factor in establishing bond strengths between metal ions and the hybrid states of nitrogen and oxygen. The highly electronegative metals coördinate more strongly with the *low* bonding electronegativity states of nitrogen and oxygen ($-N<$ and $-O^-$) since these forms exert the lowest nuclear repulsions. The metal ions of low electronegativity, on the other hand, since the system tends to distribute charge between the metal ion and the ligands to where they both have the same electronegativity, can donate enough charge to the bond to minimize nuclear repulsion effects. Therefore, they tend to form more stable bonds with the high bond electronegativity states of nitrogen and oxygen since the electronegativity product term is larger in these cases. Restating the above—when the metal ion involved is one of low enough electronegativity, nuclear repulsion forces are minimized and bond strength increases as a function of the product of the electronegativities of the partners; while in the case of the highly electronegative metal ions, nuclear repulsion forces between the partners are effective since both try to pull the electrons between them close to their respective nuclei. Variations in the two effects with $X'_m$ are continuous as indicated in Fig. 5.

The effect of nuclear repulsion may also be used to explain the changing ratios of log $K_f$ to $pK_D$, the acid dissociation constant of the chelating agent for a series of related chelate compounds. Figure 6 shows a plot of the log $K_f$ (average) values for a series of $\beta$-diketones with $CuCl_2$, $NiCl_2$ and $BaCl_2$ in the 75 vol. % dioxane solution.[7]

Inductive effects pulling charge away from the oxygen atoms increase the degree of dissociation of the $\beta$-diketone by increasing the bond-weakening effect of nuclear repulsion between the enol oxygen atom and the proton more rapidly than the increase in bond strength attributable to an increase in the electronegativity product of the partners. The observed nuclear repulsion effects are much smaller for the less electronegative metal ions since they can donate charge to the bond while the proton cannot. Hence the enolate ions increasingly prefer to associate with metal ions rather than protons as $pK_D$ decreases. For this reason the acidic trifluoro-$\beta$-diketones are effective chelating agents for many metal ions in acidic solution. It should be noted that the ratio of log $K_f$ to $pK_D$ increases going from barium the least electronegative metal ion shown to copper the most electronegative metal ion.

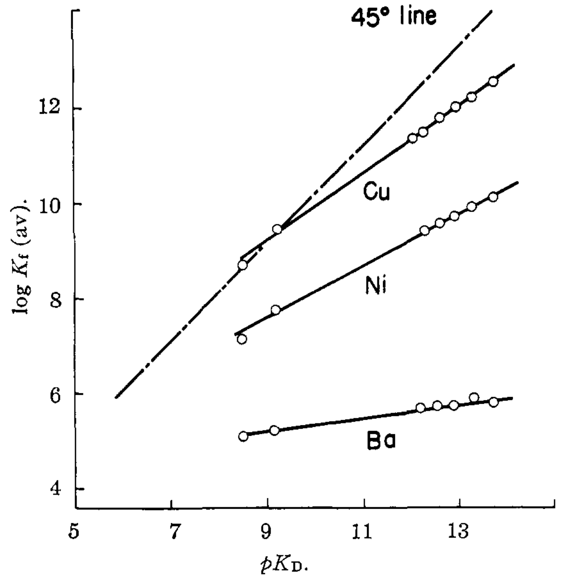

Fig. 6.—The effect of nuclear repulsion on the ratio of log $K_f$ to $pK_D$.

STATE COLLEGE, PENNA.

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

# Sexadentate Chelate Compounds. VII

BY FRANCIS P. DWYER, NAIDA S. GILL,[1] ELEONORA C. GYARFAS AND FRANCIS LIONS

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The bis-salicylidene derivatives of 3,4-bis-($\gamma$-amino-$\alpha$-thiapropyl)-toluene, 3,4-bis-($\delta$-amino-$\alpha$-thiabutyl)-toluene, 1,4-bis-($o$-aminophenyl)-1,4-dithiabutane, and the 5-bromosalicylidene derivative of 1-amino-6-($o$-aminophenyl)-3,6-dithiahexane have been prepared. The formation of the usual cationic complexes with cobalt demonstrates that replacement of the polymethylene bridges between the coördinating atoms by one side of a benzene ring does not destroy the sexadentate character of the chelate compounds.

