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THERMOCHEMICAL BOND ENERGY STUDIES OF VARIOUS TRANSITIONAL METAL BIS-BETA-DIKETONE COMPOUNDS AND THEIR INNER ORBITAL SPLITTINGS BY BOMB CALORIMETRY

A Dissertation
Presented to
the Faculty of the Graduate School
University of the Pacific

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

by

Charles Irvin Drew

January 1971

This dissertation, written and submitted by

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Dated January 25, 1971

THERMOCHEMICAL BOND ENERGY STUDIES OF VARIOUS TRANSITIONAL METAL BIS-BETA-DIKETONE COMPOUNDS AND THEIR INNER ORBITAL SPLITTINGS BY BOMB CALORIMETRY

Abstract of Dissertation
Charles Irvin Drew

The thermochemical technique of static bomb calorimetry was used to determine the heats of combustion for some twenty chelated metal complexes. Studied were the first row transitional metals (Mn^{+2} through Zn^{+2}) bis-beta diketone complexes of acetylacetone and their related ligands and the acetylacetonates of Pd^{+2}, Pt^{+2}, Be^{+2}, Ce^{+3}, Tl^{+1}, and Zr^{+4}.

Solid purified samples of from 1 to 2 grams were combusted in a pressurized oxygen atmosphere to the reaction products H_2O (l), CO_2 (g) and metallic oxides. The temperature change for the exothermic reactions was standardized with benzoic acid to give the enthalpy of combustion in kcal/mole. The majority of the data for the combustion reaction are in error of 1/2 of 1% or less.

The heat of combustion data were used in a suitable Born-Haber thermochemical cycle to determine the average bond energy for the metal to ligand bond. The bond cleavage can be expressed in either terms of an ionic or a coordinated bond break, known as heterolytic and homolytic cleavage respectively, depending on the choice of the thermochemical cycle. The homolytic bond energy cycle is suitable for the calculation of the average bond energy.

For the acetylacetonate complexes of Mn^{+2} through Zn^{+2}, the heterolytic thermochemical cycle was used. Thus, the heterolytic bond energies obtained are shown to vary with the electronic configuration of the central metal. These variations are predicted by crystal field theory.

A plot of the total heterolytic bond energies versus atomic number will, with a knowledge of the spin state of the metal ions, give an estimation of 10Dq values for the complexes. For the complexes investigated, 10Dq values are in good agreement with those obtained by the more accurate spectroscropic method.

A second series of compounds invertigated consisted of various ligands similar to acetylacetone. The copper and nickel complexes were synthesized with benzoylacetone, dibenzoylmethane and salicylaldehyde. It was expected that a pattern of decreasing bond energy could be found by the systematic replacement of first one and then the other methyl groups by a phenyl group (the substituent effect). No clear pattern emerged.

This investigation provides the framework for future investigations to give a more quantitative understanding of metal chelated complexes and their metal-ligand bond energies.

ACKNOWLEDGEMENT

Grateful acknowledgement in making this endeavor possible is given to Dr. Emerson Cobb for financial and moral encouragement; to the University of the Pacific for three National Science Foundation traineeships in 1966-1967, 1967-1968, 1968-1969 and for supplemental support; to my committee chairman, Dr. Richard P. Dodge, for his guidance; and to my wife, Carol, for her presence and patience.

TABLE OF CONTENTS

LIST OF TABLES

PAGE

LIST OF FIGURES

PAGE

CHAPTER I

INTRODUCTION

The amount of quantitative thermochemical data available on chelated coordination compounds is rather limited in comparison to that for organic or simple inorganic compounds. While within recent years some progress has been made (27, 39, 40, 41), there still remains much to be done before a theory can be postulated making possible the calculation of any chelated bond energy (38). The transitional metal acetylacetonates are especially convenient for such a study as they possess the useful physical properties of volatility, stability and solubility in organic solvents (40).

A useful method for the calculation of the bond energies is the use of the Born-Haber cycle in which the heat of formation of the transitional metal acetylacetonates can be determined by measuring all the quantities in the cycle. For many of these compounds the only unknown quantity remaining to be measured is the heat of combustion. Then, by application of Hess's law of summation, the heat of chelation for the gas phase reaction can be calculated. A portion of this chelation process is the metal to ligand bond formation (hereafter designated as M-L for the general term and M-O where L is the oxygen).

A useful way of looking at bond energy terms is found in crystal field theory. The orbitals of the transitional metals are directional and bonding occurs between specific configurations. Thus, certain of the five "d" orbitals are more closely directed towards an oxygen atom of the ligand. These "directional" orbitals are increased in energy and hence the term inner orbital splitting. This inner orbital splitting, known as the crystal field stabilization energy (hereafter known as c.f.s.e.) is dependent upon the electronic configuration of the metal. For the case of d^o, d^5--high spin--and d^{10}, no inner orbital splitting can be detected. Hence, a straight line drawn between d^5 and d^{10} in a plot of total M-L bonding energy versus atomic number for homogeous series reveals the case of no c.f.s.e. The difference between the actual plot and the straight line gives the c.f.s.e. for each compound. The c.f.s.e. data is useful as it varies with the strength of the bonding energy, the ligand involved, and with the metal.

In this work, M-L bond energy data have been determined on three types of compounds. First, the divalent transitional metal acetylacetonate complexes of manganese through zinc are combusted to determine the M-L bond energy and the c.f.s.e. In addition, the heat of combustion of Cu and Ni complexes with ligands of benzoylacetone, dibenzoylmethane, and salicylaldehyde is reported along with combustion data for seven assorted acetylacetonate compounds of the second and third transitional row metals.

CHAPTER II

NATURE OF THE BETA-DIKETONE CHELATED COMPOUNDS

The group of chelate ligands known as the ßeta-diketones, of which acetylacetone is the simplest, undergo structural changes when forming a chelated ring. Normally, acetylacetone exists as a mixture of the keto form--24%--and the enol form--76%. In chelation, however, all is converted to the enol form which behaves as an acid and loses a proton forming an anion. The anionic structure behaves as the bidentate ligand which "bites" the metal.

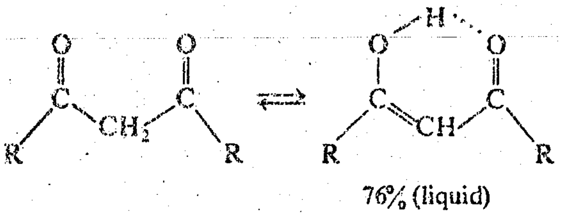


FIGURE 1

KETO-ENOL TAUTOMERISM OF ACETYLACETONATE (from ref. 15, p.369)

When the enolated bidentate forms a chelate ring, an important change in the electronic structure of the ligand occurs and the two oxygen atoms become equivalent. Infrared study verifies this effect. The absorption band of the conjugated carbonyl groyp, C=O (1650 - 1750 cm^{-1}), present in the ligand disappears upon chelation and a new band indicative of the resonance system appears at 1520 and 1590 cm^{-1} (20).

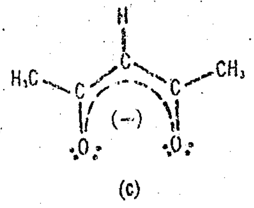


FIGURE 2

ANIONIC FORM OF ACETYLACETONATE LIGAND (from ref. 30)

As might be expected, this new resonance system within the chelate ring is considerably more stable. For acetylacetonate complexes, the increase due to the formation of the new resonance system appears to be about 2 - 3 kcal/mole for each chelate ring formed. The salicylaldehyde complexes do not exhibit this additional resonance stabilization and the infrared spectra of the salicylaldehyde complexes differs only slightly from that of the free ligand.

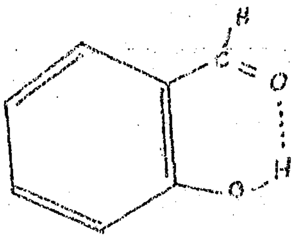


FIGURE 3

SALICYLALDEHYDE

It should be expected, however, that all other chelates in this investigation will display the resonance stabilization phenomena as shown by the derivatives of acetylacetone.

A. MOLECULAR STRUCTURE OF THE CHELATED COMPLEXES

It is naive to begin a quantitative study of these complexes without at least a rudimentary knowledge of the stereochemical factors with which we are dealing. Initially, classical methods were able to establish the structure of some of the transitional metal chelated complexes, but classical methods are limited to stable complexes. Some complexes are not stable enough to endure the physical process of separation of the optical or geometrical isomers: in addition, classical methods are limited in structural deduction to only previously imagined possibilities. X-ray diffraction analysis, for these reasons, has been completed on many of the transitional metal chelated compounds (3).

We shall assume in all instances in this work, as the experimental evidence suggests, that the beta-diketone anion is coordinated through the two oxygens of the ligand to the metal. There are, however, three other possibilities: 1) the coordination may occur with only one oxygen, as is the case for the mercury (II) acetylacetonate: 2) it may be bonded to the alpha carbon (platinum (IV)); 3) bonding may occur from the metal to the carbon-carbon double bond as shown in the acidified Werner complex, $HPt(AA)_2Cl$ (11).

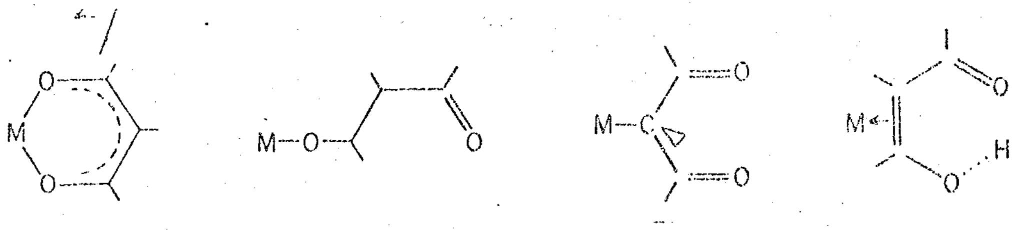
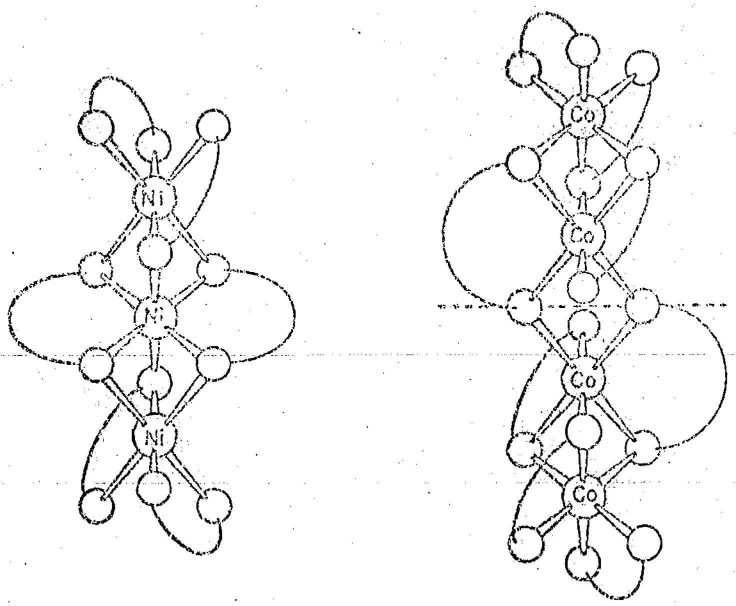


FIGURE 4

ACETYLACETONE AS A LIGAND
(from ref. 11, p.581)



Nickel Acetylacetonate Trimer   *Cobalt Acetylacetonate Tetramer*

FIGURE 5

POLYMERIC FORM OF Co AND Ni ACETYLACETONATES (from ref. 30, p.46)

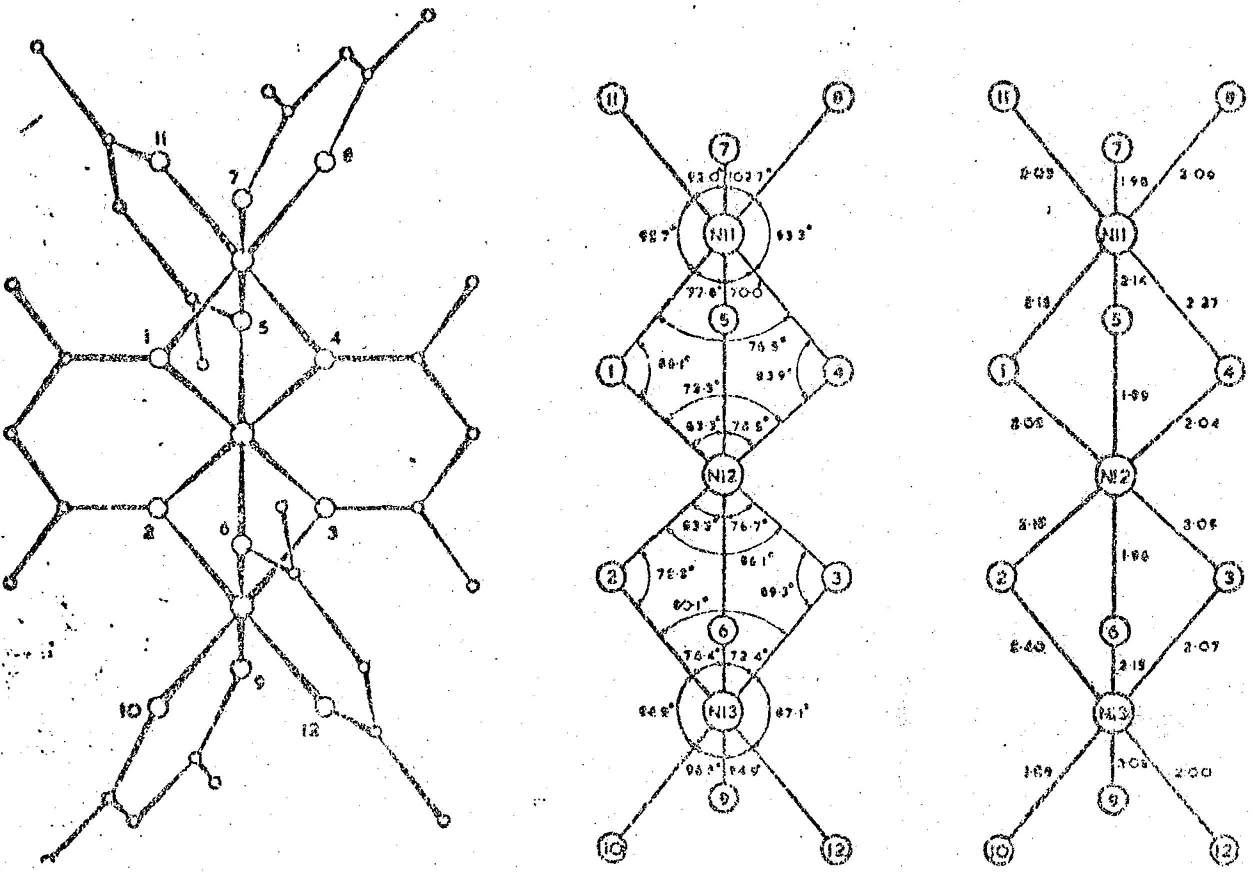


FIGURE 6

X-RAY DIFFRACTION OF Ni ACETYLACETONATE (from ref. 4, p.461)

In general, the anhydrous first row transitional metal (II) complexes were found to polymerize into either trimeric or tetrameric complexes due to their preference for six coordination (see page 6 for Co(II) and Ni(II) acetylacetonate structure).

