

TABLE V  
 SATURATION EFFECT IN POLYSUBSTITUTED ACIDS

	$pK_a$		$pK_a$		$pK_a$		$pK_a$
CH <sub>4</sub>	40						
CH <sub>3</sub> NO <sub>2</sub>	11	CH <sub>3</sub> COCH <sub>3</sub>	20	CH <sub>3</sub> SO <sub>2</sub> CH <sub>3</sub>	23	CH <sub>3</sub> CN	25
CH <sub>2</sub> (NO <sub>2</sub> ) <sub>2</sub>	4	CH <sub>2</sub> (COCH <sub>3</sub> ) <sub>2</sub>	9	CH <sub>2</sub> (SO <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	14	CH <sub>2</sub> (CN) <sub>2</sub>	12
CH(NO <sub>2</sub> ) <sub>3</sub>	0	CH(COCH <sub>3</sub> ) <sub>3</sub>	6	CH(SO <sub>2</sub> CH <sub>3</sub> ) <sub>3</sub>	0	CH(CN) <sub>3</sub>	0

ratio of the rates for water and for hydroxide ion should not change too much in going from acetone to other monosubstituted acids of the same strength and the ratio has been assumed constant. The acid ionization constants obtained in this way have been checked by seeing that the corresponding reverse rate constants,  $k_2$ , did not exceed the theoretical limiting value of *ca.*  $10^{13}$  l./mole min. predicted by Onsager's theory<sup>36</sup> for ion recombination. There are reasons why the rate of recombination of two oppositely charged ions could be less than given by this theory, but it is difficult to see how it could be greater. The estimated constants are shown in parentheses in Table IV. The order of effect of the common activating groups on the acidity of acids of the CH<sub>3</sub>X type is thus NO<sub>2</sub> > CO > SO<sub>2</sub> > COOH > COOR > CN  $\approx$  CONH<sub>2</sub> > halogen. This is not the same order as would be obtained from a consideration of acids of the HOX type which gives<sup>37</sup> SO<sub>2</sub> > NO<sub>2</sub> > COOH  $\approx$  CN > CO > halogen.

It can be misleading to estimate the ionization constant of a di- or trisubstituted acid from those of the monosubstituted acids. This is illustrated in Table V. Evidently there is a saturation effect

(36) L. Onsager, *J. Chem. Phys.*, **2**, 599 (1934).

(37) See G. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, Chapter VI.

which sets in more strongly the greater the electron withdrawing power of the substituting group.

**Primary and Secondary Acids and Bases.**—Several years ago Lewis and Seaborg<sup>38</sup> suggested that there was a fundamental difference, not of degree but of kind, between primary acids and bases which react with each other instantaneously, and secondary acids and bases which are slow in all their neutralization reactions. Now both the forward and reverse reactions of equation (1) are typical acid-base reactions and in Table IV are recorded rate constants covering a range of twenty-four powers of ten. These include rates which are far too slow to measure (half-lives of thousands of years), rates which are as fast as the reactants can diffuse toward each other and collide, and all possible values in between. Thus there seems to be no evidence for Lewis and Seaborg's sharp distinction into primary and secondary acids and bases. Rather we have a gradual transition from slowly reacting, or pseudo, acids and bases to rapidly reacting, or normal, acids and bases.

**Acknowledgment.**—The authors are indebted to the Research Corporation for a grant which made this work possible.

(38) G. N. Lewis and G. T. Seaborg, *THIS JOURNAL*, **61**, 1886 (1939); G. N. Lewis, *J. Franklin Inst.*, **226**, 293 (1938).

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

## Sexadentate Chelate Compounds. VI

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The bis-salicylidene derivatives of 1,9-diamino-3,6-dithianonane (EET base) and 1,10-diamino-3,7-dithiadecane (ETT base) have been prepared and caused to react with cobalt salts to give crystalline complex cobalt(III) salts whose structures have been correlated with those of the bases from which they are derived.

