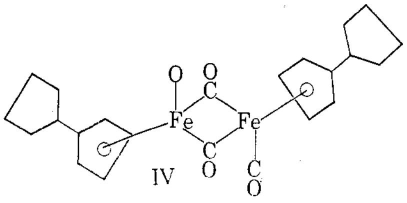
TABLE III

ULTRAVIOLET SPECTRA

Compound	ϵ_{220}	$\lambda_{\text{shoulder}}$, mμ	$\epsilon_{\text{shoulder}}$	$\lambda_{\max}$, mμ	$\epsilon_{\max}$
$C_{10}H_{14}Fe(CO)_3$	2.3×10^4	228	2.2×10^4	313	2.3×10^3
$C_{12}H_{18}Fe(CO)_3$	6.7×10^4	233	4.7×10^4	308	2.3×10^3
$C_{14}H_{22}Fe(CO)_3$	6.7×10^4	230	6.0×10^4	297	2.6×10^3

spectrum (carbonyl stretching bands (CS_2 solution, NaCl optics) at 2041, 1996, 1957, and 1783 cm.$^{-1}$) to be di-π-(cyclopentylcyclopentadienyl)tetracarbonyldiiron (IV) analogous to the well-known di-π-cyclopentadienyltetracarbonyldiiron[13] (carbonyl stretching bands (CS_2 solution, NaCl optics) at 2041, 2000, 1957, and 1786 cm.$^{-1}$). We found no evidence that tricarbonyl-(1,1′-bicyclopentenyl)iron(0) could be converted to IV. Thus, the essential rearrangement must have occurred before I was formed.



IV

[13] H. Zeiss, Ed., "Organometallic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1960, Chapter X.

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Metal–Oxygen Bonds in Complexes: Raman Spectra of Trisacetylacetonato and Trisoxalato Complexes of Aluminum, Gallium, and Indium[1]

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The Raman spectra of the complex oxalates and acetylacetonates of aluminum, gallium, and indium have been studied, principally for information on the nature and strength of their metal–oxygen bonds. Highly polarized, low frequency Raman lines have been found which are attributable to the metal–oxygen symmetric stretching modes, and an interesting correlation with the C—O and C═O stretching frequencies is found in the oxalate series. $\partial\bar{\alpha}/\partial Q$ values have been calculated for these M–O bonds from the Raman line intensities and found to be unusually large (Al = 1.33, Ga = 1.37, In = 1.47 Å.^{2} (a.w.)$^{-1/2}$) in the acetylacetonate series, indicating metal–oxygen π-bonding in these very stable complexes.

Metal–oxygen bonds have recently been the subject of much interest in complex coordination compound chemistry, but little application of the powerful technique of Raman spectroscopy has been made to date. A considerable amount of infrared work has been reported dealing with the symmetries and vibrational frequency assignments of coordination compounds of metals with the chelating ligands oxalate, $C_2O_4^{2-}$, and acetylacetonate, $C_5H_7O_2^-$. Assignment of the abundance of spectral lines in such complexes to the normal modes of vibration has been a difficult task, especially in the interesting low frequency region below ∽800 cm.$^{-1}$ where metal–oxygen stretching fundamentals occur. This difficulty has led to contradictions[2–9] in the recent literature over the location of metal–oxygen stretching modes. Correct assignments must precede any calculation of force constants, and hence of metal–oxygen bond strengths. The unique selection rules for Raman spectra and the information on depolarization ratios obtainable with the Raman method are of considerable importance for solving this problem of frequency assignments.

