

761. *Some Transition Metal Complexes of Bisdiethylamino-phenylphosphine.**

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Complexes of bisdiethylaminophenylphosphine with nickel(II), cobalt(II), palladium(II), platinum(II), and copper(I) are reported. Copper(I) iodide gives both a 1 : 1 and a 2 : 1 complex; the former is a tetramer, and the latter a monomer apparently involving three-co-ordinate copper.

In a previous paper,¹ the formation of complexes of the bisdialkylaminophenylphosphines with mercury(II) iodide was reported; this work has now been extended in the case of the diethyl compound to a selection of transition metals in their common valency states. The complexes isolated are shown in the Table. In each case the conclusion drawn previously from the examination of the mercury(II) complexes, that the bisdialkylaminophenylphosphines behave always as simple monophosphine ligands is supported. There is a marked contrast between these transition-metal complexes and the mercury(II) compounds in that their preparation requires carefully controlled conditions, notably the use of low temperatures. Qualitatively these transition-metal complexes appear much less

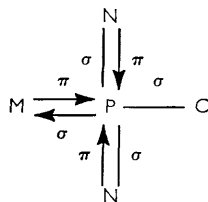
* Presented in part at the 7th Internat. Conference on Co-ordination Chemistry, Stockholm, 1962.

¹ Ewart, Payne, Porte, and Lane, *J.*, 1962, 3984.

Complexes prepared [L = Ph·P(NEt₂)₂].

	Colour	M. p.	Δ_m in Ph·NO ₂ (concn. 10 ⁻³ M)	$\mu_{\text{eff.}}$ (B.M.)
L ₂ Ni(NCS) ₂	Red	99—105°	17.3	Diamagnetic
L ₂ Co(NCS) ₂	Green	98—102	21.8	4.34
L ₂ CoCl ₂	Green	~70 (decomp.)	6.4	4.53
L ₂ CoBr ₂	Green	112—114	8.1	4.43
L ₂ PdCl ₂	Yellow	109—111	4.0	Diamagnetic
L ₂ PtCl ₂	Yellow	100—104	0.0	Diamagnetic
(LCuI) ₄	White	194—198	0.0	—
L ₂ CuI.....	White	103	0.0	—

stable than the mercury(II) complexes and less stable than the transition-metal complexes of the alkylarylphosphines.² The origin of these differences must lie in the electron distribution within the N–P–N system and the extent to which phosphorus *d*-orbitals remain available as acceptor orbitals. In complexes such as this, where considerable back-donation occurs, the metal is in competition with nitrogen for the use of the available acceptor orbitals of the phosphorus. A model of bisdiethylaminophenylphosphine, with tetrahedrally hybridised nitrogen and phosphorus atoms, appears to show that all the five *d*-orbitals of phosphorus are capable of some degree of overlap with the nitrogen filled *p*-orbital. The bonding could be represented thus:



The cobalt and nickel complexes decomposed if the solids were left in contact with the solutions at temperatures $>0^\circ$, or if left damp with solvent after filtration. Once separated and thoroughly freed from solvent, the complexes could be stored unchanged indefinitely in an evacuated tube, but if left in contact with moist air changes in colour occurred and the materials became sticky. The palladium(II) and platinum(II) complexes were considerably less prone to these changes. The nature of the changes has not been elucidated, the products being sparingly soluble in all solvents except dilute aqueous strong acids, and of indefinite composition. Complexes containing hydroxy- or alkoxy-groups are possible. Attempts to isolate the nickel(II) chloride and bromide complexes were unsuccessful because of the speed of solvolysis. However, complex formation in the initial stages of the reaction was clearly indicated by a marked change in colour when the solutions were mixed.