Extension of the arguments put forward in Part III<sup>3</sup> of this series of papers to the structure of the complex ions derived from cobalt(III) and the sexadentate chelate compounds prepared by condensing salicylaldehyde with 1,9-diamino-3,6-dithianonane (EET base) and 1,10-diamino-3,7-dithiadecane (ETT base) would strongly suggest that the former should be capable of existence only in enantiomorphous forms structurally similar to those obtained from the bis-salicylidene derivative of EEE base,<sup>4</sup> whilst there could be the possibility of the latter existing in two structurally isomeric

pairs of enantiomorphs. Experiment has now shown that the facts agree with this prediction.

At one end of the molecule of EET base there is an ethylene chain between the nitrogen atom and the sulfur atom. At the other end the second nitrogen atom is separated from the other sulfur atom by a trimethylene chain. For convenience the former may be designated the E end and the latter the T end of the molecule. When a molecule of the bis-salicylidene derivative of EET base loses two protons and wraps itself round a triply positively charged cobalt atom it should be possible, arguing on analogy with the complexes derived from TET base, for the oxygen-nitrogen-sulfur atom sequence at the T end of the molecule to take up one or the other of two configurations. In one the oxygen, nitrogen and sulfur atoms would lie

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(3) F. P. Dwyer, N. S. Gill, E. C. Gyarfás and F. Lions, *THIS JOURNAL*, **74**, 4188 (1952).

(4) Cf. Part I, F. P. Dwyer and F. Lions, *ibid.*, **72**, 1545 (1950).

in a plane (as in the complex ions derived from EEE base or from TET base (green form)). In the other configuration the oxygen, nitrogen and sulfur atoms would be arranged vicinally (as in the complex ions from TET base (brown form)). On the other hand, the spatial demands of the second oxygen-nitrogen-sulfur atom sequence at the E end of the molecule require a planar arrangement of these donor atoms and debar the vicinal arrangement. When the bis-salicylidene derivative of EET base functions as a sexadentate both oxygen-nitrogen-sulfur atom sequences must be simultaneously arranged in planes, or both must have vicinal arrangements of their three donor atoms. Hence it is obvious that the bis-salicylidene derivative of EET base can coordinate with cobalt(III) only in such a way as to give complexes structurally similar to those derived from EEE base.

It might be thought that the bis-salicylidene derivative of ETT base, which has an exactly similar ethylene bridge between nitrogen and sulfur atoms at one end and a trimethylene bridge between the second nitrogen and sulfur at the other would be similarly constrained to coordinate with cobalt(III) to give complex salts existing only in the form corresponding to the complex salts derived from EEE base. However, the lengthening of the chain between the two sulfur atoms from ethylene to trimethylene must increase the flexibility of the molecule and lead to the possibility of some angular rotation of the bonds attaching a sulfur atom to carbon atoms about the axis of the bond between the sulfur and cobalt. It is true that the cobalt(III) complex salts derived from ETE base exist only in the green form, but it is also true that those derived from TTT base exist only in the brown form. Hence, it seemed reasonable to anticipate the possibility of existence of two pairs of enantio-

morphous ions (green and brown) derived from cobalt(III) and the bis-salicylidene derivative of ETT base. Experiment has shown this to be true, but it is worthy of comment that the brown form is the unstable form, is difficult to isolate and passes very readily into the green form. The green 1,9-bis-(salicylideneamino)-3,6-dithianonane cobalt(III) iodide and the green 1,10-bis-(salicylideneamino)-3,7-dithiadecane cobalt(III) iodide have both been obtained in optically active enantiomorphs, whose rates of racemization are not significantly different from those of the corresponding salts from EEE base.

The EET base used in these experiments was prepared by condensing 1-N-phthalimido-5-bromo-3-thiapentane<sup>5</sup> with the sodium salt of  $\gamma$ -mercapto-propylphthalimide<sup>6</sup> to 1,9-bis-N-phthalimido-3,6-dithianonane and then removing the phthalic acid residues by the method of Ing and Manske.<sup>7</sup> 1,10-Diamino-3,7-dithiadecane (ETT base) was similarly prepared by condensing trimethylene-bromohydrin with the sodium salt of  $\beta$ -N-phthalimidoethylmercaptan<sup>8</sup> to 1-N-phthalimido-3-thiahexan-6-ol, conversion of this with phosphorus pentabromide to the corresponding bromide and condensation of this bromide with the sodium salt of  $\gamma$ -propylphthalimide<sup>6</sup> to 1,10-bis-N-phthalimido-3,7-dithiadecane from which the phthalic acid residues were removed by the method of Ing and Manske.<sup>7</sup> The methods for conversion of the bis-salicylidene derivatives of these two bases to the corresponding cobalt(III) complex salts, described in the Experimental section, were arrived at only after much abortive experimentation and must be carefully adhered to for success in the preparations. Absorption spectra curves are shown in Fig. 1.

