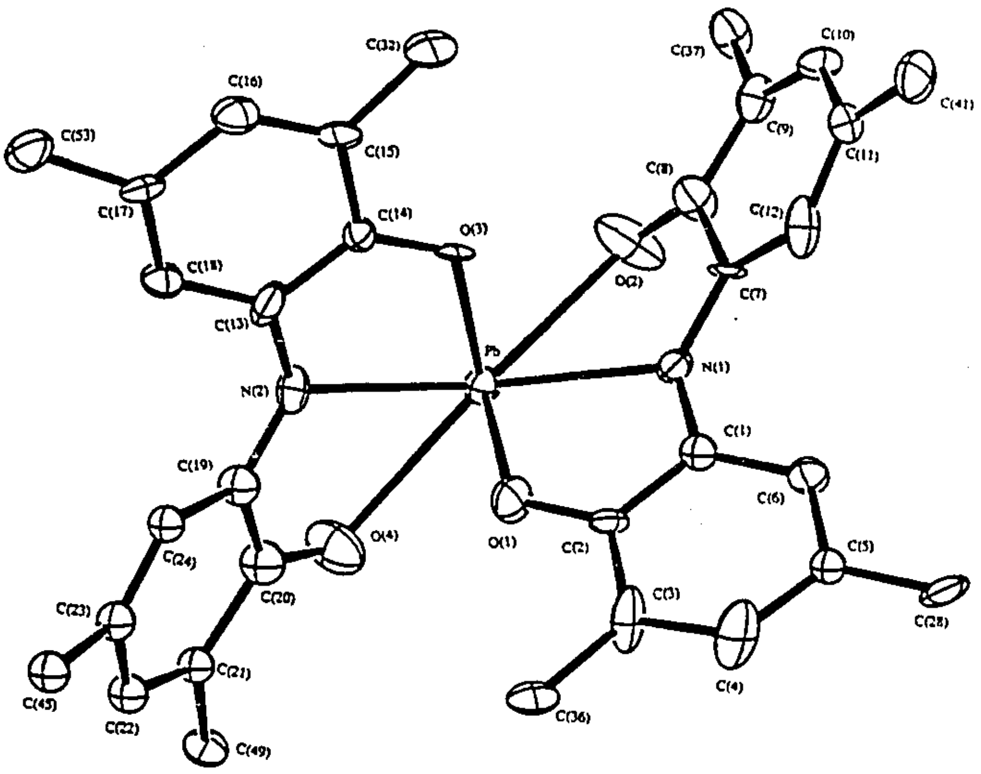


FIGURE 7.2

Cell Packing Diagram of Pb(Cat-N-BQ)$_2$

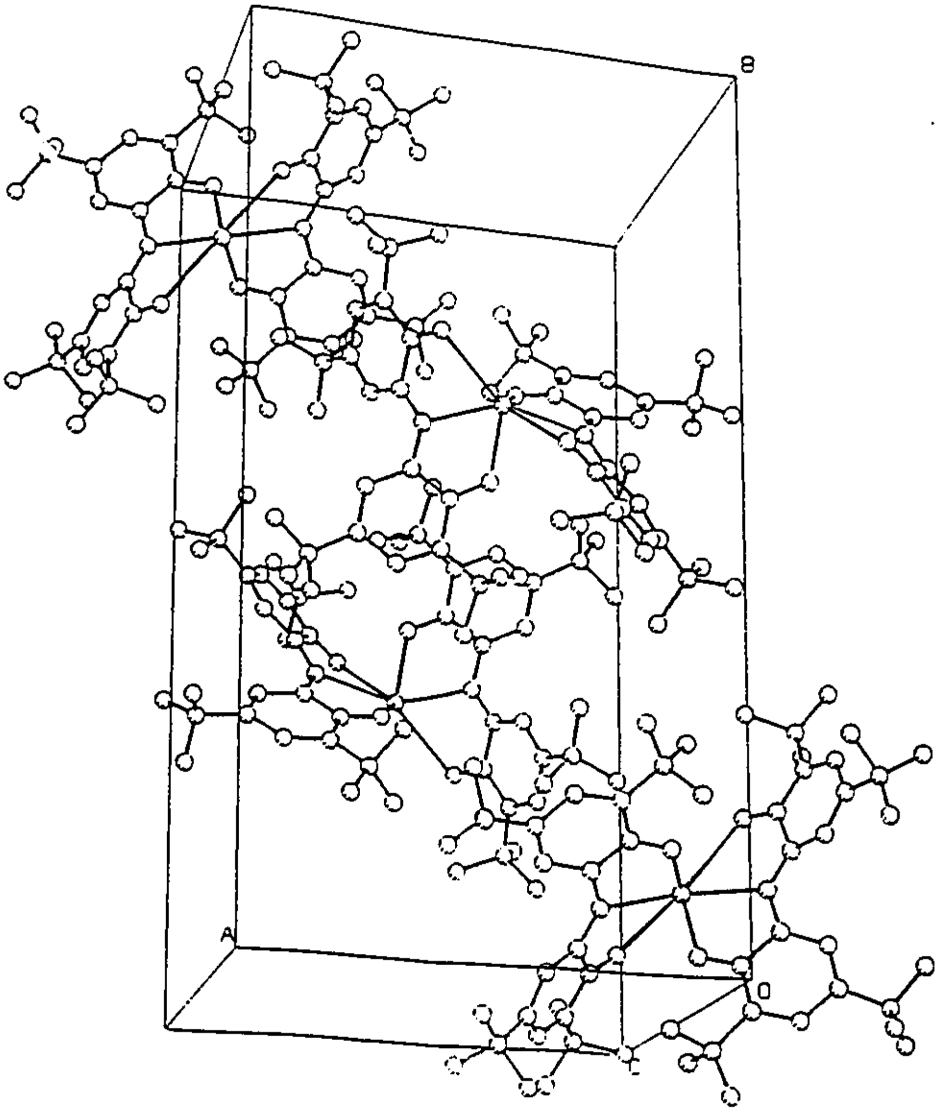


TABLE 7.4

Final Positional Coordinates and Thermal Parameters for Non-Hydrogen Atoms of Pb(Cat-N-BQ)$_2$ with Estimated Standard Deviations (e.s.d.'s) in Parentheses

Atom	x	y	z	B(eq)
Pb	0.04466(6)	0.12323(3)	0.33697(5)	2.91(3)
O(1)	0.034(1)	0.0474(4)	0.263(1)	3.4(6)
O(2)	-0.078(1)	0.2060(6)	0.308(1)	6(1)
O(3)	0.098(1)	0.1578(5)	0.216(1)	4.0(7)
O(4)	0.148(1)	0.0659(7)	0.470(1)	7(1)
N(1)	-0.097(1)	0.1156(7)	0.208(1)	3.1(1)
N(2)	0.217(1)	0.1012(5)	0.330(1)	2.8(7)
