EFFECT OF COORDINATION ON THE STRUCTURE OF TRIS(*N,N*-DIMETHYLAMINOMETHYL)PHOSPHINE OXIDE

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Crystals of tris(*N,N*-dimethylaminomethyl)phosphine oxide (tmpo) are hexagonal, space group $P6_3$; a = 8.723(5), c = 10.636(5) Å, Z = 2, R = 0.039 for 384 observed reflections. The complex $[Co(tmpo)_2(H_2O)_2](ClO_4)_2$, forms orthorhombic crystals, space group *Pbca*, a = 19.16(1), b = 10.576(2), c = 17.043(4) Å, Z = 4, R = 0.069 for 1 409 observed reflections. The molecule is centrosymmetric, with the Co atom lying in the centre. The tmpo is coordinated through the oxygen atom and one of the nitrogen atoms. The coordination of the ligand brings about very small changes in the bond lengths and angles except for the P=O bond. The coordinated water molecules play a major part in the structure of $[Co(tmpo)_2(H_2O)_2](ClO_4)_2$.

Aminoalkylphosphine oxides are rather rare ligands in coordination chemistry. Dodoff and coworkers[1] studied complexes of *P,P*-dimethyl-*P*-aminomethylphosphine oxide (dapo) with Co(III), Cr(III) and Cu(II) and suggest that the ligand in them is bidentate, bonded through the oxygen and nitrogen atoms. Du Preez and coworkers[2,3] studied complexes of *P*-(N,N-dimethylaminomethyl)-*P,P*-diphenylphosphine oxide (dmpo) and *P*-(*N,N*-dimethylaminoethyl)-*P,P*-diphenylphosphine oxide (depo) with Co(II), Ni(II) and Cu(II) and determined the crystal and molecular structure of the $[Cu(dmpo)_2Cl]_2[CuCl_4]$ complex[3]. This structure involves the tetrahedral $[CuCl_4]^{2-}$ anion and the $[Cu(dmpo)_2Cl]^+$ cation where the coordination number of the Cu atom is five. The coordination environment of copper adopts the form of a square pyramid with the Cl atom in its apex and two O atoms and two N atoms in the basal plane. The metal atom lies approximately 0.48 Å above the basal plane. The dmpo ligand is bonded as a chelating N,O-donor. The Cu, O, P, C, N atoms form a nonplanar five-membered ring[3]. A similar five-membered ring, viz. Pt–O–P–C–N, which, however, is planar, was found in the $[Pt(pdpo)Br_4]$ complex where pdpo is *P*-(2-pyridyl)-*P,P*-dimethylphosphine oxide[4].

Unlike the above ligands[1 – 3], the symmetric tris(*N,N*-dimethylaminomethyl)phosphine oxide (tmpo) contains four donor atoms in the molecule and thus can be theoretically

coordinated to a metal atom in seven different ways. The present work is concerned with the crystal structure of tmpo and $[Co(tmpo)_2(H_2O)_2](ClO_4)_2$ and with the effect of the coordination on the geometry of the symmetric tmpo molecule.

EXPERIMENTAL

Tris(*N,N*-dimethylaminomethyl)phosphine oxide was prepared following ref.[5]. Single crystals of the compound, which were obtained by cooling slowly its 20% solution in methanol in a refrigerator, were washed with a minimal volume of acetone cooled to −15 °C, and dried in air. For $C_9H_{24}N_3OP$ (221.3) calculated: 48.95% C, 10.95% H, 19.00% N, 14.00% P; found: 48.93% C, 10.90% H, 19.27% N, 14.06% P. Phosphorus was determined gravimetrically.

