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METAL HALIDE COMPLEXES OF ORTHO-QUINONES

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METAL HALIDE COMPLEXES

OF

ORTHO—QUINONES

BY

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INTRODUCTION

Previous workers have reported several cases in which metal halides react with ortho-quinones in non-aqueous media to form highly colored crystalline complexes. 9,10-Phenanthrenequinone has received most of the attention. Meyer[1] found that it forms complexes with zinc chloride, ferric chloride, stannic chloride, mercuric chloride and aluminum chloride. A study of complexes containing 9,10-phenanthrenequinone and halides of the zinc-group metals was performed by Knox and Innes[2]. 9,10-Phenanthrenequinone also forms complexes with hydrochloric acid[3], nitric acid[4], sulfuric acid[4] and perchloric acid[5]. Several other quinones have been studied briefly. Complex formation has been noted between para-quinone and stannic chloride[1], α -naphthoquinone and anti-mony pentachloride[1], β -napthoquinone and stannic chloride[1], and 1,2-chrysenequinone and perchloric acid[6]. A good but old review of the literature has been compiled by Pfeiffer[7]. So far, ortho-quinone complexes have been studied from a strictly preparative standpoint; nothing has been done to elucidate their structures.

The purpose of the present study was two-fold. First, it was desired to develop a simple general procedure for the preparation of ortho-quinone-metal halide complexes, a procedure which would permit the inclusion of metal halides not studied previously. Secondly, it was intended to choose

several typical complexes and to perform experiments on them in order to obtain some information on how the quinone and metal halide were bound together. These experiments were to include determinations of molecular weights, x-ray diffraction studies, magnetic measurements and spectral studies. In addition the quinonone itself was to be varied in an effort to determine what influence the structure of the ligand had on complex formation.

Section I describes the synthetic procedure that was developed as well as the modifications required in special cases. The metal halides that were studied are discussed in terms of their ability to form complexes with ortho-quinones. Some attention is given to the influence of quinone structure in regard to complex formation. The complexes themselves are classified in terms of their stoichiometric relationships and are assigned tentative formulations. Special notice is taken of the behavior of the complexes when treated with solvents of different polarity.

Section II contains the structural study of the com-- plexes. It is divided into six parts: molecular weight determinations, thermogravimetric analysis, x-ray diffraction studies, spectra in the visible region, spectra in the infra- red region and magnetic measurements. Each part includes a brief description of the experimental techniques and procedures that were used. The results are discussed in terms of their applicability to the elucidation of the structure and bonding of ortho-quinone-metal halide complexes. Orders of stability

are developed from considerations relating to the effect of
the various metal halides on the carbonyl groups of the qui-
none. Conclusions concerning stereochemistry and bond type
are drawn from evidence provided by the magnetic measurements.

Section III is the experimental section. Detailed
descriptions of the procedures used in preparing and analyzing
the complexes are given. The techniques mentioned in Section
II, the structural study, are also described more thoroughly.

An appendix which contains tables of important data
which are too large to be conveniently placed within the
above sections follows Section III. The bibliography in turn
follows the appendix.

SECTION I

PREPARATION OF THE COMPLEXES

The synthetic procedure for metal halide—quinone com-
plexes developed by earlier workers in quite simple. A hot
saturated solution of metal halide in glacial acetic acid is
added to a similar solution of quinone. A pure crystalline
product is formed on cooling. This method is perfectly
adequate for metal halides which do not react preferentially
with acetic acid and which are readily available in a pure,
anhydrous form. Unfortunately, most of the halides investi-
gated here do not fall into this category. They readily
react with water to form hydrates and usually are purchased
as such. Subsequent treatment to remove water often results
in an inferior product of doubtful purity. Pure, anhydrous
halides can be obtained at a higher cost, but this does not
preclude the necessity of special techniques to keep out
water during handling. A much more convenient method for
appreciably hygroscopic halides is outlined below.

It has been found that anhydrous solutions of many
metal bromides can be prepared easily by direct bromination
of the metal in methanol[8]. These solutions contain bromide
as pure as the original metal and can be introduced into a
reaction mixture rapidly and efficiently. Incorporation with
the original procedure for the complexes is as follows. The
bromide solution is concentrated by boiling in order to remove

most of the methanol. Glacial acetic acid is added and the
solution is heated nearly to the boiling point. Then a hot
solution of quinone in glacial acetic acid is added. Con-
siderable darkening of the solution occurs at this point, and
crystallization of the complex usually takes place at once.
If not, excess solvent can be removed by boiling or by strip-
ping under vacuum. All of the complexes listed in Table I
were prepared by the above method except for those involving
molybdenum pentachloride and mercuric bromide. The molybde-
num chloride complexes were prepared by dissolving molybdenum
pentachloride in glacial acetic acid and adding a solution of
quinone in glacial acetic acid. Acetone was found to be a
more suitable reaction medium for the mercuric bromide com-
plexes. These procedures are described more fully in Section
III.

Several ortho-quinones were studied: 9,10-phenan-
threnequinone, 1,2-chrysenequinone, acenaphthenequinone, and
2-nitrophenanthrenequinone. These were chosen for the follow-
ing reasons. First of all, it was known that 9,10-phenan-
threnequinone exhibits complexing ability. Therefore, it was
chosen as a standard. The others were chosen to see what
effects, if any, variations in the quinone structure had on
complex formation. 1,2-Chrysenequinone, which contains an
additional aromatic ring as well as a carbonyl system similar
to that of 9,10-phenanthrenequinone, would provide an oppor-
tunity to determine the influence of increased ligand size.
Acenaphthenequinone would serve to illustrate the effect of

increasing the distance between the carbonyl oxygens by de-creasing the size of the quinone ring. The influence of an electron withdrawing group could be studied by determining the complexing ability of 2-nitrophenanthrenequinone.

The results were quite interesting. It was found that 9,10-phenanthrenequinone and 1,2-chrysenequinone form stable complexes with a large number of metal halides. On the other hand, acenaphthenequinone and 2-nitrophenanthrene-quinone proved to be quite unreactive in most cases. From this it can be said that the major requirement for complex formation of this type is a six-membered quinoidal ring such as that present in 9,10-phenanthrenequinone. Acenaphthene-quinone with its five-membered ring simply does not fit into the stereochemical picture. The carbonyl oxygens are just too far apart. Increasing the size of the ligand by one ring does not seem to exert an appreciable influence on complex formation. The complexes of 1,2-chrysenequinone can be pre-pared just as readily as those of 9,10-phenanthrenequinone, and they exhibit similar stability. The results obtained with 2-nitrophenanthrenequinone were rather surprising. It seemed almost certain that this quinone would have a tendency to react at least somewhat like that of 9,10-phenanthrenequinone. The quinone grouping is the same sterically speaking, and the number and position of the rings are identical. It did not seem that the presence of a nitro group would seriously affect complex formation. But such is not the case. Rather than attribute this low reactivity to steric effects, it seems much

more logical to emphasize the electronic influence of the nitro group. The nitro group exerts an electron withdrawing effect on the rest of the molecule, and the resulting decrease in carbonyl polarization lowers the tendency of the quinone to act as a ligand.

A wide variety of metal halides was studied in order to establish which ones formed stable complexes with ortho-quinones. Bromides were used in most cases since they can be prepared conveniently as mentioned above. Several commercially available chlorides were studied also: molybdenum pentachloride, titanium tetrachloride, antimony pentachloride, phosphorus pentachloride and arsenic trichloride. It was found that 9,10-phenanthrenequinone and 1,2-chrysenequinone form stable complexes which contain manganese, iron, cobalt, nickel, zinc, cadmium, mercury, indium, tin, molybdenum and uranium. Their empirical formulas, together with analytical data and colors, are given in Table I. All four of the quinones studied form highly colored complexes with titanium tetrachloride and antimony pentachloride in carbon tetrachloride. However, these are so unstable that they cannot be separated from the reaction mixture without extensive decomposition. The details are given in Section III. No reaction was observed with phosphorus pentachloride or arsenic trichloride. Nor was it possible to isolate a complex containing cupric bromide. The acetic acid procedure is of little value in this case since copper tends to come out much more readily as the acetate. Other solvents such as chloroform and acetone were tried and found to be un-

satisfactory.

