for the arginine and argininate complexes, respectively.

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[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND ORGANIC CHEMISTRY, UNIVERSITY OF SYDNEY]

Sexadentate Chelate Compounds. III[1]

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A series of sulfur-containing α,ω-diamines of the general formula $NH_2\cdot(CH_2)_x\cdot S\cdot(CH_2)_y\cdot S\cdot(CH_2)_z\cdot NH_2$, where x, y and z have values of 2 or 3, has been prepared and the bases condensed with salicylaldehyde or 2-hydroxy-1-naphthaldehyde. The resultant Schiff bases behave as sexadentate chelate compounds and can occupy all six coördination positions about a cobalt$^{(III)}$ ion. For certain of them no less than four different unsymmetrical spatial arrangements of the chelate moiety about the central cobalt atom are possible (two pairs of enantiomers) and this capacity has been correlated with the structure of the chelate. Most of the complex salts prepared have been resolved into optical isomers, and the molecular rotations of some of these are extremely high, one of them possessing the highest molecular rotation so far recorded.

The amine groups and the sulfur atoms in diamines of the general formula $NH_2\cdot(CH_2)_x\cdot S\cdot(CH_2)_y\cdot S\cdot(CH_2)_z\cdot NH_2$, where x, y and z have values of two or three, are separated by ethylene or trimethylene bridges; and a convenient nomenclature distinguishing between them designates them simply by a combination of the letters E and T (representing the ethylene or trimethylene bridges). Thus, the base 1,8-diamino-3,6-dithia-octane ($x = y = z = 2$), the metallic derivatives of whose bis-salicylidene and bis-(2-hydroxy-1-naphthylmethylene) condensation products were discussed in Part I,[3] would be designated EEE; 1,9-diamino-3,7-dithianonane (x, $z = 2$; $y = 3$) would be ETE; 1,10-diamino-4,7-dithiadecane (x, $z = 3$; $y = 2$) would be TET, and so on. This paper describes the preparation of sexadentate chelate compounds by condensation of the symmetrical bases ETE, TET and TTT with salicylaldehyde or 2-hydroxy-1-naphthaldehyde and their coördination with cobalt$^{(III)}$ ions. Discussion of the compounds derived from the unsymmetrical bases EET and ETT is reserved for a later paper.

The bases ETE, TET and TTT were prepared by methods exactly similar to that already described[3] for EEE, the appropriate ω-bromo-alkylphthalimide (2 moles) being condensed in alkaline absolute ethanolic solution with the requisite α,ω-dithiol paraffin to the bis-phthalimido derivative of the base, and this being then hydrolyzed by the method of Ing and Manske.[4]

Loss of two protons from a molecule of such a Schiff base as the bis-salicylidene derivative of any one of the bases EEE, ETE, TET or TTT and union of the residue with a cobalt$^{(III)}$ ion leads to formation of a complex ion in which the organic residue is attached through the oxygen, nitrogen and sulfur atoms to the central cobalt atom. The organic residue is thus attached to the metal atom in five successive "chelate loops," and the complex ion may be very clearly formulated in a two-dimensional diagram such as I, the successive chelate loops being numbered from 1 up to 5.

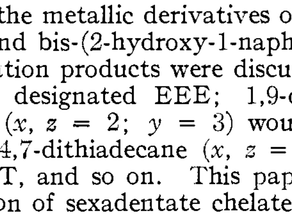

Fig. 1.—I.

Now, it was pointed out in Part I[3] that in the 1,8-bis-(o-hydroxyarylideneamino)-3,6-dithiaoctane cobalt$^{(III)}$ salts (from EEE base) the spatial requirements of the sulfur and nitrogen atoms demand a planar arrangement of each of the oxygen–nitrogen–sulfur atom sequences, starting from each end of the sexadentate moiety; and probably, also, substantially, of the 1,2- and 4,5-chelate loops containing them. Lengthening of the chain of carbon atoms between the two sulfur atoms from 2 to 3 (ETE base) would convert chelate loop 3 from a five-membered ring to a six-membered ring but would not be expected to produce any great effect other than, perhaps, some symmetrical buckling in the chelate loop 3; although it should be remembered that coördination compounds derived from the dialkyl ethers of 1,2-dithiol ethane are considerably more stable with their five-membered chelate ring than are any coördination compounds derived from the ethers of α,ω-dithiol paraffins in which the polymethylene chain between the sulfur atoms is longer than ethylene.[5]

In fact, experiment showed that the Schiff bases from ETE behaved normally, or, rather, similarly to those derived from EEE base, yielding characteristic green binary complex cobalt$^{(III)}$ salts comparable to the analogous ones derived from EEE base and capable of resolution into dextro and levo forms.

On the other hand, in the complexes derived from TET and TTT, expansion of the five-membered sulfur- and nitrogen-containing chelate loops 2 and 4 to six-membered chelate loops might be expected to present difficulties in the way of maintenance of

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[1] For the previous communication in this series see F. P. Dwyer, F. Lions and D. P. Mellor, THIS JOURNAL, **72**, 5037 (1950).

[2] Commonwealth Research Assistant, University of Sydney.

[3] F. P. Dwyer and F. Lions, THIS JOURNAL, **72**, 1545 (1950).

[4] H. R. Ing and R. H. F. Manske, *J. Chem. Soc.*, 2348 (1926).

[5] *Cf.* L. Tschugaeff, *Ber.*, **41**, 2222 (1908); *Compt. rend.*, **154**, 33 (1912); L. Tschugaeff and A. Kobljanski, *Z. anorg. Chem.*, **83**, 8 (1913); L. Tschugaeff and W. Subbotin, *Ber.*, **43**, 1200 (1910).

