COMPLEXES OF TRIS(*N*-PIPERIDINOMETHYL)PHOSPHINE OXIDE WITH ZINC AND CADMIUM

Pavel VOJTISEK[1] and Ivana CISAROVA[2]

Department of Inorganic Chemistry, Charles University, 128 40 Prague 2, Czech Republic;
e-mail: [1] pavojt@prfdec.natur.cuni.cz, [2] cisarova@prfdec.natur.cuni.cz

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Dedicated to Professor Jaroslav Podlaha on the occasion of his 60th birthday.

A number of compounds which can by their stoichiometry be classified into several groups have been prepared by reaction of tris(*N*-piperidinomethyl)phosphine oxide (tppo) with Zn(II) and Cd(II) salts. The structure of two Zn(II) complexes differing by their Zn : tppo ratio and of one Cd(II) complex has been determined by the X-ray diffraction technique. The results show that in all the cases tppo is bound as divalent chelate N,O-donor, but the geometry of coordination sphere of M(II) decisively affects the steric arrangement of the five-membered chelate ring. Structures of the compounds studied are entirely different from those of Zn(II) complexes of sterically less demanding *P*,*P*-dimethyl-*P*-aminomethylphosphine oxide (dmao). On the other hand, the way of coordination of tppo is the same as that found in the case of the Co(II) complex of tris(*N*,*N*-dimethylaminomethyl)phosphine oxide.

Key words: Tris(*N*-piperidinomethyl)phosphine oxide; Complexes of aminoalkylphosphine oxides; X-Ray diffraction; Chelate ring formation.

Aminoalkylphosphine oxides are typical examples of electro-neutral ligands with a phosphoryl group at α-position with respect to nitrogen atom of the amino group. From among the group of ligands of this type, the complex-forming behaviour has been described in the cases of the symmetrical tris(*N*,*N*-dimethylaminomethyl)phosphine oxide[1,2] (tmpo) and several nonsymmetrical ligands with various substituents at the phosphorus atom. Du Preez[3,4] prepared complexes of Co(II), Cu(II) and Ni(II) with *P*-(*N*,*N*-dimethylaminomethyl)-*P*,*P*-diphenylphosphine oxide (dmpo) and *P*-(*N*,*N*-dimethylaminoethyl)-*P*,*P*-diphenylphosphine oxide (depo). Dodoff[5,6] and more recently Borisov[7] studied in detail the complex-forming behaviour of *P*-aminoethyl-*P*,*P*-dimethylphosphine oxide (dmao). The last paper quoted describes a number of complexes with Ni(II), Pd(II) and particularly Zn(II). The authors[7] also determined the structure of two Zn(II) complexes of different stoichiometries: Zn(dmao)Br_2 and Zn$(dmao)_2I_2$. Both these structures are interesting in that dmao is always bound as a bridge N,O-donor and not in the chelate way observed for similar ligands dmpo (ref.[4]) and tmpo (ref.[1]). Both described Zn(II) complexes have the same tetrahedral arrangement at the metal atom and both the compounds are polymeric in nature.

The present paper is focused on complexes of the symmetrical tris(*N*-piperidinomethyl)phosphine oxide (tppo) with Zn(II) and Cd(II), particularly on the effect of complex-forming ability of the anion on the stoichiometry and structure of the compounds formed.

EXPERIMENTAL

Tris(*N*-piperidinomethyl)phosphine oxide (tppo)

The substance was prepared by a known way[8] from yellow phosphorus, piperidine and formaldehyde and recrystallized from petroleum ether immediately before each preparation of the complexes; m.p. 120–121 °C (petroleum ether) (ref.[8] gives m.p. 119–120 °C). For $C_{18}H_{36}N_3OP$ (341.5) calculated: 63.4% C, 10.6% H, 11.35% N, 9.07% P; found: 63.7% C, 10.8% H, 12.30% N, 9.03% P. ^{31}P NMR spectrum (EtOH–MeOH): 52.0 ppm, ^{1}H NMR spectrum ($CDCl_3$): 2.69 ppm (d), $^{2}J(P,H) = 7.1$ Hz (PCH_2N), 2.4–2.5 ppm (m), 1.3–1.6 (m) (NC_5H_{10}).

$[Zn(tppo)_2(H_2O)_2(ClO_4)_2]$ (**1**)

The complex was prepared by mixing a solution of $Zn(ClO_4)_2 . 6 H_2O$ (0.75 g, 2 mmol) in EtOH–H_2O mixture (3 : 1, 20 ml) with a solution of tppo (1.5 g, 4.4 mmol) in EtOH–H_2O mixture (9 : 1, 25 ml) at room temperature. The white microcrystalline solid separated after several minutes and was collected by filtration through a sintered glass filter, washed (EtOH, Et_2O) and dried on the filter. Yield 60%, m.p. 150–152 °C. For $C_{36}H_{76}Cl_2N_6O_{12}P_2Zn$ (983.3) calculated: 6.31% P, 6.66% Zn; found: 6.08% P, 6.41% Zn.