The complexes can be classified according to type as shown in Table II. This classification is based on the oxidation number of the metal species and the number of quinones present in the empirical formula. Tentative structural formulations based on the most common coordination number of the metal are suggested. These are partially substantiated by the results of a thermogravimetric study of PhQ·ZnBr$_2$ (see Section II).

One of the more striking characteristics of the complexes is their color. Nearly all of them are dark purple, almost black in appearance. This is a particularly unusual phenomenon, especially in cases like the zinc complexes. Zinc compounds are generally pure white, but PhQ·ZnBr$_2$ and ChQ·ZnBr$_2$ are intense violet and black. The relationship between color and stability is dwelt upon more fully in Section II.

The complexes are stable enough to be handled in the open air, but they should be stored under dry conditions as a precaution. They are readily decomposed by water and other polar solvents into the original components. For example, the phenanthrenequinone-zinc bromide complex yields a precipitate of phenanthrenequinone and an aqueous solution of zinc bromide when treated with water. This, of course, admirably simplifies the problem of elementary analysis. The quinone is determined directly by weighing, and the aqueous solution is analyzed for the metal and the halide by conventional methods. The

complexes are nearly insoluble in non-polar solvents such as chloroform, benzene and toluene. They are insoluble in ligroin. It seems that any dissolving that does occur, takes place via decomposition. When a sample of $PhQ \cdot ZnBr_2$ was treated with dry benzene, the color of the benzene changed from colorless to faint yellow. A nearly identical color can be obtained by dissolving 9,10-phenanthrenequinone itself in benzene. An aqueous extract of the benzene used to treat the complex gave a negative test for bromide. Repeated treatments of the sample with fresh benzene gave similar results. There was no decrease in the intensity of the yellow color as would be expected had the complex been contaminated with excess quinone. These results indicate that the solvent actually breaks down the complex, removes the quinone and leaves the bromide behind. The only thing that seems to retard this process is the fairly low solubility of the quinone in benzene.

Strangely enough, complex formation can take place in the presence of water. Small amounts of 9,10-phenanthrenequinone and zinc bromide were mixed and ground together under anhydrous conditions. No color change was observed after several minutes. When the mixture was exposed to the atmosphere, the color slowly changed from pale yellow to dark brown. On longer standing the dark brown color gradually changed back to yellow. Apparently what happens is that the anhydrous zinc bromide picks up water from the air and thereby furnishes a reaction medium in which complex formation can take place.

Then when the amount of water becomes excessive, the complex undergoes decomposition. Basically the same thing can occur in acetic acid. This concentration effect becomes important in preparing the complexes for if the solutions are too dilute, complex formation does not take place.

SECTION II

STRUCTURAL STUDY OF THE COMPLEXES

Several questions pertaining to the nature of ortho-quinone—metal halide complexes immediately arise. How are the components bound together? Are the carbonyl groups directly involved? Do the empirical formulae give a true representation of the actual species? Can any conclusions be drawn concerning steric anc structural relationships? Is it possible to determine the relative tendencies of the various metal halides to react with ortho—quinones? In order to find answers to these questions a number of methods of study were explored. These included molecular weight determinations, thermogravimetric analysis, x-ray diffraction studies, spectral studies and magnetic measurements. A survey of these techniques showed that spectral studies, particularly in the infrared, and magnetic measurements would yield of the greatest amount of information. For this reason most of the emphasis in this work is placed on the interpretation of observed magnetic moments and infrared spectra.

Molecular Weight Determinations.— Unfortunately, cryoscopic and ebullioscopic molecular weight determinations proved to be unsuccessful. The main reason is that in solution the complexes are dissociated considerably except at high or nearly saturated concentrations. The Rast method gave ridiculously low values with camphor, borneol and naphthalene as

solvents. In another attempt the result of a freezing point determination of a $PhQ \cdot ZnBr_2$-glacial acetic acid solution was precipitation of the quinone. If the molecular weights of the complexes are to be determined in the future, it is suggested that x-ray methods be used. This will require accurate measurements of density and unit cell dimensions which are not available at the present time. Considerable work will be involved, but this technique is about the only course of action left.

Thermogravimetric Analysis of $PhQ \cdot ZnBr_2$.— A thermogravimetric analysis of the phenanthrenequinone—zinc bromide complex provided evidence that the formulation $PhQ \cdot ZnBr_2$ is not correct. A plot of weight vs. temperature had a break in the curve at a point corresponding to just one-half of the total amount of quinone present in the complex. This suggests that a better formulation would be $[Zn(PhQ)_2][ZnBr_4]$.

The decomposition proceeds as follows. In an atmosphere of dry nitrogen there is no loss in sample weight until a temperature of about $300^{\circ}C$ is reached. At this point the weight drops rapidly until one-half of the quinone is lost. As the temperature gradually rises to $490^{\circ}C$, the weight continues to decrease, but at a slower rate. At $490^{\circ}C$ a constant weight corresponding to about 25–30% of the original sample is reached. The residue is a tar which solidifies on cooling. If the atmosphere in the furnace is changed from nitrogen to air and if heating is continued at $490^{\circ}C$, further weight loss occurs until nearly all of the sample is removed. A minute

amount of grey ash is left — about 3% of the original weight.

Apparently what happens is that after the initial loss of quinone, the remaining organic portion undergoes incomplete decomposition to yield a tar. By the time the temperature has reached 490°C, most of the zinc bromide (m.p., 390°C) has been removed by volatilization. Then when air is introduced, the tar oxidizes completely. The remaining ash might be zinc oxide.

X-ray Diffraction Studies.— X-ray powder patterns were obtained for 9,10-phenanthrenequinone, $PhQ \cdot ZnBr_2$, $PhQ \cdot CdBr_2$, $PhQ \cdot MoO_2Cl_2$, $2PhQ \cdot HgBr_2$ and $3PhQ \cdot FeBr_3$. The Bragg angle (θ) and the interplanar distance (d) were determined for each line appearing on the patterns. The relative intensities (I/I_0) of the lines were estimated visually. The values for θ, d and I/I_0 are given in Tables III through VIII, and plots of I/I_0 vs. d appear in Figure 1. Inspection of these plots and recorded data for the halides shows that the patterns of the complexes are distinct from those of the components. These differences show that some sort of interaction does occur between the components and that the products obtained are not simply mixtures of quinone and metal halide. As might be expected, the patterns are quite complicated. Any determination of unit cell parameters for the complexes using powder data would be accomplished best by computer techniques.

Spectral Studies in the Visible Region.— The intense colors of the complexes indicated that it might be useful to study their spectra in the visible region. A representative

complex, PhQ·ZnBr$_2$, was chosen to test the technique. Several problems were encountered. First of all, the solvents usually employed in this kind of work were unsuitable for solubility reasons. As a result, the spectra had to be run in glacial acetic acid. Secondly, if the concentration of complex is such that a readable spectrum is produced, the amount of dissociation is so great that the spectrum of the complex is identical to that of the quinone itself. If the amount of PhQ·ZnBr$_2$ is increased until the color of the solution becomes a faint red indicative of association to form the complex, complete absorption occurs. All of the above spectra were taken relative to pure glacial acetic acid. Then it was decided to run a differential spectral analysis in which the spectrum of the complex was taken relative to the parent quinone. This method gave good results. A sharp peak was observed in the green region at 513 mμ. The quinone itself absorbs in the violet and near ultraviolet at 415 and 320 mμ. The presence of absorption in the green region is more or less expected since the color of PhQ·ZnBr$_2$ is violet with a tinge of rod.

Another way to obtain a differential spectrum would be to run a solution of complex against both of the components. In the reference compartment two cells would be placed in tandem, one containing a solution of halide and the other a solution of quinone. The sample compartment would contain two cells placed in a similar fashion. Both of these cells would be filled with a solution made by mixing equal volumes of the

halide and quinone solutions. The absorption measured would
be the difference between the mixed and unmixed components.
This method would be more appropriate for metal species such
as Co(II) and Ni(II) which are colored and absorb in the
visible region.

