Crystal Structures of Two Isomers of 1,10-bis(salicyclideneamino)-4,7-dithiadecanecobalt(III) Iodide

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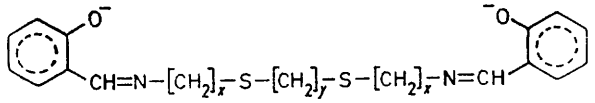
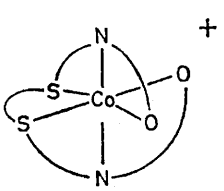
Crystal structure determinations have been carried out on recrystallized samples of the 'brown' and 'green' forms of the title compound $[Co(O{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}[CH_2]_3{\cdot}S{\cdot}[CH_2]_2{\cdot}S{\cdot}[CH_2]_3{\cdot}N{:}CH{\cdot}C_6H_4{\cdot}O)]^+I^-$, (I) and (II) respectively, by X-ray diffraction, using diffractometer data, and refined by least squares to *R* 0.043 (I) and 0·042 (II) for 581 and 3 427 reflections. Crystals of (I) are monoclinic, space group *C*2, *a* = 13.155(6), *b* = 11.915(4), *c* = 7.685(3) Å, β = 106.69(4)°, *Z* = 2. Crystals of (II) are triclinic, space group $P\bar{1}$, *a* = 20.010(8), *b* = 13.321(4), *c* = 10.086(4) Å, α = 68.74(3), β = 93.41(3), γ = 92.90(3)°, *Z* = 4. (II) contains a methanol solvent molecule in the lattice and comprises two types of cation, one in which the S,O,N from the same half of the ligand are coplanar, and a second, identical with that found in (I), in which the two ligand oxygen atoms are mutually *trans*. An absolute configuration is suggested for (I). Both cation types contain two-fold rotation axes, that in (I) being imposed crystallographically.

ONE of the classic co-ordination isomerization types is exemplified by the cobalt(III) complexes of the ligands:

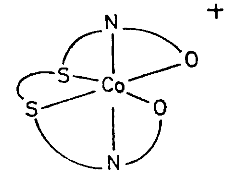


designated eee, ete, tet, *etc.*, according to whether x,y = 2 = 'ethylene' = e or x,y = 3 = 'trimethylene' = t.[1,2] For eee and ete derivatives it was predicted that the spatial requirements of the chelate loops and ligand atoms would enforce planarity of the O–N–S sequences and lead to isolation of only one pair of optical isomers



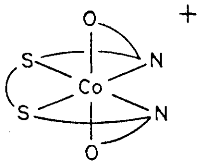
(A)

of type A. Salts of eee and of ete were found to be 'green' and resolvable. With derivatives of tet and ttt ligand constraints are released and it was predicted that a new pair of enantiomers should be possible with non-planar O–N–S sequences:

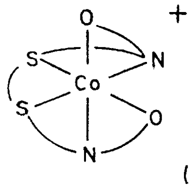


(B)

A second resolvable 'brown' series of salts was obtained from ligands of this type and the hypothesis considered confirmed. A later suggestion that further isomers were possible[3] cast doubt on the assignment of the configuration as (B) rather than (C) or (D):



(C)



(D)

and it was suggested that (C) was the more likely.

Small amounts of the original samples prepared by Dwyer *et al.*[2] were used for the present crystallographic study, namely, $(-)_D[Co(tet)]I$ (green) and $(+)_D[Co(tet)]I$ (brown). Both derivatives were recrystallized from

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[1] F. P. J. Dwyer and F. Lions, *J. Amer. Chem. Soc.*, 1950, **72**, 1545.

[2] F. P. Dwyer, N. S. Gill, E. C. Gyarfas, and F. Lions, *J. Amer. Chem. Soc.*, 1952, **74**, 4188.

[3] B. Bosnich and A. T. Phillip, *J. Amer. Chem. Soc.*, 1968, **90**, 6352.

methanol as rapidly as possible by evaporation at room temperature in an attempt to provide crystals sufficiently large for the crystallography, while seeking to limit racemization and isomerization; after several attempts, a couple of small suitable crystals was obtained in each case, but the limited quantity of the recrystallized sample available precluded determination of its optical rotation.

We now describe the structure determination of these recrystallized ' brown ' and ' green ' derivatives, denoted (I) and (II) respectively. We note, however, that crystals of both (I) and (II) were brown, as was also stated in the original report in which the ' green ' form, initially a green powder yielding a green methanolic solution, crystallized as ' brown plates.' This has been commented on elsewhere[4] where it is observed that [Co(eee)]I formed dark brown crystals and that a further preparation provided dark green-brown crystals. The result of the present investigation casts some light on this anomaly.

