

papers<sup>10,11</sup> of this series the low relaxation times found for diphenyl ether and several structurally analogous compounds were attributed to dipole orientation through a mesomeric shift of charge accompanying rotation of the phenyl ring within the molecule. An alternative explanation in terms of dipole orientation through molecular inversion, perhaps, accompanied by twisting seemed less probable, though not definitely excluded by the information available. Table III summarizes the values of the relaxation times which have been attributed to ring rotation in diphenyl ether and closely related ethers.

It was the extremely low value found for the relaxation time of diphenyl ether that indicated the relaxation mechanism to be predominantly an intramolecular process, and this indication was strengthened by the smallness of the effect of the great increase in viscosity accompanying change of the solvent from benzene to Nujol.<sup>10</sup> A simple elastic bending of the molecule would be expected to give rise to absorption at much higher frequencies, while a molecular inversion would be expected to absorb at lower frequencies. Rotation of the phenyl group in the molecule accompanied by shift in mesomeric moment seemed to offer a reasonable explanation of the observed absorption. The substitution of a nitro group in the *para* position of the ring should increase the relaxation for rotation by much less than it would for inversion, while the

protusion of a nitro group in the *ortho* position should hinder rotation much more than it would in the *para* position and hinder inversion less than it would in the *para* position. The much higher relaxation time for the intramolecular relaxation of bis-(*o*-nitrophenyl)-ether as compared to that of the *para* compound in Table III points to ring rotation rather than inversion as the intramolecular relaxation process. The low relaxation time for bis-(*p*-bromophenyl)-ether in Nujol and the smallness of the difference between it and the value for the unsubstituted compound in Nujol similarly point to ring rotation as the relaxation mechanism. The shorter of the two relaxation times obtained for cyclohexyl phenyl ether, although longer than the value for diphenyl ether, is significant in showing the presence of an intramolecular relaxation mechanism when only one aromatic ring is present in a molecule of this general type. Further measurements on related compounds are necessary for a fuller understanding of the unexpectedly high values for these two relaxation times.

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## Infrared Spectra of Metal Chelate Compounds. II. Infrared Spectra of Acetylacetonates of Trivalent Metals<sup>1</sup>

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The infrared spectra of acetylacetonates of four trivalent metals have been measured in the range between 4000 and 400  $\text{cm}^{-1}$ . With the application of perturbation theory to a previously worked out normal coordinate treatment of the Cu(II) complex, the vibrational frequencies have been calculated for each metal. 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) complex are somewhat weaker. The band at 490  $\text{cm}^{-1}$  in the Al(III) complex has been assigned to the Al-O stretching mode, based on a study of four Al(III) complexes of various  $\beta$ -diketones. A relatively large force constant of the Al-O stretching mode in these complexes suggests that the bond is strongly covalent.

### Introduction

Studies of the effects of changing the metal on the infrared spectra of metal chelate compounds have been reported on various types of ligands such as  $\beta$ -diketones,<sup>2</sup> acetylacetonate-ethylenediimine and related compounds,<sup>3</sup> 8-hydroxyquinoline,<sup>4</sup> oxalic acid<sup>5</sup> and imidazole derivatives.<sup>6</sup> In these previous investigations, the effect of changing the

metal was deduced in most cases from shifts of the carbonyl bands which frequently can be identified empirically without much ambiguity.

It should be mentioned, however, that such an empirical approach encounters serious difficulties in some cases. For example, it is almost impossible to assign the bands between 1600 and 1400  $\text{cm}^{-1}$  in the metal chelate compounds of  $\beta$ -diketones since: (1) the bond orders of the C=O and the C=C bonds are similar and both absorb in this region and (2) their relative positions are sensitive to a change in the metal. Furthermore, in such a chelate ring system, coupling between various vibrational modes is serious and the concept of "group frequency" is not generally applicable. For example, Bellamy *et al.*,<sup>7</sup> empirically adopted the strongest band in

(1) This work was supported by the Office of Ordnance Research under Contracts No.'s DA-19-020-ORD-3243 and DA-19-020-ORD-5119.

