# Spectroscopic and Configurational Assignments for *cis*-Bisdiamine Complexes

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DISSYMMETRIC cobalt(III) complexes of the type *cis*-$Co(en)_2L_2^{3+}$ give absorption and circular dichroism spectra similar to those of the corresponding trisdiamine complex if the ligand L is an amine, and the electronic states of such a *cis*-complex may be directly related[1] to those of the parent $D_3$ complex $Co(en)_3^{3+}$. It is now observed that the circular dichroism spectrum of *cis*-$Co(en)_2L_2^{3+}$ has a different form if the ligand L is well separated in the spectrochemical series from neutral nitrogen, consisting of two bands with the same sign in the region of the octahedral $T_{1g}$ absorption if L = $CN^-$ (Figure). This observation indicates that the electronic states of *cis*-$Co(en)_2(CN)_2^+$, which has

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[1] S. F. Mason and B. J. Norman, *Chem. Comm.*, 1965, 73.

$C_2$ symmetry, approximate more closely to those of the corresponding $C_{2v}$ complex *cis*-$Co(NH_3)_4(CN)_2^+$ than to those of $Co(en)_3^{3+}$.

Yamatera has shown[2] that the electronic states of a variety of cobalt(III) complexes may be related to those of octahedral cobalt(III). Following the method of Yamatera the wavefunctions for the electronic states of $C_2$ and $C_{2v}$ cobalt(III) complexes may be expressed as linear combinations of those for the corresponding states of trigonal ($D_3$) cobalt(III) complexes. The lowest excited state of octahedral cobalt(III) is triply-degenerate ($T_{1g}$) and it breaks down in $D_3$ complexes into components with $A_2$ and $E_a$ symmetry, and in $C_2$ complexes into two components with $B$ symmetry and one with $A$ symmetry. In general the orbital composition of the two $B$ states of the complexes *cis*-$Co(en)_2L_2^{3+}$ are not symmetry-determined, except in two limiting cases. In the one, *e.g.* *cis*-$Co(en)_2(NH_3)_2^{3+}$, the electronic states approximate to those of $Co(en)_3^{3+}$ and they are distinguished by their $C_2$ symmetry and direct descent from $D_3$ parentage as $A(E_a)$, $B(E_a)$ and $B(A_2)$. In the other, *e.g.* *cis*-$Co(en)_2(CN)_2^+$, the electronic states approximate to those of the corresponding $C_{2v}$ complex and they have the forms,

$$\Psi(A_2) = \Psi A(E_a) \qquad (1)$$

$$\Psi(B_2) = (1/\sqrt{3})[\sqrt{2}\,\Psi B(A_2) + \Psi B(E)_a] \qquad (2)$$

$$\Psi(B_1) = (1/\sqrt{3})[\sqrt{2}\,\Psi B(E_a) - \Psi B(A_2)] \qquad (3)$$

and the energies ($E$) and rotational strengths ($R$) listed (Table).

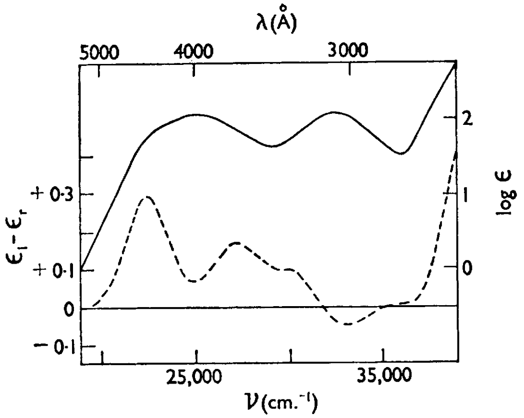
A sum rule for the rotational strengths of trigonal ($D_3$) complexes indicates[3] that,

$$R(E_a) + R(A_2) = 0 \qquad (4)$$

but experimentally it is found[4] for trigonal cobalt(III) and chromium(III) complexes that

$$|R(E_a)| > |R(A_2)| \qquad (5)$$

although the two rotational strengths have opposed signs and nearly equal magnitudes. The inequality of eqn. (5) carries over[1] from $Co(en)_3^{3+}$ to the component rotational strengths of *cis*-$Co(en)_2(NH_3)_2^{3+}$, and if eqn. (5) applies equally to the component rotational strengths of the complexes *cis*-$Co(en)_2L_2^{3+}$ with electronic states of the $C_{2v}$ limiting form, such complexes should give two circular dichroism bands of the same sign, reflecting the sign of the trigonal parent $E_a$ rotational strength, in the wavelength region of the octahedral $T_{1g}$ absorption. The band areas of the major and the minor circular dichroism band should have values in the ratio 2 : 1, and the minor band should be displaced in frequency twice as far as the major from the centre of gravity of the $A_2$ and the $E_a$ circular dichroism bands of $Co(en)_3^{3+}$ (Table). It is observed (Figure) that the two positive long-wavelength circular dichroism bands of *cis*-(+)-$Co(en)_2(CN)_2^+$ have areas with the approximate ratio of 2 : 1, and that the major and the minor band are displaced respectively by 2350 and 6900 cm.$^{-1}$ from the mean frequency of the $A_2$ and $E_a$ circular dichroism bands of $Co(en)_3^{3+}$. Since the two circular dichroism bands are positive in sign, and reflect the sign of the parent trigonal rotational strength $R(E_a)$, *cis*-(+)-$Co(en)_2(CN)_2^+$ has the same absolute configuration as (+)-$Co(en)_3^{3+}$.