EXPERIMENTAL

The crystals used were for (I), a prism 0.04 × 0.04 × 0.12 mm, and for (II), a spheroid, *ca.* 0.12 mm in diameter. Unit cells were calibrated by a least-squares fit of the angular parameters of 15 reflections with 2θ *ca.* 15° (I) and 20° (II), centred in the counter aperture of a Syntex $P\bar{1}$ four-circle diffractometer. A unique data set in the range $2\theta < 40°$ was collected for both structures with Mo-K_α radiation ($\lambda = 0.71069$ Å) (the limit being imposed primarily by the weakness of the data as a result of small crystal sizes) yielding 581 (I) and 4 668 (II) independent reflections. In (I) all reflections were used in the structure solution and refinement; in (II), 3 427 with $I > 3\sigma(I)$ were considered observed and used as the data set. For (I), Friedel-pair reflections were collected in the range $2\theta < 20°$. The data of (I) were corrected for the very small absorption effects in order to enable confident assignment of absolute configuration; no such correction was applied to the data of (II).

Crystal Data.—(I). $C_{22}H_{26}CoIN_2O_2S_2$, $M = 600.5$, Monoclinic, $a = 13.155(6)$, $b = 11.915(4)$, $c = 7.685(3)$ Å, $\beta = 106.69(4)°$, $U = 1\ 153.9(8)$ Å^3, $D_m = 1.79(2)$, $Z = 2$, $D_c = 1.73$ g cm^{-3}, $F(000) = 600$, μ(Mo-K_α) = 21.4 cm^{-1}. Space group $C2$ (C_2^3, No. 5). Neutral-atom scattering factors,[5,6] those for Co and I being corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$).[7]

(II). $C_{22}H_{26}CoIN_2O_2S_2\cdot(0.5CH_3OH)$, $M = 1\ 233$, Triclinic, $a = 20.010(8)$, $b = 13.321(4)$, $c = 10.086(5)$ Å, $\alpha = 68.74(3)$, $\beta = 93.41(3)$, $\gamma = 92.90(3)°$, $U = 2\ 500(2)$ Å^3, $D_m = 1.65(1)$, $Z = 4$, $D_c = 1.64$ g cm^{-3}, $F(000) = 1\ 236$, μ(Mo-K_α) = 19.8 cm^{-1}. Space group $P\bar{1}$ ($C_i{}'$, no. 2), scattering factors for (I). M.p. 170 °C.

Both structures were solved by the heavy-atom method and refined by least squares; in (I), full-matrix least-squares were used, while in (II) 9 × 9 block-diagonal least-squares were used, the parameters of each of the cationic $CoN_2O_2S_2$ cores being refined jointly in order to approximate to a full-matrix procedure. Anisotropic thermal parameters of the form $\exp -2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)$ were employed for all non-hydrogen atoms. Hydrogen-atom positions were estimated geometrically [r(C–H) 1.0 Å] and included as invariants in the refinement. In (II), a difference map showed the presence of an elongated region of electron density which appeared to represent a methanol molecule; it was included as such in the refinement, and appeared to refine satisfactorily and with a meaningful C–O distance, albeit with very high thermal motion, reducing R by >0.01. At convergence no parameter shift in either structure exceeded 0.2 σ, R being 0.043 (I) and 0.042 (II), and $R' \{= (\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{\frac{1}{2}}\}$ being 0.039 and 0.054. A weighting scheme of the form $w = [\sigma^2(F_o) + n \times 10^{-4}(F_o)^2]^{-1}$ was found appropriate for the two structures, for $n = 2$ (I) and 4 (II). The parity of (I) was confirmed as being correct initially by a ratio test of the R value compared with that of the opposite parity, 0.045; subsequent comparison of reflections for which the $|F_c|$ difference exceeded 4% was made for those reflections for which the intensities of the Friedel pairs differed by $>3\sigma$. Because of the weakness of the data set only 6 such reflections were found to satisfy this criterion, all of which confirmed the choice of parity.

Structure amplitudes, a Table of Bijvoet pairs used in the parity assignment for (I), thermal parameters, and details of phenyl ring planes are deposited as Supplementary Publication No. SUP 21640 (26 pp., 1 microfiche).* Computation was carried out on a CDC 6200 machine at the University of Western Australia, with a local variant of the ' X-Ray '72 ' program system.[8]

Each ligand is divided into two parts, a and b. In (II) the cation identical with that in (I) is designated 1; the other is 2. Carbon atoms are numbered according to the following scheme. Results are shown in Tables 1 and 2.

TABLE 1

Atomic fractional cell with least-squares estimated standard deviations in the final digit in parentheses (The atom labelling system is explained in the text.)