C(1)	-0.113(1)	0.0685(9)	0.172(1)	4(1)
C(2)	-0.039(1)	0.0353(7)	0.208(1)	3(1)
C(3)	-0.050(2)	-0.0167(7)	0.176(1)	3(1)
C(4)	-0.131(2)	-0.0305(8)	0.117(1)	4(1)
C(5)	-0.206(1)	0.0049(7)	0.087(1)	3(1)
C(6)	-0.195(1)	0.0537(7)	0.118(1)	3(1)
C(7)	-0.136(1)	0.1600(8)	0.173(1)	3.2(4)
C(8)	-0.126(1)	0.2050(8)	0.231(1)	3.8(5)
C(9)	-0.176(1)	0.2520(8)	0.197(1)	2.5(4)
C(10)	-0.218(1)	0.2556(7)	0.113(1)	3.0(4)
C(11)	-0.217(1)	0.2119(7)	0.051(1)	2.9(4)
C(12)	-0.179(1)	0.1671(7)	0.077(1)	2.6(4)
C(13)	0.252(1)	0.1326(8)	0.269(1)	2.6(4)
C(14)	0.185(1)	0.1624(7)	0.214(1)	3(1)
C(15)	0.216(1)	0.198(1)	0.154(1)	5(1)
C(16)	0.312(2)	0.199(1)	0.153(1)	5(1)

