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Infrared Spectra and Structure of Acetylacetonato Platinum(II) Complexes. I. Infrared Spectra and Normal Coordinate Analysis of Potassium Dichloro(acetylacetonato)platinate(II)[1]

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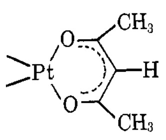
The infrared spectra of potassium dichloro(acetylacetonato)platinate(II) and three of its deuterated analogs have been obtained in the region 4000–70 cm^{-1}. Normal coordinate analyses have been carried out on these four species considering all atoms in the complex anion except methyl hydrogens. A modified Urey–Bradley force field was necessary. The force constants and band assignments obtained as well as the force field modification are discussed. The present results seem to suggest the revision of several band assignments obtained previously by the 1:1 (metal/ligand) approximate calculation for 1:2 and 1:3 complexes using the simple Urey–Bradley force field.

Introduction

The versatility of acetylacetone as a ligand was first demonstrated by Werner[3] and more recently by several investigators.[4,5] It provides a system in which the variety of metal–ligand bonding shown below[4,6] may be studied using spectroscopic methods. The purpose of this series of investigations is to analyze the infrared spectra of acetylacetonato Pt(II) complexes involving these three types of coordination and to characterize their infrared spectra and chemical bonding.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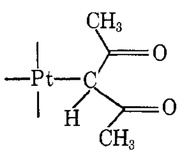
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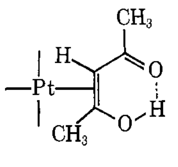
III

Among the three structures mentioned above, the chelated structure I is most common, and a number of infrared studies have already been made on acetylacetonato complexes of this type.[7] In order to analyze the infrared spectra of type I compounds, we[8] have previously carried out normal coordinate analyses of bis- and tris-acetylacetonato complexes of several first and second row transition metals. These conclusions, however, used the simple Urey–Bradley force field and were based on a 1:1 (metal/ligand) approximation, which ignores the interaction between ligands. Since the coordinate bond stretching and bending vibrations are affected appreciably by vibrational interactions between ligands, it was anticipated that the 1:1 approximate calculation would not give accurate results for those bands which appear in the low-frequency region. Also, at the time of this earlier research, no deuterated acetylacetonato complexes were prepared and no spectral data were available below 400 cm^{-1}.

Since then, several investigators[9,10] have published the far-infrared spectra of metal acetylacetonato complexes, and this situation has prompted us to carry out a rigorous normal coordinate analysis including the low-frequency bands. For this purpose, we have prepared the 1:1 complex ion, $[Pt(acac)Cl_2]^-$, and three of its deuterio analogs, and have obtained their infrared spectra from 4000 to 70 cm^{-1}. We have carried out a normal coordinate analysis of this 1:1 complex ion con-

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[2] To be submitted by G. T. B. to the faculty of Illinois Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] A. Werner, *Ber.*, **34**, 2584 (1901).

[4] J. Lewis, *Nature*, **202**, 589 (1964).

[5] R. A. D. Wentworth and C. H. Brubaker, Jr., *Inorg. Chem.*, **3**, 1472 (1964).

[6] B. N. Figgis, J. Lewis, R. F. Long, R. Mason, R. S. Nyholm, P. J. Pauling, and G. B. Robertson, *Nature*, **195**, 1278 (1962).

[7] For example, see K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 216.

[8] K. Nakamoto and A. E. Martell, *J. Chem. Phys.*, **32**, 588 (1960); K. Nakamoto, P. J. McCarthy, A. Ruby, and A. E. Martell, *J. Am. Chem. Soc.*, **83**, 1066, 1272 (1961).

[9] R. D. Gillard, H. G. Silver, and J. L. Wood, *Spectrochim. Acta*, **20**, 63 (1964).

[10] J. P. Dismukes, L. H. Jones, and J. C. Bailar, Jr., *J. Phys. Chem.*, **65**, 792 (1961).

sidering all the atoms except methyl hydrogens. It should be emphasized that the present calculation does not involve any approximation concerning the ligand–ligand interaction, since all the groups attached to the Pt atom are taken into consideration.

Experimental Section

Preparation of the Compounds.—Potassium dichloro(acetylacetonato)platinate(II) was prepared[3] by dissolving 0.415 g (1.0 mmole) of potassium tetrachloroplatinite(II) in 1.25 ml of boiling water, adding 0.95 ml (9.2 mmoles) of acetylacetone and 0.5 ml of 7.8 *M* potassium hydroxide, and shaking vigorously for 10 min while maintaining the temperature at 65°; 1.0 ml of additional potassium hydroxide was added and a small precipitate of bis(acetylacetonato)platinum(II) was separated by filtration. On standing yellow-orange plates corresponding to the formula $K(C_5H_7O_2)PtCl_2$ were obtained; they contained a small amount of a more soluble product (bright yellow crystals) corresponding to the formula $K(C_{10}H_{14}O_4)_2PtCl$. The mixture was dissolved in warm water and the pH was adjusted with HCl to a value of approximately 5. The small precipitate was removed by filtration and discarded; potassium dichloro(acetylacetonato)platinate(II) was allowed to crystallize and was separated in 28% yield.

Anal. Calcd for $C_5H_7O_2Cl_2PtK$: C, 14.86; H, 1.75; Cl, 17.54. Found: C, 15.01; H, 1.72; Cl, 17.09.

Potassium dichloro(acetylacetonato-d_1)platinate(II) was prepared from acetylacetone deuterated at the γ carbon. Acetylacetone was deuterated by heating 1.0 ml of it on a steam bath in 4.0 ml of D_2O acidified with a drop of $POCl_3$ for 2 hr; 0.5 g (1.2 mmoles) of K_2PtCl_4 was then added together with 0.5 g (8.9 mmoles) of solid KOH, and the mixture was warmed and shaken vigorously. The precipitate was purified by recrystallization from D_2O.