The Raman intensity of the *p*th normal mode of vibration of a molecule, Q_p, is given by the expression

$$I_p = \frac{KM(\nu_0 - \nu)^4}{\nu[1 - \exp(-h\nu/kT)]}\, 45\left(\frac{\partial\bar{\alpha}}{\partial Q_p}\right)^2\left(\frac{6}{6 - 7\rho}\right) \qquad (1)$$

where M is the molar concentration of the species, ν_0 is the Rayleigh frequency, ν is the Raman frequency shift, ρ is the degree of depolarization, $\bar{\alpha}$ is the mean molecular polarizability, and K is a constant. The quantity $\partial\bar{\alpha}/\partial Q_p$ (written $\bar{\alpha}'$ henceforth) is zero for all vibrational modes other than totally symmetric ones, but for these totally symmetric modes $\bar{\alpha}'$ has been shown to be related to the strength and degree of covalency of the bonds being stretched in this *p*th normal mode.[10,11] Evaluation of the quantity $\bar{\alpha}'$ for

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[1] This work was supported by the Directorate of Chemical Sciences, U. S. Air Force Office of Scientific Research.

[2] K. Nakamoto and A. Martell, *J. Chem. Phys.*, **32**, 588 (1960).

[3] K. Nakamoto, R. J. McCarthy, A. Ruby, and A. Martell, *J. Am. Chem. Soc.*, **83**, 1066 (1961).

[4] K. Nakamoto, P. J. McCarthy, and A. Martell, *ibid.*, **83**, 1272 (1961).

[5] C. Djordjevic, *Spectrochim. Acta*, **17**, 448 (1961).

[6] K. E. Lawson, *ibid.*, **17**, 248 (1961).

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

[8] M. J. Schmelz, T. Miyazawa, S. Mizushima, T. J. Lane, and J. V. Quagliano, *Spectrochim. Acta*, **9**, 51 (1957).

[9] J. Fujita, *J. Phys. Chem.*, **61**, 1014 (1957).

[10] L. A. Woodward and D. A. Long, *Trans. Faraday Soc.*, **45**, 1131 (1949).

[11] G. W. Chantry and R. A. Plane, *J. Chem. Phys.*, **32**, 319 (1960).

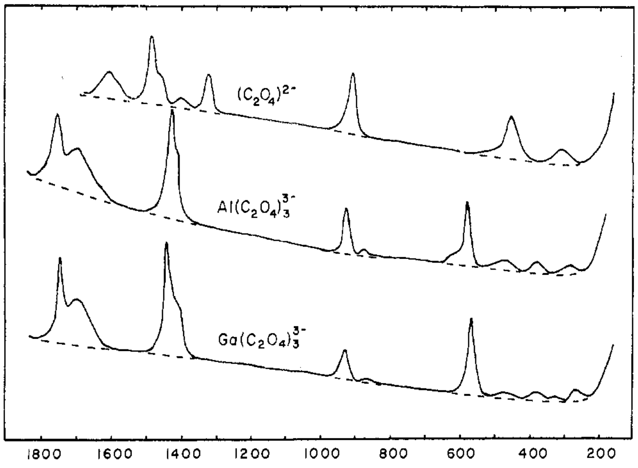

Fig. 1.—The Raman spectra of $(C_2O_4)^{2-}$, $Al(C_2O_4)_3{}^{3-}$, and $Ga(C_2O_4)_3{}^{3-}$.

the metal–oxygen symmetric stretching mode of the analogous oxalate and acetylacetonate complexes should therefore shed light on the nature of the differences in their metal–oxygen bonds and the extent to which the metal atoms in the acetylacetonate complexes are involved in benzenoid-type resonance with the unsaturated ligand rings.

Experimental

The compounds used were synthesized as described below.

Potassium Trioxalatoaluminate, $K_3Al(C_2O_4)_3$.—A near-quantitative yield was obtained from dissolution of freshly precipitated aluminum hydroxide in an aqueous solution of potassium bioxalate.[12] The product was recrystallized from aqueous solution.

Ammonium Trioxalatogallate, $(NH_4)_3Ga(C_2O_4)_3$.—Neogi and Dutt's adaptation of the $K_3Al(C_2O_4)_3$ synthesis was used.[13] The product was recrystallized from aqueous solution.

