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UNCOMMON CO-ORDINATING AGENTS—I
P,P,P′,P′-TETRAETHYLETHYLENEDIPHOSPHINE*

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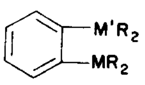
Abstract—The preparation of tetraethylethylenediphosphine (TEP) and some of its complexes is described. The complexes are compared with similar arsenic and nitrogen compounds. The ionic nature of the diamagnetic octahedral cobalt (III) complexes, $[Co(TEP)_2X_2]X$ ($X = Cl, Br, I$) is indicated by their conductance in nitrobenzene and in water ($X = Cl$). The complex $Co(TEP)_2I_2$ has one unpaired electron and, since the conductivity in nitrobenzene shows the presence of two ions, it is presumably five-co-ordinate in that solvent. It is thought to be octahedral in the solid state. A complex with the empirical formula $Co(TEP)Br_2$ is probably a salt-like dimer $[Co(TEP)_2]CoBr_4$ containing planar $[Co(TEP)_2]^{2+}$ and tetrahedral $CoBr_4{}^{2-}$. The complexes $M(TEP)X_2$ ($M = Zn, Cd, Hg, Pb, Ni$; $X = Br$ and $M = Pd, Ni$; $X = Cl$) as well as $[M(TEP)_2](ClO_4)_2$ ($M = Pb, Ni$) were isolated. Those of nickel (II) are diamagnetic and presumably planar. $Ni(TEP)Br_2$ was oxidized to $Ni(TEP)Br_3$ which has one unpaired electron, confirming the presence of nickel (III). With the coinage metals, the compounds $[Cu(TEP)_2]\,[Cu(TEP)X_2]$, $[Ag(TEP)_2]AgI_2$ and $IAuPEt_2C_2H_4PEt_2AuI$ were studied. The first two are conducting in nitrobenzene and the gold(I) complex is non-conducting. Its bridge structure is supported by its molecular weight in chloroform. It can be oxidized to $I_3Au(TEP)AuI_3$.

Many *o*-phenylene compounds (I) in which M and M′ are arsenic, phosphorus, nitrogen or any combination of them have been prepared and the properties of their co-ordination compounds investigated extensively.(1,2) In the alkyl series, the complexes of N-substituted ethylenediamines have been examined.(3) The palladium



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(1) R. S. Nyholm and G. J. Sutton, *J. Chem. Soc.* 560 (1958) and references therein; *J. Chem. Soc.* 564, 567, 572 (1958); J. E. Fergusson and R. S. Nyholm, *Chem. & Ind.* 1555 (1958); N. F. Curtis, J. E. Fergusson and R. S. Nyholm, *Chem. & Ind.* 625 (1958); H. L. Nigam and R. S. Nyholm, *Proc. Chem. Soc.* 321 (1958); J. Chatt and F. A. Hart, *Chem. & Ind.* 1474 (1958).

(2) (a) F. G. Mann and F. H. C. Stewart, *J. Chem. Soc.* 1269 (1955);
(b) E. R. H. Jones and F. G. Mann, *Ibid.* 4472 (1955); W. Cochran, F. A. Hart and F. G. Mann, *Ibid.* 2816 (1957);
(c) F. A. Hart and F. G. Mann, *Chem. & Ind.* 574 (1956); *J. Chem. Soc.* 3939 (1957); J. Chatt and F. A. Hart, *Chem. & Ind.* 147 (1958);
(d) F. G. Mann and H. R. Watson, *J. Chem. Soc.* 3945, 3950 (1957).

(3) (a) F. G. Mann and H. R. Watson, *J. Chem. Soc.* 2772 (1958);
(b) F. Basolo and R. K. Murmann. *J. Amer. Chem. Soc.* **76**, 211 (1954); **74**, 5234 (1952);
(c) R. G. Pearson, C. R. Boston and F. Basolo, *Ibid.* **75**, 3089 (1953);
(d) H. Irving and J. M. M. Griffiths, *J. Chem. Soc.* 213 (1954);
(e) F. G. Mann, *Ibid.* 2904 (1927);
(f) I. Lifschitz *et al.*, *Z. Anorg. Chem.* **242**, 97 (1939);
(g) P. Pfeiffer and H. Glaser, *J. Prakt. Chem.* [2] **151**, 134 (1938); [2] **153**, 300 (1939);
(h) R. N. Keller and L. J. Edwards, *J. Amer. Chem. Soc.* **74**, 215 (1952);
(i) F. Basolo, *Ibid.* **75**, 227 (1953).

complexes of alkyldiarsines(II) have also been studied.(4) Recently a preliminary report of a nickel(0) complex containing P,P,P′,P′-tetraethylethylenediphosphine* (III) has appeared.(5) This paper deals with a more extensive investigation of the metal

$$\underset{\text{II}}{R_2AsCH_2CH_2AsR_2} \qquad \underset{\text{III}}{(C_2H_5)_2PCH_2CH_2P(C_2H_5)_2}$$

complexes of tetraethylethylenediphosphine. This diphosphine yields co-ordination compounds containing phosphorus which are similar to complexes of ethylenediamine and which can be compared with them. Tetraethylethylenediphosphine and ethylenediamine are not strictly analogous, but ethylenediamine forms stronger complexes than N-substituted ethylenediamines and trialkylphosphines form more stable complexes than phosphines, so that the chelates of these two bidentate ligands represent the most stable compounds in each series.

RESULTS AND DISCUSSION

Tetraethylethylenediphosphine. Tetraethylethlenediphosphine was prepared by the stepwise alkylation of phosphine in liquid ammonia at —78°C. None of the intermediates were isolated and the crude tetraethyldiphosphine was obtained in

$$PH_3 \xrightarrow[C_2H_5Br]{Na} C_2H_5PH_2 \xrightarrow[C_2H_5Br]{NaNH_2} (C_2H_5)_2PH \xrightarrow[ClC_2H_4Cl]{NaNH_2} (C_2H_5)_2PCH_2CH_2P(C_2H_5)_2$$

overall yields up to 54 per cent. It was isolated and analysed as the dihydroiodide. The use of sodium amide as the base was adapted from the work of WAGNER and BURG.(6)

Trimethylenediphosphine has been prepared by LEFFLER and TEACH(7) in a similar manner. They report that ethylenediphosphine and P, P′-diethylethylenediphosphine are unstable at room temperature. HITCHCOCK and MANN(8) have prepared $(C_6H_5)C_2H_5PC_2H_4PC_2H_5(C_6H_5)$, using virtually the same method. Except for the nickel(0) compound of tetraethylethylenediphosphine, the co-ordinating ability of none of the diphosphines has been investigated.