### Experimental

**1,9-Bis-N-phthalimido-3,6-dithianonane.**—A hot solution of 1-N-phthalimido-5-bromo-3-thiapentane<sup>5</sup> (41.6 g.) in absolute ethanol (110 ml.) was added to an ethanolic solution of the sodium salt of  $\gamma$ -mercapto-propylphthalimide (from sodium (3.05 g.), absolute ethanol (100 ml.) and the mercaptan (29.3 g.)) and the mixture refluxed for 3.5 hr. Most of the ethanol was removed by distillation, water added and the aqueous layer decanted from the precipitated oil. On stirring and contact with dry ether this crystallized and was recrystallized from an ethanol-acetone (70:30) mixture and obtained in colorless needles (yield 43%), m.p. 85°.

*Anal.* Calcd. for  $C_{23}H_{22}N_2O_4S_2$ : C, 60.8; H, 4.9; N, 6.2. Found: C, 60.3; H, 4.8; N, 6.2.

**1,9-Bis-(salicylideneamino)-3,6-dithianonane.**—The above described bis-phthalimido compound (25.5 g.) was suspended in ethanol (250 ml.) boiling under reflux and hydrazine hydrate (20 ml. of 50%) added. The refluxing was continued for 2 hr. after which hydrochloric acid (25 ml.) was added and refluxing continued for 0.5 hr. As much ethanol as possible was then distilled off, water added, the precipitated phthalhydrazide removed and the 1,9-diamino-3,6-dithianonane (EET base) recovered from the aqueous solution with alkali and ether as a colorless oil (yield quantitative).

**Its diacetyl derivative** formed colorless needles (from chloroform-petroleum ether), m.p. 103°.

*Anal.* Calcd. for  $C_{11}H_{22}N_2O_2S_2$ : N, 10.1. Found: N, 10.0.

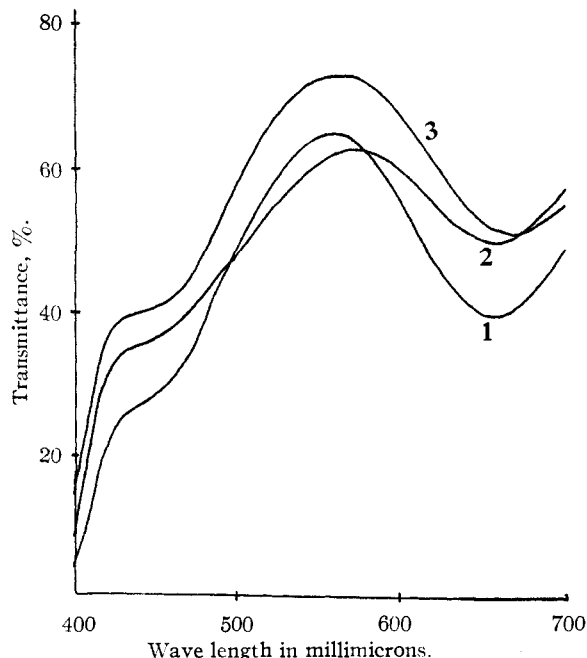


Fig. 1.—1, Co(EEE)Cl·H<sub>2</sub>O, 0.2% soln. in H<sub>2</sub>O; 2, Co(ETT)I, vac., 0.02% soln. in H<sub>2</sub>O; 3, Co(EET)I, vac., 0.017% soln. in H<sub>2</sub>O; all in 1-cm. cell.

(5) S. Gabriel, *Ber.*, **24**, 3098 (1891).

(6) S. Gabriel and W. E. Lauer, *ibid.*, **23**, 88 (1890).

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

(8) S. Gabriel, *Ber.*, **24**, 1111 (1891).

The bis-5'-bromosalicylidene derivative formed yellow prisms (from ethanol), m.p. 112°.