Potassium Oxalatoindate.—The methods used to produce aluminum and gallium complex oxalates were not successful when adapted to the indium salt. A white crystalline solid was obtained on treating gelatinous $In(OH)_3$ with hot potassium bioxalate solution, but, unlike the Al and Ga products, this precipitate was only sparingly soluble in water. Moeller[14] has analyzed a similar reaction product and found the empirical formula $K_2C_2O_4 \cdot 2K_3[In(C_2O_4)_3)] \cdot 7H_2O$, but concluded that this was in reality a mixture, the only complex indium oxalate present being $K[In(C_2O_4)_2]$.

Aluminum Trisacetylacetonate, $Al(C_5H_7O_2)_3$.—Good yields were obtained by the addition of an ammoniacal solution of freshly distilled acetylacetone (2,4-pentanedione) to an aqueous solution of aluminum sulfate.[15] The pale yellow product was dried and purified by sublimation at *ca.* 156° under 0.5 mm. pressure, followed by two successive recrystallizations from benzene. The crystals obtained in regular hexagonal plate form remained pale yellow.

Gallium and Indium Trisacetylacetonates.—These compounds were obtained in very poor yield from the method used for the aluminum compound. However, near-quantitative yields resulted from the method of Morgan and Drew[16] wherein aqueous ammonia was slowly added to a refluxing mixture of an aqueous solution of the metal sulfate with acetylacetone. Purification was again achieved by recrystallizations from benzene.

Anal. Calcd. for $In(C_5H_7O_2)_3$: C, 43.71; H, 5.14. Found: C, 43.74; H, 5.19. Calcd. for $Ga(C_5H_7O_2)_3$: C, 49.02; H, 5.77. Found: C, 49.08; H, 6.00.

The Raman spectra of the oxalate complexes were obtained from aqueous solutions; those of the acetylacetonates were obtained from both benzene and carbon tetrachloride solutions, two solvents being used to eliminate solvent interferences. A Cary Model 81 Raman spectrophotometer was used to produce the spectra. Polaroid cylinders surrounding the Raman tube were calibrated with CCl_4, $CHCl_3$, CH_2Cl_2, and C_6H_6 liquids and were used for measuring the degrees of depolarization of the Raman lines.

Results

The Raman spectra obtained from near-saturated aqueous solutions of $K_3[Al(C_2O_4)_3]$ and $(NH_4)_3[Ga(C_2O_4)_3]$ are listed in Table I and reproduced in Fig. 1 together with the spectrum of the free oxalate ion obtained from a saturated aqueous solution of $K_2C_2O_4$. The free oxalate spectrum (*e.g.*, 1490 cm.$^{-1}$) was not given by the complex solutions, showing that no appreciable dissociation of the complex ions $[Al(C_2O_4)_3]^{3-}$ and $[Ga(C_2O_4)_3]^{3-}$ took place in the aqueous solutions. The frequency assignments made for the free oxalate ion are on the basis of a nonplanar configuration of D_2 symmetry. For this, a normal coordinate treatment, using a Urey–Bradley force field, has been reported.[8]

TABLE I[a]

RAMAN FREQUENCIES AND ASSIGNMENTS[8,17] FOR THE IONS $(C_2O_4)^{2-}$, $[Al(C_2O_4)_3]^{3-}$, AND $[Ga(C_2O_4)_3]^{3-}$

(1) $(C_2O_4)^{2-}$

Frequency, cm.$^{-1}$	Description	D_2 assignment	Type
310	w, b, dp	$\nu_7(B)$	CO_2 rock
460	m, b, p	$\nu_3(A)$	$\delta(OCO)$
905	m, sh, p	$\nu_2(A)$	$\nu(C—C)$
1315	m, sh, dp	$\nu_{11}(B)$	$\nu_s(C—O)$
1390	w, b, dp	$\nu_9(B)$	CO_2 wag
1450	m, sh, dp	$\nu_6(B)$	CO_2 wag
1490	s, sh, p	$\nu_1(A)$	$\nu_s(C{=}O)$
1600	m, b, dp	$\nu_8(B)$	$\nu_a(C—O)$
1647		$\nu_5(B)$	$\nu_a(C{=}O)$

