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Final Report

on

Infrared Spectra of Metal Chelate Compounds

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I. The Problem Studied

The purpose of this research project was to investigate the infrared spectra of metal chelate compounds based on theoretical normal coordinate analyses and to make complete band assignments, especially in the lower frequency region, where the metal-ligand vibrations occur. During the period from Jan. 1, 1960 to Aug. 31, 1961, the following studies have been completed:

- (1) Perturbation calculations on acetylacetonato complexes of trivalent metals.
- (2) Perturbation calculations on acetylacetonato complexes of divalent metals.
- (3) Perturbation calculations on addition compounds of metal acetylacetonates.
- (4) Perturbation calculations on metal complexes of substituted acetylacetonates.
- (5) A normal coordinate analysis on 1:1 oxalato complexes.
- (6) Normal coordinate analyses on 1:2 and 1:3 oxalato complexes.
- (7) Normal coordinate analyses on Co(III) carbonato complexes.
- (8) Normal coordinate analyses on 1:1 and 1:3 α -diimine Fe(II) complexes.

All of the work listed above has been either published or accepted for publications as indicated in Sec. IV of this report.

II. The Work performed

(a) Preparation of Compounds and Spectral Measurements.- More than seventy metal chelate compounds have been prepared and their infrared spectra obtained by the use of a Perkin-Elmer Model 21 infrared spectrophotometer equipped with NaCl, KBr and CsBr optics.

(b) Normal Coordinate Analyses. - Normal coordinate analyses have been made on chelate rings of acetylacetonato, oxalato, carbonato and α -diimine complexes of various metals. For oxalato and α -diimine complexes, calculations have been made for 1:1 as well as 1:2 and 1:3 metal-ligand complex models to determine the order of magnitude of vibrational coupling between ligands. Most of the calculations have been made using IBM 704 and 709 electronic computers at the M.I.T. computation center, Cambridge, Massachusetts.

III. The Results Obtained

The results obtained are summarized as follows: (1) Based on the results of normal coordinate analyses, most of the infrared bands observed in a wide range of frequencies have been assigned theoretically. Erroneous band assignments made by previous investigators have been corrected.

(2) Force constants obtained by normal coordinate analyses have proved to be valuable in elucidating the electronic structure of chelate rings in metal chelate compounds. In particular, the metal-ligand stretching force constants which were obtained for the first time by this investigation, have provided valuable information on the stabilities of the metal chelate compounds studied.

More specific information is provided by the following abstracts of individual papers.

(1) Acetylacetonates of Trivalent Metals. - With the application of perturbation theory to a previously worked out normal coordinate analysis of the Cu(II) complex, the vibrational frequencies have been calculated for the acetylacetonato complexes of Co(III), Cr(III), Fe(III) and Al(III).

From the calculated force constants, it has been concluded that the metal-oxygen bonds in the Co(III) and Cr(III) complexes are fairly strong and those of the Fe(III) complexes are somewhat weaker. The band at 490 cm^{-1} in the Al(III) complex has been assigned to the Al-O stretching mode, based on a study of four Al(III) complexes of β -diketones. A relatively large force constant of the Al-O stretching mode in these complexes suggests that the bond is strongly covalent.

(2) Acetylacetonates of Divalent Metals.- The vibrational frequencies of acetylacetonates of Pd(II), Cu(II), Ni(II), Co(II), Zn(II) and Be(II) have been calculated using the perturbation method. The calculated frequencies and assignments have been used to (1) elucidate the complex spectra in the $1600 \sim 1400\text{ cm}^{-1}$ region; (2) correlate the electronic structures of strong and weak chelates with the calculated force constants and (3) show the relationship between the force constant and thermodynamic data based on formation constants from solution equilibria. Also, three chelate compounds of beryllium have been studied to locate the characteristic infrared absorption bands of the Be-O bonds.