(2) J. Lecomte, *Discussions Farad. Soc.*, **9**, 125 (1950); C. Duval, R. Freymann and J. Lecomte, *Bull. soc. chim. France*, **19**, 106 (1952).

(3) K. Ueno and A. E. Martell, *J. Phys. Chem.*, **59**, 998 (1955); **60**, 934 and 1270 (1956).

(4) R. G. Charles, H. Freiser, R. Friedel, L. E. Hildard and W. D. Johnston, *Spectrochim. Acta*, **8**, 1 (1956).

(5) J. Fujita, K. Nakamoto and M. Kobayashi, *J. Phys. Chem.*, **61**, 1014 (1957).

(6) T. R. Harkins, J. L. Walter, O. E. Harris and H. Freiser, *THIS JOURNAL*, **78**, 260 (1956).

(7) L. J. Bellamy, G. S. Spicer and J. D. H. Strickland, *J. Chem. Soc.*, 4653 (1952); L. J. Bellamy and R. F. Branch, *ibid.*, 4487 (1954).

this range as a carbonyl stretching, whereas Holtzclaw and Collman<sup>8</sup> and West and Riley<sup>9</sup> preferred the highest frequency band for this assignment.

Although previous workers have studied the spectra of a number of metal chelate compounds of  $\beta$ -diketones in the sodium chloride region, no investigations ever have been made in the potassium bromide region. Studies of the spectra in the lower frequency region are highly important in the metal chelate compounds since the metal-ligand absorptions usually appear in this range.

Therefore, it was considered important to measure the spectra with potassium bromide optics and to assign the bands theoretically. In a previous paper,<sup>10</sup> a normal coordinate treatment was carried out on the bis-(acetylacetonato)-Cu(II) complex. In the present work, calculation of vibrational frequencies of acetylacetonates of various metals was carried out by applying the perturbation method to the results of the previous calculations. In the present series of infrared studies on the metal chelate compounds, the effects of (1) changing the metal and (2) of substitution on the chelate ring, will be studied in detail from a theoretical viewpoint. This paper deals with the effect of changing the metal in acetylacetonates of trivalent metals.

### Experimental

**Spectral Measurements.**—A Perkin-Elmer Model 21 infrared spectrophotometer equipped with NaCl and KBr optics was used to obtain the spectra in the range between 4000 and 400  $\text{cm}^{-1}$ . The KBr disk method was employed for the preparation of the sample. Calibration of the frequency reading was made with Polystyrene film (NaCl region), with 1,2,4-trichlorobenzene (KBr region) and with water vapor for both regions.

**Preparation of Compounds.**—All the compounds were prepared according to the methods described in the literature.<sup>11</sup> Purity of each compound was checked by measurements of the melting point and of the ultraviolet spectrum.

### Results and Discussion

**I. Qualitative Discussion.**—Figure 1 illustrates the feature of the spectra of acetylacetonates of Co(III), Cr(III), Fe(III) and Al(III) together with that of Cu(II) for which theoretical band assignments have been made in the previous paper.<sup>10</sup> It is seen that some bands are shifted while others are not shifted by a change in the metal. From the previous theoretical assignments, it is evident that the bands not sensitive to the metal are:  $\text{CH}_3$  degenerate deformation ( $1415 \sim 1385 \text{ cm}^{-1}$ );  $\text{CH}_3$  symmetric deformation ( $1370 \sim 1356$ ); C-H in-plane bending ( $1195 \sim 1190$ );  $\text{CH}_3$  rocking ( $1028 \sim 1020$ ); C- $\text{CH}_3$  stretching ( $937 \sim 930$ ); and C-H out-of-plane bending ( $800 \sim 770$ ) vibrations.

On the other hand, the bands between 700 and 400  $\text{cm}^{-1}$  and between 1600 and 1400  $\text{cm}^{-1}$  are sensitive to the nature of the metal. Our previous normal coordinate treatment indicates that the bands at 684 and 654  $\text{cm}^{-1}$  in the Cu(II) complex are due to the ring deformation plus Cu-O stretching and to C- $\text{CH}_3$  stretching plus Cu-O stretching vibrations, respectively. The band at 455  $\text{cm}^{-1}$

(8) H. F. Holtzclaw and J. P. Collman, *THIS JOURNAL*, **79**, 3318 (1957).