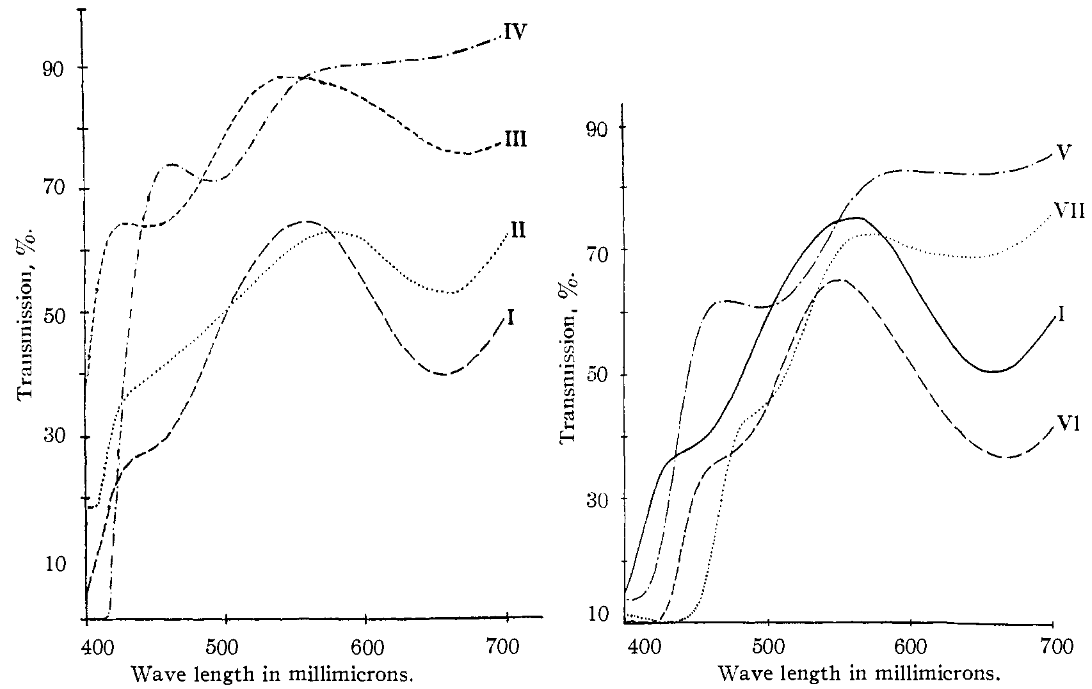

Fig. 2.—All measurements were made in a 1-cm. cell at 20°: I, 1,8-bis-(salicylideneamino)-3,6-dithiaoctane cobalt(III) chloride (from EEE base), 0.02% solution in water; II, 1,9-bis-(salicylideneamino)-3,7-dithianonane cobalt(III) iodide monohydrate (from ETE base), 0.02% solution in water; III, 1,10-bis-(salicylideneamino)-4,7-dithiadecane cobalt(III) iodide (green salt) (from TET base), 0.04% solution in water; IV, 1,10-bis-(salicylideneamino)-4,7-dithiadecane cobalt(III) chloride (brown salt) (from TET base), 0.04% solution in 50% aqueous methanol; V, 1,11-bis-(salicylideneamino)-4,8-dithiaundecane cobalt(III) bromide dihydrate (from TTT base), 0.02% solution in 30% aqueous methanol; VI, 1,10-bis-(2′-hydroxy-1′-naphthylmethyleneamino)-4,7-dithiadecane cobalt(III) bromide monohydrate (green salt) (from TET base), 0.03% solution in 30% aqueous methanol; VII, 1,10-bis-(2′-hydroxy-1′-naphthylmethyleneamino)-4,7-dithiadecane cobalt(III) bromide trihydrate (brown salt) (from TET base), 0.03% solution in 30% aqueous methanol.

a planar orientation of the chelate loop systems 1–2 and 4–5 because of atom crowding. Models indicate the high probability for each nitrogen atom of non-coincidence of the plane containing its three valence links with the plane containing the corresponding oxygen–nitrogen–sulfur atom sequence, and suggest that a similar spatial arrangement of the chelate loops to that shown in Fig. 3 of Part I should even be possible. Experiment showed that from the Schiff bases derived from TET it is possible to prepare two series of isomeric complex cobalt$^{(III)}$ salts. Salts belonging to the first series have the characteristic green color and absorption spectrum (Fig. 2) of the complex cobalt(III) salts derived from EEE and ETE, can be resolved into optically active enantiomers and are to be formulated similarly to them (Fig. 2 of Part I).[3] Under conditions described in detail in the experimental section these green salts are readily converted into corresponding brown isomeric salts with quite different light absorption (Fig. 2), and it is noteworthy that an optically active green salt yields mainly the corresponding brown salt in optically active form. At the same time some racemization occurs and it is possible to isolate small amounts of the *dl*-green salt and the *dl*-brown salt from the mother liquors. The retention of asymmetry during isomerization is most easily explained by assuming that the metal–sulfur and the metal–nitrogen ligands remain intact during the change but that the terminal oxygen atoms interchange positions in the octahedral complex (change from the configuration of Fig. 2 to that of Fig. 3 of Part I). It is also worthy of comment that the brown complex cobalt$^{(III)}$ chloride can be re-converted, at least partially, to the green complex chloride, II.

Further support for the above hypothesis derives from the fact that the complex cobalt$^{(III)}$ salts from TTT are obtainable only in the brown form and cannot be obtained in the green modification. In these TTT salts atom crowding has probably been intensified so much that the configuration of Fig. 2 (Part I)[3] is no longer possible.

It is worthy of comment that attempts to carry out the resolution into optical enantiomers of several of the complexes described in this paper using optically active acids such as *d*-α-bromocamphor-π-sulfonic acid, *d*-camphor-10-sulfonic acid, *d*-tartaric acid and *l*-mandelic acid led only to formation of intractable gums. Success, however, was readily attained by the use of tartar emetic and formation of the *d*-antimonyl tartrates. Comment should also be made on the high molecular rotations of several of the optically active complex salts described (Table I). Thus, the molecular rotations (sodium D line) of the optically active forms of 1,10-bis-(2′-hydroxy-1′-naphthylmethyleneamino)-4,7-dithiadecane cobalt$^{(III)}$ bromide trihydrate were found to be +87.030° and −84.200°. So far as we are aware these are the highest ever recorded. Further, it should be noted that the green isomer of 1,10-bis-(salicylideneamino)-4,7-dithiadecane co-

