catena-Poly[[[bis(2-pyridyl) ketone-*N*,*N'*]-copper(II)]-di-μ-chloro]

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Abstract

The crystal structure of the title compound, [CuCl$_2$-(C$_{11}$H$_8$N$_2$O)]$_n$, has been determined at room temperature. The structure consists of dimeric [Cu$_2$Cl$_4$(DPK)$_2$] units [DPK is bis(2-pyridyl) ketone] arranged in linear chains along the *b*-axis direction. Each Cu atom is surrounded by a distorted octahedral arrangement of two N atoms from a DPK ligand and four Cl atoms, two of which are at appreciably longer distances. Comparisons with the related compound [CuCl$_2$(2,2-bipyridine)]$_n$ are reported.

Comment

It is known that Cu^{II} coordination compounds adopt many different stereochemical forms. Even with simple ligands, a wide range of geometries is obtained (Cotton & Wilkinson, 1988). The same versatility can be ascribed to bis(2-pyridyl) ketone (DPK) when it acts as a ligand in a metal ion coordination complex. The title compound, [CuCl$_2$(DPK)]$_n$, (I), was prepared and its structure solved in the triclinic *P*$\bar{1}$ space group. The asymmetric unit formally contains [CuCl$_2$(DPK)], but examination of the structure reveals that translation of a centrosymmetric [Cu$_2$Cl$_4$(DPK)$_2$] dimer along the *b* axis leads to a polymeric form in the crystalline state.

(I)
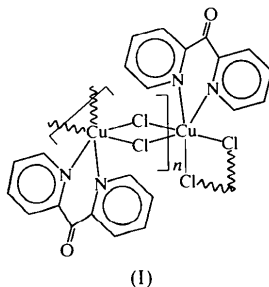
The compound has a polymeric linear structure based on dimeric units (Fig. 1). Metallic centers are joined by two Cl bridges and are surrounded by a tetragonally distorted octahedral environment. Each dimeric unit consists of a pair of octahedra sharing one edge defined by one chloride ligand (Cl1) and its symmetry equivalent across an inversion center. A basal plane in each octahedron contains one Cu atom, two N atoms belonging to the same DPK ligand molecule and two chlorines, one involved in bridging the monomeric units of the dimer (Cl1) and the other involved in bridging the translational repeats of the dimers required for polymerization (Cl2). The two apical positions of each Cu center are occupied by one proximal bridging chlorine (Cl1) and the more distant Cl atom shared with the next unit of the polymer.
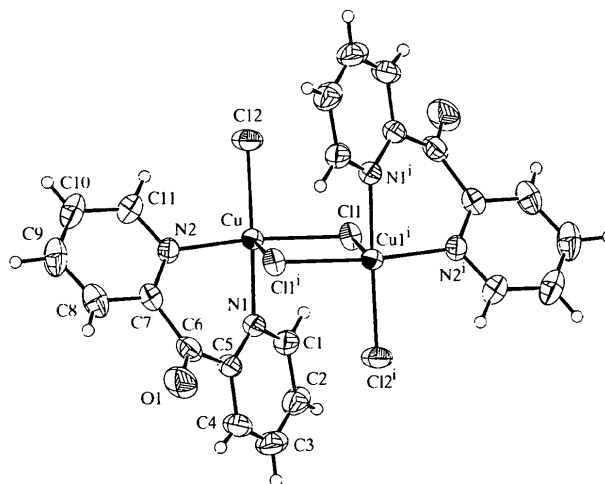

Fig. 1. *ZORTEP* drawing (Zsolnai & Pritzkow, 1995) showing one [Cu$_2$(DPK)$_2$Cl$_4$] dimeric unit with the atom-labeling scheme. All displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by spheres of arbitrary radii. [Symmetry code: (i) 1 − *x*, 2 − *y*, 1 − *z*.]

Within the basal plane of the Cu centers, the Cu—Cl distances are 2.3010 (8) and 2.2665 (7) Å, and the Cu—N distances are 2.027 (2) and 2.039 (2) Å; these values are close to normal bonding distances reported in the literature for similar compounds (Bakker *et al.*, 1971; Wang *et al.*, 1986; Garland *et al.*, 1988; Basu *et al.*, 1998). The longer bond distances to the apical Cl atoms are 2.7511 (9) Å [Cu—Cl1^i; symmetry code: (i) 1 − *x*, 2 − *y*, 1 − *z*], which is internal to the dimer, and 3.1325 (11) Å [Cu—Cl2^{ii}; symmetry code: (ii) 1 − *x*, 2 − *y*, −*z*] to the Cl atom of the next dimeric unit. Inside each dimeric unit, a Cu···Cu^i distance of 3.6599 (11) Å is found. The distance between Cu atoms of consecutive units is 4.0974 (10) Å (Cu···Cu^{ii}). This is consistent with a description of the structure as a polymer of

translationally repeating dimeric units. In contrast, the crystal structure of the previously studied compound [CuCl₂(2,2-bipyridine)]ₙ [(II); Garland *et al.*, 1988] shows the formation of linear chains of monomers, instead of the dimers observed in the present case.