The apparent exceptions can be traced to monomers which are not anhydrous. For example, it has been shown recently that the presumed anhydrous $Zn(AA)_2$ is the monohydrated complex with the water acting as a ligand to form a 5 - coordinated irregular trigonal bipyramid (21). Other hetero-ligand complexes of this nature are known such as the square pyramidal vanadyl complex, $VO(AA)_2$ (9).

Four coordinated acetylacetonate complexes are known in the Beryllium compound which is of tetrahedral configuration (10). Beryllium's first row transitional analogue is four coordinated $Cu(AA)_2$ which forms a nearly planar arrangement with slight Jahn-Teller distortions (34). Without exception, all other known Copper (II) beta-diketone complexes are square planar. The acetylacetonates of Pd (II) and Pt (II) are also square planar.

Being a stereochemical phenomenon, polymerization does not occur if the ligand is sterically hindered in such a manner that the only possible structure is the stoichiometrically expected complex. Thus, the trimeric nickel (II) acetylacetonate is converted from the octahedral trimer to a square planar monomer when the acetylacetonate is replaced by dipivaloylmethane (2, 2, 6, 6, tetramethyl-3, 5-heptanedione)(11).

In this investigation, it was found that the Ni (II) acetylacetonates and benzoyl acetonates are polymers, but the dibenzoylmethanate compound is a square planar monomer. This is consistent with the findings for dipivaloylmethane. It is uncertain at this point whether the salicylaldehyde Ni (II) complex is six or four coordinated. Calculations are carried out for both possibilities with the results: for four coordination, M-L = 71.5 kcal/mole; for six coordination, M-L = 47.7 kcal/mole. In view of the generally decreasing strength of the salicylaldehyde complexes, six coordination seems favorable. However, the lower than expected value suggests that the salicylaldehyde does not coordinate in the same manner as the acetylacetone.

Eight coordination is possible with beta-diketone compounds and is known for the $Zr(AA)_4$ and $Ce(AA)_4$. The structure for both these compounds is shown below displaying an Archimedean square anti-prism of $\sim D_2$ symmetry.

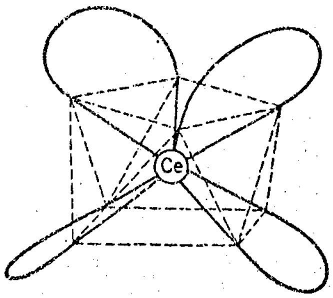


FIGURE 7

EIGHT COORDINATED CONFIGURATION (from ref. 30, p. 36)

The eight coordinated "pinwheel" anti-prism has not been discovered and it seems unlikely that it will appear due to steric hindrance.

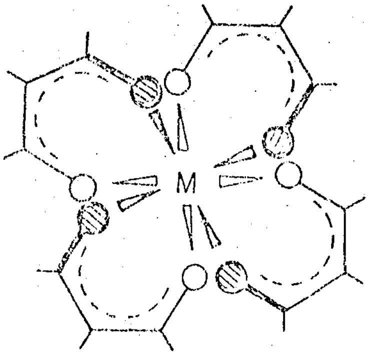


FIGURE 8

PINWHEEL STRUCTURE (from ref. 11, p. 584)

Complexes with a coordination number of two are formed with the monovalent metals. Examples are the acetylacetonates of Ag(I) and Ti(I). Two coordination also occurs with the Hg(II) acetylacetonate which is an anomaly.

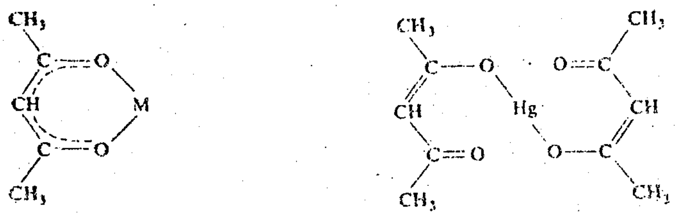


FIGURE 9

TWO COORDINATION (from ref. 20, p. 105)

CHAPTER III

EXPERIMENTAL - MATERIALS AND METHODS

A. General

The heats of combustion were determined with a static oxygen bomb calorimeter (Parr, Serial No. 1269). Due to rather large uncertainity ($\pm$ 10 cal) in the heat of combustion data, reduction to the standard states (Washburn corrections) were not applied.

The observed heat of reaction for the samples is taken to be the idealized heat of combustion yielding the oxides in their standard states. Since corrections of this type never amount to more than a few tenths of 1 % of the total heat of combustion, it is a valid approximation (36). Hence, the correct term for heats of combustion in this paper is "heats of a combustion reaction."

The heats of sublimation for those compounds investigated were taken for the most part from Joseph T. Truemper, "A Study of the Volatile Characteristics of Various Metal-Beta-Diketones Chelate Compounds" (35).

In accurate determinations, the metal oxides formed in the combustion reaction must be identified. However, work which is merely preliminary in nature need not determine accurately the nature or ratio of metal oxides as the differences in heats of formation of the transitional metal oxides are not very great. We are looking for trends in a large number of compounds. Accurate determinations on one particular compound must, however, eliminate errors due to the uncertainty of the combustion products (i.e., by x-ray diffraction analysis or by use of rotating bomb calorimetry).

B. Description of the Calorimeter

The Parr Instrument Company Series 1200 adiabatic oxygen bomb calorimeter jacket was used with a Parr 1106 inverted oxygen bomb. The jacket temperature was controlled by a Parr 1500 electric water heater. Thus, hot or cold water could be added to the jacket as needed during combustion to maintain adiabatic conditions during the entire run.

The oxygen bomb was immersed in the calorimeter bucket which was weighed to contain 1800 grams of deionized water. The oxygen bomb is constructed of Illium, an alloy which protects the bomb against attack by hot gases or acids produced during combustion. The electrodes are 667 alloy material and the capsule support loop is platinum--10 % iridium. The 1106 inverted bomb has a capacity of 340 ml. It is self-sealing under pressure with a double valve head and equipped with three legs attached to the screw cap so that the bomb can be fired in an inverted position with all fittings at the bottom instead of at the top. The Parr fuse wire used has a heat of combustion of 1400 cal/gram or 2.3 cal/cm. Approximately 10 cm of wire was placed so as to just touch the pellet.

The samples were weighed approximately and pelletized in a simple Parr pellet press. The sample to be burnt was then carefully dusted to remove any loose particles and weighed in the previously weighed combustion crucible.

Before assembling the bomb, one ml of deionized water was added to ensure that the atmosphere within the bomb was saturated with water vapor. Thus, the reaction of combustion can be said to yield water in the liquid state. The heat of solution of any CO_2 dissolved in water is taken as negligible.

Next, the assembled bomb was filled with oxygen (reagent grade) to a pressure of 35 atmospheres as indicated by a Parr No. 1824 snap coupling oxygen gauge. To avoid correction for trapped atmospheric nitrogen which would be converted to a nitric oxide, the bomb was flushed by purging with oxygen. (Due to an internal stem on the exhaust outlet, the 1 ml of water was not exhausted.)

The sealed and pressurized bomb is then placed in the weighed water bucket which is placed in the calorimeter. After the stirring motor is activated, the external water jacket is adjusted to the temperature of the internal bucket and allowed to equilibrate for at least 300 seconds.

After noting the temperature of the bucket water, the sample was ignited by a large electrical current which momentarily flows through the iron fuse wire. The red hot wire ignites the sample which then burns easily in the pressurized oxygen atmosphere.

The temperature rise is measured by a Parr mercurial thermometer, Serial No. 7D8687, with the aid of a 4 power Parr 3003 thermometer reading lens. Corrections in the observed temperature reading were made by reference to a correction chart supplied with the thermometer. These corrections were made by the Parr Company in comparison with a platinum resistance thermometer certified by the National Bureau of Standards (see Appendix for Test Certificate).

Before recording the final temperature rise, 400 seconds were allowed to pass at which time the rise was considered a maximum (see graph on page 16). To avoid stem corrections, care was taken throughout the entire run that the bucket temperature was close to the ambient temperature. No significant error is introduced if the stem and bulb temperatures do not differ more than 1/6 of the range of the thermometer. This means that the bucket temperature must be within $\pm$ 2.66°C. of the ambient.

TABLE I

TIME-TEMPERATURE DETERMINATION -- BENZOIC ACID

Time (sec.)	Temperature (degrees C.)
0	26.309
5	26.309
10	26.309
15	26.4
20	26.6
25	26.8
30	27.2
35	27.4
40	27.6
45	27.8
50	28.0
55	28.2
60	28.3
65	28.5
70	28.58
90	28.70
100	28.80
120	28.88
150	28.920
190	28.930
200	28.933
260	28.938
400	28.938

Delta T = 2.629°C.

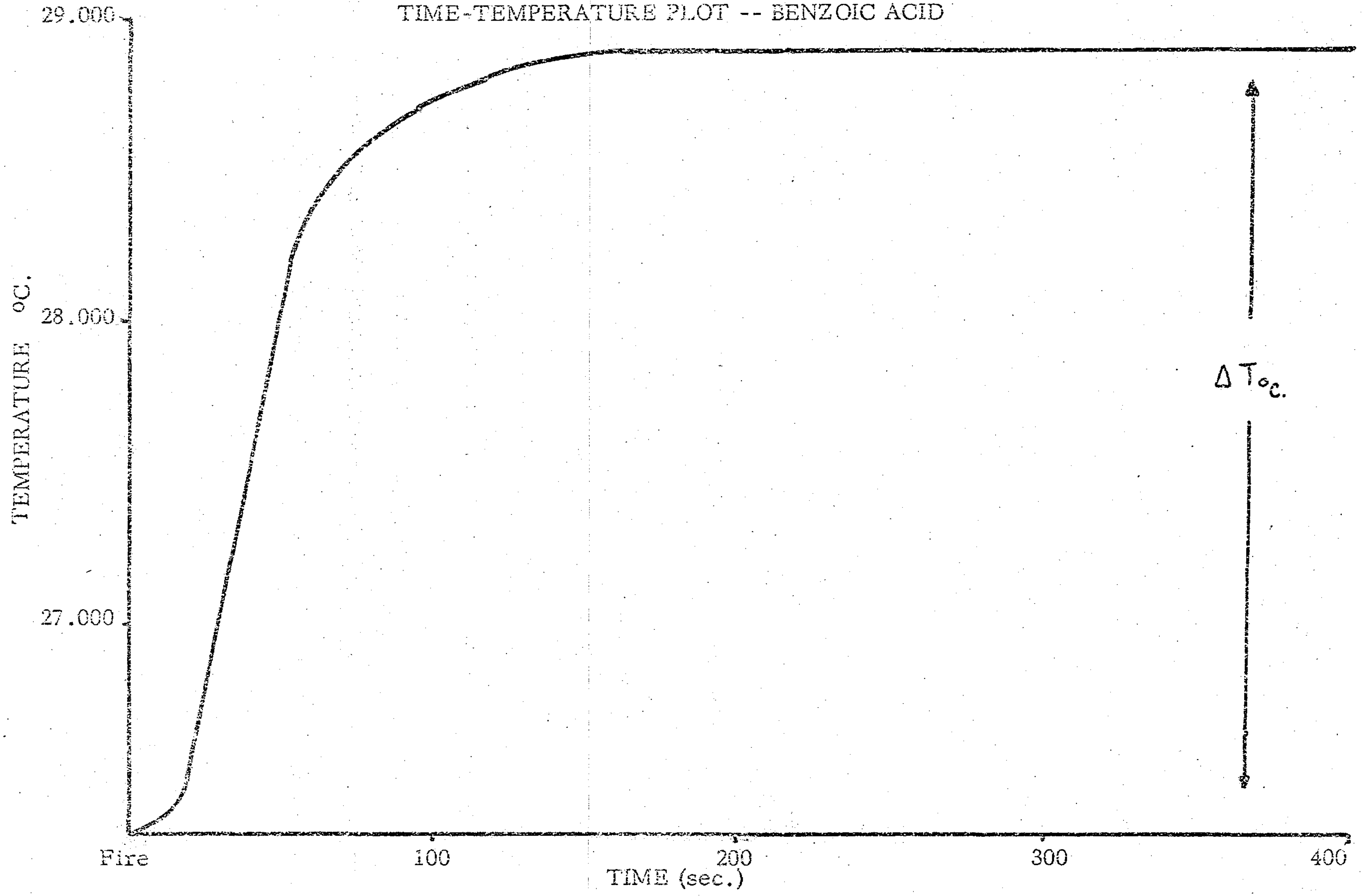
Pellet Weight = 1.1146 grams

6318 Cal/Gram (Standard)

$$\frac{(6318\ \text{cal/gram})(1.1146\ \text{grams})}{2.629\ \text{degrees}} = 2678\ \text{Calories per Degree}$$

(one determination)

FIGURE 10
TIME-TEMPERATURE PLOT -- BENZOIC ACID



C. Calibration of the Calorimeter

Bomb calorimeters are, basically, devices in which the heat of combustion is compared with some known amount of electrical energy. It is the accepted practice to compare the heat of combustion of the substance under investigation with benzoic acid which has been suitably purified. All calibrations were done using benzoic acid supplied by the Parr Instrument Company and standardized for calorific purposes. The heat of combustion of this benzoic acid was given as 6318 cal/gram.