TABLE I

	Degrees			
	$[\alpha]^{20}_D$	$[M]^{20}_D$	$[\alpha]^{20}_{5461}$	$[M]^{20}_{5461}$
1,8-Bis-(salicylideneamino)-3,6-dithiaoctane cobalt$^{(III)}$ iodide			+8,800	+50,160
			−8,800	−50,160
1,9-Bis-(salicylideneamino)-3,7-dithianonane cobalt$^{(III)}$ iodide	+ 6,930	+40,620		
	− 7,240	−42,780	−7,180	−42,100
1,10-Bis-(salicylideneamino)-4,7-dithiadecane cobalt$^{(III)}$ iodide (Green salt)	+11,800	+70,870	+5,100	+30,980
	−11,630	−69,850	−5,040	−30,650
1,10-Bis-(salicylideneamino)-4,7-dithiadecane cobalt$^{(III)}$ iodide (Brown salt)	+ 1,400	+ 8,400	−5,350	−32,200
	− 1,400	− 8,400	+5,400	+32,400
1,10-Bis-(2′-hydroxy-1′-naphthylmethyleneamino)-4,7-dithiadecane cobalt$^{(III)}$ bromide trihydrate (Green salt)	+12,300	+87,030	+9,400	+66,500
	−11,900	−84,200	−8,800	−61,730

balt$^{(III)}$ iodide which is dextrorotatory in sodium light (sodium D line) or in the mercury green light (Hg_{5461} line) when isomerized to the brown isomer is levorotatory in sodium light but dextrorotatory in the mercury green light—a phenomenon undoubtedly to be correlated with the altered absorption spectrum.

It should finally be mentioned that interaction in methanol solution of any of these Schiff bases with the acetates of nickel, iron$^{(II)}$, copper or zinc led to formation of complexes which could be obtained as pale green, red, dark green or yellow powders, respectively. They were ill-defined and were obtained only in small yields. They were soluble in chloroform and could be re-precipitated from chloroform solution by petroleum ether as powders which contained chloroform of crystallization. This was lost at 100°, the powders changing to gums. Analyses were unsatisfactory and the compounds were not further examined.

Experimental

Analyses.—Considerable difficulty was experienced in obtaining accurate analytical results for carbon, hydrogen and nitrogen in the complex salts described despite their submission to several micro-analytical laboratories. The best success was obtained by our University of Sydney micro-analyst, Mrs. E. Bielski, who developed a technique of very slow combustion in a very hot tube which proved satisfactory. We gratefully acknowledge our indebtedness.

Rotations.—Unless otherwise stated all rotations were measured in a 1-dm. tube, immediately after preparation of the solutions. However, racemization was not observed to occur at room temperature in solutions of any of the optically active substances described.

α,ω-Bis-phthalimidodithiaparaffins.—A solution of the requisite dithiol (1 mole) in absolute ethanol was added to a cooled absolute ethanolic solution of sodium ethoxide (2 moles). Then a hot absolute ethanolic solution of the appropriate ω-bromo-alkylphthalimide (2 moles) was added and the mixture refluxed for 3–4 hours, or until it was no longer alkaline. Next, most of the alcohol was distilled off and sufficient water added to the cooled residue to dissolve the sodium bromide formed during the reaction and to precipitate the product completely. This was then collected and recrystallized from glacial acetic acid.

α,ω-Diaminodithiaparaffins.—The α,ω-bis-phthalimidodithiaparaffin (1 mole) was suspended in ethanol (5–7 ml. for each gram) boiling under reflux and hydrazine hydrate solution (50% soln., 3–4 moles) added, the refluxing being continued for 2 hours. Excess of concentrated hydrochloric acid was then added and the refluxing continued for a further 0.5 hour, after which as much alcohol as possible was distilled off and a little water added. After cooling the phthalhydrazide was filtered off and washed with a little water. The combined filtrates were made strongly alkaline with solid sodium hydroxide until the base separated as an oil which was then removed by repeated extraction with ether. The combined ether extracts were dried quickly with potassium hydroxide pellets and the solvent removed leaving the base as a colorless or very pale yellow oil which could be distilled *in vacuo* if desired. The bases so obtained were not analyzed as such, but as suitable solid derivatives.

TABLE II

Compound	Formula	M.p., °C.	Yield, %	Analyses, % Calcd.	Analyses, % Found
1,9-Bisphthalimido-3,7-dithianonane[a]	$C_{23}H_{22}N_2O_4S_2$	112	95	C, 60.8 H, 4.9 N, 6.2	C, 60.5 H, 5.0 N, 6.1
1,10-Bisphthalimido-4,7-Dithiadecane	$C_{24}H_{24}N_2O_4S_2$	128	90	C, 61.5 H, 5.2 N, 6.0 S, 13.6	C, 61.3 H, 5.3 N, 5.9 S, 13.9
1,11-Bisphthalimido-4,8-dithiaundecane	$C_{25}H_{26}N_2O_4S_2$	79	97	C, 62.2 H, 5.4 N, 5.8	C, 62.0 H, 5.5 N, 5.8

[a] The quantities used were: 1,3-dithiolpropane (36 g.) in ethanol (150 ml.), β-bromoethylphthalimide in ethanol (400 ml.) and sodium (15.34 g.) in ethanol (350 ml.).

1,9-Diamino-3,7-dithianonane was a colorless oil, b.p. 147° (0.4 mm.), 88% yield. **Its diacetyl derivative** formed colorless leaflets from ethanol, m.p. 92.5°. (*Anal.* Calcd. for $C_{11}H_{22}N_2O_2S_2$: C, 47.4; H, 8.0; N, 10.1. Found: C, 47.6; H, 8.2; N, 9.8.) **The bis-5-bromosalicylidene derivative** formed yellow needles, m.p. 123° from ethanol. (*Anal.* Calcd. for $C_{21}H_{24}N_2O_2S_2Br_2$: N, 5.0. Found: N, 4.7).

