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catena-Poly[[bis(nitrato-κ^2O,O')copper(II)]-μ-propane-1,3-diylbis(diphenylphosphine oxide)-κ^2O:O']

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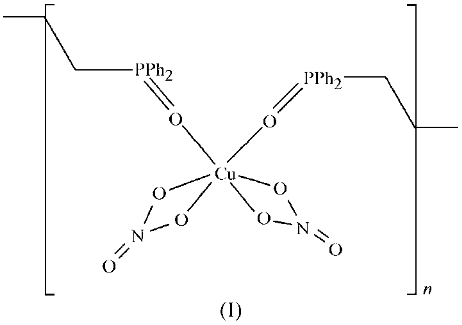
The structure of the title complex, $[Cu(NO_3)_2(C_{27}H_{26}O_2P_2)]_n$, consists of polymeric chains formed by propane-1,3-diylbis(diphenylphosphine oxide) ligands bridging between metal centres. The Cu atom lies on a twofold rotation axis and a further symmetry centre bisects the bridging bisphosphine dioxide ligand. The CuO_6 coordination geometry is a distorted octahedron, with the bidentate chelating nitrate groups adopting a *cis* configuration.

Comment

Bis(diphenylphosphino)alkane dioxides are capable of coordinating to transition metal ions *via* monodentate, bidentate chelating or bridging bonding modes. There are examples of 1,1-bis(diphenylphosphino)methane dioxide ($dppmO_2$) acting as both a chelating ligand (Arnáiz *et al.*, 2002) and a bridging ligand (Ding *et al.*, 2000); there are similar examples of 1,2-bis(diphenylphosphino)ethane dioxide ($dppeO_2$) chelating (Povey *et al.*, 1991) and bridging between metal centres (Harding *et al.*, 2007; Yang *et al.*, 2000). Although there are many structural examples of κ^2P,P' complexes of 1,3-bis(diphenylphosphino)propane (dppp) with transition metals (Davies *et al.*, 2005; Smith *et al.*, 2003; Morgan *et al.*, 2002), and reports of the catalytic efficacy of 1,3-bis(diphenylphosphino)propane dioxide ($dpppO_2$) (Ogawa *et al.*, 2004), there are few examples of $dpppO_2$ complexes of transition metals. One such complex, $MoO_2Cl_2(dpppO_2)$ (Oh & Mo, 1995), consists of discrete mononuclear units containing a chelating $dpppO_2$ ligand. We report here the structure of a further transition metal complex of $dpppO_2$, the title compound, $[Cu(NO_3)_2(dpppO_2)]_n$, (I) (Fig. 1), prepared as an extension of our work with the bisphosphine dioxide complexes of the lanthanide elements.

The structure of (I) consists of polymeric chains formed by $dpppO_2$ ligands bridging between metal centres. The metal complex is centrosymmetric, with the Cu atom sitting on a twofold rotation axis. The coordination geometry about copper is a distorted octahedron with four short [Cu—O(P) = 1.922 (2) Å and Cu–O(N) = 1.996 (2) Å] and two long Cu—O bonds [Cu—O(N) = 2.428 (2) Å]. The distortion from octahedral geometry is attributed to Jahn–Teller distortion, weak intramolecular C—H···O interactions and the small bite angle of the bidentate nitrate ligands [O—Cu—O = 57.94 (6)°]. The geometry may also be described as distorted tetrahedral by considering the nitrate ligands to be bound through a single coordination site. The N···Cu···N angle [110.89 (8)°] supports this description, but the other bond or interatom angles deviate significantly from those of the ideal polyhedron (Table 1).



(I)

The PO groups are bound to the Cu atom in a *cis* conformation. This contrasts with the *trans* configuration observed in $Cu(Ph_3PO)_2(NO_3)_2$ (Ferrari *et al.*, 1986) but is consistent with the geometry of $Ni(Cy_3PO)_2(NO_3)_2$ (Cy is cyclohexyl; Kennedy *et al.*, 1997). The Cu—O(P) and P—O bond distances are typical for coordinated phosphine oxides, *viz.* 1.923 (2)

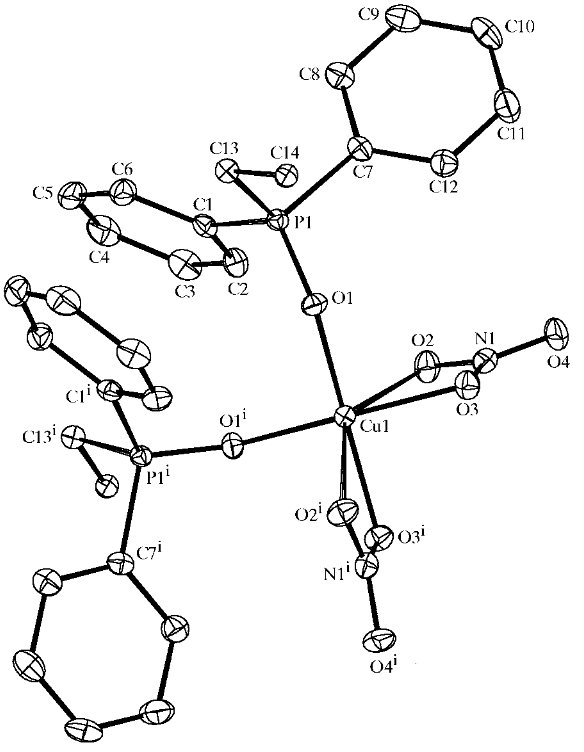


Figure 1
A view of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. [Symmetry code: (i) $-x + 1, y, -z + \frac{1}{2}$.]