The standard procedure for experimental calibration conditions was followed as is recommended by the Permanent Committee on Thermochemistry of the International Union of Chemistry. The recommendations for procedure are: the initial oxygen pressure to be 30 - 35 atmospheres; 3 grams of benzoic acid per liter of bomb volume should be burned; 3 ml of water per liter of bomb volume should be added; other samples should be of sufficient size to give about the same temperature rise as given by this amount of benzoic acid (36). (Experimentally, the rise was approximately 2.30°C.)

D. Chemicals

1. Beta Diketones

Salicylaldehyde - The commercially available Eastman Kodak Company product was used. It was distilled at a B.P. of 196.5°C.

1-Phenyl-1, 3 butanedione - This compound was commercially available and the J. T. Baker Company product (mp - 58-60°C.) was used as received.

1,3 Diphenyl-1,3 propanedione (dibenzoylmethanate) - This compound was commercially available and the J. T. Baker Company product (mp -- 76-78°C.) was used as received.

2. Metal Chelate Compounds

Bis-(acetylacetonato)manganese(II) - The commercially prepared Alfa Inorganics Industry product was used. The light tan powder was dried without water loss. Although this compound appears as a polymer in solution and is presumed a polymer in anhydrous solid states (22), the following information indicates, however, that this is most likely a four coordinated monomer and probably square planar in structure. The mp was sharp at 256°C. to 257°C. but the anhydrous polymer does not melt below 360°C. Repeated attempts at drying gave no change in the mp. In addition, the bond energy M-L for the experimental compound highly indicates a four coordination. Thus, it appears that there are two possible structures for anhydrous bis-(acetylacetonato)Mn(II): 1) the anhydrous, 6-coordinated polymer obtained by drying diaquobis (acetylacetonato)Mn(II)(22); and 2) a 4-coordinated square planar monomer (8). High spin state in either case is shown with magnetic susceptibility of 5.88 B.M. (22).

Bis-(acetylacetonato)iron(II) - The commercially available K & K Laboratories Inc. product was used. The dark red powder was dried without water loss. Indicated structure is a 6 coordinated trimer -- a high spin complex of 5.4 B.M. (13).

Bis-(acetylacetonato)nickel(II) - The commercially available K & K Laboratories Inc. product was used. This pale green powder was dried without water loss. It is a trimer (see x-ray diffraction, p. 7).

Bis-(acetylacetonato)cobalt(II) - The commercially available K & K Laboratories Inc. product was used. Cobalt is a tetramer with a coordination number of six for each cobalt atom.

Bis-(acetylacetonato)copper(II) - The commercially available Alfa Inorganics product was used. The chalk like deep blue crystalline material dried with slight water loss. Indicated structure is a four coordinated, square planar species.

Bis-(acetylacetonato)Zinc(II) - This was commercially available by Alfa Inorganics Inc. The pure white crystalline material indicated water loss on drying. The structure investigated was the monohydrate species. Graddon (21) has reported this as a five coordinated, trigonal bipyramid with water acting as the fifth ligand.

Bis-(acetylacetonato)palladium(II) - Available from Alfa Inorganics, the yellowish substance was run as received. Probable structure is square planar.

Bis-(acetylacetonato)platinum(II) - Available from Alfa Inorganics, the greenish-yellow substance was run as received. The probable structure is square planar.

3. Preparation of Synthesized Complexes

The following method was used for the preparations involving liquid diketone acetyltrifluoroacetone. A 5% metal ion solution of the nitrate salts was buffered with 5 grams of sodium acetate per 100 ml of solution. Then, an excess of the buffered metal ion solution was shaken with the stoichiometric amount of diketone. The shaking was continued until the reaction was complete. The same method was used with the solid diketones (benzoylacetone and 1,3 diphenyl-1,3 propanedione) with the exception that an excess of the buffered metal ion solution was added slowly, with shaking, to the concentrated alcoholic solution of the diketone. This order of addition was used in order to avoid the precipitation of the diketone which is insoluble in water.

The salicylaldehyde complexes were synthesized by adding half saturated solutions of the metal acetate salts in 50% alcoholic solutions to stoichiometric amounts of salicylaldehyde. The reactants were shaken until the reaction appeared complete. In all cases high yields from 75-90% were obtained.

Following the precipitation of the metal chelate compounds by the methods above, the precipitate was collected by filtration, washed, recrystallized and subsequently dried in a drying oven for 32 hours (90 - 100°C.). The specific details follow. Metal percentage analyses were carried out for all synthesized compounds by Schwarzkoph Microanalytical Laboratories, Woodside, N.Y.

1. <u>Bis-(acetyltrifluoroacetonato)copper(II)</u> - The deep blue precipitate was washed with water, recrystallized from benzene, and dried. The observed

values for the mp, which are recorded in the literature, are 189°C. (35) and 200°C. (35). Anal. Calcd. for $(C_5H_4F_3O_2)_2Cu$:Cu, 16.94. Found: Cu, 17.19.

2. Bis-(acetyltrifluoroacetonato)nickel(II) - The green precipitate included at least two different products. The more soluble product in the organic layer was isolated, washed with water and again with benzene. The observed mp was 240 - 250°C. with decomposition. (Literature (35), 230°C.) Anal. Calcd. for $(C_5H_4F_3O_2)_2Ni$:Ni, 17.09. Found: Ni, 16.09%.

3. Bis-(benzoylacetonoacetonato)copper(II) - This greenish-blue precipitate was washed with water and recrystallized from ethanol-water and dried. Observed sharp mp was at 197°C. Literature confirms a mp of 197°C. (35). Anal. Calcd. for $(C_{10}H_9O_2)_2Cu$:Cu, 16.35%. Found: Cu, 16.62%.

4. Bis-(benzoylacetonato)nickel(II) - The greenish precipitate was washed with water and recrystallized from benzene and dried. The mp observed was 178 - 179°C. (Literature (35), 178°C.) Anal. Calcd. for $(C_{10}H_9O_2)_2Ni$:Ni, 15.32%. Found: Ni, 15.28%.

5. Bis-(dibenzoylmethanato)copper(II) - The pale greenish precipitate was washed with water and recrystallized from ethanol-water solution and dried. The observed mp was 230°C. with a crystal change and decomposition, melting at 307°C. Anal. Calcd. for $(C_{15}H_{11}O_2)_2Cu$:Cu, 12.33%. Found: Fu, 12.40%.

6. Bis-(dibenzoylmethanato)nickel(II) - The gold-green precipitate was

washed and recrystallized from hot ethanol-water solution and dried. The observed mp. was 305-307°C. showing fairly sharp melting point. No report of the isolation of a crystalline product could be found in the literature. Anal. Calcd. for $(C_{15}H_{11}O_2)_2Ni$:Ni, 11.57%. Found: Ni, 11.33%.

7. Bis-(salicylaldehydo)copper(II) - The dark green crystalline precipitate was washed with water and ethanol and ether and dried. The compound melted with decomposition beginning at 265°C. Anal. Calcd. for $(C_7H_5O_2)_2Cu$:Cu, 20.64%. Found: Cu, 20.94%.

8. Bis-(salicylaldehydo)nickel(II) - The bright green precipitate was washed and dried. Melting with decomposition occurred at 330°C. Anal. Calcd. for $(C_7H_5O_2)_2$ Ni:Ni, 19.37%. Found: Ni, 17.73%.

9. Bis-(salicylaldehydo)cobalt(II) - The reddish-brown precipitate was washed and dried. Decomposition began at 320°C. Anal. Calcd. for $(C_7H_5O_2)_2$ Co:Co, 19.93%. Found: Co, 19.32%.

All of the above compounds were combusted with the exception of the trifluoroacetonates. In this case, adequate combustion equipment was not available to handle the halide compounds.

E. Oxides.

The metallic oxides produced during each determination were sampled and collected. As explained previously, the nature and equipment used in the project makes complete analysis of the oxides prohibitive. The accurate analysis of each oxidized product involves x-ray diffraction and the difficulties encountered in collecting all oxides produced during a single determination is better accomplished with a rotating bomb calorimeter. Many of the complexes exhibited a combustion phenomenon known as spalling whereby the combustion products are thrown out of the combustion crucible and splatted over the walls of the bomb charnber (29). Further difficulties in exact analysis are encountered when one considers the possibilities of the formation of hydrated oxides and metal hydroxides.

However, a description and probable composition of each oxide is listed below. We are assuming that these are the only oxides produced by the combustion reactions although this is obviously an idealization. In the case of Fe^{+2} oxide, it was observed that two types of residue were present--solid magnetite Fe_3O_4 and reddish Fe_2O_3. Analysis by weight content revealed that the approximate ratio of Fe_3O_4 to Fe_2O_3 is 2:1. It was assumed that no hydrated oxides were formed.

TABLE II

METALLIC OXIDES FORMED IN COMBUSTION REACTIONS

COMPLEX	OXIDE	DESCRIPTION
$Mn(C_5H_7O_2)_2$	MnO_2	black amorphous solid
$Fe(C_5H_7O_2)_2$	$Fe_3O_4 : Fe_2O_3$ 2:1	reddish-brown and metallic pellets
$Co(C_5H_7O_2)_2$	Co_3O_4	greenish-brown
$Ni(C_5H_7O_2)_2$	NiO	green
$Cu(C_5H_7O_2)_2$	CuO	black
$(H_2O)Zn(C_5H_7O_2)_2$	ZnO	white powder
$Pd(C_5H_7O_2)_2$	PdO	black powder
$Pt(C_5H_7O_2)_2$	Pt	silvery
All other Cu compounds	CuO	black
All other Ni compounds	NiO	green
$Tl(C_5H_7O_2)_1$	Tl_2O_3	black amorphous powder
$Zr(C_5H_7O_2)_4$	ZrO_2	yellowish
$Ce(C_5H_7O_2)_3$	Ce_2O_3	gray-green powder
$Be(C_5H_7O_2)_2$	BeO	white

CHAPTER IV

DATA

The results of experimental work are tabulated and processed in this chapter (see Appendix for raw data). In addition to the presentation of data, representative calculations are shown in detail for one compound -- bis-(salicylaldehydato)copper(II).

A. Standardization

Tables XIII and XIV (see Appendix) contain the data for two different standardizations of the bomb calorimeter. They obviously have different values as they represent standardizations with different amounts of deionized water in the calorimetry bucket. Most of the experimental work was done with the second more precise calibration. The data are marked with an asterisk where the second calibration standard is used.

B. Heats of Combustion

Tables XIII through XXXIII contain the data for the heats of combustion of each compound which was experimentally tested. At least four runs were made for each compound determination except for the compounds of platinum and palladium where only 2 grams of sample were available for analysis.

The summary for heat of combustion data is found in Table III (see p.26).

TABLE III

EXPERIMENTALLY DETERMINED HEATS OF COMBUSTION

COMPOUND	MOLECULAR WEIGHT	ΔE_c (cal/g)	ΔE_c (kcal/mole)	Δn	ΔH_c (kcal/mole)	%ERROR
$Mn(AA)_2$	253.16	-5002.1 ± 24.6	-1266.3 ± 6.22	-2.50	-1267.8	.49%
$Fe(AA)_2$	254.07	-4261.2 ± 37.1	-1082.6 ± 9.4	-2.25	-1083.9	.86%
$Co(AA)_2$	257.15	-4189.2 ± 26.5	-1077.3 ± 6.80	-1.88	-1078.4	.63%
$Ni(AA)_2$	256.93	-4171.0 ± 9.99	-1071.6 ± 2.56	-2.00	-1072.8	.23%
$Cu(AA)_2$	261.75	-4613.6 ± 17.36	-1207.6 ± 4.54	-2.00	-1208.8	.37%
$(H_2O)Zn(AA)_2$	281.60	-4255.1 ± 36.2	-1198.2 ± 10.19	-2.00	-1200.0	.85%
$Cu(BA)_2$	385.90	-6251 ± 22.68	-2413.0 ± 8.75	-3.00	-2414.8	.36%
$Ni(BA)_2$	381.30	-5859 ± 24.06	-2234.7 ± 9.17	-3.00	-2236.5	.41%
$Cu(DBM)_2$	510.04	(-6837.4)	-3487.3	+1.00	-3486.7	
$Ni(DBM)_2$	505.21	(-6711.2)	-3390.6	+1.00	-3390.0	
$Cu(SA)_2$	305.78	-5081.7 ± 53.52	-1553.9 ± 16.36	-1.00	-1554.5	1.05%
$Ni(SA)_2$	300.94	-4903.3 ± 12.56	-1517.1 ± 3.77	-1.00	-1517.7	.25%
$Co(SA)_2$	301.17	-4861.9 ± 17.9	-1464.28 ± 5.39	-1.66	-1465.1	.36%
$Pd(AA)_2$	304.62	-4021.0 ± 29.3	-1224.8 ± 8.9	-2.00	-1226.0	.72%
$Pt(AA)_2$	393.31	-3133.4 ± 48.5	-1232.4 ± 19.0	-1.50	-1233.2	1.54%
$Be(AA)_2$	207.23	(-6109)	-1265.96	-2.00	-1267.1	
$Ce(AA)_3$	437.45	(-3932.9)	-1720.4	-3.00	-1722.2	
$Tl(AA)_1$	303.48	(-2001.3)	-607.3	-1.50	- 608.1	
$Zr(AA)_4$	487.77	-3806.4 ± 16.9	-1856.66 ± 8.24	-4.00	-1859.02	.44%

Corrections to constant pressure enthalpy changes were made by using the first law relationship where Δn is the change in the number of moles of gaseous molecules for the combustion reaction.

$$\Delta H_c = \Delta E_c + \Delta nRT$$

The enthalpy of combustion in kcal/mole calculated in Table III is utilized in Table IV as one of the eight additive quantities which make up the thermochemical cycle. The Born Haber cycle for bis-salicylaldehyde is found on page 31. All other quantities, aside from the heat of combustion reactions, are known as standard reference values or have been determined in the recent literature. The other seven quantities which make up the thermochemical cycle are described below with the source of the data. As an example, the values used for bis-salicylaldehyde Cu (II) will be calculated for each quantity.

