Reactions of Co-ordinated Molecules. Part 9.† Calculation of Carbonyl-stretching Force Constants of Metallo-acetylacetonate Molecules: Evidence supporting Intramolecular π Bonding

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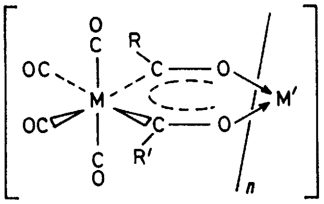
The carbonyl-stretching force constants of three complexes containing the metallo-acetylacetonate moiety, *cis*-$[Al\{(OCMe)_2M(CO)_4\}_3]$ and *cis*-$[Re(MeCO \cdots H \cdots OCMe)(CO)_4]$ (M = Mn or Re), have been calculated using the Cotton–Kraihanzel approximation. The results permit the assignment of the normal modes of the carbonyl ligands of the metallo-acetylacetonate group to the experimentally observed stretching frequencies. The values of the force constants, k_2, are related to the magnitude of the intramolecular bonding between the two axial-carbonyl ligands and the metallo-acetylacetonate ligand. Laser Raman data are presented to support the band assignment.

In earlier papers of this series we reported the preparation and characterization of a number of complexes of the type shown below which contain the metallo-β-diketonate group, *cis*-$(OC)_4M(RCO)(R'CO)$, where M = Mn or Re.[1-3] The metallo-β-diketonate ligand is isoelectronic and isostructural with a β-diketonate



ligand, and it represents the formal substitution of the methine group of a β-diketonate anion by the metal complex, *cis*-$[M(CO)_4]$. When $M' = Al$ or Ga, $n = 3$, and a tris-chelate complex is formed. If $M' = H^+$, then $n = 1$ and the neutral metallo-β-diketone molecule is isolated as the enol tautomer.

The i.r. spectra of these complexes in the terminal carbonyl region have four bands indicating that the local-oscillator approximation holds. Each metallo-β-diketonate ligand acts as an isolated *cis*-$[M(CO)_4L_2]$ complex. With this assumption, the four observed frequencies were assigned tentatively to the four i.r.-active normal modes using qualitative reasoning based on the relative intensities of the bands.[3] However, the assignment of two of the four bands was particularly uncertain because of their closeness in frequency and an angular distortion of two of the carbonyl ligands.

The present paper utilizes the Cotton–Kraihanzel approximation to calculate the stretching force constants of the carbonyl ligands of three metallo-acetylacetonate complexes (R, R' = Me). For each complex, only one of the six possible assignments is correct and the same assignment holds for all the three complexes. Laser Raman data support this assignment. A comparison of the values of the force constants indicates a possible correlation of the value of the axial-carbonyl force constant with the degree of bonding between the π-electron system of the metallo-acetylacetonate ligand and these two carbonyl ligands.[4]

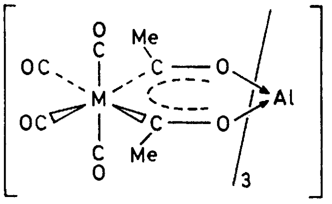
EXPERIMENTAL

The complexes *cis*-$[Al\{(OCMe)_2Mn(CO)_4\}_3]$ (1), *cis*-$[Al\{OCMe)_2Re(CO)_4\}_3]$(2), and *cis*-$[Re(MeCO \cdots H \cdots OCMe)(CO)_4]$ (3) were prepared by literature procedures.[1-3] The i.r. spectra were recorded on a Perkin-Elmer 727 spectrometer of *ca.* 0.01 mol dm^{-3} solutions in cyclohexane in 0.1-mm sodium chloride cavity cells using the pure solvent as a reference. Band wavenumbers are reported in cm^{-1} and were calibrated with a polystyrene film. The wavenumbers of complex (1) obtained in this way were within 2 cm^{-1} of the values obtained *via* calibration with gaseous CO and DCl.

Laser Raman spectra were recorded on a Beckman model 700 laser Raman spectrometer using a 2-W argon laser having a green line at 5 145 Å. The Raman spectra and polarization measurements were recorded in benzene–methylene chloride (9 : 1) and benzene solutions for complexes (2) and (3), respectively. Solutions of complex (1) decomposed within 30 s when exposed to the laser beam. The polarization ratio, ρ, was calculated by normal procedures.[5]

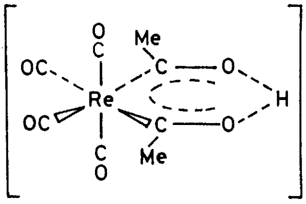
RESULTS AND DISCUSSION

The three complexes studied are shown below:



(1) M = Mn

(2) M = Re



(3)

The carbonyl region of the i.r. spectrum of (1) has been displayed previously[3] and consists of four bands, A—D, where A is the band of highest frequency. The spectra of the other two complexes have nearly identical patterns with some slight differences in band frequencies. Each $M(CO)_4$ group of (1) and (2) is independent of the other two identical groups since coupling between the carbonyl oscillators of different $M(CO)_4$ groups is not

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† Part 8; C. M. Lukehart and G. P. Torrence, *Inorg. Chem.*, 1978, **17**, in the press.

