

86. Complexes of Palladium and Platinum with Certain Chelate Compounds.

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The complexes formed by bivalent palladium and platinum with a number of chelate compounds are described. The chelate components employed each contain an acidic group (CO₂H, SH, or OH) and a donor atom (N, S, or As) (some of them new compounds). All these form palladium complexes, but, in a number of cases, no platinum complex was obtained.

In previous investigations (Livingstone, Plowman, and Sorenson, *J. Proc. Roy. Soc., New South Wales*, 1950, **84**, 28; Livingstone and Plowman, *ibid.*, p. 188; 1951, **85**, 116) the palladium complex of *o*-methylthiobenzoic acid was described and also a number of halogen-bridged complexes containing this chelating compound. The purpose of the present work was to ascertain whether bivalent palladium and platinum would form complexes with a number of chelate components. All the organic compounds used contain one acid group in the molecule, so that if they reacted with bivalent palladium, the compounds formed would be of the inner complex type such as diglycinepalladium(II) (Pinkard, Sharrat, Wardlaw, and Cox, *J.*, 1934, 1012). These complexes are of especial interest since they are theoretically capable of forming bridged complexes when treated with palladium salts containing an atom or group which can act as a bridge.

The ligands used by us are shown in the Table, together with the properties of the complexes formed. The acidic groups were CO₂H, SH, or OH, and the co-ordinating groups were NH₂, SR, or AsMe₂. It will be seen that palladium yielded a complex in all cases, but platinum in only seven of the thirteen cases.

The ligands marked with an asterisk are new compounds. Their syntheses, and those of the analogues, *o*-propylthio-, *o*-pentylthio-, and *o*-octylthio-benzoic acid, are recorded in the Experimental section.

Although the palladous and platinous complexes formed by these chelate ligands are all theoretically capable of showing geometrical isomerism, only one isomer of each complex was obtained. It was assumed to have the *trans*-configuration.

Complexes of bivalent palladium and platinum with certain chelate groups.

	Pd ^{II} complex	Pt ^{II} complex
I Anthranilic acid	Yellow; m. p. 245°; i. ¹	Puce; decomp.; i. ³
II 3-Amino-2-naphthoic acid	Buff; decomp.; i.	Pale yellow; impure
III <i>o</i> -Methylthiobenzoic acid	Canary-yellow; m. p. 193°; w; sp.s. ²	None
IV <i>o</i> - <i>n</i> -Butylthiobenzoic acid *	Yellow; m. p. 159°; sp.s.	„
V <i>o</i> -Benzylthiobenzoic acid	Canary-yellow; m. p. 169°; sp.s.	„
VI <i>o</i> -Octadecylthiobenzoic acid *	Yellow; m. p. 106–108°; sp.s.	„
VII 1 : 2-Di-(<i>o</i> -carboxyphenylthio)ethane	Orange-brown; decomp.; i.	Pale yellow; decomp.; i.
VIII <i>o</i> -Carboxyphenyldimethylarsine	Yellow; m. p. 168°; w; s. ¹	None
IX <i>o</i> -Aminophenol	Buff; decomp.; i.	„
X <i>o</i> -Aminobenzenethiol	Buff; decomp.; i.	Deep yellow; impure
XI <i>o</i> -Methylthiobenzenethiol *	Pink; m. p. 157°; s.	Deep yellow; m. p. 158°; sp.s.
XII 3-Dimethylarsinopropane-1-thiol *...	Orange; m. p. 180°; w; s.	Yellow; m. p. 187°; s.
XIII 3-Ethylthiopropene-1-thiol *	Impure	Yellow; m. p. 168°; i.

¹ Livingstone and Plowman, *loc. cit.*, 1950. ² Livingstone, Plowman, and Sorenson, *loc. cit.*
³ Grinberg and Kats, *J. Gen. Chem. (U.S.S.R.)*, 1950, **20**, 248.

w, Soluble in water; unless otherwise stated, these complexes are insoluble in water. s., Soluble; sp.s.; sparingly soluble; i., insoluble, in organic solvents such as alcohol, acetone, nitrobenzene, and chloroform.

EXPERIMENTAL

o-*n*-Butylthiobenzoic Acid.—Thiosalicylic acid (30 g.), potassium hydroxide (25 g.), and *n*-butyl bromide (40 g.) were refluxed in absolute alcohol (400 ml.) under nitrogen for 1 hr., then poured into water (1 l.); the mixture was acidified with hydrochloric acid, and filtered.

