*Infrared Spectra of Metal Chelate Compounds. X. A Normal Coordinate Analysis of Dithiooxalato Complexes**

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In general, the infrared spectra of metal chelate compounds are markedly different from those of the pure ligands in the low frequency region. This is mainly due to the difference in vibrational coupling, which in turn is a result of differences in steric configuration and electronic structure.

In order to assign the low frequency bands of metal chelate compounds, it is essential to carry out normal coordinate analysis on the metal chelate ring, including the coordinate bonds. Such attempts have already been carried out on acetylacetonato,[1] oxalato,[2] and carbonato[3] complexes, and the results have proved to be highly important in estimating the strength of the metal-oxygen bonds[4] and in elucidating the electronic structure of the chelate ring.[5] It is, therefore, desirable to extend this work to metal chelate compounds containing other coordinate bonds.

Infrared studies on metal chelate compounds containing metal sulfur bonds are very few. Chatt et al.[6] have, however, reported the infrared spectra of *N*-alkyl, *N*, *N*-dialkyl dithiocarbamato, and xanthato complexes in the NaCl region, and we have carried out a normal coordinate analysis of dithiocarbamato complexes.[7] In view of the scarcity of work on metal chelate compounds containing metal-sulfur bonds, we decided to undertake a similar study on dithiooxalato complexes. Accordingly, we prepared the dithiooxalato complexes of four metals, and obtained their infrared spectra over the wide range of frequency between 4000 and 280 cm^{-1}. We also carried out a normal coordinate analysis of the platinum(II) dithiooxalato complex in order to estimate the force constants as well as to make complete theoretical band assignments.

Experimental

Preparation of Compounds.—Bis(dithiooxalato)-nickel(II), palladium, and platinum(II),[8] and tris-(dithiooxalato)-cobalt(III)[9] were prepared according to the methods described in the literature and were recrystallized several times from an aqueous solution.

Spectral Measurements.—Infrared spectra were obtained on a Perkin-Elmer Model 21 infrared spectrophotometer equipped with NaCl and CsBr optics. The KBr disk method was used for the spectra in the NaCl region, whereas the Nujol mull technique was employed for the spectra in the CsBr region. Frequency calibrations were made with polystyrene film (NaCl region), with 1,2,4-trichlorobenzene (CsBr region), and with water vapor (both regions).

Procedure and Calculations

Figure 1 shows the 1 : 1 (metal/ligand) model of the dithiooxalato complex used for normal

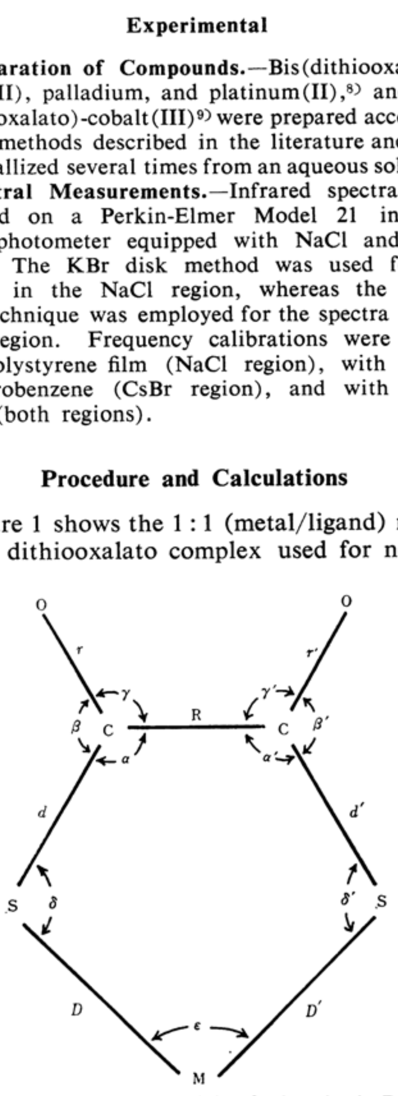

Fig. 1. Molecular model of the 1 : 1 Pt(II) dithiooxalato complex.