Potassium dichloro(acetylacetonato-d_6)platinate(II) was prepared in the same manner as above using, however, acetylacetone deuterated in the methyl positions. The deuterated acetylacetone (d_8) was prepared by refluxing 1.0 ml of acetylacetone in 10.0 ml of D_2O in the presence of potassium carbonate for 8 hr. This exchange process was repeated three times with fresh portions of D_2O. The acetylacetone was extracted with ether and the ether removed under vacuum. The completely deuterated acetylacetone (d_8) thus obtained was exchanged with H_2O slightly acidified with $POCl_3$, and the methyl deuterated compound (d_6) was isolated by extraction with ether.

Potassium dichloro(acetylacetonato-d_7)platinate(II) was prepared in the same manner as the nondeuterated compound using completely deuterated acetylacetone in D_2O solution.

Bis(acetylacetonato)platinum(II) compounds were prepared by the reaction between excess acetylacetone or deuterated acetylacetone and potassium tetrachloroplatinite(II) according to the methods described in the literature.[3,11]

The degree of isotopic substitution was verified by a comparison of the nmr spectra of the deuterated ligands.

Spectral Measurements

A Beckman IR 12 double-beam infrared spectrophotometer was used to obtain the spectra from 4000 to 650 cm^{-1}. The KBr disk method was employed in this region. The spectra between 700 and 200 cm^{-1} were measured with a Beckman Model IR-7 infrared spectrophotometer equipped with CsI optics. For these spectra the Nujol mull technique and CsI plates were used, as well as polyethylene pellets. The spectra between 300 and 70 cm^{-1} were measured with a Beckman IR 11 far-infrared spectrophotometer. For these spectra polyethylene pellets[12] were used. Calibration of frequency readings was made with polystyrene film, 1,2,4-trichlorobenzene, and water vapor.

Method of Calculation

The molecular model of dichloro(acetylacetonato)platinate(II) ion is shown in Figure 1, in which X is chlorine and R is the methyl group which is treated as a single atom having a mass of 15.035 (atomic units). This 11-atom model will have 27 normal vibrations which are classified into four species, $10\ A_1 + 3\ A_2 + 5\ B_1 + 9\ B_2$, under C_{2v} symmetry. The 19 in-plane vibrations consisting of the species $10\ A_1 + 9\ B_2$ are separated from the remaining eight out-of-plane vibrations and are the subject of this paper. The only out-of-plane vibration to be expected in the high-frequency region (above 600 cm^{-1}) is the C–H bending mode, which can be easily identified upon deuteration. Other out-of-plane bendings are expected to appear in the low-frequency region (below 600 cm^{-1}). Figure 1 also shows the 26 internal coordinates used for the calculation of the 19 in-plane vibrations. As a first step, the *G* and *F* matrices were constructed using these 26 internal coordinates. These matrices were reduced to 21st order and separated into 11th order A_1 and 10th order B_2 matrices through coordinate transformations, which removed 5 redundancies (concerned with the sum of the angles around each C atom and the Pt atom and one concerned with the sum of the six angles in the ring). The two remaining redundancies were left in the calculation, since they cannot be removed as readily as those mentioned above.

Table I lists the symmetry coordinates used in our calculation. The *G* matrix elements were evaluated using the molecular parameters: $r_1 = r_1' = 1.28$ A, $r_2 = r_2' = 1.39$ A, $r_3 = r_3' = 1.53$ A, $r_4 = r_4' = 1.97$ A, $r_5 = r_5' = 2.30$ A, $R = 1.08$ A, $\alpha_{12} = \alpha_{12}' = \alpha_{23} = \alpha_{23}' = \alpha_{31} = \alpha_{31}' = 120°$, $\delta_1 = \delta_1' = 114°$, $\delta = 132°$, $\beta = \beta' = 129°$, $\gamma_{44} = \gamma_{45} = \gamma_{45}' = \gamma_{55} = 90°$. These values are similar to those obtained from the X-ray analysis of $K[Pt(acac)_2Cl]$.[6]

The *F* matrix elements were expressed by using a modified Urey–Bradley force field of the type

$$V = V(\text{simple UBFF})^{13} + 2\rho[(\Delta r_1)(\Delta r_2) + (\Delta r_2)(\Delta r_2') + (\Delta r_2')(\Delta r_1') + (\Delta r_1)(\Delta r_1') - (\Delta r_1)(\Delta r_2') - (\Delta r_2)(\Delta r_1')]$$

where ρ is a stretching–stretching interaction constant. The second term in the above expression takes a form similar to that used for the benzene molecule by Scherer and Overend.[14] Here the contributions of each type of interaction are considered equal and are expressed in terms of a single interaction constant ρ. The reasons for this modification will be discussed in the following section.

Finally, two secular equations of the form $|GF -$

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[11] A. A. Grinberg and I. N. Chapurskii, *Russ. J. Inorg. Chem.*, **4**, 137 (1959).

[12] Polyethylene pellets were made by pressing in an evacuated die, as 20% by weight intimate mixtures in Microthene 500, and then heating at 60 to 90° until the opaque pellet became clear as the polyethylene melted.

[13] T. Shimanouchi, *J. Chem. Phys.*, **17**, 245 (1949).

[14] J. R. Scherer and J. Overend, *Spectrochim. Acta*, **17**, 719 (1961).

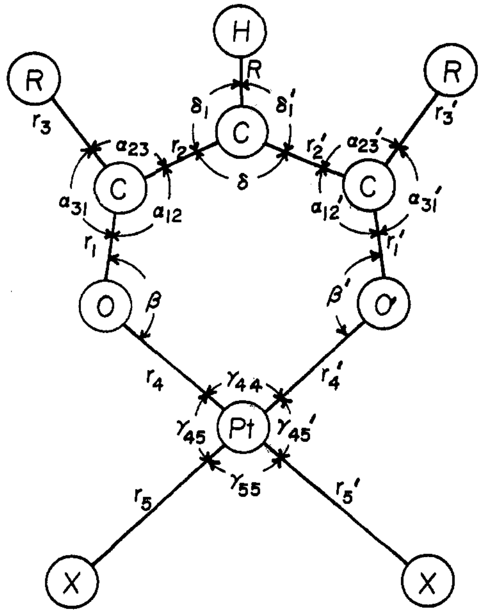

Figure 1.—Molecular model and internal coordinates.