The *product*, recrystallized from 50% alcohol (300 ml.), had m. p. 100—101° (29.2 g.) (Found: C, 62.9; H, 6.9%; equiv., 210. $C_{11}H_{14}O_2S$ requires C, 62.8; H, 6.7%; equiv., 210). Similarly were prepared *o-n-propylthio*-, m. p. 124° (Found: C, 60.8; H, 5.8%; equiv., 195. $C_{10}H_{12}O_2S$ requires C, 61.2; H, 6.2%; equiv., 196), *o-pentylthio*-, m. p. 104—105° (Found: C, 64.4; H, 7.2%; equiv., 224. $C_{12}H_{16}O_2S$ requires C, 64.3; H, 7.2%; equiv., 224), *o-n-octylthio*-, m. p. 80° (Found: C, 67.6; H, 8.3%; equiv., 266. $C_{15}H_{22}O_2S$ requires C, 67.8; H, 8.4%; equiv., 267), and *o-n-octadecylthio-benzoic acid*-, m. p. 101.5° (Found: C, 73.7; H, 10.3%; equiv., 408. $C_{25}H_{42}O_2S$ requires C, 73.8; H, 10.4%; equiv., 406).

1: 2-*Di-(o-carboxyphenylthio)ethane*.—An alcoholic solution (500 ml.) of thiosalicylic acid (20 g.), potassium hydroxide (16 g.), and ethylene dibromide (12.2 g.) was refluxed under nitrogen for 90 min., then poured into water and acidified with hydrochloric acid. The white precipitate was filtered off and dried (yield, 18.5 g.). The *product* was not appreciably soluble in hot alcohol, benzene, acetone, or ether, but readily soluble in hot pyridine. Recrystallized from pyridine, it yielded colourless elongated prisms (14.8 g.), m. p. 297° (Found: C, 57.7; H, 4.3%; equiv., 166. $C_{16}H_{14}O_4S_2$ requires C, 57.5; H, 4.2%; equiv., 167).

Synthesis of o-Methylthiobenzenethiol. — o-Methylthioaniline. The following preparation is more satisfactory than that described by Hofmann (*Ber.*, 1887, 20, 1788). *o*-Mercaptoaniline (30 g.) was treated in alcohol (125 ml.) with sodium (5.4 g.) in small pieces. Methyl iodide (33 g.) was added and the whole refluxed for 40 min., then cooled and poured into water (1 l.). The oil, extracted in ether, was dried, recovered by evaporation, and distilled. The sulphide (20.3 g.) had b. p. 126—128°/15 mm., n_D^{17} 1.6264. Beilstein's "Handbuch," Vol. XIII, p. 297, and Suppl. 1, p. 124, lists 133°/15 mm., n_D^{17} 1.6263.

o-Methylthiobenzenethiol. o-Methylthioaniline (10.3 g.) was diazotized with dilute sulphuric acid (40 ml.) and sodium nitrite (5.7 g.) at 5—8° and added, with stirring, to a solution of sodium ethyl xanthate (40 g.) in water (100 ml.), at 75—85°, during 15 min. The reaction was very violent at the beginning, nitrogen being evolved immediately and a red oil separating. Finally, the mixture was warmed at 90° for 10 min. and then cooled. The red oil was separated, and the aqueous layer was extracted with ether and the ether evaporated. The two lots of oil were combined and refluxed with alcohol (120 ml.) containing potassium hydroxide (17 g.) for 2½ hr. The red liquor was filtered to yield a considerable quantity of white crystals. The filtrate was concentrated to 45 ml., then poured into water (500 ml.), and the crystals were added to this mixture. The resulting solution was acidified with hydrochloric acid and extracted with ether, and the extracts were washed with water and dried. After evaporation of the ether, the crude oil (12.3 g.) was distilled under reduced pressure in an atmosphere of coal gas. Considerable decomposition occurred during the distillation, leaving a tarry residue. The water-white fraction (b. p. 100—105°/2 mm.; 2.4 g.) was collected. This *thiol* gave a positive test for thiol with alkaline sodium nitroprusside (Found: C, 54.1; H, 5.1. $C_7H_8S_2$ requires C, 53.8; H, 5.2%).

Preparation of 3-Dimethylarsinopropane-1-thiol. — 3-Chloropropyl-dichloroarsine, prepared as described by Gough and King (*J.*, 1928, 2439), had b. p. 132—136°/25 mm. 3-Chloropropyl-dimethylarsine, prepared by Barclay and Nyholm's method (*Chem. and Ind.*, 1953, 378), had b. p. 59—62°/10 mm. (Found: C, 32.9; H, 6.4. Calc. for $C_5H_{12}ClAs$: C, 32.9; H, 6.6%).