TABLE I
Crystal data, measurement and refinement details for tmpo

Parameter	Data
Space group	$P6_3$ (No. 173), $Z = 2$
a, b, c, Å	8.723(5), 8.723(5), 10.636(5)
$\alpha = \beta, \gamma$, °	90, 120
Cell volume, Å^3	700.9(8)
D_m, D_x, g cm^{-3}	1.08(8), 1.040
Radiation	CuK_α, $\lambda = 1.5418$ Å
Absorption correction	Not applied, $\mu = 14.8$ mm^{-1}
$F(000)$	244
Temperature, K	296
Crystal dimensions, mm	0.75 × 0.15 × 0.20
No. of reflections for lattice parameter determination	18 ($9 < \theta < 17°$)
Diffractometer	Syntex $P2_1$
Scan mode	$2\theta - \theta$
Standard reflections	3 after every 97
(variation)	(<2%)
Intervals h, k, l	⟨0, 12⟩, ⟨0, 12⟩, ⟨0, 20⟩
No. of reflections measured	391
No. of reflections used ($I \geq 1.96\sigma(I)$)	384
Residual electron density, e Å^{-3}	0.14, −0.36
$(\Delta/\sigma)_{max}$ for non-H atoms	0.038
Function minimized	$w(\|F_o\| - \|F_c\|)^2$
Weight	$\sigma^{-2}(F_o)$, derived from $\sigma(F_o)/F_o = 1/2\ \sigma_2(I)/I$ and $\sigma_2(I) = (\sigma_1^2(I) + 0.03\ I^2)^{1/2}$
Second extinction correction	Type 1, $g = 0.70(6) \cdot 10^{-6}$ (ref.[13])
R, wR	0.039, 0.038

The $[Co(tmpo)_2(H_2O)_2](ClO_4)_2$ complex was prepared by reacting 4.4 mmol of $Co(ClO_4)_2 . 6 H_2O$ and 9.0 mmol of tmpo in 50 ml of 96% ethanol at 30 °C. The system was allowed to stand at room temperature, and hexagonal crystals of pink colour, suitable for X-ray treatment, separated in 50 h. The crystals were washed with ethanol and acetone and dried between filter paper sheets. For $C_{18}H_{52}Cl_2N_6O_{12}P_2Co$ (736.4) calculated: 8.00% Co, 9.63% Cl, 4.89% P; found: 8.1% Co, 9.8% Cl, 5.1% P.

The density of the complex was determined by the flotation method in a heptane–chloroform mixture, the density of tmpo was determined likewise in a saturated solution of tmpo in acetone. Crystal data, along with some experimental details, for tmpo and for the complex are given in Tables I and II, respectively. The structures of the two compounds were elucidated by direct methods (MULTAN 80, ref.[6]) and by the Patterson and Fourier techniques (SHELX 76, ref.[7]). The coordinates, thermal parameters (anisotropic for the non-hydrogen atoms and isotropic for the hydrogen atoms), scale factor and secondary isotropic

TABLE II
Crystal data, measurement and refinement details for $[Co(tmpo)_2(H_2O)_2](ClO_4)_2$

Parameter	Data
Space group	*Pbca* (No. 61), $Z = 4$
a, b, c, Å	19.16(1), 10.576(2), 17.043(4)
$\alpha = \beta = \gamma$, °	90
Cell volume, Å^3	3454.7(8)
D_m, D_x, g cm^{-3}	1.399(2), 1.414
Radiation	MoK$_\alpha$, $\lambda = 0.71069$ Å
Absorption correction	Not applied, $\mu = 6.37$ mm^{-1}
$F(000)$	1656
Temperature, K	296
Crystal dimensions, mm^3	0.10 × 0.15 × 0.25
No. of reflections for lattice parameter determination	22 ($5 < \theta < 20°$)
Diffractometer	Hilger–Watts
Scan mode	$2\theta - \theta$
Standard reflections	3 after every 30
(variation)	(<2%)
Intervals h, k, l	⟨0, 18⟩, ⟨0, 11⟩, ⟨0, 17⟩
No. of reflections measured	2 109
No. of reflections used ($I < 1.96\sigma(I)$)	1 409
Residual electron density, e Å^{-3}	0.82, −0.33
$(\Delta/\sigma)_{max}$ for non-H atoms	0.100
Function minimized	$w(\|F_o\| - \|F_c\|)^2$
Weight	$\sigma^{-2}(F_o)$, derived from $\sigma(F_o)/F_o = 1/2\ \sigma_2(I)/I$ and $\sigma_2(I) = (\sigma_1^2(I) + 0.03\ I^2)^{1/2}$
R, wR	0.069, 0.073

extinction coefficient (for tmpo only) were refined simultaneously by the full matrix least squares method (SHELX 76, ref.[7]). The scattering factors for the neutral atoms were taken from ref.[8]. The hydrogen atoms of the methyl groups were held in the theoretical positions during the refinement of the structure of the Co compound. The molecular geometry was calculated by using the PARST program[9].