In an endeavor to obtain more experimental evidence bearing on the structure of the complex ions derived from cobalt(III) and the various azomethine bases which have been shown capable of functioning as sexadentate chelate compounds[2] it was considered that it would be of value to prepare a series of diamines based on the structure I but in which one or more of the polymethylene bridges between hetero atoms had been replaced by one side of a benzene ring. Atoms attached to a benzene ring are constrained to lie in the plane of that ring. Thus, for example, in the complex ions derived from cobalt(III) and the bis-salicylidine derivative of 1,4-bis-($o$-aminophenyl)-1,4-dithiabutane (BEB base,[3] II) each benzene ring

$$NH_2—(CH_2)_x—S—(CH_2)_y—S—(CH_2)_z—NH_2$$

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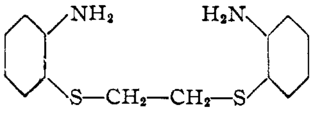
(1) Commonwealth Research Assistant, University of Sydney.

(2) *Cf.* F. P. Dwyer and F. Lions, THIS JOURNAL, **72**, 1545 (1950); F. P. Dwyer, N. S. Gill, E. C. Gyarfas and F. Lions, *ibid.*, **74**, 4178 (1952); **74**, 3134 (1952); **75**, 1526 (1953); **75**, 2443 (1953).

(3) The nomenclature suggested is, for brevity, similar to that introduced in Part III and designates an $o$-phenylene group as B. It was found convenient in preparing compounds with such an $o$-phenylene group replacing the $-(CH_2)_y-$ bridge of I to use the available 3,4-dithioltoluene. The substituent methyl group does not increase the possibilities of isomerism in the final Co(III) complex ions as can be shown by a model. The base 3,4-bis-($\gamma$-amino-$\alpha$-thiapropyl)-toluene is designated in this paper as EBE base.



II

should be fairly rigidly held in the plane containing its attached nitrogen and sulfur atoms and the cobalt atom. The flexing of the chelate moiety to encompass the central cobalt atom must then largely occur at the donor nitrogen and sulfur atoms.

In this paper are described the preparations of the bis-salicylidene derivatives of 3,4-bis-(γ-amino-α-thiapropyl)-toluene (EBE base, III), 3,4-bis-(δ-amino-α-thiabutyl)-toluene (TBT base, IV) and 1,4-bis-(*o*-aminophenyl)-1,4-dithiabutane (BEB base, II) together with that of the bis-(5-bromosalicylidene) derivative of 1-amino-6-(*o*-aminophenyl)-3,6-dithiahexane (EEB base, V). Each Schiff base reacts readily with cobalt(II) salts in presence of an oxidizing agent to give complex cobalt(III) salts in which the chelate compound functions as a sexadentate.

In the complex cobalt(III) ions derived from III it would not be anticipated that the introduction of the benzene ring between the two sulfur atoms would cause any serious alteration of the arrangement of the oxygen–nitrogen–sulfur atom sequences present in the complex ions derived from EEE base. No change in the number of atoms in loop 3[4] has occurred and the complex ions from III must be assumed to be structurally similar to the complex ions from EEE. The complex cobalt(III) salts from III give red-brown colored solutions whilst those from EEE are green. However, the absorption curves are similar.

Of the sexadentate chelate compounds described in this paper the most interesting should be that derived from TBT base (IV). It will be remembered (Part III) that TET base reacts with salicylaldehyde to give a sexadentate which yields two series of isomeric racemic complex cobalt(III) salts of very unequal stability. The structural constraints in TBT imposed by the presence of the benzene ring limit complex formation to one series only of complex cobalt(III) salts which give green colored solutions. The absorption curve of the iodide in the visible is similar to that of the complex cobalt(III) iodide from EEE base.