An alcoholic solution of sodium hydrogen sulphide was prepared by dissolving sodium (7.7 g.) in absolute alcohol (300 ml.), and passing hydrogen sulphide into the solution until it was colourless to phenolphthalein. This was added gradually to a solution of 3-chloropropyl-dimethylarsine (60 g.), in alcohol (50 ml.), in an atmosphere of coal gas. Little reaction took place until the mixture was heated, whereupon sodium chloride was precipitated. The mixture was refluxed for 30 min., then cooled, and filtered. The alcohol was distilled off and the residue was distilled under reduced pressure (coal gas), yielding 3-dimethylarsinopropane-1-thiol (26.0 g.), b. p. 54—58°/3 mm., n_D^{20} 1.5296 (Found: C, 33.2; H, 7.1. $C_5H_{13}SAs$ requires C, 33.3; H, 7.3%). The compound gives a violet colour with alkaline sodium nitroprusside. The water-white liquid showed no coloration or precipitation when kept under coal gas in a refrigerator for 2 years.

3-Ethylthiopropane-1-thiol.—To a solution from sodium (30 g.) in alcohol (500 ml.) was added ethanethiol (75 g.) in alcohol (100 ml.), followed by 3-chloropropan-1-ol (114 g.) during 10 min. Sodium chloride separated and the temperature rose to about 60°. When the addition was complete, the mixture was refluxed for 1½ hr., then filtered and evaporated. Distillation in coal gas *in vacuo* gave water-white 3-ethylthiopropan-1-ol (86.2 g.), b. p. 98—99°/10 mm., n_D^{20} 1.4843 (Found: C, 50.2; H, 10.1. $C_5H_{12}OS$ requires C, 50.0; H, 10.1%).

This alcohol (85.5 g.) was treated in ligroin with thionyl chloride during 15 min., then refluxed for 1½ hr., after which no more hydrogen chloride was evolved. About 3 g. of black oil were

formed, which was discarded. The ligroin was distilled off and the product distilled, yielding 3-ethylthiopropyl chloride (75 g.), b. p. 65–66°/10 mm., n_D^{20} 1.4843 (Found: C, 43.5; H, 8.0. $C_5H_{11}Cl$ requires C, 43.3; H, 8.0%).

Sodium ethyl sulphide, prepared as before, from sodium (37.5 g.) and alcohol (500 ml.), was treated gradually with the preceding chloride (225 g.), and the whole refluxed for 30 min. Hydrochloric acid was added until the mixture was just acid. The sodium chloride was filtered off, and the alcohol removed by distillation at the water pump. Distillation under reduced pressure gave 3-ethylthio propane-1-thiol (179 g.), b. p. 47°/1 mm., n_D^{25} 1.5135 (Found: C, 44.2; H, 8.7. $C_5H_{12}S_2$ requires C, 44.1; H, 8.9%). The colourless product gave a violet colour with alkaline sodium nitroprusside.

Bis-3-amino-2-naphthoatopalladium(II).—To 3-amino-2-naphthoic acid (1.05 g.), dissolved in one equivalent of sodium hydroxide solution (50 ml.), at 60°, was added potassium chloropalladate(II) (0.9 g.), dissolved in water (20 ml.). There was an immediate precipitation of the buff-coloured *palladium complex*, which was filtered off, washed with hot water, then acetone, and dried at 120° (Found: C, 55.3; H, 3.5; Pd, 22.5. $C_{22}H_{16}O_4N_2Pd$ requires C, 55.2; H, 3.4; Pd, 22.3%).

A solution of potassium chloroplatinate(II), similarly treated, gave after a few minutes impure yellow crystals.

Bis-(o-n-butylthiobenzoato)palladium(II).—*o-n*-Butylthiobenzoic acid (2.5 g.), in one equivalent of sodium hydroxide solution (50 ml.), was treated with an aqueous solution of potassium chloropalladate(II) (1.9 g.) at room temperature. An oil separated, which crystallized. The product was filtered off and recrystallized from 50% aqueous acetone. Fine yellow crystals (2.0 g.) of the *palladium complex* were obtained, having m. p. 159° (Found: C, 49.5; H, 4.9; Pd, 20.4. $C_{22}H_{26}O_4S_2Pd$ requires C, 50.3; H, 5.0; Pd, 20.3%). The conductivity of the complex at 25° was: in nitrobenzene, $\Lambda_{1000} = 0.03$ mho; in water, $\Lambda_{2000} = 11$ mho.