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TABLE I. SYMMETRY COORDINATES FOR IN-PLANE VIBRATIONS

A_1 species	$s_1=(1/\sqrt{2})(\Delta r+\Delta r')$	ν(C=O)
	$s_2=(1/\sqrt{2})(\Delta d+\Delta d')$	ν(C-S)
	$s_3=(1/\sqrt{2})(\Delta D+\Delta D')$	ν(M-S)
	$s_4=\Delta R$	ν(C-C)
	$s_5{}^*=(1/\sqrt{2})(\Delta\beta-\Delta\gamma+\Delta\beta'-\Delta\gamma')$	δ(CO)
	$s_6=(1/\sqrt{20})(-\Delta\alpha-\Delta\alpha'-\Delta\delta-\Delta\delta'+4\Delta\varepsilon)$	ring def.
	$s_7=(1/2)(\Delta\alpha+\Delta\alpha'-\Delta\delta-\Delta\delta')$	ring def.
B_2 species	$s_8=(1/\sqrt{2})(\Delta r-\Delta r')$	ν(C=O)
	$s_9=(1/\sqrt{2})(\Delta d-\Delta d')$	ν(C-S)
	$s_{10}=(1/\sqrt{2})(\Delta D-\Delta D')$	ν(M-S)
	$s_{11}{}^*=(1/\sqrt{2})(\Delta\beta-\Delta\gamma-\Delta\beta'+\Delta\gamma')$	δ(CO)
	$s_{12}=(1/2)(\Delta\alpha-\Delta\alpha'+\Delta\delta-\Delta\delta')$	ring def.
	$s_{13}=(1/2)(\Delta\alpha-\Delta\alpha'-\Delta\delta+\Delta\delta')$	ring def.

* Not normalized (see Ref. 1)

ν, stretching mode; δ, bending mode

TABLE II. FORCE CONSTANTS OF THE Pt(II) DITHIOOXALATO COMPLEX (10^5 dyn./cm.)

Stretching	Bending	Repulsive
K_1(C=O) = 8.85	H_1(S-C-C) = 0.30	F_1(C······O) = 0.30
K_2(C-S) = 3.30	H_2(O-C-S) = 0.40	F_2(O······S) = 0.40
K_3(Pt-S) = 2.30	H_3(O-C-C) = 0.35	F_3(C······S) = 0.10
K_4(C-C) = 2.60	H_4(Pt-S-C) = 0.05	F_4(C······Pt) = 0.05
	H_5(S-Pt-S) = 0.05	F_5(S······S) = 0.35

coordinate analysis. Since the symmetry of this model is C_{2v}, the fifteen normal vibrations are grouped into four species. The in-plane vibrations ($6A_1+5B_2$) can be separated from the out-of-plane vibrations ($2A_2+2B_1$) because they do not interact with each other. Thus, only the eleven in-plane vibrations are calculated in this paper. Most of the out-of-plane vibrations are expected to appear beyond our observable region, since the dithiooxalato complex consists of relatively heavy atoms. The symmetry coordinates used for the calculation are shown in Table I. The $\boldsymbol{G}$ and $\boldsymbol{F}$ matrices are similar to those previously reported for the oxalato complex.²⁾ In evaluating the $\boldsymbol{G}$ matrix elements of the platinum(II) complex, the following molecular parameters were used: $r=r'=1.28$ Å, $R=1.47$ Å, $d=d'=1.80$ Å, $D=D'=2.32$ Å, $\alpha=\alpha'=\beta=\beta'=\gamma=\gamma'=120°$, $\delta=\delta'=105°$, and $\varepsilon=90°$. Both the A_1 and B_2 species involve one redundant condition which is a complicated function of the bond distances and angles. It is not necessary, however, to eliminate these redundancies from the calculation since they give "zero frequencies" in the final result. Thus, one seventh-order (A_1) and one sixth-order (B_2) secular equation of the form, $|\boldsymbol{GF}-E\lambda|=0$, were solved using an IBM 709 computer.

The Urey-Bradley force field¹⁰⁾ was used to express the potential energy. Except for those relating to the Pt-S bonds, force constants were transferred from molecules with similar structures¹¹⁾ and were adjusted so as to obtain the best fit with the observed spectrum. Table II lists the best set of force constants thus obtained. Table III compares the observed frequencies with those calculated with this set of force constants. In order to make theoretical band assignments, the potential energy distribution¹²⁾ in each normal vibration was

TABLE III. COMPARISON OF CALCULATED AND OBSERVED FREQUENCIES FOR THE Pt(II) DITHIOOXALATO COMPLEX (cm^{-1})

		Obs.	Calcd.
A_1	λ_1	1594	1568
	λ_2	1083	1102
	λ_3	573	557
	λ_4	436 422	420
	λ_5	322	324
	λ_6	—	170
B_2	λ_7	1594	1629
	λ_8	939	960
	λ_9	515	533
	λ_{10}	398	380
	λ_{11}	322	322

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10) T. Shimanouchi, *J. Chem. Phys.*, **17**, 245, 734, 848 (1949).

