Single-crystal Infrared Study of Dicarbonyl(acetylacetonato)rhodium(I)

By **David M. Adams** * and **William R. Trumble**, Department of Chemistry, University of Leicester, Leicester LE1 7RH

The absorption spectrum of single crystals of $Rh(CO)_2$(acac) in polarised i.r. light has enabled direct and unambiguous differentiation of in-plane from out-of-plane modes.

THE co-ordinated acetylacetonate ligand (acac) has a relatively complex vibrational spectrum and much attention has been devoted to its assignment. The earliest attempts at complete assignment were based upon normal co-ordinate analysis (NCA) of the in-plane vibrations,[1] considering only one ring of $Cu(acac)_2$. A more recent calculation treating $Cu(acac)_2$ as a 29-atom problem and $Fe(acac)_3$ as a 43-body problem [2] broadly supported Nakamoto's earlier calculation, only to be faced with a new treatment [3] which reversed part of the high-frequency band assignment.

The majority of the *physical* evidence upon which assignments rest is not entirely unambiguous in its interpretation. The beautifully complete isotopic substitution studies (^{2}H, ^{13}C, ^{18}O) of Junge and Musso [4] did much to settle the assignment above 600 cm^{-1}, but conflicting interpretations followed for the ν(M–O) region from ^{18}O substitution,[5] and the use of metal isotopes.[6] More reliable evidence as to which bands are associated with ν(M–O) followed study of the dependence of low-frequency bands upon change of metal.[7] A partial i.r. study of the monoclinic single crystals of $Cu(acac)_2$ has been reported but interpretation is not direct.[2]

What is missing from all this work is a *direct physical demonstration* of which bands are due to in-plane or out-of-plane motion. We report the results of a single-crystal i.r. study of $Rh(CO)_2$(acac) which provides this information, and helps in understanding the dicarbonyl vibrations as well.

In the solid state $Rh(CO)_2$(acac) is notable for the pronounced dichroic appearance of its crystals. They are iridescent green by reflection but red by transmission. A mull of the material is a typical rhodium(I) red. The molecules are stacked in columns with a Rh–Rh distance of 3·27 Å, but a slight displacement of the molecules relative to each other results in adoption of a triclinic cell, $P\bar{1}$, with $z = 2$. In contrast, packing in $Rh(CO)_2(CF_3COCHCOCF_3)$ is regular resulting in an orthorhombic cell.[8] The chains in $Rh(CO)_2$(acac) run parallel to *b* with a centre of inversion relating the two planar molecules.

Although the indicatrix of a triclinic crystal bears no necessary relation to the crystal axes, thereby enormously complicating optical and Raman studies, when using radiation of i.r. wavelengths which are comparable to the crystal thickness there will be negligible splitting into ordinary and extra-ordinary rays. For i.r. study, it follows that we may select any direction we please. The material crystallises as thin platelets elongated along *b*. We have therefore studied it in transmission using radiation polarised either parallel or perpendicular to the chain axis, thereby selectively exciting modes which are perpendicular or parallel to the set of molecular planes.

Selection Rules.—For one $Rh(CO)_2$(acac) molecule internal modes span the C_{2v} representation $12a_1 + 11b_1$ (in-plane modes), and $4a_2 + 6b_2$ (out-of-plane modes) where the molecular plane is *zx* and methyl is treated as a point mass. Approximate internal co-ordinate contributions are shown in the Table.

Coupling of the modes of the two molecules in the primitive cell takes place *via* the site symmetry C_1. Thus, each mode in C_{2v} (of whatever species) will generate an $A_g + A_u$ pair in the factor group C_i. We

$$\begin{array}{ccccc} C_{2v} & & C_1 & & C_i \\ a_1, a_2, b_1, b_2 & \longrightarrow & A & \xrightarrow{\times 2} & A_g\ \text{(Raman)} + A_u\ \text{(i.r.)} \end{array}$$

were unable to obtain Raman spectra from this crystal using red, blue, or green excitation since even very low applied laser powers drilled holes in the crystals, and no greater success was obtained using a powder sample in a rotating cell. Since we have only the i.r. evidence we cannot estimate the extent of the Davydov splitting, and the *number* of internal modes found will be that predicted on the basis of *one* C_{2v} molecule (*i.e.* A_u modes only). We emphasise that in strict group theoretical terms no distinction can be made between any of the modes observed in the i.r.