Bis-(o-benzylthiobenzoato)palladium(II).—A solution of potassium chloropalladate(II) (9.75 g.) in water (100 ml.) was slowly poured into a boiling aqueous solution (200 ml.) containing *o*-benzylthiobenzoic acid (14.6 g.) and sodium hydroxide (2.4 g.). The immediate yellowish-orange precipitate was filtered off and recrystallized from 60% aqueous acetone (2.5 l.). The recrystallized complex was washed with acetone and dried over phosphoric oxide. The bright yellow prisms (16 g.) are soluble in chloroform and moderately soluble in aqueous acetone, and melt at 169° (with decomp.) (Found: C, 56.5; H, 3.8; Pd, 18.0. $C_{28}H_{22}O_4S_2Pd$ requires C, 56.7; H, 3.7; Pd, 18.0%). Λ_{3000} in nitrobenzene at 25° = 0.

Bis-(o-octadecylthiobenzoato)palladium(II).—*o*-Octadecylthiobenzoic acid (2.0 g.) was dissolved in one equiv. of 0.1M-sodium hydroxide and the solution diluted to 150 ml. Potassium chloropalladate(II) (0.8 g.), in water (40 ml.), was added at 90°. A pale yellow turbid liquor resulted. On being heated with acetone (75 ml.) for several minutes, the precipitate became granular, and, after the solution had cooled, the complex was filtered off and washed first with water, then with acetone, in which it was slightly soluble (2.1 g.; m. p. 106–108°) (Found: C, 65.5; H, 9.1; Pd, 11.6. $C_{60}H_{82}O_4S_2Pd$ requires C, 65.4; H, 9.1; Pd, 11.6%). Λ_{2000} in nitrobenzene = 0.2 mho.

1:2-Di-(o-carboxyphenylthio)ethanepalladium(II).—1:2-Di-(*o*-carboxyphenylthio)ethane (1 g.) was treated with one equiv. of 0.5M-sodium hydroxide, and the small amount of undissolved organic acid was filtered off. The filtrate was poured into a solution of potassium chloropalladate(II) (1 g.) in hot water (15 ml.). A crystalline precipitate was formed immediately. After being heated on the steam-bath for a further 15 min., the mixture was filtered, and the orange crystals were washed with hot water, then acetone. The *complex* (1.15 g.) is practically insoluble in water and organic solvents (Found: C, 42.9; H, 2.7; Pd, 24.6. $C_{16}H_{12}O_4S_2Pd$ requires C, 43.8; H, 2.8; Pd, 24.3%).

1:2-Di-(o-carboxyphenylthio)ethaneplatinum(II).—1:2-Di-(*o*-carboxyphenylthio)ethane (1 g.), dissolved in one equiv. of 0.5M-sodium hydroxide, was added to a solution of potassium chloroplatinate(II) (1.25 g.) in hot water (15 ml.). No precipitation occurred but, on the addition of one drop of dilute acetic acid, a cream-coloured precipitate was formed. The mixture was digested on the water-bath for 15 min. and the *platinum complex* was then filtered off and washed with water and acetone (yield, 1.12 g.) (Found: C, 36.2; H, 2.3; Pt, 36.7. $C_{16}H_{12}O_4S_2Pt$ requires C, 36.4; H, 2.3; Pt, 37.0%).

Bis-o-aminophenolpalladium(II) Monohydrate.—*o*-Aminophenol (1 g.) was dissolved in water (40 ml.), containing sodium hydroxide (0.3 g.); to this was added potassium chloropalladate(II) (1.5 g.) in water (30 ml.). The buff-coloured complex, which was immediately precipitated, was washed with hot water, then acetone (in which it is virtually insoluble) and dried *in vacuo*

over phosphoric oxide (Found: C, 42.2; H, 3.8; N, 8.3; Pd, 31.2. $C_{12}H_{12}O_2N_2Pd, H_2O$ requires C, 42.3; H, 4.1; N, 8.2; Pd, 31.2%).

No precipitate or colour change occurred when potassium chloroplatinate(II) was used in this reaction.

Bis-o-aminobenzenethiolpalladium(II).—*o*-Aminobenzenethiol (1 g.) was treated with one equiv. of 0.5M-sodium hydroxide and then an aqueous solution of potassium chloropalladate(II) (1.25 g.). A chocolate-coloured amorphous precipitate was formed which, on being boiled for some time with aqueous acetone, became crystalline and much paler. The buff-coloured crystals (1.22 g.) were washed with hot water, then acetone. The compound is insoluble in water and organic solvents (Found: C, 40.7; H, 3.4; Pd, 30.2. $C_{12}H_{12}N_2S_2Pd$ requires C, 40.6; H, 3.4; Pd, 30.1%).