The basal plane of the octahedron is slightly distorted from planarity, with displacements of 0.2375 (9), -0.2004 (9), -0.1809 (8) and 0.1958 (8) Å for atoms N1, N2, Cl1 and Cl2, respectively. The Cu atom is displaced by -0.0520 (7) Å in the direction of the Cl1^i atom. Angles between *cis* atoms bonded to the Cu center are between 82.56 (3) and 104.87 (3)°, deviating from the 90° angle expected for a regular octahedron of donor atoms. These distortions arise from the steric requirements of the DPK ligand with the two N atoms belonging to a chelate ring. The crystal structure of free DPK (Garland *et al.*, 1986) is almost planar, with the ketone C atom maintaining a trigonal geometry and the planar pyridine rings forming a dihedral angle of about 8°. In this complex, the ketone group of DPK is unchanged after coordination, but the dihedral angle between the pyridine rings is 44.22 (12)°, thereby aligning the coordination positions of the N atoms with the Cu center. As a consequence, the chelate N—Cu—N angle is 87.28 (9)°, adding almost no strain to the chelate ring. The C5—C6 and C6—C7 distances [1.506 (4) and 1.503 (4) Å, respectively] appear to be long for Csp^2— Csp^2 single bonds (1.46 Å). This is a consequence of the bending of the pyridine rings which inhibits the delocalization of π-electrons of each ring through the entire molecule. Deveson *et al.* (1996) have observed the same effect in *catena*-[(μ_2-nitrato-O,O')-[bis(2-pyridyl) ketone](nitrato-O)copper(II)]. All other interatomic distances and angles in the ligand show no significant deviations from free ligand values.

The dimeric chains along the c axis (Fig. 2) show a 'zigzag' distribution of Cu atoms, with a Cu^i···Cu···Cu^{ii} angle of 141.007 (19)°. Although structure (II) shows the differences mentioned above, the equivalent Cu···Cu···Cu angle has a value of 143.31 (2)°.

There is an interaction between equivalent N2-containing pyridine rings of symmetry-related molecules [at $(-x, 2-y, -z)$ and $(2-x, -y, 2-z)$] belonging to two parallel chains. The perpendicular distance between rings is 3.651 Å and the distance between ring centroids is 4.064 Å; Fig. 2 shows this interaction.

Experimental

CuCl₂ and DPK (1:1 stoichiometric ratio) were dissolved in anhydrous acetonitrile. The resulting green solution was evaporated slowly at room temperature. After 5 d, green needle-shaped crystals of suitable size for data collection had appeared.

Crystal data

[CuCl₂(C₁₁H₈N₂O)]	Mo $K\alpha$ radiation
$M_r = 318.65$	$\lambda = 0.71069$ Å
Triclinic	Cell parameters from 24
$P\bar{1}$	reflections
$a = 8.7543$ (11) Å	$\theta = 20.15$–$24.58°$
$b = 9.9307$ (15) Å	$\mu = 2.330$ mm^{-1}
$c = 7.3140$ (16) Å	$T = 293$ (2) K
$\alpha = 108.537$ (14)°	Needle
$\beta = 106.347$ (14)°	0.35 × 0.10 × 0.10 mm
$\gamma = 85.225$ (12)°	Green
$V = 578.48$ (17) Å^3	
$Z = 2$	
$D_x = 1.829$ Mg m^{-3}	
D_m not measured	

Data collection

Rigaku AFC-7S diffractometer	2356 reflections with $I > 2\sigma(I)$
$\theta/2\theta$ scans	$R_{int} = 0.049$
Absorption correction:	$\theta_{max} = 27.5°$
ψ scan (Molecular	$h = -5 \rightarrow 11$
Structure Corporation,	$k = -12 \rightarrow 12$
1993)	$l = -9 \rightarrow 9$
$T_{min} = 0.496$, $T_{max} = 0.800$	3 standard reflections
2944 measured reflections	every 150 reflections
2669 independent reflections	intensity decay: none