The complexes with copper(I) are of particular interest. Depending on the ratio of copper(I) iodide to ligand, either a 1 : 1 or a 2 : 1 complex is obtained. The 1 : 1 complex is a tetramer, which is in line with the general proposition. The 1 : 2 complex is monomeric in benzene and nitrobenzene, and in the latter solvent it is a non-conductor. Similar behaviour was observed by Cass, Coates, and Hayter³ with *p*-dimethylaminophenyldimethylphosphine, *p*-dimethylaminophenyldiethylphosphine, and dimethylphenylphosphine and silver(I) or copper(I) iodide; however, it was not then possible to obtain molecular-weight results for the 2 : 1 copper(I) complexes owing to their low solubility. These workers established the monomeric nature of the 2 : 1 silver(I) iodide adducts with the ligands listed above, and since the compounds were non-conductors in nitrobenzene and benzene they are to be regarded as examples of 3-co-ordination. By an analogous

² Ahrland and Chatt, *Chem. and Ind.*, 1955, 96.

³ Cass, Coates, and Hayter, *J.*, 1955, 4007.

argument, the 2:1 complex, which we report, appears also to be an example of 3-coordination, this time in the chemistry of copper(I). Ahrland and Chatt² have discussed the occurrence of three-coordination in the case of phosphine and silver(I), and this discussion appears to be directly applicable to copper(I). It is intended to confirm the three-co-ordinate form of this copper(I) complex by a more direct structural method.

On the basis of its diamagnetic character and colour, the nickel(II) complex is square-planar, and the cobalt complexes on similar reasoning are tetrahedral. The equivalent conductances of the nickel and cobalt(II) thiocyanate complexes correspond to those expected for 1:1 electrolytes. The halide complexes all have relatively low conductances and are probably, as with the triarylphosphine complexes, either weak electrolytes or non-electrolytes.

EXPERIMENTAL

Bisthiocyanatodi(bisdiethylaminophenylphosphine)nickel(II).—Potassium thiocyanate (1.13 g., 0.0116 mole), dissolved in boiling ethanol (25 ml.), was added to nickel(II) nitrate hexahydrate (1.73 g., 0.00596 mole) dissolved in ethanol (25 ml.). Potassium nitrate was filtered off and the green alcoholic solution of nickel thiocyanate was added dropwise with stirring, under nitrogen, to bisdiethylaminophenylphosphine (3.28 g., 0.0131 mole) dissolved in ethanol (25 ml.) and kept at -50° . The resulting red crystalline complex was filtered off under nitrogen and dried *in vacuo* (1.538 g., 38%), m. p. $99-105^{\circ}$ [Found: N, 12.4; Ni, 8.8%; *M*, 355 (cryoscopic in nitrobenzene). $C_{30}H_{50}N_6NiP_2S_2$ requires N, 12.4; Ni 8.6%; *M*, 680].

Bisthiocyanatodi(bisdiethylaminophenylphosphine)cobalt(II).—As described above, potassium thiocyanate (0.424 g., 0.00436 mole) was added to cobalt(II) nitrate hexahydrate (0.609 g., 0.00209 mole), and the resulting solution of cobalt(II) thiocyanate added to bisdiethylaminophenylphosphine (0.997 g., 0.00209 mole). A green crystalline complex (0.447 g., 33%), m. p. $98-102^{\circ}$, was obtained (Found: N, 12.2; S, 9.2. $C_{30}H_{50}CoN_6P_2S_2$ requires N, 12.4; S, 9.4%).

Dichlorodi(bisdiethylaminophenylphosphine)cobalt(II).—Cobalt chloride hexahydrate (0.354 g., 0.00149 mole) was dehydrated at 180° in the presence of hydrogen chloride and added slowly in ethanol (15 ml.) to bisdiethylaminophenylphosphine (0.780 g., 0.00309 mole) as described previously. A green crystalline product (0.475 g., 50.3%), m. p. *ca.* 70° (decomp.), was obtained (Found: N, 8.5; Cl, 10.9. $C_{28}H_{50}Cl_2CoN_4P_2$ requires N, 8.5; Cl, 11.2%).

Dibromodi(bisdiethylaminophenylphosphine)cobalt(II).—The green anhydrous cobalt(II) bromide (0.431 g., 0.00197 mole), under the conditions described above, gave a pale green dibromo-complex (1.152 g., 84.7%), m. p. $110-112^{\circ}$ (Found: N, 7.5; Br, 21.8. $C_{28}H_{50}Br_2CoN_4P_2$ requires N, 7.7; Br, 21.9%).