C(17)	0.380(1)	0.1706(7)	0.208(1)	2.5(4)
C(18)	0.349(1)	0.1379(7)	0.267(1)	3(1)
C(19)	0.256(1)	0.0579(7)	0.367(1)	2(1)
C(20)	0.211(1)	0.0372(9)	0.444(1)	4(1)
C(21)	0.254(1)	-0.0056(8)	0.493(1)	3(1)
C(22)	0.318(1)	-0.0316(8)	0.457(1)	3(1)
C(23)	0.357(1)	-0.0164(8)	0.381(1)	3(1)
C(24)	0.327(1)	0.029(1)	0.339(1)	4(1)
C(25)	0.045(2)	-0.063(1)	0.305(2)	7(2)
C(26)	-0.001(2)	-0.1098(8)	0.164(2)	8(2)
C(27)	0.115(2)	-0.036(1)	0.171(2)	7(2)
C(28)	-0.295(2)	-0.0168(9)	0.031(1)	5(1)
C(29)	-0.361(2)	0.027(1)	-0.006(2)	8(2)
C(30)	-0.276(2)	-0.043(1)	-0.053(2)	10(2)
C(31)	-0.343(2)	-0.052(2)	0.083(2)	10(2)
C(32)	0.145(2)	0.2312(7)	0.092(1)	3(1)
C(33)	0.084(2)	0.262(1)	0.142(2)	7(2)
C(34)	0.088(2)	0.195(1)	0.022(2)	6(1)
C(35)	0.194(2)	0.269(1)	0.039(2)	6(1)
C(36)	0.023(2)	-0.0584(8)	0.207(2)	5(1)
C(37)	-0.179(1)	0.3008(8)	0.259(2)	4(1)
C(38)	-0.080(2)	0.3203(9)	0.285(2)	4.9(6)
C(39)	-0.240(2)	0.342(1)	0.214(2)	9(2)
C(40)	-0.218(2)	0.2847(9)	0.342(2)	6(1)
C(41)	-0.255(2)	0.2232(8)	-0.050(1)	3.3(4)
C(42)	-0.185(2)	0.258(1)	-0.086(2)	10(2)
C(43)	-0.350(2)	0.245(1)	-0.068(2)	11(2)
C(44)	-0.261(2)	0.172(1)	-0.105(2)	9.0(9)
C(45)	0.427(2)	-0.048(1)	0.347(2)	5(1)
C(46)	0.373(2)	-0.099(1)	0.306(2)	8(2)
C(47)	0.502(2)	-0.069(1)	0.420(2)	11(2)
C(48)	0.474(2)	-0.026(1)	0.276(2)	8(2)

C(49)	0.215(2)	-0.023(1)	0.576(1)	4(1)
C(50)	0.230(2)	0.018(1)	0.649(2)	8(2)
C(51)	0.111(2)	-0.037(1)	0.554(2)	8(2)
C(52)	0.265(2)	-0.071(1)	0.617(2)	8(2)
C(53)	0.485(2)	0.1755(8)	0.210(2)	5(1)
C(54)	0.506(2)	0.230(1)	0.211(4)	17(3)
C(55)	0.503(3)	0.163(3)	0.118(4)	24(5)
C(56)	0.546(2)	0.155(3)	0.280(4)	27(5)

TABLE 7.5

Interatomic Distances (Å) and Angles (°) for Non-Hydrogen Atoms of $Pb(Cat\text{-}N\text{-}BQ)_2$ with Estimated Standard Deviations (e.s.d's) in Parentheses