(2) $[Al(C_2O_4)_3]^{3-}$ and $[Ga(C_2O_4)_3]^{3-}$

Frequencies (cm.$^{-1}$) and description		D_3 assignments	Type
$[Al(C_2O_4)_3]^{3-}$	$[Ga(C_2O_4)_3]^{3-}$		
275 w, dp	265 w, dp	..	CCO, OMO, COM, deformations
...	325 vw, dp	..	
370 w, dp	375 vw, dp	..	
470 w, b, dp	460 vw, b, dp	E	δ
585 m, sh, p	573 s, sh, p	A_1	$\nu_s(M—O)$
600 w, b, dp	...	E	$\nu_a(M—O)$?
865 vw, dp	860 vw, dp	A_1	$\delta(OCO)$
920 m, sh, p	915 m, sh, p	A_1	$\nu(C—C)$
1410 s, sh, dp	1400 s, dp	E	$\nu_a(C—O)$
1420 vs, sh, p	1425 vs, sh, p	A_1	$\nu_s(C—O)$
1685 s, b, dp	1685 s, dp	E	$\nu_a(C{=}O)$
1750 vs, sh, p	1730 s, sh, p	A_1	$\nu_s(C{=}O)$

[a] w, weak; m, medium; s, strong; v, very; sh, sharp; b, broad; p, polarized; dp, depolarized; δ, deformation; ν_s, symmetric stretch; ν_a, asymmetric stretch.

The complex oxalate frequency assignments have been made by an adaptation of the results of a normal coordinate treatment on a 1:1 model, *viz.*

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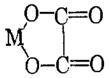
[12] J. C. Bailar, Jr., and E. M. Jones, *Inorg. Syn.*, **1**, 35 (1939).
[13] P. Neogi and N. K. Dutt, *J. Indian Chem. Soc.*, **15**, 83 (1938).
[14] T. Moeller, *J. Am. Chem. Soc.*, **62**, 2444 (1940).
[15] R. C. Young, *Inorg. Syn.*, **2**, 25 (1946).
[16] G. T. Morgan and H. D. K. Drew, *J. Chem. Soc.*, **119**, 1059 (1921).



which has C_{2v} symmetry, to the over-all D_3 symmetry of the whole 1:3 anionic complex.[8,17] Coupling of vibrational modes between the three oxalate groups in a complex is probably only slight except in the case of the metal–oxygen modes, where coupling will obviously be strong. The lines assigned to symmetric stretching of the metal–oxygen bonds are forbidden in the infrared spectrum, but the frequencies, the high intensities, and the low degrees of depolarization of these lines make their assignments in the Raman spectrum quite clear (see Discussion).

In order to characterize more completely the metal–oxygen symmetric stretching modes, their Raman line intensities were measured quantitatively by comparison with internal standards,[11] and these data were used to calculate the $\bar{\alpha}'$ values for the modes. Integrated line intensities were used throughout, the usual precautions being taken to place these on an absolute scale.[11] Accumulated errors in these corrected line intensities probably amount to ±5%, leading to a propagated error in the $\bar{\alpha}'$ values reported of *ca.* ±9%, a figure which does not affect the validity of the conclusions based on the $\bar{\alpha}'$ values. For the aluminum complex it was only possible to measure the combined intensity and polarization of the 585 and 600 cm.$^{-1}$ pair of strongly overlapping lines. The 585 cm.$^{-1}$ symmetric stretch line was polarized, but the other weaker line was obviously depolarized. Equation 1 may be rewritten

$$(\bar{\alpha}')^2 = K''I\left[\frac{6 - 7\rho}{6}\right]$$

where K'' is a constant for the mode considered. Denoting the polarized and depolarized overlapping lines by subscripts 1 and 2, respectively, leaving the combination with no subscript, one may write

$$I = I_1 + I_2$$

and

$$\rho I = \rho_1 I_1 + \rho_2 I_2$$

whence

$$\rho = \frac{\rho_1 I_1 + \rho_2 I_2}{I}$$

Therefore

$$(\bar{\alpha}')^2 = K''I\left[\frac{6 - 7\rho}{6}\right] = K''\left[\frac{6I - 7\rho_1 I_1 - 7\rho_2 I_2}{6}\right]$$

Now since one line is depolarized

$$(\bar{\alpha}')^2 = K''I_1\left[\frac{6 - 7\rho_1}{6}\right]$$

It is seen that the intensity and depolarization measurements of the band combination give the same value for $\bar{\alpha}'$ as the polarized band would alone, provided that the weaker line is completely depolarized.