(9) R. West and R. Riley, *J. Inorg. Nuclear Chem.*, **5**, 295 (1958).

(10) K. Nakamoto and A. E. Martell, *J. Chem. Phys.*, **32**, 588 (1960).

(11) See, for example, N. V. Sidgwick, "Chemical Elements and their Compounds," Oxford University Press, London, 1950.

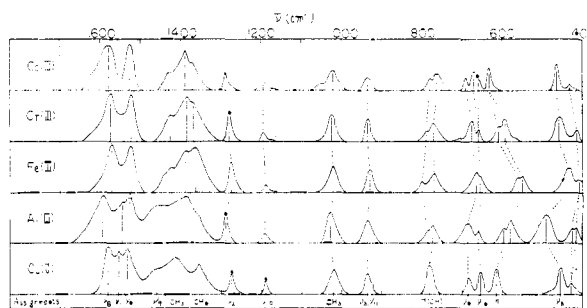


Fig. 1.—Infrared spectra of acetylacetonates of trivalent metals.

also was proved to be an almost pure Cu-O stretching vibration. Thus the band shifts in the lower frequency region between various metals are reasonably understood from the previous band assignments based on the normal coordinate treatment.

The spectra between 1600 and 1400  $\text{cm}^{-1}$  are also metal-sensitive. On an empirical basis, one would expect one C=C and two C=O stretching bands for the 1:1 complex model in this range. Fig. 1 indicates that Co(III), Cr(III) and Fe(III) exhibit three bands whereas Al(III) and Cu(II) exhibit four bands between 1600 and 1400  $\text{cm}^{-1}$ . For reasons mentioned above, however, it is almost impossible to make any reliable empirical assignments in this region, and only a theoretical approach of the type given below can be of value in this respect.

**II. Method of Calculation.**—In the normal coordinate treatment made on the chelate ring of bis-(acetylacetonato)-Cu(II),<sup>10</sup> the result of changing the metal is such that the  $\mathbf{G}$ -matrix is slightly changed from that of the Cu(II) complex, because of variations in the mass of the metal and in the metal-oxygen bond distance.<sup>12</sup> The  $\mathbf{F}$  matrix is also changed since the metal-oxygen stretching force constants as well as other force constants will be altered. It is possible, however, to regard these variations as perturbation terms in the original  $\mathbf{H}^0$  matrix ( $\mathbf{H}^0 = \mathbf{G}^0\mathbf{F}^0$ ) of the Cu(II) complex if their contributions to the new  $\mathbf{H}$  matrix are relatively small. Thus by the use of perturbation theory, one can calculate the approximate frequencies for each metal without solving higher order secular equations.<sup>13</sup> For the Cu(II) complex, the relation

$$(\mathbf{L}^0)^{-1}\mathbf{G}^0\mathbf{F}^0\mathbf{L}^0 = \Lambda^0$$

holds, where 0 denotes the Cu(II) complex. For the chelates of the other metals, the secular equation is given by

$$|\mathbf{H} - \mathbf{E}\lambda| = 0 \quad \text{where} \quad \mathbf{H} = (\mathbf{L}^0)^{-1}\mathbf{G}\mathbf{F}\mathbf{L}^0$$

Since the  $\mathbf{G}$  and  $\mathbf{F}$  matrices of the chelate compounds of the metal, x, are slightly different from those of the Cu(II) complex, the  $\mathbf{H}$  matrix can

(12) A normal coordinate treatment was made on the 1:1 complex of acetylacetonato copper, although the actual complex is a square planar 1:2 chelate. This assumption makes it possible to use the perturbation method for the calculation of vibrational frequencies of the metal chelates of other metals which have various configurations around the central metal. If interactions between ligands is considered, however, all the metal-oxygen stretching force constants will be slightly decreased (see ref. 10).

(13) E. B. Wilson, J. C. Decius and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., New York, N. Y., 1955, p. 229.