Pb	O(1)	2.26(1)	C(7)	C(8)	1.46(3)
Pb	O(2)	2.78(1)	C(7)	C(12)	1.49(2)
Pb	O(3)	2.28(1)	C(8)	C(9)	1.47(3)
Pb	O(4)	2.74(1)	C(9)	C(10)	1.31(2)
Pb	N(1)	2.59(1)	C(9)	C(37)	1.59(2)
Pb	N(2)	2.59(1)	C(10)	C(11)	1.48(3)
O(1)	C(2)	1.27(2)	C(11)	C(12)	1.32(2)
O(2)	C(8)	1.24(2)	C(11)	C(41)	1.56(3)
O(3)	C(14)	1.27(2)	C(13)	C(14)	1.40(2)
O(4)	C(20)	1.29(2)	C(13)	C(18)	1.43(2)
N(1)	C(1)	1.35(2)	C(14)	C(15)	1.43(3)
N(1)	C(7)	1.36(2)	C(15)	C(16)	1.40(3)
N(2)	C(13)	1.39(2)	C(15)	C(32)	1.53(3)
N(2)	C(19)	1.34(2)	C(16)	C(17)	1.39(3)
C(1)	C(2)	1.41(3)	C(17)	C(18)	1.36(2)
C(1)	C(6)	1.38(3)	C(17)	C(53)	1.52(3)
C(2)	C(3)	1.44(2)	C(19)	C(20)	1.53(3)
C(3)	C(4)	1.39(3)	C(19)	C(24)	1.41(3)
C(3)	C(36)	1.54(3)	C(20)	C(21)	1.42(3)
C(4)	C(5)	1.44(3)	C(21)	C(22)	1.34(3)
C(5)	C(6)	1.35(3)	C(21)	C(49)	1.53(3)
C(5)	C(28)	1.53(3)	C(22)	C(23)	1.43(3)
C(23)	C(24)	1.37(3)			
C(23)	C(45)	1.48(3)			
C(36)	C(25)	1.46(3)			
C(36)	C(26)	1.50(3)			
C(36)	C(27)	1.64(3)			

C(28)	C(29)	1.53(3)
C(28)	C(30)	1.50(4)
C(28)	C(31)	1.47(3)
C(32)	C(33)	1.50(3)
C(32)	C(34)	1.55(3)
C(32)	C(35)	1.52(3)
C(37)	C(38)	1.51(3)
C(37)	C(39)	1.49(3)
C(37)	C(40)	1.52(3)
C(41)	C(42)	1.53(3)
C(41)	C(43)	1.46(3)
C(41)	C(44)	1.55(3)
C(45)	C(46)	1.61(3)
C(45)	C(47)	1.52(3)
C(45)	C(48)	1.48(3)
C(49)	C(50)	1.52(3)
C(49)	C(51)	1.54(3)
C(49)	C(52)	1.52(4)
C(53)	C(54)	1.46(3)
C(53)	C(55)	1.49(5)
C(53)	C(56)	1.36(4)