$[Zn(tppo)_2(H_2O)_2](NO_3)_2$ (**2**)

The complex was prepared by mixing a solution of $Zn(NO_3)_2 . 6 H_2O$ (1 g, 3.4 mmol) in Me_2CO–H_2O mixture (9 : 1, 25 ml) with a solution of tppo (2 g, 5.8 mmol) in the same solvent (20 ml) at 50 °C. The solution became turbid (white), a colourless crystalline solid separated after several minutes and was collected by filtration, washed with Me_2CO and dried as compound **1** above. Yield 85%, m.p. 90–91 °C. For $C_{36}H_{76}N_8O_{10}P_2Zn$ (877.4) calculated: 49.6% C, 8.79% H, 8.03% N, 7.11% P, 7.45% Zn; found: 49.2% C, 8.42% H, 8.13% N, 7.18% P, 7.51% Zn.

$[Zn(tppo)Cl_2]$ (**3**)

The complex was prepared by mixing a solution of $ZnCl_2$ (0.1 g, 0.7 mmol) in Me_2CO (5 ml) with a solution of tppo (0.3 g, 0.9 mmol) in the same solvent (10 ml) at about 40 °C. A small amount of precipitate (<0.01 g) separated after several minutes was removed by filtration through a sintered glass filter No. 4, and the clear filtrate was left to stand at 0 °C 12 h. The white crystals formed were isolated as complex **2** above. Yield 80%, m.p. 200–202 °C. For $C_{18}H_{36}Cl_2N_3OPZn$ (477.4) calculated: 45.3% C, 7.60% H, 11.46% Cl, 8.81% N, 6.49% P, 13.70% Zn; found: 46.0% C, 8.02% H, 14.60% Cl, 8.82% N, 6.50% P, 13.80% Zn.

[Zn(tppo)Br_2] (**4**)

The complex was prepared by the same procedure as complex **3** above from $ZnBr_2$ (0.5 g, 2.2 mmol Zn) and tppo (1 g, 2.9 mmol) in Me_2CO. Yield 60%, m.p. 211–213 °C. For $C_{18}H_{36}Br_2N_3OPZn$ (566.7) calculated: 38.2% C, 6.41% H, 28.20% Br, 7.42% N, 5.48% P, 11.51% Zn; found: 38.6% C, 6.60% H, 28.20% Br, 7.30% N, 5.40% P, 11.59% Zn.

[Zn$(tppo)_2I_2$] (**5**)

The complex was prepared by reacting a solution (5 ml) of ZnI_2 (0.3 mmol Zn) in Me_2CO with a solution of tppo (0.2 g, 0.6 mmol) in Me_2CO (8 ml) at boiling temperature (reflux). After 2–3 min, a small amount of white precipitate separated and was removed by filtration. The clear filtrate was left to stand at 0 °C ca 50 h, and the microcrystalline solid separated was collected by filtration in vacuo, washed (Me_2CO, Et_2O), and dried in vacuum. Yield 50%, m.p. 179–180 °C. For $C_{36}H_{72}I_2N_6O_2P_2Zn$ (1 002.1) calculated: 43.2% C, 7.24% H, 25.40% I, 8.40% N, 6.19% P, 6.53% Zn; found: 43.5% C, 6.95% H, 25.28% I, 8.18% N, 6.20% P, 6.64% Zn.

[(H_3tppo)($ZnCl_4$)Cl] (**6**)

$ZnCl_2$ (0.14 g, 1 mmol) was treated with 36% HCl (0.3 ml) and Me_2CO (8 ml), whereupon a solution of tppo (0.34 g, 1 mmol) in Me_2CO (8 ml) was added. The white voluminous precipitate formed immediately and was stirred 3 h to give a crystalline solid which was isolated in the same way as compound **2** above. Yield almost 100%, m.p. 206–207 °C. For $C_{18}H_{39}Cl_5N_3OPZn$ (587.1) calculated: 36.9% C, 6.19% H, 30.19% Cl, 7.16% N, 5.28% P, 11.14% Zn; found: 37.1% C, 6.38% H, 29.88% Cl, 6.68% N, 5.16% P, 10.97% Zn.

[Cd$(tppo)_2(H_2O)_2$]$(ClO_4)_2$ (**7**)

The complex was prepared by mixing a solution of $Cd(ClO_4)_2 . 2 H_2O$ (0.6 g, 1.5 mmol) in Me_2CO (20 ml) with a solution of tppo (1 g, 2.9 mmol) in Me_2CO (20 ml). The resulting solution became turbid and the white crystalline solid separated after shaking and was isolated in the same way as compound **5** above. Yield 70%, m.p. 260 °C. For $C_{36}H_{76}Cl_2N_6O_{12}P_2Cd$ (1 020.3) calculated: 11.00% Cd, 6.24% P; found: 11.10% Cd, 6.19% P.