1. The heats of oxidation for the molecular compositions of each compound are listed in column one of Table IV. The heat of oxidation is calculated as the heat of formation of the metallic oxides and oxidation products (the heat of formation of elements in their standard states being zero). For each compound combusted, the heat of oxidation is determined as:

$$\Delta H_{ox} = 1/a \; \Delta H_f M_a O_b + \Delta H_f CO_2 + \Delta H_f H_2O$$

The heat of formation of CO_2 and H_2O is taken as -94.0518 kcal/mole and -68.3174 kcal/mole respectively (31). The source for the heat of formation of the oxide is the Handbook of Chemistry and Physics (23, p.1832).

e.g. Bis-Salicylaldehyde Cu(II)

$CuO = -37.1$ kcal/mole

$14 \times \Delta H_f\, CO_2 = 1316.7$ kcal/mole

$5 \times \Delta H_f\, H_2O = 341.6$ kcal/mole

$\Delta H_{ox} = 1695.4$ kcal/mole

2. ΔHv is the heat of vaporization of metal (see <u>Handbook of Chemistry and Physics</u> (23, p.1832).

$$\Delta H_{Cu,\ vap} = -81.52 \text{ kcal/mole}$$

3. The heats of formation of the various ligands used, H_{fL} , have been previously determined (40). The values are given in Table IV for each separate determination.

e.g. Salicylaldehyde: $\Delta H_{fL} = 66.7$ kcal/mole

4. The heat of vaporization of the ligands has been determined elsewhere for these compounds. Where the data are lacking estimates are made from analogous compounds. Experimentally, $\Delta H_{vap.}$ values were determined by use of the Clausius-Clapeyron equation. (35)

e.g. Salicylaldehyde: $\Delta H_{L,\ vap.} = 11.4$ kcal/mole

5. The heat of transition from the keto to the enol form is listed in the fifth column. For salicylaldehyde there is no transition. For acetylacetone, this is 2.61 kcal/mole (23).

6. The sixth quantity in the cycle is the heat of formation of the chelated complex. Essentially this is the unknown quantity and is determined once all the other additive quantities of the cycle are known.

7. The seventh quantity is the heat of vaporization of the complex. It is determined experimentally (35). Where experimental quantities are unavailable, estimations are made from analogous compounds.

e.g. Bis-(salicylaldehydato)Cu(II): $\Delta H_{\text{comp. vap.}} = 20.4$ kcal/mole(39)

The bond energies for the metal to ligand are calculated for each component in the last columns of Table IV (39). These values represent the average for each metal to oxygen bond strength. As will be explained in the following chapter, these values are the homolytic bonding energies for the process:

$$M{:}O = M^{\cdot} + O^{\cdot}$$

In making these calculations, it is assumed that the heat of chelation of the complex is the enthalpy related to the breaking of two O-H bonds (one for each ligand), the formation of either 4, 5, or 6 M-O bonds, and the heat of formation of one H-H bond.

e.g. bis-(salicylaldehydato)Cu(II)

$$\Delta H_{f,\ chel} = -2E(O\text{-}H) - 4E(Cu\text{-}O) + E(H\text{-}H)$$

$$-91.56 = -2(-110\ \text{kcal/mole}) - 4E(Cu\text{-}O) + (-103\ \text{kcal/mole})$$

$$4E(Cu\text{-}O) = 208.56\ \text{kcal/mole}$$

$$E(Cu\text{-}O) = 52.14\ \text{kcal/mole}$$

Of course, it is imperative to know coordination numbers before the bonding energies can be determined. A summary of the homolytic bond energies with their coordination numbers and probable structures is given on the following page for the compounds investigated. For references to the structures of the compounds, see Chapter II.

FIGURE 11

THERMOCHEMICAL CYCLE FOR EVALUATION OF BOND ENERGIES IN BIS(SALICYLALDEHYDATO)Cu(II)

$$\begin{tikzcd}
Cu(g) & + & 2\,C_7H_6O_2(g) - H_2(g) \arrow[r, "\Delta H_{f,\,chel}"] & Cu(C_7H_5O_2)_2\,(g) \arrow[d, "-\Delta H_{comp,\,vap}"] \\
 & & 2\,C_7H_6O_2(\ell) \arrow[u, "2\Delta H_{L,\,vap}"'] & Cu(C_7H_5O_2)_2\,(s) \arrow[d, "\Delta H_C"] \\
Cu(s) \arrow[uu, "\Delta H_{Cu,\,vap}"'] & +\ 14C(s)\ + & 17O_2(g) + 6H_2(g) - H_2(g) \arrow[u, "2\Delta H_{f,\,L}"'] \arrow[r, "\Delta H_{ox}"] & CuO(s) + 14CO_2(g) + 5H_2O(\ell)
\end{tikzcd}$$

$$\Delta H_{ox} = \Delta H_{Cu,\,vap} + 2\Delta H_{f,\,L} + 2\Delta H_{L,\,vap} + \Delta H_{f,\,chel} - \Delta H_{comp,\,vap} + \Delta H_C$$

$$\Delta H_{f,\,chel} = -2E(O\text{-}H) + 4E(Cu\text{-}O) + E(H\text{-}H)$$

TABLE IV
DATA USED IN CALCULATION OF BOND ENERGY

COMPOUND	ΔH_{ox}	ΔH_v	$\Delta H^o_{f, L}$	$\Delta H_{L, vap}$	ΔH_{trans}	$\Delta H_{f\ chel}$	$\Delta H_{3\ vap}$	ΔH_c	$\Delta E(M\text{-}O)$ total	$\Delta E(M\text{-}O)$
$Mn(AA)_2$	-1545.0^{a} ± 0.050	-68.34^{a} ± 0.05	201.9^{g} ± 0.8	-23.0^{e}	-5.22^{b} ± 0.05	-156.85^{l}	15.0^{j}	-1267.8^{f} ± 6.22	-273.8	68.5
$Fe(AA)_2$	-1485.2^{a}	-96.68^{b}	201.9^{g}	-23.0^{e}	-5.22^{b}	-309.1^{l}	15.0^{j}	-1083.9^{f} ± 9.4	-426.1	71.0
$Co(AA)_2$	-1487.7^{a}	-101.6^{b}	201.9^{g}	-23.0^{e}	-5.22^{b}	-322.2^{l}	15.0^{j}	-1078.4^{f} ± 6.8	-439.2	73.2
$Ni(AA)_2$	-1476.4^{a}	-101.3^{b}	201.9^{g}	-23.0^{e}	-5.22^{b}	-316.2^{l}	15.0^{j}	-1072.8^{f} ± 2.36	-433.2	72.2
$Cu(AA)_2$	-1455.7^{a}	-81.52^{b}	201.9^{g}	-23.0^{e}	-5.22^{b}	-139.66^{l}	15.0^{j}	-1208.8^{f} ± 4.54	-256.7	64.17
$(H_2O)Zn(AA)_2$	-1571.5^{a}	-31.19^{b}	201.9^{g}	-23.0^{e}	-5.22^{b}	-214.01^{l}	15.0^{j}	-1200.0^{f} ± 10.19	-331.1	66.22
$Pd(AA)_2$	-1439.0^{a}	-93.0^{b}	201.9^{g}	-23.0^{e}	-5.22^{b}	-117.32^{l}	15.0^{j}	-1226.0^{f}	-234.3	58.6
$Pt(AA)_2$	-1418.6^{a}	-121.6^{b}	201.9^{g}	-23.0^{e}	-5.22^{b}	-118.32^{l}	15.0^{j}	-1233.2^{f}	-235.3	58.8
$Cu(BA)_2$	-2532.9^{a}	-81.52^{b}	162.4^{h}	-40.0^{d}	-5.22^{c}	-77.74^{l}	6.5^{k}	-2413.0^{f}	-194.7	48.6
$Ni(BA)_2$	-2553.6^{a}	-101.3^{b}	162.4^{h}	-40.0^{d}	-5.22^{c}	-293.2^{l}	10.1^{k}	-2234.7^{f}	-410.2	68.4
$Cu(DBM)_2$	-3610.0^{a}	-81.52^{b}	201.9^{g}	-36.0^{n}	-5.22^{b}	97.04^{l}	15.0^{j}	-3482.3^{f}	-214.0	53.5
$Ni(DBM)_2$	-3630.0^{a}	-101.3^{b}	201.9^{g}	-36.0^{n}	-5.22^{b}		15.0^{j}	-3390.6^{f}	-233.5	58.4

COMPOUND	ΔH_{ox}	ΔH_v	$\Delta H^o_{f,L}$	$\Delta H_{L,vap}$	ΔH_{trans}	ΔH_f chel	ΔH_3 vap	ΔH_c	E(M-O) total	E(M-O)
Be(AA)$_2$	-1562.9[a]	-76.63[b]	201.9[g]	-23.0[e]	-5.22[b]	184.9[l]	15.0[j]	-1256.9[f]	301.9	75.5
Ce(AA)$_3$	-2345.8[a]	?	302.85[g]	-34.5[e]	-7.83[b]			-1720.4[f]		
Tl(AA)$_1$	-759.0[c]	-44.5[b]	100.95[g]	-11.5[e]	-2.61[b]	101.9[l]	15.0[j]	-607.3[f]	160.4	80.2
Zr(AA)$_4$	-3101.4[a]	-125.0[b]	403.8[g]	-46.0[e]	-10.44[b]	992.3[l]	?	-1859.0[f]		
Cu(SA)$_2$	-1695.4[a]	-81.52[b]	133.41[i]	-22.8[e]		91.5[l]	20.4[e]	-1553.9[f]	208.5	52.1
Ni(SA)$_2$	-1716.1[c]	-101.3[b]	133.4[i]	-22.8[e]		169.3[l]	20.4[e]	-1517.1[f]	286.3	71.5
Co(SA)$_2$	-1728.0[a]	-101.6[b]	133.4[i]	-22.8[e]		234.6[l]	20.4[e]	-1464.3[f]	356.6	58.6

(a) N.B.S. Circular 500. (b) "Handbook of Chem. and Phys." (c) B. Jakuszewski, Chem. Abstr., 54, 16161. (d) D. T. Farrar and M.M. Jones, J. Phys Chem., 68, 1720 (1964). (e) J.L. Wood and M.M. Jones, J. Phys.Chem., 67, 1049 (1963). (f) This paper. (g) G.R. Nicholson, J.Chem. Soc., 2431 (1957). (h) D.T. Farrar and M.M. Jones, J. Phys. Chem., 67, 1049 (1963). (i) J.L. Wood and M.M. Jones, J. Phys. Chem., 68, 1720 (1964). (j) see ref. 35. (k) E.W. Berg and J.T. Truemper, J. Phys. Chem. 64, 487 (1960). (l) Calculated as described in text. (m) The standard deviations for ΔH_{ox}, $\Delta H_{L,vap.}$ and ΔH_{trans} are all 0.05 kcal/mole or less (D.T. Farrar and M.M. Jones, J.Phys.Chem., 68, 1720 (1964). (n) Calculated from Troutons rule for the Heat of vaporization.

TABLE V

COMPOUNDS, STRUCTURE AND M-L BOND ENERGY

COMPOUND	COORDINATION NUMBER	STRUCTURE	ΔH(M-L HOMOLYTIC BOND ENERGY)(kcal/mole)
$Mn(AA)_2$	4	sq. planar monomer	68.5 ± 1.5
$Fe(AA)_2$	6	oct. trimeric polymer	71.0 ± 1.6
$Co(AA)_2$	6	oct. tetrameric polymer	73.2 ± 1.1
$Ni(AA)_2$	6	oct. trimeric polymer	72.2 ± 0.4
$Cu(AA)_2$	4	sq. planar monomer	64.2 ± 1.1
$(H_2O)Zn(AA)_2$	5	trigonal bipyramid	66.7 ± 2.0
$Pd(AA)_2$	4	sq. planar	58.6 ± 2.2
$Pt(AA)_2$	4	sq. planar	58.8 ± 4.6
$Cu(BA)_2$	4	sq. planar	48.6 ± 2.2
$Ni(BA)_2$	6	oct.polymer	68.4 ± 1.5
$Cu(DBM)_2$	4	sq. planar	(53.5)
$Ni(DBM)_2$	4	sq. planar	(58.4)
$Cu(SA)_2$	4	sq. planar	52.1 ± 4.1
$Ni(SA)_2$	6	oct. polymer	47.7 ± 0.9
$Co(SA)_2$	6	oct. polymer	58.6 ± 1.3
$Be(AA)_2$	4	tetrahedral monomer	(75.5)
$Ce(AA)_3$	6	oct. monomer	*
$Tl(AA)_1$	2	linear monomer	(80.2)
$Zr(AA)_4$	8	archimedeal anti-prism	*

* Not sufficient ΔH_{vap} data available to calculate bond energy.

CHAPTER V

DISCUSSION OF RESULTS

The homolytic bond energies described in the last chapter result from the heat of formation of the chelated structure of the neutral atoms in the gaseous state. Although analysis of neutral atoms could lead to a determination of the ligand field effect, traditionally the gaseous reference state chosen is that of charged ionic species. Thus, there is a necessity to convert the bond energy data from a homolytic to a heterolytic cleavage:

$$M{:}L = M^{+} + {:}L^{-} \qquad \Delta H = \text{heterolytic bond cleavage energy} \qquad (5\text{-}1)$$

Homolytic and heterolytic bonding are related in the following manner (40).