*Anal.* Calcd. for  $C_{21}H_{24}Br_2N_2O_2S_2$ : N, 5.0. Found: N, 5.0.

Condensation of this EET base in ethanol solution with salicylaldehyde (2 moles) was readily effected by warming and 1,9-bis-(salicylideneamino)-3,6-dithianonane obtained in yellow leaflets, m.p. 54°.

*Anal.* Calcd. for  $C_{21}H_{24}N_2O_2S_2$ : C, 62.7; H, 6.5; N, 7.0. Found: C, 62.7; H, 6.6; N, 7.1.

*dl*-1,9-Bis-(salicylideneamino)-3,6-dithianonane Cobalt(III) Iodide Monohydrate.—Cobalt(II) chloride hexahydrate (0.4 g.) was added to a boiling solution of 1,9-bis-(salicylideneamino)-3,6-dithianonane (0.5 g.) in methanol (50 ml.) and then at once a hot solution of sodium acetate (0.4 g.) in methanol containing hydrogen peroxide (5 ml. of 3%). The deep green solution was then poured into a large dish and allowed to evaporate at room temperature (about 3 days) to a volume of about 25 ml. Water (50 ml.) was then added followed by potassium iodide (3 g.). The resulting brown precipitate appeared to consist of the complex cobalt(III) iodide and a very sparingly soluble complex triiodide. It was dissolved in hot water, a little sodium thiosulfate added and then solid potassium iodide. Cooling to 0° caused precipitation of the pure iodide in black needles, m.p. 196° (yield 0.35 g.).

*Anal.* Calcd. for  $Co(C_{21}H_{24}N_2O_2S_2)I \cdot H_2O$ : Co, 9.8; I, 21.0; N, 4.6. Found: Co, 9.8; I, 21.1; N, 4.5.

This salt was soluble in cold water to a green solution. On heating this changed to greenish-brown, but the green color was restored on cooling. All attempts to prepare a brown isomeric salt failed.

*d*-1,9-Bis-(salicylideneamino)-3,6-dithianonane Cobalt(III) *d*-Antimonyl Tartrate Pentahydrate.—A solution of the *dl*-salt (4.0 g.) in hot water (60 ml.) was shaken with silver *d*-antimonyl tartrate (2.67 g.) until precipitation of silver iodide was complete. After addition of a little filter pulp and filtration the filtrate was evaporated until a tarry oil commenced to separate. On cooling in ice and scratching, this crystallized. The evaporation was continued until approximately 2.8 g. of solid had been collected. After several recrystallizations from hot water it was obtained in glistening black rods which char at about 270°.

*Anal.* Calcd. for  $Co(C_{21}H_{24}N_2O_2S_2)(C_4H_4O_7Sb) \cdot 5H_2O$ : Co, 7.1; Sb, 14.6; N, 3.4;  $H_2O$ , 10.8. Found: Co, 7.1; Sb, 14.5; N, 3.3;  $H_2O$ , 10.7.

A 0.02% aqueous solution at 20° (1-dm. tube) gave  $\alpha_D^{20}$  1.30°, whence  $[\alpha]^{20}_D + 6,500^\circ$ .

*d*-1,9-Bis-(salicylideneamino)-3,6-dithianonane Cobalt(III) Iodine Dihydrate.—Hydrochloric acid (5 ml. of 2 *N*) was added to a hot solution of the above described *d*-antimonyl tartrate (1.5 g.) in water (30 ml.) and the solution immediately cooled to room temperature. The precipitated antimony oxychloride was removed by filtration and solid potassium iodide added to the filtrate. The brown precipitate which came down was collected and recrystallized to constant rotation from hot water containing a little potassium iodide. It formed black nodular prisms, m.p. 192°.

*Anal.* Calcd. for  $Co(C_{21}H_{24}N_2O_2S_2)I \cdot 2H_2O$ : C, 40.5; H, 4.5; N, 4.5; Co, 9.5; I, 20.4. Found: C, 40.7; H, 4.6; N, 4.6; Co, 9.5; I, 20.4.