[Cd$(tppo)_2(H_2O)_2$]$(NO_3)_2$ (**8**)

The complex was prepared in the same way as compound **7** above from $Cd(NO_3)_2 . 4 H_2O$. Yield 90%, m.p. 84–85 °C. For $C_{36}H_{76}N_8O_{10}P_2Cd$ (920.4) calculated: 47.0% C, 8.34% H, 12.23% Cd, 7.62% N, 6.74% P; found: 46.7% C, 8.30% H, 12.34% Cd, 7.32% N, 6.83% P.

[Cd(tppo)Br_2] (**9**)

The complex was prepared in the same way as **3** above from $CdBr_2 . 6 H_2O$. Yield 65%, m.p. 175–177 °C. For $C_{18}H_{36}Br_2N_3OPCd$ (613.7) calculated: 35.3% C, 5.92% H, 26.09% Br, 18.30% Cd, 6.85% N, 5.06% P; found: 35.1% C, 6.11% H, 25.86% Br, 18.80% Cd, 6.78% N, 5.11% P.

(H_3tppo)Cl_3 (**10**)

The compound was prepared by reacting tppo (2 g, 5.9 mmol) in a 1 : 1 mixture of petroleum ether and toluene (80 ml) with excess gaseous HCl at 15–20 °C. The white microcrystalline precipitate was allowed to stand with the solution at room temperature 5 h and at 0 °C 5 h, whereupon it was collected by filtration in vacuo, washed with ice cold Et_2O, and dried over P_2O_5 in vacuum. Yield 90%, m.p. 260–261 °C. For $C_{18}H_{39}Cl_3N_3OP$ (450.9) calculated: 48.0% C, 8.73% H, 23.60% Cl, 9.33% N, 6.88% P; found: 48.2% C, 8.18% H, 23.45% Cl, 9.30% N, 6.82% P.

$(H_3tppo)(ClO_4)_3$ (**11**)

The compound was prepared by dissolving tppo (0.2 g, 0.6 mmol) in a 7 : 1 mixture of ethanol and water (4 ml) and adding 2.8 M $HClO_4$ (1.5 ml). The solution was evaporated over P_2O_5, and the solid which separated after 20 days was collected, washed with Me_2CO and Et_2O, and kept over P_2O_5 in vacuum. Yield 50%, m.p. 152–153 °C. For $C_{18}H_{39}Cl_3N_3O_{13}P$ (642.9) calculated: 4.82% P; found: 4.75% P.

Structure Determination

The crystals of complexes **2**, **3**, **8** suitable for X-ray diffraction measurements were selected from repeated preparations carried out at concentrations three times lower than those described above. The densities of the compounds were determined by the flotation method using a heptane–chloroform mixture.

Complex **2**: $C_{36}H_{76}N_8O_{10}P_2Zn$, m.w. 877.4, monoclinic, space group $P2_1/c$ (No. 14), a = 11.494(2) Å, b = 10.384(2) Å, c = 19.983(4) Å. β = 91.31(2)°, V = 2 384.0(8) $Å^3$, Z = 2, D_c = 1.256 g cm^{-3}, D_m = 1.280(4) g cm^{-3}, $F(000)$ = 976. A colourless crystal of the dimensions 0.16 × 0.18 × 0.18 mm was measured at 293(2) K using a CAD4 diffractometer with graphite monochromator, radiation MoKα, λ = 0.71073 Å. The lattice parameters were determined from 25 reflections (θ = 15–16°). The intensities were measured by a θ–2θ scan in the θ interval of ⟨2.04°,24.76°⟩, h interval of ⟨0,13⟩, k interval of ⟨0,12⟩, and l interval of ⟨–23,23⟩. The absorption was neglected (μ = 0.640 mm^{-1}). Three standard reflections were measured always after 1 h and their intensity varied in the limits from –2.0% to +2.4%. Altogether 4 170 reflections were measured, R_σ = 0.085 (3 961 independent ones, R_{int} = 0.026).

Complex **3**: $C_{18}H_{36}Cl_2N_3OPZn$, m.w. 477.8, monoclinic, space group $P2_1/n$ (non-standard No. 14), a = 7.669(1) Å, b = 15.046(1) Å, c = 20.750(2) Å. γ = 102.07(1)°, V = 2 341.4(4) $Å^3$, Z = 4, D_c = 1.355 g cm^{-3}, $F(000)$ = 1 008. A slightly yellowish plate of the dimensions 0.57 × 0.21 × 0.78 mm was measured as **2** above in the θ interval of ⟨1.70°,24.97°⟩, h interval of ⟨–9,9⟩, k interval of ⟨–17,17⟩, and l interval of ⟨0,42⟩. The absorption was neglected (μ = 1.358 mm^{-1}), the intensity variation of standard reflections was in the limits from –2.1% to +2.0%. Altogether 8 245 reflections were measured, R_σ = 0.023 (4 109 independent ones, R_{int} = 0.019).