[1] C. M. Lukehart, G. P. Torrence, and J. V. Zeile, *J. Amer. Chem. Soc.*, 1975, **97**, 6903.

[2] C. M. Lukehart and J. V. Zeile, *J. Amer. Chem. Soc.*, 1976, **98**, 2365.

[3] C. M. Lukehart, G. P. Torrence, and J. V. Zeile, *Inorg. Chem.*, 1976, **15**, 2393.

[4] C. M. Lukehart and G. P. Torrence, *Inorg. Chim. Acta*, 1977, **22**, 131.

[5] S. K. Freeman, 'Applications of Laser Raman Spectroscopy,' Wiley, New York, 1974, p. 29.

observed. The local-oscillator approximation applies and each $M(CO)_4$ moiety can be treated as a *cis*-disubstituted octahedral complex of the type, *cis*-$[M(CO)_4L_2]$, possessing C_{2v} symmetry. The observed frequencies for each complex are shown in Table 1.

TABLE 1

Observed carbonyl-stretching bands of the complexes (1)—(3) in cyclohexane solution

	Band (cm^{-1})			
Complex	A	B	C	D
(1)	2 065m	1 985s(sh)	1 978s	1 960m
(2)	2 048m	1 989s(sh)	1 982s	1 959m
(3)	2 099m	2 000s(sh)	1 993s	1 962m

The *cis*$[M(CO)_4L_2]$ spectrum is characterized by four i.r. active carbonyl-stretching modes. Following the qualitative work of Orgel [6] and the quantitative study of Cotton,[7] the four bands can be assigned tentatively. The two axial-carbonyl ligands, which lie out of the ML_2 plane, give two bands ($A_1^{(2)}$ and B_1 symmetry) where the $A_1^{(2)}$ band is of higher frequency and much weaker intensity than the B_1 band. The two equatorial-carbonyl ligands, which lie in the ML_2 plane, also give two bands ($A_1^{(1)}$ and B_2 symmetry) where both peaks have nearly equal intensity. Unfortunately, the relative positions of these two sets of bands cannot be predicted from symmetry considerations alone. The tentative assignment of the bands observed for complex (1) is: peak A ($A_1^{(2)}$, axial); peak B ($A_1^{(1)}$, equatorial); peak C (B_1, axial); and peak D (B_2, equatorial).

TABLE 2

The calculated force constants and B-band frequency for each assignment of the complexes (1)—(3)

		Observed bands and assignments				Force constants/Nm^{-1}			
Complex		$A_1^{(2)}$	$A_1^{(1)}$	B_1	B_2	k_1	k_2	k_i	Calculated wavenumber of band B (cm^{-1})
(1)	1	A	C	B	D	*	*	*	
	2	A	B	D	C	1 611	1 613	31	1 987
	3	A	D	B	C	1 621	1 531	41	1 895
	4	A	C	D	B	1 589	1 616	32	1 964
	5	A	D	C	B	1 546	1 639	30	1 938
	6	A	B	C	D	1 580	1 637	28	1 978
(2)	1	A	C	B	D	*	*	*	
	2	A	B	D	C	1 612	1 601	25	1 986
	3	A	D	B	C	1 619	1 527	33	1 902
	4	A	C	D	B	1 600	1 602	26	1 974
	5	A	D	C	B	1 543	1 633	23	1 940
	6	A	B	C	D	1 572	1 631	22	1 975
(3)	1	A	C	B	D	*	*	*	
	2	A	B	D	C	1 644	1 634	40	2 001
	3	A	D	B	C	1 656	1 521	52	1 873
	4	A	C	D	B	1 622	1 637	41	1 979
	5	A	D	C	B	1 545	1 679	37	1 933
	6	A	B	C	D	1 590	1 675	36	1 986

* Imaginary roots obtained.