TABLE I

COMPARISON OF OBSERVED AND CALCULATED FREQUENCIES IN METALLIC ACETYLACETONATES (CM. <sup>-1</sup> )											
Obsd.	Co(III)		Cr(III)		Fe(III)		Al(III)		Cu(II)		Predominant modes
	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.		
1578	1576	1575	1576	1572	1575	1590	1590	1580	1580	1580	C=C str. ( $\nu_8$ )
1527	1532	1524	1531	1526	1529	1545	1548	1554	1544	1544	C=O str. ( $\nu_1$ )
						1530		1534			
1430	1480	1427	1480	1425	1477	1466	1487	1464	1489	1489	CO str. + CH bend. ( $\nu_9$ )
1390	..	1385	..	1390	..	1387	..	1415	..	..	CH <sub>3</sub> deg. def.
1372	..	1370	..	1365	..	1387	..	1356	..	..	CH <sub>3</sub> sym. def.
1284	1263	1281	1263	1276	1262	1288	1250	1274	1264	1264	CC str. + CCH <sub>3</sub> str. ( $\nu_2$ )
1195	1224	1195	1224	1190	1221	1191	1222	1190	1226	1226	C-H in-plane bend. ( $\nu_{10}$ )
1022	..	1025	..	1022	..	1028	..	1020	..	..	CH <sub>3</sub> rock.
934	936	934	935	930	926	935	939	937	936	936	CCH <sub>3</sub> str. + CO str. ( $\nu_3$ )
		902		901		895		885		901	CCH <sub>3</sub> str. ( $\nu_{11}$ )
780	..	788	..	800	..	773	..	781	..	..	C-H out-of-plane bend.
771		772		770							
764											
691	671	677	667	663	648	685	675	684	659	659	Ring def. + M-O str. ( $\nu_4$ )
671	641	658	638	654	602	658	645	654	628	628	C-CH <sub>3</sub> bend + M-O str. ( $\nu_{12}$ )
662											
633	..	609	..	559	..	594	..	614	..	..	Out-of-plane?
		594		549		577					
466	465	459	461	434	433	490	494	455	457	457	M-Ostr. ( $\nu_5$ )
432	..	416	..	411	..	425	..	427	..	..	Out-of-plane?
						416					
..	373	..	373	..	373	..	373	..	373	373	Ring def. ( $\nu_{13}$ )
..	311	..	307	..	273	..	320	..	302	302	M-O str. ( $\nu_{14}$ )
..	276	..	277	..	265	..	281	..	272	272	C-CH <sub>3</sub> bend ( $\nu_6$ )
..	200	..	202	..	199	..	202	..	197	197	Ring def. ( $\nu_7$ )

be written as

$$H = (L^0)^{-1}(G^0 + \Delta G_x)(F^0 + \Delta F_x)L^0 \\ = \{\tilde{L}^0 + (L^0)^{-1}\Delta G_x\} \{(\tilde{E}^0)^{-1}A^0 + \Delta F_x L^0\}$$

The approximate frequencies are calculated from the equation

$$\lambda_i = H_{ii} + \sum_k^k \frac{H_{ik}H_{ki}}{H_{ii} - H_{kk}}$$

In practice, the metal-oxygen bond distance in the  $G$  matrix was taken from the available structural data or otherwise estimated by taking an intermediate value between ionic and covalent radii. Small variation of these values would not cause serious errors in estimating the force constants. In the  $F$  matrix, only the M-O (metal-oxygen) and C=O stretching force constants were considered to be variable as a first approximation. Evidently such an assumption does not give satisfactory results in the vibrations involving C=C stretching, C-CH<sub>3</sub> stretching and other bending modes. In spite of this expectation, only these two force constants were adjusted to obtain the best agreements with the observed values since variations of other force constants are essentially small, and this paper mainly concerns the relative shifts of the metal-sensitive bands in a series of acetylacetonates of various metals.

Most of the computations have been made with the I.B.M. 704 computer. The mass, bond distance and the force constant used in the calculations are listed in Table II.<sup>14</sup> Table I lists the calculated and observed frequencies in each metal.