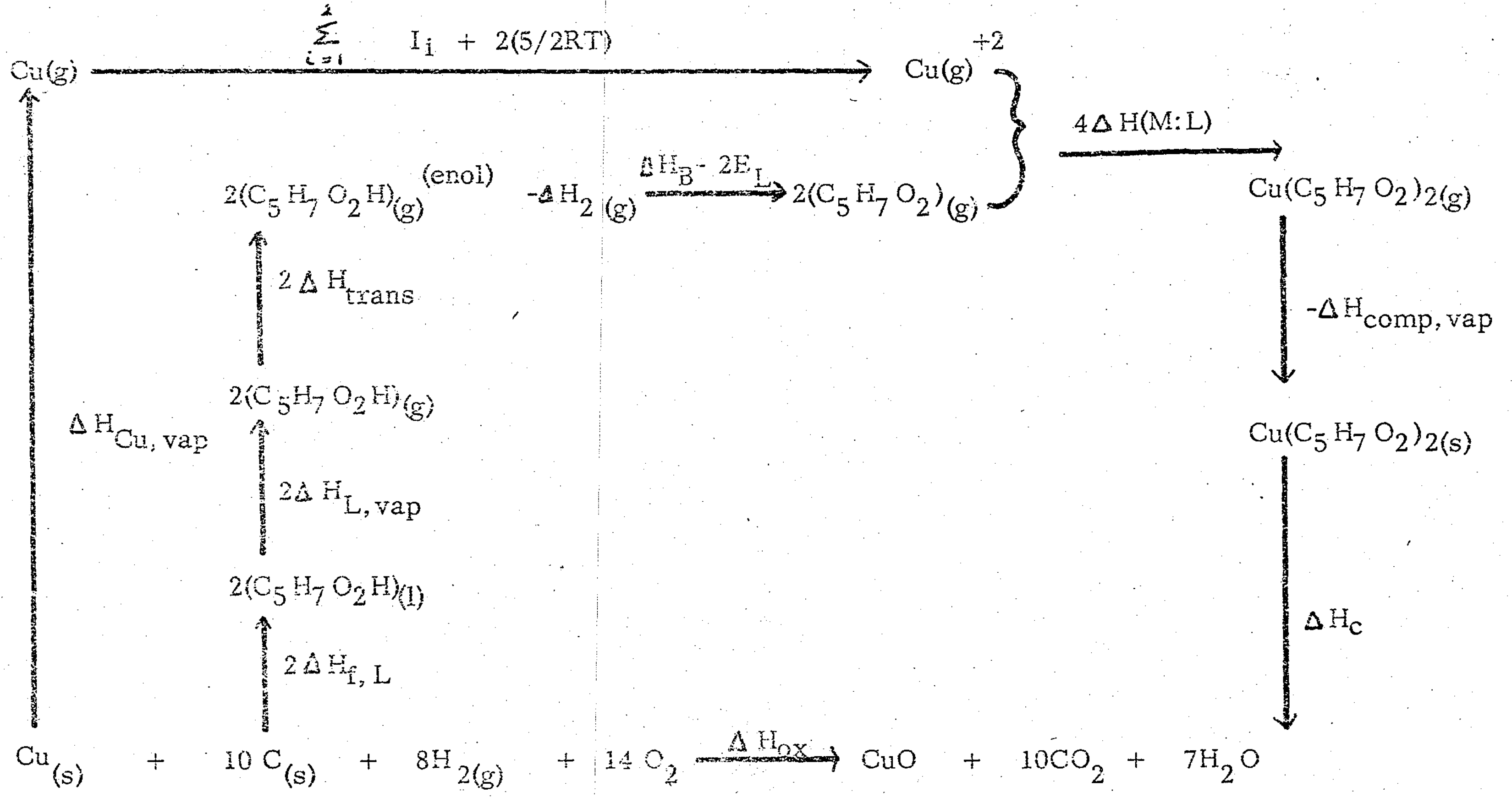
$$6\,\Delta H(M{:}L)_{homo} = 6\,\Delta H(M{:}L)_{hetero} + \sum_{i=1}^{2} I_i + 2(5/2\,RT) - E_L \qquad (5\text{-}2)$$

$\sum_{i=1}^{2} I_i$ is the ionization potential summation and E_L is the electron affinity of the ligand, and the term $2(5/2\,RT)$ is used to convert the ionization energies to 298°K.

In effect, then, what we are now viewing is known as the lattice energy and a new thermochemical cycle must be constructed to take into account a bond cleavage of a heterolytic nature. Such a cycle follows.

FIGURE 12

THERMODYNAMIC CYCLE FOR EVALUATION OF HETEROLYTIC BOND ENERGY IN BIS(ACETYLACETONATO)Cu(II)



$$\Delta H_{ox} = \Delta H_{vap} + \sum_{i=1}^{2} I_i + 2(5/2RT) + 2\Delta H_{f,\,ligand} + 2\Delta H_{vap} + 2\Delta H_{trans} + H_B - E_L + 4\Delta H(M:L) - \Delta H_{comp,\,vap} + \Delta H_c$$

$$\Delta H_B = -2E(O-H) + E(H-H)$$

TABLE VI

HETEROLYTIC BONDING -- ACETYLACETONATES

	$E(M\text{-}O)_{homo}$	$6\Delta E(M\text{-}L)_{homo}$	I	$+2(5/2RT)$	$-2EL$	$6\Delta E(M\text{-}L)_{hetero}$
Mn	68.5 ± 1.55	411.0	531.2	2.96	-15.68	929.48 ± 9.30
Fe	71.0 ± 1.60	426.0	555.2	2.96	-15.68	968.6 ± 9.40
Co	73.2 ± 1.10	439.7	574.2	2.96	-15.68	1001.2 ± 6.80
Ni	72.2 ± 0.43	433.2	594.6	2.96	-15.68	1015.1 ± 2.56
Cu	64.2 ± 1.13	385.2	646.0	2.96	-15.68	1018.5 ± 6.78
Zn	66.2 ± 2.04	397.2	630.2	2.96	-15.68	1014.7 ± 12.24

In analyzing the series of acetylacetonates Mn through Zn, we must make adjustments for differing coordination numbers and structures. Therefore, we are using the total heterolytic bonding strength as 6 times that of the adjusted bond strength. In reality, this does not correlate with the structure of all of the complexes as not all are 6 coordinated. However, for our purposes this "adjusted"plot to a uniform structure creates a difficulty only in the meaning of graphically obtained $-\Delta H$. One complex not corresponding to 6 coordination is Cu^{+2} . However, the 10 Dq value for Cu may be adjusted by using the relationship of the magnitude of 10Dq for octahedral to square planar complexes in a ratio of 10 to 9.

A. CRYSTAL FIELD STABILIZATION ENERGIES

The heterolytic bonding calculated with the use of equation 5-2 can be used in visualizing a variable relationship between the energy needed to form the heterolytic bonds and the atomic number. This relationship is predicted by crystal field theory and gives us an indication of the crystal field stabilization energies created by the presence of unfilled "d" orbitals in a ligand field.

This method is outlined by George and Mc Clure (19) with the use of the following relationship:

$$-\partial H = -(4n_t - 6n_e)Dq + P \qquad \text{(for octahedral coordination)} \qquad (5\text{-}3)$$

where: $-\partial H$ is the observed stabilization

n_t is the number of t_{2g} electrons

n_e is the number of e_g electrons

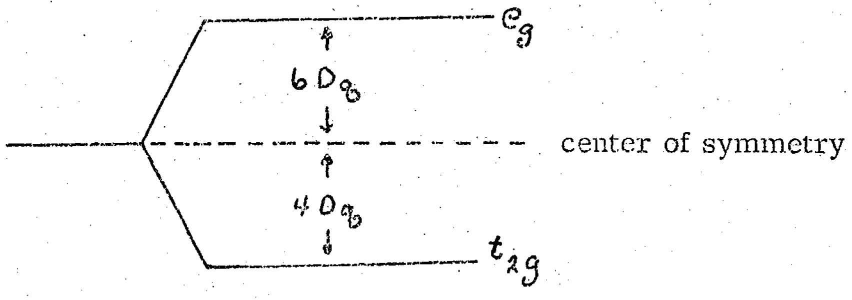
P is the pairing energy

The method used is that of plotting the total heterolytic bond energy versus the atomic number of the metal ions. To use this theory we must assume a linear relationship between the thermodynamic quantity and the atomic number in the absence of the ligand field. In addition, we must assume that there exists a "center of symmetry" among the split d-orbitals created by the ligand field.

The "center of symmetry" concept in effect states that for the octahedral case, there exists three d-orbitals -- the t_{2g} orbitals (d_{xy}, d_{xz}, d_{yz}) -- that are destabilized by an amount equal to the stabilization of two e_g orbitals ($d_{x^2-y^2}$, d_{z^2}).

FIGURE 13

SPLITTING OF D ORBITALS BY CRYSTAL FIELD
(for octahedral configuration)



In the octahedral case, this means that the two e_g orbitals are oriented directly at the ligands (along the xyz axes) and thus are "increased" in energy. The remaining t_{2g} orbitals are decreased in energy by an equal amount.

The $-\Delta H$ value is determined graphically from the plot on page 41. Then with the use of equation 5-3 and knowledge of the electronic configurations of the ions, the Dq values are calculated. The quantity known as 10 Dq is the energy difference between two sets of orbitals which have become split due to the field imposed on them. The Dq values can be calculated in various manners, the most accurate of which is spectroscopically. However, a correlation between the 10 Dq values obtained spectroscopically and thermodynamically is extremely interesting since the derivations are based on entirely different theorectical models. The less accurate thermodynamic method used here, however, has the added advantage of giving quantitative information concerning the strength of the bonds involved with the metal.

FIGURE 14

TOTAL HETEROLYTIC BOND ENERGY-ATOMIC NUMBER PLOT FOR DIVALENT Mn - Zn ACETYLACETONATES

METAL	$6\Delta H(M-L)$
Mn	929.4 ± 9.30
Fe	968.6 ± 9.40
Co	1001.2 ± 6.80
Ni	1015.1 ± 2.56
Cu	1018.5 ± 6.78
Zn	1014.7 ± 12.24

- - - - - Dotted line indicates no crystal field stabilization

FIGURE 14

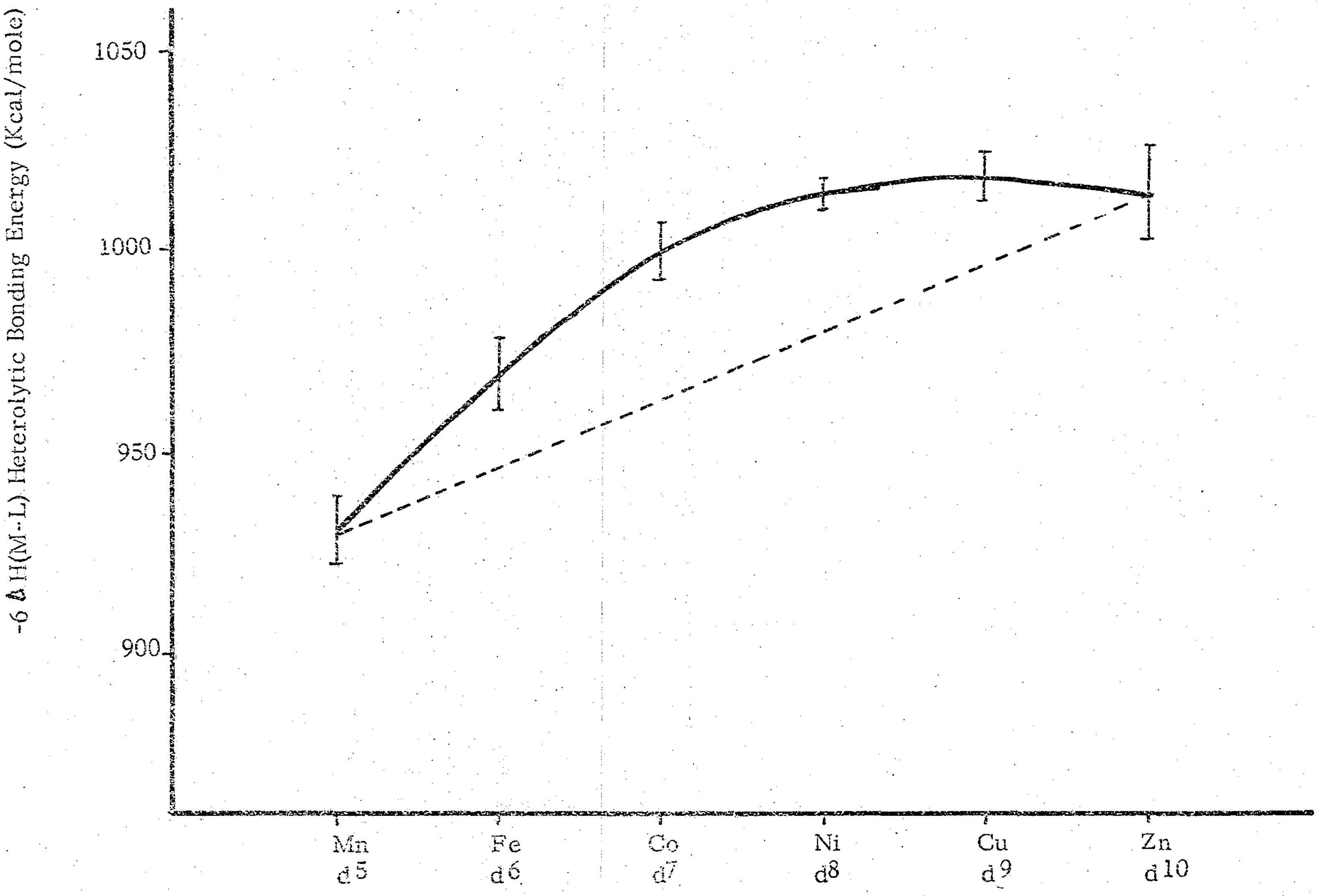

-6 ∆ H(M-L) Heterolytic Bonding Energy (Kcal/mole)
1050
1000
950
900
Mn
d5
Fe
d6
Co
d7
Ni
d8
Cu
d9
Zn
d10

TABLE VII

10 Dq VALUES OBTAINED FROM FIGURE 14

ELECTRONIC CONFIGURATION	COMPLEX	t_{2g}	e_g	$-\Delta H$	Dq (kcal)	10Dq (kcal)	10Dq (cm^{-1})
d^5	Mn^{+2} (highspin)	3	2	0			
d^6	Fe^{+2} (highspin)	4	2	23 = 4Dq	5.75	57.5	20,125
d^7	Co^{+2}	5	2	38.2 = 8Dq	4.78	47.8	16,673
d^8	Ni^{+2}	6	2	35 = 12Dq	2.92	29.2	10,220
d^9	Cu^{+2}	6	3	23 = 6Dq	3.83	38.3	13,400
d^{10}	Zn^{+2}	6	4	0			

Spectroscopic values of 10Dq or c.f.s.e. are obtained by taking the visible absorption spectrum for the compound and correlating the absorption bands with the ground level energy diagrams derived from the symmetry and electronic state of the particular ion. Correlations between energy level diagrams and the absorption spectra are made by observing the Laporte selection rules of spin allowed and spin forbidden electron transitions. Examples of spectroscopically determined c.f.s.e. are explained later in this chapter.