Cobalt complexes. Tetraethylethylenediphosphine (hereafter called diphosphine and abbreviated TEP) forms complexes with cobalt(II) and (III). Air oxidation of solutions of cobalt (II) salts and the diphosphine gives a series of cobalt(III) complexes with the formula $[Co(TEP)_2X_2]X$(X = Cl, Br and I). The green bromo and chloro compounds are soluble in water and seem to hydrolyse slowly to a yellow solution. The green colour can be restored, at least in the early stages of hydrolysis, by addition of the appropriate hydrohalic acid. The brown iodo salt is insoluble in water. All three of the cobalt(III) complexes are conducting in nitrobenzene (Table 1). Their molar conductances (35–39 mhos) are a little higher than the 20–30 mhos usually found for 1 : 1 electrolytes at 20–25° in the concentration range 0·001–0·01 M(9). The

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* Can also be named ethylenebis(diethylphosphine)

(4) J. CHATT and F. G. MANN, *J. Chem. Soc.* 1622 (1939).

(5) J. CHATT and F. A. HART, *Chem. & Ind.* 1474 (1958).

(6) R. I. WAGNER and A. B. BURG, *J. Amer. Chem. Soc.* 75, 3869 (1953).

(7) A. J. LEFFLER and E. G. TEACH, *The Preparation of Some Alkyl Diphosphines*, 133rd National A.C.S. Meeting, San Francisco, April (1958).

(8) C. H. S. HITCHCOCK and F. G. MANN, *J. Chem. Soc.* 2081 (1958).

(9) (a) A. KABESH and R. S. NYHOLM, *J. Chem. Soc.* 38 (1951);
(b) C. M. HARRIS and R. S. NYHOLM, *Ibid.* 4375 (1956).

larger values are probably due to the higher temperatures at which the measurements were made. The conductivity of the chloro complex (Table 1) in water shows that two ions are present and substantiates its uni-univalent character in nitrobenzene. All of the compounds are diamagnetic or slightly paramagnetic, indicating an octahedral configuration in which all the electrons are paired. What evidence there is (see below) might indicate that the halogen atoms are in the *trans* positions.

TABLE 1.—MOLAR CONDUCTANCE OF DIPHOSPHINE COMPLEXES

Compound	Molar conductance in $PhNO_2$			Molar conductance in H_2O	
	Temp. (°C)	Conc. ($M \times 10^{-3}$)	Λ_M	Temp. (°C)	Λ_{1024}
$[Co(TEP)_2I_2]I$	29	1·02	35·7		
$[Co(TEP)_2Br_2]Br$	28	0·79	36·9		
$[Co(TEP)_2Cl_2]Cl$	25	0·97	39·1	29	120
$[Co(TEP)_2I]I$	29	0·79	35·4		
$[Co(TEP)_2]CoBr_4$	29	0·62	16·4	26·5	233*
$Ni(TEP)Br_3$	28	0·60	3·8		
$[Cu(TEP)_2]$ $[Cu(TEP)I_2]$	28	5·60	29·4		
$[Ag(TEP)_2]AgI_2$	28	0·95	15·0		
$IAu(TEP)AuI$	28	1·22	0·9		
$Zn(TEP)Br_2$	28·5	1·41	0		
$Cd(TEP)Br_2$	28	5·0	0·3		

* Based on the empirical formula $Co(TEP)Br_2$.

In structure and method of preparation, the diphosphine complexes of cobalt(III), $[Co(TEP)_2X_2]X$, are similar to the analogous ethylenediamine and o-phenylenebis(dimethylarsine)(10) compounds (Formula I, $M = M' = As$, $R = Me$). Apparently, the only previously reported complex of cobalt(III) and a phosphine is $Co(PEt_3)_2Cl_3$.(11)

The complexes of cobalt(II) are prepared in the absence of air. With a 2 : 1 ratio of diphosphine to cobalt, compounds of the empirical formulas $Co(TEP)_2I_2$ and $Co(TEP)Br_2$ were isolated. The molar conductance of the brown iodo compound in nitrobenzene is 35·4 mhos, indicating that two ions are present. This means that the cobalt is five-co-ordinate in nitrobenzene if any possible solvation by the solvent is ignored. The compound is insoluble in water so that its conductivity in that solvent could not be determined. $Co(TEP)_2I_2$ has a magnetic moment of 2·2 B.M. which indicates one unpaired electron. Both square planar and spin-paired tetragonal cobalt(II) complexes have a theoretical moment corresponding to one unpaired electron (1·73 B.M.) when calculated by the "spin only" formula, but, because of more orbital contribution the values for the square planar configuration are usually higher. The ranges of values usually found are 2·1–2·9 B.M. and

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(10) F. H. BURSTALL and R. S. NYHOLM, *J. Chem. Soc.* 3570 (1952).
(11) R. G. WILKINS, *Nature, Lond.* **167**, 434 (1951).

1·7–2·0 B.M. for four- and six-co-ordinate complexes respectively.(12) The magnetic moment for $Co(TEP)_2I_2$ is almost between the expected ranges; however, the octahedral (or tetragonal) structure is preferred for the solid state of this compound because the infrared spectra of $Co(TEP)_2I_2$ and all of the cobalt(III) compounds, $[Co(TEP)_2X_2]X$, are very similar. The individual variations in absorption frequencies among the cobalt(III) complexes are as great as the differences between each of them and the cobalt(II) iodo compound. If the five-co-ordinate cobalt compound is a square pyramid as expected, then the two diphosphine molecules are probably at the base. Such an arrangement would suggest a *trans* structure for solid $Co(TEP)_2I_2$ and probably also for the cobalt(III) complexes.

Penta-co-ordinate cobalt(II) is not unexpected for it is in accord with the crystal field theory.(13) Other cobalt(II) compounds which are probably five-co-ordinate are $Co(TAS)I_2$(14) and Co(SPA)(15) (TAS = methyl-*bis*-(3-dimethylarsinopropyl)arsine and SPA = *bis*-salicylaldehyde-γ,γ'-diaminodipropylamine). Nyholm and co-workers have shown that *o*-phenylenebis(dimethylarsine) (PDA) complexes of Pd(II)(9b,16a), Ni(II)(17), Pt(II)(17) and Au(III)(16) have conductances in nitrobenzene which support five-co-ordinate structures in that solvent. The complexes have the general formula $[M^{+n}(PDA)_2X]^{+n-1}$ (X usually halide) if any possible co-ordination by nitrobenzene is ignored. In the solid state, the $M^{II}(PDA)_2I_2$ complexes have four arsenic atoms in a plane and the two iodine atoms in a distorted octahedral arrangement.(17)