(14) Refinements of the force constants also were made for Cu(II). Thus the force constants of Cu(II) listed in Table II are slightly different from those previously reported.

TABLE II

MASS, BOND DISTANCE AND FORCE CONSTANT IN ACETYLACETONATES OF TRIVALENT METALS

Throughout the calculations,  $K(\text{C}=\text{C}) = 5.35$ ,  $K(\text{C}-\text{CH}_3) = 3.60$  were used. Other force constants are the same as before.<sup>10</sup>

Metal	At. wt.	Metal-oxygen distance (Å.)	Force const. (10 <sup>6</sup> dyne/cm.)	
			$K(\text{M}-\text{O})$	$K(\text{C}=\text{O})$
Co(III)	58.94	1.95	2.40	6.70
Cr(III)	52.01	1.95	2.30	6.70
Fe(III)	55.85	1.95	1.65	6.70
Al(III)	26.98	1.90	2.60	6.80
Cu(II)	63.54	1.95	2.20	6.90

It is seen that agreements between these two values are quite satisfactory in view of the approximate nature of the calculation.

**III. Results of the Calculations.**—Table II indicates that the M-O force constants of the Co(III) and Cr(III) complexes are larger and the corresponding C=O force constants smaller than those of the Cu(II) complex. This result suggests that, in the former complexes, the M-O bond orders are relatively higher and C=O bond orders are relatively lower than those of the Cu(II) complex. It is conceivable that partial double bonding due to  $d\pi-p\pi$  overlap is relatively increased in these trivalent metal chelates. On the other hand, the M-O force constant in the Fe(III) complexes is very low, indicating that the Fe-O bonds are weak. This result is consistent with the magnetic data<sup>15</sup> which indicate that the Fe-O bonds in this compound are ionic.

Table I indicates that the calculated frequencies are in perfect agreement with the observed ones for  $\nu_6$  but not for  $\nu_4$  and  $\nu_{12}$  vibrations. This differ-

(15) I. C. Jackson, *Proc. Roy. Soc. (London)*, **A140**, 695 (1935).

ence is due to the fact that  $\nu_5$  is an almost pure M-O stretching vibration, whereas  $\nu_4$  and  $\nu_{12}$  are more complex vibrations, which involve coupling between M-O stretching and other vibrations. By adjusting force constants of bonds other than the M-O and carbonyl groups, somewhat better agreement would probably be obtained. However, the results of the calculations illustrated in Table I are sufficient to show that  $\nu_4$  and  $\nu_{12}$  are metal-sensitive and shift to higher frequencies as the M-O force constant increases. The nature of the bands which occur between  $\nu_{12}$  and  $\nu_5$  in Fig. 1 is not obvious from the present calculations. It is seen, however, that these bands are also metal-sensitive. It is conceivable that they are derived from one of the out-of-plane ring vibrations, which were not treated in the present calculation.

In the region between 1600 and 1400  $\text{cm.}^{-1}$ , more than three bands are observed in all the compounds studied. On the basis of the present calculations, the highest frequency band is assigned to the  $\nu_3$ -vibration (ca. 75% C=C stretching plus 25% C=O stretching modes).<sup>16</sup> Since the main character of the bands is C=C stretching, the fact that their frequencies are the least sensitive of this group of bands to the nature of the metal is understandable. The second highest frequency band is assigned to  $\nu_1$ -vibration (ca. 75% C=O stretching plus 25% C=C stretching) and is more sensitive to a change in the metal than  $\nu_3$ -vibration. As is seen in Table I, two bands at 1545 and 1530  $\text{cm.}^{-1}$  in the Al(III) complex and at 1554 and 1534  $\text{cm.}^{-1}$  in the Cu(II) complex were tentatively assigned to the  $\nu_1$ -vibration. The lowest frequency band is assigned to the  $\nu_9$ -vibration (50% C=O stretching plus 50% C-H in-plane bending), although the calculated frequency is always higher than the observed values. This may be due to the fact that the C-H in-plane bending force constant is slightly