The thermodynamic model of c.f.s.e. assumes that a relation can be made between c.f.s.e. and the total binding energies for a series of compounds This correlation holds, however, only if all other quantities comprising the total binding are constant or vary in a consistent, predictable manner(17, p.75). The factors which must be predictable are the various attraction and repulsion forces between the ligand and the central metal ion and the effective ionic radius of the metal ions. All these factors contribute to the thermodynamic but not to the spectroscopic c.f.s.e. values. For the above reasoning, a slightly curved dotted line is drawn between Mn and Zn in the c.f.s.e. plot on page 41 to emphasize that the relationship may not be linear. Calculations for the $-\Delta H$ values are made, however, assuming only a linear relationship. Accounting for force pairing energy is unnecessary since the d^5, d^6, d^7 ions are in the high spin state.

One advantage in working with the divalent metal series over their trivalent counterparts is that better c.f.s.e. correlations are expected for the divalent series since the "variable" attraction and repulsion forces are somewhat smaller for the divalent series. (Compare Wood's data on trivalent acetylacetonate with this work (40)).

B. SPECTROCSOPIC AND THERMODYNAMIC COMPARISONS OF C.F.S.E.

A comparison between the 10Dq data obtained thermodynamically and spectroscopically for the hydrated divalent ions (Mn^{+2} - Zn^{+2}) and that obtained thermodynamically for divalent acetylacetonates is shown in the table below.

TABLE VIII

10Dq VALUES FOR DIVALENT FIRST ROW TRANSITION COMPOUNDS IN CM^{-1}

		$M(H_2O)_6^{+2}$		$M(AA)_2$
		Spectra 10 Dq	Heat of Hydration 10 Dq	Heat of Chelation 10 Dq
d^5	Mn^{+2}	--	--	--
d^6	Fe^{+2}	10,000	15,000	20,125 [a]
d^7	Co^{+2}	9,300	14,000	16,673
d^8	Ni^{+2}	8,900	10,000	10,220
d^9	Cu^{+2}	12,000	15,000	13,400
d^{10}	Zn^{+2}	--	--	--
		1*	2*	3*

* Source:

1. From the visible absorption spectra (17)
2. Estimated from the lattice energies and heats of hydration (17)
3. Experimentally from this work

a. The absorption shift for $Fe(H_2O)_6^{+2}$ is at 10,000 cm^{-1} whereas the absorption shift for $Fe(AA)_2$ should lie above 20,000 cm^{-1} to give a red compound. Figure 16 indicates that this shift should double the 10Dq value.

As is expected, the thermodynamic data are higher than the spectroscopic values for both types of compounds. Nevertheless, there is fair agreement between the thermodynamic and spectroscopic data.

The d^6 case of Fe^{+2} provides an interesting example for a comparison of the aqueous hydrate with the acetylacetonate. In solution, the ferrous ion has a pale green color due to a weak absorption band in the red at 10,000 cm^{-1} (see Figure 15). The bis-(acetylacetonato)Fe(II) is a dark red compound, indicating that the absorption band has shifted considerably up the visible color spectrum toward the blue. This weak absorption for both high spin aqueous ferrous ion and acetylacetonate ferrous complex is due to the spin allowed transition;

$$^5T_{2g} \longrightarrow {}^5E_g$$

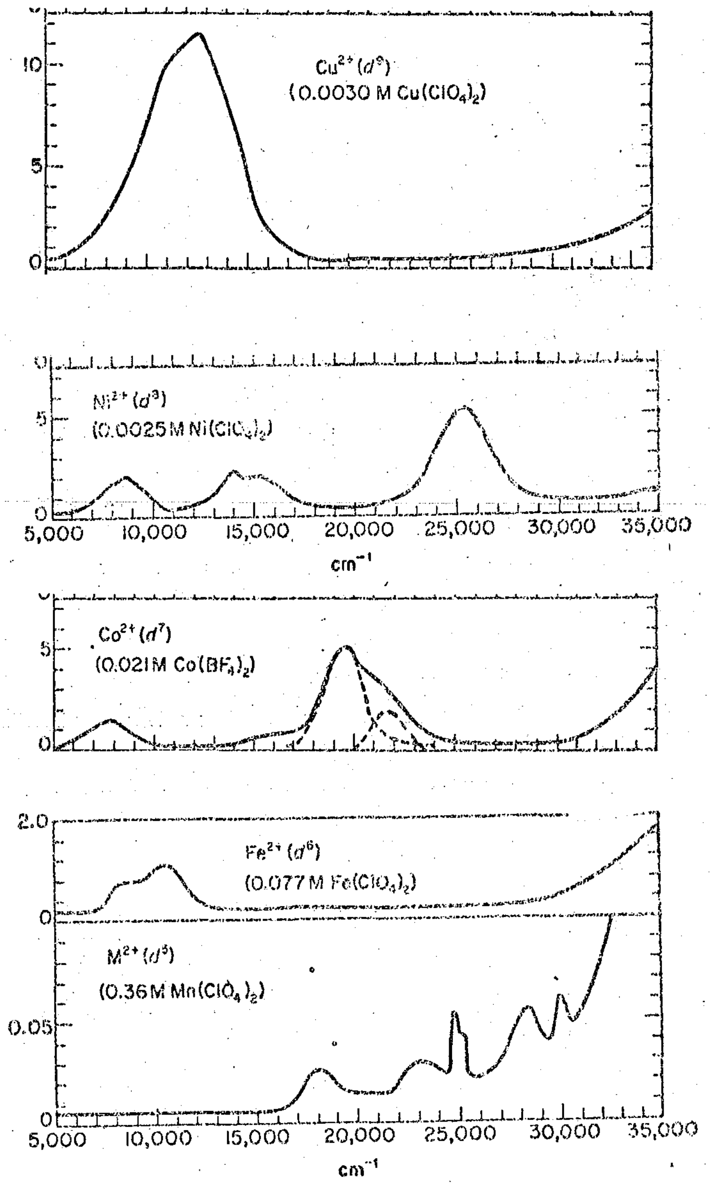
From the energy diagram for d^6 (Figure 16), it is observed that the difference between the energy levels T_{2g} and E_g increase rapidly with slight changes in the 10Dq value. Thus, it is expected that color change from pale green for $Fe(H_2O)_6^{+2}$ to red for acetylacetonate Fe(II) would indicate an increase in the 10Dq value of the crystal field splitting energy. Indeed, this was experimentally observed (10,000 cm^{-1} for $Fe(H_2O)_6^{+2}$ compared to 20,000 cm^{-1} for acetylacetonate Fe(II)).

What has been observed for the ferrous ion is that a replacement of water molecules by other ligands results in a change of the 10Dq c.f.s.e. Obviously, the acetylacetonate oxygen ligand atoms are more closely bound to the metal than are the loosely arranged water molecules. Thus, a greater ligand field is created by the acetylacetonates.

FIGURE 15

THE ABSORPTION SPECTRA OF AQUEOUS SOLUTIONS OF THE FIRST TRANSITION SERIES IONS (from ref. 17, 221-4)

M	$M(H_2O)_6^{+2}$ Color	$M(AA)_2$ Color
Copper	Deep Blue	Deep Blue
Nickel	Light Green	Light Green
Cobalt	Pink	Pink
Iron	Pale Green	Dark Red
Manganese	Pale Pink	Light Tan



The acetylacetonates of Cu^{+2}, Ni^{+2}, and Co^{+2} correspond, however, very closely in color to their respective aqueous ions, showing that the 10 Dq values should be approximately the same. This indicates similar structure and electronic states.

It should be noted that many of the synthesized copper and nickel complexes underwent a color change when the acetylacetonate ligand was replaced by salicylaldehyde, benzoylacetonate or dibenzoylmethanate (see Chapter III). This indicates a greater ligand field strength and different 10 Dq values should be expected for these complexes.

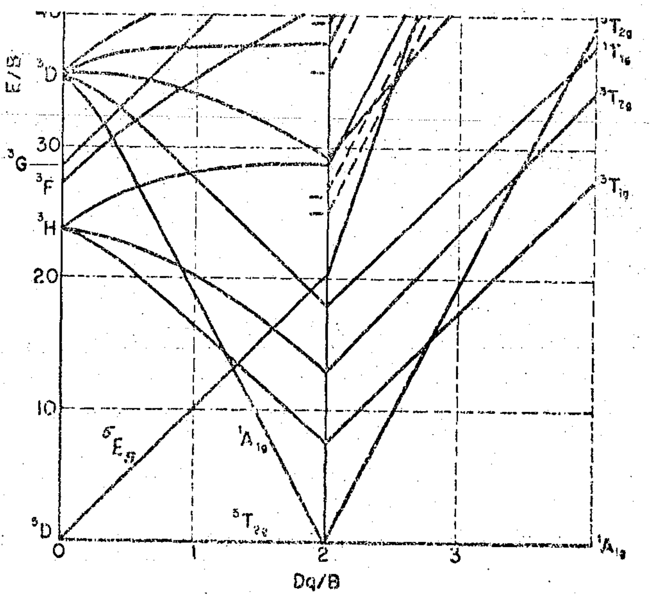


FIGURE 16

THE ENERGY DIAGRAM OF d^6(e.g., Fe^{+2})
(from ref. 17, p.164)

CHAPTER VI

ADDITIONAL DATA ON LIGAND VARIATION AND OTHER ACETYLACETONATES

In addition to the divalent acetylacetonates of the first row transitional metals, the following compounds were investigated.

TABLE IX

HOMOLYTIC BOND ENERGIES FOR ADDITIONAL LIGAND VARIATION COMPOUNDS

COMPOUND	ΔH_C (Kcal/mole)	$\Delta E(M-L_{homo})$ (Kcal/mole)	COORD.#
$Cu(BA)_2$	-2413.0 ± 8.75	48.6 ± 2.2	4
$Ni(BA)_2$	-2234.7 ± 9.17	68.4 ± 1.5	6
$Cu(DBM)_2$	-3487.3	(53.3)	4
$Ni(DBM)_2$	-3390.6	(58.4)	4
$Cu(SA)_2$	-1553.9 ± 16.36	52.1 ± 4.1	4
$Ni(SA)_2$	-1517.1 ± 3.77	47.7 ± 0.9	6
	-1517.1	71.5	4
$Co(SA)_2$	-1464.3 ± 5.39	58.6 ± 1.3	6
	-1464.3	87.0	4
$Be(AA)_2$	-1265.9	(75.5)	4
$Zr(AA)_4$	-1856.3 ± 8.24		8
$Pd(AA)_2$	-1226.0 ± 8.9	58.6 ± 2.2	4
$Ce(AA)_3$	-1720.4		6
$Pt(AA)_2$	-1233.2 ± 19.0	59.0 ± 4.6	4
$Tl(AA)_1$	-607.3	(80.2)	2

It was originally thought that systematic ligand variation would show definite trends in M-L bond energy. Thus, it was assumed that electron withdrawing groups on the ligand would weaken the M-L bond energy and electron donating groups would strengthen the bond.

One basis for such a correlation is the Hammett equation which has been used to show variation in the stability constants and presumably in the M-L bond strength (due to electron donating and withdrawing groups)(16).

The sample of compound investigated here was small, but no coherent variations were found in this work by replacing the ligand methyl groups with phenyl groups (see Fig. 17). Other thermochemical bond energy investigations of ligand variations with Fe^{+2} (14) and Ni^{+2} (39) have found no correlation between either resonance or electron donating ability of the ligand and M-L bond energy.

If the above assumption is true and no correlation exists, then one might conclude that electron withdrawing and donating groups affect the reaction kinetics and not the reaction thermodynamics. That is to say that electronic and resonance variation affect the stability constants but not the bond energy.

It is of interest to note that in Fig. 17 the plot of the symmetrical ligand groups of the acetylacetonates and the dibenzoylmethanate complexes shows approximately parallel positive slopes. The asymmetrical ligand groups of the benzoylacetonate and the salicylaldehyate complexes, on the other hand, have approximately parallel negative slopes. This leads one to speculate that symmetry may play an important rôle in relating the coordinate bond energy to the ligand environment.

The alternate possibility to explain Figure 17 is that the experimental errors for the data obtained and the lack of accurate heat of vaporization data for the complexes do not allow any speculation concerning the nature of the ligand and its effect on the heterolytic energy.

Further investigation into this area is suggested as a future project.