TABLE I

SYMMETRY COORDINATES FOR IN-PLANE VIBRATIONS

Species	Symmetry coordinate	Vibrational mode[a]
A_1	$S_1 = (1/\sqrt{2})(\Delta r_1 + \Delta r_1')$	CO str
	$S_3 = (1/\sqrt{2})(\Delta r_2 + \Delta r_2')$	CC str
	$S_5 = (1/\sqrt{2})(\Delta r_3 + \Delta r_3')$	CR str
	$S_7 = (1/\sqrt{2})(\Delta r_4 + \Delta r_4')$	PtO str
	$S_9 = \Delta R$	CH str
	$S_{11} = (1/\sqrt{2})(\Delta r_5 + \Delta r_5')$	PtCl str
	$S_{13}{}^b = (1/\sqrt{2})(\Delta\alpha_{23} - \Delta\alpha_{31} + \Delta\alpha_{23}' - \Delta\alpha_{31}')$	CR bend
	$S_{15} = (1/2)(-\Delta\alpha_{12} - \Delta\alpha_{12}' + \Delta\beta + \Delta\beta')$	Ring def
	$S_{17} = (1/\sqrt{12})(\Delta\alpha_{12} + \Delta\alpha_{12}' - 2\Delta\delta + \Delta\beta + \Delta\beta' - 2\Delta\gamma_{44})$	Ring def
	$S_{19} = (1/\sqrt{2})(\Delta\delta - \Delta\gamma_{44})$	Ring def
	$S_{21}{}^b = (2\Delta\gamma_{55} - \Delta\gamma_{45} - \Delta\gamma_{45}')$	$PtCl_2$ bend
B_2	$S_2 = (1/\sqrt{2})(\Delta r_1 - \Delta r_1')$	CO str
	$S_4 = (1/\sqrt{2})(\Delta r_2 - \Delta r_2')$	CC str
	$S_6 = (1/\sqrt{2})(\Delta r_3 - \Delta r_3')$	CR str
	$S_8 = (1/\sqrt{2})(\Delta r_4 - \Delta r_4')$	PtO str
	$S_{10} = (1/\sqrt{2})(\Delta r_5 - \Delta r_5')$	PtCl str
	$S_{12}{}^b = (1/\sqrt{2})(\Delta\alpha_{23} - \Delta\alpha_{31} - \Delta\alpha_{23}' + \Delta\alpha_{31}')$	CR bend
	$S_{14}{}^b = (\Delta\delta_1 - \Delta\delta_1')$	CH bend
	$S_{16} = (1/2)(\Delta\alpha_{12} - \Delta\alpha_{12}' + \Delta\beta - \Delta\beta')$	Ring def
	$S_{18} = (1/2)(\Delta\alpha_{12} - \Delta\alpha_{12}' - \Delta\beta + \Delta\beta')$	Ring def
	$S_{20}{}^b = (\Delta\gamma_{45} - \Delta\gamma_{45}')$	$PtCl_2$ rock

[a] R denotes the CH_3 group. [b] These coordinates are not normalized (see ref 7). However, this causes only minor changes in the interpretation of normal modes in terms of symmetry coordinates.

$E\lambda| = 0$ were solved using an IBM 7094 computer. The fact that one "zero frequency" was obtained in each species provided a good check of our calculation. Table II lists the set of force constants which gives the best fit to the observed frequencies for the dichloro(acetylacetonato)platinate(II) ion and its three deuterio analogs. Table III compares the observed frequencies with those calculated for the four isotopic species. The agreement is very satisfactory; the average error is 1.5% for the 76 observed frequencies and the maximum error is 4.5% (ν_5 of the d_7 compound). It is to be expected that, in general, the normal vibrations related to the methyl group contain more error than other modes due to our treatment of the methyl group as a single atom. The last column of Table III contains an approximate description of each normal mode in terms of the symmetry coordinates listed in Table I. They were obtained from the calculation of the potential energy distribution[15] for the d_0 compound shown in Table IV.

TABLE II

FORCE CONSTANTS FOR

DICHLORO(ACETYLACETONATO)PLATINATE(II) ION (MDYNES/A)

(I) Stretching

$K(\text{C}\overset{\cdots}{-}\text{O}) = 6.50$
$K(\text{C}\overset{\cdots}{-}\text{C}) = 5.23$
$K(\text{C—CH}_3) = 3.58$
$K(\text{Pt—O}) = 2.46$
$K(\text{C—H}) = 4.68$
$K(\text{Pt—Cl}) = 1.78$

(II) Bending

$H(\text{O—C—C}) = 0.33$
$H(\text{R—C—C}) = 0.38$
$H(\text{O—C—R}) = 0.23$
$H(\text{C—C—C}) = 0.26$
$H(\text{H—C—C}) = 0.18$
$H(\text{C—O—Pt}) = 0.13$
$H(\text{O—Pt—O}) = 0.13$
$H(\text{O—Pt—Cl}) = 0.05$
$H(\text{Cl—Pt—Cl}) = 0.04$

(III) Repulsive

$F(\text{O}\cdots\text{C}) = 0.54$
$F(\text{R}\cdots\text{C}) = 0.52$
$F(\text{O}\cdots\text{R}) = 0.37$
$F(\text{C}\cdots\text{C}) = 0.47$
$F(\text{H}\cdots\text{C}) = 0.50$
$F(\text{C}\ldots\text{Pt}) = 0.20$
$F(\text{O}\ldots\text{O}) = 0.20$
$F(\text{O}\ldots\text{Cl}) = 0.09$
$F(\text{Cl}\ldots\text{Cl}) = 0.08$

(IV) Stretching–Stretching Interaction

$\rho = 0.43$

Modification of the Simple Urey–Bradley Force Field.—As noted above, the infrared spectra of methyl-deuterated acetylacetonato complexes were obtained for the first time in this investigation. These new spectral data necessitated the revision of some of our previous band assignments which were made without confirmation by the spectra of deuterated compounds. One of them is the band at 1380 cm^{-1} of the nondeuterated compound. This band was assumed to be the degenerate deformation of the CH_3 group, since its frequency is close to the group frequency of this mode.[16] As seen in Figure 2, the spectra of the d_6 and d_7 compounds, in which both the CH_3 groups are completely deuterated, still exhibit strong bands at 1380–1368 cm^{-1}. Furthermore, the spectrum of the nondeuterated compound in this region clearly consists of two bands closely located, one at 1380 cm^{-1} and the other at 1363 cm^{-1} (shoulder). The separation of these two peaks increases slightly in the d_1 compound.