Complex **8**: $C_{36}H_{76}N_8O_{10}P_2Cd$, m. w. 920.4, monoclinic, space group $P2_1/c$ (No. 14), a = 11.600(3) Å, b = 10.287(2) Å, c = 20.268(5) Å. β = 90.03(3)°, V = 2 418.5(11) $Å^3$, Z = 2, D_c = 1.312 g cm^{-3}, D_m = 1.344(8) g cm^{-3}, $F(000)$ = 1 012. A colourless crystal of the dimensions 0.14 × 0.08 × 0.16 mm was measured as **2** above. The lattice parameters were determined from 25 reflections (θ = 2–13.5°). The measurement was carried out in the θ interval of ⟨2.65°,27.56°⟩, h interval of ⟨0,15⟩, k interval of ⟨0,13⟩, and l interval of ⟨0,26⟩. The absorption was neglected (μ = 0.574 mm^{-1}), the intensity variation of standard reflections was in the limits from –2.1% to +1.1%. Altogether 2 988 reflections were measured, R_σ = 0.047.

The structure of all the three complexes was solved by the Patterson and Fourier method and refined by the least squares treatment (full-matrix, based on F^2) (SHELXS86, SHELXL93) (refs[9,10]). The hydrogen atoms were placed at the theoretical positions (structures **2** and **8**) or found on the difference map and refined isotropically (structure **3**). In the case of compound **8** the hydrogen atoms of the coordinated H_2O molecule were not found near the heavy atom of Cd. The minimized function always was $\Sigma w(F_o^2 - F_c^2)^2$, where $w = 1/[\sigma^2|F|^2 + (0.0487P)^2 + 1.21P]$ for compound **2**, $w = 1/[\sigma^2|F|^2 + (0.0634P)^2 + 0.63P]$ for compound **3**, and $w = 1/[\sigma^2|F|^2 + (0.0720P)^2 + 3.47P]$ for compound **8**, where

$P = (F_o^2 + 2F_c^2)/3$. The final values of refinement for the individual structures were as follows: **2** 406 parameters, $\Delta_{max}/\sigma = 0.004$ for non-hydrogen atoms, $R = 0.043$, $R_w = 0.094$ for 2 031 observed ($I > 2\sigma(l)$) reflections, $GOF = 0.992$, the residual electron densities 0.48 and –0.29 e/Å^3; **3** 380 parameters, $\Delta_{max}/\sigma = 0.004$ for non-hydrogen atoms, $R = 0.036$, $R_w = 0.091$ for 3 319 observed ($l > 2\ \sigma\ (l)$) reflections, $GOF = 1.071$, residual electron densities 0.62 and –0.77 e/Å^3; **8** 296 parameters, $\Delta_{max}/\sigma = 0.005$ for non-hydrogen atoms, $R = 0.052$, $R_w = 0.126$ for 1 666 observed ($I > 2\sigma(l)$) reflections, $GOF = 1.034$, residual electron densities 0.44 and –0.44 e/Å^3.

The infrared spectra were measured in Nujol or in KELF using a Perkin–Elmer 684 apparatus at room temperature.

RESULTS AND DISCUSSION

The synthesized Zn(II) and Cd(II) compounds are colourless microcrystalline substances which cannot be dissolved in common solvents without being decomposed. Therefore, they could not be recrystallized, and the preparation of single crystals had to start from dilute solutions of starting compounds and was successful only with the complexes **2**, **3** and **8** at random after carrying out a rather large number of repeated syntheses. It is necessary to obey the conditions of syntheses described in Experimental (particularly the choice of solvent and the content of water in it) to obtain the substances in defined microcrystalline form. At lower water content the yields are low, whereas, on the other hand, an excess of water results in formation of voluminous precipitates of varying composition, usually with metal content higher than that corresponding to the stoichiometry of complex.

Compounds in which coordination of tppo is presumed can be classified into three groups. The first includes the hydrated compounds with the ratio of metal : tppo = 1 : 2, the second includes anhydrous complexes with the 1 : 1 ratio, and the third is only formed by the complex [Zn(tppo$_2$)I$_2$](**5**). The results of IR spectra (Table I) show that the phosphoryl group is coordinated in all these compounds. The lowering of ν(P–O) value is about 35–40 cm^{-1}, being roughly the same for both the Zn(II) and Cd(II) complexes and independent of stoichiometry of the compound. Hence it can be presumed that tppo is coordinated in practically identical way in all these compounds.

In contrast to that, in compounds **6**, **10**, and **11** the ν(P–O) value is shifted by ca 30–35 cm^{-1} in the opposite direction (Table II). This effect corresponds to protonation of tppo at all its nitrogen atoms, which also agrees with results of the analyses. Therefore, compounds **6**, **10**, and **11** must be formulated as salts of the [H$_3$tppo]$^{(3+)}$ cation. A similar shift in ν(P–O) was also observed[2] during the protonation of tmpo.