A 0.01% aqueous solution at 20° (1-dm. tube) gave  $\alpha_D^{20} + 0.80^\circ$  and  $\alpha_{5461} + 0.61^\circ$ , whence  $[\alpha]^{20}_D + 8,000^\circ$ ,  $[\alpha]^{20}_{5461} + 6,100^\circ$ ,  $(M)^{20}_D + 49,800^\circ$  and  $(M)^{20}_{5461} + 38,000^\circ$ .

*l*-1,9-Bis-(salicylideneamino)-3,6-dithianonane Cobalt(III) Iodide Dihydrate.—The levorotatory filtrate from the precipitation of the above described *d*-antimonyl tartrate was precipitated fractionally with potassium iodide. The least soluble fraction was inactive, the succeeding fractions increasingly levorotatory. Repeated systematic fractional crystallization from hot water (and adding potassium iodide) eventually gave the pure *levo* salt; black nodular prisms, m.p. 192°.

*Anal.* Found: C, 40.2; H, 4.6; N, 4.5; Co, 9.5; I, 20.2.

A 0.01% aqueous solution at 20° (1-dm. tube) gave  $\alpha_D^{20} - 0.79^\circ$  and  $\alpha_{5461} - 0.60^\circ$ , whence  $[\alpha]^{20}_D - 7,900^\circ$ ,  $[\alpha]^{20}_{5461} - 6,000^\circ$ ,  $(M)^{20}_D - 49,200^\circ$  and  $(M)^{20}_{5461} - 37,300^\circ$ .

1-N-Phthalimido-6-bromo-3-thiahexane.— $\beta$ -N-Phthalimidoethyl mercaptan<sup>8</sup> (30.1 g.) was dissolved in hot ethanol

(75 ml.) and the solution added to a cooled solution of sodium (3.45 g.) in absolute ethanol (90 ml.). Trimethylene-bromohydrin (20.9 g.) was then added and the mixture refluxed for 2 hr. Most of the ethanol was then distilled off, water added to the cooled residue and the separated oil taken up and dried with anhydrous sodium sulfate in ether. After removal of the ether the oil was treated in a dish with an equal weight of phosphorus pentabromide. When the frothing had subsided the reaction mixture was warmed at 100° for 15 minutes to complete the reaction and then poured into water. The product separated as a brown oil which could not be induced to crystallize (yield 85%). It was dried in a vacuum desiccator over concentrated sulfuric acid.

1,10-Bis-N-phthalimido-3,7-dithiadecane.—A hot solution of the crude bromide just described (42.6 g.) in absolute ethanol (150 ml.) was added to an ethanolic solution of the sodium salt of  $\gamma$ -mercaptopropylphthalimide (from sodium (3 g.), absolute ethanol (110 ml.) and the mercaptan<sup>8</sup> (28.7 g.)) and the mixture refluxed for 3.5 hr. After removal of the ethanol and addition of water the oily product slowly solidified on standing and was recrystallized from ethanol containing acetone. It was difficult to obtain pure but was eventually obtained in colorless prisms, m.p. 77–80° (yield 75%).

*Anal.* Calcd. for  $C_{24}H_{24}N_2O_4S_2$ : C, 61.5; H, 5.2; N, 6.0. Found: C, 61.4; H, 5.4; N, 6.1.

1,10-Diamino-3,7-dithiadecane.—Removal of the phthalic acid residues from the above described bis-phthalimido compound was carried out similarly to the preparation of EET base. The product was eventually obtained as a colorless oil, b.p. 159–161° (0.6 mm.), yield 40%. For analysis it was converted into its bis-(2'-hydroxy-1'-naphthylmethylene) derivative, yellow needles, m.p. 96° (from ethyl acetate).

*Anal.* Calcd. for  $C_{30}H_{32}N_2O_2S_2$ : C, 69.7; H, 6.2; N, 5.4. Found: C, 69.9; H, 6.4; N, 5.6.

The bis-salicylidene derivative of this ETT base was a yellow oil which could not be induced to crystallize. After preparation in ethanol solution from stoichiometric proportions of the base (1 mole) and salicylaldehyde (2 moles) it was washed with petroleum ether and then used.