In addition to internal modes the following lattice modes occur. Translatory (optical branch), $3A_g$; rotatory, $3A_g + 3A_u$. Only the three A_u modes are i.r. active and, since the molecules may be presumed to have a large permanent dipole moment, these modes should appear with reasonable intensity. Although no group theoretical distinction can be made between the three rotatory modes, since they arise by virtue of in-phase and out-of-phase coupling of motion about three orthogonal

---

[1] K. Nakamoto and A. E. Martell, *J. Chem. Phys.*, 1960, **32**, 588.

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

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

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

[5] S. Pinchas, B. L. Silver, and I. Laulicht, *J. Chem. Phys.*, 1967, **46**, 1056.

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

[7] R. D. Hancock and D. A. Thornton, *J. Mol. Struct.*, 1969, **4**, 361.

[8] N. A. Bailey, E. Coates, G. B. Robertson, F. Bonati, and R. Ugo, *Chem. Comm.*, 1967, 1041.

axes (see Figure) we expect that one will be excited by $\mathbf{E}(\perp)$ and two by $\mathbf{E}(\parallel)$.

EXPERIMENTAL

We thank Dr. R. D. W. Kemmitt for a sample of $Rh(CO)_2$-(acac). Crystals were grown by vacuum sublimation, by evaporation of an ether solution, and by crystallisation from cyclopropane in a Carius tube, the latter method giving larger plates. Several crystals were aligned on plates of potassium bromide or polyethylene and held in position by a smear of Vaseline. In the region 20—600 cm^{-1} spectra were obtained using a Beckman-RIIC FS-720 interferometer system; a home-made cryostat was used for spectra at liquid-nitrogen temperature. The region 400—1600 cm^{-1} was covered using a Digilab interferometer through the courtesy of Dr. Denney of Cambridge Scientific Instruments Ltd. Perkin-Elmer wire-grid polarisers on silver chloride on polyethylene substrates were used as appropriate. Raman experiments were attempted with a Coderg T800 spectrometer.

RESULTS AND ASSIGNMENT

Results are shown in the Table. Extinctions between the $\mathbf{E}(\parallel)$ and $\mathbf{E}(\perp)$ spectra were very good and provide strong support for an interpretation based upon C_{2v} molecular geometry.

Vibrational bands/cm^{-1} and assignment for Rh(acac)-$(CO)_2$. Numbers in parentheses are from experiments at liquid nitrogen temperature

$\mathbf{E}(\perp)$	$\mathbf{E}(\parallel)$	Assignment
50 (55)		$\nu(R_z)$
	64 (66)	$\nu(R_{x,y})$
77 (80)		
	112 (113 br)	$\nu(R_{x,y})$
115 (113 br)		
	167 (164)	Out-of-plane deformation
180 (178)		
	202 br (202)	Out-of-plane deformation
225 (225)		
236 (238)		
264 (264)		
289 (289)		
405 (405)		ν(Rh–CO)/δ(RhCO)
450 (450)		
458 (458)		ν(Rh–CO); ring deformation (in-plane)
	498 (495)	π(RhCO)
506 (505)		δ(RhCO)/ν(Rh–CO)
630		δ(RhCO)
	670	Ligand out-of-plane deformation
686		
	790	π(C–H)
942		
962		
	1020	$\rho_r(CH_3)$
1025		
1130		
1203		
	1220	
1276		

Out-of-plane Modes: the $\mathbf{E}(\parallel)$ *Spectrum*.—The highest out-of-plane modes of the co-ordinated (acac) ligand are known from isotopic evidence to be associated with methyl. $\delta(CH_3)_a$ and $\delta(CH_3)_s$ appear in both $\mathbf{E}(\parallel)$ and $\mathbf{E}(\perp)$ spectra, though with different intensities. The methyl rock mode at 1020 cm^{-1} is unique to the $\mathbf{E}(\parallel)$ spectrum and equivalent modes are found in $\mathbf{E}(\perp)$. This clearly shows that the methyl group cannot be treated on the C_{3v} local symmetry approximation and that its vibrations must be classified under at least C_{2v}.

Between 20 and 800 cm^{-1} seven bands appear in $\mathbf{E}(\parallel)$. Eight bands are expected if C_{2v} is a good approximation to the molecular symmetry (*i.e.* $6b_2$, plus $2A_u$ rotatory modes) but since, in principle, a_2 modes may also appear we must search for evidence of their presence. They are inactive in C_{2v} and only active in the factor group C_i by virtue of site symmetry; if they appear at all they will be weak. It is difficult to distinguish between b_2 and a_2 modes since the same internal co-ordinates tend to generate symmetry co-ordinates in both species. The best region for this purpose is undoubtedly that in which π(RhCO) modes occur (see below), but this shows no sign of a band which must be attributed to a_2. We conclude from this, and from the *number* of $\mathbf{E}(\parallel)$ modes found, that a_2 modes do not appear in the $\mathbf{E}(\perp)$ spectrum of $Rh(CO)_2$(acac); in other words, the site field is weak.

