Single-crystal Vibrational Spectrum of Hexa(imidazole)cobalt(II) Nitrate

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An essentially complete assignment has been deduced for the title complex from single-crystal Raman and i.r. spectral evidence and differs substantially from that of earlier qualitative work, which is reinterpreted. ν(M–N) Modes in imidazole complexes are shown to lie in the 190—250 cm^{-1} region, thereby supporting earlier qualitative studies of ν(M–N) for pyridine and related complexes. A prominent feature of the results is the extreme weakness of the M–N breathing mode in the Raman spectra, and the series of strong M–N–C deformational mode bands.

THE chemical literature is well provided with reports of qualitative work on the vibrational spectra of polycrystalline co-ordination complexes. In general, such work has now ceased to be acceptable in journals of the first rank. It nevertheless represents the bulk of our knowledge of inorganic spectroscopy and its principal results are frequently used diagnostically. In many cases, examination of the evidence for such qualitative assignments shows that they are little more than informed guesses although, if quoted often enough, they begin to assume a higher status. The situation becomes particularly confused for complexes with polyatomic ligands: the M–L stretching modes are generally of greatest chemical interest as they may correlate with factors such as ligand-field stabilization energy (l.f.s.e.), but are accompanied by a plethora of rather ill defined ligand torsions and other skeletal modes of little interest. Metal–nitrogen stretching modes are among the most commonly quoted qualitative assignments, especially where the neutral ligand is a heterocyclic molecule, but it is just this kind of complex for which qualitative assignment evidence is least convincing. We report a single-crystal study of a typical complex of this type. The aims of the work were (*a*) to determine the complete low-frequency spectra, which has not been done before, and (*b*) to use the experimentally determined symmetry labels, and any other information, to make a full assignment. The salt [Co(imidazole)$_6$][NO$_3$]$_2$ is almost uniquely suitable for our purpose. It crystallises [1,2] with a unimolecular rhombohedral cell; the molecular point group, site group, and factor group are all S_6. It may be regarded as an 'oriented gas' with no complicating features due to either site or correlation fields. Selection rules are shown in Table 1. The nickel and cadmium [3] analogues are isostructural with the cobalt complex and have also been used in this study.

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[3] A. D. Mighell and A. Santoro, *Acta Cryst.*, 1971, **B27**, 2089.

TABLE 1

Selection rules for [Co(imidazole)$_6$][NO$_3$]$_2$

S_6	T	R(Co)	R(NO$_3$)	N_i(NO$_3$)	N_i(I)	N_i(ML$_6$)	Activities
A_g	1	1	1	2	9	5	Raman $x^2 + y^2, z^2$
E_g	1	1	1	2	9	5	Raman $x^2 - y^2$, xy; xz, yz
A_u	1		1	2	9	6	I.r. (z)
E_u	1		1	2	9	6	I.r. (x,y)

T = Translatory modes; R(Co) and R(NO$_3$) are rotatory modes of the cation and nitrate respectively; N_i(NO$_3$), N_i(I), and N_i(ML$_6$) are internal vibrations of nitrate, the imidazole ligands with hydrogen atoms neglected, and the ML$_6$ skeleton.

Correlation

	O_h	S_6		O_h	S_6
ν_1	a_{1g}	a_g	ν_4	t_{1u}	$a_u + e_u$
ν_2	e_g	e_g	ν_5	t_{2g}	$a_g + e_g$
ν_3	t_{1u}	$a_u + e_u$	ν_6	t_{2u}	$a_u + e_u$

RESULTS AND DISCUSSION

The data are shown in Tables 2 and 3 and Figures 1 and 2. All the internal modes of nitrate and of imidazole are above 400 cm^{-1}. Our study is of the low-frequency region in which the selection rules (Table 1) show that a total of eight bands should be found for each of the four symmetry species. The meaning of the column N_i(ML$_6$) may be further clarified by subdivision into contributions from the MN$_6$ skeleton (*i.e.* $2A_g + 2E_g + 3A_u + 3E_u$) and from bends of the M–N–C angles and torsions of the co-ordinated ligands (*i.e.* $3A_g + 3E_g + 3A_u + 3E_u$). The MN$_6$ part is accurately octahedral but the overall molecular symmetry is lowered to S_6 by the disposition of the ligands. The MN$_6$ vibrations should therefore show little departure from predictions on the basis of O_h symmetry: the relation is shown by the correlation appended to Table 1, which indicates that ν_3,ν(M–N) and ν_4,δ(M–N) should be identified by the occurrence of near coincidences in A_u and E_u spectra, and ν_5 by a similar A_g,E_g pair.