In contrast to $Co(TEP)_2I_2$, green $Co(TEP)Br_2$ has a magnetic moment of 3·7 B.M. per cobalt atom. Tetrahedral cobalt(II) complexes have a theoretical moment of 3·88 B.M. corresponding to three unpaired electrons when it is calculated by the "spin only" formula. In practice, however, the values are higher due to orbital contribution and the range usually found for tetrahedral structures is 4·3–4·8 B.M.(12) Thus the value of 3·7 B.M. for $Co(TEP)Br_2$, calculated per cobalt atom, is lower than expected for a tetrahedral arrangement. Another structure for $Co(TEP)Br_2$ is the salt-like dimer $[Co(TEP)_2]$ $CoBr_4$. The observed magnetic moment would then be a mean of the magnetic moments for $[Co(TEP)_2]^{2+}$ and $CoBr_4^{2-}$. In the pyridinium salt, $CoBr_4^{2-}$ has a magnetic moment of 4·67 B.M.(18) which leaves a remainder of 2·3 B.M. for $[Co(TEP)_2]^{2+}$. This corresponds to one unpaired electron and is in the range expected (2·1–2·9 B.M.) for a square planar cobalt(II) complex.(12) It is also in line with the value of 2·2 B.M. for the one unpaired electron in six-co-ordinate $Co(TEP)_2I_2$.

The conductivity of $[Co(TEP)_2]$ $CoBr_4$ in nitrobenzene is 16·4 mhos. This value is much lower than expected because 2 : 2 electrolytes should have higher conductances than the 20–30 mhos found for 1 : 1 electrolytes. The lower value may be due to a rearrangement

$$[Co(TEP)_2]CoBr_4 \rightleftarrows 2\ Co(TEP)Br_2$$

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(12) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.* 12 (1954).
(13) F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions* p. 59. John Wiley, New York (1958).
(14) G. A. Barclay and R. S. Nyholm, *Chem. & Ind.* 378 (1953).
(15) M. Calvin and C. H. Barkelew, *J. Amer. Chem. Soc.* **68**, 2267 (1946).
(16) (a) C. M. Harris, R. S. Nyholm and N. A. Stephenson, *Rec. Trav. Chim.* **75**, 687 (1956);
(b) C. M. Harris and R. S. Nyholm, *J. Chem. Soc.* 63 (1957).
(17) C. M. Harris, R. S. Nyholm and N. C. Stephenson, *Nature, Lond.* **177**, 1127 (1956).
(18) R. S. Nyholm, *Quart. Rev.* **7**, 377 (1953).

in nitrobenzene. Alternatively, if the compound exists as Co(TEP)Br_2 in the solid state, its small conductance (8·2 mhos based on the simple formula) may be due to dissociation into the ionic structure.

The molar conductance of Co(TEP)Br_2 in water (Λ_{1024} = 233 mhos based on the simple formula) indicates the presence of three ions per cobalt atom. Hydrolysis of either the non-ionic or ionic structure is consistent with this behaviour. The reading was taken 3 min after dissolution which liberated no diphosphine. While the evidence from magnetic and conductivity data is inconclusive, it seems to favour formulation of the complex as [Co(TEP)$_2$]$CoBr_4$ containing planar [Co(TEP)$_2$]$^{2+}$ and tetrahedral $CoBr_4{}^{2-}$.

Square planar complexes of cobalt(II) with *o*-phenylenebis(dimethylarsine) containing two molecules of base, [Co(PDA)$_2$]X_2, have been isolated.(19) With cobalt(II), ethylenediamine is inclined to form six-co-ordinate complexes containing three molecules of base,(20) so that diphosphine tends to resemble the diarsine chelating agent.

Both of the brown iodo cobalt complexes, [Co(TEP)$_2I_2$]I and Co(TEP)$_2I_2$, can be changed to green by heating for long periods *in vacuo* over phosphorus(V) oxide. Traces of moisture turn the complexes brown and reheating turns them green again. Green and brown Co(TEP)$_2I_3$ give the same analysis, but Co(TEP)$_2I_2$ loses approximately 10 per cent of its diphosphine on such treatment. Too much heating converts them into blue compounds. Green Co(TEP)$_2I_2$ has a magnetic moment of 3·9 B.M. (three unpaired electrons), but enough green Co(TEP)$_2I_3$ was not available for a magnetic measurement. The infra-red spectra of these two green compounds and that of green [Co(TEP)$_2$] $CoBr_4$ are very similar. The main feature of their spectra is a quite broad absorption frequency at approximately 1100 cm^{-1}. This similarity, along with the magnetic moment of green Co(TEP)$_2I_2$, might be interpreted as suggesting a similarity in structure for all of these compounds.

Nickel complexes. Two diphosphine complexes with the formula Ni(TEP)X_2 (X = Cl, Br) were prepared. The chloro compound contained only one molecule of diphosphine even though a 2 : 1 ratio of diphosphine to nickel was used in its preparation. With the very poor co-ordinating anion, perchlorate, the 2 : 1 complex [Ni(TEP)$_2$](ClO_4)$_2$ was isolated. All of the complexes are diamagnetic, indicating a square planar structure.

Attempts to oxidize Ni(TEP)Cl_2 with chlorine in solution, suspension or in the solid state led to unstable or ill-defined products. Oxidation of a dilute solution of Ni(TEP)Br_2 in benzene by bromine gave a green-black precipitate which analysed fairly well for the empirical formula Ni(TEP)Br_3. The magnetic moment of this complex was 2·0 B.M., indicating one unpaired electron and confirming the presence of nickel(III). The complex was very insoluble in water, but in solvents such as ethanol, acetone and chloroform, in which it was slightly soluble, it appeared to give momentarily a green solution which then turned brown. The green colour persisted longest in nitrobenzene, in which it was essentially non-conducting. This indicates a five-co-ordinate structure, ignoring any possible co-ordination by nitrobenzene. The evidence seems to indicate a polymeric octahedral nickel(III) compound

(19) R. S. NYHOLM, *J. Chem. Soc.* 2071 (1950).

(20) J. BJERRUM, G. SCHWARZENBACH and L. G. SILLEN, *Stability Constants, Part I: Organic Liquids* p. 5. The Chemical Society, London (1957).

in the solid state which tends to decompose when it is dissolved, rather than a penta-co-ordinate square pyramid such as found for $Ni(PEt_3)_2Br_3$.(21)

CHATT and HART(5) have prepared $Ni(TEP)(CO)_2$, which contains nickel(0) and tetraethylethylenediphosphine. Attempts to co-ordinate two molecules of diphosphine failed. With *o*-phenylenebis(diethylphosphine) (PEP) (Formula I, $M = M' = P$, $R = C_2H_5$) a compound of analogous composition is formed, as well as a complex containing only the phenylenediphosphine, $Ni(PEP)_2$.