*The electronic absorption spectrum* ——————
*and the circular dichroism spectrum* - - - - - - - - - - -
*of* cis-(+)-$Co(en)_2(CN)_2^+$ *in aqueous solution.*

The complexes *cis*-$Co(en)_2(NH_3)L^{3+}$ with L = $Br^-$, $Cl^-$, or $H_2O$ give[5] two circular dichroism bands with the same sign and an approximate band area ratio of 1 : 2 in the region of the long-wavelength absorption band. These complexes approximate to $C_{4v}$ symmetry if the perturbation due to the

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[2] H. Yamatera, *Bull. Chem. Soc. Japan*, 1958, **31**, 95.

[3] S. Sugano, *J. Chem. Phys.*, 1960, **33**, 1883; N. K. Hamer, *Mol. Phys.*, 1962, **5**, 339; T. S. Piper and A. Karipides, *Mol. Phys.*, 1962, **5**, 475; H. Poulet, *J. Chim. phys.*, 1962, **59**, 584.

[4] R. E. Ballard, A. J. McCaffery, and S. F. Mason, *Proc. Chem. Soc.*, 1962, **331**; *J. Chem. Soc.*, **1965**, forthcoming; A. J. McCaffery and S. F. Mason, *Proc. Chem. Soc.*, 1962, **388**; *Mol. Phys.*, **1963**, **6**, 359.

[5] J. P. Mathieu, *Bull. Soc. chim. France*, 1936, 476.

ligand L is stronger than that due to the chelation. In $C_{4v}$ metal amine complexes the octahedral $T_{1g}$ transition of cobalt(III) breaks down into components with $A_2$ and $E$ symmetry, which are respectively undisplaced and displaced by $\delta/4$ (Table) from the energy of the parent hexamine transition,[2] and the complexes *cis*-$Co(en)_2(NH_3)L^{3+}$ with electronic states of the limiting $C_{4v}$ form should give circular dichroism bands due to the $A_2$ and $E$ transitions with the same sign and a band–area ratio of 1 : 2 (Table). The circular dichroism spectrum of *cis*-$Co(en)_2(NH_3)L^{3+}$ with L = $Br^-$, $Cl^-$, or $H_2O$ in the region of the long-wavelength absorption consists[5] of a minor band lying at approximately the mean frequency of the $A_2$ and $E_a$ bands of $Co(en)_3{}^{3+}$ and a major band which is the further displaced from that frequency the larger is the separation between the ligand L and neutral nitrogen in the spectrochemical series. Both the major and the minor circular dichroism bands are positive in sign for the isomers *cis*-(+)-$Co(en)_2(NH_3)L^{3+}$ with L = $Br^-$, $Cl^-$, or $H_2O$, which accordingly are assigned the same absolute configuration as (+)-$Co(en)_3{}^{3+}$.

TABLE

The energies $E$ and rotational strengths $R$ of electronic transitions from the ground state to components of the octahedral $T_{1g}$ state of cobalt(III) in the complexes *cis*-$Co(en)_2L_2{}^{3+}$ with electronic states approximating to the $C_{2v}$ form, and in the complexes *cis*-$Co(en)_2(NH_3)L^{3+}$ with electronic states approximating to the $C_{4v}$ form. The energies are expressed relative to $E_0$, the centre of gravity of the energies of the $A_2$ and $E_a$ transitions in $Co(en)_3{}^{3+}$, in terms of $\delta$ which is the difference between $E_0$ and the energy of the $T_{1g}$ transition of $CoL_6{}^{3+}$. The rotational strengths are given as combinations of $R(A_2)$ and $R(E_a)$, which are the rotational strengths of the $A_2$ and the $E_a$ transition of $Co(en)_3{}^{3+}$.

| Symmetry form | Component state | Rotational strength | Energy |
|---|---|---|---|
| $C_{2v}$ | $B_1$ | $(1/3)[R(A_2) + R(E_a)]$ | $E_0 + \delta/2$ |
| | $A_2$ | $(1/2)R(E_a)$ | $E_0 + \delta/4$ |
| | $B_2$ | $(2/3)R(A_2) + (1/6)R(E)_a$ | |
| $C_{4v}$ | $A_2$ | $(1/3)[R(A_2) + R(E_a)]$ | $E_0$ |
| | $E$ | $(2/3)[R(A_2) + R(E_a)]$ | $E_0 + \delta/4$ |

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