Vibronic Intensity in Hexa-aminecobalt(III) Ion

By R. A. D. WENTWORTH

(*W. A. Noyes Laboratory, University of Illinois, Urbana, Illinois, U.S.A.*)

RECENTLY, Mason and Norman[1] have suggested that in $Coen_3^{3+}$ the N–H and C–H vibrations are responsible for a significant share of the intensity of the spectroscopically accessible *d–d* transitions.

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[1] S. F. Mason and B. J. Norman, *Chem. Comm.*, 1965, 48.

However, Dingle's polarized crystal spectra[2] of $(\pm)$-$(Coen_3Cl_3)_2$,NaCl,$6H_2O$ indicates that only vibrations within the CoN_6 octahedron are important. Further evidence against an intensity mechanism involving N–H vibrations is provided from a study of the solution and crystal spectra of salts of $Co(NH_3)_6{}^{3+}$ and their deuterated analogues (see Table).

TABLE

The Spectra of $Co(NH_3)_6{}^{3+}$ and $Co(ND_3)_6{}^{3+}$

Compound	ν_{max}(kK)	ϵ_{max}	I × 10^{-4}†	ν_{max}(kK)	ϵ_{max}	I × 10^{-4}
$Co(NH_3)_6{}^{3+}$ *	21·05	56	17·4	29·50	45	16·2
$Co(ND_3)_6{}^{3+}$ **	21·10	55	16·6	29·54	44	16·2

* In H_2O. ** in D_2O. See also reference 3.

† The band intensity taken as $\epsilon_{max}\nu_{\frac{1}{2}}$.

In solution, the extinction coefficients and band intensities of the transitions in the perchlorates of $Co(NH_3)_6{}^{3+}$ and $Co(ND_3)_6{}^{3+}$ [3] are almost identical. The relatively minor decreases upon isotopic substitution can most probably be attributed to the smaller quanta of a Co–ND_3 skeletal vibration, whose importance is shown below, and not to an N–D vibration as previously suggested[1] for isotopically substituted $Coen_3{}^{3+}$.

Significant evidence against the intensity mechanism of Mason and Norman is provided from the crystal spectrum of the hexagonal[4] $Co(NH_3)_6Co(CN)_6$. At 80°K, progressions of at least 12 vibrational quanta superimposed on the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition of the hexa-ammine moiety are clearly visible. These are most easily distinguished around the band maxima at 4720 Å but extend from ~ 4100 to ~ 5400 Å. Isotopic substitution shifts the band maxima to 4650 Å, with the first component discernable between 5200—5300 Å. With $Co(NH_3)_6Co(CN)_6$, the vibrational structure of the band can be explained in terms of a uniquantal progression of a 420 ± 10 cm.$^{-1}$ vibration and its combinations with a 390 ± 10 cm.$^{-1}$ vibration. Deuteration lowers these to 380 ± 10 and 340 ± 15 cm.$^{-1}$ respectively. These frequencies are obviously too small to accommodate intraligand motions, and it is clear that, as with $Coen_3{}^{3+}$, only skeletal vibrations of the CoN_6 octahedron appear to contribute to the intensity of the $^1T_{1g}$ absorption.

Finally, it has been suggested[1] that on chelation the reduction in the separation of the band maxima of the $^1T_{1g}$ and $^1T_{2g}$ absorptions (~16B) reflects partial delocalization of the metal t_{2g} electrons into σ-antibonding orbitals common to the entire chelate ring. This may be so; however, when comparing the similar values of this separation in $Co(NH_3)_6{}^{3+}$ and $Coen_3{}^{3+}$ (8,400 vs., 8100 cm.$^{-1}$), a detailed analysis of low-temperature data will be necessary to ensure that very similar vibrational patterns are contained within the band envelopes of both cases. If they are not, then small shifts in the band maxima will certainly be observed, and do not necessarily reflect changes in the mutual repulsion parameter.

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[2] R. Dingle, *Chem. Comm.*, 1965, 304.

[3] Prepared by repeated recrystallization from D_2O (99·8 atom %) until there was no further decrease in the N–H absorption at 3300 cm.$^{-1}$

[4] O. Hassel and J. R. Salvesen, *Z. phys. Chem.*, 1927, **128**, 345. The space group is $C^2{}_{31}$ and the site symmetry of the chromophoric ion in question is either C_3 or S_6. The σ and π spectra are identical indicating that the distortions from O_h symmetry must be small. Since the site symmetry is unknown, however, the important issues concerning electric dipole selection rules and the possible Jahn–Teller distortion of the $^1T_{1g}$ state remain undecided.