TABLE 7.5 *cont'd*

atom	atom	atom	angle	atom	atom	atom	angle
O(1)	Pb	O(3)	87.5(5)	C(4)	C(3)	C(36)	119(2)
O(1)	Pb	N(1)	65.3(5)	C(3)	C(4)	C(5)	123(2)
O(1)	Pb	N(2)	76.9(5)	C(4)	C(5)	C(6)	117(2)
O(3)	Pb	N(1)	76.3(5)	C(4)	C(5)	C(28)	117(2)
O(3)	Pb	N(2)	66.1(5)	C(6)	C(5)	C(28)	126(2)
N(1)	Pb	N(2)	127.2(5)	C(1)	C(6)	C(5)	121(2)
Pb	O(1)	C(2)	121(1)	N(1)	C(7)	C(8)	117(2)
Pb	O(3)	C(14)	122(1)	N(1)	C(7)	C(12)	125(2)
Pb	N(1)	C(1)	116(1)	C(8)	C(7)	C(12)	118(2)
Pb	N(1)	C(7)	117(1)	O(2)	C(8)	C(7)	124(2)
C(1)	N(1)	C(7)	126(2)	O(2)	C(8)	C(9)	118(2)
Pb	N(2)	C(13)	111(1)	C(7)	C(8)	C(9)	118(2)
Pb	N(2)	C(19)	121(1)	C(8)	C(9)	C(10)	121(2)
C(13)	N(2)	C(19)	127(2)	C(8)	C(9)	C(37)	121(2)
N(1)	C(1)	C(2)	110(2)	C(10)	C(9)	C(37)	117(2)
N(1)	C(1)	C(6)	124(2)	C(9)	C(10)	C(11)	121(2)
C(2)	C(3)	C(6)	125(2)	C(10)	C(11)	C(12)	122(2)
O(1)	C(2)	C(1)	126(2)	C(10)	C(11)	C(41)	116(2)
O(1)	C(2)	C(3)	119(2)	C(12)	C(11)	C(41)	121(2)
C(1)	C(2)	C(3)	114(2)	C(7)	C(12)	C(11)	119(2)
C(2)	C(3)	C(4)	120(2)	N(2)	C(13)	C(14)	115(2)
C(2)	C(3)	C(36)	122(2)	N(2)	C(13)	C(18)	123(2)

atom	atom	atom	angle	atom	atom	atom	angle
C(14)	C(13)	C(18)	121(2)	C(22)	C(23)	C(24)	118(2)
O(3)	C(14)	C(13)	122(2)	C(22)	C(23)	C(45)	122(2)
O(3)	C(14)	C(15)	120(2)	C(24)	C(23)	C(45)	121(2)
C(13)	C(14)	C(15)	118(2)	C(19)	C(24)	C(23)	121(2)
C(14)	C(15)	C(16)	116(2)	C(5)	C(28)	C(29)	110(2)
C(14)	C(15)	C(32)	121(2)	C(5)	C(28)	C(30)	112(2)
C(16)	C(15)	C(32)	123(2)	C(5)	C(28)	C(31)	111(2)
C(15)	C(16)	C(17)	127(2)	C(29)	C(28)	C(30)	103(2)
C(16)	C(17)	C(18)	116(2)	C(29)	C(28)	C(31)	110(2)
C(16)	C(17)	C(53)	125(2)	C(30)	C(28)	C(31)	110(2)
C(18)	C(17)	C(53)	119(2)	C(15)	C(32)	C(33)	112(2)
C(13)	C(18)	C(17)	121(2)	C(15)	C(32)	C(34)	107(2)
N(2)	C(19)	C(20)	114(2)	C(15)	C(32)	C(35)	112(2)
N(2)	C(19)	C(24)	128(2)	C(33)	C(32)	C(34)	112(2)
C(20)	C(19)	C(24)	118(2)	C(33)	C(32)	C(35)	106(2)
O(4)	C(20)	C(19)	116(2)	C(34)	C(32)	C(35)	107(2)
O(4)	C(20)	C(21)	124(2)	C(3)	C(36)	C(25)	113(2)
C(19)	C(20)	C(21)	118(2)	C(3)	C(36)	C(26)	113(2)
C(20)	C(21)	C(22)	117(2)	C(3)	C(36)	C(27)	102(2)
C(20)	C(21)	C(49)	118(2)	C(25)	C(36)	C(26)	111(2)
C(22)	C(21)	C(49)	124(2)	C(25)	C(36)	C(27)	109(2)
C(21)	C(22)	C(23)	126(2)	C(26)	C(36)	C(27)	108(2)