The solution data, the instrument corrected Raman intensities and depolarization values, and the $\bar{\alpha}'$ values calculated from eq. 1 are given in Table II. The $\bar{\alpha}'$ value used for the nitrate ion internal standard was calculated from the relationship

$$\left(\frac{\partial\bar{\alpha}}{\partial Q}\right)_{NO_3} = \sqrt{3}M_O^{-1/2}\left(\frac{\partial\bar{\alpha}}{\partial r_{N-O}}\right)$$

where M_O is the oxygen atomic weight and r_{N-O} is the mean N–O bond distance. Chantry and Plane's[11] value of $(\partial\bar{\alpha}/\partial r_{N-O}) = 1.64$ Å.^{2} was used.

TABLE II

$[Al(C_2O_4)_3]^{3-}$ AND $[Ga(C_2O_4)_3]^{3-}$ COMPLEXES: DATA FOR AND RESULTS OF CALCULATION FOR METAL–OXYGEN VIBRATIONS

	Al complex	NO_3^- standard	Ga complex	ClO_4^- standard
Concn., M	0.616	0.319	1.32	0.659
$\Delta\nu$, cm.$^{-1}$	585 (+600)	1050	573	940
I, cm.^{2}	56.3	43.8	98.4	71.1
ρ	0.575[a]	0.17	0.27	0.06
$\bar{\alpha}'$, Å. (a.w.)$^{-1/2}$	0.286	0.710	0.441	0.865

[a] Value for combination of bands due to symmetric and asymmetric stretching modes.

Similarly, the $\bar{\alpha}'$ for the perchlorate ion was obtained from

$$\left(\frac{\partial\bar{\alpha}}{\partial Q}\right)_{ClO_4} = 2M_O^{-1/2}\left(\frac{\partial\bar{\alpha}}{\partial r_{Cl-O}}\right)$$

using

$$\left(\frac{\partial\bar{\alpha}}{\partial r_{Cl-O}}\right) = 1.73 \text{ Å.}^2$$

Unlike the oxalate complexes, the trisacetylacetonate complexes of aluminum, gallium, and indium are electrically neutral molecules and are insoluble in water. Benzene was found to be the best solvent for all three complexes, and the Raman spectra given in Table III and Fig. 2 were all obtained from near-saturated solutions of each of the compounds in benzene, though carbon tetrachloride solutions gave the same frequencies and relative intensities of the lines characterizing the complexes. The assignments given are derived from the infrared results,[2–5] with the notable exception of the metal–oxygen stretching mode which, using a molecular model of D_3 symmetry, is forbidden in the infrared. The spectrum of the aluminum complex was obtained from λ 4358 and λ 4047 mercury line excitation, and instrument corrected intensities of Raman lines excited by each of these mercury arc lines were found to be within 3% of each other, thus confirming that no resonance Raman effect was present.

The intensities of the ν_s(M–O) lines from the complex compounds were measured relative to the 610 cm.$^{-1}$ line of the benzene solvent. Though not the most intense benzene line, this line was the closest, in both frequency and intensity, to the ν_s(M–O) lines measured. In order to place the measured Raman line intensities on an absolute scale, the intensity of the 610 cm.$^{-1}$ benzene line was measured relative to the 460 cm.$^{-1}$ $\nu_1(A_1)$ line of carbon tetrachloride by

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(17) J. Fujita, A. E. Martell, and K. Nakamoto, *J. Chem. Phys.*, **36**, 324 (1962).