From deuteriation evidence from related complexes [4] there is no doubt that the 790 cm^{-1} band is a C–H deformation mode: we provide direct proof that it is a π(C–H) mode. Comparison of our spectra with those of other (acac) complexes [2] which do not contain carbonyl groups allows identification of vibrations due to these two parts of the molecule. Only one π(RhCO) mode is allowed (b_2) and is at 498 cm^{-1}: it is the only $\mathbf{E}(\parallel)$ band between 200 and 670 cm^{-1} so there can be little doubt as to its origin. This observation unequivocally places π(RhCO) relative to δ(RhCO) and ν(Rh–C) which appear in $\mathbf{E}(\perp)$. For comparison we note that ν(Pt–C) in $[PtCl_3\cdot CO]^-$ was identified by its Raman solution polarisability at 529 cm^{-1}, but that δ(PtCO) and π(PtCO) could not be differentiated experimentally: they are at 481 and 490 cm^{-1}, and the lower band was arbitrarily assigned to the out-of-plane π(PtCO) mode.[9]

The 670 cm^{-1} band must arise from a ligand distortion with a major contribution from C–CH_3 motion. There remain four observed modes between 20 and 200 cm^{-1}, a region in which three internal plus two lattice modes are expected. We note that the 200 cm^{-1} band is broad, even at liquid-nitrogen temperature, and may contain two nearly coincident contributions. If this is so then the band at 112 cm^{-1} must be due to a rotatory mode (as well as that at 64 cm^{-1}); the modes at 167 and 200 cm^{-1} are principally ring deformations.

In-plane Modes: the $\mathbf{E}(\perp)$ *Spectrum*.—The $\mathbf{E}(\perp)$ spectrum is necessarily more crowded. With the exception of ν(C–H), the two ν(CO) modes, and the internal vibrations of the methyl groups, we expect $10a_1 + 10b_1$ bands plus one rotatory lattice mode in the range 20—1600 cm^{-1}. It is convenient to consider the spectrum in two regions.

Above 600 cm^{-1}. The pattern of absorption closely follows that well established for large numbers of other complexes of (acac) and requires no comment. Details are given in the Table.

In the ν(CO) region each of the molecular modes (a_1 and b_1) yields an A_g (Raman) + A_u (i.r.) doublet. We find, however, that there are three bands, at 2080 (ex a_1), 2015, 2000 cm^{-1} (ex b_1). There are also weak ^{13}CO satellites at 2058, 1977, and 1968 cm^{-1}. This observation cannot be accommodated by the selection rules of the triclinic cell, but it can be rationalised if we take a vibrationally effective cell of orthorhombic symmetry. Taking the

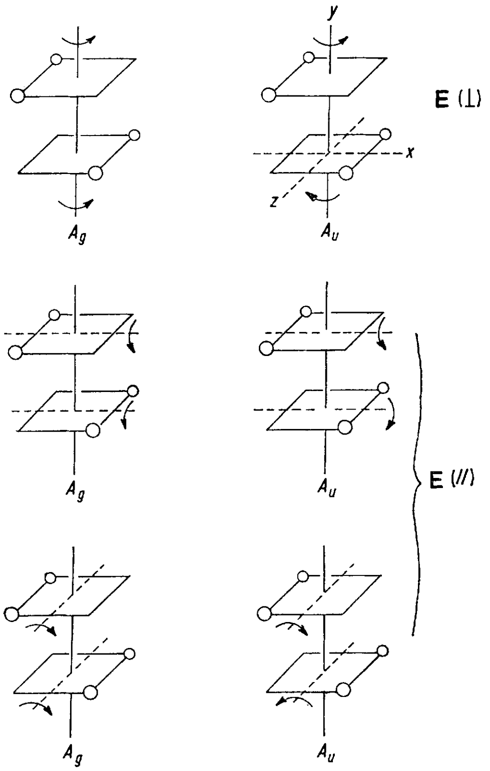
---

[9] R. G. Denning and M. J. Ware, *Spectrochim. Acta*, 1968, **24A**, 1785.

group *Ama*2, $z = 4$, as found for the closely related Rh(CO)$_2$(CF$_3$COCHCOCF$_3$), where (yz) is now the molecular plane it follows that

$$\begin{array}{cccc} C_{2v}\text{ (molecule)}, & C_s\text{(site)} & \xrightarrow{\times 2} & C_{2v}^{16} \\ a_1 + b_2 & 2A' & & 2(A_1 + B_2) \end{array}$$

where all four modes are i.r.-active. On this basis we assign the 2080 cm^{-1} band to the B_2 component of the coupled a_1 modes, and the 1977 and 1968 cm^{-1} pair to the B_2 and A_1 components of the coupled b_2 modes.