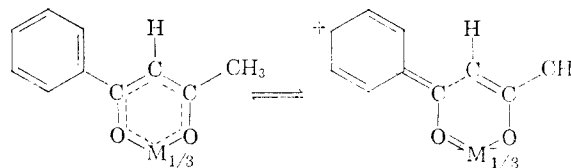
(16) The fact that the highest frequency band in this range is a C=C stretching and not a C=O stretching vibration would be difficult to predict on an empirical basis. However, this result is theoretically quite reasonable because: (1) the C=O bond orders are considerably lowered in the chelate ring and (2) the coupling between two relatively isolated C=O stretching modes is weak, whereas the coupling between two adjacent C=C stretching modes is relatively strong.

high. Since the  $\nu_9$ -band is partly overlapped by a strong  $\text{CH}_3$  degenerate deformation mode (1415 ~ 1390  $\text{cm.}^{-1}$ ), the band maxima are sometimes obscure.

**Aluminum-Oxygen Bond.**—Table I indicates that the band at 490  $\text{cm.}^{-1}$  in the Al(III) complex is an Al-O stretching band and the corresponding force constant is  $2.60 \times 10^6$  dyne/cm. (Table II). This value is larger than that of the Cu-O bond which has partial double bond character. Thus we conclude that the Al-O bond is strongly covalent although different from the transition metals in that  $d\pi$ - $p\pi$  bonding does not occur.

In order to confirm the band assignment, the infrared spectra of three Al(III) complexes of various  $\beta$ -diketones were compared. Since all three compounds (the 1:3 chelates of acetylacetonone, benzoylacetonone and dibenzoylmethane with Al(III)) exhibit absorptions between 490 and 450  $\text{cm.}^{-1}$  which do not exist in the free ligands, the assignments on the Al-O bonds are supported by these additional data. In this connection it should be noted that the band at 483  $\text{cm.}^{-1}$  in aluminum oxalate which was not assigned previously<sup>5</sup> now can be assigned to the Al-O stretching mode.

It was also observed that the Al-O stretching band shifts to lower frequency as the methyl group of acetylacetonone is replaced by the phenyl group. As will be discussed in a subsequent publication the same band shifts to higher frequency by the same substitution in the case of transition metal chelates. It is conceivable that the resonance involving  $d\pi$ - $p\pi$  bonding such as



does not occur in the Al(III) complexes.

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## Products of the Thermal Decomposition of Some Cobalt Ammine Azides

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The thermal decompositions of solid  $[\text{Co}(\text{NH}_3)_6](\text{N}_3)_2$ ,  $[\text{Co}(\text{NH}_3)_5\text{N}_3](\text{N}_3)_2$ , *cis*- and *trans*- $[\text{Co}(\text{NH}_3)_4(\text{N}_3)_2]\text{N}_3$  and  $\text{Co}(\text{NH}_3)_5(\text{N}_3)_2$  at 120 to 150° have been studied and the products characterized. The first four compounds behave similarly. Under varying conditions smooth reactions can yield  $\text{N}_2$ ,  $\text{NH}_3$  and  $\text{CoN}$  or  $\text{Co}(\text{NH}_3)_2(\text{N}_3)_2$ . Alternately explosions to  $\text{Co}$ ,  $\text{N}_2$ ,  $\text{NH}_3$  and  $\text{H}_2$  can occur. The triammine differs, exploding violently with no evidence of preliminary reactions.

### Introduction

Recent reviews summarize the information available on the reactions of azide compounds.<sup>2-4</sup> In brief, two principal types of azides are most often

(1) Ohio State University, Columbus, Ohio.

(2) W. E. Garner, "Chemistry of the Solid State," Butterworths Scientific Publications, London, 1955, Chap. 9.

studied: covalent azides (*i.e.*,  $\text{HN}_3$ ,  $\text{CH}_3\text{N}_3$ ) in which the azide group is associated with a single molecule and simple metal azides with the

(3) F. P. Bowden and A. D. Yoffe, "Fast Reactions in Solids," Academic Press, Inc., New York, N. Y., 1958.

(4) B. L. Evans, A. D. Yoffe and P. Gray, *Chem. Revs.*, **59**, 515 (1959).