Several important conclusions can be drawn from the
fact that the complex absorbs radiation of a longer wave-
length or lower energy than does the quinone. Molecules can
absorb or emit energy in transitions between different elec-
tronic energy levels. Since electronic energy levels are
associated with the molecular orbitals in a compound, changes
in the energy gap between excited and ground states indicate
the presence of a factor which effects these orbitals. In
the case of $PhQ \cdot ZnBr_2$, the zinc bromide has effectively
reduced the energy gap for the quinone and made it easier
for the quinone electrons to be delocalized into orbitals
utilized in binding the two together. The increased delocal-
ization results in absorption at a longer wavelength. This
is comparable to the effect of increased conjugation. The
electrons are spread out over a larger system, the energy gap
is reduced, and absorption is shifted towards the red. Ab-
sorption in this region indicates that the difference in
energy between at least one electronic energy level and the
ground state is not particularly large. In fact, the energy
required for transition of an electron between these levels
is of the order of that required to hold two electrons in a
covalent bond — about 30–100 kcal. The ability to absorb

energy corresponding to the wavelengths of this region is not a characteristic of highly stable compounds. This coincides with the general properties of ortho-quinone-metal halide complexes. They certainly cannot be considered highly stable.

It would be interesting to study the effect on the absorption band produced by different metal halides. To do this by solution spectrophotometry would be inconvenient and rather noisome unless a more suitable solvent than glacial acetic acid could be found. A better approach would be to work with the solids as such and use a reflectance technique.

Studies in the Infrared Region.— A great deal of information is available concerning the factors responsible for variations of the frequency and intensity of the infrared absorption band resulting from carbonyl stretching vibrations. Since it seemed likely that the bonding between the metal halide and the quinone involved the carbonyl groups, it was decided to study the infrared spectra of the complexes, particularly in the 1700–1500 cm^{-1} region. Fortunately, the complexes do not decompose in either Nujol or Halocarbon oil. These were used to prepare mulls from which the spectra were obtained.

The infrared spectrum of 9,10-phenanthrenequinone contains two strong, sharp bands in the 1700–1500 cm^{-1} region. The first absorption, at 1674 cm^{-1}, is the carbonyl band. The second is an aromatic band, and it occurs at 1595 cm^{-1}. While both absorptions are strong, the aromatic band has a slightly lower intensity. The spectra of the 9,10-phenanthrenequinone complexes are characterized by a decrease in the frequency of

the carbonyl band and an increase in the intensity of the aromatic band. In nearly all cases the aromatic band becomes so strong that its intensity is greater than that of the carbonyl band. This effect does not create any complications in the 9,10-phenanthrenequinone series since the carbonyl bands are well defined in most cases and can be assigned frequency values without any trouble. For example, $PhQ \cdot ZnBr_2$ absorbs at 1626 cm^{-1} and 1587 cm^{-1}. The latter band is the stronger. Except as noted below, the spectra of the other complexes in this series are similar in appearance. The frequencies of the carbonyl and aromatic bands are given in Table IX. The last column shows the difference between the carbonyl absorption of the complex and that of the parent quinone. Shifts ranging from 9 cm^{-1} to 114 cm^{-1} were observed.

$3PhQ \cdot Fe\ Br_3$ gives a rather poor spectrum. There is a broad band between 1675 and 1635 cm^{-1}. The most intense absorption occurs at 1665 cm^{-1}. The aromatic band occurs at 1587 cm^{-1}. The $PhQ \cdot SnBr_4$ spectrum contains only one band in the 1700-1500 cm^{-1} region. It occurs at 1560 cm^{-1} and probably is a combination of the carbonyl and aromatic absorptions. This is the largest shift observed for any of the complexes, a decrease of 114 cm^{-1}. In $PhQ \cdot MoO_2Cl_2$ a third band appears at 1552 cm^{-1} which might be aromatic in nature. It is not present in the corresponding bromide.

The fact that the frequency of the carbonyl band of 9,10-phenanthrenequinone differs from those of the complexes

supports the contention that the carbonyl groups are directly involved in the bonding. It is expected that co-ordination through the quinone oxygens will result in a reduction of the double bond character of the carbonyl groups and shift the carbonyl band to a lower frequency. This is analogous to the well-known behavior of carbonyl groups subjected to hydrogen bonding or chelation.

If it is assumed that the decrease in frequency of the carbonyl absorption is a measure of the strength of the oxygen-metal bond, orders of stability can be derived. However, a certain amount of caution has to be exercised in making comparisons between the various metal species. It is not safe to include metals of different oxidation states in the same series. Furthermore, the number of ligands per metal should not vary within a given series. Accordingly, complexes of Types II, III and V have been omitted from the following orders of stability:

a) for complexes of Type I, $Co \rangle Zn \sim Mn \rangle Cd$;

b) for complexes of Type IV, $Ni \rangle Hg$;

c) for complexes of Type VI, $MoO_2Br_2 \rangle MoO_2Cl_2$.

In the 1,2-chrysenequinone series the situation is not quite so simple. The quinone itself absorbs strongly at 1659 cm^{-1} and 1594 cm^{-1}. A weak band appears at 1577 cm^{-1}. This is most likely another aromatic band. As in the 9,10-phenanthrenequinone series, the intensity of aromatic absorption increases at the expense of carbonyl absorption. Deciding just which bands are due to carbonyl stretching is

a problem, however. For an example, consider $ChQ \cdot MnBr_2$ in which four strong bands appear between 1620 and 1570 cm^{-1}. The two bands at 1587 cm^{-1} and 1572 cm^{-1} undoubtedly are the aromatic bands. Those at 1617 cm^{-1} and 1605 cm^{-1} indicate either that both carbonyl groups have the same frequency and some new absorption band is present or that the two carbonyl groups absorb at different frequencies. A plausible explanation for the latter can be developed from considerations of the steric environment of the dione grouping. Although the carbonyl frequency usually is affected more by its immediate surroundings than by the rest of the molecule, the presence of another ring in 1,2-chrysenequinone must produce some difference between the carbonyl groups, however slight. This difference is hardly appreciable in 1,2-chrysenequinone itself, although a close examination of the carbonyl band reveals that it is a composite rather than a clean-cut single as in symmetrical 9,10-phenanthrenequinone. When 1,2-chrysenequinone becomes bonded to a metal halide, the steric effect of the extra ring becomes more important, and the difference between the carbonyls is greater. The difference is sufficiently large to result in splitting the original carbonyl bnad. This effect is also observed in $ChQ \cdot ZnBr_2$, $ChQ \cdot CdBr_2$ and $ChQ \cdot UO_2Br_2$. The problem becomes more complicated when the shift to lower frequency is such that the carbonyl bands overlap the aromatic bands. Nor does the increased intensity of the aromatic bands help matters any. $ChQ \cdot CoBr_2$ falls into this category. The aromatic bands occur at 1586 cm^{-1} and 1572 cm^{-1}. There is

a band of medium intensity at 1613 cm^{-1}, and a shoulder appears on the 1586 cm^{-1} band at about 1595 cm^{-1}. These two absorptions at 1613 cm^{-1} and 1595 cm^{-1} apparently are the carbonyl bands. ChQ·In Br_3 is similar except for a broad band at 1562 cm^{-1}. In 2ChQ·NiBr$_2$ there are only two strong bands, and these are at 1586 cm^{-1} and 1568 cm^{-1}. No definite assignment of the carbonyl frequency can be made. The data for the 1,2-chrysenequinone series is given in Table X.