The E_g species Raman spectra showed the eight bands predicted. Since all crowd into the region below 200 cm^{-1} it is certain that there will be much interaction between the various internal co-ordinate sets. It is also clear that the set contains the octahedral ν_2,ν(M–N) vibration; we identify this with the highest band, 195 cm^{-1}, as the M–N–C bends and torsions are unlikely to be higher in frequency than the associated stretch.

TABLE 2

Raman wavenumbers (cm^{-1}) and intensities (arbitrary units) for single-crystal [Co(imidazole)$_6$][NO$_3$]$_2$ and for polycrystalline nickel and cadmium analogues, all at liquid-nitrogen temperature

	[Co(imidazole)$_6$][NO$_3$]$_2$						
Assignment [a]	$x(zz)y$	$x(zx)y$	$x(yz)y$	$x(yx)y$	ν/cm^{-1}	M = Ni [b]	M = Cd [b]
E_g ν_L		100	100		46	46m	41s
A_g ν_L (translatory)	200				53	↑	↑
E_g ν_L		250	300		68		
E_g ν_L		250	300	10	79	↓	↓
A_g } ν_5, δ(M–N)	500	20(sh)	20(sh)	5	93	96s	80s
E_g }		90	90	30	102	102(sh)	99w
E_g δ + τ		90	90	80	125	125m	113m
A_g δ + τ	15				140		
E_g δ + τ		15	10	5	153		
A_g δ + τ	60				167		
E_g δ + τ		50	50	15	169	179w	130w
A_g δ + τ	30				183		139vw
E_g ν_2, ν(M–N)		60	70	40	195	214m	161m

[a] δ + τ Indicates δ(MNC) and torsions of imidazole about the M–N bonds; ν_L = lattice mode. [b] These powder spectra show large regions of nearly continuous emission which can only be separated by single-crystal work.

TABLE 3

I.r. absorption wavenumbers (cm^{-1}) for single-crystal [Co(imidazole)$_6$][NO$_3$]$_2$ and polycrystalline nickel and cadmium analogues

	A_u		E_u		Mulls [c]		
Assignment [a]	b	c	b	c	M = Co	M = Ni	M = Cd [d]
ν_L			52w	56w	56w	57w	
ν_6, δ(M–N)	74s	78s	73m	74m	78s	83s	68s
δ + τ	102s	102s			102m	107m	} 92s
δ + τ			120m	128m	124w (sh)	120w (sh)	}
ν_4, δ(M–N)	142w	146m	137m	140m	138vs	140vs	114(sh)
δ + τ			177s	178s	182s	193s	124s
δ + τ			202s	206s	206s	220s	144s
δ + τ	(sh)	226m			219w (sh)	232w (sh)	
ν_3, ν(M–N)	248vs	250vs	241s	248s	250vs	272vs	165vs
Combination					273wm		180(sh)

[a] See footnote *a* in Table 2. [b] At room temperature. [c] At liquid-nitrogen temperature. [d] The equivalences of these bands to those of the cobalt complex are uncertain due to the large shifts involved.

The E_u i.r. spectrum showed seven of the eight predicted bands and, in particular, showed strong absorption at *ca.* 250 cm^{-1}, much higher than the highest A_g or E_g Raman bands. By a similar argument, the highest band is attributed to ν_3,ν(M–N); it is almost coincident with a strong A_u band, as required by the correlation of

Table 1. Comparison of the A_u and E_u spectra reveals two other near coincidences (146, 140 and 78, 74 cm^{-1}) which are accordingly regarded as originating as ν_4 and ν_6.

A curious feature of the A_g Raman spectra was the weakness of the emission at shifts greater than 100 cm^{-1} and only five of the eight predicted bands were present. It appears that ν_1,a_g is missing altogether, in contrast to the generally held rule of thumb that skeletal breathing modes are the most intense in the Raman spectra. For hexa-ammine, hexa-aqua, and hexa-halogeno-species the order $\nu_1 > \nu_2$ is invariable: it is therefore most probable that, for [Co(imidazole)$_6$]$^{2+}$, ν_1 is greater than ν_2 and, hence, is above 200 cm^{-1}. We note that the ν(M–S) breathing mode in [Ni(thiourea)$_4$Cl$_2$] could not be located in the Raman spectra.[4] The near coincidence of A_g,E_g bands at 167, 169 cm^{-1} must be accidental and not due to ν_5 as this bending mode must be well below the positions of ν_1, ν_2, and ν_3; it is likely that the 93, 102 cm^{-1} pair have a major contribution from ν_5.