Attempts at resolution of the complex cobalt(III) iodide from II were unsuccessful. The complex salts derived from III and IV were readily resolved with the help of potassium *d*-antimonyl tartrate. Publication of the results of racemization studies of the optically active salts is being withheld for the present. It may be noted that whilst one of the enantiomers of the complex cobalt(III) iodide from EBE showed no appreciable racemization after boiling for 10 minutes in aqueous methanol, the optically active salts from TBT lost 30% of their activity under the same conditions.

EBE base was prepared by alkylation of 3,4-dithioltoluene with γ-bromoethylphthalimide followed by hydrazinolysis according to the method of Ing and Manske.[5] TBT base was similarly prepared, but using γ-bromopropyl phthalimide instead of the lower homolog. BEB base was prepared by causing the sodium salt of *o*-nitrothiophenol to react with ethylene dibromide and then reducing the product with zinc dust and aqueous ethanolic calcium chloride solution. EEB base was prepared by causing the sodium salt of *o*-nitrothiophenol to react with 1-phthalimidoethyl-3-thia-5-bromopentane[6] to form 1-phthalimido-6-(*o*-nitrophenyl)-3,6-dithiahexane from which the phthalyl group was removed with the help of hydrazine leaving a nitro base which was reduced to EEB with zinc dust and aqueous methanolic calcium chloride solution.

## Experimental

All rotations were measured at 20° in a 1-dm. tube.

**3,4-Bis-(γ-phthalimido-α-thiapropyl)-toluene.**—To a cooled solution of sodium ethoxide (from sodium 4.6 g.) and absolute ethanol (150 ml.) were added first a warm solution of 3,4-dithioltoluene (15.6 g.) in absolute ethanol (30 ml.) and then after thorough mixing, a hot solution of β-bromoethylphthalimide (50.8 g.) in absolute ethanol (130 ml.). The mixture was refluxed for 3.5 hours after which most of the ethanol was distilled off and water added to the residue. The precipitated solid was collected, washed with water and recrystallized from glacial acetic acid; colorless needles, m.p. 138°, yield 81%.

*Anal.* Calcd. for $C_{27}H_{22}N_2O_4S_2$: C, 64.5; H, 4.4; N, 5.6. Found: C, 64.5; H, 4.4; N, 5.6.

**3,4-Bis-(δ-phthalimido-α-thiabutyl)-toluene** was prepared similarly (yield 90%) from 3,4-dithioltoluene and γ-bromopropylphthalimide; pale yellow prisms from acetone, m.p. 115–116°.

*Anal.* Calcd. for $C_{29}H_{26}N_2O_4S_2$: C, 65.6; H, 4.9; N, 5.3. Found: C, 65.7; H, 5.0; N, 5.4.

**3,4-Bis-(γ-amino-α-thiapropyl)-toluene (EBE Base, III).**—Hydrazine hydrate (32 ml. of 50%) was added to a suspension of 3,4-bis-(γ-phthalimido-α-thiapropyl)-toluene (45.1 g.) in ethanol (350 ml.) boiling under reflux. Excess concentrated hydrochloric acid (40 ml.) was added after 2 hours, and the refluxing continued for 0.5 hour, after which as much ethanol as possible was distilled off and a little water added. The phthalhydrazide which precipitated was removed by filtration and washed with a little water and the combined filtrates made strongly alkaline with solid sodium hydroxide. The oily base which separated was collected and dried in ether and distilled; colorless oil, b.p. 190° (0.6 mm.), yield 90%. It was analyzed as its **diacetyl derivative**; colorless needles, m.p. 116° (from chloroform–petroleum ether).

*Anal.* Calcd. for $C_{15}H_{22}N_2O_2S_2$: C, 55.2; H, 6.8; S, 19.6. Found: C, 55.0; H, 6.5; S, 20.0.

**3,4-Bis-(γ-salicylideneamino-α-thiapropyl)-toluene** from EBE base (1 mole) and salicylaldehyde (2 moles) in boiling ethanol formed yellow needles, m.p. 82°.