The structures **2** and **8** of complexes [M(tppo)$_2$(H$_2$O)$_2$](NO$_3$)$_2$, which both belong to the first group, are very similar to each other (Figs 1 and 2). The coordinates of non-hydrogen atoms are given in Tables II and III for complexes **2** and **8**, respectively. Selected bond lengths and bond angles are listed in Table V. The crystal structures of these compounds are consisted of slightly deformed (elongated in the direction of the M–N bond) octahedral centrosymmetrical cation [M(tppo)$_2$(H$_2$O)$_2$]$^{(2+)}$ (Figs 1 and 2) and noncoordinated anions $NO_3^{(1-)}$ which are connected to the cation by only one hydrogen bond of medium strength. A coordinated H_2O molecule acts as a proton “donor”, and one of oxygen atoms in anion acts as a proton “acceptor”. In the case of Zn(II) complex the length of this bond is 2.648(6) Å, in Cd(II) complex it is 2.871(12) Å, i.e. somewhat longer (Table V). Tppo is coordinated in this cation as a N,O-chelate through O(1) oxygen and one of the nitrogen atoms (N(1)), as it is the case for tmpo in a similar complex with Co(II) (ref.[1]). The H_2O molecules as well as oxygen atoms of phosphoryl group are at *trans*-position to each other.

TABLE I
Infrared data (cm^{-1}) for prepared compounds

Compound	ν(P–O)	$\Delta\nu$(P–O)[a]	Bands of anions	Coordinated H_2O
1	1 120 (s,b)	–35	475 (w) ν_2[b], 620 (m) ν_4	1 635 (w,b) δ
	1 094 (sh)[c]	–33	1 098 (s,b) ν_3	3 390 (m,b) ν
2	1 120 (vs)	–35	816 (w) ν[d], 1 380 (vs) ν_3	1 620 (vw) δ
	1 098 (s)	–37		3 200 (w,b) ν
3	1 115 (sh)	–40	–	–
	1 086 (vs)	–49		
4	1 118 (s)	–37	–	–
	1 096 (vs)	–39		
5	1 117 (s)	–38	–	–
	1 087 (vs)	–48		
6	1 183 (vs)	+28	265 (s) ν_1 ?[e]	3 050 (m)[f]
	1 172 (vs)	+37	281 (s) + 294 (s) ν_3	
7	1 124 (s)	–31	625 (m) ν_4[b], 929 (sh) ν_1	1 640 (vw) δ
	1 088 (vs)[c]	–47	1 095 (vs) ν_3	3 460 (m,b) ν
8	1 122 (vs)	–33	815 (w) ν[d], 1 380 (vs) ν_3	1 620 (vw) δ
	1 099 (s)	–36		3 220 (w,b) ν
9	1 118 (vs)	–37	–	–
	1 098 (vs)	–37		
10	1 190 (s)	+35	–	3 010–3 030 (m,b)[f]
	1 170 (w)	+35		
11	–	–	464 (w) ν_2[b], 620 (vs) ν_4	3 060–3 070 (m,b)[f]
	1 153 (vs,b)[c]	+18	949 (m) ν_1, 1070–1 110 (vs,b) ν_3	
tppo	1 155 (vs)	–	–	–
	1 135 (vs)	–		

[a] $\Delta\nu$(P–O) gives the shift of the ν(P–O) bands after coordination or protonization. [b] For perchlorate anion (T_d). [c] Partial overlap with bands of perchlorate anion. [d] For nitrate anion (D_{3h}). [e] For tetrachlorozincate (T_d). [f] N–H bands.

The structure of anhydrous complex [Zn(tppo)Cl_2] (**3**) (for coordinates see Table IV, for selected bond lengths and angles see Table V), which belongs to the second group,

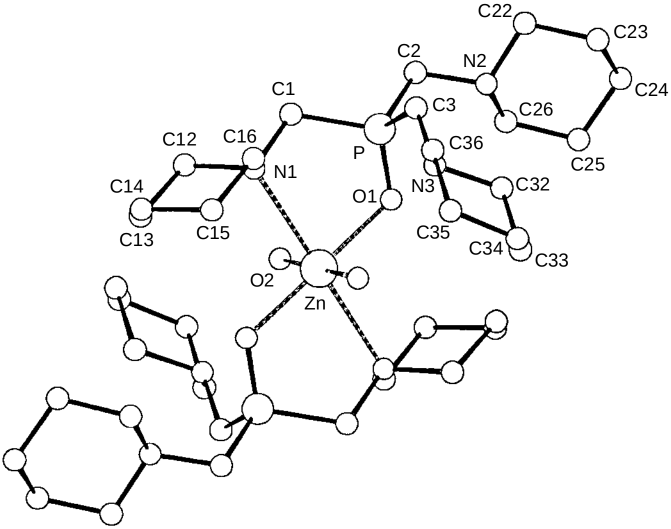

FIG. 1
Perspective view of the cation $[Zn(tppo)_2(H_2O)_2]^{2+}$ from **2** with the atom labelling