RESULTS AND DISCUSSION

The atomic coordinates of all the refined atoms in the two structures are given in Tables III and IV, respectively, the atomic distances and angles are given in Tables V and VI, respectively. The C–H distances for the refined hydrogen atoms lay within the interval of 0.83 to 1.04 Å in both structures.

The crystal structure of tmpo is composed of discrete molecules (Fig. 1). The P=O bond lies in the crystallographic 6_3-axis, which is also the three-fold axis of the discrete molecule. The bond lengths and angles are consistent with typical values in similar structures[10,11].

The structure of $[Co(tmpo)_2(H_2O)_2](ClO_4)_2$ comprises octahedral $[Co(tmpo)_2(H_2O)_2]^{2+}$ cations and tetrahedral ClO_4^- anions. The coordination sphere of the Co(II) atom forms a distorted octahedron (the resulting symmetry approaches D_{4h}). The Co–O(1) and Co–O(2) distances are identical within the limits of error, viz. 2.079(7) Å. The Co–N(1) distance is appreciably longer, viz. 2.271(7) Å: typical values for the Co–N(tertiary

TABLE III
Fractional coordinates (. 10^4) of all refined atoms in tmpo with estimated standard deviations (e.s.d.'s) in parentheses. $U_{eq} = (1/3)(U_{11} + U_{22} + U_{33})$

Atom	x/a	y/b	z/c	U_{eq}(. 10^3), Å^2
P	0	0	0	44(0)
O	0	0	−1393(7)	65(1)
N	2785(3)	−490(3)	560(4)	63(1)
C(1)	2140(3)	737(3)	744(4)	55(1)
C(2)	3616(7)	−243(8)	−663(5)	103(2)
C(3)	4011(6)	−281(7)	1571(6)	95(2)
H(1A)	1663(66)	686(62)	1437(69)	104(15)[a]
H(1B)	2889(46)	1815(60)	406(34)	67(8)[a]
H(2A)	4165(77)	−1041(67)	−893(42)	111(16)[a]
H(2B)	4779(75)	1137(77)	−817(51)	117(15)[a]
H(2C)	2673(95)	−636(87)	−1291(67)	143(24)[a]
H(3A)	4288(81)	−1110(67)	1462(62)	111(17)[a]
H(3B)	3382(68)	−429(57)	2380(61)	102(13)[a]
H(3C)	4853(71)	862(63)	1620(45)	77(10)[a]

[a] Isotropic displacement parameter.

amine) and Co–OH_2 distances are 2.22(3) and 2.08(6) Å, respectively[11]. Only two Co–O (phosphine oxide) bond lengths are known[11] and both of them are shorter (1.990 and 1.940 Å) than the Co–O(1) bond.

The tmpo ligand is coordinated as a bidentate ligand through the O(1) and N(1) atoms, forming thus a five-membered ring. The Co–N(1)–C(1)–P–O(1) five-membered ring is not planar. The distances of the P and C(1) atoms from the Co–O(1)–N(1) plane (the equatorial plane of the coordination polyhedron) are 0.57(1) and 0.79(1) Å, respectively. Coordination of a similar kind has been observed for dmpo in $[Cu(dmpo)_2Cl_2][CuCl_4]$ (ref.[3]) where the symmetry of the Cu(II) coordination sphere approaches the square pyramid, the Cu–N distances being somewhat shorter (2.010(6) Å) than the Cu–O distances (2.064(5) Å) (ref.[3]).

The ClO_4^- anion remains beyond the Co(II) coordination sphere, as expected. The Cl–O distances lie within the region of 1.39(2) – 1.30(1) Å, except for the Cl–O(6) bond for which an unreasonably low value of 1.26(1) Å was obtained. For the O(3)–O(6) oxygen atoms the U_{eq} values obtained are also one order of magnitude higher than for the other non-hydrogen atoms, which indicates a partial disorder of the oxygen atoms in the perchlorate anion and accounts for the somewhat higher *R*-factor value.