TABLE III

RAMAN FREQUENCIES AND VIBRATIONAL MODES FROM THE COMPLEXES $Al(acac)_3$, $Ga(acac)_3$, AND $In(acac)_3$ (acac = ACETYLACETONATE)

Line frequencies ($cm.^{-1}$) and description			
$Al(acac)_3$	$Ga(acac)_3$	$In(acac)_3$	Type
220 w, dp	208 vw, dp	230 w, dp	δ(ring), in plane
340 vw	283 vw, dp	...	δ(C–CH)
400 m, sh, dp	420 vw, dp	410 vw, dp	δ(ring), in plane
420 w, dp	...	...	δ(ring), out of plane
465 s, sh, p	460 s, sh, p	444 m, sh, p	ν_s(M–O)
495 mw, sh, dp	525 vw, dp	...	ν_a(M–O)
570 mw, sh, dp	570 w, p	570 w, dp	$C\text{–}C{<}^{C}_{C}$ wag
690 m, sh, sl. p	685 m, dp	675 mw, dp	ν(M–O) + δ(ring) coupled
938 mw, sh, dp	...	...	$\nu(C\text{–}CH_3)$
956 mw, sh, p	950 m, p	940 mw, p	$\nu(C\text{–}CH_3)$ + ν(C–O) coupled
1033 mw, sh, p	1030 w	...	CH_3 rock
1190 ms, sh, dp	1199 m, dp	1205 w, dp	δ(CCH)
1298 vvs, sh, p	1280 vs, p	1273 s, p	ν_s(C–C)
1373 s, sh, dp	1375 s, dp	1373 m, dp	$\delta(CH_3)$
1450 w	1530 vw, dp	...	...
1600 w	...	...	ν(C–O)
2927 vs, sh	2930 vs	2928 m, p	ν(C–H) Fermi resonance
2952 s, sh	2950 m	2950 w, p	doublet

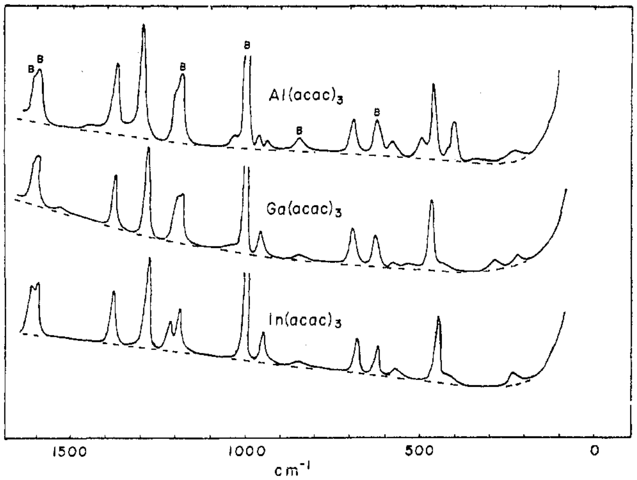

Fig. 2.—The Raman spectra of $Al(acac)_3$, $Ga(acac)_3$, and $In(acac)_3$ (acac = $C_5H_7O_2$; B = benzene solvent line).

running the spectrum of a benzene–carbon tetrachloride (10:1 volume) liquid mixture. This gave a result, corrected for frequency and instrument sensitivity, of $(I_{610}/I_{460}) = 0.0918$, where the I values are molar intensities. However, it has recently been shown that the molar intensities of benzene and of carbon tetrachloride are mutually distorted in mixtures of these two liquids, due to some form of strong intermolecular association, though no such distortion is found from mixtures of each of these solvents with cyclohexane.[18] Accordingly, the ratio (I_{610}/I_{460}) was redetermined indirectly from a 1:10 volume cyclohexane–benzene mixture and a 1:2 volume carbon tetrachloride–cyclohexane mixture. In the region of interest, cyclohexane gave Raman lines at 380 (w, p), 425 (w, dp), 805 (vs, p), 1028 (s, dp), and 1160 (m, p) $cm.^{-1}$. The intensity of the 805 $cm.^{-1}$ line was used as the intermediate for the benzene–carbon tetrachloride comparison, whereby the frequency and sensitivity corrected indirect ratio $(I_{610}/I_{460}) = 0.140$ was obtained. The original, direct ratio is seen to be 34% low. Using this indirect intensity ratio and Chantry and Plane's[11] value for $(\partial\bar{\alpha}/\partial r_{C-Cl}) = 2.00$ Å.^{2} to obtain $(\partial\bar{\alpha}/\partial Q)$ for carbon tetrachloride from the relation

