

An unusual eight-coordinated copper complex: bis(4,7-diphenyl-1,10-phenanthroline)dinitratocopper(II)

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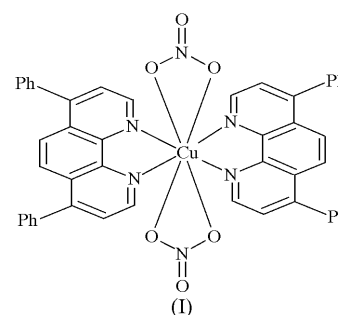
In the title monomer, $[\text{Cu}(\text{NO}_3)_2(\text{C}_{24}\text{H}_{16}\text{N}_2)_2]$, the copper(II) cation is eight-coordinate within an octahedral-like polyhedron. The coordination polyhedron is formed by two chelating diphenylphenanthroline groups that define the highly distorted CuN_4 equatorial plane and two weakly bound bidentate (chelating) nitrate groups in the apical or axial positions. The complex crystallizes in the monoclinic space group $C2/c$; a twofold axis passes through the copper(II) cation and bisects the two nitrate ligands. This gives the molecule C_2 point-group symmetry, rendering only half of the molecule independent.

Comment

Hydrothermal synthesis refers to the generation of a product by a chemical reaction in a sealed heated solution above ambient pressure. The mechanisms involved in hydrothermal processes are not yet fully understood, but the ability of this type of process to generate novel products unattainable by other methods is well known. Products of such reactions often have peculiar characteristics regarding binding affinity (Moghimi *et al.*, 2003), coordination numbers (Feng & Xu, 2001), connectivity (Walton, 2002), *etc.* An example of novel connectivity can be found, for instance, in carboxylic acid complexes of metal ions. Specifically, in high-temperature phases, carboxylic acid groups are usually multidentate and the organic ligand acts as a template during the condensation of the oxygen–metal coordination network. In contrast, carboxylic acids are preferentially monodentate at room temperature and infinite structures are normally obtained (Livage *et al.*, 2001).

Regarding copper nitrates, although there are a number of such complexes with the anion acting in a chelating mode, a

search in the November 2005 (and updates) version of the Cambridge Structural Database (CSD; Allen, 2002) revealed that the reported cases correspond to fourfold (nine cases), fivefold (27 cases), sixfold (88 cases) or even sevenfold coordination (one case) of the metal. To our knowledge, no eight-coordinate Cu^{II} complexes with chelating nitrate ions have been reported to date. We present here the first example of an eight-coordinate Cu^{II} system, specifically, a copper diphenylphenanthroline (DPP) nitrate derivative, $[\text{Cu}(\text{DPP})_2(\text{NO}_3)_2]$, (I), obtained serendipitously as a by-product of a hydrothermal synthesis (see *Experimental*). This unusual complex exhibits the unprecedented case of two chelating nitrate ligands in a rare eightfold coordination mode for the copper(II) cation.



The compound is a monomer built up around a twofold axis that passes through the metal centre, rendering only half of the whole coordination polyhedron independent. Despite the fact that the copper ion is formally linked to eight donor atoms, it exhibits a pseudo-octahedral environment in which the distorted equatorial plane is defined by four N atoms from two chelating DPP ligands, and the 'out-of-plane' positions are occupied by four O atoms from the two chelating nitrate ions. The axial nitrate ions are located on the twofold axis, which