During the process of our calculation, we have found that the simple Urey–Bradley force field[13] predicts little separation between the antisymmetric and symmetric $\text{C}\overset{\cdots}{-}\text{O}$ stretching modes. It further predicts a large separation of the corresponding $\text{C}\overset{\cdots}{-}\text{C}$ stretching modes, because the two $\text{C}\overset{\cdots}{-}\text{C}$ bonds interact strongly through a common atom. On this basis, it was anticipated that three bands (two $\text{C}\overset{\cdots}{-}\text{O}$ and the antisymmetric $\text{C}\overset{\cdots}{-}\text{C}$ stretching) would appear in the region 1600–1500 cm^{-1}. An investigation at liquid nitrogen temperature, with the resulting decrease in band width, increase in intensity, and increase in resolution, did not

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(15) Y. Morino and K. Kuchitsu, *J. Chem. Phys.*, **20**, 1809 (1952).

(16) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962.

TABLE III

A COMPARISON OF OBSERVED AND CALCULATED FREQUENCIES OF POTASSIUM DICHLORO(ACETYLACETONATO)PLATINUM(II) AND ITS DEUTERATED ANALOGS[a]

	d_0 compound		d_1 compound		d_6 compound		d_7 compound		
	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Predominant modes
					A₁ Species				
ν_1	. . .	3086	. . .	2268	. . .	3086	. . .	2268	S_9
ν_2	1563 s	1561	1553 s	1555	1558 s	1560	1542 s	1555	S_1
ν_3	1288 m	1271	1286 m	1269	1310 w 1248 w	1260	1310 w 1248 w	1258	$S_3 + S_5$
ν_4	952 m	935	920 m	917	945 m	930	888 m	912	$S_5 + S_3 + S_{15}$
ν_5	703 w	693	672 w	690	651 m	677	646 m	675	$S_7 + S_{15} + S_5$
ν_6	478 m	491	477 m	491	473 m	467	451 m	466	$S_7 + S_{15}$
ν_7	327 s	331	327 s	331	327 s	331	327 s	331	S_{11}
ν_8	283 w	285	282 w	283	280 w	271	280 w	269	$S_{17} + S_{13}$
ν_9	228 m	231	228 m	230	225 m	223	222 m	222	$S_{17} + S_{15} + S_{13}$
ν_{10}	132 m	134	132 m	134	132 m	134	132 m	134	S_{21}
					B₂ Species				
ν_{11}	1538 s	1538	1500 s	1508	1538 s	1536	1496 s	1506	S_4
ν_{12}	1380 s	1386	1373 s	1369	1380 s	1385	1368 s	1368	S_2
ν_{13}	1212 w	1221	865 w[c]	864	1210 w	1217	876 w[c]	849	S_{14}
ν_{14}	941 m	921	960 m	982	892 m	890	960 m	963	S_6
ν_{15}	650 s	646	650 s	635	619 s	641	619 s	630	S_8
ν_{16}	448 m	444	442 m	441	448 m	432	411 m	428	$S_{16} + S_{12}$
ν_{17}	339 s	334	339 s	333	339 s	330	339 s	330	S_{10}
ν_{18}	283 w	280	282 w	279	280 w	268	280 w	268	$S_{12} + S_{16} + S_8$
ν_{19}	128 m	130	128 m	130	128 m	130	128 m	130	S_{20}
					Not Calculated				
	1429 m		1430 m		1035 m		1038 w		CH_3 deg def
	1363 sh		1372 sh		1018 m		1024 m		CH_3 sym def
	1033 m		1035 m		972 m		970 m		CH_3 rock
	1018 m		1015 m		958 m		960 m		CH_3 rock
	817 s		620 m		809 s		617 s		π CH[d]
	380 w		377 w		370 w		368 w		π skeletal[d]
	95 m		95 m		95 m		95 m		π skeletal[d]

[a] Intensity designations: s, strong; m, medium; w, weak; sh, shoulder; vw, very weak. [b] For the d_0 compound. [c] These bands were observed only at liquid nitrogen temperature. [d] Out-of-plane mode.

TABLE IV

THE POTENTIAL ENERGY DISTRIBUTION FOR DICHLORO(ACETYLACETONATO)PLATINATE(II) ION[a]

A₁ Species

Symmetry coordinate		Observed frequency (cm⁻¹)								
	3086[b]	1563	1288	952	703	478	327	283	228	132
S_1	0.00	*1.00*	0.02	0.27	0.00	0.00	0.00	0.00	0.00	0.00
S_3	0.03	0.13	*1.00*	*0.37*	0.01	0.08	0.00	0.01	0.00	0.00
S_5	0.01	0.04	*0.33*	*1.00*	*0.35*	0.26	0.00	0.00	0.00	0.00
S_7	0.00	0.00	0.01	0.00	*1.00*	*1.00*	0.00	0.00	0.05	0.00
S_9	*1.00*	0.00	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.00
S_{11}	0.00	0.00	0.00	0.00	0.00	0.00	*1.00*	0.00	0.03	0.00
S_{13}	0.00	0.00	0.00	0.06	0.00	0.20	0.00	*0.92*	*0.30*	0.00
S_{15}	0.00	0.01	0.02	*0.54*	*0.75*	*0.46*	0.00	0.00	*0.39*	0.00
S_{17}	0.00	0.00	0.00	0.04	0.03	0.25	0.03	*1.00*	*1.00*	0.03
S_{19}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S_{21}	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.05	*1.00*