This assignment requires a quantitative confirmation for two reasons. First, the spectra of most, if not all, of the previously reported *cis*-$[M(CO)_4L_2]$ complexes show the C band as the weaker shoulder of the more intense B band giving an assignment: A ($A_1^{(2)}$, axial); B (B_1, axial); C ($A_1^{(1)}$, equatorial); and D (B_2, equatorial).[8] Secondly, the *X*-ray structural determinations of (1) and (3) reveal that the two axial-carbonyl ligands are tilted toward the plane of the metallo-acetylacetonate ligand thereby defining a co-ordination axis which deviates significantly from 180°.[1,2]

In complex (1), the C(axial)–Mn–C(axial) angle of 156.3° is 9.1° more bent than the other two axes of the co-ordination octahedron, whilst in complex (3) the C(axial)–Re–C(axial) angle of 170.6° is 7.7° more bent than the other two co-ordination axes. This pronounced tilting should cause the A_1(axial) band to gain intensity at the expense of the B_1 (axial) band, which contributes more uncertainty to the correct assignment of bands B and C. We undertook a quantitative study of these spectra to resolve these questions.

The secular equations as derived from the Cotton–Kraihanzel approximation for the *cis*-$[M(CO)_4L_2]$ complex were taken from the literature.[9] The three carbonyl-stretching force constants which must be determined are k_1 (equatorial CO), k_2 (axial CO), and k_i (the interaction force constant).

The correct assignment is obtained by the following procedure.[9] The frequencies of A, C, and D are used to calculate k_1, k_2, and k_i. Band B is not used because it is a shoulder and the observed frequency is probably the most inaccurate (too high in this case). Since the highest-energy mode must be the $A_1^{(2)}$ band, there are six possible combinations of assignments for the other three bands.[9] The force constants are calculated for each assignment. The correct assignment is the one having real positive values for the force constants where k_2 is significantly greater than k_1 and where the calculated frequency for band B is closest to the experimental value. Table 2 shows the calculated force constants and band

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[6] L. E. Orgel, *Inorg. Chem.*, 1962, **1**, 25.

[7] F. A. Cotton, *Inorg. Chem.*, 1964, **3**, 702.

[8] C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, 1963, **2**, 533.

[9] F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, 1962, **84**, 4432.

B frequency for all six possible assignments of each complex.

Assignment (1) of each complex gives imaginary roots and can be neglected, (2) and (3) have k_2 either less than or nearly equal to k_1 and can be eliminated, and (4) and (5) have either k_2 being very nearly equal to k_1 or a very low calculated value for band B. Assignment (6) of each complex meets all the above criteria, and is therefore the correct assignment. The calculated value of the wavenumber of band B is lower than the observed value for each complex [by 7 cm^{-1} for complex (1) and by 14 cm^{-1} for complexes (2) and (3)]. This trend is expected and it should be stressed that all the computational and theoretical error is absorbed by this frequency.[9] The quantitative assignment is in agreement with the previous qualitative assignment.[3]

The laser Raman data for complexes (2) and (3) support this assignment. Complex (3) gave the better Raman spectrum due to its excellent solubility in benzene. In the Raman spectrum of (3), peak A was the most intense peak in the carbonyl region, and peak B was more intense than C or D although B and C were not completely resolved. This is strong empirical evidence that peaks A and B are the totally symmetric vibrations.[10] Also peak A was a polarized band, $\rho = 0.41$, thereby confirming it as an A_1 vibrational mode.

Even though complex (2) was not very soluble, peak A was visible in the Raman spectrum, and this peak was polarized also, $\rho = 0.57$, thus providing strong evidence that the peak of highest frequency is a totally symmetric vibration. Solutions of this complex showed slight decomposition within 5 min of exposure to the laser beam. The rapid decomposition of complex (1) in the laser beam prevented its analysis by laser Raman spectroscopy.

Since complexes (1)—(3) are quite similar one would not expect a large spread in the values of the individual force constants. The values of k_1 and k_i fall within the ranges $1\,580 \pm 10$ and 29 ± 7 Nm^{-1} respectively, the uncertainty being that usually considered as normal in the Cotton–Kraihanzel method. The substitution of a proton for an aluminium ion or a rhenium atom for manganese does not significantly affect the value of k_1. However, the value of k_2 for the metallo-enol complex, (3), is 41 Nm^{-1} larger than the average value of k_2 ($1\,634 \pm 3$ Nm^{-1}) for the two aluminium complexes, (1) and (2). This is a significant difference. If the value of a force constant reflects bond order, then it appears that the C–O bonds of the axial-carbonyl ligands of complex (3) are of higher bond order than the C–O bonds of those ligands of complexes (1) and (2).

This result may support our explanation of the tilting of these axial-carbonyl ligands in complexes (1) and (3).[4] According to this bonding mechanism, the C–O bond order of the axial-carbonyl ligands of complex (1) should be reduced relative to complex (3). This is the trend observed in the values of k_2 for these complexes. Presumably, complex (2) would show a tilting of the axial-carbonyl ligand of the same degree as found in complex (1).

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[7/095 *Received*, 19*th January*, 1977]

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[10] J. Tang and A. C. Albrecht, ' Raman Spectroscopy,' vol. 2, ed. H. A. Szymanski, Plenum, New York, 1970, p. 58.