1,10-Diamino-4,7-dithiadecane was a colorless oil (yield 95%). **Its diacetyl derivative** formed colorless leaflets, m.p. 122° from ethanol. (*Anal.* Calcd. for $C_{12}H_{24}N_2O_2S_2$: N, 9.6. Found: N, 9.6.) **The bis-5-bromosalicylidene derivative** formed yellow leaflets, m.p. 96° from ethanol. (*Anal.* Calcd. for $C_{22}H_{26}N_2O_2S_2Br_2$: N, 4.9. Found: N, 4.8.) **The di-picrate** formed deep yellow needles, m.p. 134° from ethanol. (*Anal.* Calcd. for $C_{20}H_{18}N_8O_{14}S_2 \cdot C_2H_5OH$: N, 15.8; EtO–, 6.3. Found: N, 15.8; EtO–, 6.3.)

1,11-Diamino-4,8-dithiaundecane was a colorless oil (yield 96%). **Its diacetyl derivative** formed colorless leaflets, m.p. 93° from chloroform and petroleum ether. (*Anal.* Calcd. for $C_{13}H_{26}N_2O_2S_2$: N, 9.1. Found: N, 9.1.) **The bis-5-bromosalicylidene derivative** formed yellow leaflets, m.p. 58° from ethanol. (*Anal.* Calcd. for $C_{23}H_{28}N_2O_2S_2Br_2$: N, 4.8. Found: N, 4.6.)

α,ω-Bis-(*o*-hydroxyarylideneamino)-dithiaparaffins.—Hot ethanolic solutions of the diamino-dithiaparaffin (1 mole) and the *o*-hydroxy aldehyde (2 moles) were mixed then boiled for a few minutes. On cooling the Schiff base usually separated as an oil which could be induced to crystallize and then be recrystallized from ethanol.

1,9-Bis-(salicylideneamino)-3,7-dithianonane (I).—Minute yellow prisms, m.p. 41°. (*Anal.* Calcd. for $C_{21}H_{26}N_2O_2S_2$: C, 62.7; H, 6.5; N, 7.0. Found: C, 62.4; H, 6.6; N, 7.0.)

1,10-Bis-(salicylideneamino)-4,7-dithiadecane (II).—Yellow leaflets, m.p. 79.5°. (*Anal.* Calcd. for $C_{22}H_{28}N_2O_2S_2$: C, 63.4; H, 6.8; N, 6.7. Found: C, 63.0; H, 6.7; N, 6.7.)

1,11-Bis-(salicylideneamino)-4,8-dithiaundecane (III).—Yellow needles, m.p. 46.5°. (*Anal.* Calcd. for $C_{23}H_{30}N_2O_2S_2$: C, 64.1; H, 7.0; N, 6.5. Found: C, 63.8; H, 7.1; N, 6.5.)

1,10-Bis-(2′-hydroxy-1′-naphthylmethyleneamino)-4,7-dithiadecane (IV).—Yellow leaflets from benzene, m.p. 154.5°. (*Anal.* Calcd. for $C_{30}H_{32}N_2O_2S_2$: C, 69.7; H, 6.2; N, 5.4. Found: C, 69.4; H, 6.3; N, 5.4.)

dl-**1,9-Bis-(salicylideneamino)-3,7-dithianonane Cobalt(III) Iodide Monohydrate.**—A solution of cobalt(II) acetate tetrahydrate (2.88 g.) in hot methanol (100 ml.) was added to a solution of the Schiff base I (4.03 g.) in hot methanol (200 ml.) and the mixture maintained at the boiling point for 5 minutes, a slight cloudiness in the resulting red-brown solution being cleared by addition of just sufficient hot methanol. Air was then drawn through the hot solution for 0.5 hour, after which water (200 ml.) was added and the passage of air continued for a further 3 hours. Finally, the solution was diluted with water (400 ml.), heated to 80° for 0.5 hour and then allowed to stand overnight. After removal of small amounts of a brown decomposition product which had separated the solution was warmed to 50° and 20% potassium iodide solution (100 ml.) added. On cooling and scratching the cobalt(III) complex iodide was precipitated in bluish-black shining crystals which were collected and recrystallized from hot water containing a little potassium iodide. The pure salt crystallized in black prisms or dark brown plates, m.p. 243° (dec.). It was sparingly soluble in cold water to a green solution but moderately soluble in hot water to an intensely greenish-brown solution. The solution in alcohol was brown, but the substance was insoluble in acetone, benzene or ether.

Anal. Calcd. for $Co(C_{21}H_{24}N_2O_2S_2)I \cdot H_2O$: Co, 9.8; I, 21.0; C, 41.7; H, 4.3; N, 4.6. Found: Co, 9.8; I, 21.0; C, 41.4; H, 4.4; N, 4.9.

The perchlorate could be obtained as a very sparingly soluble precipitate by addition of sodium perchlorate to a solution of the iodide, but was not further studied.

dl-**1,9-Bis-(salicylideneamino)-3,7-dithianonane Cobalt(III) Chloride Dihydrate.**—A solution of the above-described iodide (2 g.) in hot water (50 ml.) was shaken with silver chloride (5 g.) for 15 minutes. After filtration from silver halides the deep green solution was evaporated to dryness (water-bath) and the resulting greenish-brown gum dissolved in hot methanol (50 ml.). A few drops of water were added, then ether. The substance soon crystallized in dark brown prisms which, after drying over calcium chloride, melted at 193°.

Anal. Calcd. for $Co(C_{21}H_{24}N_2O_2S_2)Cl \cdot 2H_2O$: Co, 11.1; Cl, 6.7. Found: Co, 11.1; Cl, 6.6.

dl-**1,9-Bis-(salicylideneamino)-3,7-dithianonane Cobalt(III)** ***d*****-Antimonyl Tartrate Hexahydrate.**—The above-described iodide (8.0 g.) was dissolved in hot water (200 ml.) and freshly prepared silver chloride (20 g.) added. The hot mixture was shaken for 10 minutes to effect transformation to the more soluble chloride after which filter-pulp was added and the silver halides filtered off. After washing the precipitate with a little hot water the deep-green filtrate and washings were evaporated on a water-bath to a volume of 160 ml. A solution of potassium *d*-antimonyl tartrate (2.02 g., 2 moles) in hot water (70 ml.) was then added gradually with scratching, a dark brown crystalline solid being precipitated. After cooling in ice the solid was collected and recrystallized from hot water containing a little potassium antimonyl tartrate. It came out in prismatic needles and leaflets, m.p. 253° (dec.), and was moderately soluble in hot water, sparingly in alcohol and insoluble in acetone.