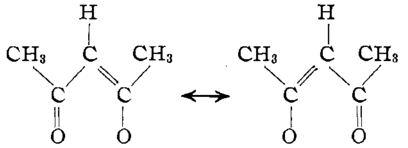
B₂ Species

	Observed frequency (cm⁻¹)								
	1538	1380	1212	941	650	448	339	283	128
S_2	0.20	*1.00*	0.16	0.07	0.00	0.00	0.02	0.03	0.00
S_4	*1.00*	0.17	0.04	0.05	0.00	0.02	0.00	0.00	0.00
S_6	0.03	0.01	0.13	*1.00*	0.00	0.01	0.00	0.02	0.00
S_8	0.00	0.00	0.02	0.00	*1.00*	0.00	0.07	*0.39*	0.00
S_{10}	0.00	0.00	0.00	0.00	0.00	0.00	*1.00*	*0.55*	0.00
S_{12}	0.01	0.01	0.01	0.00	0.17	*0.32*	0.13	*1.00*	0.00
S_{14}	0.27	0.19	*1.00*	0.05	0.04	0.00	0.01	0.00	0.00
S_{16}	0.00	0.00	0.00	0.01	0.06	*1.00*	0.07	*0.51*	0.00
S_{18}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S_{20}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	*1.00*

[a] If there are more than two relatively large contributions, only the term which contributes more than 0.3 is used to represent the vibrational coupling. [b] Calculated frequency (cm⁻¹).

demonstrate the presence of more than two bands in this region. This apparent contradiction can be explained by considering the well-known delocalization of the π electrons in the chelate ring. It provides an electronic mechanism for an interaction between the C$\overset{\cdots}{-}$O stretching vibrations, which should, therefore, be separated. As a result, it is reasonable to anticipate that one of the C$\overset{\cdots}{-}$O stretching bands is lowered to 1380 cm^{-1} and would be unaffected by deuteration of the methyl groups. It was found that no combination of reasonable changes in force constants in the simple Urey–Bradley force field can result in the separation of more than 200 cm^{-1} required to support this assignment.

Accordingly, a modification of the force field was made with the introduction of a new interaction force constant. Since the acetylacetonato complexes may be considered as pseudo-aromatic compounds, it is reasonable to treat them analogously to the benzene molecule. The origin of this vibrational interaction is similar to that of the Kekulé type interaction introduced by Scherer and Overend[14] for their calculations of benzene. In the present case, we consider the resonance between structures



Theoretically, we expect slightly different interaction constants between various pairs of stretching internal coordinates. Since our experimental data are not sufficient to determine each of these constants, we have chosen to use the same constant ρ for all types of interaction as a first approximation. This is reasonable because the C$\overset{\cdots}{-}$O and C$\overset{\cdots}{-}$C bond orders are similar. Although the Pt—O bonds could also be included in the above resonance system, we did not do so because the Pt—O stretching frequency is too low to couple seriously with the C$\overset{\cdots}{-}$C stretching modes. In the present case, ρ assumes a value of 0.43 mdyne/A, which is comparable to 0.35 mdyne/A determined for benzene. The slightly larger value which we have obtained may be indicative of a very small dissimilarity in the lengths of the C$\overset{\cdots}{-}$O bonds.

Results and Discussion

(I) **Band Assignments.**—Figure 2 illustrates the infrared spectra of potassium dichloro(acetylacetonato)platinate(II) and its three deuterio analogs from 2000 to 70 cm^{-1}. The spectra above 2000 cm^{-1} are not shown, since no significant absorptions are seen except the C–H and C–D stretching bands. The spectrum between 1600 and 1200 cm^{-1} is most interesting; it changes remarkably upon deuteration of the C–H and C–H$_3$ hydrogens. Both the d_0 and d_6 compounds exhibit two closely spaced bands at *ca.* 1560 and 1540 cm^{-1}. Upon deuterium substitution on the γ carbon, the separation of these two bands increases as the 1540 cm^{-1} band is shifted to *ca.* 1500 cm^{-1}. According to our calculation (Table IV), the bands near 1560 cm^{-1} are due to almost pure C$\overset{\cdots}{-}$O stretching (ν_2, A$_1$ species), whereas the bands near 1540 cm^{-1} (ν_{11}, B$_2$ species) are the C$\overset{\cdots}{-}$C stretching modes coupled slightly with the C—H in-plane bending mode. Upon deuteration, this coupling disappears completely since the C—D in-plane bending frequency is too low to couple with the C$\overset{\cdots}{-}$C stretching mode. Apparently this decoupling is responsible for the shift of ν_{11} from 1540 to 1500 cm^{-1}.

In the d_0 compound, three bands are closely located between 1430 and 1360 cm^{-1}: 1429 (medium), 1380 (strong, sharp), and 1363 cm^{-1} (shoulder). As seen in Figure 2, two bands at 1429 and 1363 cm^{-1} disappear completely in the d_6 and d_7 compounds. It is, therefore, reasonable to assign them to the degenerate and symmetric deformation of the methyl groups.[17] As stated previously, the strong band at 1380 cm^{-1} appears in all the compounds studied and has been assigned to the C$\overset{\cdots}{-}$O stretching (ν_{12}, B$_2$ species) coupled slightly with the C—H bending mode. Again, this band is shifted by *ca.* 10 cm^{-1} upon deuteration on the γ carbon, since the contribution of the C—H bending mode diminishes. The next band at 1288 cm^{-1} of d_0 is assigned to the C$\overset{\cdots}{-}$C stretching coupled with the C—CH$_3$ stretching mode (ν_3, A$_1$ species). In the d_6 and d_7 compounds this band seems to split into two peaks (1310 and 1248 cm^{-1}), although the origin of this splitting is not clear. The weak band at 1212 cm^{-1} of d_0 is assigned to the C—H in-plane bending mode (ν_{13}, B$_2$ species), which is shifted to *ca.* 870 cm^{-1} upon deuteration of the CH hydrogen.