The water molecules coordinated to Co(II) play an important part. They are involved not only in coordination to Co(II) but also in hydrogen bonds, one of which connects the complex cation to the perchlorate anion through the O(3) atom (the O(2)...O(3) distance is 3.04(2) Å, the O(2)–H(22)–O(3) angle is 136(3)°), while the other connects the water molecule to one of the uncoordinated nitrogen atoms in the tmpo molecule (Fig. 2). The length of this O(2) hydrogen bond orients one *N,N*-dimethylaminomethyl group approximately in the direction of the Co–O(2) bond (the Co–O(1)–P–C(4) torsion angle is 105.5(2)°).

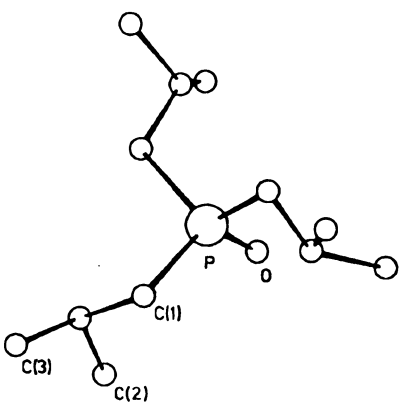

FIG. 1
Perspective view of the tmpo molecule with atom numbering

TABLE IV

Fractional coordinates (. 10^4) of all refined atoms in $[Co(tmpo)_2(H_2O)_2](ClO_4)_2$ with e.s.d.'s in parentheses. $U_{eq} = (1/3)(U_{11} + U_{22} + U_{33})$

Atom	*x/a*	*y/b*	*z/c*	U_{eq}(. 10^3), Å^2
Co	0	0	0	41(1)
P	1200(1)	1458(2)	775(1)	49(1)
O(1)	1044(3)	325(5)	268(4)	50(2)
C(1)	421(5)	2414(10)	839(7)	58(4)
N(1)	-85(4)	2113(7)	216(4)	52(3)
C(2)	93(6)	2835(9)	-508(6)	69(4)
C(3)	-795(5)	2455(10)	470(7)	72(4)
C(4)	1426(7)	1044(11)	1772(6)	64(4)
N(2)	937(5)	124(9)	2098(5)	73(3)
C(5)	1236(9)	-1127(12)	2091(9)	132(7)
C(6)	707(9)	501(19)	2878(8)	143(8)
C(7)	1924(6)	2402(17)	460(7)	58(4)
N(3)	1834(4)	2966(7)	-302(6)	66(3)
C(8)	2078(6)	2123(11)	-924(7)	87(5)
C(9)	2193(6)	4189(11)	-362(8)	89(5)
O(2)	-184(5)	-228(7)	1193(4)	62(3)
Cl	3556(2)	98(3)	2208(2)	78(1)
O(3)	3964(6)	-937(11)	2366(8)	164(6)
O(4)	2957(10)	-630(20)	2105(14)	272(12)
O(5)	3608(12)	611(14)	1521(8)	257(12)
O(6)	3569(11)	818(11)	2794(8)	258(11)
H(1A)	531(46)	3301(99)	844(53)	71(30)[a]
H(1B)	205(38)	2412(69)	1394(49)	41(22)[a]
H(4A)	1410(54)	1991(103)	1992(57)	91(34)[a]
H(4B)	1909(54)	822(86)	1707(56)	69(33)[a]
H(7A)	2304(48)	1966(81)	523(46)	47(30)[a]
H(7B)	1925(47)	2923(89)	829(55)	57(34)[a]
H(21)	245(59)	-36(93)	1588(63)	85(32)[a]
H(22)	-524(48)	-262(89)	1361(53)	42(33)[a]

[a] Isotropic displacement parameter.

Comparison of the bond lengths and angles in the free tmpo ligand and in its coordinated form demonstrates that the coordination mainly affects the P=O bond. Due to the coordination of the phosphoryl group, the electron density shifts partly from the oxygen atom to the metal atom. As a result, the P=O bond order decreases and the bond length increases. The changes in the remaining part of the tmpo molecule, which are due to the formation of the five-membered chelate ring, are less marked.