Anal. Calcd. for $Co(C_{21}H_{24}N_2O_2S_2)(C_4H_4O_7Sb) \cdot 6H_2O$: Co, 6.9; Sb, 14.3; H_2O, 12.7. Found: Co, 7.0; Sb, 14.3; H_2O, 12.6.

l-**1,9-Bis-(salicylideneamino)-3,7-dithianonane Cobalt(III)** ***d*****-Antimonyl Tartrate Heptahydrate.**—The *dl*-antimonyl tartrate described above was dissolved in just sufficient water at 90° with vigorous shaking, and after filtration the dark greenish-brown solution was cooled to room temperature, the sides of the container being scratched. The bluish-black crystals that separated were found to be strongly levorotatory while the mother liquor was dextrorotatory. The mother liquor was reserved for the isolation of the dextro form. The crystals were recrystallized several times as before until the pure levo form of the *d*-antimonyl tartrate was obtained in black prismatic needles, m.p. 260°.

An aqueous solution containing 13.44 mg. per 100 ml. gave −1.47° in a 2-dm. tube for the sodium D line, whence $[\alpha]^{20}_{\text{D}}$ −5470°.

Anal. Calcd. for $Co(C_{21}H_{24}N_2O_2S_2)(C_4H_4O_7Sb) \cdot 7H_2O$: Co, 6.76; Sb, 13.97; H_2O, 14.5. Found: Co, 6.8; Sb, 13.9; H_2O, 14.4.

d-**1,9-Bis-(salicylideneamino)-3,7-dithianonane Cobalt(III)** ***d*****-Antimonyl Tartrate Pentahydrate.**—The mother liquor from which the above described levo form had been separated was treated with saturated potassium antimonyl tartrate solution. The precipitated salt was redissolved in water at 90° and saturated potassium antimonyl tartrate solution (50 ml.) added to the hot solution, which was then cooled to room temperature with scratching of the walls of the containing vessel. The crystalline solid which separated was strongly dextrorotatory and was recrystallized, using the same method, repeatedly until its specific rotation was constant. It crystallized in black leaflets, m.p. 235°.

An aqueous solution containing 11.36 mg. per 100 ml. gave +0.61° for the sodium D line, whence $[\alpha]^{20}_{\text{D}}$ +5,370°.

Anal. Calcd. for $Co(C_{21}H_{24}N_2O_2S_2)(C_4H_4O_7Sb) \cdot 5H_2O$: Co, 7.06; Sb, 14.6; H_2O, 10.8. Found: Co, 7.1; Sb, 14.5; H_2O, 10.9.

l-**1,9-Bis-(salicylideneamino)-3,7-dithianonane Cobalt(III) Iodide.**—A solution of the above described *d*-antimonyl tartrate of the levo cobalt(III) complex (0.5 g.) in hot water (50 ml.) was treated with a few drops of dilute hydrochloric acid and the resulting antimony oxychloride removed by filtration. Solid potassium iodide was then added to the warm solution to incipient crystallization and the complex iodide caused to precipitate by cooling in ice. After washing with cold dilute potassium iodide solution the precipitate was redissolved in hot water and reprecipitated with potassium iodide as before. It was washed with a little ice-water, dried on a porous tile and then recrystallized from warm methanol, being thus obtained in brown nodular prisms, m.p. 235°, by the addition of ether. This optically active complex iodide was much more soluble in water than the *dl*-iodide.

An aqueous solution containing 8.56 mg. per 100 ml. at 20° gave rotations of −1.24° for the sodium D line and −1.23° for the Hg line 5461 in a 2-dm. tube; whence $[\alpha]^{20}_{\text{D}}$ −7.240° and $[\alpha]^{20}_{5461}$ −7.180° and $[M]^{20}_{\text{D}}$ −42,780° and $[M]^{20}_{5461}$ −42,100°. The observed rotation (sodium D line) had fallen to −1.16° after 20 minutes and to −1.10° after 30 minutes at 100°. It was noteworthy that the solution became greenish-brown on heating but that the color was restored to green on cooling.

Anal. Calcd. for $Co(C_{21}H_{24}N_2O_2S_2)I$: Co, 10.1; I, 21.6; C, 43.2; H, 4.1. Found: Co, 10.0; I, 21.5; C, 42.9; H, 4.3.

d-**1,9-Bis-(salicylideneamino)-3,7-dithianonane Cobalt(III) Iodide.**—This salt was prepared from the dextrorotatory antimonyl tartrate by a method exactly similar to that used for its enantiomer, and crystallized similarly in brown nodular prisms, m.p. 235°. An aqueous solution containing 9.88 mg. per 100 ml. at 20° showed a rotation of +1.37° for the sodium D line, in a 2-dm. tube, whence $[\alpha]^{20}_{\text{D}}$ +6,930° and $[M]^{20}_{\text{D}}$ +40,620°.

Anal. Found: Co, 10.0; I, 21.7; C, 42.8; H, 4.3.

When it was recrystallized from water this substance crystallized with two molecules of water of crystallization. (*Anal.* Calcd. for $Co(C_{21}H_{24}N_2O_2S_2)I \cdot 2H_2O$: Co, 9.5; I, 20.4. Found: Co, 9.4; I, 20.3.)

dl-**1,10-Bis-(salicylideneamino)-4,7-dithiadecane Cobalt(III) Iodide Dihydrate (Green Salt).**—Cobalt(II) chloride hexahydrate crystals (0.4 g.) was added to a boiling methanolic solution of the Schiff base II (0.5 g. in 100 ml.) and then a boiling solution of sodium acetate crystals (0.4 g.) in methanol (30 ml.) to which 3% hydrogen peroxide (5 ml.) had been added was rapidly added with shaking. More hydrogen peroxide (5 ml. of 3%) was at once added and then the solution was poured immediately into a 10″-evaporating dish cooled in ice. If larger amounts were used or the cooling of the mixture was too slow almost all of the complex cobaltic salt was obtained in the brown modification. Saturated potassium iodide solution (5 ml.) was added to the green methanol solution and then ether in excess. The precipitate formed was collected, freed from ether and then fractionally extracted with hot water while a green solution resulted. The combined green extracts were then cooled and filtered free from a small amount of brown residue, which was reserved. Addition of solid potassium iodide to the cold green solution led to precipitation of the green complex salt as a brown to black precipitate, which was recrystallized from hot water with the help of potassium iodide (yield 60%). The black prismatic needles finally obtained had m.p. 173° and were soluble in alcohol but insoluble in benzene or chloroform.

