Vibrational M–O Bands of Acetylacetone–Metal Complexes

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The Raman spectra of normal and ^{18}O-labelled trisacetylacetonatochromium(III) were measured in the 100—1 600 cm^{-1} region using a laser source. Since the *ca.* 355 cm^{-1} band is hardly affected by ^{18}O-labelling it cannot be due to a Cr–O stretching vibration as suggested on the basis of ^{50}Cr–^{53}Cr shifts. The predominantly antisymmetrical Cr–O stretching (a_2 and e) vibrations are assigned to the normal complex i.r. absorption band at 592 cm^{-1}.

THE bands appearing in the i.r. absorption spectra of powdered trisacetylacetonato-chromium(III) and -manganese(III) at *ca.* 592, and 592 and 566 cm^{-1}, respectively, were assigned [1] to an M–O stretching mode of vibration of these complexes on the basis of the high $^{16}O_2$–$^{18}O_2$ isotopic shifts observed for these bands, which amount to 15—19 cm^{-1}. The parallel 614 cm^{-1} band of bisacetylacetonatocopper(II) was assigned similarly on the basis of its (16 and 17 cm^{-1}) isotopic shifts to 598 and 597 cm^{-1} in the case of the [$^{18}O_2$]- and [2,4-$^{13}C_2$,$^{18}O_2$]-isotopomers, respectively.[2] Junge and Musso also attributed the 678 cm^{-1} absorption band of the palladium complex ($^{16}O_2$–$^{18}O_2$ shift 21 cm^{-1}) and that at 747 cm^{-1} in the case of bisacetylacetonato-beryllium ($^{16}O_2$–$^{18}O_2$ shift 10 cm^{-1}) to an M–O stretching mode of vibration.[2]

This assignment of the 592—614 cm^{-1} bands of these chromium(III) and copper(II) complexes, respectively, was rejected by Nakamoto *et al.*[3] on the ground that it is in disagreement with the low 0.7 and 0.2 cm^{-1} isotopic shifts observed by them for these bands on exchanging ^{50}Cr for ^{53}Cr and ^{63}Cu for ^{65}Cu, although these exchanges can be calculated to yield shifts of only *ca.* 3.5 and 2 cm^{-1} for a 600 cm^{-1} diatomic M–O oscillator and *very appreciably* lower values for the corresponding metal complexes (where the metal atom is in the *centre* of a octahedral or square-planar oxygen atom configuration). These authors therefore attributed the 592 cm^{-1} band to an out-of-plane ring deformation mode of vibration and identified the Cr–O stretching bands with the absorptions observed in the i.r. spectrum of the chromium complex at *ca.* 460 and 355 cm^{-1}, which are reported to exhibit ^{50}Cr–^{53}Cr shifts of 3.0 and 3.9 cm^{-1}, respectively.[3]

It seemed thus very appropriate to study the effect of ^{18}O-labelling on the 355 cm^{-1} vibration of this complex in order to find out whether it really is a Cr–O stretching vibration and as such sensitive to ^{18}O-labelling or whether the small ^{50}Cr–^{53}Cr shifts observed are meaningless being so near to experimental error in the determination of absorption frequencies on potassium bromide pellets in the 300—600 cm^{-1} region. The Raman spectra of normal and 84% ^{18}O-labelled trisacetylacetonato-chromium(III) have therefore been compared in the 100—1 600 cm^{-1} region using a laser source Raman spectrometer.

EXPERIMENTAL

Normal and ^{18}O-labelled trisacetylacetonatochromium(III) were from Miles-Yeda Ltd. The labelled sample showed 84.0 atom % ^{18}O and 0.7 atom % ^{17}O.

The Raman spectrometer used was similar to that described in detail,[4] consisting mainly of a Spex double monochromator, model 1401, and a krypton laser operated at 647.1 nm.

Measurements were carried out on capillary tubes filled with crystals of the metal complex studied. The frequencies of medium to strong Raman bands reported here are believed to be correct to within 1 cm^{-1}.

RESULTS

Table 1 gives the frequency of the Raman bands observed for normal and ^{18}O-labelled trisacetylacetonatochromium-(III), their relative intensities (relative to the strongest Raman band of the spectrum, taken to be 100), and the frequency of the i.r. absorption bands in the 100—1 600 cm^{-1} region.

It can be seen from Table 1 that many vibrations which appear in the i.r. absorption spectrum of the crystalline chromium complexes as strong bands are not observed in the Raman spectrum. These vibrations include the 1 569 cm^{-1} C–O stretching vibration as well as those at 1 423, 1 380, 801, 766, 661, 612, and 592 cm^{-1}. This fact seems to be due partly to the Raman spectrum inactivity of the i.r.-active A_2 species vibrations of the D_3 point group to which the isolated trisacetylacetonatochromium(III) molecule belongs [5] and partly to the high background of the Raman spectrum of the strongly red coloured complex, which masks weak Raman bands.