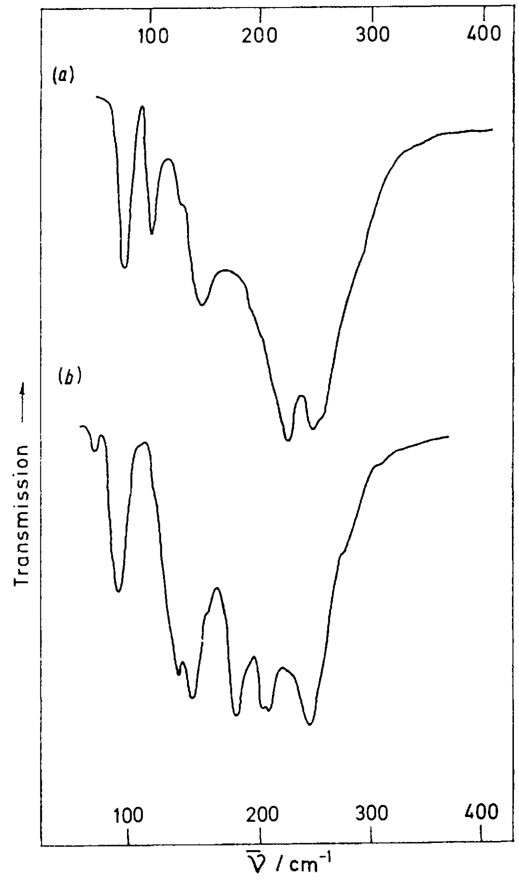

FIGURE 1 I.r. absorption spectra at liquid-nitrogen temperature of [Co(imidazole)$_6$][NO$_3$]$_2$ in polarised light: (*a*) A_u species, (*b*) E_u species

Examination of the form of the lattice modes indicates reasons for the non-appearance of some of them in the spectra. Further, since nitrate lacks a permanent

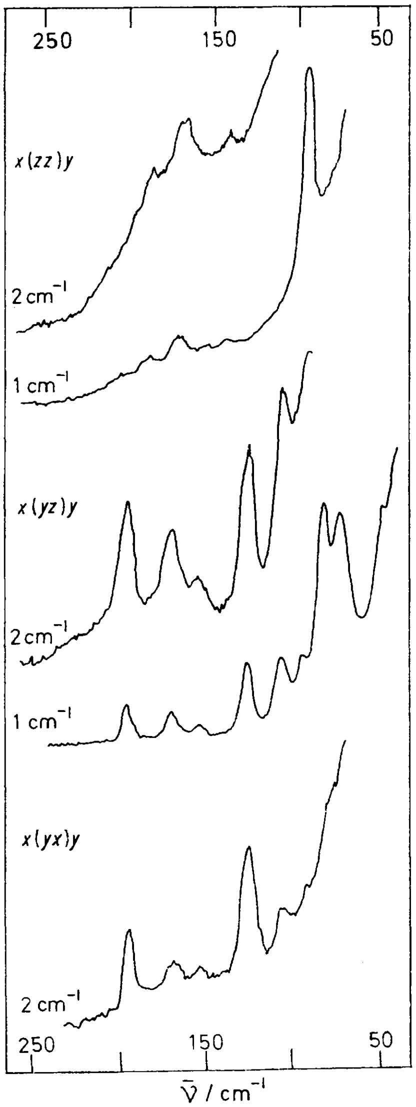

FIGURE 2 Single-crystal Raman spectra of [Co(imidazole)$_6$]-[NO$_3$]$_2$ at liquid-nitrogen temperature. Spectral slit width 1 or 2 cm^{-1} as shown, 632·8 nm excitation, *ca.* 25 mW at the sample

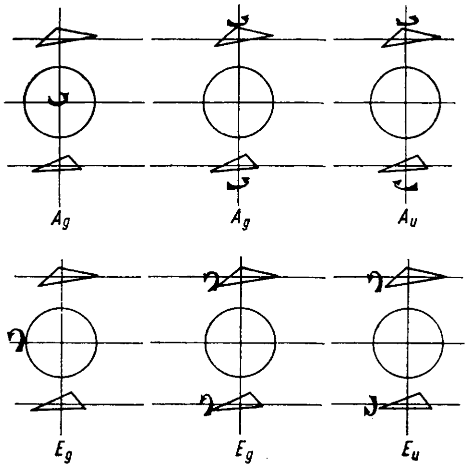

FIGURE 3 Schematic representation of the rotatory lattice modes of [Co(imidazole)$_6$][NO$_3$]$_2$