*Anal.* Calcd. for $C_{25}H_{26}N_2O_2S_2$: C, 66.6; H, 5.8; N, 6.2. Found: C, 66.2; H, 5.8; N, 6.1.

**3,4-Bis-(δ-amino-α-thiabutyl)-toluene (TBT Base, IV)** was obtained from its bis-phthalimido derivative similarly to EBE base as a colorless oil, b.p. 198–200° (0.5 mm.), yield 80%. Its **diacetyl derivative** formed colorless nodules, m.p. 82–83° (from chloroform–petroleum ether).

*Anal.* Calcd. for $C_{17}H_{26}N_2O_2S_2$: N, 7.9. Found: N, 8.2.

**3,4-Bis-(δ-5′-bromosalicylideneamino-α-thiabutyl)-toluene** formed yellow needles, m.p. 112.5° (from ethanol).

*Anal.* Calcd. for $C_{27}H_{28}Br_2N_2O_2S_2$: N, 4.44. Found: N, 4.5.

**3,4-Bis-(δ-salicylideneamino-α-thiabutyl)-toluene** formed yellow needles, m.p. 80° (from ethanol).

*Anal.* Calcd. for $C_{27}H_{30}N_2O_2S_2$: C, 67.7; H, 6.3; N, 5.9. Found: C, 67.4; H, 6.1; N, 6.1.

***dl*-3,4-Bis-(γ-salicylideneamino-α-thiapropyl)-toluene Cobalt(III) Iodide Dihydrate.**—*A boiling solution of cobalt-*

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(4) See Fig. 1 of Part III.

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

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

(II) acetate tetrahydrate (1 g.) in methanol (20 ml.) was added to a boiling solution of the bis-salicylidene derivative of EBE base (2 g.) in methanol (100 ml.) and immediately afterwards hydrogen peroxide (5 ml. of 3%) was added, the solution becoming mulberry red in color. After careful evaporation in the air at room temperature to a volume of about 80 ml. excess 10% aqueous potassium iodide solution was added. The resulting dark brown amorphous precipitate was collected and recrystallized from hot aqueous acetone with the help of potassium iodide and was obtained in black nodular prisms, m.p. 217°.

*Anal.* Calcd. for $[Co(C_{25}H_{24}N_2O_2S_2)]I\cdot 2H_2O$: C, 44.8; H, 4.2; N, 4.2; Co, 8.8; I, 18.9. Found: C, 44.9: H, 4.4; N, 4.4; Co, 8.8; I, 19.1.

***d*-3,4-Bis-(γ-salicylideneamino-α-thiapropyl)-toluene Cobalt(III) *d*-Antimony Tartrate Tetrahydrate.**—To a solution of the above-described racemic iodide (0.8 g.) in the minimum volume of 50% aqueous acetone was added a solution of *d*-potassium antimonyl tartrate (0.2 g.), in water (8 ml.). The resulting precipitate of the *d*-complex–*d*-antimonyl tartrate was recrystallized to constant rotation from aqueous acetone and obtained in black micro-prisms.

*Anal.* Calcd. for $[Co(C_{25}H_{24}N_2O_2S_2)](C_4H_4O_7Sb)\cdot 4H_2O$: Co, 6.8; N, 3.2; $H_2O$, 8.3. Found: Co, 6.7; N, 3.3; $H_2O$, 9.5.

A 0.01% solution in water containing 5% acetone gave $\alpha_D$ +0.19° whence $[\alpha]^{20}_D$ +1900° and $[M]^{20}_D$ +16,400°.

***d*-3,4-Bis-(γ-salicylideneamino-α-thiapropyl)-toluene Cobalt(III) Iodide Monohydrate.**—The *d*-complex–*d*-antimonyl tartrate just described was dissolved in aqueous acetone and 10% aqueous potassium iodide solution added. The black precipitate was collected and recrystallized from aqueous acetone, black nodular prisms of the pure *d*-complex iodide, m.p. 219°, being thus obtained.