Compound (I) (Co, S, and O × 10^4, others × 10^3)

Atom	x	y	z
Co	5 000(—)	0 655(2)	10 000(—)
S	5 537(3)	−0 681(3)	8 405(5)
O	3 682(6)	0 571(7)	8 165(11)
N	556(1)	174(1)	863(1)
C(1)	325(1)	144(1)	714(2)
C(2)	214(1)	140(1)	626(2)
C(3)	165(1)	226(2)	515(2)
C(4)	221(1)	320(1)	490(2)
C(5)	329(1)	324(1)	572(2)
C(6)	383(1)	237(1)	683(2)
C(7)	496(1)	241(1)	749(2)
C(8)	670(1)	176(1)	874(2)
C(9)	703(1)	072(2)	782(2)
C(10)	692(1)	−039(1)	876(2)
C(11)	554(1)	−191(1)	981(2)
I	0	0	0

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* For details, see Notices to Authors, No. 7, *J.C.S. Dalton*, 1975, Index issue.

[4] Footnote in N. A. P. Kane-Maguire and T. E. MacDermott, *Austral. J. Chem.*, 1963, **16**, 1360.

[5] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[6] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

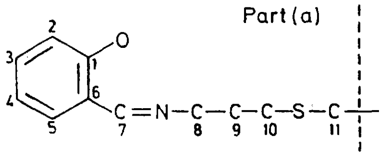
[7] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[8] ' X-Ray ' system, Technical Report TR 192, Computer Science Centre, University of Maryland, U.S.A., version of June 1972.

TABLE 1 (*Continued*)

Compound (II) (Co and I $\times 10^5$, others $\times 10^4$)

Atom	*x*	*y*	*z*
Cation (1), part (a)			
Co	10 155(6)	22 406(10)	43 021(14)
S	1 747(1)	2 289(2)	6 045(3)
O	1 783(3)	2 278(5)	3 284(7)
N	1 015(4)	3 815(6)	3 674(8)
C(1)	1 904(4)	3 047(7)	2 026(9)
C(2)	2 337(5)	2 825(8)	1 143(11)
C(3)	2 507(5)	3 594(9)	−0 143(12)
C(4)	2 245(7)	4 607(9)	−0 565(12)
C(5)	1 833(6)	4 861(9)	0 292(11)
C(6)	1 655(5)	4 087(7)	1 593(9)
C(7)	1 285(5)	4 420(7)	2 501(11)
C(8)	0 786(5)	4 325(8)	4 628(12)
C(9)	1 275(6)	4 211(9)	5 890(13)
C(10)	1 363(6)	3 068(11)	6 920(12)
C(11)	1 676(6)	0 908(9)	7 300(12)
Cation (1), part (b)			
S	1 018(1)	0 436(2)	5 201(3)
O	0 296(3)	2 105(5)	5 514(6)
N	0 423(4)	2 068(6)	2 804(8)
C(1)	−0 317(5)	2 404(7)	5 071(9)
C(2)	−0 732(5)	2 564(7)	6 035(10)
C(3)	−1 390(5)	2 858(8)	5 632(11)
C(4)	−1 655(5)	2 980(8)	4 275(12)
C(5)	−1 253(5)	2 810(8)	3 300(11)
C(6)	−0 576(4)	2 532(7)	3 701(9)
C(7)	−0 214(5)	2 267(8)	2 687(10)
C(8)	0 655(5)	1 564(8)	1 811(11)
C(9)	0 764(6)	0 360(8)	2 557(13)
C(10)	1 297(6)	0 081(7)	3 774(13)
C(11)	1 741(6)	0 211(9)	6 452(13)
Cation (2), part (a)			
Co	60 495(6)	75 975(9)	22 432(12)
S	5 374(1)	9 005(2)	1 266(2)
O	6 566(3)	6 341(5)	2 838(6)
N	6 399(3)	7 958(5)	3 864(7)
C(1)	6 698(4)	5 744(7)	4 168(9)
C(2)	6 829(5)	4 638(7)	4 462(10)
C(3)	6 997(5)	3 997(8)	5 835(13)
C(4)	7 032(5)	4 372(8)	6 986(11)
C(5)	6 894(5)	5 437(8)	6 690(11)
C(6)	6 717(4)	6 120(7)	5 304(9)
C(7)	6 631(5)	7 254(7)	5 038(9)
C(8)	6 431(5)	9 069(7)	3 812(9)
C(9)	5 742(5)	9 533(8)	3 679(10)
C(10)	5 474(6)	9 963(8)	2 161(11)
C(11)	4 547(5)	8 413(8)	1 675(12)
Cation (2), part (b)			
S	5 216(1)	6 683(2)	3 940(3)
O	6 771(3)	8 497(5)	1 239(6)
N	5 770(4)	7 177(6)	0 621(7)
C(1)	6 727(5)	9 054(7)	−0 151(9)
C(2)	7 155(5)	9 974(7)	−0 703(9)
C(3)	7 145(5)	10 564(8)	−2 142(11)
C(4)	6 722(5)	10 260(8)	−3 096(10)
C(5)	6 319(5)	9 370(8)	−2 572(10)
C(6)	6 297(4)	8 758(7)	−1 118(9)
C(7)	5 911(5)	7 773(7)	−0 675(10)
C(8)	5 841(6)	6 091(7)	0 813(11)
C(9)	4 816(6)	5 813(8)	1 535(11)
C(10)	4 913(5)	5 566(8)	3 126(11)
C(11)	4 514(5)	7 571(8)	3 132(12)
Anions			
I(1)	56 176(5)	27 067(6)	29 356(9)
I(2)	14 915(4)	78 913(7)	03 011(8)
Solvent			
C	7 001([illegible])	1 533(27)	1 932(53)
O	6 636(14)	1 963(24)	0 591(30)