In conclusion, the tmpo ligand is found to be coordinated in the same manner as the dmpo ligand[3], coordination through an oxygen atom and a nitrogen atom (associated with the formation of a five-membered ring) being preferred to the coordination

TABLE V
Bond lengths (in Å) and angles (in °) in tmpo (non-hydrogen atoms only) with e.s.d.'s in parentheses

Bond	Length	Bonds	Angle
P–O	1.482(7)	O–P–C(1)	115.7(1)
P–C(1)	1.823(3)	P–C(1)–N	112.8(2)
C(1)–N	1.450(3)	C(1)–N–C(2)	111.2(3)
N–C(2)	1.452(5)	C(1)–N–C(3)	109.7(3)
N–C(3)	1.462(4)	C(2)–N–C(3)	111.1(3)

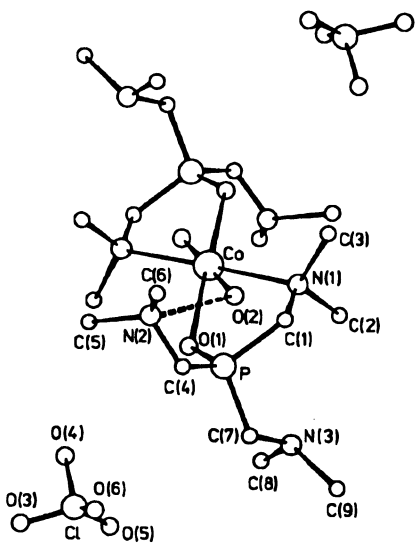

FIG. 2
Perspective view of the $[Co(tmpo)_2(H_2O)_2]^{2+}$ cation and ClO_4^- anions with atom numbering. (N(2)...O(2) is hydrogen bond, see text)

through two nitrogen atoms associated with the formation of a six-membered ring. The coordination does not affect the geometry of the tmpo molecule appreciably: the ligand is a weak σ-donor and the metal–ligand interaction is predominantly electrostatic by nature. This is consistent with the bonding and coordination situation of phosphine oxides in general[12].

TABLE VI
Bond lengths (in Å) and angles (in °) in $[Co(tmpo)_2(H_2O)_2](ClO_4)_2$ (non-hydrogen atoms only) with e.s.d.'s in parentheses

Bond	Length	Bond	Length
Co–N(1)	2.271(7)	N(1)–C(2)	1.49(1)
Co–O(1)	2.080(6)	N(1)–C(3)	1.47(1)
Co–O(2)	2.078(7)	C(4)–N(2)	1.46(1)
P–O(1)	1.508(6)	N(2)–C(5)	1.44(1)
P–C(1)	1.81(1)	N(2)–C(6)	1.46(2)
P–C(4)	1.81(1)	C(7)–N(3)	1.44(1)
P–C(7)	1.79(1)	N(3)–C(8)	1.46(1)
C(1)–N(1)	1.47(1)	N(3)–C(9)	1.47(1)
Bonds	**Angle**	**Bonds**	**Angle**
N(1)–Co–O(1)	82.6(2)	O(1)–P–C(7)	115.1(5)
O(2)–Co–O(1)	88.1(3)	C(1)–P–C(4)	113.2(4)
O(2)–Co–N(1)	86.7(3)	C(1)–P–C(7)	110.3(6)
Co–N(1)–C(1)	106.4(6)	C(4)–P–C(7)	103.4(5)
Co–N(1)–C(2)	110.7(5)	P–C(1)–N(1)	112.3(7)
Co–N(1)–C(3)	110.8(6)	P–C(4)–N(2)	111.5(7)
C(1)–N(1)–C(2)	109.7(8)	P–C(7)–N(3)	114.0(8)
C(1)–N(1)–C(3)	110.0(7)	C(4)–N(2)–C(5)	111(1)
C(2)–N(2)–C(3)	109.2(8)	C(4)–N(2)–C(6)	111(1)
P–O(1)–Co	116.6(3)	C(5)–N(2)–C(6)	112(1)
O(1)–P–C(1)	108.4(4)	C(7)–N(3)–C(8)	111.3(9)
O(1)–P–C(4)	113.2(4)	C(7)–N(3)–C(9)	111.8(9)
		C(8)–N(3)–C(9)	109.7(9)

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