*Anal.* Calcd. for $[Co(C_{25}H_{24}N_2O_2S_2)]I\cdot H_2O$: C, 46.0; H, 4.0; N, 4.3; Co, 9.0; I, 19.4. Found: C, 45.8; H, 3.9; N, 4.4; Co, 9.0; I, 19.3.

A 0.01% solution in water containing 5% acetone gave $\alpha_D$ +0.18° and $\alpha_{5461}$ +0.07°, whence $[\alpha]^{20}_D$ +1800°, $[\alpha]^{20}_{5461}$ +700°, $[M]^{20}_D$ +12,000° and $[M]^{20}_{5461}$ +4600°.

**1,3,4-Bis-(γ-salicylideneamino-α-thiapropyl)-toluene Cobalt(III) Iodide Monohydrate.**—Addition of potassium iodide to the mother liquor remaining after precipitation of the *d*-complex–*d*-antimonyl tartrate (*vide supra*) gave a precipitate which after many fractional crystallizations from aqueous acetone with rejection of the least soluble fractions eventually yielded black nodular prisms of the *l*-complex iodide, m.p. 219°.

*Anal.* Found: C, 45.8; H, 4.3; N, 4.5; Co, 9.1; I, 19.3.

A 0.01% solution in water containing 5% acetone gave $\alpha_D$ −0.18° and $\alpha_{5461}$ −0.07°, whence $[\alpha]^{20}_D$ −1800°, $[\alpha]^{20}_{5461}$ −700°, $[M]^{20}_D$ −12,000° and $[M]^{20}_{5461}$ −4600°.

***dl*-3,4-Bis-(δ-salicylideneamino-α-thiabutyl)-toluene Cobalt(III) Iodide.**—The bissalicylidene derivative of TBT base (1.2 g.) and cobalt(II) chloride hexahydrate (0.6 g.) were dissolved in boiling methanol (350 ml.) and then a boiling solution of sodium acetate (0.6 g.) and hydrogen peroxide (3 ml. of 3%) in methanol (25 ml.) added. The resulting deep-green solution was at once poured into a large ice-cooled dish and the methanol allowed to evaporate at room temperature overnight. The residue was extracted with warm water (50 ml.) and the green solution freed from a brown impurity by filtration after which excess potassium iodide solution was added. The green micro-crystalline precipitate which formed was collected and recrystallized by solution in methanol to which ether was then added. It formed black nodular prisms, m.p. 166°.

*Anal.* Calcd. for $[Co(C_{27}H_{28}N_2O_2S_2)]I$: C, 48.9; H, 4.3; N, 4.2; Co, 8.9. Found: C, 48.7; H, 4.4; N, 4.3; Co, 8.9.

**1,3,4-Bis-(δ-salicylideneamino-α-thiabutyl)-toluene Cobalt(III) *d*-Antimonyl Tartrate Pentahydrate.**—Silver *d*-antimonyl tartrate (slightly more than 1 mole) and hot water (50 ml.) were added to the above described *dl*-complex iodide and the mixture was vigorously shaken for 10 minutes, after which the solution was filtered free of solids and evaporated to 25 ml., when about half the dissolved salt crystallized on cooling to room temperature. After collection and repeated recrystallization from very small volumes of water it was obtained pure as the *l*-complex–*d*-antimonyl tartrate.

*Anal.* Calcd. for $[Co(C_{27}H_{28}N_2O_2S_2)](C_4H_6O_7Sb)\cdot 5H_2O$: N, 3.1; Co, 6.5. Found: N, 3.0; Co, 6.5.

A 0.02% solution in water containing 10% of methanol gave $\alpha_D$ −0.40°, whence $[\alpha]^{20}_D$ −2000° and $[M]^{20}_D$ −18,000°.

**1,3,4-Bis-(δ-salicylideneamino-α-thiabutyl)-toluene Cobalt(III) Iodide Monohydrate.**—The *l*-complex–*d*-antimonyl tartrate just described was dissolved in water and potassium iodide added. The resulting green precipitate was collected and recrystallized from methanol to which ether was added and obtained as a green micro-crystalline powder, m.p. 167°.