DISCUSSION

The unit cells of both (I) and (II) (depicted in Figures 1 and 2 respectively) contain discrete mononuclear

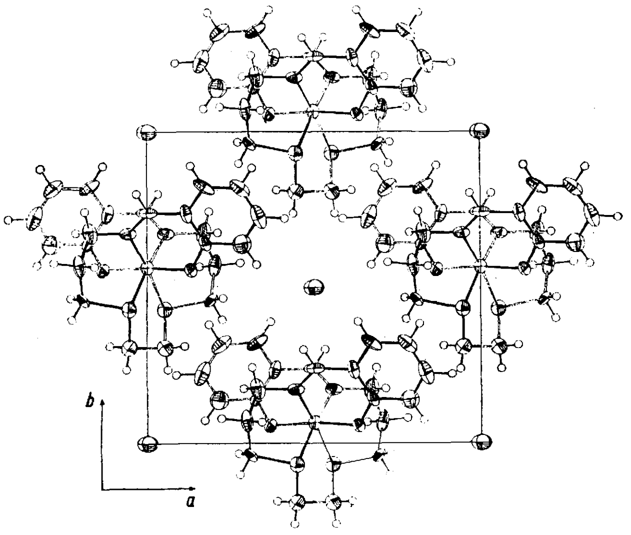


FIGURE 1 Unit cell contents of (I) projected down *c*, showing 50% thermal ellipsoids. Hydrogen atoms are shown with an arbitrary diameter of 0.1 Å. Note that the axial system is right-handed and the suggested absolute configuration is as shown

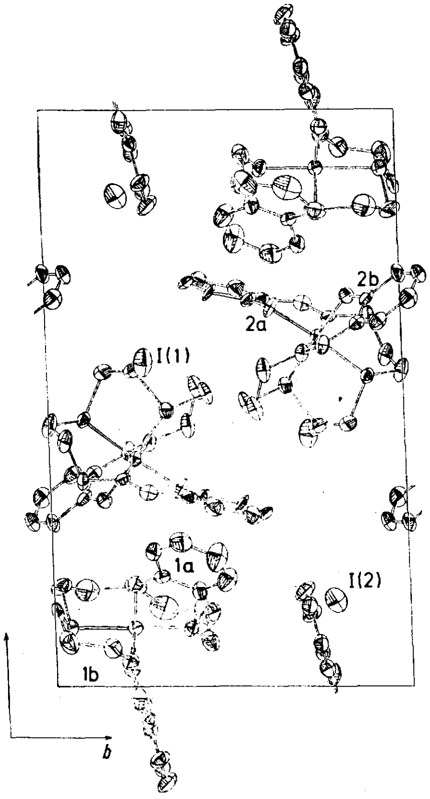


FIGURE 2 Unit-cell contents of (II) projected down *c*, showing 50% thermal ellipsoids; the methanol solvent molecule has been omitted for clarity

cations and, in the case of (II), probably a solvent molecule. The lattice of (I) is particularly simple, both

TABLE 2

Interatomic distances (Å) and angles (°) in the cation geometry; primes denote atoms from the alternate half of the cation