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and 1.508 (2) Å compared with 1.941 (4) and 1.509 (5) Å in $Cu(Ph_3PO)_2(NO_3)_2$ (Ferrari *et al.*, 1986), and 1.967 (4) and 1.498 (5) Å in $[Cu\{(Ph_2PO)_2C_2H_4\}Br_2]_n$ (Yang *et al.*, 2000). The P—O, P—C and C—C bond lengths in (I) do not differ significantly from those of the chelating $dpppO_2$ ligand in $MoO_2Cl_2(dpppO_2)$ [1.496 (6)–1.499 (6), 1.80 (1)–1.84 (1) and 1.54 (1)–1.56 (1) Å; Oh & Mo, 1995].

The nitrate ligands are bidentate and bound asymmetrically, with Cu—O(N) distances of 1.996 (2) and 2.428 (2) Å, respectively, and this is reflected in the N—O bond lengths [1.296 (2) and 1.254 (2) Å]. The difference between the Cu—O bond lengths [0.432 (3) Å] is similar to that observed in (2-methylpyrazine)copper(II) [0.467 (5) Å; Amaral *et al.*, 2001] and intermediate between those of $Cu(Ph_3PO)_2(NO_3)_2$ [0.232 (8) Å; Ferrari *et al.*, 1986] and $[Cu(C_5H_3N_2O_2)(NO_3)(H_2O)]_n$ [0.621 (6) Å; Zheng *et al.*, 2005]. Nitrate groups on adjacent Cu atoms of the polymer are on the same side of the chain (Fig. 2). This contrasts with the $dppeO_2$ complex of $CuBr_2$ (Yang *et al.*, 2000), in which the anionic ligands display an alternating arrangement. The differences in these arrangements are accommodated by the additional C atom in the aliphatic chain of the bridging diphosphonate molecule of (I) and the conformation of the aliphatic chains. In the $dppeO_2$ ligand, the C—C bond exhibits an *anti* conformation, with the P═O bonds oriented in an antiparallel arrangement. Both C—C bonds of the aliphatic chain of the $dpppO_2$ ligand in (I) also show an *anti* conformation, but in this case the P═O bonds are arranged to produce an O═P···P═O dihedral angle of 77.7 (1)°. In the complex $MoO_2Cl_2(dpppO_2)$ (Oh & Mo, 1995), both C—C bonds adopt a *gauche* conformation to accommodate chelation. The free $dpppO_2$ ligand has been reported to crystallize as a hydrate (Calcagno *et al.*, 2000) in which the $dpppO_2$ molecule does not exhibit the twofold rotational symmetry observed in (I). In the structure of the hydrate, the alkyl chain of the hydrogen-bonded $dpppO_2$ molecule consists of one *anti* C—C bond and one *gauche* C—C bond, shifting the orientation of the P═O bonds towards the more favourable antiparallel alignment.

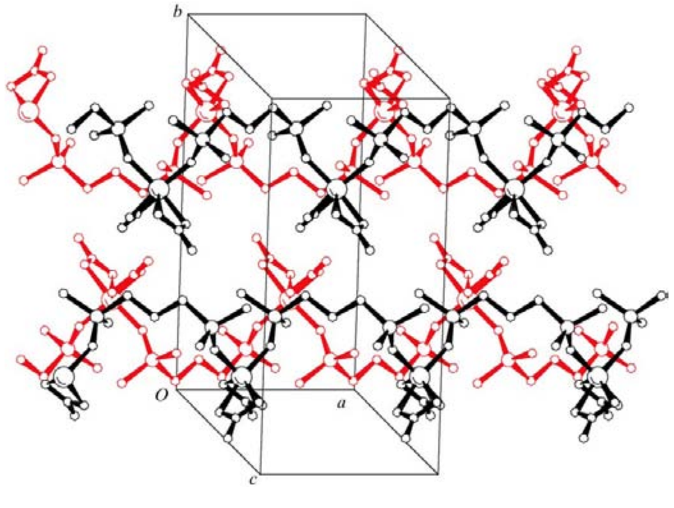

Figure 2
The packing of (I), showing polymeric chains running along the [100] direction. H atoms and phenyl groups have been omitted for clarity.