Refinement

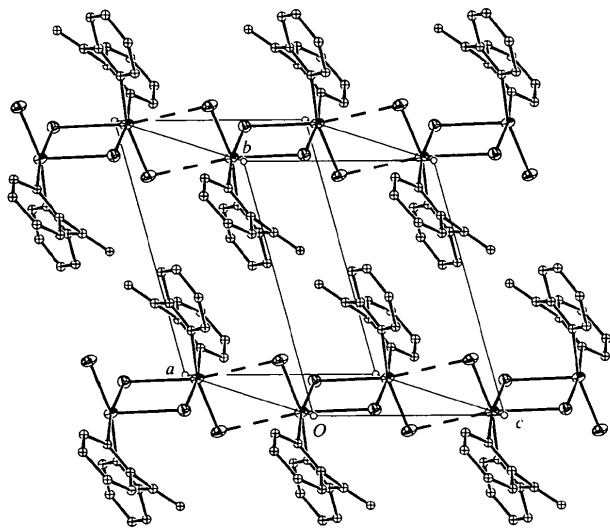|	
Refinement on F^2	$(\Delta/\sigma)_{max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.032$	$\Delta\rho_{max} = 0.434$ e Å^{-3}
$wR(F^2) = 0.096$	$\Delta\rho_{min} = -0.684$ e Å^{-3}
$S = 1.035$	Extinction correction: none

Fig. 2. A unit-cell packing diagram of (I). Note that chains are along the c-axis direction and interactions are between parallel pyridine rings. H atoms have been excluded for clarity.

2669 reflections
186 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0347P)^2 + 0.3555P]$
where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from
International Tables for
Crystallography (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Cu—N1	2.027 (2)	Cu—Cl1	2.3010 (8)
Cu—N2	2.039 (2)	Cu—Cl1^i	2.7511 (9)
Cu—Cl2	2.2665 (7)	Cu—Cl2^{ii}	3.1325 (11)
N1—Cu—N2	87.28 (9)	Cl2—Cu—Cl1^i	102.48 (3)
N1—Cu—Cl2	165.46 (7)	Cl1—Cu—Cl1^i	87.59 (3)
N2—Cu—Cl2	94.90 (6)	N1—Cu—Cl2^{ii}	83.48 (6)
N1—Cu—Cl1	88.87 (6)	N2—Cu—Cl2^{ii}	82.66 (6)
N2—Cu—Cl1	171.11 (6)	Cl2—Cu—Cl2^{ii}	82.56 (3)
Cl2—Cu—Cl1	90.82 (3)	Cl1—Cu—Cl2^{ii}	104.87 (3)
N1—Cu—Cl1^i	92.03 (6)	Cl1^i—Cu—Cl2^{ii}	166.61 (2)
N2—Cu—Cl1^i	84.53 (6)	Cu—Cl1—Cu^i	92.41 (3)

Symmetry codes: (i) $1 - x, 2 - y, 1 - z$; (ii) $1 - x, 2 - y, -z$.

Refined C—H distances are in the range 0.84 (3)–0.97 (3) Å.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *MSC/AFC Diffractometer Control Software*. Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ZORTEP* (Zsolnai & Pritzkow, 1995). Software used to prepare material for publication: *PLATON* (Spek, 1990).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1092). Services for accessing these data are described at the back of the journal.

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Tris(1,10-phenanthroline)nickel(II) dinitrate thiourea monohydrate

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Abstract

The structure of the first nickel coordination complex with 1,10-phenanthroline (phen) containing thiourea as a cocrystallization molecule is reported. The title compound, $[Ni(C_{12}H_8N_2)_3](NO_3)_2 \cdot CH_4N_2S \cdot H_2O$, crystallizes in the centrosymmetric space group $C2/c$. The crystal structure is formed by $[Ni(phen)_3]^{2+}$ cations, water and thiourea molecules positioned on a twofold axis, with the nitrate anions in general positions. The packing is directed by electrostatic interactions, stacking of phen molecules and hydrogen bonds between the crystallization molecules and the nitrate anions.

Comment

This work reports the crystal structure of the compound tris(1,10-phenanthroline)nickel(II) dinitrate thiourea monohydrate, (I). The structure is composed of

(I)
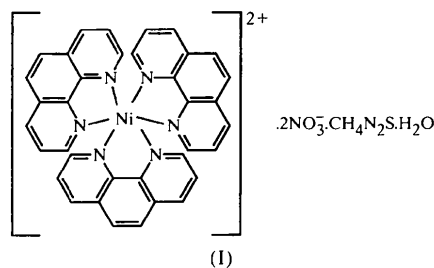
$[Ni(phen)_3]^{2+}$ cations, two nitrate anions, one water and one thiourea molecule per cation. Although the presence of thiourea has been reported in other cocrystal structures, there are no reports of its cocrystallization with phen or with other nickel complexes. The crystal structure is properly described in the centrosymmetric space group $C2/c$ with the asymmetric unit comprising half of the $[Ni(phen)_3]^{2+}$ cationic complex, half of the cocrystallization solvates and one independent nitrate anion. The Ni atom, as well as the O51, C31 and S31 atoms, are positioned on a twofold axis of symmetry to maintain the necessary 1:2 cation–anion ratio. Tris(1,10-