		Compound (II)			
		Molecule (1)		Molecule (2)	
	Compound (I)	Part (a)	Part (b)	Part (a)	Part (b)
Co–O	1.897(7)	1.886(7)	1.904(7)	1.898(6)	1.913(6)
Co–O–C(1)	123.0(8)	123.0(6)	124.8(6)	124.3(7)	122.6(5)
O–C(1)	1.32(2)	1.34(1)	1.31(1)	1.31(1)	1.33(1)
C(1)–C(2)	1.42(2)	1.39(2)	1.39(2)	1.43(1)	1.41(1)
O–C(1)–C(2)	118(1)	118.2(8)	117.9(8)	116.9(9)	118.1(9)
O–C(1)–C(6)	124(1)	123.4(9)	123.0(9)	124.3(9)	123.8(8)
C(1)–C(6)	1.40(2)	1.40(1)	1.40(1)	1.40(1)	1.41(1)
C(2)–C(1)–C(6)	118(1)	118.3(8)	119.1(8)	118.9(8)	118.1(8)
C(2)–C(3)	1.37(2)	1.38(1)	1.39(1)	1.37(1)	1.38(1)
C(1)–C(2)–C(3)	121(1)	121.4(9)	120.3(9)	118.5(9)	120.6(9)
C(3)–C(4)	1.38(3)	1.38(2)	1.39(2)	1.42(2)	1.40(1)
C(2)–C(3)–C(4)	121(1)	119(1)	121(1)	123(1)	121(1)
C(4)–C(5)	1.37(2)	1.37(2)	1.39(2)	1.38(1)	1.36(1)
C(3)–C(4)–C(5)	119(1)	121(1)	120(1)	118(1)	118(1)
C(5)–C(6)	1.40(2)	1.40(1)	1.42(1)	1.40(1)	1.40(1)
C(4)–C(5)–C(6)	122(1)	120(1)	119(1)	121(1)	123(1)
C(5)–C(6)–C(1)	119(1)	120(1)	121(1)	121(1)	119(1)
C(1)–C(6)–C(7)	121(1)	121.9(8)	123.2(8)	120.5(7)	121.5(7)
C(5)–C(6)–C(7)	119(1)	117.9(9)	115.8(9)	118.5(9)	118.9(9)
C(6)–C(7)	1.44(2)	1.41(2)	1.44(2)	1.45(1)	1.43(1)
C(7)–N	1.28(2)	1.30(1)	1.30(1)	1.29(1)	1.30(1)
C(6)–C(7)–N	127(1)	127.4(9)	125.3(9)	125.8(9)	126.9(9)
N–Co	1.94(1)	1.959(7)	1.937(8)	1.947(8)	1.957(9)
C(7)–N–C(8)	116(1)	118.6(8)	115.5(9)	115.2(8)	115.5(9)
C(7)–N–Co	122(1)	121.2(8)	122.9(8)	123.5(7)	122.0(7)
Co–N–C(8)	121(1)	119.7(5)	121.2(6)	121.3(5)	121.9(6)
N–C(8)	1.48(2)	1.47(1)	1.50(2)	1.46(1)	1.48(1)
N–C(8)–C(9)	112(1)	113(1)	112.1(8)	112.5(8)	115.6(9)
C(8)–C(9)	1.55(2)	1.52(2)	1.53(1)	1.52(1)	1.52(2)
C(9)–C(10)	1.53(2)	1.51(2)	1.53(2)	1.50(1)	1.52(2)
C(8)–C(9)–C(10)	113(1)	115(1)	114(1)	112(1)	111(1)
C(10)–S	1.79(1)	1.81(2)	1.80(1)	1.81(1)	1.81(1)
C(9)–C(10)–S	109(1)	109.7(9)	109.8(9)	116.3(7)	115.8(6)
S–C(11)	1.82(2)	1.82(1)	1.82(1)	1.80(1)	1.81(1)
S–Co	2.243(5)	2.238(4)	2.241(3)	2.252(3)	2.254(3)
C(10)–S–C(11)	103.9(6)	103.9(6)	104.2(6)	104.8(6)	102.6(5)
C(10)–S–Co	104.1(5)	105.8(4)	103.9(3)	112.3(3)	110.1(4)
Co–S–C(11)	101.2(6)	101.3(4)	100.9(4)	103.6(3)	105.5(3)
S–C(11)–C(11′)	106(1)	105.9(8)	107.3(8)	113.2(7)	114.2(8)
C(11)–C(11′)	1.52(2)	1.49(2)		1.49(1)	
O–Co–N	92.4(4)	92.2(3)	92.6(3)	91.2(3)	92.2(3)
O–Co–S	85.5(3)	84.9(2)	85.8(2)	171.2(2)	171.4(2)
N–Co–S	87.0(4)	86.8(3)	85.5(2)	97.6(2)	95.8(2)
O–Co–O′	174.0(4)	173.6(2)		92.8(3)	
N–Co–N′	96.5(5)	98.2(3)		175.2(3)	
S–Co–S′	89.6(2)	89.6(1)		89.3(1)	
O–Co–N′	91.6(4)	92.2(3)	91.2(3)	84.6(3)	85.6(3)
O–Co–S′	90.3(3)	90.4(2)	89.9(2)	90.8(2)	88.3(2)
N–Co–S′	175.5(4)	175.4(3)	174.3(3)	86.6(2)	86.7(2)

cations and anions being located on special positions on two-fold axes in a centred array. The cation of (I) is of type (C) as suggested by Bosnich and Phillip.[3]

Where crystals of (I) are optically active, those of (II) are not, being a 1 : 1 mixture of the racemates of two distinct cation types; since one of these, (1), is identical to (I), the original 'green' compound may well correspond to the other, type (A), (2). The present derivative is presumably the least soluble product of the racemization–isomerization process and its composition provides a possible explanation of the 'brown crystals' of the green form observed both by us and others.[1-4]

The essentially catoptric nature of the rotatory dispersion curves of the $(-)_D$ 'green' and $(+)_D$ 'brown' forms in the visible region was first used as support [9] for Dwyer and Lions assertion about the stereochemistry of the isomer interchange occurring by interchange of the terminal oxygen atoms.[2] Clearly those two terminal chelates do invert their configuration in the interchange but it does not effectively alter the ligand field and it was pointed out later [3] that the spectral difference between the ions was more reasonably interpreted by way of the structural assignments for the two isomers found in the present study.