atom	atom	atom	angle	atom	atom	atom	angle
C(9)	C(37)	C(38)	107(2)	C(46)	C(45)	C(47)	103(2)
C(9)	C(37)	C(39)	113(2)	C(46)	C(45)	C(48)	108(2)
C(9)	C(37)	C(40)	109(2)	C(47)	C(45)	C(48)	108(2)
C(38)	C(37)	C(39)	110(2)	C(21)	C(49)	C(50)	111(2)
C(38)	C(37)	C(40)	110(2)	C(21)	C(49)	C(51)	112(2)
C(39)	C(37)	C(40)	108(2)	C(21)	C(49)	C(52)	111(2)
C(11)	C(41)	C(42)	108(2)	C(50)	C(49)	C(51)	109(2)
C(11)	C(41)	C(43)	114(2)	C(50)	C(49)	C(52)	107(2)
C(11)	C(41)	C(44)	109(2)	C(51)	C(49)	C(52)	106(2)
C(42)	C(41)	C(43)	112(2)	C(17)	C(53)	C(54)	107(2)
C(42)	C(41)	C(44)	107(2)	C(17)	C(53)	C(55)	107(2)
C(43)	C(41)	C(44)	106(2)	C(17)	C(53)	C(56)	120(2)
C(23)	C(45)	C(46)	106(2)	C(54)	C(53)	C(55)	99(3)
C(23)	C(45)	C(47)	113(2)	C(54)	C(53)	C(56)	105(4)
C(23)	C(45)	C(48)	117(2)	C(55)	C(53)	C(56)	116(4)

states, the reported structures of these complexes are all very similar to each other, with the Schiff base ligands always occupying meridional sites of an octahedron, giving a complex molecule of approximately D_{2d} symmetry. All the M-O, C-O as well as C-N bonds are almost structurally equivalent in each of these structures, indicating that charge delocalization occurs over the entire molecule.

The structure of $Pb(C_{56}H_{80}N_2O_4)_2$, however, is significantly different from the typical features of the transition metal complexes. Although the coordination geometry of this complex could be viewed as substantial distortion from either an octahedron or a trigonal prism, it does not closely approximate any standard stereochemistry. This distortion might be a combined effect of the larger atomic radius of lead, compared to those of the first row transition metal elements or perhaps more importantly to the existence of a stereochemically active lone pair of electrons on the lead(II) cation.

There are several noticeable features of this structure there can be compared with the structure of the transition metal complexes. The coordinated ligand in this complex is clearly a much more localized form of Cat-N-BQ, with two different C_6 rings and two different oxygen atoms. The N-M-N principal axis in D_{2d} transition metal complexes of this ligand system usually has a bond angle close to 180° (175.0° for N_1-Fe-N_2 to 177.9° for N_1-Co-N_2), but the N-Pb-N angle in this complex is only 127.2°. The dihedral angle between the two C_6-rings of the ligand containing O_1, N_1 and O_2 is also significantly greater in this complex (36.8°) than in the case of the iron complex (11.7°) or the manganese complex (13.4°). The N_1-Pb-O_1 and N_1-Pb-O_2 angles are 65.3° and 62° respectively, compared to the *ca.* 80° for the transition metal complexes, also indicating a different overall interaction of the ligand with lead.

The average bond length of Pb-O_1 and Pb-O_3 in this complex is 2.27 Å, which is much longer than 2.01 Å of Pb-O in $Ph_3Pb(OSiPh_3)$[230] for Pb in the +4 oxidation states, and slightly shorter than the Pb-O bonds (av. 2.337 Å) in a macrocyclic Schiff base Pb(II) complex $C_{24}H_{28}Cl_2N_4O_{12}Pb$.[231] The Pb-N lengths (av. 2.59 Å) and Pb-O_2, Pb-O_4 bond lengths (av. 2.76 Å) are in the range found for Pb-N and Pb-O coordination bonds; for example, 2.539 Å (av) and 2.668 (av) Å for Pb-N and Pb-O in a lead(II) tetraimine Schiff base complex $PbL_2(NCS)_2$ MeOH,[232] 2.645-3.060 Å for Pb-O in a series of crown ether complexes of $Pb(NO_3)_2L$ (L = crown ethers),[233] 2.64 Å, and 2.71-2.78 Å for Pb-N and Pb-O in $Pb(C_{20}H_{44}N_4O_4)(NO_3)_2(C_3H_8O)$.[234] We notice that the differences in the C-O bond distances are small and the measured Pb-O bond distances give same significant figures as other bonds in this crystallographic data. This may due to the quality related problem of the single crystal used in the measurement. Further confirmation experiment on this respect seems needed.