Potassium chloroplatinate(II), similarly treated, gave impure yellow crystals, which became green when kept in a desiccator for several days.

Bis-o-methylthiobenzenethiolpalladium(II).—*o*-Methylthiobenzenethiol (0.6 g.) was treated with one equiv. of 0.5M-sodium hydroxide and an aqueous solution (10 ml.) of potassium chloropalladate(II) (0.64 g.). An amorphous product was precipitated, but after the mixture had been heated for some time the precipitate crystallized. The pink complex (0.61 g.), m. p. 157°, is soluble in acetone to a pinkish-purple solution, and in chloroform and nitrobenzene to yield red solutions (Found: C, 40.2; H, 3.3; Pd, 25.3. $C_{14}H_{14}S_4Pd$ requires C, 40.3; H, 3.4; Pd, 25.6%). Conductivity at 25°: in acetone, $\Lambda_{500} = 0.06$ mho; in nitrobenzene, $\Lambda_{500} = 0.02$ mho.

Bis-o-methylthiobenzenethiolplatinum(II).—A solution of potassium chloroplatinate(II) (0.52 g.) in water (10 ml.) was added to a suspension of *o*-methylthiobenzenethiol (0.39 g.) in one equiv. of 0.5M-sodium hydroxide. After a few minutes, fine yellow crystals were slowly precipitated. The product was filtered off and heated with a small quantity of acetone. The compound (0.31 g.), m. p. 158°, is moderately soluble in acetone and nitrobenzene (Found: C, 32.8; H, 2.7; Pt, 38.6. $C_{14}H_{14}S_4Pt$ requires C, 33.2; H, 2.8; Pt, 38.6%). Conductivity at 25°: in acetone, $\Lambda_{1000} = 0.06$ mho; in nitrobenzene, $\Lambda_{1000} = 0.01$ mho.

Bis-(3-dimethylarsinopropane-1-thiol)palladium(II).—A solution of potassium chloropalladate(II) (1.25 g.) in water (15 ml.) was added slowly, with stirring, to a suspension of 3-dimethylarsinopropane-1-thiol (2.1 g.) in one equiv. of 0.5M-sodium hydroxide. Orange crystals were precipitated, but they were contaminated with excess of thiol. The precipitate was filtered off and washed with water, then acetone, and recrystallized from acetone. The complex (1.38 g.), m. p. 180°, is moderately soluble in water and acetone, readily soluble in chloroform, benzene, and nitrobenzene (Found: C, 25.9; H, 5.1; Pd, 23.1%; *M*, cryoscopically in 0.42% nitrobenzene solution, 467; in 0.28% nitrobenzene solution, 477; in 0.37% benzene solution, 465. $C_{10}H_{24}S_2As_2Pd$ requires C, 25.8; H, 5.3; Pd, 23.0%; *M*, 465). Conductivity at 25°: in water, $\Lambda_{1000} = 7$ mho; in nitrobenzene, $\Lambda_{1000} = 0.1$ mho.

Bis-(3-dimethylarsinopropane-1-thiol)platinum(II).—A solution of potassium chloroplatinate(II) (2.0 g.), as in the preceding experiment, gave a complex which after final trituration with ligroin and recrystallization from 90% acetone (125 ml.) yielded yellow crystals (1.2 g.), m. p. 187° (Found: C, 21.8; H, 4.2. $C_{10}H_{24}S_2As_2Pt$ requires C, 21.7; H, 4.4%). Conductivity in nitrobenzene at 25°: $\Lambda_{1000} = 0.1$ mho.

Bis-(3-ethylthiopropane-1-thiol)platinum(II).—The thiol (5.05 g.) was treated with one equiv. of 0.5M-sodium hydroxide and then an aqueous solution of potassium chloroplatinate(II) (7.5 g.) with vigorous stirring. The red colour disappeared from the solution and a yellow oil, which gradually became crystalline, was produced. The crude product was filtered off, washed with water, then boiled with acetone, and collected. The yellow crystals (4.92 g.) are insoluble in water, acetone, chloroform, and nitrobenzene. The compound softens at about 145° and melts at 167° to a pale amber liquid which does not decompose below 250° (Found: C, 25.2; H, 4.6; Pt, 42.4. $C_{10}H_{22}S_4Pt$ requires C, 25.8; H, 4.7; Pt, 41.9%).

Potassium chloropalladate(II) gave only a yellow amorphous precipitate.

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