The $(+)_D$ 'brown' isomer has the probable configuration shown and the catoptric nature of the rotatory dispersion (r.d.) and circular dichroism (c.d.) curves in the visible region could be accommodated by the isomerization process depicted provided the orientation of the terminal chelates is the major contributor to the

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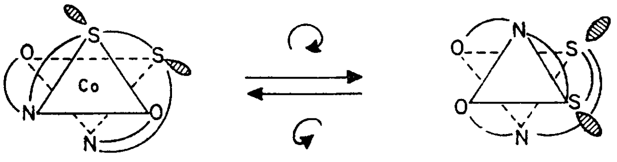
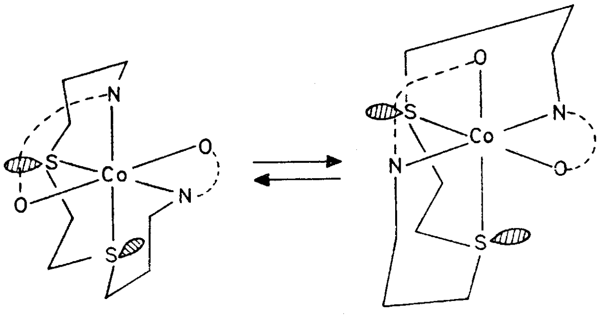
[9] A. M. Sargeson, 'Chelating Agents and Metal Chelates,' Academic Press, New York, U.S.A., **1964**.

rotatory strength in this region. Clearly the chelate pairs have a Λ orientation for the ' brown ' form.

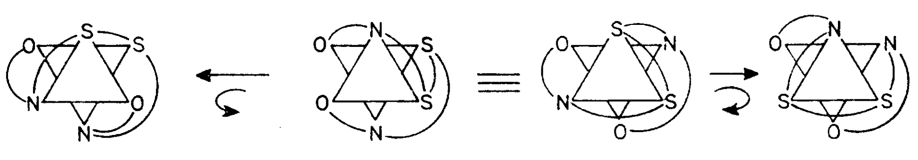


(C) (+)$_{\mathrm{D}}$ 'brown'   (A) (−)$_{\mathrm{D}}$ 'green'

The absolute configuration suggested for the (+)$_{\mathrm{D}}$ ' brown ' isomer is contrary to that predicted by the exciton c.d. study. Unfortunately, the other structural result involves racemic pairs and the absolute configuration of the 'green' isomer cannot be defined unequivocally. If the isomer interconversion occurs as shown $(A)\rightleftarrows(C)$ by a relatively simple trigonal twist then the absolute configuration of the ' green ' isomer follows as shown. This is the same as the configuration predicted previously.[3] A consequence of this interconversion is that the chiral *S* centres invert: *S*(brown)$\rightleftarrows$*R*(green). There is some doubt about the ease of such interconversions. Early work with a co-ordinated dialkyl sulphide indicated inversion to be slow[10] but more recent n.m.r. studies indicate that the activation energy for inversion of such chiral centres may be *ca.* 5 kcal mol^{-1}. If this is true it serves as no real impediment to rearrangement on the time scale involved here.[11-13] Although these studies have been conducted with Pt$^{\mathrm{II}}$ and Rh$^{\mathrm{III}}$ primarily, there is no expectation that Co$^{\mathrm{III}}$ will be grossly different. There is clearly a dilemma between the two sets of information which at the moment is unresolved.* An alternative interpretation of the interconversion[3] therefore is that the chiral *S* centres direct the stereochemistry. A complex succession of edge displacements could lead to the interconversion shown, where the chirality of the *S* centres is retained along with that of the terminal chelates. This leads to the assignment of the absolute configuration of the (−)$_{\mathrm{D}}$ green isomer, as shown, which is also the inverse of that described previously.[3] The present disagreement with the exciton analysis could come from several sources and clearly needs to be re-examined. Equally clearly, it is not possible to reach a conclusion about the absolute configuration of the (−)$_{\mathrm{D}}$ ' green ' isomer from the present work, and a single-crystal *X*-ray study of the (+)$_{\mathrm{D}}$ ' green ' [Co(eee)]I isomer is now contemplated to resolve the problem.