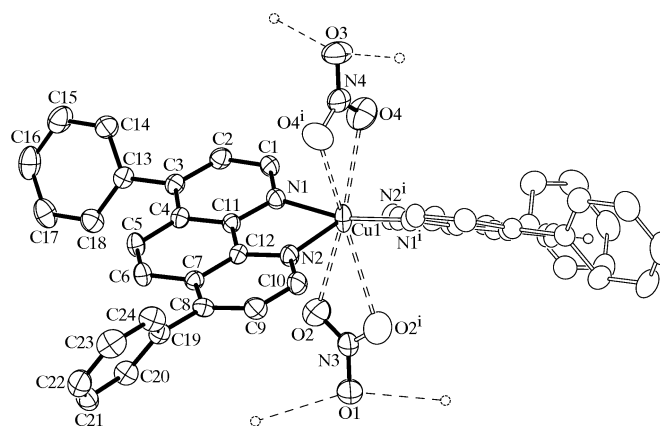


Figure 1

A view of the molecule of (I), showing the atom-numbering scheme used. Principal ellipsoids and full bonds denote the independent part of the structure; empty ellipsoids and hollow bonds represent the symmetry-generated part. Displacement ellipsoids are drawn at the 50% probability level. Double broken lines show the weak coordination of the nitrate anion; single broken lines represent hydrogen bonds for which the molecule acts as an acceptor. The symmetry codes are as in Table 1.

bisects the apical O atom of the upper and lower nitrate ligands in addition to the Cu^{II} ion. Fig. 1 shows a molecular diagram of (I), where the way in which the eightfold coordination is achieved is clearly evident.

The DPP ligands bind to the cation through four very even Cu–N bonds [distance range 2.009 (3)–2.012 (3) Å], but in a dramatically distorted fashion. Specifically, in order to alleviate conformational restraints due to steric hindrance (see below), the phenanthroline group binds in a twisted [$\Delta_1 \simeq 31.8 (1)^\circ$] as well as a slanted [$\Delta_2 \simeq 9.4^\circ$] fashion. The resulting dihedral angle between the symmetry-related coordination planes of 33.2 (1) $^\circ$ is thus significant. (Δ_1 is the angle between the N1–N2 and N1ⁱ–N2ⁱ vectors; Δ_2 is the angle between the Cu1–X1 and Cu1–X1ⁱ vectors, where X1 is the mid-point of the N1–N2 vector.)

The interaction of the copper cation with the nitrate ligands is rather weak, with the Cu–O coordination distances appearing (on first inspection) to be long enough to be borderline bonding/non-bonding. Thus, the ‘bonding’ assignment remained doubtful until bond valence calculations (Brown & Altermatt, 1985) produced values of $2 \times 0.071 = 0.142$ for the O4/O4ⁱ pair and $2 \times 0.039 = 0.078$ for the O2/O2ⁱ pair. These values are larger than the lower limit of 0.06 proposed by Liebau (2000) for a cation–donor contact to be considered as a weak bonding interaction. Despite the two nitrate coordination interactions being weak, their internal bond lengths do reflect the effect of their involvement upon coordination. Thus, nitrate atom N3, with its considerably weaker bond valence (2×0.039), exhibits perfect resonance in its double bond such that the three N–O distances are indistinguishable. Nitrate atom N4, instead, is involved in a slightly stronger interaction (the bond valence is 2×0.071) and shows some localization of the double bond between N4 and O3, the uncoordinated apical O atom of the nitrate ion.

The position of the coordinated nitrate groups seems to be a compromising equilibrium between the attractive force to the metal centre and the steric hindrance or repulsion produced by the DPP N atoms. The relative orientation of the chelating anions (they coordinate almost orthogonal to each other, their planes being rotated by 76.6 $^\circ$) and the twisting of the coordination planes of both DPP groups seems to be the way in which the system achieves such a balance. This is clearly seen if we compare the distances between the coordinated nitrate O [O2, O2ⁱ, O4 and O4ⁱ; symmetry code: (i) $-x, y, -z + \frac{1}{2}$] and the basal N atoms (N1, N1ⁱ, N2 and N2ⁱ). If only these atoms are considered then each (coordinated) nitrate O atom is located at the apex of a triangular pyramid having three of these N atoms as the base, at very similar distances to the apex (3.04–3.16 Å). This ‘equilibrium’ situation contrasts with what would have been the case if no twisting were present, in which case two of these N atoms would appear 3.30–3.45 Å away, but the third would be within van der Waals contact (2.55–2.80 Å). The angle between the DPP coordination planes is 39.9 (1) $^\circ$, and this represents the largest deformation we could trace in the equatorial plane of an octahedral-like copper polyhedron.