Magnetic Measurements.— The magnetic properties of coordination compounds often provide a good deal of information pertaining to structure and bond type. This is particulartly true of complexes of transition metal ions which have incomplete shells of electrons. Knowledge of the behavior of such substances in the presence of a magnetic field can lead to the determination of the number of unpaired electrons per molecule or ion. In many cases it is possible to deduce from this number whether a complex is of the spin—free or spin—paired type, and whether outer or inner orbital bonding occurs. Such considerations can lead to conclusions pertaining to the stereochemistry of the complex if the number of ligands is known. The quantity measured is the magnetic susceptibility, X'_M. The relationship between X'_M and the magnetic moment, μ, can be expressed approximately as

$$\mu = 2.84 \, (X'_M T)^{1/2}$$

where μ is in Bohr Magnetons, X'_M is in c.g.s. units and T is in degrees Kelvin. The number of unpaired electrons, n, can

be obtained from μ by means of the "spin only formula",

$$\mu = \left[n(n+2)\right]^{1/2}$$

The magnetic susceptibilities of the manganese, iron, cobalt and nickel complexes were determined by the Gouy method (Sect. III, p. 30). From these data the magnetic moments were calculated and compared with theoretical values obtained from the "spin only formula". The results are listed in Tables XI and XII.

The observed moments of the manganese complexes agree with the theoretical moment calculated for five unpaired electrons. From this it can be concluded that the manganese is in the bivalent state and that the bonding is of the spin-free or weak field type. If the ligand field were strong, the observed moments would have corresponded to one unpaired electron. Since the manganese complexes probably are better formulated as in $\left[Mn(PhQ)_2\right]\left[MnBr_4\right]$ rather than $PhQ \cdot MnBr_2$, the number of ligand bonds per metal is four. These bonds cam be accommodated in the 4 s and 4 p levels. Such conditions give rise to sp³ bonding and a tetrahedral arrangement of the ligand bonds about the metal. From a steric point of view these are the most probable or least hindered positions.

The moments for the iron complexes also indicate spin-free bonding with five unpaired electrons. A strong field would have produced one unpaired electron. Here there are three quinones or six ligand bonds surrounding the iron. The

3d level cannot be used, but the 4 s, 4 p and 4 d levels are available. Use of these levels results in sp^3d^2 outer orbital bonding and an octahedral configuration.

The formulation of the cobalt complexes is analogous to that of manganese, viz., $[Co(PhQ)_2][CoBr_4]$ rather than $PhQ \cdot CoBr_2$. The magnetic moments observed show that there are three unpaired electrons for every cobalt. The values obtained are somewhat higher than the theoretical, but they fall within the range usually found for cobalt(II). Thus it can be concluded that the cobalt complexes are also spin—free, have sp^3 type bonding, and have a tetrahedral arrangement of the quinone—metal bonds. Spin—paired cobalt(II), which would result from the presence of a strong ligand field, is not commonly found.

The nickel complexes have moments which correspond to the presence of two unpaired electrons for each nickel ion. It seems likely that these complexes exist as expressed in $[Ni(PhQ)_2]Br_2$ or $[Ni(PhQ)_2Br_2]$, since it would certainly be unusual for nickel to accommodate four quinone molecules. Here again the complexes can be described as spin—free. The configuration about the metal ion could be either tetrahedral or octahedral. It is impossible to decide which of these two configurations is correct on the basis of magnetic data since the number of unpaired electrons is the same in both cases.

These conclusions are all summarized in Table XIII. Generally speaking, the magnetic measurements indicate that the manganese(II), iron(III), cobalt(II) and nickel(II) com—

plexes have outer orbital or weak field type bonding with
the carbonyl-to-metal bonds oriented in sterically favored
directions. This orientation results in a tetrahedral con-
figuration for the manganese(II) and cobalt(II) complexes,
an octahedral configuration for the iron(III) complexes and
either a tetrahedral or an octahedral configuration for the
nickel(II) complexes.

SECTION III

EXPERIMENTAL PROCEDURES

Preparation of the Quinones.— 9,10-Phenanthrene-
quinone[9], 1,2-chrysenequinone[10], and acenaphthenequinone[11]
were prepared and purified by methods already cited in the
literature. The author is indebted to Dr. H. M. Haendler for
a generous sample of 2-nitrophenanthrenequinone.

Metal Bromides in Methanol[8].— One tenth of a gram-
atomic weight of metal was covered with 250 ml. of methanol
(b.p., 64.5-64.7°). A slight excess of bromine was added
cautiously in small portions. The mixtures were either
allowed to stand or refluxed gently until the reaction ceased.
The solutions were filtered and used in the procedure below.

General Procedure for Preparing the Complexes.— Thirty
ml. of metal bromide-methanol solution was concentrated to
about 5 ml. by boiling. To this was added a hot filtered
solution of 0.01 m. of quinone in 60 ml. of glacial acetic
acid. The color changed immediately to deep brown or black.
If crystallization did not occur at once, the solution was con-
centrated by boiling. More rapid crystallization can also be
obtained by using an excess of bromide. This does not affect
product purity. The crystalline product was filtered hot on
a fritted glass funnel, washed several times with ligroin, and
dried at reduced pressure in a vacuum desiccator.

<u>Procedure Using MoCl$_5$.—</u> To a hot filtered solution of 0.01 m. of quinone in 60 ml. of glacial acetic acid was added a solution of 2.7 g. (0.01 m.) of molybdenum penta-chloride (Climax Molybdenum Co.) in 10 ml. of glacial acetic acid. The solution darkened and black crystals formed immediately. The product was filtered, washed with ligroin and dried at reduced pressure.

<u>Procedure Using HgBr$_2$.—</u> A mixture of 0.005 m. of quinone and 1.8 g. (0.005 m.) of mercuric bromide (Baker's Analyzed Reagent) was covered with 50 ml. of acetone and allowed to reflux for two hours. The color of the solid portion gradually changed to dark red. The product was filtered, washed with ligroin and dried at reduced pressure.

<u>Procedure Using TiCl$_4$ or SbCl$_5$.—</u> A solution of 0.005 m. of chloride in 10 ml. of dry carbon tetrachloride was added to a suspension of 0.005 m. of powdered quinone in 30 ml. of dry carbon tetrachloride. The mixture was allowed to stand at room temperature. The original yellow or orange color of the quinone changed as indicated below. None of these products could be separated from the reaction mixture without considerable decomposition.

Quinone	Color of Complex	
	SbCl$_5$	TiCl$_4$
9,10-Phenanthrenequinone	brown	black
1,2-Chrysenequinone	black	brown
Acenaphthenequinone	blue-green	red
2-Nitrophenanthrenequinone	black	black

<u>General Procedure for Elementary Analysis</u>.— A weighed
sample of complex was covered with about 30 ml. of hot water
and allowed to stand. When room temperature had been reached,
the quinone was filtered and determined directly by weighing.
The filtrate was diluted to 250 ml. in order to provide a con-
venient volume of solution for the halide and metal analysis.
Halide was determined by treating a 100 ml. aliquot with ex-
cess silver nitrate and back—titrating with thiocyanate.
Ferric ammonium sulfate was used as an indicator. The metal
was determined on a second aliquot. The final form of the
metal is given in Table I. Exceptions to this procedure are
given below.

<u>Analysis of the Molybdenum Complexes</u>.— A weighed
sample of complex was decomposed by heating nearly to dryness
with 30 ml. of 25 percent aqueous sulfuric acid and 10 ml. of
concentrated nitric acid. The treatment was repeated to en-
sure complete removal of the organic and halogen portions.
Molybdenum was determined as lead molybdate on the residue.

<u>Analysis of the Tin Complexes</u>.— A weighed sample was
digested in 30 ml. of 3 M nitric acid. The residue, a mixture
of quinone and stannic oxide, was filtered and ignited to
remove the quinone. Then tin was determined as the oxide by
weighing. Bromide was determined as in the general procedure
on a separate sample.

<u>Analysis of the Indium Complexes</u>.— After weighing,
the sample was decomposed in dilute aqueous ammonia to pre—

cipitate both the quinone and the indium. The precipitate
was filtered, ignited to remove the quinone and weighed to
determine indium as the oxide. Bromide was determined as
above on the combined filtrate and washings.