*Anal.* Calcd. for $[Co(C_{27}H_{28}N_2O_2S_2)]I\cdot H_2O$: Co, 8.7; N, 4.1. Found: Co, 8.6; N, 4.2.

A 0.02% solution in water containing methanol (10%) gave $\alpha_D$ −0.40° and $\alpha_{5461}$ −0.13°, whence $[\alpha]^{20}_D$ −2000°, $[\alpha]^{20}_{5461}$ −650°, $[M]^{20}_D$ −13,600° and $[M]^{20}_{5461}$ −4400°. The substance racemized in solution, very slowly at room temperature but rapidly at 80°.

***d*-3,4-Bis-(δ-salicylideneamino-α-thiabutyl)-toluene Cobalt(III) Iodide Monohydrate.**—The mother liquor remaining after the separation of the crude *l*-complex–*d*-antimonyl tartrate described above was fractionally precipitated with potassium iodide. The less-soluble fraction had only a small rotation. The more soluble was strongly dextrorotatory. This fraction was recrystallized several times from a mixture of methanol and ether always preserving the more soluble fraction. Eventually the pure *d*-complex iodide was obtained as a green micro-crystalline powder, m.p. 167°.

*Anal.* Found: Co, 8.6; N, 4.2.

A 0.02% solution in water containing methanol (10%) gave $\alpha_D$ +0.40° and $\alpha_{5461}$ +0.13, whence $[\alpha]^{20}_D$ +2000°, $[\alpha]^{20}_{5461}$ +650°, $[M]^{20}_D$ 13,600° and $[M]^{20}_{5461}$ +4400°.

**1,4-Bis-(*o*-nitrophenyl)-1,4-dithiabutane.**—To a cooled solution of sodium ethoxide (from sodium (4.6 g.) and absolute ethanol (90 ml.)) were added successively a hot solution of *o*-nitrothiophenol (31 g.) in absolute ethanol (250 ml.) and a solution of ethylene dibromide (18.8 g.) in absolute ethanol (20 ml.), and the mixture was then refluxed for 3 hours. After removal of most of the ethanol and addition of water, the product was isolated and recrystallized from glacial acetic acid, and obtained in yellow needles, m.p. 206.5°, yield 82%.

*Anal.* Calcd. for $C_{14}H_{12}N_2O_4S_2$: C, 50.0; H, 3.6; N, 8.3. Found: C, 50.1; H, 3.9; N, 8.6.

**1,4-Bis-(*o*-aminophenyl)-1,4-dithiabutane (BEB Base, II).**—Zinc dust (15 g.) was added to a suspension of the above described dinitro compound (2.35 g.) in aqueous methanol (50 ml. of 80%) containing calcium chloride (0.5 g.) and the mixture gently refluxed for 2 hours. It was then filtered hot and the crystalline product (85% yield) recovered by gentle evaporation of the filtrate; colorless needles from methanol, m.p. 77.5°.

*Anal.* Calcd. for $C_{14}H_{16}N_2S_2$: C, 60.8; H, 5.8; N, 10.1. Found: C, 60.8; H, 5.9; N, 10.2.

**The diacetyl derivative** formed colorless needles (ethanol), m.p. 199°.

*Anal.* Calcd. for $C_{18}H_{20}N_2O_2S_2$: N, 7.8. Found: N, 7.6.

**The bis-δ-bromosalicylidene derivative** formed yellow needles (from ethyl acetate), m.p. 190°.

*Anal.* Calcd. for $C_{28}H_{22}Br_2N_2O_2S_2$: ·N, 4.4. Found: N, 4.6.

The dipicrate formed minute yellow needles, m.p. 202° from ethanol.

*Anal.* Calcd. for $C_{26}H_{22}O_{14}N_8S_2$: N, 15.3. Found: N, 15.4.

**The bis-salicylidene derivative** formed yellow needles (ethanol–pyridine mixture), m.p. 187°.

*Anal.* Calcd. for $C_{28}H_{24}N_2O_2S_2$: C, 69.4; H, 5.0; N, 5.8. Found: C, 69.6; H, 5.1; N, 5.8.