(+) $_{\mathrm{D}}$, 'brown'   (−) $_{\mathrm{D}}$,'green'



(C)   (A)   (A)   (D)

It has been noted elsewhere that the facile interconversion between ' green ' and ' brown ' forms is solvent dependent.[4] The simple mode for interconversion of the (−)$_{\mathrm{D}}$ ' green ' to (+)$_{\mathrm{D}}$ ' brown ' through the anticlockwise twist about the trigonal axis or a complex set of edge displacements for the N and O atoms will accommodate the retention of optical activity. However, qualification of these mechanisms is required to accommodate racemization. A succession of trigonal twists or edge displacements will generate three diastereoisomers but no racemic pairs. This implies that racemization must occur either *via* inversion at the *S* centres or *via* a trace of a labile Co$^{\mathrm{II}}$ species. For the last possibility the rates of electron transfer could be rapid. The Co$^{\mathrm{II}}$ species should be close to the spin ' crossover ' point and may even be low spin (*cf.* the pyridine 2-aldimine analogues of these thia-amines[14] which were among the first low-spin Co$^{\mathrm{II}}$ ions described).

The geometry of the two cation types is generally very similar. The conformations of the six-membered rings are all chairs and the ethanedisulphide chelate in the (+)$_{\mathrm{D}}$ ' brown ' isomer has a λ conformation. The racemic ' green ' form shows both λ and δ forms. Information about the planarities of various moieties and deviations is summarized in Table 3. Significant differences of other than a trivial nature were found only about the cobalt atom, where the relative dispositions of the ligand atom changes, and the sulphur atom, where appreciable changes are found in the surrounding angular geometry of C(9)–C(10)–S,

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* There also appears to be an error in Section 4 of ref. 3, where the configuration assignment is discussed in terms of c.d. bands at 14 000 and 16 500 cm^{-1}. Presumably they should be read as 24 000 cm^{-1} and 26 500 cm^{-1}.

[10] F. G. Mann, *J. Chem. Soc.*, 1930, 1745.

[11] E. W. Abel, R. P. Bush, F. J. Hopton, and C. R. Jenkins, *Chem. Comm.*, 1966, 58.

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[13] R. A. Walton, *J. Chem. Soc.*, 1967, 1852.

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TABLE 3

Equations of least-squares planes in the form $pX + qY + rZ = s$, where the orthogonal Å frame is defined by X parallel to a, Z in the ac plane. Atom deviations (in square brackets) are in Å as are σ, the estimated standard deviations of the defining atoms

The cationic core planes

(*a*) cations (I) and (II) (1) (values given in that order)

Plane	10^4p	10^4q	10^4r	s	σ	χ^2
CoS_2N_2	7 213	0 000	6 926	8.251	0.05	110.5
	8 084	0 383	−5 873	−1.753	0.05	228.6

[Co 0.00, 0.00; N(a) 0.05, 0.06; S(a) −0.05, −0.05; S(b) (0.05), 0.05; N(b) (−0.05), −0.06; C(11a) 0.45, 0.49; C(11b) (−0.45), −0.37; C(10a) 1.38, 1.36; C(10b) (−1.38), −1.40; C(9a) 1.16, 1.16; C(9b) (−1.16), −1.25; C(8a) 1.18, 1.19; C(8b) (−1.18), −1.21; C(7a) −0.92, −0.95; C(7b) (0.92), 0.95]

Plane	10^4p	10^4q	10^4r	s	σ	χ^2
Co, N(a), O(a), O(b), S(b)	−4 920	7 236	4 841	1 923	0.03	45.6
	5 752	0 043	8 180	5.432	0.04	97.6

[Co 0.05, 0.06; N(a) −0.01, −0.01; S(b) −0.01, 0.00; O(a) −0.02, −0.03; O(b) (−0.02), −0.03; C(1a) 0.53, 0.55; C(6a) 0.82, 0.80; C(7a) 0.42, 0.38; C(1b) 0.93, 0.91; C(8a) −0.68, −0.68; C(10b) 0.98, 0.93; C(11b) −1.73, −1.74]

Angle between this plane and associated phenyl ring: 24.0, 23.2°

Plane	10^4p	10^4q	10^4r	s	σ	χ^2
Co, N(b), O(a), O(b), S(a)	4 920	7 236	−4 841	−0.903	0.03	34.3
	−0 823	9 964	−0 214	2.458	0.04	102.1

[Co 0.05, 0.06; N(b) −0.01, −0.03; S(a) −0.01, −0.03; O(a) −0.02, 0.00; O(b) −0.02, 0.00; C(1b) 0.53, 0.47; C(6b) 0.82, 0.70; C(7b) 0.42, 0.33; C(8b) −0.68; −0.65; C(1a) 0.93, 0.94; C(10a) 0.98, 0.98; C(11a) −1.73, −1.73]