Analysis of the Mercury Complexes.— The determination
of quinone was carried out according to the general procedure,
except that the sample had to be digested several hours to
ensure complete decomposition.

Thermogravimetric Analysis of $PhQ \cdot ZnBr_2$.— The
apparatus used was that described by Wendlandt[12]. Basically,
it consists of a modified torsion balance (Sauter) from which
the sample is suspended into a furnace. Temperature change is
followed by a Micromax recorder. Changes in sample weight
during heating are recorded directly on a revolving drum con-
nected in line to the torsion bar. The balance is maintained
at the null point by an application of the photoelectric ef-
fect. The decompositions were performed with the generous
help of D. W. Kingston, builder of the apparatus (M.S., Univ.
of N. H., 1962). Two runs were made.

In the first run a 73.2 mg. sample of $PhQ \cdot ZnBr_2$ was
used. This weight corresponded to 86.5 scale divisions (s.d.)
on the torsion balance. Throughout the run, the heating
chamber was swept out with dry nitrogen to eliminate air oxi-
dation and to prevent any decomposition products from col-
lecting on the sample container and suspension system. The
temperature was raised slowly to $238°C$ at which point a slight
loss in weight occurred. Then the temperature was increased

further until the rate of weight loss became appreciable.
Here, at 300°C, the temperature was kept constant until de-
composition slowed down. Then the temperature was increased
gradually to 490°C. During this time the weight of the
sample slowly dropped to 22.3 s.d. where it remained constant.
On inspection the residue proved to be a tar which quickly
hardened to a black mass on cooling. An inflection point was
observed on the thermogram at 65.5 s.d.

A 42.0 mg. (49.4 s.d.) sample was used in the second
run. The furnace was swept with dry nitrogen as before and
heated at a rate of about 5 deg./min. until a temperature of
480°C was reached. At this point the sweeping was done by
air instead of nitrogen in order to remove the organic portion
by oxidation. On continued heating at 490°C the weight of the
sample decreased to a constant value of 1.4 s.d. The residue
was an ash-like substance. Inflections on the thermogram
occurred at 38.65 s.d. and 14.2 s.d.

The results are tabulated below. The observed in-
flection points are compared with those calculated for the
loss of all of the quinone and the loss of one-half of the
total amount of quinone.

Run	Wt. of sample (s.d.)	Inflection points (s.d.)		
		Calcd. for total am't	Calcd. for 1/2 total am't	Observed
1	86.5	45.0	65.7	65.5
2	49.4	25.7	37.5	35.2

X-ray Diffraction Data.— Powder patterns were obtained for 9,10-phenanthrenequinone, PhQ·ZnBr$_2$, PhQ·CdBr$_2$, 2PhQ·HgCl$_2$, 3PhQ·FeBr$_3$ and PhQ·MoO$_2$Cl$_2$. The samples were finely ground and mounted in 0.3 mm. capillaries. The patterns were taken with the 57.3 mm. Phillips camera using copper and iron radiation (1.5418 Å and 1.9373 Å, resp.). The values determined for θ, the angle of diffraction, and d, the interplanar distance, are given in Tables III through VIII. The relative intensities, I/I_0, were estimated visually.

Visible Spectra.— The spectrum of PhQ·ZnBr$_2$ in glacial acetic acid was obtained for the region between 1000 and 320 m u. A differential method was used. A solution which was 4×10^{-4} M in 9,10-phenanthrenequinone and 0.2 M in zinc bromide was run against a reference solution of 4×10^{-4} M 9,10-phenanthrenequinone. A band appeared at 513 mμ with an absorbance of 1.68 (ϵ, 4247). The quinone itself absorbed at 415 mμ (abs., 0.66; ϵ, 1659) and 320 mμ (abs., 1.73; ϵ, 4362). An excess of zinc bromide had to be used since a solution which was 4×10^{-4} M in complex alone gave a curve identical to that of the quinone. Here, glacial acetic acid was used as the reference. The instrument employed was a Beckman Model DU Spectrophotometer.

Infrared Spectra.— The spectra of the complexes and their parent quinones were obtained from Nujol and Halocarbon oil mulls. The instrument was a Perkin-Elmer Model 21 Double Beam Recording Infrared Spectrophotometer with sodium chlo-

ride optics.

Magnetic Measurements.— The magnetic susceptibilities of the manganese, iron, cobalt and nickel complexes were determined by the Gouy method[13]. The sample container, a double—ended Gouy tube, was suspended between the poles of a magnet (Newport Instruments, Model C Electromagnet) from a converted semi—micro analytical balance (Spoerhase vorm. Staudinger, Giessen). The left pan of the balance had been removed and replaced by a tare consisting of a brass container filled with lead shot. From the bottom of the tare a gold chain led down through the floor of the balance. The tube was attached to the end of the chain by a copper yoke. The entire suspension system was enclosed to prevent drafts from interfering during weighing. The chain was adjusted so that the bottom of the sample in the tube just reached the center of the pole gap of the magnet. The height of the sample was about 4.4 cm. This is sufficient to meet the requirement that one end of the sample be in a region essentially out of the influence of the magnet. The magnetic field was maintained at about 7000 gauss. Higher values resulted in too rapid an increase in sample temperature. This is to be avoided since the susceptibility of paramagnetic substances is temperature dependent. In addition to not using a higher field, the magnet was operated for a period of time no longer than that required for rapid weighing. The susceptibilities were calculated from the expression

$$10^6 X = \frac{\alpha \pm \beta \, F'}{w}$$

where X is the magnetic susceptibility, α is a constant allowing for the displaced air and equal to 0.029 times the sample volume, β is the tube calibration constant, w is the weight of the sample and F' is the force on the sample.

The sample volume was determined with mercury at 22°. The Gouy tube was filled until the meniscus just split the mark. After obtaining the weight of mercury required, the volume was calculated from the specific volume of mercury (0.0738 ml./g. at 22°). The average value for the sample volume was 0.5428 ± 0.0002 ml. The resulting value for α is 0.01574.

The tube was calibrated with $HgCo(CNS)_4$ to obtain a value for β . First of all, the force on the empty tube was found to be +0.2 mg. Then the calibrant was packed into the tube as follows. About 10 percent of the total weight of solid was introduced, and the bottom of the tube was tapped firmly on a wooden block until no further settling occurred. This was repeated until the level of the solid reached the volume mark. Then the total force on calibrant plus tube was measured. Subtracting the force on the tube gave the force on the calibrant, F'. Since these measurements were carried out at 25.5°, the value of $10^6 X$ for the calibrant had to be corrected. The mass susceptibility of $HgCo(CNS)_4$ is 16.44 x 10^{-6} at 20° and dX/dT is 0.33%[14]. So at 25.5°, $10^6 X$ for $HgCo(CNS)_4$ is 16.14. These values were substituted into the expression mentioned above. An average of three determinations showed that β equaled 0.181 ± 0.001.

The calibration was checked against the mass sus-
ceptibility of $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ [15]. For this substance

$$10^6 X = \frac{9500}{T + 1}$$

For $25.5°$ the calculated value of $10^6 X$ is 31.81. The ob-
served value was 31.77.

The mass susceptibilities of the complexes were
measured in the same fashion and at the same temperature,
$25.5°$. These were converted to mole susceptibilities and
corrected for the diamagnetic contributions of the ligands
(ref. 13, p.417). The magnetic moments were calculated from
the relationship

$$\mu = 2.84(X'_M T)^{1/2}$$

where μ is the magnetic moment in Bohr Magnetons, X'_M is
the corrected mole susceptibility and T is the absolute
temperature.