$$\left(\frac{\partial\bar{\alpha}}{\partial Q}\right)_{CCl_4} = 2M_{Cl}^{-1/2}\left(\frac{\partial\bar{\alpha}}{\partial r_{C-Cl}}\right)$$

the $\bar{\alpha}'$ values for each of the complex acetylacetonates were calculated. Table IV summarizes the essential data and results from these experiments.

TABLE IV

DATA FOR AND RESULTS OF $\bar{\alpha}'$ CALCULATION FOR METAL–OXYGEN VIBRATIONS IN $Al(acac)_3$, $Ga(acac)_3$ AND $In(acac)_3$

	Al	Ga	In	CCl_4
Concn., M	0.842	0.852	0.757	...
Δ, $cm.^{-1}$	465	460	444	460
Molar (I_{M-O}/I_{CCl_4})	5.48	6.74	7.00	1.00
ρ	0.24	0.28	0.27	0.06
$\bar{\alpha}'$, Å.^{2} (a.w.)$^{-1/2}$	1.33	1.37	1.47	0.671

Discussion

The spectra of the aluminum and gallium oxalate complexes resemble each other very closely, the difference observed being largely due to the different masses of the metal atoms. Thus, as predicted, the difference in masses of the metal atoms causes the metal–oxygen asymmetric stretching modes, wherein the metal moves, to be shifted more than the symmetric stretching mode, wherein the metal remains stationary. The latter shift may be taken as an indication of the relative metal–oxygen bond strengths. Summarizing the most significant spectral features, *viz.*

	Al	Ga
M—O sym. stretch, $cm.^{-1}$	585	573
C—O sym. stretch, $cm.^{-1}$	1420	1425
C═O sym. stretch, $cm.^{-1}$	1750	1730

It appears that the Ga—O bond is very slightly weaker than the Al—O bond, and that the shifts in the C—O

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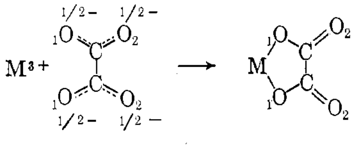
[18] Yu. G. Borok'ko and Ya. K. Syrkin, *Opt. Spectry.*, **9**, 358 (1960).

and C═O bond frequencies can accordingly be explained by the following model.


I II

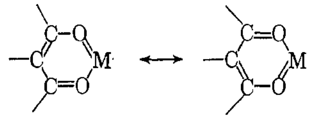
I and II represent the extremes of no bonding and full covalent bonding, respectively, of metal to oxygen. I incorporates a planar oxalate ion wherein the carbon–oxygen bonds are all equivalent, C═O indicating one and one half bonds between the atoms. Using this model, as the metal–oxygen bond strength increased, so the $C—O_1$ bonds would weaken and the $C═O_2$ bonds become stronger. Taking the symmetric stretching frequencies as a measure of bond strength, the results are seen to be explained by this hypothesis, at least in a qualitative manner, though the differences in bond strengths between the aluminum and gallium complex oxalates are obviously only very small.