Dichlorodi(bisdiethylaminophenylphosphine)palladium(II).—Potassium tetrachloropalladate(II) (0.308 g., 0.00401 mole) in water (25 ml.) was shaken with bisdiethylaminophenylphosphine (2.093 g., 0.00830 mole) in ether (75 ml.). The ethereal layer was separated, dried (CaH_2), and allowed to evaporate slowly, to give a yellow dichloro-complex (1.611 g., 59%), m. p. $109-111^{\circ}$ (Found: N, 8.0; Cl, 10.0. $C_{28}H_{50}Cl_2N_4P_2Pd$ requires N, 8.2; Cl, 10.4%).

Dichlorodi(bisdiethylaminophenylphosphine)platinum(II).—Potassium tetrachloroplatinate(II) (0.360 g., 0.000867 mole), dissolved in water (7 ml.) and acetone (12 ml.), was added to bisdiethylaminophenylphosphine (0.442 g., 0.00175 mole). The potassium chloride was filtered off and the resulting yellow solution gave a pale yellow product, m. p. $100-104^{\circ}$, on being kept (Found: N, 7.41; Cl, 9.1. $C_{28}H_{50}Cl_2N_4P_2Pt$ requires N, 7.3; Cl, 9.2%).

Di-iodobisdiethylaminophenylphosphinecopper(I).—Copper(I) iodide (1.299 g., 0.00688 mole), dissolved in saturated potassium iodide solution (50 ml.), was added to bisdiethylaminophenylphosphine (3.220 g., 0.0238 mole), dissolved in ethanol (50 ml.) and cooled to 0° . The white precipitate (4.290 g., 96.7%) was filtered off, washed with water, and dried *in vacuo*. Recrystallisation from ethanol gave complex, m. p. 103° (Found: N, 8.3; Cu, 8.9; I, 19.0. $C_{28}H_{50}CuIN_4P_2$ requires N, 8.1; Cu, 9.1; I, 18.3%). The molecular weight was determined ebullioscopically in benzene (*M*, 627), and cryoscopically in nitrobenzene (*M*, 703) and in benzene (*M*, 679) ($C_{28}H_{50}CuIN_4P_2$ requires *M*, 695).

Iodobisdiethylaminophenylphosphinecopper(I).—Copper(I) iodide (0.285 g., 0.00150 mole), dissolved in saturated potassium iodide solution, was added to di-iodobisdiethylaminophenylphosphinecopper(I) (1.132 g., 0.00163 mole) in boiling ethanol. The white monoiodo-complex produced (1.183 g., 0.0026 mole) melted at $194-198^{\circ}$ [Found: N, 6.3; Cu, 14.2; I, 28.8%;

M (cryoscopic in C_6H_6 , 1669, 1848. $C_{14}H_{25}CuIN_2P$ requires N, 6.3; Cu, 14.3; I, 28.7%; *M*, 1771). The 1 : 1 complex was also made directly by adding bisdiethylaminophenylphosphine to copper(I) iodide in equimolar quantities.

Magnetic Moments.—Except for the palladium chloride complex, these were measured on a Gouy-type balance, calibrated by means of mercury(II) tetrathiocyanatocobaltate(II).⁴

Several samples of the palladium dichloride complex gave values of high magnetic susceptibility (4–6 B.M.). Careful purification led to the expected diamagnetic complex, but the nature of the paramagnetic impurity or alternative form was not elucidated. We are grateful to Professor J. Lewis of the University of Manchester for assistance with measurements of the magnetic susceptibility of the purified palladium complex.

Conductance Measurements.—These were made at 25° in nitrobenzene (purified by storage over a molecular sieve, followed by distillation under reduced pressure) at concentrations around $10^{-3}M$ by means of a Phillips PR 9500 conductance bridge.

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⁴ Nyholm and Figgis, *J.*, 1958, 4190.