Although there are cases of nitrate ligands chelating a copper cation in the literature, there are no examples of such a

clear ‘bifurcated’ apical behaviour, with the whole ligand acting as a unique entity for coordination purposes. The cases surveyed in the CSD usually display extremely distorted cationic environments owing to the small bite angle of the anion, which is often in the range 72–75 $^\circ$. (Approximate octahedral or square-planar coordination geometries for Cu^{II} have expected L–Cu–L bond angles of 90 $^\circ$.) In the case of (I), the nitrate bite angle is much smaller (Table 1) and supports the view that the chelate acts as an effective single apical bond. On the other hand, the large ‘equatorial’ distortions in (I) are due to ‘inter-ligand’ steric hindrance (bumping) rather than ‘intra-ligand’ limitations (small bite angle). Although the cause of this deformation is clear (*viz.* the interaction with the chelating apical donors), the subtle reasons leading to preferred bidentate binding of the nitrate ions over simple monodentate coordination are not. Perhaps some theoretical calculations on the preferred denticity of the nitrate ions in (I) will be needed to elucidate this point. It is possible that the severe conditions employed during the hydrothermal synthesis of (I) might play a decisive role in the stabilization of such an uncommon coordination polyhedron for Cu^{II}.

The monomers interact with each other through two non-conventional C–H \cdots O bonds (Table 2) involving both non-coordinating nitrate O atoms. As the latter are located on special positions (a twofold axis), the interaction is mirrored and the result is a bridge between two molecules having the O atom as the common acceptor. Fig. 1 shows the way in which both bonds act roughly at right angles to one another. As expected for a system cluttered with aromatic rings, some π – π and C–H \cdots π interactions are also present (Table 3). They involve both pendant phenyl rings, which in (I) appear more prone than their phenanthroline counterparts to these types of interactions owing to their protruding character and their rotational freedom. This allows the substituent phenyl rings to adapt to packing constraints, leading to significant deviations from the planar phenanthroline core [dihedral angles of 50.3 (1) and 57.9 (1) $^\circ$], to the extent that they end up being almost perpendicular to each other [a dihedral angle of 81.8 (1) $^\circ$].

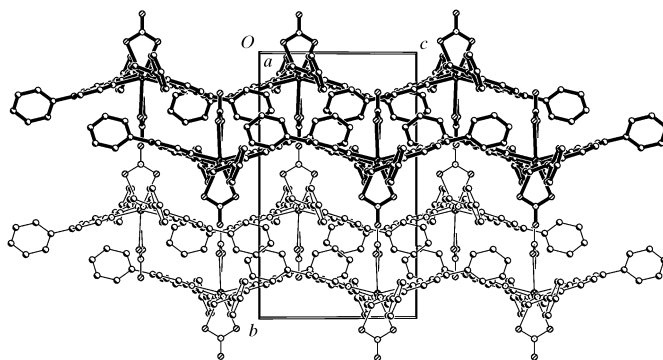


Figure 2
Packing view down the *a* axis, showing a cross-section of the layers stacked along the *b* axis.

Both the C5—H5···O1ⁱⁱ hydrogen bond and the π interactions presented in Table 3 facilitate the formation of weakly bonded 'corrugated' planes parallel to (101) (Fig. 2). In turn, the stacking along the *b* axis of the latter two-dimensional structures to form the three-dimensional arrangement in the structure is mainly stabilized by the remaining C9—H9···O3ⁱⁱⁱ hydrogen bond.

Experimental

The original scope of the synthesis was to obtain a hybrid organic-inorganic compound, that is, one with an inorganic structure host (\cdots P—O—V \cdots) and a copper(II) phenanthroline complex as guest (Feng & Xu, 2001). In the process of adjusting the hydrothermal synthesis conditions to obtain the hybrid compound, the title eight-coordinate copper(II) complex was obtained serendipitously. For the synthesis of (I), a mixture of Cu(NO₃)₂·3H₂O (0.5 mmol), V₂O₅ (0.25 mmol), 4,7-DPP (1.0 mmol), H₃PO₄ (5 ml, 0.0087 mmol) and Zn (0.5 mmol) was sealed in a Teflon-lined acid digestion bomb and heated at 393 K for 6 d under autogenous pressure, followed by slow cooling to room temperature. The resulting solid product consisted of pale-green crystals of the title compound.