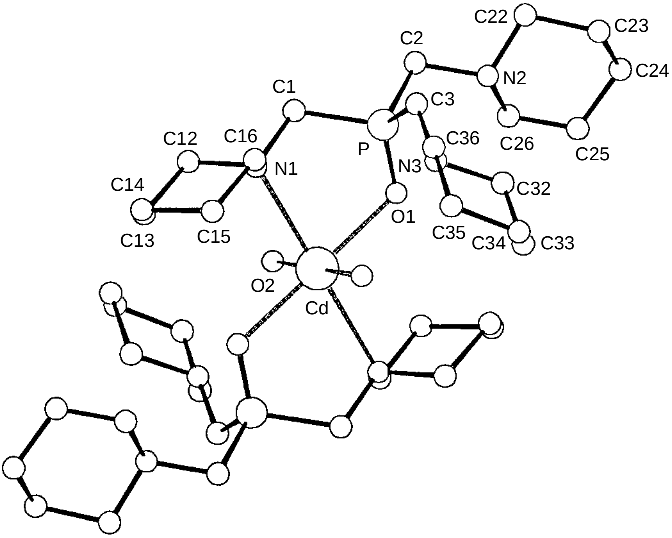

FIG. 2
Perspective view of the cation $[Cd(tppo)_2(H_2O)_2]^{2+}$ from **8** with the atom labelling

TABLE II
Atomic coordinates (. 10^4) and equivalent isotropic displacement parameters (Å^2 . 10^3) for **2**. U_{eq} is defined as one third of the trace of the orthogonalized $\boldsymbol{U}_{ij}$ tensor

Atom	*x*	*y*	*z*	U_{eq}
Zn	0	0	0	51(1)
P	1082(1)	–39(1)	1442(1)	46(1)
O1	1282(2)	321(2)	719(1)	45(1)
C3	1734(5)	–1613(5)	1666(2)	56(1)
N3	2059(3)	–2378(3)	1080(2)	48(1)
C32	3246(4)	–998(5)	861(3)	62(1)
C33	3578(5)	2733(6)	238(3)	77(2)
C34	3524(6)	–4189(7)	349(4)	96(2)
C35	2337(6)	–4567(6)	618(3)	82(2)
C36	2026(5)	–3780(5)	1235(3)	66(1)
C2	1726(5)	1105(6)	2032(3)	62(1)
N2	2981(3)	1135(3)	1929(2)	53(1)
C22	3665(5)	1027(7)	2554(3)	78(2)
C23	4961(6)	906(8)	2406(4)	97(2)
C24	5364(7)	2058(8)	2016(4)	104(2)
C25	4607(7)	2215(8)	1376(4)	103(2)
C26	3326(6)	2269(6)	1547(3)	79(2)
C1	–489(4)	–35(6)	1576(2)	53(1)
N1	–1147(3)	–649(3)	1008(2)	49(1)
C12	–2370(4)	–167(6)	1027(2)	59(1)
C13	–3151(5)	–817(6)	497(3)	68(2)
C14	–3134(5)	–2271(6)	565(3)	75(2)
C15	–1890(5)	–2765(5)	573(3)	68(2)
C16	–1154(5)	–2085(5)	1110(2)	57(1)
O2	–689(3)	1795(3)	89(1)	56(1)
N4	9324(6)	1214(5)	6461(3)	90(2)
O41	9967(5)	1499(5)	6008(3)	140(2)
O42	9638(6)	626(8)	6910(3)	214(4)
O43	8333(7)	489(8)	6396(4)	215(4)

first of all differs by the geometry of the coordination sphere of Zn(II) (Fig. 3). The relatively bulkier chloride anions only allow the coordination number of 4, hence the complex formed is approximately tetrahedral. The coordination shell of Zn(II) is formed by two Cl^- anions, the O(1) oxygen of the phosphoryl group, and again one of

TABLE III
Atomic coordinates (. 10^4) and equivalent isotropic displacement parameters ($Å^2 . 10^3$) for **3**. U_{eq} is defined as one third of the trace of the orthogonalized $\boldsymbol{U}_{ij}$ tensor

