Optically Active Co-ordination Compounds. Part XXXVII.[1] Chiroptical Properties of the Ethylenediaminebis(1,10-phenanthroline)cobalt(III) Ion

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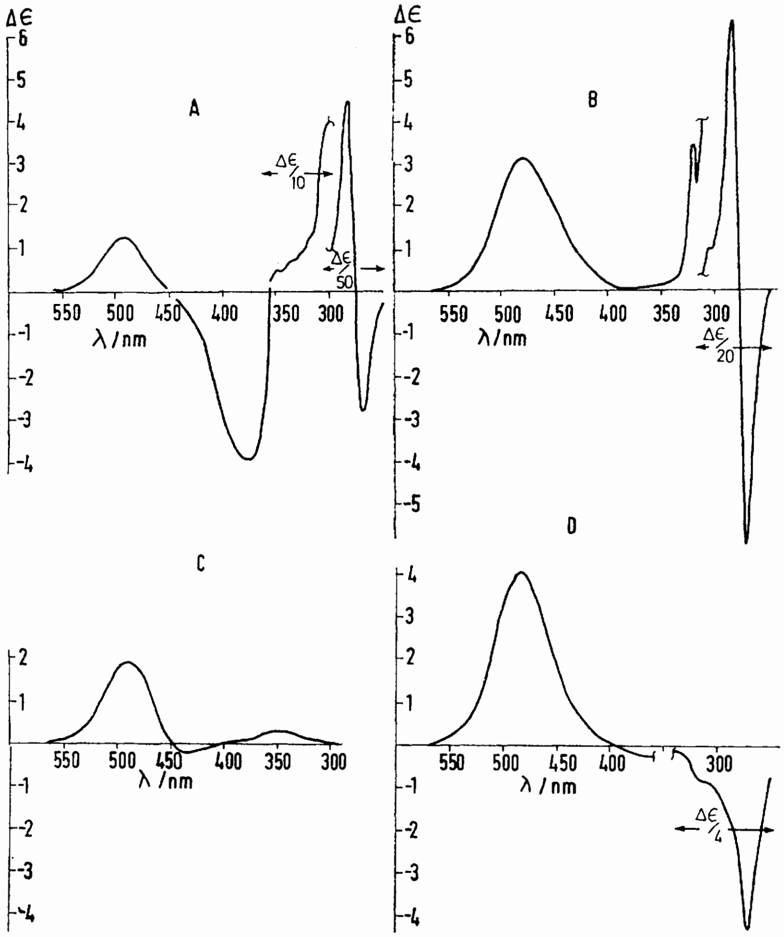
The ion $[Co(en)(phen)_2]^{3+}$ has been resolved into enantiomers by use of (−)tris(cysteinesulphinato)cobaltate(III). Contributions in its c.d. spectrum from the ' exciton ' bands of the *cis*-bis(1,10-phenanthroline) moiety, and from the *d–d* bands of the cobalt ion, provide a correlation between the empirical configurational assignment based on *d–d* bands and the assignment based on the inherently dissymmetric exciton region.

We have now completed the series of resolutions for the complexes $[Co(en)_x(phen)_{3-x}]^{3+}$ (A, $x = 0$; B, $x = 1$; C, $x = 2$; D, $x = 3$) by resolving B, the ethylenediaminebis(1,10-phenanthroline)cobalt(III) ion. This is the first complete series in which the end-members involve fully saturated ligands {*i.e.* D, $[Co(en)_3]^{3+}$} and fully unsaturated ligands {*i.e.* A, $[Co(phen)_3]^{3+}$}. Interestingly, the four less-soluble diastereoisomeric salts formed with the novel resolving agent[2] (−)-$[Co(cysu)_3]^{3-}$ all contain cations having the Λ configuration.

The c.d. spectra are presented in the Figure. The exciton c.d.[3] for B, where only two *cis*-di-imine ligands couple, is, as expected, considerably smaller than that for A, or other tris-complexes. The c.d. in the exciton region of other tris-bis pairs {*e.g.*[4] $[Ru(phen)_3]^{2+}$ and $[Ru(phen)_2(py)_2]^{2+}$} shows the same feature.



C.d. spectra of A, $[Co(phen)_3]^{3+}$ (355—300 nm, Δε/10: <300 nm, Δε/50): B, $[Co(en)(phen)_2]^{3+}$ (<310 nm, Δε/20): C, $[Co(en)_2(phen)]^{3+}$ (<340 nm, Δε/4): D, $[Co(en)_3]^{3+}$

This finding reinforces an earlier demonstration[5] of the same point which used the species (+)-$[Co(phen)_3]^{3+}$ (A of this work). Despite the presence of anomalously large c.d. absorption at *ca.* 380 nm (our value for Δε, −3·9, is larger than that recorded[5]) the exciton and longest wavelength c.d. bands gave self-consistent assignments of configuration (Λ).

