An Analysis of the Electronic Spectra of Bisaminecobalt Halides. The Effect of Low Symmetry and of Steric Hindrance

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WE have studied the electronic absorption spectra (5000—30,000 cm.$^{-1}$) of thirty-three tetrahedral complexes of formula $(\text{Amine})_2\text{CoX}_2$ where the amine is quinoline, isoquinoline, 2,6-dimethylpyrazine, pyridine, or a 2-, 3-, or 4-substituted pyridine, and X is Cl, Br, I, NCS, NCO, or NCSe. The Table illustrates typical examples of the spin-allowed absorption observed in the near-infrared and visible regions of the spectrum.

The results may be generalised:

(*a*) The visible absorption spectra are typical for tetrahedral cobalt derivatives and show no phenomena attributable to the lower symmetry (C_{2v}).

(*b*) For a given halide or pseudo-halide, the absorption maxima in the visible region are independent of the amine to a close degree of approximation.

(*c*) The near-infrared absorption consists of three components whose total bandwidth is some 1500—2000 cm.$^{-1}$ greater than the bandwidth observed in corresponding tetrahedral $\text{CoX}_4{}^{2-}$ derivatives.[1] These are assigned tentatively (in C_{2v} symmetry) to the transitions $^4A_1 \rightarrow {}^4A_2$, $^4A_1 \rightarrow {}^4B_2$, $^4A_1 \rightarrow {}^4B_1$ in order of increasing energy, respectively. Such assignments are based on a calculation derived from reasonable assumed single electron energies, and from the earlier polarisation data of Ferguson.[2]

(*d*) Two of the three near-infrared maxima are roughly independent of the amine for a given halide. The third, and highest energy component, is roughly constant for all sterically unhindered amines but drops in energy by as much as 1000 cm.$^{-1}$ when a sterically hindered amine is employed.

Such behaviour which has not been previously observed may be rationalised by consideration of

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[1] F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Amer. Chem. Soc.*, 1961, **83**, 4690.

[2] J. Ferguson, *J. Chem. Phys.*, 1960, **32**, 528.

the effect of lengthening the cobalt–nitrogen bond on the $^4A_2$, $^4B_2$, and $^4B_1$ term energies. The $^4B_1$ term is expected to decrease markedly, should bond lengthening occur to minimise steric repulsion. The other terms would not be appreciably affected.

Absorption spectra in chloroform, and calculated 10Dq *and* B *values*

	λ_{max} (ε) (cm.$^{-1}$)	10Dq	B (cm.$^{-1}$)
IQ_2CoBr_2	16,640 (551), 15,950sh (950), 15,270 (1091), 9259 (85), 6830 (97), 5866 (88)	4428	659
2-$MePy_2CoBr_2$	16,620sh (336), 15,730sh (584), 15,200 (735), 8537 (61), 6874 (76), 5832 (54)	4185	673
4-$EtPy_2CoBr_2$	16,690 (502), 15,820sh (857), 15,360 (955), 9264 (71), 6906 (85), 5955 (73)	4462	654

IQ = isoquinoline, MePy = methylpyridine, EtPy = ethylpyridine.

(*e*) Charge-transfer energies and quartet doublet transitions are not greatly affected by varying the amine.

(*f*) The mean crystal field splitting energy 10Dq, and the Racah parameter B have been calculated. Sterically hindered ligands give rise to lower values of 10Dq, and higher values of B, than unhindered amines. With variation of halide, 10Dq follows the sequence

$$I < Br < Cl < NCO \simeq NCS < NCSe$$

and B follows the sequence

$$I < NCS < Cl \simeq NCO < Br$$

(the variation of B overall is small).

Recently, Goodgame and Goodgame[3] have considered the near-infrared spectra of a few of the compounds covered in this study. They report that in some cases part of the ν_1 absorption ($^4A_2 \rightarrow {}^4T_2$ in T_d) was observed near 4000—4500 cm.$^{-1}$. We have also observed absorption in this region, but since we have also noted similar absorption in compounds such as (quinoline)$_2$ZnCl$_2$, we defer assigning these bands until we have completed a more detailed analysis of the absorption in this region. Certainly, amine combination bands or overtones occur in this region and may partly or wholly obscure the desired ν_1 absorption.

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[3] D. M. L. Goodgame and M. Goodgame, *Inorg. Chem.*, 1965, **4**, 139.