DISCUSSION

As is evident from Table 1 the *ca.* 355 cm^{-1} vibration of the Cr^{III} complex is absolutely *insensitive* to ^{18}O-labelling as its frequency remains the same, within experimental error, also in the case of the [$^{18}O_2$]acetyl-

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[1] S. Pinchas, B. L. Silver, and I. Laulicht, *J. Chem. Phys.*, 1067, **46**, 1506.

[2] H. Junge and H. Musso, *Spectrochim. Acta*, 1968, **24A**, 1219.

[3] K. Nakamoto, C. Udovich, and J. Takemoto, *J. Amer. Chem. Soc.*, 1970, **92**, 3973.

[4] H. H. Classen, H. Selig, and J. Shamir, *Appl. Spectroscopy*, 1969, **23**, 8.

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

acetonate. This proves unequivocally that this vibration does *not* affect to any significant extent the position of the oxygen atoms in this molecule and hence *cannot be a* Cr–O *stretching vibration* as suggested on the basis of the ^{50}Cr–^{53}Cr shift of 3.9 cm^{-1} [3] and the large variation of this vibration [5] with the change of the chromium atom for an atom such as Co^{III} (386 cm^{-1}) or Fe^{III} (289 cm^{-1}). This band must thus be assigned to a ring in-plane C–C–C bending mode of vibration. A deformation vibration of this type was calculated by Nakamoto to have a frequency of *ca.* 370 cm^{-1} in the case of the cobalt, copper, *etc.* complexes.[6]

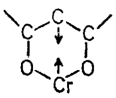
TABLE 1

Raman and i.r. band frequencies (cm^{-1}) of normal and ^{18}O-labelled trisacetylacetonatochromium(III)

Normal complex			^{18}O-labelled complex		
Raman	Intensity	I.r.	Raman	Intensity	I.r.
		103 [a,5]			
125	54		124	46	
170	25				
184	33	179 [a,3]	184	19	
231	5	224 [a,3]	225	7	
256	12	250 [a,3]	252	10	
356	12	355 [a,5]	354	17	
416	5	416 [1]	411	6	408sh [1]
457	100	456 [1]	447	100	451 [1]
563	10		562	11	
		592 [1]			573 [1]
		612 [b,3]			
		661 [1]			658 [1]
684	10	678 [1]	672	16	667 [1]
		766 [1]			766 [1]
		801 [1]			801 [1]
944	15	~940 [1]	936	24	936 [1]
1 030	5	1 029 [1]	1 026	6	1 018 [1]
1 061	3		1 059	4	
1 196	14	1 197 [1]	1 189	19	1 188 [1]
1 281	46	1 276 [1]	1 279	50	1 272 [1]
1 368	19	1 356 (shoulder) [1]	1 369	38	
		1 380 [1]			1 375 [1]
		1 423 [c,1]			1 424 [1]
1 435	2		1 439	4	
1 513	68	1 519 [1]	1 512	19	1 519 [1]
		1 569 [1]			1 556 [1]

[a] For Nujol mull or solution. [b] For KBr pellet. [c] This value was misprinted in Table 1 of ref. 1.

The 3.9 cm^{-1} ^{50}Cr–^{53}Cr shift observed for this frequency seems thus to be unreally large even though this mode of vibration does involve *some* movement of the metal atom relative to the other atoms of the ring, as seen from the Scheme.



SCHEME Movement of the Cr^{III} atom during the 355 cm^{-1} vibration

Taking into account that the experimental error in the absolute determination of the frequency of absorption bands in the 300—400 cm^{-1} region is usually not better than 1—2 cm^{-1} (especially in the case of potassium bromide pellets which are not homogeneous, are notorious for interacting with the ions of the investigated compounds, and are known to change their characteristic absorption with time) one tends to conclude that these small ^{50}Cr–^{53}Cr shifts are of a very limited significance. A further indication in this direction is the fact that the 416 cm^{-1} band of the normal Cr^{III} complex, which shows an ^{18}O-shift of 5 cm^{-1} in the Raman spectrum and *ca.* 8 cm^{-1} in the i.r. absorption (see Table 1) and hence is definitely a vibration which affects the CrO_2 system, exhibits no ^{50}Cr–^{53}Cr shift whatsoever.[3]

The variation of the 355 cm^{-1} frequency as a result of exchange of the Cr^{III} atom for an Fe^{III} or Co^{III} atom seems to be due mainly to the different $O\text{-}\widehat{M}\text{-}O$ angle brought about by this exchange since it has been found that while the average $O\text{-}\widehat{Cr}\text{-}O$ angle [7] is 91.1°, $O\text{-}\widehat{Fe}\text{-}O$ [8] is *ca.* 87° and $O\text{-}\widehat{Co}\text{-}O$ [9] is 88°.