APPENDIX

FIGURES AND TABLES

Figure 1. Relative Intensity (I/I_o) vs. Interplanar Distance (d)
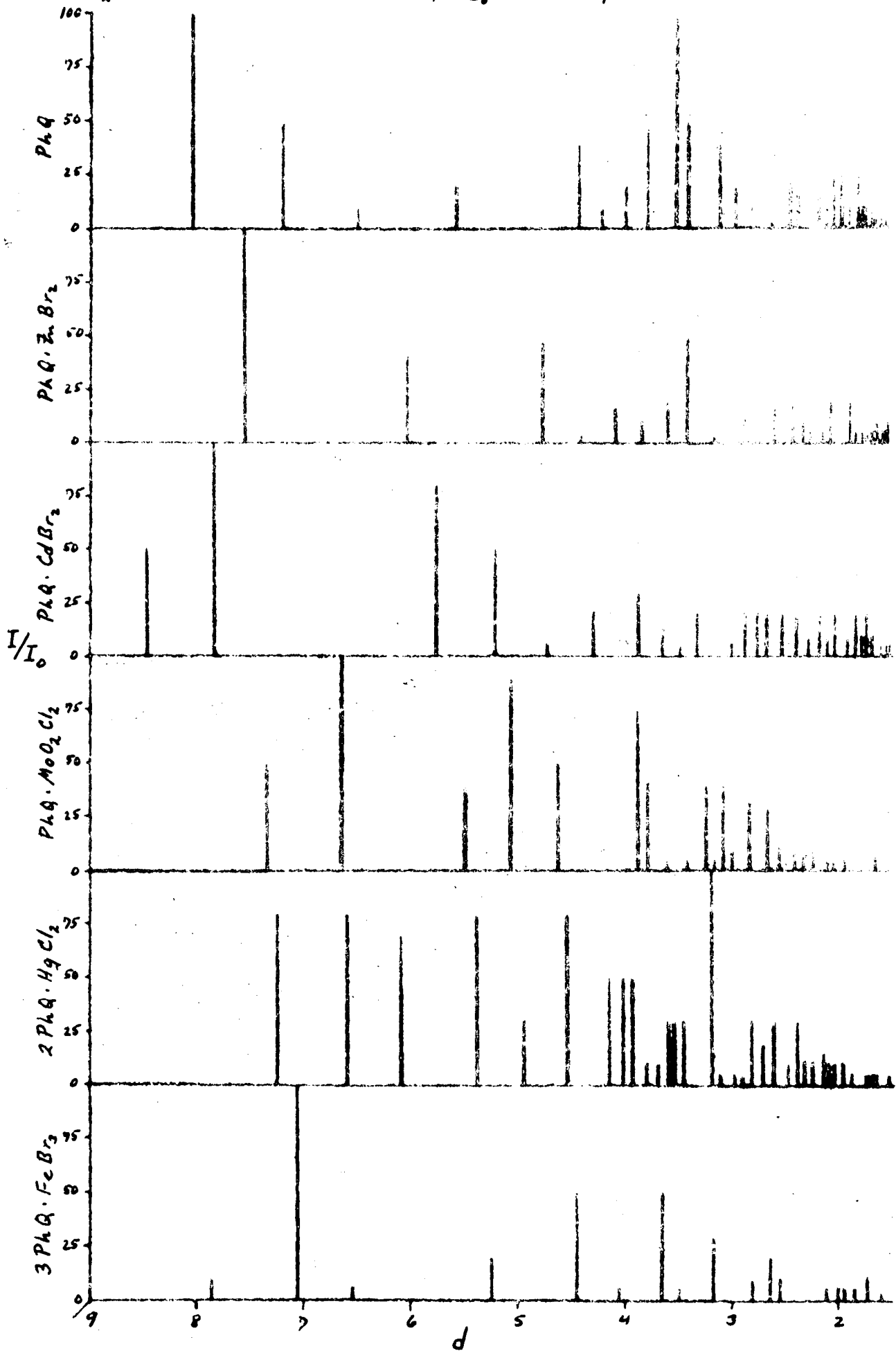
Figure 2. Differential Spectrum of $PhQ \cdot ZnBr_2$

I PhQ $(4 \times 10^{-4} M)$ & $ZnBr_2$ $(0.2M)$
vs. PhQ $(4 \times 10^{-4} M)$ in acetic acid.

II PhQ $(4 \times 10^{-4} M)$ in acetic acid.
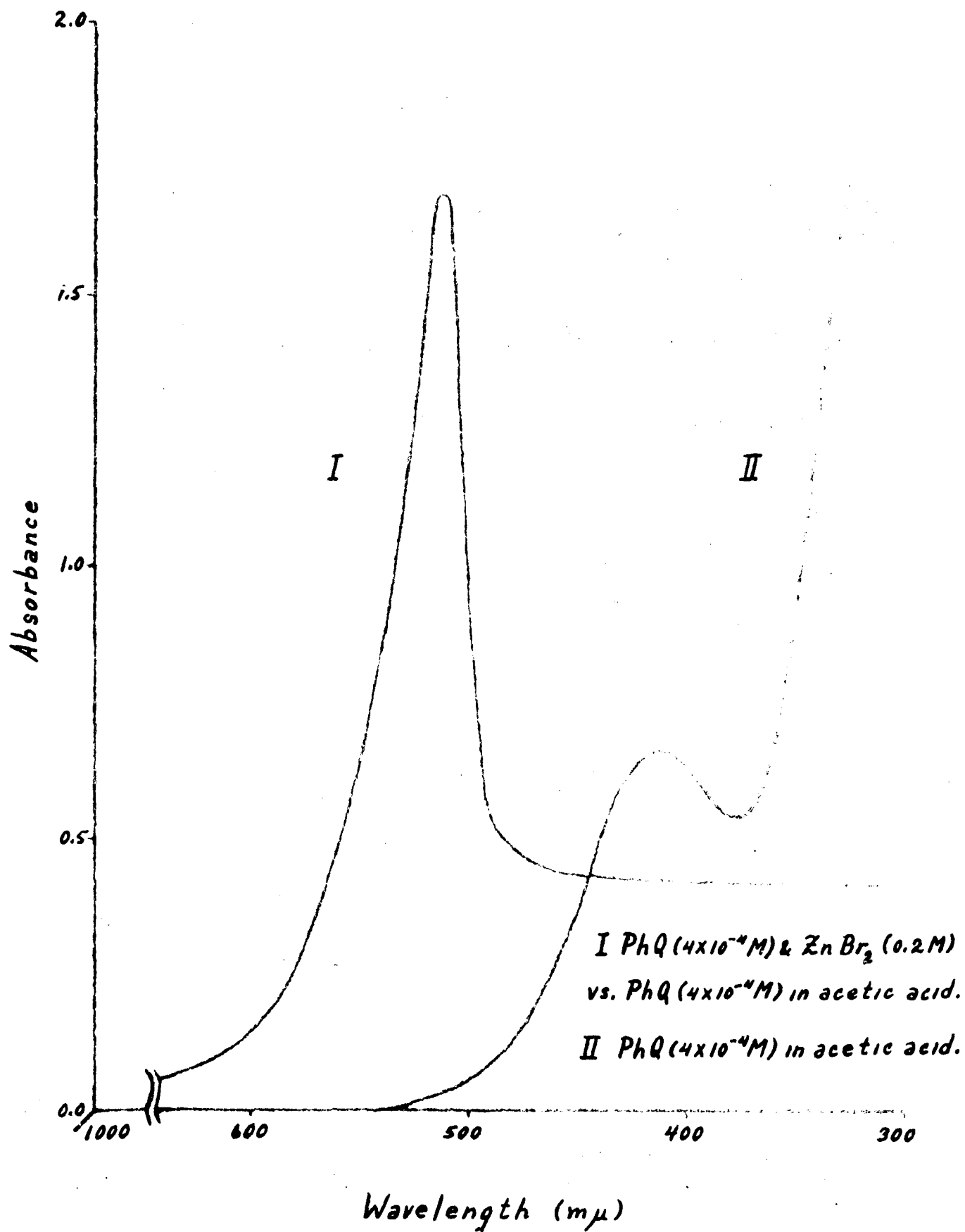
TABLE I