*dl*-1,10-Bis-(salicylideneamino)-3,7-dithiadecane Cobalt(III) Iodide (Green Form).—The oily anil just described (4.16 g.) was dissolved in boiling methanol (200 ml.), the solution cooled rapidly to 60° and then treated with a cold solution of cobalt(II) acetate tetrahydrate (2.38 g.) and hydrogen peroxide (15 ml. of 3%) in methanol (50 ml.). The gray precipitate of cobalt(II) complex which first separated soon redissolved giving a deep red-brown solution. The solution was cooled immediately in an ice-bath and a current of air drawn through it to complete the oxidation and evaporate the methanol. When the volume had been reduced to about 30 ml. (about 30 hr.) the dark brown sirupy liquid was diluted with water (300 ml.) and allowed to stand for 2–3 days exposed to the air. After removal of a dark tarry product by filtration, fractional precipitation with 20% potassium iodide solution was carried out. The iodide of the brown cobalt(III) complex first separated as a brown powder (see below), leaving a deep green solution from which the green form of the iodide was precipitated in black micro-prisms. It was recrystallized first from hot water and then from methanol to which ether was added; black micro-prisms, m.p. 218° (yield 2.5 g.) being obtained. This salt dissolved in methanol or acetone to brown solutions which became green on addition of water. Boiling of the aqueous solution led to decomposition and separation of a black tar. Isomerization to the brown form was not observed by prolonged heating in any solvent.

*Anal.* Calcd. for  $Co(C_{22}H_{26}N_2O_2S_2)I$ : C, 44.0; H, 4.4; N, 4.7; Co, 9.8. Found: C, 43.6; H, 4.4; N, 4.5; Co, 9.9.

*dl*-1,10-Bis-(salicylideneamino)-3,7-dithiadecane Cobalt(III) Iodide Monohydrate (Brown Form).—The first-obtained brown amorphous precipitate mentioned above (about 1 g.) was sparingly soluble in water, methanol, acetone and chloroform to brown solutions. It was purified by warming with a suspension of freshly precipitated silver chloride in 1:1 aqueous methanol, the very much more soluble complex chloride passing into solution. The solution was then rapidly filtered and the brown iodide obtained

as a micro-crystalline precipitate, m.p. 165°, by addition of potassium iodide. The brown chloride is rapidly transformed in solution into the green salt. Heating on the water-bath soon transforms the brown iodide to the green iodide.

*Anal.* Calcd. for  $\text{Co}(\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_2\text{S}_2)\text{I}\cdot\text{H}_2\text{O}$ : C, 42.7; H, 4.6; N, 4.5; Co, 9.5. Found: C, 42.5; H, 4.6; N, 4.6; Co, 9.6.

*d*-1,10-Bis-(salicylideneamino)-3,7-dithiadecane Cobalt-(III) *d*-Antimonyl Tartrate Dihydrate.—The *dl*-iodide (green form) (3.2 g.) was suspended in water (40 ml.) at 80° and shaken with freshly precipitated silver chloride. After filtration the precipitate of silver halides was washed with a little dilute sodium nitrate solution in order to desorb adhering complex salt and the green filtrate evaporated rapidly to a volume of 40 ml. After removal of a small amount of tarry decomposition product potassium *d*-antimonyl tartrate (1.8 g.) in hot water (8 ml.) was added, the mixture cooled to room temperature and allowed to stand overnight. The crop of small brown plates which had separated was collected, the filtrate evaporated to about 30 ml., allowed to stand and a second crop of crystals obtained. The two crops were combined and recrystallized from hot water; minute brown plates which charred on heating being obtained.

*Anal.* Calcd. for  $\text{Co}(\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_2\text{S}_2)(\text{C}_4\text{H}_4\text{O}_7\text{Sb})\cdot 2\text{H}_2\text{O}$ : N, 3.5; Sb, 15.3. Found: N, 3.5; Sb, 15.3.

A 0.02% aqueous solution at 20° (1-dm. tube) gave  $\alpha_D +0.035^\circ$ , whence  $[\alpha]^{20}_D +1,750^\circ$ .