Complexes of nickel(II) with *o*-phenylenebis(dimethylarsine) containing one, two or three molecules of base have been isolated,(22) the one containing two molecules being most easily prepared. It is believed to be five-co-ordinate in nitrobenzene. Oxidation to nickel(III)(22) and even nickel(IV)(23) has been accomplished. Nickel(0) compounds containing one(22a) and two(5) molecules of diarsine have been prepared. Ethylenediamine and nickel(II) tend to form *tris* compounds, but this tendency is reduced with N-monoalkyl derivatives and still further decreased with N-N′-dialkylethylenediamines.(3b) A *bis* complex of N,N′-dimethylethylenediamine has been prepared,(3e) but attempts to form complexes of nickel and N,N,N′,N′-tetramethylethylenediamine were unsuccessful.(3a) In composition and ability to stabilize the different oxidation states of nickel, tetraethyldiphosphine more closely resembles the diarsines.

Coinage metal complexes. The silver(I) and copper(I) complexes isolated, $[Cu(TEP)_2][Cu(TEP)I_2]$ and $[Ag(TEP)_2]AgI_2$, are very similar. The ionic structures are assigned on the basis of the conductivities in nitrobenzene. The conductivity of the silver compound is lower than the 20–30 mhos usually found for 1 : 1 electrolytes, a property in which it resembles the analogous silver compound of *o*-diethylphosphinophenyldiethylarsine(2b) (Formula I, $M = P$, $M' = As$, $M = C_2H_5$, abbreviated P–As). Copper(I) compounds of the general formula $[M(P\text{–}As)_2]A$ in which A is halogen or CuX_2^- ($X = Cl,Br$) as well as the silver(I) compound, in which A is iodide, have normal conductivities, but the silver complex in which A is AgI_2^- has a lower conductivity. The explanation suggested is a dissociation into a neutral three-co-ordinate species:

$$[Ag(base)_2]AgI_2 \rightleftarrows 2\ Ag(base)I$$

Attempts to resolve the compounds $[Cu(P\text{–}As)_2]I$ and $[Au(P\text{–}As)_2]I$ were not successful, but X-ray studies proved they were tetrahedral. Copper complexes of diarsines(2b,9a) have similar formulas and are thought to be tetrahedral. Copper(I) and silver(I) iodo monophosphines have a tetrameric structure $[M(PR_3)I]_4$ in which the central atoms are tetrahedral.(24)

Silver(I) and ethylenediamine (en) form the compounds $[AgH(en)]^{2+}$, $Ag(en)^+$, $Ag_2(en)^{2+}$, $Ag(en)_2^+$ as well as the dimer $Ag_2en_2^{2+}$.(25) The silver is probably linear in all of them and the ethylenediamine monodentate or bridging. Cryoscopic measurements on $[Ag_2en_2]SO_4$ support the dimeric structure which probably contains a

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(21) K. A. JENSEN and B. NYGAARD, *Acta. Chem. Scand.* **3**, 474 (1949).

(22) R. S. NYHOLM, *J. Chem. Soc.* (a) 2061 (1950); (b) 2906 (1952).

(23) R. S. NYHOLM, *J. Chem. Soc.* 2602 (1951).

(24) F. G. MANN, D. PURDIE and A. F. WELLS, *J. Chem. Soc.* 1503 (1936); 1828 (1937); F. G. MANN and A. F. WELLS, *Nature, Lond.* **140**, 502 (1937); A. F. WELLS, *Z. Krist.* **94**, 447 (1936).

(25) G. SCHWARZENBACH, H. AKERMAN, B. MAISSEN and G. ANDEREGG, *Helv. Chim. Acta* **35**, 2337 (1952); P. JOB, *C. R. Acad. Sci., Paris* **176**, 442 (1923); **184**, 1066 (1927).

ten-membered ring. Copper(I) forms the compound $Cu(en)_2^+$ in which ethylenediamine is monodentate.(26) Thus, in its ability to form four-co-ordinate compounds with silver(I) and copper(I), the disphophine is similar to the diarsines.

The gold(I) complex is of a different type, having the empirical formula $Au_2(TEP)I_2$. It is almost non-conducting in nitrobenzene. Its molecular weight of 820 (ebulliscopic in chloroform) compared to the calculated 854·5 indicates that the diphosphine serves as a bridge. The gold is probably linear two-co-ordinate to give the structure IAu(TEP)AuI. The difference in behaviour of gold(I) as compared to silver(I) and copper(I) is probably due to the reluctance of gold(I) to form four-co-ordinate structures. Yet 4-methyl-*o*-phenylenebis(diethylphosphine),(2c) *o*-diethylphosphinophenyldiethylarsine(2b), and *o*-phenylenebis(dialkylarsines)(2b,16) form complexes which contain two molecules of base and are four-coordinate. These phenylene chelates have a rigid structure in which the co-ordinating atoms are held in a position favorable for chelation, while tetraethylethylenediphosphine can form a bridge more readily.

Oxidation of $Au_2(TEP)I_2$ by iodine gives a black compound of the composition $Au_2(TEP)I_6$. It is probably also bridged, with the gold(III) having a square planar structure as $I_3Au(TEP)AuI_3$. This reaction is very similar to the oxidation of gold(I) monophosphine complexes, $Au(PR_3)X$, to square planar gold(III) compounds, $Au(PR_3)X_3$.(27,28)

Oxidation of $[Au(PDA)_2]I$ produces $[Au(PDA)_2I_2]I$, which preliminary X-ray studies show to have a *trans* octahedral structure. $Au(PDA)_2(NO_3)_3$ is five-coordinate in nitrobenzene, but completely ionized in water to four-co-ordinate $[Au(PRA)_2]^{3+}$, the perchlorate of which was also isolated.(16) With ethylenediamine, gold(III) forms the complexes $[Au(en)X_2]X$ and $[Au(en)_2]X_3$(29) but these compounds were not prepared by oxidation of gold(I) complexes as are the diarsines and diphosphines. A bridging structure like that of $Au_2(TEP)I_6$ has been postulated for $(CH_3)_3AuNH_2C_2H_4NH_2Au(CH_3)_3$.(30) With gold(III) it is difficult to decide whether the diphosphine compound is more similar to those of ethylenediamine or of the diarsines.