Formulas, Colors and Analytical Data

Formula	Anal.,calcd.%		Anal.,found%		Metal Method	Color
$PhQ \cdot MnBr_2$	PhQ	49.23	PhQ	49.10		
	Mn	12.99	Mn	12.75	Anthranilate	Purple
	Br	37.79	Br	37.70		
$ChQ \cdot MnBr_2$	ChQ	54.60	ChQ	54.72		
	Mn	11.61	Mn	11.50	Anthranilate	Black
	Br	33.79	Br	33.56		
$PhQ \cdot CoBr_2$	PhQ	48.76	PhQ	48.75		
	Co	13.80	Co	13.53	Anthranilate	Purple
	Br	37.43	Br	37.30		
$ChQ \cdot CoBr_2$	ChQ	54.14	ChQ	54.19		
	Co	12.36	Co	12.30	Anthranilate	Black
	Br	33.51	Br	33.48		
$PhQ \cdot ZnBr_2$	PhQ	48.04	PhQ	48.04		
	Zn	15.09	Zn	14.97	Anthranilate	Violet
	Br	36.88	Br	36.84		
$ChQ \cdot ZnBr_2$	ChQ	53.42	ChQ	53.19		
	Zn	13.52	Zn	13.65	Anthranilate	Black
	Br	33.06	Br	33.00		
$PhQ \cdot CdBr_2$	PhQ	43.34	PhQ	43.35		
	Cd	23.40	Cd	23.35	Anthranilate	Brown
	Br	33.27	Br	33.17		
$ChQ \cdot CdBr_2$	ChQ	48.68	ChQ	48.85		
	Cd	21.19	Cd	21.08	Anthranilate	Brown
	Br	30.13	Br	30.17		

Table I cont.—

Formula	Anal., calcd. %		Anal., found %		Metal Method	Color
$PhQ \cdot InBr_3$	In	20.39	In	20.03	Oxide	Brown
	Br	42.61	Br	40.19		
$ChQ \cdot InBr_3$	In	18.73	In	18.50	Oxide	Black
	Br	39.13	Br	38.96		
$PhQ \cdot SnBr_4$	Sn	18.36	Sn	18.36	Oxide	Black
	Br	49.44	Br	49.23		
$ChQ \cdot SnBr_4$	Sn	17.04	Sn	17.04	Oxide	Violet
	Br	45.89	Br	45.72		
$2PhQ \cdot NiBr_2$	PhQ	65.58	PhQ	65.33		
	Ni	9.24	Ni	9.23	Dimethyl glyoxime	Black
	Br	25.17	Br	24.97		
$2ChQ \cdot NiBr_2$	ChQ	70.27	ChQ	70.15		
	Ni	7.99	Ni	8.08	Dimethyl glyoxime	Black
	Br	21.75	Br	21.69		
$2PhQ \cdot HgBr_2$	PhQ	53.60	PhQ	53.48		Orange
$2ChQ \cdot HgBr_2$	ChQ	58.90	ChQ	59.00		Red
$3PhQ \cdot FeBr_3$	PhQ	67.88	PhQ	67.73		
	Fe	6.07	Fe	6.17	Oxide	Brown
	Br	26.05	Br	26.05		
$3ChQ \cdot FeBr_3$	ChQ	72.38	ChQ	72.51		
	Fe	5.22	Fe	5.23	Oxide	Black
	Br	22.40	Br	22.30		

Table I cont.—

Formula	Anal., calcd. %		Anal., found %		Metal Method	Color
$PhQ \cdot MoO_2Br_2$	Mo	19.35	Mo	19.33	Lead Molybdate	Black
$PhQ \cdot MoO_2Cl_2$	Mo	23.57	Mo	23.35	Lead Molybdate	Black
$ChQ \cdot MoO_2Cl_2$	Mo	20.99	Mo	20.75	Lead Molybdate	Violet
$ChQ \cdot UO_2Br_2$	ChQ	37.53	ChQ	40.00		Brown
	Br	23.23	Br	21.21		

TABLE II

Classification of the Complexes

Type	Example	
	Empirical Formulation	Suggested Formulation
I	$PhQ \cdot ZnBr_2$	$\left[Zn(PhQ)_2 \right]\left[ZnBr_4 \right]$
II	$PhQ \cdot InBr_3$	$\left[In(PhQ)Br_2 \right] Br$
III	$PhQ \cdot SnBr_4$	$\left[Sn(PhQ)Br_2 \right] Br_2$ [a]
		$\left[Sn(PhQ)Br_4 \right]$ [b]
IV	$2PhQ \cdot NiBr_2$	$\left[Ni(PhQ)_2 \right] Br_2$ [a]
		$\left[Ni(PhQ)_2Br_2 \right]$ [b]
V	$3PhQ \cdot FeBr_3$	$\left[Fe(PhQ)_3 \right] Br_3$
VI	$PhQ \cdot MoO_2Cl_2$	$\left[Mo(PhQ)O_2 \right] Cl_2$

Note:

a)   If configuration is tetrahedral.

b)   If configuration is octahedral.

TABLE III

Powder Pattern Data for 9,10—Phenanthrenequinone

θ	d	I/I_0
5.50	8.043	100
6.15	7.196	50
6.80	6.511	10
7.95	5.574	20
10.00	4.439	40
10.50	4.230	10
11.15	3.986	20
11.75	3.786	50
12.65	3.520	100
13.10	3.401	50
14.35	3.110	40
15.00	2.979	20
15.90	2.814	10
17.10	2.622	5
18.25	2.462	30
18.85	2.386	20
20.65	2.186	20
21.35	2.118	10
22.25	2.036	20
22.65	2.009	20
23.10	1.965	10
23.70	1.918	10

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TABLE IV

Powder Pattern Data For PhQ·ZnBr$_2$

θ	d	I/I_o
4.83	9.207	20
5.87	7.538	100
8.32	6.051	40
9.27	4.786	50
10.07	4.409	5
10.87	4.088	20
11.62	3.827	10
12.32	3.613	20
13.07	3.409	50
13.57	3.286	1
14.12	3.160	5
14.67	3.044	1
15.52	2.881	20
16.27	2.752	1
17.12	2.615	20
18.42	2.440	20
19.07	2.359	10
19.77	2.279	5
20.97	2.154	5
21.67	2.088	20
23.92	1.901	20
24.57	1.854	5

Table IV cont.—

θ	d	I/I_0
25.37	1.799	5
26.27	1.742	5
26.87	1.706	5
27.67	1.660	10
28.87	1.597	5
29.57	1.562	10
31.27	1.485	1
32.32	1.442	1

TABLE V

Powder Pattern Data for PhQ·CdBr$_2$

θ	d	I/I_o
4.43	9.981	5
5.23	8.457	50
5.63	7.858	100
7.67	5.776	80
8.47	5.234	50
9.37	4.735	5
10.32	4.303	20
11.42	3.893	30
12.17	3.657	10
12.72	3.501	5
13.42	3.322	20
14.07	3.171	100
14.87	3.004	5
15.52	2.881	20
16.22	2.760	20
16.77	2.672	20
17.77	2.526	20
18.52	2.427	20
19.47	2.313	10
20.67	2.185	20
21.32	2.120	10
22.27	2.034	20

Table V cont.—

θ	d	I/I_o
23.37	1.943	10
24.92	1.830	20
25.52	1.789	10
26.02	1.757	20
27.27	1.683	10
28.52	1.615	5
29.12	1.584	5
30.27	1.529	5
31.37	1.481	5
31.77	1.464	10
32.77	1.424	5
33.27	1.405	5
34.02	1.378	10
34.77	1.352	5
35.77	1.319	5
36.97	1.282	5
38.27	1.245	5
39.52	1.211	10
40.47	1.188	5
41.47	1.164	1
42.17	1.148	1
42.97	1.131	5
43.67	1.116	5

TABLE VI

Powder Pattern Data for PhQ·MoO$_2$Cl$_2$

θ	d	I/I_0
___*	___	5
6.12	9.090	5
6.92	8.040	5
7.57	7.353	50
8.37	6.654	100
9.17	6.078	1
10.12	5.513	40
11.02	5.067	90
12.07	4.632	50
12.12	4.614	5
14.42	3.890	75
14.82	3.787	40
15.62	3.598	5
16.57	3.397	5
17.42	3.236	40
17.82	3.165	5
18.42	3.066	40
18.97	2.980	10
19.87	2.850	35
20.32	2.789	1
21.12	2.688	30
22.22	2.561	10
22.72	2.508	1

*Unreadable; line cut by aperture.