11) S. Mizushima and T. Shimanouchi, "Infrared Absorption and the Raman Effect," Kyoritsu, Tokyo (1959).

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TABLE IV. THE POTENTIAL ENERGY DISTRIBUTION IN EACH NORMAL VIBRATION

		Symmetry coordinate							Assignment
A_1		s_1	s_2	s_3	s_4	s_5	s_6	s_7	
	λ_1	**1.00**	0.02	0.00	0.10	0.01	0.00	0.02	ν(C=O)
	λ_2	0.07	**0.76**	0.00	**1.00**	0.45	0.00	0.04	ν(C-C)+ν(C-S)
	λ_3	0.10	**1.00**	0.25	0.16	0.16	0.06	0.06	ν(C-S)
	λ_4	0.01	0.13	**1.00**	0.26	0.06	0.03	0.11	ν(Pt-S)
	λ_5	0.00	0.00	0.17	0.20	**1.00**	0.00	0.12	δ(CO)
	λ_6	0.00	0.01	0.37	0.02	0.00	**1.00**	**1.00**	ring def.
B_2		s_8	s_9	s_{10}	s_{11}	s_{12}	s_{13}		
	λ_7	**1.00**	0.07	0.00	0.03	0.03	0.09		ν(C=O)
	λ_8	0.19	**0.94**	0.00	**1.00**	0.07	0.00		δ(CO)+ν(C-S)
	λ_9	0.18	0.25	**0.80**	**1.00**	0.06	**0.86**		δ(CO)+ring def.+ν(Pt-S)
	λ_{10}	0.08	**0.97**	0.02	0.41	0.03	**1.00**		ring def.+ν(C-S)
	λ_{11}	0.01	0.05	**1.00**	0.11	0.09	0.00		ν(Pt-S)

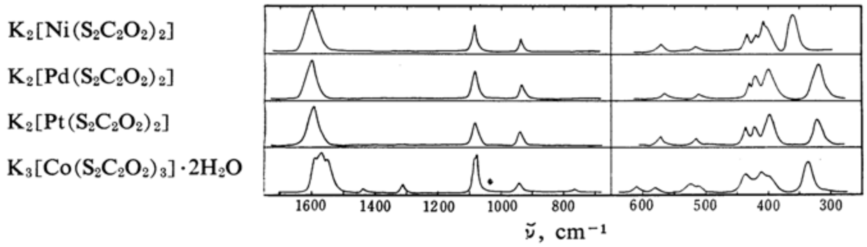

Fig. 2. Infrared spectra of dithiooxalato complexes of various metals.

calculated with respect to each symmetry coordinate. The results are shown in Table IV, along with numbers indicating the relative contribution from each symmetry coordinate.

Results and Discussion

Figure 2 shows the infrared spectra of 1 : 2 and 1 : 3 dithiooxalato complexes with various metals. It is noted immediately that the spectra of the various divalent metal complexes are very similar to one another. Thus, the band assignments obtained for the platinum(II) complex are in the main applicable to the other divalent metal complexes. Although the calculation was carried out using the 1 : 1 complex model, it has already been demonstrated that errors due to this approximation are fairly small.[2)]

According to the results shown in Tables III and IV, the strong bands observed near 1600 cm^{-1} (λ_1, λ_7) are assigned to the C=O stretching modes. In the platinum(II) complex, this band appears at 1594 cm^{-1}, and the corresponding force constant is calculated to be 8.85×10^5 dyn./cm. In the $[Pt(ox)_2]^{2-}$ ion, however, the stretching bands due to the uncoordinated C=O bonds were observed at 1674 cm^{-1}, and the corresponding force constant was estimated to be 9.30×10^5 dyn./cm. This comparison seems to suggest that the C=O bonds in dithiooxalato complexes are weaker than those in oxalato complexes.

As is seen in Fig. 2, all the compounds exhibit two bands at about 1080 (λ_2) and 940 cm^{-1} (λ_8). Table IV indicates that the former is a coupled vibration between C–C and C–S stretching modes, whereas the latter is a coupled vibration between C–S stretching and CO bending modes. A similar pattern of vibrational coupling occurs in the oxalato complex,[2)] where the bands near 1400 and 900 cm^{-1} are assigned to the coupled vibrations between C–C and C–O stretching, and between C–O stretching and CO bending modes, respectively.