For acetylacetonate complexes, primary information on bond characteristics is obtained from Raman intensity measurements. For this $\partial\bar{\alpha}/\partial r$ values rather than the $\bar{\alpha}'$ ($=\partial\bar{\alpha}/\partial Q$) values calculated should properly be used.[11] However, assuming a simple MO_6 model for the acetylacetonate complexes, the transformation is of the form

$$\left(\frac{\partial\bar{\alpha}}{\partial Q}\right)_{MO_6} = \sqrt{6}M_O{}^{-1/2}\left(\frac{\partial\bar{\alpha}}{\partial r_{M-O}}\right)$$

Comparing this with the analogous equation for CCl_4 given earlier, it is apparent that like the $\partial\bar{\alpha}/\partial Q$ values given, the $\partial\bar{\alpha}/\partial r$ values for the complex acetylacetonates will be unusually high compared with the corresponding values for the oxalate complexes given in Table II. One way in which the increased $\bar{\alpha}'$ could not indicate increased $\partial\bar{\alpha}/\partial r$ for acetylacetonates is for the effective mass of O to be larger for the oxalates, but this possibility seems most unlikely. Another possibility which must be considered is that the vibrational modes assigned as ν_s(M–O) involve some contribution from other motions within the molecules, such as ring deformations. However, the sharp, polarized nature of these lines (see Tables II and IV and Fig. 1 and 2) together with their close correspondence in frequency with similarly assigned lines from infrared spectra[2-6] indicates that this possibility also is unlikely. The absence of other highly polarized lines in the close vicinity of these ν_s(M–O) lines, and the lack of intensity enhancement in the oxalate complexes (note the similar ρ values for the ν_s(M–O) lines in the oxalate and acetylacetonate series), further supports this conclusion.

The large values of $\bar{\alpha}'$ obtained for the acetylacetonates are consistent with the great stability of these compounds relative to acetylacetonates of a wide range of transition metals studied by various workers using the infrared technique.[2-5] A structure involving benzenoid resonance in each of the acetylacetonate–metal rings has been suggested by Calvin and Wilson[19] to explain the high stability of some transition metal acetylacetonates (*e.g.*, Co(III), Cr(III), Pd(II)), *viz.*



Holm and Cotton[20] have elaborated this in proposing donation of electrons from oxygen to the metal (O pπ → M dπ), donation in the opposite direction being less likely since oxygen has no vacant orbitals. Aluminum, gallium, and indium have no unfilled inner d-orbitals to take part in pπ–dπ bonding of this type, but in view of the Raman data obtained it appears likely that outer d-orbital hybridization plays a significant part in the stabilization of the acetylacetonates of these metals. That large values of $\bar{\alpha}'$ are associated with π-bonding has been well established by Chantry and Plane.[11] Additional evidence for this type of metal–oxygen π-bonding in analogous compounds is provided by n.m.r. results.[21]

Table IV shows an increase in $\bar{\alpha}'$ for the metal–oxygen vibrations in the complex acetylacetonate series in going from aluminum ($\bar{\alpha}' = 1.33$), to gallium ($\bar{\alpha}' = 1.37$), to indium ($\bar{\alpha}' = 1.47$), which is much less marked than the corresponding increase in the complex oxalates of aluminum ($\bar{\alpha}' = 0.286$) and gallium ($\bar{\alpha}' = 0.441$). This difference in behavior can also be accounted for by the π-bonding proposal made above for the acetylacetonate series in the following manner. First it must be recognized that the quantity $\bar{\alpha}'$ associated with the metal–oxygen stretches is made up of contributions from the polarizability derivatives of both bonding and nonbonding electrons.[10] In going from aluminum (atomic number 13) to gallium (atomic number 49) the effect of increasing atomic polarizability is manifested in the increasing $\bar{\alpha}'$ values found for both series of complexes, but the additional contribution of the π-bonding minimizes the effect in the acetylacetonates. The small frequency differences between the metal–oxygen vibrations within each of the series can be taken as evidence of very similar metal–oxygen bond force constants for the complexes within each of the series.

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[19] M. Calvin and K. W. Wilson, *J. Am. Chem. Soc.*, **67**, 2003 (1945).
[20] R. H. Holm and F. A. Cotton, *ibid.*, **80**, 5658 (1958).
[21] R. E. Hester, *Chem. Ind.* (London), 33 (1963).