Anal. Calcd. for Co($C_{22}H_{26}N_2O_2S_2$)I·2H_2O: C, 41.5; H, 4.8; Co, 9.53; I, 20.51; mol. wt., 618. Found: C, 41.7; H, 5.0; Co, 9.4; I, 20.4; mol. wt. in α-naphthol (m.p. 94.7°, *K* 18.79) 243.

dl **- 1,10 - Bis - (salicylideneamino) - 4,7 - dithiadecane Cobalt(III) Iodide (Brown Salt).**—The brown residue obtained in the preparation of the green salt was dissolved in hot methanol, an equal volume of water was added and then potassium iodide in excess, the complex iodide separating as a brown precipitate. Alternatively, the original preparative mixture, or a solution of the green salt in methanol could be refluxed for an hour, diluted with an equal volume of water and the complete iodide precipitated. It recrystallized from hot 70% methanol in brown micaceous flakes, m.p. 195°, which were sparingly soluble in water and acetone.

Anal. Calcd. for Co($C_{22}H_{26}N_2O_2S_2$) I: C, 44.0; H, 4.4; Co, 9.81; I, 21.13; mol. wt., 600. Found: C, 43.6; H, 4.8; Co, 9.8; I, 21.0; mol. wt. (in α-naphthol), 293.

dl **- 1,10 - Bis - (salicylideneamino) - 4,7 - dithiadecane Cobalt(III) Chloride Monohydrate (Brown Salt).**—The iodide just described was suspended in hot 20% aqueous methanol and shaken with freshly prepared silver chloride for 20–30 minutes. The solids were removed by filtration and the filtrate rapidly evaporated to dryness. The resulting brown residue was recrystallized from hot water and thus obtained in monoclinic prisms or in plates, m.p. 187°, which were much more soluble in water or in ethanol than the iodide. An aqueous solution maintained at 90–100° slowly acquired a greenish color. When equilibrium had been established between 20 and 30% had been converted to the green salt, and the green iodide could be isolated by fractional precipitation with potassium iodide. By retransformation of the unchanged brown iodide to the chloride and repetition of the heating process it was possible after several such operations to make the conversion of the brown salt to the green salt almost quantitative.

Anal. Calcd. for Co($C_{22}H_{26}N_2O_2S_2$)Cl·H_2O: Co, 11.18; Cl, 6.73. Found: Co, 11.2; Cl, 6.7.

The equivalent conductivities of *M*/1,000 and *M*/5,000 solutions of the brown chloride were 122 and 118.5 ohms^{-1}, respectively, consistent with a binary electrolyte.

d **- 1,10 - Bis - (salicylideneamino) - 4,7 - dithiadecane Cobalt(III)** ***d*****-Antimonyl Tartrate Pentahydrate (Green Salt).**—The racemic iodide (4 g.) was dissolved in hot water (80 ml.) and the solution shaken with excess silver chloride for some time, then filtered. Potassium *d*-antimonyl tartrate (1 g., 0.5 mole) was added to the hot solution of the chloride and the mixture cooled to room temperature. The black prisms and plates of the *d*-complex *d*-antimonyl tartrate which separated were filtered from the solution of the *l*-complex chloride and washed with a little ice-water. They were recrystallized by taking up in the minimum quantity of hot water, adding a little potassium antimonyl tartrate and allowing to cool.

Anal. Calcd. for Co($C_{22}H_{26}N_2O_2S_2$)($C_4H_4O_7$Sb)·5H_2O: Co, 6.95; Sb, 14.33; H_2O, 10.85. Found: Co, 6.95; Sb, 14.5; H_2O, 10.8.

A 0.02% solution in aqueous methanol gave α_D +1.71°, whence $[\alpha]^{20}_D$ +8,550°.

d **- 1,10 - Bis - (salicylideneamino) - 4,7 - dithiadecane Cobalt(III) Iodide (Green Salt).**—A solution of the *d*-complex *d*-antimonyl tartrate just described in the minimum volume of 50% methanol at 40° was treated with saturated potassium iodide solution. The brown microcrystalline precipitate of the dextro iodide which came down on cooling in ice was much more soluble in water than the racemate, and was recrystallized to constant rotation by transformation to the chloride with silver chloride in the minimum volume of hot water followed by fractional precipitation with solid potassium iodide. The substance was finally recrystallized from warm methanol by the addition of ether and obtained in brown plates, m.p. 174°.

Anal. Calcd. for Co($C_{22}H_{26}N_2O_2S_2$)I: C, 44.0; H, 4.4; Co, 9.81; I, 21.13. Found: Co, 9.8; I, 21.2.

An aqueous solution containing 0.0267 g. per 250 ml. gave α_D +1.26° and α_{5461} +1.09° (2-dm. tube), whence $[\alpha]^{20}_D$ +11,800° and $[\alpha]^{20}_{5461}$ +5,100 and $[M]^{20}_D$ +70,870° and $[M]^{20}_{5461}$ +30,980°.

l **- 1,10 - Bis - (salicylideneamino) - 4,7 - dithiadecane Cobalt(III) Iodide (Green Salt).**—The solution of the levo chloride remaining after the separation of the *d*-complex *d*-antimonyl tartrate (*vide supra*) was treated with potassium antimonyl tartrate (1 g.) and cooled in ice, the small precipitate which separated being discarded. Saturated potassium iodide solution was added to the filtrate fractionally so as to produce two precipitates. The first precipitate had only small optical activity and was rejected. The strongly levorotatory second precipitate was transformed to the chloride using the minimum volume of water and again fractionally precipitated as the iodide, the first fraction being again rejected and the process repeated on the more soluble fractions until they possessed constant rotation. The final fraction was recrystallized from warm methanol with the help of ether and obtained in brown plates, m.p. 174–175°.