Crystal data

[Cu(NO ₃) ₂ (C ₂₄ H ₁₆ N ₂) ₂]	<i>Z</i> = 4
<i>M_r</i> = 852.34	<i>D_x</i> = 1.492 Mg m ⁻³
Monoclinic, <i>C2/c</i>	Mo <i>K</i> α radiation
<i>a</i> = 20.337 (2) Å	μ = 0.64 mm ⁻¹
<i>b</i> = 17.7445 (18) Å	<i>T</i> = 298 (2) K
<i>c</i> = 12.7349 (13) Å	Block, pale green
β = 124.350 (2)°	0.22 × 0.16 × 0.14 mm
<i>V</i> = 3794.2 (7) Å ³	

Data collection

Bruker SMART CCD area-detector diffractometer	13919 measured reflections
φ and ω scans	4281 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2001)	2759 reflections with <i>I</i> > 2σ(<i>I</i>)
<i>T</i> _{min} = 0.86, <i>T</i> _{max} = 0.92	<i>R</i> _{int} = 0.070
	θ _{max} = 28.1°

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0549P)^2 + 1.6794P]$
$R[F^2 > 2\sigma(F^2)] = 0.066$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.140$	(Δ/σ) _{max} < 0.001
<i>S</i> = 1.06	$\Delta\rho$ _{max} = 0.45 e Å ⁻³
4281 reflections	$\Delta\rho$ _{min} = -0.27 e Å ⁻³
278 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

Cu1—N1	2.009 (3)	N3—O1	1.232 (6)
Cu1—N2	2.012 (3)	N3—O2	1.233 (4)
Cu1—O4	2.634 (3)	N4—O3	1.226 (5)
Cu1—O2	2.847 (3)	N4—O4	1.238 (3)
N1—Cu1—N1 ⁱ	166.56 (15)	O4—Cu1—O4 ⁱ	47.43 (12)
N2—Cu1—N2 ⁱ	152.17 (16)	O2—Cu1—O2 ⁱ	43.77 (13)

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

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C5—H5···O1 ⁱⁱ	0.93	2.51	3.295 (4)	142
C9—H9···O3 ⁱⁱⁱ	0.93	2.51	3.323 (4)	146

Symmetry codes: (ii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (iii) $-x, -y, -z + 1$.

Table 3

Key π — π and C—H··· π contacts (Å, °) in (I).

ccd is the centre-to-centre distance, sa the (mean) slippage angle, ipd the (mean) interplanar distance, Cg4 the centroid of the C13–C18 ring and Cg5 the centroid of the C19–C24 ring.

<i>Cg</i> ··· <i>Cg</i>	ccd	sa	ipd
<i>Cg</i> 4··· <i>Cg</i> 4 ^{iv}	4.245 (2)	35.70	3.45
<i>Cg</i> 5··· <i>Cg</i> 5 ^v	3.815 (3)	20.10	3.58
C23—H23··· <i>Cg</i> 4 ^{vi}	2.86	13.02	2.82

Symmetry codes: (iv) $-x + 1, -y, -z + 1$; (v) $-x + 1/2, -y + 1/2, -z + 2$; (vi) *x, y, z + 1*.

H atoms were placed at calculated positions (C—H = 0.93 Å) and allowed to ride on their parent C atoms [*U*_{iso}(H) = 1.2*U*_{eq}(C)].

Data collection: SMART-NT (Bruker, 2001); cell refinement: SAINT-NT (Bruker, 2000); data reduction: SAINT-NT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL-NT (Sheldrick, 2000); software used to prepare material for publication: SHELXTL-NT and PLATON (Spek, 2003).

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