The bands near 570 cm^{-1} (λ_3) are due to an almost pure C–S stretching mode, and the corresponding force constant is calculated to be 3.30×10^5 dyn./cm. This value is similar to that obtained for thiourea (3.20×10^5 dyn./cm.),[13)] but it is larger than that of diethylthioether (2.50×10^5 dyn./cm.),[11)] which has pure C–S single bonds. The strengthening of the C–S bonds can be accounted for if it is assumed that electron migration occcurs from C=O to C–S bonds in dithiooxalato complexes. It is also interesting to compare the C–S stretching bands in the dithiooxalato and dithiocarbamato platinum(II) complexes.[6)] The C–S stretching

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[13)] A. Yamaguchi, S. Mizushima, T. J. Lane, C. Curran and J. V. Quagliano, *J. Am. Chem. Soc.*, **80**, 527 (1958).

force constant of the former is larger than that of the latter (3.00×10^5 dyn./cm.), whereas the C–S stretching frequency of the former is lower than that of the latter (622 cm^{-1}). This result clearly demonstrates the structural dependence of the vibrational frequency.

According to the results shown in Table IV, the weak bands at ca. 515 cm^{-1} (λ_9) are due to a coupling mode between the CO bending, ring deformation and Pt–S stretching vibrations. The bands at 398 (λ_{10}) and 322 (λ_5) cm^{-1} are the ring deformation coupled with the C–S stretching mode and with the CO bending mode respectively.

The Pt–S stretching vibrations are assigned to the bands observed at 436 and 422 (λ_4) and 322 (λ_{11}) cm^{-1}. These frequencies are higher than those observed for the dithiocarbamato platinum(II) complex (375 and 288 cm^{-1}), mainly because the Pt–S stretching force constant of the dithiooxalato platinum(II) complex (2.30×10^5 dyn./cm.) is greater than that of the dithiocarbamato platinum(II) complex (2.10×10^5 dyn./cm.) This seems to suggest that the Pt–S bond of the dithiooxalato complex is slightly stronger than that of the dithiocarbamato complex. These values for the Pt–S stretching force constant would be reduced slightly if the calculation were made on the actual 1 : 2 model instead of the present 1 : 1 approximate model. In the case of the oxalato platinum(II) complex, however, the Pt–O stretching force constant obtained from the 1 : 2 model was only about 6% smaller than that calculated on the 1 : 1 approximate model.[2]

It has been recognized that such sulfur-containing ligands as thioethers and thiols form strong coordinate bonds with platinum(II).[14] The Pt–S bonds may be strengthened in the dithiocarbamato and dithiooxalato complexes, since they presumably involve pertial $d\pi$-$p\pi$ or $d\pi$-$d\pi$ bonding. Therefore, the relatively large Pt–S force constants obtained here are not surprising. This is also in good accord with the chemical observation that the $[Pt\cdot(C_2O_2S_2)_2]^{2-}$ ion is formed immediately after a solution of $K_2(C_2O_2S_2)$ is added to that of $K_2[PtCl_4]$ (The Pt–Cl stretching force constant is estimated to be 1.50×10^5 dyn./cm.[15])

Figure 2 indicates that, except for the lowest frequency band (λ_{11}), the spectra of the dithiooxalato complexes are little sensitive to the nature of the metal. This result is rather unusual, since all the metal chelate compounds studied so far exhibit several metal-sensitive bands in the low-frequency region. The origin of this anomaly can only be understood through normal coordinate analyses of individual complexes; this remains a problem to be solved in the future.

Summary

The infrared spectra of dithiooxalato complexes of platinum(II), palladium(II), nickel(II) and cobalt(III) have been obtained in the range between 4000 and 280 cm^{-1}. A normal coordinate analysis has been carried out for the 1 : 1 (metal/ligand) model of the dithiooxalato platinum(II) complex. The results indicate that the Pt–S stretching bands are at ca. 430 and 320 cm^{-1} and that the corresponding force constant is 2.30×10^5 dyn./cm.

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[14] For example, see "The Chemistry of the Coordination Compounds," Ed. by J. C. Bailar, Jr., Reinhold, New York (1956), p. 49.

[15] J. Hiraishi, I. Nakagawa and T. Shimanouchi, the 16th Annual Meeting of the Chemical Society of Japan, Tokyo, 1963.