***dl*-1,4-Bis-(*o*-salicylideneaminophenyl)-1,4-dithiabutane Cobalt(III) Iodide.**—Cobalt(II) chloride hexahydrate (1.2 g.) was added to a boiling solution of the bis-salicylidene derivative of BEB base just described (2.4 g.) in absolute ethanol (200 ml.) and the boiling was maintained until a clear greenish-brown solution had resulted. A solution of sodium acetate crystals (2 g.) and hydrogen peroxide (10 ml. of 3%) in methanol (25 ml.) was then added and the mixture boiled for a few minutes. The dark red-brown solution was diluted with water until it became cloudy and allowed to cool when it was filtered free of a slight precipitate. The complex iodide was then precipitated by the addition of sodium iodide, collected and recrystallized from methanol with the help of ether. It came out in black nodular prisms, m.p. 239°, very sparingly soluble in water to a red-brown solution.

*Anal.* Calcd. for $[Co(C_{28}H_{22}N_2O_2S_2)]I$: Co, 50.3; H, 3.3; N, 4.2; Co, 8.8; I, 19.0. Found: C, 50.3; H, 3.4; N, 4.3; Co, 8.9; I, 19.1.

All attempts to resolve this salt proved abortive.

**1-Phthalimido-6-(*o*-nitrophenyl)-3,6-dithiahexane.**—Hot solutions of *o*-nitrothiophenol (11.6 g.) in absolute ethanol (125 ml.) and of 1-phthalimido-5-bromo-3-thiapentane (23.6 g.) in absolute ethanol (90 ml.) were added successively to a cooled solution of sodium ethoxide (from sodium (1.73 g.) and absolute ethanol (35 ml.)) and the mixture then refluxed for 3 hours. Most of the alcohol was then distilled off, water added and the washed solid product collected and recrystallized from acetone. It formed yellow needles, m.p. 122°, yield 82%.

*Anal.* Calcd. for $C_{18}H_{16}N_2O_4S_2$: C, 55.7; H, 4.2; N, 7.2. Found: C, 55.4; H, 4.3; N, 7.4.

**1-Amino-6-(*o*-nitrophenyl)-3,6-dithiahexane.**—The above described phthalimido compound (11.6 g.) was suspended in boiling ethanol (100 ml.), hydrazine hydrate (5.2 ml. of 50%) added and the boiling continued under reflux for 2 hours. Hydrochloric acid (10 ml., 10 *N*) was then added and the boiling continued for 0.5 hour after which as much alcohol as possible was distilled off and water added to the residue. The precipitated phthalhydrazide was removed and solid sodium hydroxide added to the filtrate until the base separated as a yellow oil which solidified on standing and scratching. It was difficult to purify but could be partially purified by solution in alcohol and then reprecipitation with aqueous sodium hydroxide solution; or by solution in ether in which it is somewhat soluble when impure, removal of most of the solvent and allowing to crystallize. The solid base becomes oily in a vacuum desiccator and solidifies again on exposure to air. For analysis it was converted to its **5-bromosalicylidene derivative**; yellow needles, m.p. 85° from ethanol.

*Anal.* Calcd. for $C_{17}H_{17}N_2O_3S_2Br$: N, 6.3. Found: N, 6.5.

**The picrate** formed yellow needles, m.p. 169° from ethanol.

*Anal.* Calcd. for $C_{16}H_{17}N_6O_9S_2$: N, 14.2. Found: N, 14.4.

**1-(5′-Bromosalicylideneamino)-6-(*o*-(5′-bromosalicylideneamino)-phenyl)-3,6-dithiahexane.**—Zinc dust (11.5 g.) and a solution of calcium chloride (0.4 g.) in water (1.2 ml.) were added to a solution of 1-amino-6-(*o*-nitrophenyl)-3,6-dithiahexane (2.7 g.) in aqueous methanol (38 ml. of 80%). The mixture was then heated under reflux for 2 hours, filtered hot and the alcohol removed, leaving a brown oil (crude EEB base). A solution of 5′-bromosalicylaldehyde (2 moles) in ethanol was added to a hot ethanolic solution of this crude base (1 mole). After boiling for a minute or two the product separated as an oil which was induced to crystallize and was recrystallized from ethyl acetate; yellow prisms, m.p. 103°.