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[1] Part XXXVI, R. D. Gillard, P. R. Mitchell, and C. F. Weick, *J.C.S. Dalton*, 1974, 1635.

[2] L. S. Dollimore and R. D. Gillard, *J.C.S. Dalton*, 1973, 933.

[3] S. F. Mason, *Inorg. Chim. Acta Rev.*, 1968, **2**, 89.

[4] B. Bosnich, *Accounts Chem. Res.*, 1969, **2**, 266.

[5] S. F. Mason and B. J. Norman, *J. Inorg. Nuclear Chem. Letters*, 1967, **3**, 285.

Most notably, the exciton region for B shows the typical pattern[3] (giving an assignment of Λ configuration) and a very clear *d—d* band (positive only) giving also[6] a Λ assignment. The two methods are in this case very clearly self-consistent.

EXPERIMENTAL

The salt $[Co(en)(phen)_2][ClO_4]_3 \cdot 2H_2O$ was obtained using essentially the method of Palade.[7] Since difficulties were encountered, details are given.

Circular dichroism spectra of $[Co(en)_x(phen)_{3-x}]^{3+}$ (x = 0—2)

(+)$[Co(en)_2(phen)]^{3+}$	λ [d]	483				316			272	
	Δε [e]	4·08				−3·24			−17·1	*a*
(+)$[Co(en)(phen)_2]^{3+}$	λ [d]	480				318	303sh	282	270	
	Δε [e]	3·10				3·4	19·7	125·1	−118·5	*b*
	λ [d]	463		349	335	317	305	281	274	
	ε [f]	113		1 820	2 770	6 510	12 550	48 600	50 900	*c*
(+)$[Co(phen)_3]^{3+}$	λ [d]	492	378	347	330sh	318sh	302sh	283	269	
	Δε [e]	1·29	−3·93	4·50	8·45	12·6	39·6	233	−140	*a*

[a] From ref. 2. [b] This work. [c] Absorption spectrum. [d] In nm. [e] The sign for Δε is + unless expressly stated. [f] Isotropic molar extinction coefficient, l mol^{-1} cm^{-1}.

The compound $[CoCl_2(phen)_2]Cl \cdot 4\frac{1}{2}H_2O$ (2·0 g), made by the method[8] of Ablov (Found: C, 47·7; H, 3·6; N, 9·15. Calc. for $C_{24}H_{25}Cl_3CoO_{4\cdot5}$: C, 47·6; H, 5·3; N, 9·20%) was suspended in hot ethanol (30—40 ml) and an aqueous solution of ethylenediamine (20% w/v; 1·5 ml) was added, whereupon the solution became yellow-orange. On cooling, yellow crystals containing the species $[Co(en)_2(phen)]^{3+}$ rapidly formed and were filtered off. Their electronic spectrum in water was identical to that of an authentic sample. The filtrate, when set aside overnight, afforded a further batch of crystals. The electronic spectrum of a solution of these crystals was unlike that of either $[Co(en)_2(phen)]^{3+}$ or $[Co(phen)_3]^{3+}$ and cation-exchange chromatography (SP-Sephadex C-25) demonstrated the presence of only one species. The crystals were redissolved in hot water and reprecipitated as the perchlorate $[Co(en)(phen)_2][ClO_4]_3 \cdot 2H_2O$ by addition of an excess of $NaClO_4$ solution (Found: C, 39·0; H, 3·1; N, 10·5. Calc. for $C_{26}H_{28}Cl_3CoN_6O_{14}$: C, 38·4; H, 3·45; N, 10·8%).

The species $[Co(en)(phen)_2]^{3+}$ was resolved using the complex K_3(+)-[Co(L-cysu)$_3$] according to the procedure given earlier.[2] The structure of the $[Co(cysu)_3]^{3-}$ anion is as yet unknown; however, we have measured the ^{13}C magnetic resonance spectrum of a saturated neutral solution in H_2O–D_2O of its potassium salt. This shows three signals of equal intensity at (p.p.m. relative to Me_4Si) 175·27 (sharp, due to CO_2H), 66·67 (broader, probably due to the CH_2), and 57·94 (sharper, due to asymmetric carbons). In view of this simplicity, it seems probable that we are dealing with a *facial*-isomer.

Analysis of the diastereoisomer showed it to be a 1 : 1 salt with seven water molecules of crystallisation (Found: C, 38·0; H, 4·3; N, 11·0. Calc. for (+)-$[Co(en)(phen)_2]$-(+)-$[Co(cysu)_3] \cdot 7H_2O$, $C_{35}H_{53}Co_2N_9O_{19}S_3$: C, 37·6; H, 4·8; N, 11·3%).

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[3/1932 *Received*, 19*th September*, 1973]

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[8] A. V. Ablov, *Russ. J. Inorg. Chem.*, 1961, **6**, 157.