Schematic arrangement of the bimolecular unit cell of Rh(CO)$_2$(acac) showing generation of rotatory lattice modes by coupling about three axes

Below 600 cm^{-1}. Several NCA's have established the broad lines of the (acac) assignment. It is clear from these that $6a_1 + 5b_1$ molecular modes will lie below 600 cm^{-1} in Rh(acac)(CO)$_2$, including the Rh(CO)$_2$ vibrations. We therefore expect twelve bands in the **E**(⊥) spectrum in this region, including the lattice mode. Twelve are observed.

Comparison with spectra of the planar complexes M(acac)$_2$, where M = Cu, Pd, or Pt, shows that all such systems have i.r. absorption *ca.* 260—290 and *ca.* 450—470 cm^{-1} due to ν(M–O) and ring deformation vibrations. Hence, there is little doubt that the 405 and 506 cm^{-1} bands are due to Rh–CO modes; ν(Rh–CO) and δ(RhCO) motion must contribute substantially to both. The second δ(RhCO) is placed at 630 cm^{-1} and the missing ν(Rh–CO) is probably a component of the doublet *ca.* 455 cm^{-1}. The frequency span of these Rh–CO assignments is normal for a polycarbonyl species; *cf.* in Fe(CO)$_2$Cl(π-C$_5$H$_5$) it is from 437 to 600 cm^{-1}.[10] The remaining low-frequency modes are complex in-plane deformations of the whole molecule and cannot be further described without the aid of an NCA.

Rotatory Lattice Modes.—Although the frequencies of the rotatory lattice modes cannot be predicted accurately without an NCA of the full unit cell, an informative estimate is simply obtained from the simple harmonic formula for a restricted rotor. Coupling of the rotatory motion about each molecular axis, i, will take place giving an A_g mode of frequency $\omega_i^+ = \{(k_i - k_i')/I_i\}^{\frac{1}{2}}$ and an A_u mode $\omega_i^- = \{(k_i + k_i')/I_i\}^{\frac{1}{2}}$ where k_i is a force constant governing the restricted rotation about axis i, and k_i' is an interaction constant such that $k_i' \ll k_i$. I_i Is the moment of inertia about axis i. If we assume initially that all three sums $(k_i - k_i')$ are equal, the ratios of the three i.r.-active rotatory lattice mode frequencies are $\nu_y : \nu_z : \nu_x = 1 : 1{\cdot}71 : 1{\cdot}23$ since the moments of inertia are $I_x = 816{\cdot}2$, $I_z = 422{\cdot}98$ a.m.u. Å^{-2} and, by a theorem, $I_y = I_x + I_z$ (y is nearly coincident with the chain axis). This clearly indicates that the rotatory mode about the chain axis, ν_y, is the lowest of all since it is associated with the greatest moment of inertia, I_y. We note that the lowest band found (50 cm^{-1}) has the correct polarisation for a lattice mode of the type discussed for ν_y. Using the above ratios we predict $\nu_x = 61{\cdot}5$ cm^{-1} (observed, 64 cm^{-1}) and $\nu_z = 85{\cdot}5$ cm^{-1} (observed, 110 cm^{-1}). The latter discrepancy suggests that one of the sums $(k_i - k_i')$ differs from the other two. Nevertheless, considering the primitive nature of the theory, the agreement provides good support for the proposed assignment.

We had also hoped to estimate the rotatory mode frequencies from the X-ray-determined vibrational mean-square amplitudes. However, an analysis of the thermal-ellipsoid data in terms of a rigid planar molecule model showed that the molecule is essentially non-rigid, as indicated by some physically meaningless values of the vibrational tensor components. In fact, this result might have been anticipated in view of the many low-frequency modes the molecule is known to possess.

We thank the S.R.C. for a grant to W. R. T. and for other support. We also thank Dr. N. A. Bailey for a copy of the X-ray data prior to publication, and Dr. P. A. Tucker for analysing the thermal ellipsoid data.

[3/2110 *Received*, 15*th October*, 1973]

---

[10] D. M. Adams, J. N. Crosby, and R. D. W. Kemmitt, *J. Chem. Soc.* (*A*), 1968, 3056.