It is thus clear that the main (probably a merged a_2 and *e*) Cr–O stretching band of trisacetylacetonatochromium(III) appears at 592 cm^{-1}, rather than at 355 cm^{-1}, as concluded by Pinchas *et al.*[1] on the basis of the 19 cm^{-1} ^{16}O–^{18}O shift of the 592 cm^{-1} frequency, in spite of the low, 0.7 cm^{-1}, ^{50}Cr–^{53}Cr shift reported for the latter. The 592 cm^{-1} band cannot be due to ' an out-of-plane ring deformation in which the oxygen atom is displaced appreciably ' as suggested by Nakamoto *et al.*[3] since such a mode is in fact a Cr–O bending vibration and a bending vibration (and especially an *out-of-plane* one) is as a rule always much lower in frequency than the corresponding stretching mode of vibration. Hence were the 592 cm^{-1} band really due to this vibration mode the Cr–O stretching vibration would have to be observed *much above* 592 cm^{-1} where no highly ^{18}O-sensitive band can be assigned to such a vibration.

Another argument against assigning the 592 cm^{-1} band to an out-of-plane Cr–O bending vibration is that the in-plane O–Cr–O bending i.r. and Raman band was found for this complex at [1] 416 cm^{-1}, as judged from its ^{18}O-shift to *ca.* 410 cm^{-1} (see Table 1). Bisacetylacetonatocopper(II) [2,10] exhibits an i.r. absorption at 431 cm^{-1} which seems to be analogous to this band and this was shown by i.r. dichroic measurements to be due to an in-plane mode of vibration,[10] thus supporting the above mentioned assignment of the 416 cm^{-1} Cr^{III} complex absorption. Since an out-of-plane bending is usually lower in frequency than the respective in-plane bending vibration the O–Cr–O out-of-plane bending must therefore be below 416 cm^{-1} and not at 592 cm^{-1}. This mode of vibration seems to bring about the Raman band at 231 cm^{-1} which shifts to 225 cm^{-1} as a result of ^{18}O-labelling (Table 1). In the case of the

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[6] K. Nakamoto, P. J. McCarthy, and A. E. Martell, *J. Amer. Chem. Soc.*, 1961, **83**, 1272.

[7] B. Morosin, *Acta Cryst.*, 1965, **19**, 131.

[8] J. Iball and C. H. Morgan, *Acta Cryst.*, 1967, **23**, 239.

[9] V. M. Padmanabhan, *Proc. Indian Acad. Sci.*, 1958, **47**, 329.

[10] M. Mikami, I. Nakagawa, and T. Shimanouchi, *Spectrochim. Acta*, 1967, **23A**, 1037.

copper(II) complex a similar band appears at 217 cm^{-1} and dichroic measurements show that this band can belong to an out-of-plane bending vibration[10] (of the B_{3u} species).

Table 2 summarises the assignment of the Raman and i.r. bands of crystalline trisacetylacetonatochromium(III) in the 200—700 cm^{-1} region, as suggested by the $^{16}O-^{18}O$ shifts observed for them.

TABLE 2

Assignment of the Raman and i.r. bands of crystalline trisacetylacetonatochromium(III) in the 200—700 cm^{-1} region

Frequency (cm^{-1})	$^{16}O-^{18}O$ Shift	Assignment
231	6	O–Cr–O out-of-plane bending
256	4	Another O–Cr–O out-of-plane bending
356	2	C–C–C in-plane bending
416	5	In-plane O–Cr–O bending
457	10	In-phase Cr–O stretching + C–CH_3 bending
563	1	Ring deformation
592	19	Out-of-phase Cr–O stretching
612		Ring deformation ?
661	3	Ring deformation
684	12	Ring deformation + Cr–O stretching

The fact that even the complete normal co-ordinate treatment of the 43-body trisacetylacetonatometal complex made by Mikami *et al.*[10] yielded the erroneous conclusions that the 355 cm^{-1} band of the Cr^{III} compound belongs to a Cr–O stretching vibration, its 592 cm^{-1} vibration does *not* possess a Cr–O stretching character, *etc.*, proves again[1] that such calculations are totally inadequate even for only moderately complex molecules.

Since it is now clear that the *ca.* 355 cm^{-1} band of trisacetylacetonatochromium(III) (and by analogy, very probably, also the 386 cm^{-1} band of the Co^{III} complex[5] and that at *ca.* 291 cm^{-1} in the case of the Cu^{II} compound,[10] *etc.*) has nothing to do with a stretching of the M–O bond it appears that all the conclusions drawn[3,5] in respect to the force constant of this bond in various complexes, on the basis of its exact frequency in these cases, are invalid.

The fact that the relative peak intensity of the 1 512 cm^{-1} C=C(C^{18}O) stretching,[1] Raman band of the ^{18}O-labelled compound (19%) is much lower than that of the respective normal complex band (68%) is analogous to the usually lower than expected intensity of the X^{18}O stretching i.r. bands[11] and other phenomena peculiar to the electronic distribution in ^{18}O-labelled compounds.[12]

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[11] S. Pinchas, D. Samuel, and I. Wassermann, *Spectrochim. Acta*, 1967, **23A**, 1307.

[12] S. Pinchas, *Nature Physical Science*, 1973, **242**, 46.