The Far Infrared Spectra of Bidentate Nitrato-complexes

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RECENT theoretical predictions of the vibrational spectra expected for isolated bidentate nitrato-groups[1] suggest that two i.r.-active metal–oxygen stretching frequencies should be observed in the 300 cm.$^{-1}$ region (assuming a metal atom of 60 a.m.u. and an M–O force constant of 1·5 mdyne/Å) In view of the difficulty of assigning structures on the basis of splitting of the 1430 cm.$^{-1}$ E_1 mode of nitrates,[2] we have examined the far i.r. spectra of nitrato-complexes $L_2M(NO_3)_2$ (L = 2-picoline, quinoline, or triphenylphosphine oxide, M = Co, Ni, Zn, or Cu) which it has been suggested[2] are of similar structure to $[Me_3PO]_2Co(NO_3)_2$ with bidentate nitrato-groups making up octahedral co-ordination.[2] The spectra shows two strong bands assignable to M–O frequencies arising from nitrato-metal interaction.

Moreover, the far-i.r. spectra of $py_2Zn(NO_3)_2$ and $py_2Cu(NO_3)_2$ show two strong bands which, from comparison with the corresponding deuterio-pyridine analogues, appear to be attributable to M–O vibrations. M–O frequencies are not observed above 275 cm.$^{-1}$ in the spectra of samples with four or more molecules of pyridine per molecule of complex [$py_4Cu(NO_3)_2$, py_6 Co, Ni, Cu, $Zn(NO_3)_2$].

$\nu(M–O)$ *for complexes* $L_2M(NO_3)_2$

	Co	Ni	Cu	Zn
Quinoline	284, 300*	294, 305*	303, 323*	274, 291*
α-Picoline	280, 306	286, 312	282, 326	280br
Triphenylphosphine oxide	256, 303	260, 325	300,356	256, 303
Pyridine			288, 328*	285, 305*

All spectra obtained as Polythene discs.
* Spectrum run at −196°.

Topping has observed similar frequencies for $RbUO_2(NO_3)_3$ at 262 and 223 cm.$^{-1}$, again assignable to bidentate nitrates,[4] while benzimidazole and benzyl benzimidazole complexes show similar frequencies.[5]

It thus appears possible that bidentate nitrato-groups give rise to characteristic frequencies in the far-i.r. region.

(*Received, September 13th,* 1968; *Com.* 1250.)

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