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[4] D. M. Adams and R. R. Smardzewski, *J. Chem. Soc.* (*A*), 1971, 10.

dipole moment, the intensities of its rotational modes should be low in i.r. absorption. The two A_g lattice modes of rotatory type (Figure 3) involve motion in planes normal to the c axis and will therefore show no intensity in (zz) spectra thereby accounting for the remaining modes of this species. By elimination, the lowest-frequency band in A_g, 53 cm^{-1}, is attributed to the sole translatory mode of that species. The A_u rotatory mode of the nitrate groups takes place also about the c axis and cannot therefore interact with radiation parallel to this axis: it will be absent from the A_u spectrum. In contrast, the E_g and E_u lattice modes satisfy all conditions for appearance.

The above arguments have accounted for most features of the observed spectra and result in the assignment shown in the Tables. It is clear that many prominent bands are due to torsional and other deformational motions of the co-ordinated imidazole molecules, vibrations of little interest and of no diagnostic value. Our assignment, arrived at solely from evidence within the spectra (with the aid of relevant arguments), leads to ν(M–N) values in the region originally indicated for co-ordinated pyridine and its derivatives and thereby supports that work.[5] Further evidence of the correctness of the assignment of the highest of the observed bands to ν(M–N) and δ(M–N–C) modes is provided by the frequency shifts on replacing Co^{II} with Ni^{II} and Cd^{II} respectively (Tables 2 and 3). There was a very close correspondence between the cobalt and nickel spectra, indicating that an equivalent assignment holds. The higher bands were higher in frequency for the Ni^{II} complex in accord with the higher l.f.s.e. associated with the d^8 configuration as compared with high-spin d^7. The much weaker bonding to Cd^{II} was shown by the collapse of the entire spectrum into the region below 200 cm^{-1}.

There have been two qualitative studies of the low-frequency vibrational spectra of imidazole complexes,[6,7] and many other very tentative attempts have been made to assign ν(M–N) modes in imidazole and other complexes of heterocyclic nitrogen-donor ligands. The assignments of Goodgame *et al.*, who made the most complete qualitative study, are almost wholly incorrect, partly for reasons which can only be appreciated from the results of our single-crystal study, but also because they entirely neglected the δ(M–N–C) and ligand torsional modes which are a major feature of the low-frequency spectra. Their ν_3 assignment is correct and its variation with change of metal correlates well with the order of l.f.s.e., *i.e.* $\mathrm{Mn^{II}} \sim \mathrm{Zn^{II}} < \mathrm{Co^{II}} < \mathrm{Ni^{II}}$. For imidazole complexes of other stoicheiometries and structures bands at *ca.* 250 cm^{-1} in the i.r. spectra were found by Goodgame *et al.* and attributed to ν(M–N), correctly in our view.

The principal lesson to be learned from this study is that the many complex deformational modes present in co-ordination complexes of large donor ligands must not be neglected when analysing such spectra. Carbonyl-bending modes, δ(MCO), are thoroughly well understood and recognised; the same view must be taken of other co-ordination complexes.

EXPERIMENTAL

Large rhombohedral crystals of $[\mathrm{M(imidazole)_6}][\mathrm{NO_3}]_2$ (M = Co or Ni) were grown by evaporation at 50 °C of aqueous solutions of the ligand and the appropriate metal nitrate in stoicheiometric quantities. The rhombohedral angle in these crystals is close to 90° and the three-fold axis must be identified by X-ray techniques. In general no faces occurred which contained this axis, except that occasionally a few hexagonal prisms of the cobalt complex appeared. This may have been due to paraffin which was used as a surface layer to restrict evaporation. The hexagonal crystals were used for the single-crystal experiments and work with the nickel complex was abandoned due to the close similarity of mull spectra of the two materials. Both forms of the cobalt complex showed identical powder spectra. The unit-cell parameters were determined by X-ray diffraction and found to be identical with the published values.

Raman spectra were determined using a Coderg T800 triple monochromator instrument, a 'cryocirc' cold cell, and 632·8 nm excitation. I.r. spectra were determined for thin crystal slices using a Beckman-RIIC FS-720 Fourier spectrometer and a home-made cryostat. Perkin-Elmer wire-grid polarisers were employed.

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