TABLE X

TOTAL HETEROLYTIC BONDING ENERGY FOR ADDITIONAL LIGAND VARIATION COMPOUNDS

(all units Kcal/mole)

COORD.#	COMPOUND	M-O	$-6\Delta E(M\text{-}O)$	ΣI_2	2(5/2RT)	$-E_L$	$6\Delta H(M\text{-}O_{hetero})$
4	$Cu(BA)_2$	48.6	-291.6	646.0	2.96	-15.69	-924.9 ± 8.75
6	$Ni(BA)_2$	68.4	-410.4	594.6	2.96	-15.69	-992.3 ± 9.17
4	$Cu(DBM)_2$	53.5	-321.0	646.0	2.96	-15.69	(-954.3)
4	$Ni(DBM)_2$	58.4	-350.5	594.6	2.96	-15.69	(-932.4)
4	$Cu(SA)_2$	52.1	-312.8	646.0	2.96	-15.69	-946.1 ± 16.36
4	$Ni(SA)_2$	71.5	-429.0	594.6	2.96	-15.69	-1010.9 ± 3.77
4	$Co(SA)_2$	87.0	-527.4	574.2	2.96	-15.69	-988.9 ± 5.39
6	$Ni(SA)_2$	47.7	-286.2	594.6	2.96	-15.69	-868.2 ± 3.77
6	$Co(SA)_2$	58.6	-351.6	574.2	2.96	-15.69	-913.1 ± 5.39

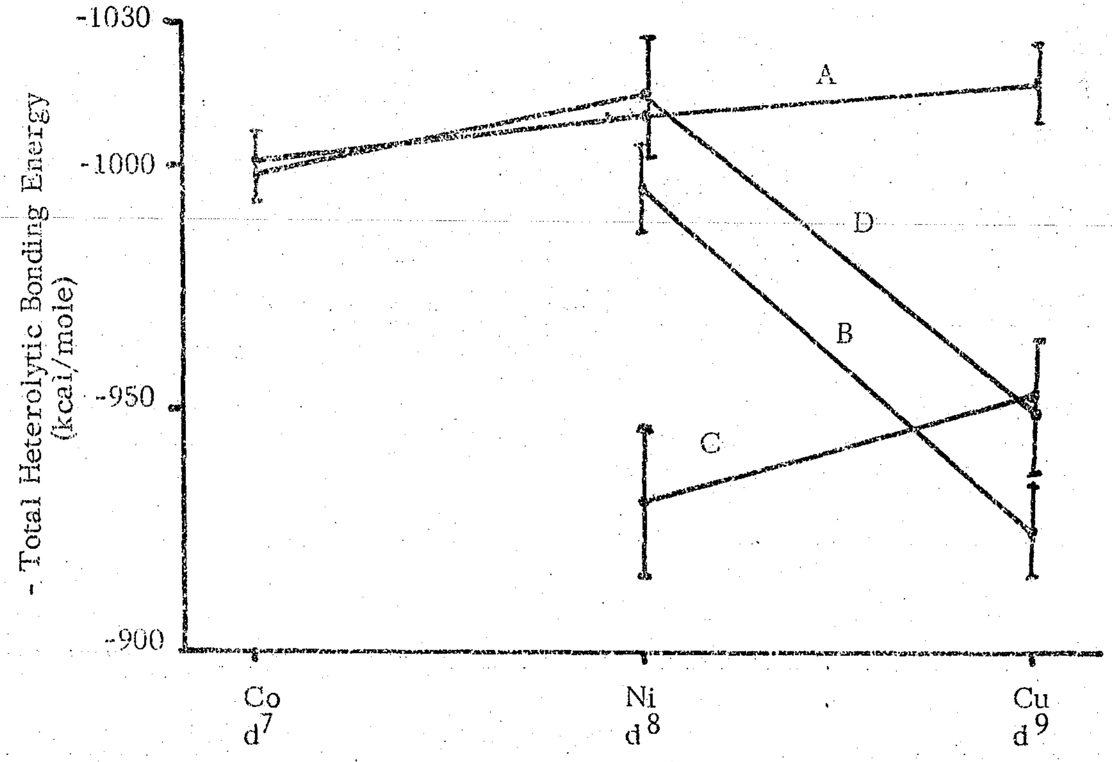
TABLE XI

TOTAL HETEROLYTIC BONDING ENERGY FOR FOUR LIGANDS (kcal/mole)

METAL	$(AA)_2$	$(BA)_2$	$(DBM)_2$	$(SA)_2$
Cu	-1018.5 ± 7	-924.9 ± 9	-954.3 ± 15	-946.1 ± 16
Ni	-1015.1 ± 3	-992.3 ± 9	-932.4 ± 15	-1010.9 ± 4
Co	-1001.2 ± 7			-988.9 ± 5

FIGURE 17

TOTAL HETEROLYTIC BONDING VS ATOMIC NUMBER FOR FOUR LIGANDS



A. acetylacetonate $(AA)_2$
B. benzoylacetonate $(BA)_2$
C. dibenzoylmethanate $(DBM)_2$
D. salicylaldehyde $(SA)_2$

CHAPTER VII

CONCLUSIONS

In this investigation it is shown that the combustion data for chelated metal complexes can offer a great deal of insight into the nature of these compounds. Not only can the M-L bond energy be calculated from the heat of chelation derived from the thermochemical cycle, but correlations can be made to show variations predicted by crystal field theory. In particular, the humped curve graph of the total heterolytic bond energy versus atomic number gives a good indication of 10 Dq values and provides a link between crystal field theory, spectroscopic data, and the bond energies for these particular compounds. This investigation of the divalent metal acetylacetonates has resulted in much better 10Dq c.f.s.e. correlation than previously obtained with the trivalent metal acetylacetonates (40).

TRENDS.

According to the molecular orbital theory, as the anti-bonding "eg" orbitals become filled, the metal to oxygen bond should weaken. Since all compounds were high spin, the "eg" orbitals of Mn^{+2}, Fe^{+2}, Co^{+2}, and Ni^{+2} all contained two electrons. But for Cu^{+2} and Zn^{+2} the anti-bonding orbitals contain three and four electrons respectively, and the data indicates a slightly lower M-L bond for these cases.

The bonds of Fe-O, Co-O and Ni-O were found to have the highest energy for the acetylacetonates complexes. These compounds are polymers and it stands to reason that there might be some attraction between the metals to form weak metal to metal bonds. However, since the metal orbitals are not directly alined, a more important contribution might be the energy gained by increased resonance stabilization of the polymeric species over the monomeric compounds.

LIMITATIONS OF THE CALORIMETRIC METHOD

The method of bomb calorimetry does have limitations and disadvantages. The bond energies are swamped by the large energy value of the total heat of combustion for the complex. To do accurate determinations, the combustion production products must be determined precisely. The accuracy is also affected by side reactions such as the formation of carbon monoxide, carbon and other products of incomplete combustion.

Since the over all error produced in the experiment is the sum of the individual errors, an effort must be made not only to reduce the number of sources of error but also the degree of error from each source. One is severely limited in the degree of accuracy when using mercury thermometers. The temperature rise must be measured with the accuracy of 0.0003°C. if the error due to the temperature measurement is to be kept at a minimum of not more than 0.01 percent. In order to obtain measurements of this precision a 25 ohm platinum resistance thermometer must be used (31). With the use of a mercury thermometer, the over all experimental error averaged between 1/2 of 1% to 1% in this work. This is not bad considering that the NBS measurements on Fossil fuel heats of combustion with the best of equipment is accurate to within only a few tenths of 1%. The greatest accuracy obtainable with this method on pure substances is 0.01% to 0.02% according to the National Bureau of Standards.

OTHER METHODS

Other methods of determining the bond energies should be investigated which could lead to smaller errors and greater accuracy. An approach which might be investigated is the use of an electrical cell to measure the heat of reaction. A modified Gibbs-Helmohotz equation suitable for enthalpy measurement has been established as follows (42):

$$H = -23{,}070 \text{ cal/volt } j \left[\mathcal{E} - T\left(\frac{\partial \mathcal{E}}{\partial T}\right)_p \right]$$

where:
H = heat of reaction (cal)
j = valence
$\mathcal{E}$ = e.m.f. (volts)
T = temperature (^{o}K.)

This equation is valid only for the case of a saturated reversible cell in which gases are liberated. The cell reaction pertinent to this study would be:

$$M^{+2} + 2\,C_5H_8O_2^{-} = M(C_5H_7O_2)_2\,(s) + H_2(g)$$

The only measurements necessary are the e.m.f. of the cell and the temperature. Since both can be accurately measured, the per cent of error should be greatly reduced.

With the use of a suitable thermochemical cycle the coordinate bond energy could be expressed for the gaseous phase reaction, thus avoiding the problem of the heat of hydration side reactions.

The possibilities of future investigations in this field are abundant. An investigation of the 2nd and 3rd row transitional metals could be undertaken to show the c.f.s.e. for the 4d and 5d orbitals. The acetylacetonates of the Lanthanide series could be investigated to show the c.f.s.e. for the 4f orbitals. Ligand variations could be altered to investigate the metal chelation bonding with elements other than oxygen. Nitrogen metal bonds of amino acids and the porphyrin groups of haemin and chlorophyll come to mind as interesting studies to be made.

SUMMARY

The heats of combustion of some twenty chelated complexes have been determined by static bomb calorimetry in order to calculate the average bond energy of the metal-ligand bond. The data from the heats of combustion were used in a suitable Born-Haber thermochemical cycle to determine either the heterolytic or homolytic cleavage energy for the metal to ligand bond. In the case of all twenty chelated complexes investigated, the central metal was chelated with coordinate bonds to either 2, 4, 6, or 8 oxygen atoms.

The six divalent first row transitional metal acetylacetonates investigated (Mn-Zn) were found to have $(M-L)_{homolytic}$ coordinate bond energies between 66 and 75 kcal/mole. The bond energy of the series was adjusted to an equivalent heterolytic bond cleavage energy. A plot of the $6\,\Delta E(M-L)_{heterolytic}$ versus atomic number showed the expected humped curve for $d^5 - d^{10}$ transsitional metals as predicted by crystal field theory.

From the plot, a graphic determination of the 10 Dq was taken which compared favorably with the more accurate spectroscopic 10 Dq values. A comparison between the color of the compounds and that expected from ground state energy diagrams for the various 10 Dq values was explained.

Compounds consisting of various ligands similar to acetylacetate were investigated to determine substituent effects. The Copper and Nickel complexes were synthesized with benzoylacetone, dibenzoylmethane, and salicylaldehyde.

It was shown that while the Ni^{+2} acetylacetonate and benzoylacetonate complexes polymerize to form a 6 coordinate complex, the dibenzoylmethanate is most probably only a 4 coordinate monomeric structure. This is due to steric repulsion of the two bulky phenyl groups.

It was expected that a pattern of decreasing bond energy could be found by the systematic replacement of first one and then the other methyl groups of the acetylacetonate type complexes (i.e., the benzoyl and dibenzoyl). No clear pattern emerged, except that in general the $(M-L)_{homo}$ bond energies were lower for R = phenyl than for R = methyl.

The salicylaldehyde complexes were studied as an example of a six ring chelated system which does not exhibit conjugate resonance stabilization as found in acetylacetonate type complexes. Again, no discernable pattern emerged indicating a substituent effect. The data did reveal, however, that the symmetry of the complexes might have an effect on the coordinate bond energies.

The third type of compounds investigated consisted of other acetylacetonate metal complexes not found in the first transitional row. In general, these acetylacetonate complexes of Pd^{+2}, Pt^{+2}, Al^{+3}, Be^{+2}, Ce^{+3}, Tl^{+1}, and Zr^{+4} were merely an assortment of available complexes not previously investigated.

The Pd^{+2} and Pt^{+2} acetylacetonates are analogous to the Ni^{+2} acetylacetonates except for their square planar structure and indicate a generally lower (M-L) bond energy for the 4d and 5d transitional metals over the 3d counterparts.

The other acetylacetonate complexes, beside showing examples of interesting stereochemistry, provide the frame work for future investigation, thus giving a more complete quantitative understanding of metal-ligand chelated bond energy beyond the first transitional row.

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APPENDIX

TABLE XII

THERMOMETER TEST CERTIFICATE

The Parr Instrument Company certifies that this thermometer has been tested for use in differential temperature measurements, as in calorimetry. The test was made by comparison with a platinum resistance thermometer certified by the National Bureau of Standards. The thermometer was held upright in a large, covered, circulating water bath with the bulb and scale completely immersed. All readings were taken with the aid of a magnifier and were estimated to one-tenth of the smallest scale division. In normal use a large portion of the stem will not be immersed and its temperature may differ slightly from the bulb temperature. This will introduce no significant error if the difference between stem and bulb temperatures is less than 1/6th of the range of the thermometer. If the temperature difference is larger, an emergent stem correction should be applied.

Positive (+) corrections in the adjoining table should be added to the observed readings. Negative (−) corrections should be subtracted. The corrections at temperatures between the test points can be determined by interpolation, or by plotting these values and drawing a correction curve.

Mercury-in-glass thermometers change slightly with age. Any significant physical change is usually confined to the bulb. This affects the scale equally throughout, therefore the thermometer will remain accurate for differential measurements. However, continued accuracy for true temperatures cannot be guaranteed.

Instructions for the proper care and handling of calorimetric thermometers are given on the reverse side of this certificate.

Catalog No. 1603

Serial No. 7D8687

TEST DATA

Reading of Thermometer	Correction to Reading
19.500°C.	-0.006°C.
21.000	- .000
22.500	- .002
24.000	- .012
25.500	- .016
27.000	- .016
28.500	- ,016
30.000	- .020
31.500	- .022
33.000	- .018
34.500	- .018

Test Date 3-28-69

Signed for PARR INSTRUMENT CO.

By ....

PARR INSTRUMENT CO. 211 - 53rd ST. MOLINE, ILL., U. S. A.