Atom	*x*	*y*	*z*	U_{eq}
Zn	1424(1)	3620(1)	2259(1)	45(1)
P	1388(1)	4488(1)	2661(1)	39(1)
Cl1	21(1)	2652(1)	1551(1)	72(1)
Cl2	2036(1)	3120(1)	3219(1)	99(1)
O1	150(2)	4647(1)	2405(1)	40(1)
N1	3733(3)	4642(2)	2025(1)	41(1)
N2	1184(3)	6557(1)	1629(1)	41(1)
N3	–269(3)	5881(1)	3759(1)	41(1)
C2	998(4)	6537(2)	2323(1)	49(1)
C3	1349(3)	5627(2)	3529(1)	43(1)
C1	3674(3)	5372(2)	2494(2)	50(1)
C12	5418(4)	4303(2)	2131(2)	55(1)
C16	3723(4)	5011(2)	1365(1)	47(1)
C22	–483(4)	6145(2)	1307(2)	61(1)
C13	5618(4)	3603(2)	1631(2)	64(1)
C35	–1599(4)	6619(2)	4634(2)	62(1)
C36	45(4)	6323(2)	4384(1)	49(1)
C32	–1740(4)	5089(2)	3795(2)	53(1)
C26	1828(5)	7487(2)	1395(2)	59(1)
C33	–3440(4)	5358(3)	4020(2)	61(1)
C34	–3169(5)	5819(3)	4667(2)	63(1)
C15	3901(4)	4322(2)	852(2)	56(1)
C14	5584(4)	3958(2)	957(2)	62(1)
C23	–213(7)	6119(3)	586(2)	86(1)
C24	480(9)	7058(3)	325(2)	97(2)
C25	2126(7)	7492(3)	677(2)	84(1)

TABLE IV
Atomic coordinates (. 10^4) and equivalent isotropic displacement parameters (Å^2 . 10^3) for **8**. U_{eq} is defined as one third of the trace of the orthogonalized $\boldsymbol{U}_{ij}$ tensor

Atom	x	y	z	U_{eq}
Cd	0	0	0	55(1)
P	1166(2)	–87(2)	1462(1)	57(1)
O1	1402(5)	289(5)	767(3)	68(2)
C3	1765(10)	–1713(8)	1671(5)	72(4)
N3	2106(6)	–2461(6)	1095(4)	62(3)
C32	3280(9)	–2094(10)	867(6)	76(5)
C33	3640(11)	–2835(12)	252(7)	109(6)
C34	3562(13)	–4304(13)	374(10)	118(8)
C35	2379(15)	–4682(10)	637(9)	109(8)
C36	2071(11)	–3881(8)	1235(6)	94(5)
C2	1759(8)	1010(10)	2080(5)	79(5)
N2	3017(7)	1063(6)	1955(4)	69(3)
C22	3677(10)	969(13)	2573(6)	105(5)
C23	4976(11)	890(14)	2405(8)	116(7)
C24	5355(12)	2056(12)	2019(8)	128(9)
C25	4602(15)	2198(16)	1421(12)	134(10)
C26	3380(13)	2195(11)	1550(8)	95(6)
C1	–408(9)	–48(10)	1603(5)	71(4)
N1	–1081(7)	–638(7)	1046(4)	64(3)
C12	–2269(9)	–111(10)	1088(6)	83(5)
C13	–3051(9)	–711(11)	558(6)	95(5)
C14	–3090(10)	–2159(11)	596(7)	92(5)
C15	–1843(9)	–2699(9)	582(6)	88(5)
C16	–1105(8)	–2073(7)	1107(5)	73(4)
O2	–789(6)	1997(5)	76(3)	74(3)
N4	9364(21)	1206(13)	486(6)	127(7)
O41	9753(26)	1337(17)	6044(11)	267(14)
O42	9719(17)	924(20)	939(6)	273(12)
O43	8408(18)	1436(19)	6327(16)	352(21)

the nitrogen atoms of tppo. The ligand is bound as an N,O-chelate, i.e. identically as in complexes **2** and **8**, which corresponds well to the results of IR spectra. If we compare the bonding distances Zn–O(1) and Zn–N(1) in the tetrahedral and the octahedral complexes, it is obvious that for the coordination number 4 the donor atoms can approach nearer to the metal atom (see Table V). This is particularly seen in the case of the bulky piperidine group which has much higher steric requirements as compared with phosphoryl group. The big steric requirements of piperidine group also make the M–N(1) bond markedly longer (2.524(4) Å) in the octahedral Zn(II) complex as compared with that in similar octahedral complex $[Co(tmpo)_2(H_2O)_2]^{(2+)}$ (where the M–N(1) bond length is[1] 2.271(7) Å), which contains a somewhat less demanding group $–N(CH_3)_2$. However, the M–O(1) bond lengths are similar: 2.061(2) and 2.080(6) Å in **2** and the tmpo complex[1], respectively. If we compare the M–O and M–N distances in complexes **2** and **8**, we can see that the Cd–O distance is longer than Zn–O by about 0.2 Å, which corresponds to the greater radius of $Cd^{(2+)}$. In contrast to that, the Cd–N and Zn–N distance are practically the same (Table V), which indicates that the approaching of nitrogen to metal (and hence the strength of M–N interaction) is mainly dictated by the steric requirements of $–NR_2$ group. On the other hand, the effect of radius of the metal, and hence the change of its polarization strength, cause a greater lengthening of P–O(1) bond in complex **2** as compared with complex **8** (Table V). This is in accordance with the predominantly electrostatic nature of the bond between phosphoryl group and metal[1,11].