(3) Addition Compounds of Metallic Acetylacetonates.- Vibrational force constants have been calculated for bis-(acetylacetonato)-Ni (II) and bis-(acetylacetonato)-oxovanadium (IV) with pyridine and bis-(acetylacetonato)-dioxouranium (VI) with pyridine and water, using the perturbation method. The effect of the coordinated adduct on the strength of the metal-oxygen bond has been discussed quantitatively in terms of the change of the metal-oxygen stretching force constants in these compounds. Remarkable changes of the frequencies and in the force constants, occurring in the formation of the addition compounds, suggest that the bonds are formed directly between the central metal ion and the oxygen or nitrogen of the added ligand.

(4) Effect of Substituents on the Infrared Spectra of Metal

Acetylacetonates. - Vibrational frequencies of metal chelate compounds of hexafluoro- and trifluoroacetylacetone, benzoylacetone and bibenzoylmethane with Cu(II) and Ni(II) have been calculated using the perturbation method. The calculated force constants provide a quantitative measure of the electronic effect of the trifluoromethyl and phenyl groups on the chelate rings.

(5) A Normal Coordinate Treatment of 1:1 Oxalato Complexes. - A normal

coordinate treatment has been made on the 1:1 (metal:ligand) model of the Cr(III) oxalato complexes. Based on this results, the metal-oxygen stretching bands of oxalato complexes of other metals have been found in the range between 600 and 300 cm^{-1} . The force constants and the band assignments obtained have been compared with those of the previous normal coordinate analysis based on the free oxalato ion. Relationships between the metal-oxygen and the carbon-oxygen stretching frequencies have been discussed.

(6) Normal Coordinate Treatment of 1:2 and 1:3 Oxalato Complexes. -

Normal coordinate treatments have been made on the square planar 1:2 oxalato complexes of Pt(II) and the octahedral 1:3 oxalato complex of Cr(III), and the results compared with those obtained with simple 1:1 complexes. It has been found that coupling between the ligands in the square planar 1:2 complex is small whereas coupling between the ligands in the octahedral 1:3 complex is appreciable. Observed differences of the spectra between 1:1 and 1:2 oxalato complexes of Pt(II) and between 1:1 and 1:3 oxalato complexes of Cr(III) and Co(III) are in good agreement with the results of these calculations.

(7) Infrared Spectra of Co(III) Carbonato Complexes.- Normal coordinate treatments have been made for the unidentate and bidentate Co(III) carbonato complexes. The theoretical band assignments and force constants obtained confirm the validity of the previous qualitative conclusions based on the differences of symmetry and the frequency shifts of the unidentate and bidentate complexes. The Co(III)-O stretching bands have been found at $440 \sim 380$ and $400 \sim 350 \text{ cm}^{-1}$ for the bidentate complexes, and at $360 \sim 340^{-1}$ for the unidentate complexes.

(8) Normal Coordinate Treatment of 1:1 and 1:3 α -Diimine Fe(II) Complexes. Normal coordinate treatment has been made on 1:1 and 1:3 α -diimine complexes of Fe(II). It has been found that the Fe-N stretching force constant is unusually high and the C=N stretching force constant is unusually low in these complexes. This result indicates the presence of strong resonance in the metal chelate ring of these α -diimine complexes. It has also been found that the 1:1 model approximation can not be applicable to strong chelates like Fe(II) α -diimine complexes because of strong vibrational coupling between ligands.