Angle between this plane and associated phenyl ring: (24.0), 19.5°

(*b*) Cation II(a)

Plane	10^4p	10^4q	10^4r	s	σ	χ^2
CoS_2O_2	2 581	2 838	9 235	11.08	0.15	2 107

[Co 0.00, O(a) −0.16, O(b) 0.16, S(a) −0.14, S(b) 0.14, C(11a) −0.67, C(11b) 0.01, C(10a) 1.48, C(10b) −1.35, C(1a) 0.65, C(1b) −0.71]

Plane	10^4p	10^4q	10^4r	s	σ	χ^2
Co, S(a), O(a), N(a), N(b)	7 634	5 382	−3 571	11.73	0.03	50.9

[Co −0.02, S(a) −0.02, O(a) −0.03, N(a) 0.03, N(b) 0.03, C(1a) −0.62, C(6a) −0.89, C(7a) −0.40, C(8a) 0.60, C(9a) −0.20, C(10a) 0.20, C(11a) −1.70, C(7b) 1.05, C(8b) −0.98]

Angle between this plane and associated phenyl ring: 26.2°

Plane	10^4p	10^4q	10^4r	s	σ	χ^2
Co, S(b), O(b), N(a), N(b)	5 970	−8 008	0 486	−4 159	0.06	246

[Co −0.01, S(b) −0.06, O(b) −0.07, N(a) 0.07, N(b) 0.06, C(1b) −0.71, C(6b) −0.94, C(7b) −0.39, C(8b) 0.82, C(9b) 0.32, C(10b) 0.71, C(11b) −1.80, C(7a) 1.08, C(8a) −1.03]

Angle between this plane and associated phenyl ring: 26.8°

C(10)–S–Co, Co–S–C(11), S–C(11a)–C(11b) (Table 2). A small *trans*-effect may be apparent in the cobalt–sulphur distance, where in cation (2) in (II), a slight increase in ⟨Co–S⟩ [2.25_3 Å] is found in comparison to the values for cation (1) in (II), and (I) ⟨Co–S⟩ [2.23_9 and 2.24_3 Å], in which the *trans*-atoms are oxygen rather than nitrogen.

For the cobalt(III)–salicylideneamine ligand system, there is nothing remarkable; the geometry parallels that observed in many previous structures. Oxygen exhibits a slight deviation (0.00—0.06 Å) on the same side of the ring plane as nitrogen (0.11—0.17 Å); cobalt, however, deviates considerably on the other side of the plane (−0.47 to −0.60 Å). Details of other ligand planes are given in Table 3, and torsion angles in the ligand strings in Table 4. There are little comparable data in the literature for cobalt(III)–mercaptide sulphur systems; the present distances are shorter than those observed in the tris complexes of cobalt(III) with the conjugated chelate ligands such as dithiocarbamate (2.27_1),[15] diethyldithiocarbamate (2.25_8),[16] *O*-ethyl thiocarbonate (2.27),[17] and dimethyl dithiophosphate (2.32 Å),[18] but surprisingly similar to those observed for the bridging mercaptide–cobalt(III) distances [2.242(2) and 2.250(2) Å] found in di-μ-ethylthio-tetrakisethyldicobalt(III).[19]

TABLE 4

Torsion angles (°) in the ligand string; values for each entry are in the sequence (I), (II) [cation section (1a), (1b), (2a), (2b)]

Co–O–C(1)–C(6)	22.0	26.3	21.4	25.8	25.9
O–C(1)–C(6)–C(7)	6.3	3.8	5.0	4.3	5.2
C(1)–C(6)–C(7)–N	−13.0	−14.5	−12.7	−15.3	−17.7
C(6)–C(7)–N–Co	−9.4	−5.9	−6.5	−4.9	−3.0
C(6)–C(7)–N–C(8)	164.9	166.0	166.2	173.5	167.9
C(7)–N–C(8)–C(9)	−104.9	−100.8	−103.1	116.4	125.2
Co–N–C(8)–C(9)	69.4	71.3	69.8	−65.2	−64.0
N–C(8)–C(9)–C(10)	−64.3	−65.3	−61.1	83.7	75.2
C(8)–C(9)–C(10)–S	69.1	65.3	66.5	−60.0	−65.4
C(9)–C(10)–S–Co	−67.7	−63.8	−68.0	24.1	43.5
C(9)–C(10)–S–C(11)	−173.2	−170.0	−173.3	−87.8	−68.4
C(10)–S–C(11)–C(11)	157.5	159.3	155.4	78.9	93.9
Co–S–C(11)–C(11)	49.8	49.6	47.8	−39.0	−22.0
S–C(11)–C(11)–S	−66.6	−65.4		41.2	

[5/1456 *Received*, 23*rd July*, 1975]

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