The stereochemistry of the chelate five-membered ring M,O(1),P,C(1),N(1) can be seen from Table V and particularly from Table VI. A comparison of values of bond angles, torsion angles at the individual bonds, and distances of P and C(1) atoms from the plane defined by M, O(1), N(1) will show that a substantial effect on the arrange-

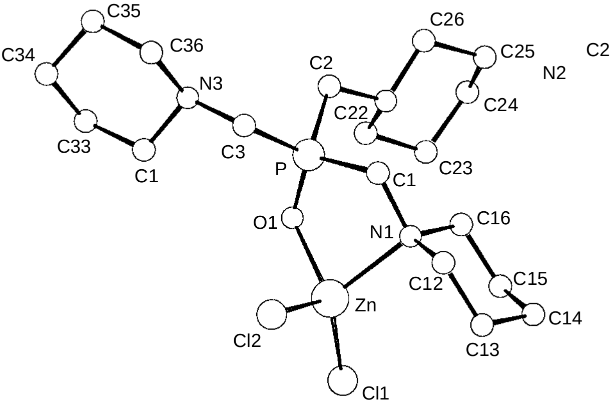

FIG. 3
Perspective view of the cation $[Zn(tppo)Cl_2]$ **3** with the atom labelling

TABLE V
Select bond distances (Å) and angles (°) in complexes **2**, **3** and **8**

Atoms	**2**	**3**	**8**
		Bond distances	
M–O1	2.061(2)	2.016(2)	2.268(4)
M–N1	2.524(4)	2.143(2)	2.550(9)
M–O2	2.034(3)	–	2.254(5)
M–Cl1	–	2.1870(9)	–
M–Cl2	–	2.2158(10)	–
P–C1	1.832(4)	1.808(3)	1.849(12)
P–O1	1.515(3)	1.510(2)	1.486(7)
P–C2	1.819(5)	1.814(3)	1.821(7)
P–C3	1.848(5)	1.831(3)	1.860(8)
N1–C1	1.493(5)	1.476(4)	1.500(9)
N1–C12	1.493(5)	1.501(3)	1.483(14)
N1–C16	1.504(5)	1.478(3)	1.481(10)
O2–O41^{i}	2.648(6)	–	2.871(12)
		Bond angles	
O1–M–N1	82.24(10)	86.83(7)	79.44(22)
O1–M–O2	93.70(10)	–	97.19(16)
N1–M–O2	87.90(12)	–	88.74(25)
O1–M–Cl1	–	111.23(5)	–
O1–M–Cl2	–	107.17(6)	–
N1–M–Cl1	–	122.96(6)	–
N1–M–Cl2	–	104.19(6)	–
Cl1–M–Cl2	–	119.17(5)	–
P–O1–M	120.2(2)	112.02(9)	118.9(4)
C1–P–O1	108.1(2)	107.46(12)	108.9(4)
N1–C1–P	111.8(3)	112.0(2)	112.8(8)
M–N1–C1	103.2(3)	103.6(2)	105.4(6)
M–N1–C12	116.1(3)	111.4(2)	114.2(6)
M–N1–C16	112.2(3)	114.2(2)	109.6(7)
C1–N1–C12	107.4(4)	108.6(2)	107.0(9)
C1–N1–C16	109.0(4)	109.1(2)	110.5(6)
C16–N1–C12	108.7(2)	109.6(2)	110.0(8)
O1–P–C2	112.9(2)	114.0(1)	114.9(5)
O1–P–C3	112.3(2)	115.0(1)	112.4(4)
C1–P–C2	106.9(2)	110.3(2)	104.6(5)
C1–P–C3	111.2(3)	103.7(1)	110.7(5)
C2–P–C3	105.3(3)	106.0(1)	105.0(4)

Symmetry code: i = –1 – *x*, –*y*, –1 – *z*.

TABLE VI
Torsion angles (°) in chelate rings and distances (Å) of the P and C(1) atoms from M–O(1)–N(1)-plane

Atoms	**2**	**3**	**8**
		Distances	
P	–0.124(4)	0.751(3)	–0.116(7)
C1	0.483(7)	0.905(4)	0.487(13)
		Torsion angles	
P–O1–M–N1	5.4(2)	–32.5(1)	5.1(3)
C1–P–O1–M	–24.9(3)	17.9(2)	–24.3(5)
N1–C1–P–O1	42.5(4)	14.5(2)	43.0(7)
M–N1–C1–P	–35.5(4)	–36.3(2)	–36.7(7)
O1–M–N1–C1	19.4(3)	39.1(2)	19.7(5)

ment of the chelate ring in space is exerted by the geometry of coordination sphere and not by the radius of cation. The values listed in Table VI show unambiguously that the conformations of chelate rings in compounds **2** and **8** are practically identical, being different from that in complex **3**.

In conclusion it can be stated that the way of coordination of tppo to Zn and Cd found in structures **2**, **3**, and **8** is entirely different from that of the sterically less demanding aminoalkylphosphine oxides studied by Borisov[7]. On the other hand, from structural point of view the complex-forming behaviour of tppo is analogous to that of tmpo[1,2].

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