Anal. Found: C, 43.4; H, 4.8; Co, 9.8; I, 21.0.

An aqueous solution containing 0.0243 g. per 250 ml. had α_D −1.13° and α_{5461} −0.49°; whence $[\alpha]^{20}_D$ −11,630°, $[\alpha]^{20}_{5461}$ −5,040, $[M]^{20}_D$ −69,850° and $[M]^{20}_{5461}$ −30,650°.

d **- 1,10 - Bis - (salicylideneamino) - 4,7 - dithiadecane Cobalt(III) Iodide (Brown Salt).**—It was possible to convert the brown racemic iodide described above by standard methods to such salts as the *d*-α-bromocamphor-π-sulfonate, the *d*-camphorsulfonate, the *d*-tartrate, the *d*-antimonyl tartrate and the *l*-mandelate, all of which salts crystallized well from different solvents but could not be separated into fractions of different rotation. Recourse was therefore had to the isomeric change of the green salts to the brown. A solution of the levo iodide (green salt) (0.5 g.) in methanol (80 ml.) and 1% potassium iodide solution (5 ml.) was refluxed (water-bath) for 10 minutes, then cooled in ice. On scratching the sides of the container a brown crystalline precipitate came down. This was removed and the refluxing continued for a further ten minutes after which, by cooling and scratching a second crop of brown crystals was obtained. The process was then repeated, four crops in all of brown crystals being obtained. The optical rotatory power of each of these was the same, so that they were combined. Examination of the methanolic mother liquor revealed almost complete loss of optical activity. It was found to contain a mixture of the racemic iodide (green salt) and the racemic iodide (brown salt) so that the refluxing process had been responsible for isomerization of the green salt to the brown salt, and, additionally, racemization. However, because of the considerably smaller solubility of the optically active form of the brown salt it could be isolated in the manner described. It was finally recrystallized from boiling methanol and formed micaceous plates, m.p. 215°.

Anal. Found: Co, 9.8; I, 21.2.

A 0.02% solution in 50% aqueous methanol gave α_D +0.28° and α_{5461} −1.07°; whence, $[\alpha]^{20}_D$ +1,400°, $[\alpha]^{20}_{5461}$ −5,350°, $[M]^{20}_D$ +8,410° and $[M]^{20}_{5461}$ −32,200°.

l **- 1,10 - Bis - (salicylideneamino) - 4,7 - dithiadecane Cobalt(III)Iodide (Brown Salt).**—This salt was prepared from the dextro complex iodide (green salt) by a method exactly similar to that used for its enantiomer and was obtained in flat plates, m.p. 215°, from methanol.

Anal. Found: C, 43.6; H, 4.6; Co, 9.8; I, 21.1.

A 0.02% solution in 50% aqueous methanol gave α_D −0.28° and α_{5461} +1.08°; whence, $[\alpha]^{20}_D$ −1,400°, $[\alpha]^{20}_{5461}$ +5,400°, $[M]^{20}_D$ −8,400° and $[M]^{20}_{5461}$ +32,400°.

An equimolecular mixture of this iodide with its enantiomer melted at 195° and this melting point was not depressed by admixture with some of the *d,l*-iodide prepared as described above.

dl **- 1,10 - Bis - (2′ - hydroxy - 1′ - naphthylmethyleneamino)- 4,7-dithiadecane Cobalt(III) Chloride Tetrahydrate (Green Salt).**—Cobalt(III) chloride hexahydrate (0.5 g.) was added to a boiling solution of the Schiff base IV (0.5 g.) in methanol (200 ml.), and then a solution of sodium acetate crystals (0.5 g.) and hydrogen peroxide (5 ml. of 3%) in methanol (15 ml.). The mixture became deep green and was cooled immediately and filtered. The filtrate was reduced in volume to about 50 ml. *in vacuo* and then water (50 ml.) was added together with solid potassium chloride. A sticky solid separated and became crystalline on standing overnight. It was recrystallized by solution in hot methanol followed by addition of water and potassium chloride, and obtained in nodular clusters of needles, m.p. 177°. It was sparingly soluble in water, soluble in chloroform but insoluble in acetone. Boiling of its solution in methanol led to isomerization to a greenish-brown sparingly soluble salt.

Anal. Calcd. for $Co(C_{30}H_{30}N_2O_2S_2)Cl\cdot4H_2O$: Co, 8.6; Cl, 5.2; C, 52.9; H, 5.6. Found: Co, 8.6, Cl, 5.4; C, 52.6; H, 5.6.

dl-**1,10-Bis-(2′-hydroxy-1′-naphthylmethyleneamino)-4,7-dithiadecane cobalt(III) bromide monohydrate (green salt)** was prepared similarly to the chloride. It was more sparingly soluble and came out in green needles, m.p. 217°.

Anal. Calcd. for $Co(C_{30}H_{30}N_2O_2S_2)Br\cdot H_2O$: Co, 8.8; Br, 11.9; C, 53.7; H, 4.8; N, 4.2. Found: Co, 8.9; Br, 11.8; C, 53.5; H, 4.8; N, 4.0.

dl-**1,10-Bis-(2′-hydroxy-1′-naphthylmethyleneamino)-4,7-dithiadecane Cobalt(III) Bromide Trihydrate (Brown Salt).**—A solution of the green salt just described in methanol was boiled under reflux for some hours, the color changing to greenish-brown. The solution was then diluted with water and solid potassium bromide added. The greenish-brown precipitate which came down was collected and recrystallized from hot aqueous methanol to which potassium bromide was added, the process being repeated several times. The salt was eventually obtained in greenish-brown needles, m.p. 203°.

Anal. Calcd. for $Co(C_{30}H_{30}N_2O_2S_2)Br\cdot3H_2O$: Co, 8.3; Br, 11.3; C, 50.9; H, 5.1; N, 4.0. Found: Co, 8.4; Br, 11.3; C, 51.2; H, 5.2; N, 4.0.

dl-**1,10-Bis-(2′-hydroxy-1′-naphthylmethyleneamino)-4,7-dithiadecane Cobalt(III)** ***d*****-Antimonyl Tartrate (Green Salt).**—A solution of the green *dl*-chloride in hot water was treated with an excess of potassium *d*-antimonyl tartrate solution. The green powder which separated after cooling was collected, washed with water in which it is only sparingly soluble and dried. It was recrystallized by solution in chloroform and then adding ether. The microcrystalline powder decomposed on heating, first becoming a gum.