Table VI cont.—

θ	d	I/I_o
23.57	2.422	10
24.57	2.330	5
25.17	2.278	1
25.57	2.244	10
26.32	2.185	1
27.02	2.132	1
27.82	2.076	5
28.32	2.042	5
29.17	1.987	1
30.17	1.927	5
30.82	1.891	1
31.42	1.858	1
32.32	1.812	1
32.37	1.809	1
33.07	1.775	1
33.47	1.756	1
34.82	1.696	1
36.57	1.626	5
37.87	1.578	1
38.57	1.554	1
39.52	1.522	1
40.22	1.500	1

TABLE VII

Powder Pattern Data For $2PhQ \cdot HgCl_2$

θ	d	I/I_o
6.10	7.255	80
6.75	6.559	80
7.25	6.109	70
8.20	5.405	80
8.95	4.955	30
9.75	4.552	80
10.70	4.152	50
11.05	4.022	50
11.30	3.934	50
11.70	3.802	10
12.05	3.693	10
12.30	3.619	30
12.55	3.548	30
12.85	3.466	30
13.35	3.339	1
13.90	3.209	100
14.30	3.121	5
14.90	2.998	5
15.30	2.921	5
15.85	2.823	30
16.50	2.714	20
17.20	2.607	30

Table VII cont.—

θ	d	I/I_o
18.05	2.488	10
18.75	2.398	30
19.30	2.332	10
19.95	2.259	10
21.05	2.146	15
21.35	2.118	10
22.05	2.053	10
23.00	1.973	10
23.45	1.937	10
24.15	1.884	5
24.80	1.838	15
25.25	1.807	10
25.95	1.762	5
26.30	1.740	5
26.65	1.719	5
27.25	1.684	5
27.90	1.647	5
28.70	1.605	1
29.70	1.556	1
30.25	1.530	5
30.85	1.503	1
31.75	1.465	10
32.50	1.435	1
33.30	1.404	1

Table VII cont.—

θ	d	I/I_o
34.25	1.370	5
35.10	1.341	1
36.15	1.307	1
36.75	1.288	1
37.25	1.274	1
37.90	1.255	1
38.40	1.241	1
38.85	1.229	1
39.40	1.215	1
40.20	1.194	5

TABLE VIII

Powder Pattern Data For $3PhQ \cdot FeBr_3$

θ	d	I/I_0
5.55	10.015	10
7.10	7.837	10
7.85	7.092	100
8.50	6.553	5
10.60	5.266	20
11.50	4.859	5
12.55	4.458	50
13.80	4.061	5
15.25	3.683	50
16.05	3.504	5
16.80	3.351	100
17.75	3.177	30
18.80	3.006	1
20.20	2.805	10
21.45	2.649	20
22.45	2.537	10
23.25	2.454	1
25.80	2.226	1
27.40	2.105	5
28.50	2.030	5
30.10	1.931	5

Table VIII cont.—

θ	d	I/I_0
31.85	1.836	5
33.95	1.735	10
37.40	1.595	3

TABLE IX

Infrared Absorption Frequencies of the Phenanthrenequinone Series

in the 1700–1500 cm^{-1} Region

Compound	Range (cm^{-1})			Decrease in the Carbonyl Frequency
	1700–1600	1600–1575	1575–1500	
PhQ	1674 s	1594 s		0
PhQ·MnBr$_2$	1629 s	1586 s		45
PhQ·CoBr$_2$	1611 m	1582 s		63
PhQ·ZnBr$_2$	1626 ms	1587 s		48
PhQ·CdBr$_2$	1639 ms	1586 s		35
PhQ·InBr$_3$	1656 ms	1589 s		18
PhQ·SnBr$_4$			1560 s	114
2PhQ·NiBr$_2$	1610 m	1582 s		64
2PhQ·HgBr$_2$	1661 s	1591 s		13
3PhQ·FeBr$_3$	1665 m, br	1587 s		9
PhQ·MoO$_2$Br$_2$	1613 ms	1581 s		61
PhQ·MoO$_2$Cl$_2$	1626 m	1585 s	1552 s	48

Note: The symbols "s" (strong) and "m" (medium) give an indication of the intensities of the absorption bands. A wide band is indicated by "br" (broad).

TABLE X

Infrared Absorption Frequencies
of the Chrysenequinone Series in the
$1700-1500$ cm^{-1} Region

Compound	Range (cm^{-1})	
	1700-1600	1600-1500
ChQ	1659s	1594ms,1577mw
ChQ·MnBr$_2$	1617s, 1605ms	1587s,1572s
ChQ·CoBr$_2$	1613mw	1586s[a],1572s
ChQ·ZnBr$_2$	1620s,1603ms	1591s,1574s
ChQ·CdBr$_2$	1622s,1609ms	1589s,1575ms
ChQ·InBr$_3$	1613m	1584s[b],1562s
ChQ·SnBr$_4$	1611m	1571s[c],1530s,br
2ChQ·NiBr$_2$	1613m	1589ms,1568s
2ChQ·HgBr$_2$	1641s	1593s,1579m
3ChQ·FeBr$_3$	1653ms	1593s,1577ms
ChQ·MoO$_2$Cl$_2$	1627w,1610w	1583ms,1555s,1537s
ChQ·UO$_2$Br$_2$	1622m,1611m	1577s,1565s

Note: a. Contains a shoulder at 1595 m.
b. Contains a shoulder at 1592 m.
c. Contains a shoulder at 1581 m.

The symbols "s"(strong), "m"(medium) and "w"(weak) give an indication of the intensities of the absorption bands. A wide band is indicated by "br"(broad).

TABLE XI

Magnetic Data for the Phenanthrenequinone Series

Complex	$10^6 X'_M$	$\mu_{obs.}$	$\mu_{calcd.}$	n	Range for compounds w/same metal species[13].
PhQ·MnBr$_2$	14,157	5.84	5.92	5	5.65–6.10
	14,196	5.85			
3PhQ·FeBr$_3$	14,100	5.83			
	15,747	6.16	5.92	5	5.70–6.0
	14,658	5.94			
PhQ·CoBr$_2$	9,219	4.71	3.88	3	4.30–5.20
	9,319	4.74			
2PhQ·NiBr$_2$	4,316	3.22	2.83	2	2.80–3.50
	4,404	3.26			

TABLE XII

Magnetic Data for the Chrysenequinone Series

Complex	$10^6 X'_M$	$\mu_{obs.}$	$\mu_{calcd.}$	n	Range for compounds w/same metal species[13]
$ChQ \cdot MnBr_2$	14,344	5.88			
	14,867	5.98	5.92	5	5.65–610
	14,832	5.98			
$3ChQ \cdot FeBr_3$	16,089	6.23			
	14,475	5.90	5.92	5	5.70.6.0
	15,250	6.06			
$ChQ \cdot CoBr_2$	10,672	5.07			
	11,072	5.16	3.88	3	4.30–5.20
	10,931	5.13			
$2ChQ \cdot NiBr_2$	5,129	3.52	2.83	2	2.80–3.50
	5,090	3.50			

TABLE XIII

Structural Relationships Derived

from Magnetic Measurements

Metal Species	n (calcd. from u_{obs}.)	Bond Type	Configuration
Mn (II)	5	sp^3	tetrahedral
Fe (III)	5	sp^3d^2	octahedral
Co (II)	3	sp^3	tetrahedral
Ni (II)	2	sp^3 or sp^3d^2	tetrahedral or octahedral

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Table III cont.—

θ	d	I/I_0
25.00	1.824	20
25.55	1.787	10
26.30	1.740	10
27.00	1.698	10
27.70	1.658	15
28.30	1.626	5
29.70	1.556	5
30.65	1.512	1
31.45	1.478	10