FIGURE 18

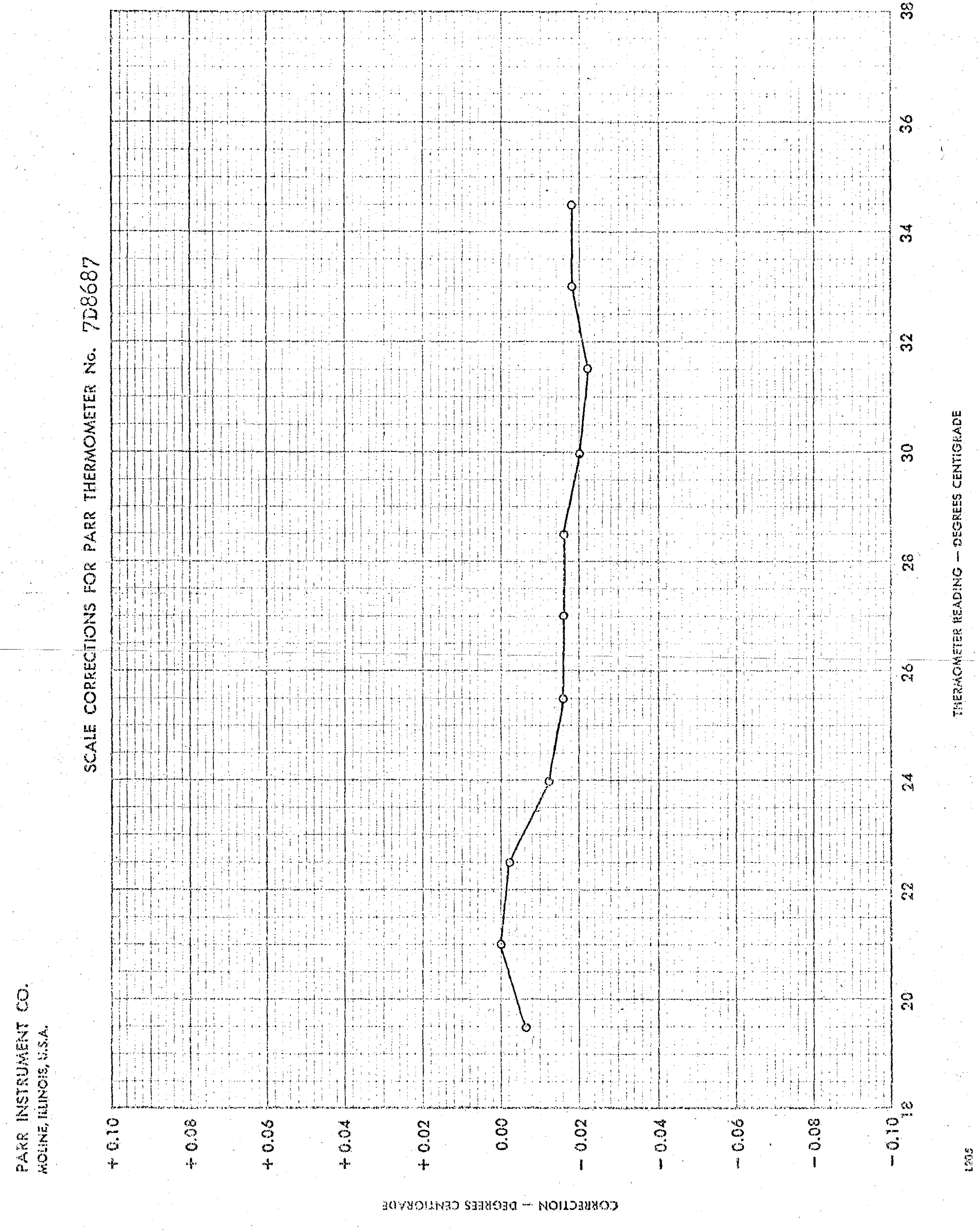
SCALE CORRECTIONS FOR PARR THERMOMETER No. 7D8687
PARR INSTRUMENT CO.
MOLINE, ILLINOIS, U.S.A.
CORRECTION — DEGREES CENTIGRADE
+ 0.10
+ 0.08
+ 0.06
+ 0.04
+ 0.02
0.00
— 0.02
— 0.04
— 0.06
— 0.08
— 0.10
THERMOMETER READING — DEGREES CENTIGRADE
18
20
22
24
26
28
30
32
34
36
38
1205

TABLE XIII

RESULTS OF CALIBRATION EXPERIMENTS USING STANDARD BENZOIC ACID
(First Standardization)

SAMPLE WEIGHT	$\Delta T^{o}C$	ΔE(cal/^{o}C)	d	d^2
1.0090	2.653	-2402.9	-5.5	30.25
1.0083	2.648	-2405.8	-2.6	6.76
0.9932	2.604	-2409.8	+1.4	1.96
1.0490	2.734	-2424.1	+15.7	246.49
0.9945	2.610	-2407.4	-1.0	1.00
1.0189	2.678	-2403.8	-4.6	21.16
1.0366	2.737	-2392.9	-15.5	240.25
1.0091	2.648	-2407.7	-0.7	.49
1.0070	2.640	-2409.9	+1.5	2.25
1.0173	2.660	-2416.3	+7.9	62.41
1.0044	2.629	-2413.7	+5.3	28.09
1.0063	2.642	-2406.4	-2.0	4.0

$$\Delta \bar{E} = -2408.4 \pm 7.3$$

TABLE XIV

RESULTS OF CALIBRATION EXPERIMENTS USING STANDARD BENZOIC ACID (Second Standardization)

SAMPLE WEIGHT	ΔT_{oC}	$\Delta E(cal/o_C)$	d	d_2
0.9400	+2.2229	-2664.4	-6.1	37.21
0.9837	+2.331	-2666.2	-4.3	18.49
0.9747	+2.306	-2670.2	0.0	0.0
0.9700	+2.292	-2673.8	+3.3	10.89
1.1146	+2.629	-2678.6	+8.1	65.61
1.3436	+3.177	-		
0.9875	+2.337	-2669.7	0.8	0.64

$$\Delta \bar{E} = -2670.5 \pm 4.7$$

TABLE XV

HEAT OF COMBUSTION OF BIS(ACETYLACETONATO)Mn(II)

SAMPLE WEIGHT (g)	$\Delta T_{^oC}$	THERMOMETER CORRECTION	FUSE CORRECTION	ΔE (cal/g)
1.4872	3.087	-.006	0.00	- 4999.1
1.3016	2.693	-.002	0.00	- 4983.0
1.2818 *	2.418	-.014	0.00	- 5037.7
1.2927 *	2.415	-.012	0.00	- 4988.9

$$\Delta \tilde{E} = -5002.1 \pm 24.59$$

* Second Calibration experiments

TABLE XVI

HEAT OF COMBUSTION OF BIS(ACETYLACETONATO)IRON(II)

SAMPLE WEIGHT (g)	$\Delta T_{^oC}$	THERMOMETER CORRECTION	FUSE CORRECTION	Δ E (cal/g)
1.1086	1.938	-.003	-.000	-4210.2
1.5787	2.796	-.000	-.000	-4265.5
1.4431 *	2.310	-.012	-5.00	-4269.7
1.3348*	2.149	-0.12	-.000	-4299.4

$$\Delta \bar{E} = -4261.2 \pm 37.1$$

* Second calibration experiments

TABLE XVII

HEAT OF COMBUSTION OF BIS(ACETYLACETONATO)COBALT(II)

SAMPLE WEIGHT (g)	ΔT^{o}_{C}	THERMOMETER CORRECTION	FUSE CORRECTION	Δ E (cal/g)
1.4875	2.568	-.000	-.000	- 4157.8
1.5238	2.662	-.013	0.000	- 4182.6
1.4107 *	2.230	-.006	0.000	- 4221.5
1.4985 *	2.354	-.004	0.000	- 4195.1

$$\Delta \bar{E} = -4189.2 \pm 26.5$$

* Second calibration experiments

TABLE XVIII

HEAT OF COMBUSTION OF BIS(ACETYLACETONATO)NICKEL (II)

SAMPLE WEIGHT (g)	$\Delta T_{^oC}$	THERMOMETER CORRECTION	FUSE CORRECTION	ΔE (cal/g)
1.3542	2.340	0.00	0.00	-4167.6
1.5718	2.729	0.00	0.00	-4181.5
1.4409 *	2.250	0.00	0.00	-4170.0

$$\Delta \bar{\bar{E}} = -4171.0 \pm 9.99$$

* Second calibration experiments

TABLE XIX

HEAT OF COMBUSTION OF BIS(ACETYLACETONATO)COPPER(II)

SAMPLE WEIGHT	$\Delta T_{^oC}$	THERMOMETER CORRECTION	FUSE CORRECTION	ΔE (cal/g)
1.3305 *	2.289	-.006	0.00	- 4594.3
1.3191 *	2.286	-.014	0.00	- 4627.9
1.3888 *	2.402	-.006	0.00	- 4618.7

$$\Delta \bar{E} = -4613.6 \pm 17.3$$

* Second calibration experiments

TABLE XX

HEAT OF COMBUSTION OF BIS(ACETYLACETONATO)ZINC(II)

SAMPLE WEIGHT (g)	$\Delta T_{^oC}$	THERMOMETER CORRECTION	FUSE CORRECTION	ΔE (cal/g)
1.5288	2.682	-.002	0.00	-4225.0
1.4423 *	2.318	-.012	0.00	-4291.9
1.4201 *	2.240	-.012	0.00	-4212.3
1.1929 *	1.916	-.003	0.00	-4289.3
1.3913 *	2.218	0.000	0.00	-4257.3

$$\Delta \bar{E} = -4255.1 \pm 36.2$$

* Second Calibration experiments

TABLE XXI

HEAT OF COMBUSTION OF BIS(ACETYLACETONATO)Pd(II)

SAMPLE WEIGHT (g)	$\Delta T_{°C}$	BENZOIC ACID WEIGHT	THERMOMETER CORRECTION	ΔE (cal/g)
0.5235	2.268	0.5326	-.012	- 4040.9
0.4601	2.576	0.6819	-.012	- 4042.3
0.4921	2.429	0.6691	0.000	- 4000.8

$$\Delta \bar{E} = -4028.0 \pm 23.5$$

TABLE XXII

HEAT OF COMBUSTION OF BIS(ACETYLACETONATO)Pt(II)

SAMPLE WEIGHT(g)	BENZOIC ACID WEIGHT	ΔT (°C)	THERMOMETER CORRECTION	ΔE (cal/g)
0.4766	0.6527	2.350	-.012	-3163.3
0.5186	0.6716	2.436	-.010	-3077.7
0.4841	0.6847	2.388	-.004	-3165.8

$$\Delta \bar{E} = -3133.4 \pm 48.5$$

TABLE XXIII

HEAT OF COMBUSTION OF TETRA-(ACETYLACETONATO) ZIRCONIUM (IV)

SAMPLE WEIGHT (g)	$\Delta T_{^oC}$	THERMOMETER CORRECTION	ΔE (cal/g)
1.6273	2.571	-.010	-3805.07
1.6935	2.669	-.006	-3795.70
1.3804	1.979	-.008	-3828.5

$$\Delta \overline{E} = -3806 \pm 16.9$$

TABLE XXIV

HEAT OF COMBUSTION OF BIS(SALICYLALDEHYDATO)COBALT(II)

SAMPLE WEIGHT (g)	ΔT_{oC}	ΔE (cal/g)
1.1144	2.029	-4863.2
1.0732	1.945	-4841.2
1.1674	2.135	-4884.7
1.2100	2.201	-4858.5

$$\Delta \overline{\overline{E}} = -4861.9 \pm 17.9$$

TABLE XXV

HEAT OF COMBUSTION OF BIS(SALICYLALDEHYDATO)COPPER(II)

SAMPLE WEIGHT (g)	$\Delta T_{^oC}$	ΔE (cal/g)
1.0867	2.039	-5010.7
1.0421	1.983	-5082.4
1.0678	2.036	-5093.6
1.0321	1.986	-5140.1

$$\Delta \bar{E} = -5081.7 \pm 53.52$$

TABLE XXVI

HEAT OF COMBUSTION OF BIS(SALICYLALDEHYDATO)NICKEL(II)

SAMPLE WEIGHT (g)	$\Delta T\ ^{o}C$	ΔE (cal/g)
1.0025	1.845	-4916.2
1.0476	1.918	-4891.1
1.0532	1.933	-4902.6

$$\Delta\bar{E} = -4903.3 \pm 12.56$$

TABLE XXVII

HEAT OF COMBUSTION OF BIS(BENZOYLACETONATO)NICKEL(II)

SAMPLE WEIGHT (g)	$\Delta T_{^{o}C}$	ΔE (cal/g)
1.0765	2.351	-5832.6
1.0210	2.242	-5864.7
1.1020	2.426	-5879.7

$$\Delta \bar{E} = -5859.0 + 24.06$$

TABLE XXVIII

HEAT OF COMBUSTION OF BIS(BENZOYLACETONATO)COPPER(II)

SAMPLE WEIGHT (g)	ΔT_{oC}	ΔE (cal/g)
1.3214	3.089	-6243.1
1.0241	2.396	-6250.4
1.0476	2.464	-6282.3
1.0432	2.433	-6228.6

$$\Delta \bar{E} = -6251.1 \pm 22.68$$

TABLE XXIX

HEAT OF COMBUSTION OF BIS(ACETYLACETONATO)BERYLLIUM(II)

SAMPLE WEIGHT (g)	$\Delta T_{°C.}$	TEMPERATURE CORRECTION	ΔE (cal/g)
1.2301	2.814	-.016	-6109.0

$\Delta \bar{E} = -6109.0$

TABLE XXX

HEAT OF COMBUSTION OF BIS(DIBENZOYLMETHATO)NICKEL(II)

SAMPLE WEIGHT (g)	$\Delta T_{°C.}$	TEMPERATURE CORRECTION	ΔE (cal/g)
1.0871	2.732	-.012	-6711.2

$\Delta \bar{E} = -6711.2$

TABLE XXXI

HEAT OF COMBUSTION OF BIS(DIBENZOYLMETHATO)COPPER(II)

SAMPLE WEIGHT	$\Delta T_{°C.}$	TEMPERATURE CORRECTION	ΔE (cal/g)
0.8957	2.297	-.002	-6837.4

$\Delta \bar{E} = -6837.4$

TABLE XXXII

HEAT OF COMBUSTION OF (ACETYLACETONATO)THALLIUM(I)

SAMPLE WEIGHT	ΔT_{oC}	TEMPERATURE CORRECTION	ΔE (cal/g)
1.7894	1.341	0.00	-2001.3

$$\Delta \bar{E} = -2001.3$$

TABLE XXXIII

HEAT OF COMBUSTION OF TRIS(ACETYLACETONATO)CEROUS (III)

SAMPLE WEIGHT	ΔT_{oC}	TEMPERATURE CORRECTION	ΔE (cal/g)
1.6759	2.736	0.000	-3931.8
0.9734	1.434	0.006	-3934.1

$$\Delta \bar{E} = -3932.9 \pm 1.6$$