Zinc, cadmium and mercury complexes. Bromo compounds containing each of these metals with one mole of diphosphine were prepared. They are assigned the structure $M(TEP)Br_2$ on the basis of the non-conducting nature of the zinc and cadmium compounds in nitrobenzene. When cadmium bromide and diphosphine react, a complex of empirical formula $Cd_3(TEP)_2Br_6$ is first precipitated. Recrystallization of this compound from dimethylformamide by addition of water gives the simple compound $Cd(TEP)Br_2$. By dissolving one mole each of $Cd(TEP)Br_2$ and cadmium bromide in dimethylformamide and precipitating with water, followed by recrystallization in the same manner, $Cd_3(TEP)_2Br_6$ is again obtained. The ease of conversion suggests that the tricadmium compound should be formulated as a mixed crystal $2Cd(TEP)Br_2 \cdot CdBr_2$, although bridged complexes of cadmium and monophosphines are well known.(3) With similar treatment $Zn(TEP)Br_2$ did not give a compound containing greater than a 1 : 1 ratio of zinc to diphosphine. The mercury

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(26) J. Bjerrum, and E. J. Nielsen, *Acta Chem. Scand.* **2**, 307 (1948); J. E. B. Randles, *J. Chem. Soc.* 802 (1941).

(27) F. G. Mann and D. Purdie, *J. Chem. Soc.* 1235 (1940).

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(29) B. P. Block and J. C. Bailar, Jr., *J. Amer. Chem. Soc.* **73**, 4722 (1951); C. S. Gibson and W. M. Colles, *J. Chem. Soc.* 2407 (1931).

(30) H. Gilman and L. A. Woods, *J. Amer. Chem. Soc.* **70**, 550 (1948).

compound, $Hg(TEP)Br_2$, is very insoluble and could not be recrystallized from any solvent, so that the analysis is not as good as might be hoped. These compounds are probably tetrahedral like the monophosphine complexes.(31)

With ethylenediamine, zinc, cadmium and mercury tend to form compounds containing three molecules of base. With tetraethylethylenediamine the compound $Cd(base)Cl_2$ has been isolated, but it is unstable in water.(3a) Precipitation of basic substances interfered with the determination of the stability constants of zinc and dialkylethylenediamines.(3d) Evidently, no compounds of diarsines with these metals have been prepared.

Palladium complex. Reaction of ammonium tetrachloropalladate(II) or dichloro-(tetrahydrogenethylenediaminetetraacetate)palladium(II) five hydrate with a molar ratio of diphosphine gives the complex $Pd(TEP)Cl_2$. Attempts to form a compound containing two molecules of diphosphine by allowing $[Pd(NH_3)_4]Cl_2$ to react with two moles of diphosphine (charcoal catalyst) or by causing $Pd(TEP)Cl_2$ to react with more diphosphine gave only the neutral mono(diphosphine) compound. With the thought that the chloride ion was such a good co-ordinating agent that it prevented the second molecule of diphosphine from reacting, the latter reaction was repeated in the presence of silver sulphate to precipitate the chloride. This procedure led to a white solid contaminated with palladium black which on recrystallization gave more palladium metal. The product may have been unstable $[Pd(TEP)_2]SO_4$.

The colourless palladium compound is probably monomeric $Pd(TEP)Cl_2$ rather than $[Pd(TEP)_2]PdCl_4$. Although no definite proof for this was obtained, all *o*-phenylene compounds of palladium with chloride containing one mole of base are yellow or colourless, while the compounds $[Pd(base)_2]PdCl_4$, which are often intermediates, are much darker.(2a,b,d,4) It is interesting that CHATT and MANN have isolated compounds of the type $[Pd(base)_2]^{2+}$ with substituted *o*-phenylenediarsines, but under identical conditions substituted ethylenediarsines give complexes containing one molecule of base. This may again be due to the rigid structure of *o*-phenylene compounds, which makes it easier to crowd the alkyl groups around the metal.

Many of the *o*-phenylene compounds in which the co-ordinating atoms are combinations of As, N and P, as well as ethylenediamines, form complexes of the compositions $Pd(base)X_2$ and $Pd(base)_2X_2$ ($X =$ halogen). Most of the compounds are probably four-co-ordinate planar. However the $Pd(PDA)_2X_2$ complexes are 1 : 1 electrolytes in nitrobenzene and have a tetragonal structure in the solid state. $[Pd(PDA)_2](ClO_4)_2$ is four-co-ordinate.(9b,16a) Dichloro- and dibromo-*bis*(*o*-dimethylaminophenyldiethylphosphine)palladium(II) are said to be five-co-ordinate in nitrobenzene and four-co-ordinate in water.(2d)

Preliminary attempts to prepare platinum(II) compounds of tetraethylethylenediphosphine were unsuccessful.

Lead complexes. Two compounds containing four-co-ordinate lead(II) were isolated. They were $Pb(TEP)Br_2$ and $[Pb(TEP)_2](ClO_4)_2$.

CONCLUSIONS

In general, the co-ordinating ability of tetraethylethylenediphosphine is more similar to that of *o*-phenylenebis(dimethylarsine) than that of ethylenediamine. Before a more valid comparison can be made, more information on the stability and chemical

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(31) R. C. EVANS, F. G. MANN, H. S. PEISER and D. PURDIE, *J. Chem. Soc.* 1209 (1940).

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reactions of the complexes is needed, particularly for the diarsines and diphosphines.

In several cases the difference between tetraethylethylenediphosphine and ethylenediamine is due to the tendency of ethylenediamine to expand the co-ordination number of a metal. With substituted ethylenediamines this tendency is reduced, but a strict comparison is not valid because the reason for complexes of lower co-ordination number for substituted ethylenediamines is due at least in part to reduced co-ordinating ability and not entirely due to steric factors. Attempts to co-ordinate ethylenediphosphine itself will be hampered by its reported instability.(7)

Probably the principal reason for the similarity of diphosphine and diarsines is the ability of both to form π-bonds. Arsenic and phosphorus atoms, but not nitrogen, have vacant *d*-orbitals so that partial double bonding can occur with metals which have electrons in their *d*-orbitals, thereby strengthening the bond. Also, the ability of diphosphines and diarsines to stabilize both lower and higher oxidation states of nickel is probably due to their ability to π-bond.(5,32)

EXPERIMENTAL

P, P, P′, P′-Tetraethylethylenediphosphine

A one litre three-necked standard taper round-bottomed flask with a side arm was fitted with an all-glass stirrer in one neck and a nitrogen inlet in another. The side arm was used as a gas outlet. The third neck of the flask was used to add solids, attach a separatory funnel or as a place for a dipstick which was used to bubble phosphine into the solution.

Air was flushed out of the system with nitrogen, which was used as a blanket throughout the experiment, and the apparatus was cooled to −78° with dry ice. Approximately 600 ml of liquid ammonia was introduced and 7·22 g (0·31 mole) of sodium was dissolved in it. Dry phosphine was bubbled through the solution with stirring until the blue colour changed to light yellow. The excess phosphine was purged with nitrogen and the dipstick was removed. The small amount of white precipitate present, probably sodium hydroxide, is not harmful.