As in the transition metal *o*-benzoquinone complexes, the increase in C-O and C-N lengths with increasing ligand charge in a series of transition metal complexes has been discussed. The change is more subtle than in the *o*-quinone complexes. Another interesting feature in these studies is the effect of the overall ligand charge for the complexes on the C_6 rings C-C bond lengths. These rings should become increasingly aromatic as the extent of ligand reduction increases. Bond lengths at ring bond 3 and 5 were particularly sensitive to the ligand charge. Since the four C-O and two C-N lengths are clearly not consistent as in the cases of transition metal complexes and the ligands in the Pb complex are much more localized, it is very difficult to compare them in these aspects. The assignment of the ligand charge according to the differences in the C-O and C-N lengths would also be difficult and inaccurate based on the limited number of solved structures. However, the C-O, C-N and C-C bond lengths in this complex are indeed very close to those values reported for $Ni(Cat\text{-}N\text{-}BQ)_2$ and quite different to the values in Mn(Cat-N-SQ) and $Ti(Cat\text{-}N\text{-}SQ)_2$ if we make a similar calculation for the ligand bond lengths as for the transition metal complexes. (See Table 7.6.) The arrangement of Bu^t

TABLE 7.6

Selected Average Bond Lengths of Metal Biquinone Complexes in (Å)

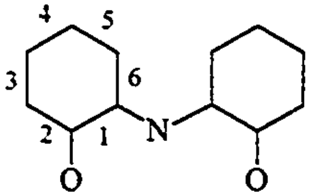
	Mn(Cat-N-BQ)$_2$[b]	Ti(Cat-N-BQ)$_2$[c]	Ni(Cat-N-BQ)$_2$[b]	Pb(Cat-N-BQ)$_2$
M-O	1.896(5)	1.88	2.031(2)	2.27(1)[a]
M-N	1.910(5)	2.15	2.019(3)	2.59(1)
C-O	1.325(7)	1.34	1.264(5)	1.27(2)
C-N	1.380(7)		1.344(5)	1.36(2)
C-C$_1$	1.417(8)		1.464(4)	1.45(3)
C-C$_2$	1.408(8)		1.450(4)	1.44(3)
C-C$_3$	1.380(9)		1.353(4)	1.36(3)
C-C$_4$	1.412(8)		1.429(4)	1.44(3)
C-C$_5$	1.367(8)		1.354(4)	1.35(3)
C-C$_6$	1.410(9)		1.430(4)	1.43(3)

a (Pb-O$_1$ + Pb-O$_3$)/2

b results from ref. 223 and 225

c results from ref. 226

ligand bond notation:



substitution in this complex is the same as those in transition metal complexes, and the space-filling molecular models (Corey-Pauling-Koltum) indicate that this is the only reasonable pattern of these complexes.

Overall, the structure of this molecule shows very interesting features as a six-coordinate Pb(II) complex distorted from idealized AX_6 geometry by the presence of a stereochemically active lone pair of electrons on Pb(II), the presence of the tridentate ligands, and the large radius of Pb(II).