Two medium bands at 1033 and 1018 cm^{-1} may be assigned to the two CH$_3$ rocking modes which are not calculated in this paper. They are shifted to *ca.* 970–960 cm^{-1} upon deuteration of the methyl groups. However, the d_6 and d_7 compounds exhibit the CD$_3$ degenerate and symmetric deformation bands between 1100 and 1000 cm^{-1}. Therefore, the spectra of all isotopic species appear somewhat similar in this region. Two bands at 952 and 941 cm^{-1} of the d_0 compound are assigned to the asymmetric and antisymmetric C–CH$_3$ stretching modes (ν_4 and ν_{14}), although the former couples with other modes. A strong band at 817 cm^{-1} of d_0 is definitely due to the C–H out-of-plane bending mode. This band disappears completely in the d_1 and d_7 compounds and is the best indication of the completeness of deuteration of the CH hydrogen.

A weak band at 703 cm^{-1} and a strong band at 650 cm^{-1} of d_0 are assigned to a ring deformation coupled with both the Pt–O stretching and the C–CH$_3$ stretching (ν_5), and the Pt–O stretching (ν_{15}) coupled slightly with the C–CH$_3$ bending mode, respectively. The former is shifted gradually to a lower frequency as more deuterium is substituted, whereas the latter is shifted to 619 cm^{-1} in the d_6 and d_7 compounds because the contribution of the C–CH$_3$ bending mode to ν_{15} is reduced in these compounds. A sharp band at 620 cm^{-1} of d_1 is attributed to the C–D out-of-plane

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(17) P. Cossee and J. H. Schachtschneider, *J. Chem. Phys.*, **44**, 97 (1966).

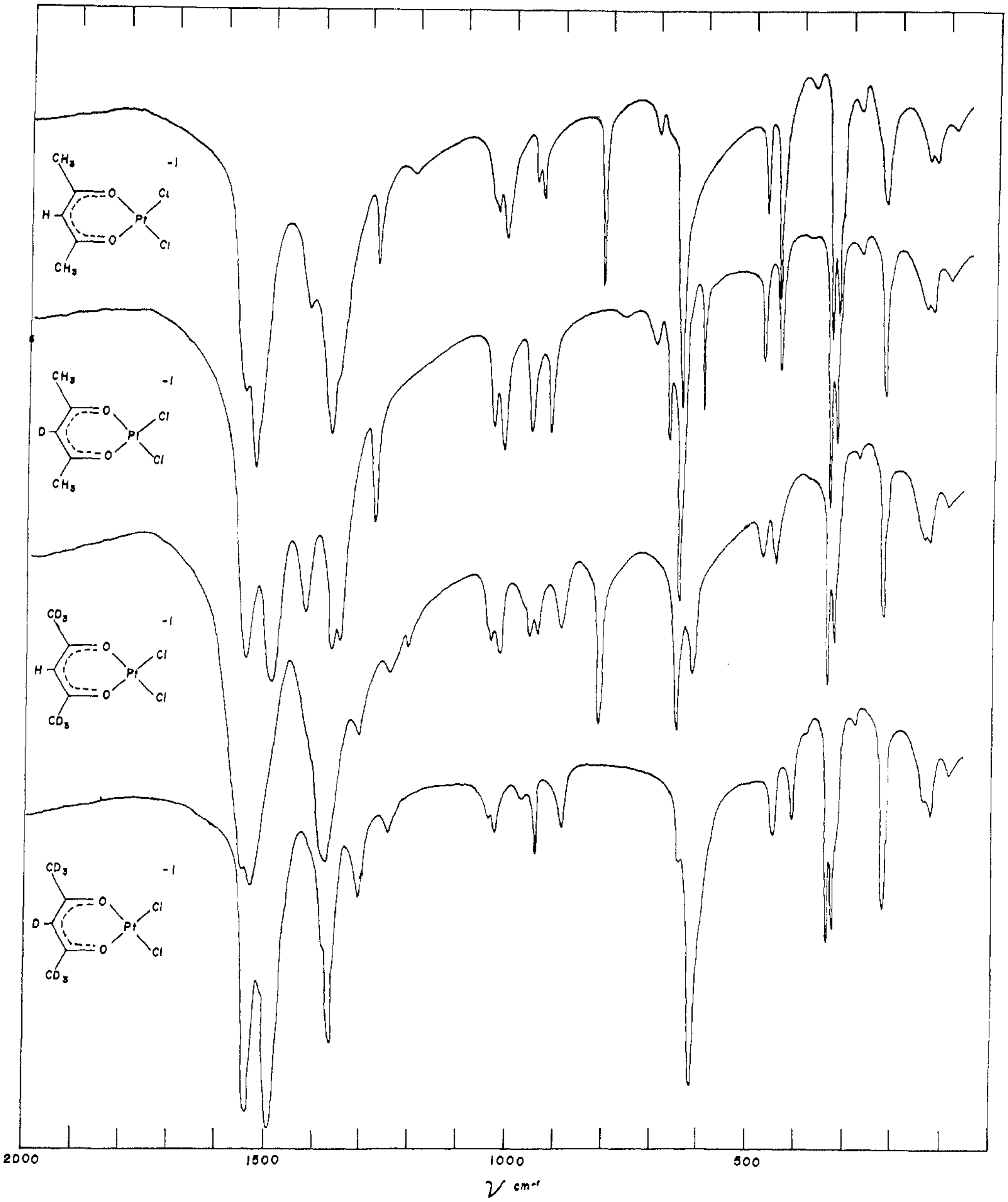

Figure 2.—Infrared spectra of potassium dichloro(acetylacetonato)platinate(II) and its three deuterio analogs.

bending mode, although the corresponding mode is overlapped with the Pt–O stretching mode (ν_{15}) in the d_7 compound.

The bands at 478 and 448 cm^{-1} of d_0 are the Pt–O stretching coupled with a ring deformation (ν_6) and a ring deformation coupled with the C–CH$_3$ bending mode (ν_{16}), respectively. Two strong bands at 339 and 327 cm^{-1} can be attributed unambiguously to the Pt–Cl stretching modes (ν_{17} and ν_7). The shape and intensity of these bands are characteristic of *cis*-dichloro Pt compounds. A weak band at 283 cm^{-1} was interpreted as an overlap of the two bands (ν_8 and ν_{18}) both of which have large contributions of the C–CH$_3$ bending mode. A medium band at 228 cm^{-1} (ν_9) appears in all the compounds studied and is assigned to a ring deformation (S_{15}) according to our calculations. Two bands at 132 and 128 cm^{-1} of d_0 are shown to be the Cl–Pt–Cl bending (ν_{10}) and PtCl$_2$ rocking (ν_{19}) modes, respectively. Finally, a medium band at 95 cm^{-1} may be due to an out-of-plane bending or a lattice mode.