With the stirrer running, 33·9 g (0·31 mole) of ethyl bromide was added dropwise and stirring was continued for 15 min after addition was completed. If the sodium bromide which precipitated during the reaction was allowed to settle, the solution was clear. A suspension of sodium amide, freshly prepared from 8·09 g (0·35 mole; 10 per cent excess) of sodium in approximately 100 ml of liquid ammonia,(33) was added and the mixture was stirred for 1 hr. This produced a green colour. The repeat addition of ethyl bromide discharged the green colour. Addition of more sodium amide turned the mixture red-orange. After one hour's stirring, it was deep red. Then ethylenedichloride was added dropwise with stirring until the red colour was discharged. Stirring was continued for 15 min. The amount of ethylenedichloride required was 13·8 g (theor. 15·4 g, 0·155 mole). The dry-ice bath was removed and the liquid ammonia was allowed to evaporate.

Two hundred millilitres of oxygen-free water (used throughout) and 300 ml of ethyl ether were added and the mixture was stirred until all the salts had dissolved. The mixture was transferred to a separating funnel, and the water layer and dark solids (elemental iron from sodium amide preparation) were separated and washed with 75 ml of ether. The combined ether extracts were washed with three 150 ml portions of water and dried over anhydrous sodium sulphate. The ether was removed under diminished pressure; the temperature of the distilling flask was then increased to 100° for a few minutes to make sure that all excess starting materials and lower phosphines were removed. The yield of crude product was 17·5 g (54 per cent). The yellow liquid was used without further purification.

Tetraethylethylenediphosphine dihydroiodide

A solution of 1·4 ml of concentrated hydroiodic acid was added to 0·26 g (1·26 mmoles) of the crude diphosphine. The reaction mixture was evaporated almost to dryness and precipitated with absolute alcohol. The crystals were dissolved in a few drops of water and heated on a steam bath.

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(32) J. CHATT, *J. Inorg. Nucl. Chem.* **8**, 515 (1958); J. CHATT and R. G. WILKINS, *J. Chem. Soc.* 4300 (1952); L. E. SUTTON, *J. Inorg. Nucl. Chem.* **8**, 23 (1958); R. S. NYHOLM, *Chem. Rev.* **53**, 263 (1953).

(33) K. W. GREENLEE and A. L. HENNE, *Inorg. Synth.* **2**, 128 (1946).

Twenty-five millilitres of absolute ethanol was added dropwise and the solution was allowed to cool slowly to room temperature. Then it was cooled in an ice-bath, and the crystals which formed were collected on a filter and washed with ethanol. After two recrystallizations, the colourless crystals were dried *in vacuo* over phosphorus(V) oxide. The compound does not have a sharp melting point, but the major portion of it melts at 181–183°. (Found: C, 25·99; H, 5·85; I, 55·00. Calc. for $C_{10}H_{25}P_2I_2$: C, 25·99; H, 5·67; I, 54·93%).

Diphosphine complexes

All of the complexes were dried *in vacuo* over phosphorus(V) oxide. If the temperature used was other than room temperature, it is listed. Most of the analytical data[*] as well as the magnetic moments and conductivities are shown in the tables.

TABLE 2.—MAGNETIC MOMENTS OF DIPHOSPHINE COMPLEXES

Compounds	Temp. (°C)	$\mu_{eff.}$ (B.M.)
$[Co(TEP)_2I_2]I$	27·0	diamagnetic
$[Co(TEP)_2Br_2]Br$	30·0	sl. paramagnetic
$[Co(TEP)_2Cl_2]Cl$	26·5	diamagnetic
$Co(TEP)_2I_2$	29·0	2·2
$[Co(TEP)_2]CoBr_4$	29·0	3·7[*]
$Ni(TEP)Br_2$	27·5	diamagnetic
$Ni(TEP)Cl_2$	28·0	diamagnetic
$[Ni(TEP)_2](ClO_4)_2$	27·5	diamagnetic
$Ni(TEP)Br_3$	28·0	2·0

[*] Per cobalt atom.

Diiodo-bis-(diphosphine)cobalt(III), *iodide*, $[Co(TEP)_2I_2]I$. A solution of 0·34 g (1·08 mmoles) of cobalt(II) iodide in 2 ml of water and 10 ml of ethanol was added to 0·44 g (2·14 mmoles) of diphosphine in 3 ml of ethanol. The solution, which turned dark brown immediately, was shaken for 4·5 hr. It was evaporated to a small volume and cooled in an ice-bath. The $[Co(TEP)_2I_2]I$ was collected on a filter, recrystallized from absolute ethanol and dried at 50°. It is insoluble in water.

Effect of heat on diiodo-bis-(diphosphine)cobalt(III) *iodide*. A sample of $[Co(TEP)_2I_2]I$ was heated at 110° *in vacuo* for 53 hr over phosphorus(V) oxide. The sample turned green, but it did not lose diphosphine. (Found: C, 28·08; H, 5·69. Calc. for $CoC_{20}H_{48}P_4I_2$: C, 28·19; H, 5·68%).

Dibromo-bis-(diphosphine)cobalt(III) *bromide*, $[Co(TEP)_2Br_2]Br$. A solution of 0·22 g (1 mmole) of cobalt(II) bromide in 5 ml of ethanol was poured into a flask containing 0·42 g (2·04 mmoles) of diphosphine in 15 ml ethanol. The mixture was refluxed for 2 hr while air bubbled through it. After evaporation to dryness, the $[Co(TEP)_2Br_2]Br$ was recrystallized from water and dried.

Dichloro-bis-(diphosphine)cobalt(III) *chloride*, $[Co(TEP)_2Cl_2]Cl$. This compound was prepared in the same manner as $[Co(TEP)_2Br_2]Br$. One-half gramme (2·42 mmoles) of diphosphine, 0·29 g (1·22 mmoles) of cobalt(II) chloride six hydrate, and 0·21 ml of 6 N hydrochloric acid in 10 ml of ethanol were allowed to react for 1·5 hr. The yield was 0·31 g (45 per cent). $[Co(TEP)_2Cl_2]Cl$ is soluble in water, ethanol, acetone, chloroform, bromoform and nitrobenzene. It is almost insoluble in benzene and carbon tetrachloride.

