

The Similarity of the Far-infrared Spectra of Complexes containing Mono- and Bi-dentate Nitrate-groups

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NUTTALL and TAYLOR¹ suggested that bidentate nitrate-groups are characterised by the presence of two frequencies in the far-i.r. region; no complexes containing monodentate nitrate-groups were, however, considered. These absorptions are assigned to M-O stretching modes and occur

important, there was no indication of the unit-cell composition. If these lattices contain more than one molecule per unit cell then two or more bands may be observed where only one would be predicted from consideration of an isolated molecule.

I.r. spectra of some nitrate-complexes

Compound ^{a,b}	Observed frequency (40—400 cm. ⁻¹)			Evidence for assumed structure: ref. no.
	Below 250 cm. ⁻¹	250—350 cm. ⁻¹	Above 350 cm. ⁻¹	
Monodentate NO₃⁻				
[Co(NH ₃) ₅ NO ₃](NO ₃) ₂	138m, 188w, 224w, 231w	250wsh, 266m, 274m, 332s, 340s		4
Cu en ₂ (NO ₃) ₂	70w, 84w, 109sbr	316w, 329w		5
Cu dben ₂ (NO ₃) ₂	68sh, 86sh, 97s, 112vs, 142m, 168w, 196m, 216w	250m, 274m, 299s, 322w	350w, 382w	6
Ni en ₂ (NO ₃) ₂	78m, 109m, 132w, 163w, 219s, 232sh, 240sh	292m, 318s	380s	7
Ni dben ₂ (NO ₃) ₂	86w, 116w, 138w, 208w, 217w, 239m	257m, 276m, 304w, 314w, 332w	369m	6
Bidentate NO₃⁻				
[Ni en ₂ NO ₃]BF ₄	70m, 82m, 96w, 108w, 178m, 208s, 220s	276w, 303w	363m	7
[Ni en ₂ NO ₃]ClO ₄	72w, 86m, 108w, 178w, 196sh, 211s, 220sh	272w, 302w	—	7
[Ni en ₂ NO ₃]I	75m, 96w, 109w, 182w, 201sh, 210s, 222s	273w, 302m, 334m	366m	7
[Ni tmd ₂ NO ₃]ClO ₄	74m, 92w, 172sh, 191s, 205s, 224m	315w, 332w	383m	7

^a All of the compounds were prepared by established procedures and were pure.

^b en = ethylenediamine; dben = dibenzylethylenediamine; tmd = trimethylenediamine.

in the region 250—350 cm.⁻¹. The assignments rest largely upon three invalid assumptions. First, it is assumed that one or more of the normal vibrational modes of the molecules involve almost exclusively stretching of the M-O bonds. In such molecules the mechanics of the system should be carefully considered, particularly when assigning a metal-ligand vibration, for it has been shown^{2,3} that even in simple systems mixing of vibrations can occur to such a degree that the assignment of metal-ligand stretching vibrations has little meaning. Secondly, even if one of the fundamental modes were shown to correspond to an M-O stretching vibration, then in a complex containing two or more coordinated nitrate-groups, unless the complex were of very high symmetry, at least two "M-O stretching modes" would be expected even if the groups were monodentate in their co-ordination. Nuttall and Taylor,¹ claiming one "M-O stretching frequency" for monodentate and two for bidentate nitrate-ligands, base their argument upon models³ which contain either one monodentate or one bidentate nitrate-group and no other ligand, whereas the complexes studied had two bidentate ligands and other donors of similar mass. Thirdly they produce no crystallographic evidence to confirm the structures of the compounds listed and, more

We have examined the solid-state, low-frequency vibrational i.r. spectra of the mono- and bi-dentate nitrate-complexes listed in the Table. The monodentate nitrate-complexes have at least two absorptions in the region 250—350 cm.⁻¹. In particular [Co(NH₃)₅NO₃](NO₃)₂, which contains⁴ one monodentate nitrate-group, has five absorptions in this region and Cu en₂(NO₃)₂, which has been shown by X-ray crystallographic analysis⁵ to have *trans*-monodentate nitrate-groups, has two. Both classes of complexes have generally similar spectra. [Ni en₂NO₃]X (X = BF₄, ClO₄, I), which contain similar complex metal cations, do not have identical i.r. spectra. Most of the complexes listed show some strong bands at both higher and lower frequencies which may just as well be assigned to "M-O stretching frequencies".

These results demonstrate that mono- and bi-dentate nitrate-groups cannot be distinguished by the use of far-i.r. spectroscopy by the qualitative recognition of typical group frequencies for each of the two cases. Also, theoretical results, obtained with simple models, cannot be compared with the spectra obtained from compounds whose detailed structures are either complicated or largely unknown.

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² I. R. Beattie and F. W. Parrett, *J. Chem. Soc. (A)*, 1966, 1784.

³ R. E. Hester and W. E. L. Grossman, *Inorg. Chem.*, 1966, 5, 1308.

⁴ See "Nouveau Traité de Chimie Minérale", ed. P. Pashal, Masson and Co., Paris 1959, vol. XVIII, p. 500.

⁵ Y. Komivana and E. C. Lingafelta, *Acta Cryst.*, 1964, 17, 1145.

⁶ A. Earnshaw, L. F. Larkworthy, and K. C. Patel, unpublished results. The electronic spectra of the dibenzylethylenediamine derivatives of Cu^{II} and Ni^{II} are very similar to those of the corresponding ethylenediamine complexes.

⁷ N. F. Curtis and Y. M. Curtis, *Inorg. Chem.*, 1965, 4, 804.