*Anal.* Calcd. for $C_{24}H_{22}N_2O_2S_2Br_2$: C, 48.5; H, 3.7; N, 4.7. Found: C, 48.5; H, 3.9; N, 5.2.

**1-(5′-Bromosalicylideneamino)-6-(*o*-(5′-bromosalicylideneamino)-phenyl)-3,6-dithiahexane Cobalt(III) Iodide.**—Cobalt(II) chloride hexahydrate (0.5 g.) was added to a boiling solution of the bis-5-bromosalicylidene derivative of EEB base just described (0.45 g.) in methanol (130 ml.) and then a solution of sodium acetate (0.5 g.) and hydrogen peroxide (4.5 ml. of 3%) in methanol (10 ml.) added. When the volume was reduced to about 50 ml. the solution was filtered and a strong aqueous solution of potassium iodide added to the filtrate. The precipitate was collected and recrystallized by allowing its solution in methanol containing a little water to evaporate slowly, when it came out in minute brown needles, m.p. 205°, which were soluble in chloroform.

*Anal.* Calcd. for $[Co(C_{24}H_{20}Br_2N_2O_2S_2)]I$: C, 37.1; H, 2.6; N, 3.6; Co, 7.57. Found: C, 37.6; H, 2.9; N, 3.8; Co, 7.7.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

# Chemistry of Arsenic–Boron Bonding: Arsine Borines and Arsinoborine Polymers

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The methylarsines form borine complexes which are more easily dissociated than the corresponding phosphine borines, but show a similar increase of stability, and difficulty of losing hydrogen, with methylation. The existence of arsine borine could not be recognized. The protolytic reactions occur far more readily than those of the phosphine borines, with formation of fairly similar polymers, such as those of the $(CH_3)_2AsBH_2$ unit. The trimer of $(CH_3)_2AsBH_2$ (m.p. 50°, b.p. est. 250°, yield 80%) is stable up to 200°, and requires such a temperature for hydrolysis—some 100° lower than for trimeric $(CH_3)_2PBH_2$. The tetramer of $(CH_3)_2AsBH_2$ (m.p. 150°, b.p. est. 352°, yield 6%) is less stable than the trimer, to which it is partially converted at 180°. A higher polymer of $(CH_3)_2AsBH_2$, formed in far larger yield (14%) than the corresponding P compound (*ca.* 1%) is converted to trimer, with less tetramer, on heating. The trimer and tetramer can be recrystallized from organic solvents in the open air. Their lesser stability and greater reactivity, relative to the $(CH_3)_2PBH_2$ polymers, can be ascribed to the relative weakness of bonding electrons in the 4 quantum level of arsenic.

The discovery of some very stable boron hydride derivatives based upon P–B bonding,[1] such as the trimers of $(CH_3)_2PBH_2$ and $(CH_3)_2PB(CH_3)_2$, led to the question whether analogous arsinoborines also would be stable and chemically fairly inert. Inasmuch as trivalent arsenic compounds generally are less strongly bonded than the analogous phosphorus compounds, it was expected that the arsinoborines would have less thermal stability and higher chemical reactivity than the analogous phosphinoborines; also the arsine borine complexes were expected to be less stable than the corresponding phosphine borines. The results of the present study agree with such expectations, although the new arsinoborines are decidedly more stable and far less reactive than most of the previously known derivatives of the boron hydrides. The structural factors leading to the stabilization of the phosphinoborines have already been discussed,[1] and similar arguments presumably would apply to the arsinoborines.

## Experimental Part

### 1. Preparation and Characterization of Methylarsines

**Arsine.**—A 70% yield of arsine was obtained by the reaction of arsenic trichloride with lithium aluminum hy-

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(1) A. B. Burg and R. I. Wagner, THIS JOURNAL, 75, 3872 (1953).