General Conclusions

This work has focused on the oxidation processes of the Main Group elements P, Sb and Te, and their low oxidation state compounds. The studies on the oxidation of Sn was also extended during the course of this research project. In comparison with other commonly used oxidants, *o*-benzoquinones allow the one-electron product semiquinones to be identified and therefore have many clear advantages in the mechanistic studies of the above processes. The identification of molecules in which the semiquinones are bonded to either tellurium or phosphorus clearly implies the intermediate formation of $R_2Te(SQ)$ or $X_3P(SQ)$, although these intermediate Te(III) and P(IV) species have not yet been isolated. Together with previous studies on oxidation processes from this laboratory, this work completes a set of investigation of the reactions of substituted *o*-quinones with the fourth row elements Cd, In, Sn, Sb and Te, and with their low oxidation compounds. With the aid of ESR spectroscopy, it has been established that the reaction mechanism actually involves a one-electron process as the first step in the reactions of each of the above systems, rather than the electron pair transfer generally assumed to occur, and there can be no doubt of the generality of this conclusion, which also applies in the case of P, Ga and Tl. The results in this laboratory and the increasing evidence over recent years of radical species[180] in the chemistry of such elements as N, P, S, Se and Te implying that the one-electron transfer processes are not restricted to transition metal chemistry, but can and do occur throughout the Periodic Table.

It is of interest to note that different products were produced in different reaction systems. In particular, previous results from this laboratory have shown both 1-electron (semiquinone) and 2 x 1-electron (catecholate) reaction products were obtained from the reactions of *o*-quinones with elemental In and Sn, and with their low oxidation state compounds. The reaction products in the present work, however, are all clearly identified as catecholate compounds. This suggests that Group 3A and 4A metals, and their low oxidation compounds may have some advantages in mechanistic studies of oxidation processes which involve Main Group substances. Even though all the reaction products in the present work are catecholates, different elements gave different oxidation state products with *o*-benzoquinones. For phosphorus systems, the reaction products are its highest state P(IV) compounds. While for tellurium systems, only Te(IV) species were produced. The antimony systems yield both Sb(III) and Sb(V) products depending on the different reactants used. These differences in reactivities are consistent with our knowledge of the chemistry of these elements.

In terms of preparative chemistry, this work offers a simple direct route to a variety of catecholate compounds. This direct high-yield 'one-pot' synthesis, which employes *o*-benzoquinones and different elements, may have some advantages over the previous route which involves the reaction of air sensitive halide compounds with 1,2-diols. In addition, these reaction products, such as $P(O_2C_6R)Br$ and Sb(cat)X, are themselves useful starting materials for further alkylation, arylation and other ligand exchange reactions.

During the course of this work, the structures of five main group catecholate complexes have been determined by x-ray crystallography. These complexes offer good examples for the structural examination of Main Group substances by the Valence Shell Electron Pair Repulsion (VSEPR) model. Their structures are generally consistent with the predictions based on this model. In each cases, there is clear evidence for a stereochemically active lone pair of electrons in the coordination kernel of the central atoms. The C-O bond distance in these complexes clearly confirm the catecholate ligands are formed by the reduction of the corresponding quinones species.

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Thesis: Synthesis and Properties of Electrically Conducting Rare Earth Metal Complexes

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Recent Academic Awards

1992	University of Windsor Conference Travel Award
1990-1991	University of Windsor Tuition Scholarship
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Areas of Competence

Syntheses: Inorganic, Organic and Organometallic Syntheses, Schlenck techniques, Dry-Box Operation

Instrument Analyses: IR, AA, UV-Visible, NMR, EPR

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Professional Experience

1987-1988 Institute of Radiation Medicine, Chinese Academy of Medical Science, Tianjin, China

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Experiment of organosilicon compounds for junior graduate students

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First year General Chemistry, Teaching TA and Solutions TA
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Publications

A. Published Papers

1. H-K Wang, Z. Tian, Z-F Wang and C. Lin, Rare-Earth Metal 7,7,8,8-Tetracyanoquinodimethane compounds with semi-conductor property Science Bulletin (Chinese) 1988, 1630-32.

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B. Manuscript in preparation

9. Z. Tian and D.G. Tuck, Preparation and Structural Studies of a Novel Schiff-base Biquinone Lead(II) Complex.

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