The Electronic Spectra of the μ-Superoxodecammine- and μ-Superoxodecacyano-dicobalt(III) Ions

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THE electronic spectrum of the μ-superoxodecamminedicobalt(III) ion, $\{(NH_3)_5CoO_2Co(NH_3)_5\}^{5+}$, has been reported[1–3] and our observations are consistent with those of Sykes.[3] The spectrum of the μ-superoxodecacyanodicobalt(III) ion, $[(CN)_5CoO_2Co(CN)_5]^{5-}$, has been reported by Mori *et al.*[4] and our observations are similar.

The main features of the electronic spectra of the two ions are shown in the Figure in which the transition energies (kcal. mole^{-1}) and corresponding molar absorption coefficients, ϵ, (M^{-1} cm.$^{-1}$) are quoted for the absorption maxima and shoulders (sh).

The hexamminecobalt(III) ion exhibits two crystal-field transitions,[5] ${}^1A_{1g} \rightarrow {}^1T_{1g}$ at 63 kcal. mole^{-1} and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ at 84 kcal. mole^{-1}. If one ammonia ligand is replaced, say, by a chloride ion the point-group symmetry changes from O_h to C_{4v} and the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ band is split and gives rise to two transitions; ${}^1A_1 \rightarrow {}^1E$ and ${}^1A_1 \rightarrow {}^1A_2$. In the chloropentamminecobalt(III) ion[5] the three transitions require the energies 55, 80, and 101 kcal. mole^{-1}.

The three bands at 43, 60, and 83 kcal. mole^{-1} of the decammine complex may be interpreted as being typical cobalt(III) absorption as first suggested by Linhard and Wiegel.[2] Such transitions are consistent with a change to C_{4v} 'local' symmetry around each of the cobalt atoms in the bridged decammine complex, the superoxide ion being shared by the two pentamminecobalt groups.

The very high intensity, 97 kcal. mole^{-1}, band may be interpreted as a charge-transfer absorption. From the photochemistry of the decammine complex in the 97 kcal. mole^{-1} band[6] it would appear that the charge transfer occurs from an orbital, centred on the Co–O_2–Co system with the major portion of the electron density on the superoxo-group, to an e antibonding orbital on one or other of the cobalt atoms. As a result of this transfer the complex dissociates to give molecular oxygen.

The effect of a change in crystal-field strength by the replacement of ammonia by cyanide ion in the bridged dicobalt complex is as would be expected for the d–d transitions: ${}^2A_1 \rightarrow {}^2E$, ${}^2A_1 \rightarrow {}^2A_1$, and ${}^2A_1 \rightarrow {}^2T_2$. These absorptions are shifted to higher energies by 16, 18, and 21 kcal. mole^{-1} respectively, compared to the decammine complex. The fourth band of the decacyano-complex is shifted to lower energy (92 kcal. mole^{-1}) and would appear from its intensity to be the corresponding charge-transfer band. Such a shift may be understood in terms of either a low lying $t_2{}^*$ orbital or to the configurational interaction of the charge-transfer band with the near d–d bands. From a consideration of intensities, it would appear that in the decammine complex the charge-transfer band interacts with the ${}^2A_1 \rightarrow {}^2T_2$ band. This would result in the charge-transfer band moving to higher energy and the ${}^2A_1 \rightarrow {}^2T_2$ band moving to lower energy as compared to their unperturbed energies. In the decacyano-complex the higher crystal-field shifts the ${}^2A_1 \rightarrow {}^2T_2$ band to a higher energy than the charge-transfer band. Configurational interaction would then force the ${}^2A_1 \rightarrow {}^2T_2$ band to higher energy. This would explain the apparent 21 kcal. mole^{-1} shift of the ${}^2A_1 \rightarrow {}^2T_2$ band.

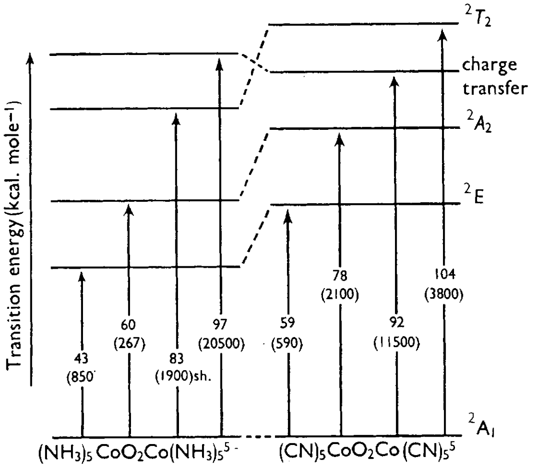

FIGURE. *The transition energies* (*kcal. mole*$^{-1}$) *and the molar absorption coefficients* (*in parenthesis*) *for the* μ-*superoxodecammine- and* μ-*superoxodecacyano-dicobalt*(III) *ions.*

The photochemistry of the decacyano-complex[7] gives further evidence for the assignment of the 92 kcal. mole^{-1} band as a charge transfer from the superoxo-group to the cobalt resulting in the evolution of molecular oxygen.

The movement of the charge-transfer band to lower energy and that of the ${}^2A_1 \rightarrow {}^2A_2$ band to higher energy are the causes of the red-brown colour of the decacyano-complex, the paramagnetic dicobalt complexes usually possessing a green colour.[8]

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