*d*-1,10-Bis-(salicylideneamino)-3,7-dithiadecane Cobalt-(III) Iodide.—The *d*-antimonyl tartrate just described was dissolved by grinding it (1 g.) with 10% sodium acetate solution (20 ml.). Solid potassium iodide was then added. The resulting brown amorphous precipitate of the *d* complex iodide was collected and washed with a little ice-water in

which it is very soluble and then transformed to the chloride by shaking with freshly precipitated silver chloride and water (15 ml.). After removal of the silver halides the active iodide was obtained in crystalline form by gently warming, adding potassium iodide and scratching. The transformation to the chloride was necessary because of the tendency of the iodide to become tarry on warming with water. The crystalline solid was eventually recrystallized twice from methanol to which dry ether was added and obtained in micaceous plates, m.p. 234°.

*Anal.* Calcd. for  $\text{Co}(\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_2\text{S}_2)\text{I}$ : N, 4.7; Co, 9.8; I, 21.1. Found: N, 4.6; Co, 9.9; I, 21.4.

A 0.01% aqueous solution at 20° gave  $\alpha_D +0.14^\circ$  (1-dm. tube), and  $\alpha_{5461} +0.11^\circ$ , whence  $[\alpha]^{20}_D +1,400^\circ$ ,  $[\alpha]^{20}_{5461} +1,100^\circ$ ,  $(M)^{20}_D +8,400^\circ$  and  $(M)^{20}_{5461} +6,600^\circ$ .

*d*-1,10-Bis-(salicylideneamino)-3,7-dithiadecane Cobalt-(III) Iodide.—The filtrate obtained from the precipitate of *d*-antimonyl tartrate mentioned above was fractionally precipitated with potassium iodide. The least soluble fractions were inactive but the more soluble were levorotatory. These were combined, transformed to the chloride with silver chloride and again fractionally precipitated, the process being repeated several times. The micaceous plates of the purified iodide eventually melted at 233°.

*Anal.* Found: N, 4.6; Co, 9.9; I, 21.3.

A 0.01% aqueous solution at 20° (1-dm. tube) gave  $\alpha_D -0.13^\circ$  and  $\alpha_{5461} -0.10^\circ$  whence  $[\alpha]^{20}_D -1,300^\circ$ ,  $[\alpha]^{20}_{5461} -1,000^\circ$ ,  $(M)^{20}_D -7,800^\circ$  and  $(M)^{20}_{5461} -6,000^\circ$ .

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

## Inner Complexes of Uranium Containing 1,3-Dicarbonyl Chelating Groups

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In a search for moderately volatile uranium compounds, a series of uranyl and a series of uranium(IV) compounds of diketones and of ketoaldehydes were prepared. The data obtained indicate that the maximum attainable vapor tensions of uranium compounds of these types are unlikely to exceed 0.1 mm. at 130°. The preparation of the compounds investigated, the vapor tensions when large enough for measurement, and a few other properties are described.

Some time ago we undertook an investigation of complex compounds of uranium to ascertain whether among such substances there might be some having at least a moderate degree of volatility. After examination of the possibilities we decided to prepare a series of uranium compounds of the 1,3-diketone type. Thirteen such uranyl derivatives and ten derivatives of tetravalent uranium were prepared. Determination of their vapor tensions by measurement of the rate of effusion of their vapors<sup>1</sup> indicated to us that there is little likelihood of finding such compounds having vapor tensions much above 0.1 mm. at 130°. Furthermore the compounds most favorable from the point of view of volatility, *i.e.*, the derivatives of uranium(IV), had only a low degree of stability at temperatures at which the vapor tensions are appreciable.

Before this investigation was completed, uranium(IV) borohydride,<sup>2</sup>  $\text{U}(\text{BH}_4)_4$ , and its methyl

derivatives<sup>3</sup> had been prepared, and had been found to have volatilities far higher than what appeared to be the maximum attainable volatility of the diketones. For this reason the investigation of the latter type of compounds was discontinued.

It seems improbable that we shall return to this investigation. For this reason the following report of the results obtained is now presented.

### Results and Discussion

Table I records the vapor tensions at 130°, and the melting points of a number of complex uranyl and uranium(IV) compounds. To save space the chelating agent is identified by formula only; the corresponding uranyl compounds have the formulas  $\text{UO}_2\text{X}_2$ , and the uranium(IV) compounds the formulas  $\text{UX}_4$ , in which X is the univalent negative ion of the chelating agent. A dash in column II means that the compound in question gave no indication of volatility, a zero that there was indication of volatility but that the vapor tension was too

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