Anal. Calcd. for $Co(C_{30}H_{30}N_2O_2S_2)(C_4H_4O_7Sb)$: Co, 6.86; Sb, 14.17. Found: Co, 6.9; Sb, 14.1.

Addition of petroleum ether (b.p. 40–70°) to a chloroform solution of this salt led to precipitation. If the process were carried out fractionally the least soluble fractions appeared to contain *d*-complex *d*-antimonyl tartrate, the intermediate fractions both *d*-complex *d*-antimonyl tartrate and *l*-complex *d*-antimonyl tartrate and the most soluble fractions *l*-complex *d*-antimonyl tartrate. The fractionation was difficult owing to the tendency of the precipitated material, especially that in the least soluble fractions, to separate in gummy form. By repeated fractionation of the least soluble fractions a product was eventually obtained whose specific rotation $[\alpha]^{20}_D$ of +3.600° remained unaltered after as many as ten recrystallizations. Because of the much higher rotation of the *l*-complex *d*-antimonyl tartrate (*vide infra*) it would appear that this product was a *partial racemate* containing 2 moles of *d*-complex *d*-antimonyl tartrate to 1 mole of *l*-complex *d*-antimonyl tartrate.

Anal. Calcd. for $Co(C_{30}H_{30}N_2O_2S_2)(C_4H_4O_7Sb)$: Co, 6.86; Sb, 14.17. Found: Co, 6.9; Sb, 14.1.

Repeated recrystallization of the more soluble fractions from the above described fractionation, using chloroform and petroleum ether, eventually led to *l*-**1,10-bis-(2′-hydroxy-1′-naphthylmethyleneamino)-4,7-dithiadecane cobalt(III)** ***d*****-antimonyl tartrate (green salt)** being isolated as a green microcrystalline powder. Its specific rotation $[\alpha]^{20}_D$ was found to be −7.600°, but it is almost certain that it was not optically pure.

Anal. Found: Co, 6.8; Sb, 14.1.

l-**1,10-Bis-(2′-hydroxy-1′-naphthylmethyleneamino)-4,7-dithiadecane Cobalt(III) Bromide Trihydrate (Green Salt).**—The *l*-complex *d*-antimonyl tartrate just described (2 g.) was suspended in methanol (30 ml.) and 10% sodium acetate solution (10 ml.) added. On shaking well most of the solid dissolved. After filtration water (3 vol.) and solid potassium bromide were added to the deep green solution to precipitate all the complex as bromide. The dried precipitate was dissolved in chloroform (30 ml.) containing methanol (5 ml.) and precipitated fractionally with moist ether. The least soluble fractions contained racemic bromide. By repeated recrystallization almost pure levo salt was obtained as a green microcrystalline powder, m.p. 190–191°. This was higher than that recorded for the pure dextro salt (*vide infra*) due to the presence of racemate. It could be shown that addition of racemate to either of the optically active enantiomers in small amounts *raised* the melting point.

Anal. Calcd. for $Co(C_{30}H_{30}N_2O_2S_2)Br\cdot3H_2O$: C, 50.9; H, 5.1; N, 4.0; Co, 8.34; Br, 11.3. Found: C, 51.1; H, 5.2; N, 3.9; Co, 8.4; Br, 11.3.

A 0.01% solution in 30% methanol gave α_D −1.19° and α_{5461} −0.88 whence $[\alpha]^{20}_D$ −11,900°, $[\alpha]^{20}_{5461}$ −8,800°, $[M]^{20}_D$ −84,200° and $[M]^{20}_{5461}$ −61,730°.

d-**1,10-Bis-(2′-hydroxy-1′-naphthylmethyleneamino)-4,7-dithiadecane Cobalt(III) Bromide Trihydrate (Green Salt).**—The partial racemate described above was converted into the complex bromides, and the dried product taken up in chloroform containing methanol and fractionally precipitated with moist ether. The dextrorotatory complex bromide separated last and was only obtained pure after repeated recrystallization as a microcrystalline powder, m.p. 180°.

Anal. Found: Co, 8.4; Br, 11.3; C, 50.9; H, 5.1; N, 4.0.

A 0.01% solution in 30% methanol gave α_D +1.23° and α_{5461} +0.94°, whence $[\alpha]^{20}_D$ +12,300°, $[\alpha]^{20}_{5461}$ +9,400°, $[M]^{20}_D$ +87,030° and $[M]^{20}_{5461}$ +66,500°.

dl-**1,11-Bis-(salicylideneamino)-4,8-dithiaundecane Cobalt(III) Bromide Dihydrate.**—Cobalt(II) chloride hexahydrate (3.2 g.) was added to a boiling solution of the Schiff base III (4 g.) in methanol (250 ml.), and then a solution of crystalline sodium acetate (2.2 g.) and 3% hydrogen peroxide (20 ml.) in methanol (100 ml.) was added. The resulting deep reddish-brown solution was filtered from traces of insoluble matter and allowed to evaporate at room temperature to about 100 ml. Water (100 ml.) was then added, followed by solid potassium bromide. After crystallization from aqueous methanol with the help of potassium bromide of the solid which had separated it was obtained in dark brown prisms, m.p. 207°, which were very sparingly soluble in water but soluble in alcohol or acetone.

Anal. Calcd. for $Co(C_{23}H_{28}N_2O_2S_2)Br\cdot2H_2O$: Co, 9.8; Br, 13.2; C, 45.8; H, 5.3; N, 4.6. Found: Co, 9.9; Br, 13.1; C, 46.0; H, 5.5; N, 4.6.

It was possible to transform this complex salt into the corresponding crystalline *d*-antimonyl tartrate, *d*-tartrate, *d*-camphorsulfonate, *d*-α-bromocamphor-π-sulfonate and *d*-hydrogen tartrate by standard methods. However, none of these salts could be separated into fractions with varying rotation by any method of fractional crystallization employed.

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