Diiodo-bis-(diphosphine)cobalt(II), $Co(TEP)_2I_2$. This compound is very sensitive to oxidation so that all operations after addition of the diphosphine were carried out under a nitrogen blanket. A filtered solution of 0·15 g (1·26 mmoles) of cobalt(II) carbonate dissolved in 0·46 ml of 47 per cent hydroiodic acid and 3 ml of water was added to a boiling solution of 0·5 g (2·50 mmoles) of diphosphine in 7 ml of ethanol. Boiling water (approximately 20 ml) was slowly added until brown needles

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[*] The microanalyses were performed by Mr. J. NEMETH, Mrs. M. BENASSI, Mr. R. NESSETT and Mrs. R. JU.

TABLE 3.—DIPHOSPHINE COMPLEXES PREPARED

Compound	Colour	Calculated			Found		
		C	H	X	C	H	X
$[Co(TEP)_2I_2]I$	dark-brown	28·19	5·68	44·68	28·22	5·99	45·11
$[Co(TEP)_2Br_2]Br$	green	33·77	6·80	33·71	34·15	7·28	33·32
$[Co(TEP)_2Cl_2]Cl$	light green	41·57	8·37	18·41	41·58	8·68	18·31
$Co(TEP)_2I_2$	brown	33·12	6·67	35·00	33·05	6·96	33·70
$[Co(TEP)_2]CoBr_4$	green	28·26	5·69	37·61	27·91	5·76	38·32
$Ni(TEP)Br_2$	red-brown	28·27	5·70	37·63	28·20	5·51	37·55
$Ni(TEP)Cl_2$	yellow-brown	35·76	7·20	21·11	35·82	7·13	21·40
$[Ni(TEP)_2](ClO_4)_2$	yellow	35·84	7·22	—	36·23	7·11	—
$Ni(TEP)Br_3$	green-black	23·80	4·79	47·50	24·04	5·45	46·12
$[Cu(TEP)_2][Cu(TEP)I_2]$	colourless	36·04	7·26	25·41	36·22	6·97	25·36
$[Ag(TEP)_2]AgI_2$	colourless	27·33	5·49	—	26·63	5·50	—
$IAu(TEP)AuI$	colourless	14·05	2·83	46·16*	14·27	2·91	46·33*
$I_3Au(TEP)AuI_3$	black	8·82	1·78	55·90	9·16	1·80	54·58
$Zn(TEP)Br_2$	colourless	27·84	5·61	37·04	27·87	5·60	37·23
$Cd(TEP)Br_2$	colourless	25·10	5·06	33·40	24·76	4·95	33·54
$Cd_3(TEP)_2Br_6$	colourless	19·54	3·94	—	19·97	4·37	—
$Hg(TEP)Br_2$	colourless	21·19	4·27	28·20	19·72	4·02	28·91
$Pd(TEP)Cl_2$	colourless	31·29	6·30	18·47	31·06	6·15	19·07
$Pb(TEP)Br_2$	colourless	20·95	4·22	27·88	20·73	4·53	27·22
$[Pb(TEP)_2](ClO_4)_2$	colourless	29·34	5·91	—	29·10	5·73	—

* Gold analysis.

formed. The mixture was cooled in an ice-bath and the $Co(TEP)_2I_2$ was collected on a filter. Part of the sample was recrystallized by dissolving in ethanol and precipitating with water.

Effect of heat on diiodo-bis-(diphosphine)cobalt(II). A sample of $Co(TEP)_2I_2$ was heated *in vacuo* over phosphorus(V) oxide for 12 hr at 122° followed by 12 hr at 130°. It turned green and lost some diphosphine (~10 per cent), as indicated by the analysis and by the odour of phosphine when the apparatus was opened. The magnetic moment of the mixture is 3·9 B.M. (Diamagnetic correction based on $Co(TEP)_2I_2$.)

	Found	Calc. for $Co(TEP)_2I_2$	Calc. for $Co(TEP)I_2$
C	30·16	33·12	23·14
H	6·05	6·67	4·66

Bis-(diphosphine)cobalt(II) *tetrabromocobaltate*(II), $[Co(TEP)_2]CoBr_4$. To 0·25 g (1·14 mmoles) of cobalt(II) bromide in 3 ml of hot absolute ethanol was added a solution of 0·43 g (2·08 mmoles) of diphosphine in 2 ml of the same solvent. The blue solution turned green, and on standing a green precipitate formed. After cooling in an ice-bath, the product was collected on a filter. When recrystallized from isopropyl alcohol, it became sticky, but it dried out at 50° to a green solid. $[Co(TEP)_2]CoBr_4$ is soluble in water, methanol, ethanol, chloroform and acetone.

Dibromodiphosphinenickel(II), $Ni(TEP)Br_2$. A hot solution of 0·38 g (1·74 mmoles) of nickel(II) bromide in 4 ml of absolute ethanol was added to 0·36 g (1·74 mmoles) of diphosphine in 2 ml of absolute ethanol. Brown crystals formed on cooling. The Ni(TEP)Br_2 was recrystallized from absolute alcohol and dried at 35°: m.p., 213°.

Dichlorodiphosphinenickel(II), Ni(TEP)Cl_2. A solution of 1·39 g (5·8 mmoles) of nickel(II) chloride six hydrate in 20 ml of absolute alcohol was added to 2·39 g (11·6 mmoles) of diphosphine in 15 ml of absolute ethanol. The resulting yellow-brown solution was evaporated until crystals formed, and was then cooled. Further evaporation gave a second crop of crystals. After recrystallization of the combined precipitates from absolute ethanol, 1·7 g of Ni(TEP)Cl_2 was obtained (89 per cent yield based on $NiCl_2 \cdot 6H_2O$). Part was again recrystallized and dried at 100°: m.p. (decomp.), 245–249°.

Bis(*diphosphine*)*nickel*(II) *perchlorate*. [Ni(TEP)$_2$](ClO_4)$_2$. Nickel(II) perchlorate six hydrate (0·42 g, 1·14 mmoles) was dissolved in 5 ml of absolute ethanol and added to 0·47 g (2·28 mmoles) of diphosphine. The yellow precipitate which formed immediately was recrystallized from methanol and dried at 55°.

Tribromodiphosphinenickel(III), Ni(TEP)Br_3. A benzene solution containing 0·0151 g (0·094 mmole) of bromme was added to a filtered solution of 0·08 g (0·189 mmole) of Ni(TEP)$_2$$Br_2$ in 80 ml of warm benzene. After cooling, the green-black precipitate was collected on a filter, and washed with benzene and ethyl ether.