Although there are no classical hydrogen bonds in the structure of (I), there are a number of intra- and intermolecular short contacts, indicating weak C—H···O and C—H···π interactions, which may stabilize ligand conformation and regulate crystal packing. In the structure of (I), two intramolecular C—H···π interactions serve to stabilize the parallel alignment of ligands within the polymer chain. These consist of methylene–phenyl and phenyl–phenyl (edge-to-face) C—H···π interactions with H···π(centroid) distances of 2.71 and 2.73 Å, respectively. In the first of these interactions, methylene atom C13 acts as a donor, *via* atom H13*B*, to the C1–C6 ring at ($-x + 1$, y, $-z + \frac{1}{2}$), and in the second interaction, phenyl atom C3 acts as a donor, *via* atom H3, to the C7–C12 ring at ($x + 1$, y, z). The observed H···π(centroid) distances are appreciably shorter than those reported for similar interactions in a series of free and solvated alkyl bis(diphenylphosphine oxides) (2.95–3.65 Å; Calcagno *et al.*, 2000).

Intramolecular C—H···O interactions between phenyl CH groups and coordinated O atoms influence the asymmetry of the bidentate nitrate ligands, in that the C—H···O interaction corresponds to the O atom with the longer Cu—O bond. Phenyl atom C2 acts as a hydrogen-bond donor, *via* atom H2, to atom O2 within the same asymmetric unit. The C···O distance [3.462 (3) Å] is shorter and the C—H···O angle (165°) is smaller than the ranges reported for structures of alkyl bis(diphenylphosphine oxides) (3.52–3.60 Å and 169–175°; Calcagno *et al.*, 2000). Further C—H···O interactions exist between polymer chains; two phenyl C—H···O interactions [C4—H4···O4($-x + \frac{3}{2}$, $y - \frac{1}{2}$, z): 3.360 (3) Å and 148°; C9—H9···O2($x - \frac{1}{2}$, $-y + \frac{1}{2}$, $-z$): 3.391 (3) Å and 129°] and one methylene C—H···O interaction [C13—H13*A*···O4($-x + \frac{1}{2}$, $y - \frac{1}{2}$, z): 3.508 (3) Å and 152°] provide a link between the nitrate groups of one polymeric chain and two further chains. The C···O distances and C—H···O angles in (I) all fall within accepted ranges for this type of interaction (3.0–4.0 Å and 90–180°; Desiraju, 1991).

Experimental

Hot ethanol solutions of $Cu(NO_3)_2\cdot 3H_2O$ and propane-1,3-diylbis(diphenylphosphine oxide) were mixed in stoichiometric quantities. Slow evaporation of the resulting solution led to the formation of pale-blue crystals of (I).

Crystal data

$[Cu(NO_3)_2(C_{27}H_{26}O_2P_2)]$
$M_r = 631.98$
Orthorhombic, *Pbcn*
$a = 7.9585\ (1)$ Å
$b = 16.8134\ (4)$ Å
$c = 21.6220\ (5)$ Å

$V = 2893.23\ (10)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.92$ mm^{-1}
$T = 120\ (2)$ K
0.32 × 0.04 × 0.01 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.758$, $T_{max} = 0.991$

25739 measured reflections
3315 independent reflections
2783 reflections with $I > 2\sigma(I)$
$R_{int} = 0.069$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.082$
$S = 1.05$
3315 reflections
184 parameters
Only H-atom displacement parameters refined
$\Delta\rho_{\max} = 0.45$ e Å^{-3}
$\Delta\rho_{\min} = -0.53$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.9224 (15)	N1—O3	1.296 (2)
Cu1—O2	2.4279 (16)	N1—O4	1.227 (2)
Cu1—O3	1.9960 (16)	P1—O1	1.5084 (16)
Cu1—N1	2.5935 (19)	P1—C13	1.796 (2)
Cu1—P1	3.2754 (6)	C13—C14	1.532 (3)
N1—O2	1.254 (2)		
O1—Cu1—O1^{i}	94.95 (9)	O2—Cu1—O3	57.94 (6)
O1—Cu1—O2	94.54 (6)	O2—Cu1—O3^{i}	95.98 (6)
O1—Cu1—O2^{i}	109.01 (6)	O3—Cu1—O3^{i}	89.19 (9)
O1—Cu1—O3	89.41 (6)	O1—Cu1—N1	91.57 (6)
O1^{i}—Cu1—O3	166.62 (6)	O1^{i}—Cu1—N1	137.68 (6)
O2—Cu1—O2^{i}	145.14 (8)	N1^{i}—Cu1—N1	110.89 (8)

Symmetry code: (i) $-x+1, y, -z+\frac{1}{2}$.

All H atoms were located from a difference map but were ultimately refined in idealized positions (aromatic C—H = 0.95 Å and methylene C—H = 0.99 Å) and constrained to ride on their parent atoms. The H atoms of each functional group were assigned a common refined isotropic displacement parameter; final H-atom displacement parameters were 0.026 (2) (aromatic) and 0.022 (4) Å^2 (methylene).

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SNOOPI* (Davies, 1983); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *enCIFer* (Allen *et al.*, 2004); software used for structure analysis: *Mercury* (Macrae *et al.*, 2006) and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ3050). Services for accessing these data are described at the back of the journal.

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