(II) Force Constants.—The Urey–Bradley force constants used to give the best fit to the observed frequencies are shown in Table II. Most of these force constants were transferred from those of benzene and the acetic acid anion.[18] It should be noted that the value for K(C—CH$_3$), 3.58 mdynes/A, includes the C···H repulsive force constant for each of the methyl hydrogens according to our approximation. If it is assumed that F(C···H) is 0.36 mdyne/A (0.32 to 0.40 mdyne/A is the magnitude of this interaction determined by Cossee and Schachtschneider[17]), this would reduce K(C—CH$_3$) to 2.50 mdynes/A, which is comparable to 2.46 mdynes/A obtained for the acetic acid anion.[18]

The value of K(Pt—Cl), 1.78 mdynes/A, is similar to

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(18) S. Mizushima and T. Shimanouchi, "Infrared Absorption and Raman Effect," Kyoritsu, Tokyo, 1958.

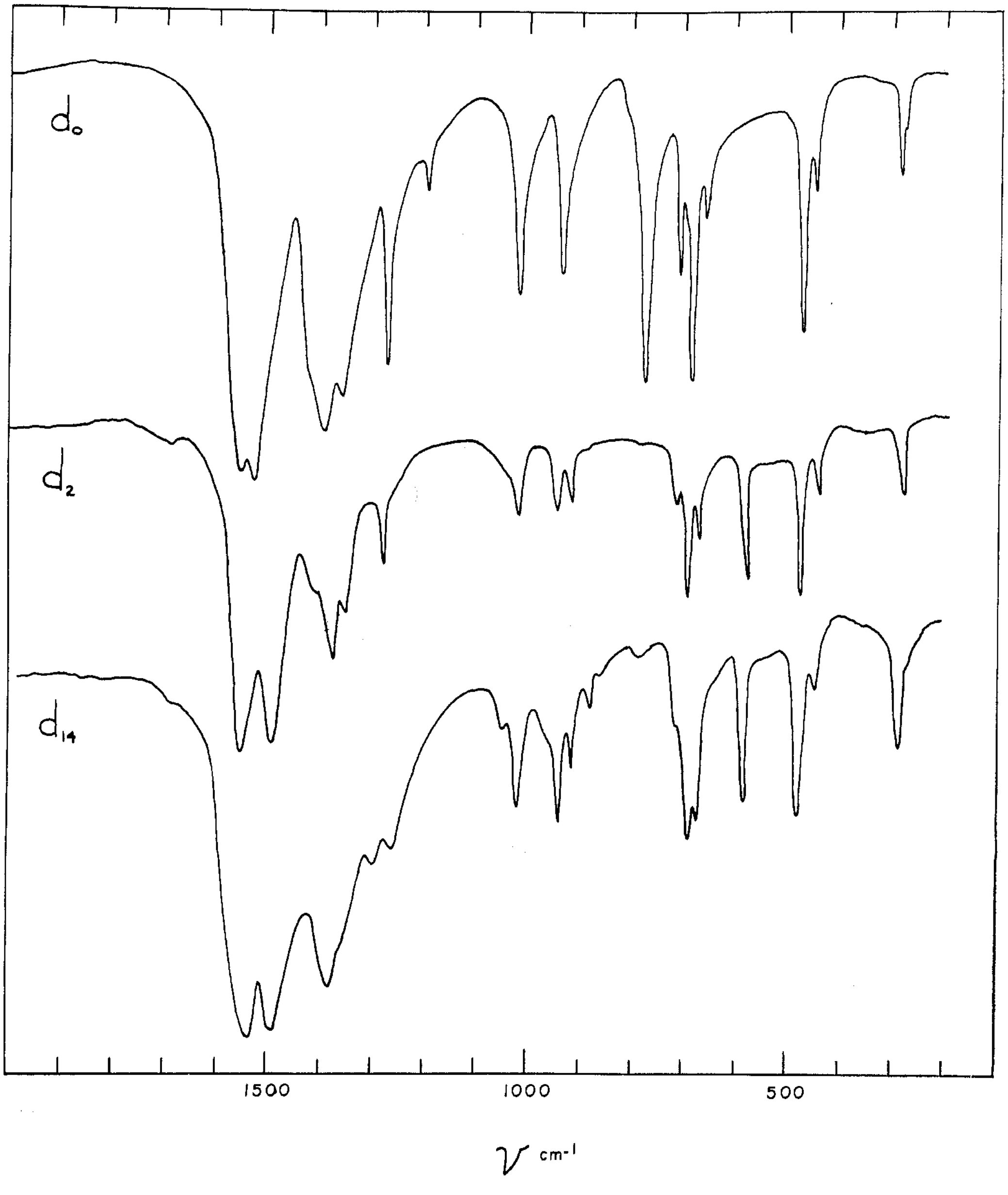

Figure 3.—Infrared spectra of bis(acetylacetonato)platinum(II) and its two deuterio analogs.

that used for *trans*-$Pt(NH_3)_2Cl_2$.[19] $K(C\overset{...}{-}O)$ used here is smaller than those obtained for the acetic acid anion (7.20 mdynes/A)[18] and acetone (10.5 mdynes/A).[17] This is consistent with the reduction in the CO bond order which occurs upon formation of the Pt—O coordinate bonds. K(Pt—O) obtained in this work is much smaller than K(Pt—CN) (3.425 mdynes/A)[20] in $K_2[Pt(CN)_4]$ and is slightly larger than $K(Pt—NH_3)$ (2.09 mdynes/A)[19] in *trans*-$Pt(NH_3)_2Cl_2$. This result may suggest that the order of the strength of these coordinate bonds may be Pt—CN >> Pt—O(acac) > $Pt(NH_3)$.