V. Reports and Publications

(a) Reports

The following status reports have been submitted under contract,
DA-19-020-ORD-5119

<u>Title of Report</u>	<u>Period Covered</u>
Quarterly Status Report No. 1	
I. A Normal Coordinate Treatment of the 1:3 Complex of N,N'-Dimethylethylenediimine	Jan. 1, 1960 - March 31, 1960
II. Infrared Spectra of Acetylacetonates of Trivalent Metals	
Quarterly Status Report No. 2	
I. Metal Chelates of N,N'-dimethylethylenediimines	April 1, 1960 - June 30, 1960
II. Infrared Spectra of Acetylacetonates of Divalent Metals	
Quarterly Status Report No. 3	
I. A Normal Coordinate Treatment of the 1:1 Complex of the Metallic Dithiooxalates	July 1, 1960 - September 30, 1960
II. Infrared Spectra of Addition Compounds of Metallic Acetylacetonates	
Quarterly Status Report No. 4	
I. A Normal Coordinate Treatment of the 1:3 Complex of the Metallic Dithiooxalates	October 1, 1960 - January 4, 1961
II. A Normal Coordinate Treatment of Metallic Oxalato Complexes	

(b) Publications

The following research papers have been published and/or accepted for publications under the contract, DA-19-020-ORD and the grant, DA-ORD-31-124-61-G61.

1. "Infrared Spectra of Metal Chelate Compounds. II. Infrared Spectra of Acetylacetonates of Trivalent Metals." K. Nakamoto, P. J. McCarthy, A. Ruby and A. E. Martell, J. Am. Chem. Soc. 83, 1066 (1961).
2. "Infrared Spectra of Metal Chelate Compounds. III. Infrared Spectra of Acetylacetonates of Divalent Metals." K. Nakamoto, P. J. McCarthy, and A. E. Martell, J. Am. Chem. Soc. 83, 1272 (1961).

3. "Infrared Spectra of Metal Chelate Compounds. IV. Infrared Spectra of Addition Compounds of Metallic Acetylacetonates." K. Nakamoto, Y. Morimoto and A. E. Martell, J. Am. Chem. Soc. 83, 4533 (1961).
4. "Infrared Spectra of Metal Chelate Compounds. V. Effect of Substituents on the Infrared Spectra of Metal Acetylacetonates." K. Nakamoto, Y. Morimoto and A. E. Martell, J. Am. Chem. Soc. 84, April (1962).
5. "Infrared Spectra of Metal Chelate Compounds. VI. A Normal Coordinate Treatment of Oxalato Metal Complexes." J. Fujita, A. E. Martell and K. Nakamoto, J. Chem. Phys. 36, 324 (1962).
6. "Infrared Spectra of Metal Chelate Compounds. VII. Normal Coordinate Treatments on 1:2 and 1:3 Oxalato Complexes." J. Fujita, A. E. Martell, and K. Nakamoto, J. Chem. Phys. 36, 331 (1962).
7. "Infrared Spectra of Metal Chelate Compounds. VIII. Infrared Spectra of Co(III) Carbonato Complexes." J. Fujita, A. E. Martell and K. Nakamoto, J. Chem. Phys. 36, 339 (1962).
8. "Infrared Spectra and Structures of α -Diimine Metal Chelate Compounds." K. Nakamoto, Advances in the Chemistry of the Coordination Compounds, Macmillan, New York, 1961, p. 437.

VI. Personnel Employed

(1) Personnel supported by the Contract, DA-19-020-ORD-5119 are:

<u>Name</u>	<u>Status</u>	<u>Period</u>
Kazuo Nakamoto	Principal Investigator Assistant Professor	Jan. 1960 - Dec. 1960
Junnosuke Fujita	Postdoctoral Fellow	April 1960 - Dec. 1960
Nancy Henry	Graduate Student	June 1960 - Sep. 1960

In addition, a trip expense to M.I.T. computation center was reimbursed to Armand Ruby (graduate student).

(2) Personnel supported by the Grant, DA-ORD-31-124-61-G61 are:

<u>Name</u>	<u>Status</u>	<u>Period</u>
Kazuo Nakamoto	Principal Investigator Assistant Professor	Jan. 1961 - Aug. 1961
Junnosuke Fujita	Postdoctoral Fellow	Jan. 1961 - May 1961
Yukiyoshi Morimoto	Research Assistant	June 1961 - Aug. 1961