Bis-(*diphosphine*)*copper*(I) *diiododiphosphinecuprate*(I), [Cu(TEP)$_2$] [Cu(TEP)I_2]. A mixture of 0·32 g (1·55 mmoles) of diphosphine and 0·46 g (2·41 mmoles) of copper(I) iodide in 5 ml of potassium iodide solution (saturated at room temperature) was shaken for 4 hr under nitrogen. The precipitate which formed was collected on a filter, washed with potassium iodide solution and water, recrystallized from benzene, and dried at 100°. [Cu(TEP)$_2$] [Cu(TEP)I_2] is insoluble in water, ethanol and acetone: m.p., 181–183°.

Bis-(*diphosphine*)*silver*(I) *diiodoargentate*(I), [Ag(TEP)$_2$]AgI_2. This compound was prepared in the same manner as the copper(I) compound, using 0·52 g (2·21 mmoles) of freshly prepared silver iodide and 0·45 g (2·18 mmoles) of diphosphine in 10 ml of potassium iodide solution and shaking 17 hr. The colourless material was recrystallized from nitrobenzene, washed with benzene and ethyl ether, and dried.

Diiodo-μ-diphosphinedigold(I), IAu(TEP)AuI. A solution of 0·5 g (2·42 mmoles) of diphosphine in 10 ml of ethanol was added to 20 ml of ethanol saturated with sodium iodide (at room temperature). The solution was heated to boiling under a nitrogen blanket and 0·78 g (2·41 mmoles) of gold(I) iodide was slowly added with rapid stirring. White crystals formed in the boiling solution. The mixture was cooled and the precipitate of Au_2(TEP)I_2 was collected on a filter and recrystallized from acetone. The molecular weight, determined ebullioscopically in chloroform, is 820 (Calc. 854·5).

Hexaiodo-μ-diphosphinedigold(III), I_3Au(TEP)AuI_3. Two millilitres of chloroform containing 0·072 g (0·283 mmole) of iodine was added to 0·12 g (0·141 mmole) of Au_2(TEP)I_2 in 5 ml of chloroform. The black crystalline precipitate which formed was collected, washed with chloroform, and dried.

Dibromodiphosphinezinc, Zn(TEP)Br_2. A solution of 0·48 g (2·13 mmoles) of zinc bromide in 3 ml of absolute ethanol was added to 0·44 g (2·12 mmoles) of diphosphine in 2 ml of the same solvent. A white precipitate formed which changed into an oil. When cooled in an ice-bath, the oil solidified and the crude product was collected on a filter. To recrystallize the product, it was dissolved in hot dimethylformamide, the solution was filtered and while it was being heated, water was slowly added until the solution became cloudy. It was heated for an additional minute or two and cooled. The Zn(TEP)Br_2 was collected on a filter and dried. It is also soluble in chloroform.

Bromodiphosphine–cadmium complexes. A solution of 1·23 g (4·52 mmoles) of cadmium bromide in 10 ml of 50–50 alcohol–water mixture was added to 0·93 g (4·51 mmoles) of diphosphine. A white precipitate formed immediately, but the mixture was shaken for 3 hr to make sure the reaction was complete. The crude material was recrystallized by the method used for Zn(TEP)Br_2 and dried at 110°. The product was Cd_3(TEP)$_2$$Br_6$.

A sample of Cd_3(TEP)$_2$$Br_6$ was recrystallized from dimethylformamide by adding water, and was dried at 55°. This yielded the simple complex Cd(TEP)Br_2. Cd(TEP)Br_2 can be converted back to Cd_3(TEP)$_2$$Br_6$ by reaction with cadmium bromide (1 : 1 molar ratio) in dimethylformamide followed precipitation with water and recrystallization. The nature of the compound which precipitates must by depend on the relative amounts of Cd(TEP)Br_2 and $CdBr_2$ present.

Dichlorodiphosphinepalladium(II), Pd(TEP)Cl_2. A hot solution of 0·25 g (1·4 mmoles) of palladium-(II) chloride and 0·15 g (2·8 mmoles) of ammonium chloride in 10 ml of water was added to 0·29 g

(1·4 mmoles) of diphosphine and shaken for 3 hr under nitrogen. The pinkish-tan precipitate was collected on a filter and then dissolved in dimethylformamide. After a small amount of red-brown precipitate was filtered off, the solution was evaporated to a small volume. White crystals formed on standing. They were recrystallized from ethanol and dried at 50°.

The complex can also be prepared from Pd(H_4EDTA)Cl_2 and diphosphine: To 0·34 g (1·65 mmoles) of diphosphine in 5 ml of ethanol was added a solution of 0·95 g (1·66 mmoles) of Pd(H_4EDTA)$Cl_2 \cdot 5H_2O$(34) in 5 ml of the same solvent. Ethylenediaminetetraacetic acid precipitated. (Found: N, 9·34. Calc. N, 9·58%) The filtrate was evaporated to a small volume and cooled. The Pd(TEP)Cl_2 was collected and recrystallized from absolute ethanol.

Several attempts were made to prepare *bis*(diphosphine) palladium(II) chloride. The reaction of tetraamminepalladium(II) chloride(35) with 2 moles of diphosphine using a charcoal catalyst gave dichlorodiphosphinepalladium(II). Attempts to make dichlorodiphosphinepalladium(II) react with diphosphine led only to recovery of the starting complex.

Dibromodiphosphinelead(II), Pb(TEP)Br_2. A filtered solution of 0·89 g (2·42 mmoles) of lead(II) bromide in 25 ml of hot potassium bromide solution (saturated at room temperature) was added to 0·33 g (1·6 mmoles) of diphosphine and the mixture was shaken for 5 hr under nitrogen. The white precipitate was filtered and washed with potassium bromide solution and then with water. The crude product was recrystallized twice from dimethylformamide and dried at 55°.

Bis-(diphosphine)lead(II) *perchlorate*, [Pb(TEP)$_2$] (ClO_4)$_2$. When a solution of 2·09 g (4·55 mmoles) of lead(II) perchlorate three hydrate in 10 ml of ethanol was added to 1·87 g (9·08 mmoles) of diphosphine in 5 ml of ethanol, an oil separated. This solidified when cooled in an ice-bath. The cream coloured precipitate was recrystallized from a 50–50 alcohol-water mixture to yield 1·47 g (40 per cent) of [Pb(TEP)$_2$] (ClO_4)$_2$. A small sample was recrystallized twice and dried: m.p. 150–152°.

Magnetic moments. Magnetic measurements were taken on a modified Curie–Cheneveau balance previously described.(36) Dimagnetic corrections were made according to SELWOOD.(37)

Conductivities. Conductivity measurements were made on a Leeds and Northup conductivity bridge (No. 4866). The nitrobenzene was fractionally crystallized three times, dried with phosphorus(V) oxide and distilled under reduced pressure. The middle fraction was used. The specific resistance of the water used was $3{\cdot}12 \times 10^6$ ohms.

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