(III) Spectra of 1:2 Complexes.—Figure 3 illustrates the infrared spectra of bis(acetylacetonato)platinum(II) and its d_2 and d_{14} analogs. A comparison of Figures 2 and 3 indicates that the general features of the spectra of the corresponding isotopic species are similar between the 1:1 and 1:2 complexes except for the Pt–Cl stretching region (350–300 cm^{-1}). This may be due to the fact that vibrational coupling between ligands is small; and furthermore, no major differences in electronic structure exist between the two series of compounds, probably because the electronegativities of oxygen and chlorine are similar. It seems, therefore, that the theoretical band assignments obtained for the 1:1 complex may be applicable to the 1:2 complex. Table V lists the observed frequencies and the probable band assignments for the 1:2 complex. It should be noted that the same trend in isotope shift is seen for the corresponding bands of the two series. Previously we[8] have assigned the infrared spectra of 1:2 and 1:3 acetylacetonato complexes based on the 1:1 approximate calculation using the simple Urey–Bradley force field. In

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[19] K. Nakamoto, P. J. McCarthy, J. Fujita, R. A. Condrate, and G. T. Behnke, *Inorg. Chem.*, **4**, 36 (1965).

[20] D. M. Sweeney, I. Nakagawa, S. Mizushima, and J. V. Quagliano, *J. Am. Chem. Soc.*, **78**, 889 (1956).

the present work, we have carried out a similar calculation using the modified force field described above. It was found that both calculations give essentially similar results for the high-frequency bands as well as for the low-frequency bands concerning the C–CH_3 bending and ring deformation modes. Although the errors in coordinate bond stretching frequencies are about 10%, this may be improved by increasing the force constant by 15–20%. A satisfactory result can, therefore, be obtained by using the 1:1 approximation within these restrictions.

In view of the present results, the following modifications of the previous band assignments[8] may be suggested: (1) The band assignments for the C$\overset{\cdots}{-}$O and C$\overset{\cdots}{-}$C stretching bands above 1500 cm^{-1} should be interchanged. (2) The band assignments for the CH_3 degenerate deformation and the lower frequency C$\overset{\cdots}{-}$O stretching should also be interchanged.

More accurate analysis of the 1:2 and 1:3 compound spectra, especially in the low-frequency region, must await a complete normal coordinate treatment considering the entire molecule.

TABLE V

BAND ASSIGNMENTS OF BIS(ACETYLACETONATO)PLATINUM(II) AND ITS DEUTERATED ANALOGS

1:1	1:2			
d_0 compound	d_0 compound	d_2 compound	d_{14} compound	Predominant mode
1563 s	1568 s	1560 s	1550 s	C$\overset{\cdots}{-}$O str
1538 s	1544 s	1501 s	1500 s	C$\overset{\cdots}{-}$C str
1429 m	1425 sh	1425 sh	1060 w	CH_3 deg def
1380 s	1405 s	1390 s	1395 s	C—O str
1363 sh	1375 m	1367 m	1029 m	CH_3 sym def
1288 m	1283 m	1283 m	1303 m 1275	C$\overset{\cdots}{-}$C str
1222 w	1204 w	885 vw	865 vw	C—H bend
1033 m 1018 m	1027 m	1030 m	946 m	CH_3 rock
952 m	945 m	954 m	946 m	C—CH_3 str
941 m		923 w	919 w	
817 s	779 s	582 s	581 s	π (C—H)
703 w	712 m	710 m	. . .	Pt—O str + ring def
650 s	690 s	688 s	688 s	Pt—O str
. . .	660 w	672 w	670 w	. . .
478 m	479 s	475 s	476 s	Pt—O str
448 m	452 m	444 m	444 m	Ring def
283 w	279 m 272 sh	279 m 272 sh	279 m 260 sh	C—CH_3 bend

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Infrared Spectra and Structure of Acetylacetonato Platinum(II) Complexes. II. Infrared Spectra and Normal Coordinate Analysis of Sodium Dichlorobis(γ-acetylacetonato)platinate(II)[1]

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Received September 22, 1966

The infrared spectra of sodium dichlorobis(γ-acetylacetonato)platinate(II) and two of its deuterated analogs have been obtained in the region 4000 to 200 cm^{-1}. Normal coordinate analyses have been carried out on these three species using a simplified molecule model. A Urey–Bradley force field was used to determine the force constants, particularly for the platinum–carbon stretching vibration. The value of 2.50 mdynes/A thus determined is compared with other platinum coordinate bond stretching force constants. Force constants and band assignments and their relation to structure are discussed.

Introduction

Several complexes of platinum(II) first prepared by Werner[3] were reported to contain acetylacetone as a unidentate ligand. It has been shown recently that in these complexes platinum is bonded to the γ-carbon atom of acetylacetone.[4–7] The unusual stability of these platinum–carbon bonds is indicated by their formation in strongly basic aqueous solutions.

The infrared spectra of metal acetylacetonato complexes have been studied by several investigators,[8] and we have recently carried out a complete normal coordinate analysis on a simple bidentate oxygen-bonded platinum complex, potassium dichloro(acetylacetonato)platinate(II),[9] for which the Urey–Bradley force field was found to be inadequate to describe the observed spectra due to interactions between resonance forms.

The possible existence of carbon-bonded metal acetylacetonates prompted us to extend our study of

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[2] To be submitted by G. T. B. to the faculty of Illinois Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] A. Werner, *Ber.*, **34**, 2584 (1901).

[4] G. Allen, J. Lewis, R. F. Long, and C. Oldham, *Nature*, **202**, 589 (1964).

[5] B. N. Figgis, J. Lewis, R. F. Long, R. Mason, R. S. Nyholm, P. J. Pauling, and G. B. Robertson, *ibid.*, **195**, 1278 (1962).

[6] J. Lewis, R. F. Long, and C. Oldham, *J. Chem. Soc.*, 6740 (1965).

[7] R. A. D. Wentworth and C. H. Brubaker, Jr., *Inorg. Chem.*, **3**, 1472 (1964).

[8] For example, see K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 216.

[9] G. T. Behnke and K. Nakamoto, *Inorg. Chem.*, **6**, 433 (1967).