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catena-Poly[{di- μ -nitrate-1:2 κ^4 O-bis[(triphenylphosphine-*P*)copper(I)]- μ -4,4'-bipyridyl-*N:N'*] Tetrahydrofuran Solvate

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Abstract

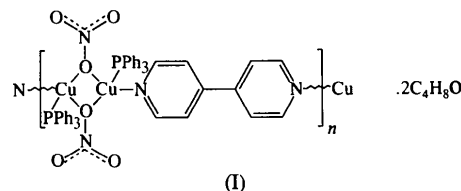
A copper(I) complex with triphenylphosphine and 4,4'-bipyridine results in a one-dimensional polymer, $\{[\text{Cu}_2(\text{NO}_3)_2(\text{C}_{18}\text{H}_{15}\text{P})_2(\text{C}_{10}\text{H}_8\text{N}_2)] \cdot 2\text{C}_4\text{H}_8\text{O}\}_n$. The Cu centers are alternately bridged by nitrate counterions and bipyridine ligands. The four-membered Cu₂O₂ ring lies on an inversion center ($\frac{1}{2}-x, \frac{1}{2}-y, -z$) and the bipyridyl ligand lies on another inversion center ($\frac{1}{2}-x, \frac{3}{2}-y, -z$). The triphenylphosphine ligand coordinates to copper providing a distorted tetrahedral coordination environment, with bond lengths Cu1—P 2.168 (1), Cu—N 2.013 (3) and Cu—O 2.177 (2) and 2.147 (2) Å. The cavities between the chains contain tetrahydrofuran solvent molecules.

Comment

Copper(I) complexes of 4,4'-bipyridine have been studied with regard to the construction of supramolecular networks (MacGillivray, Subramanian & Zaworotko,

1994; Yaghi & Li, 1995). Copper(I) is an interesting metal to study due to its well defined tetrahedral coordination geometry, high lability, and potential catalytic and magnetic capabilities (Cotton & Wilkinson, 1988). A study was initiated on the role of the counterion and ancillary ligand on the network motif.

The X-ray analysis of the crystal that resulted from the complexation of nitratobis(triphenylphosphine)copper(I) with 4,4'-bipyridine in tetrahydrofuran, (I), shows that the copper(I) ions are linked by bridging nitrate anions and 4,4'-bipyridine ligands to form stair-step undulating polymer chains.



Copper(I) adopts a distorted tetrahedral geometry, with one bond to triphenylphosphine, one to 4,4'-bipyridine and two to separate bridging nitrate O atoms (Fig. 1). The tetrahydrofuran solvent molecule is disordered over two positions and occupies the space between the triphenylphosphine ligands and adjacent chains. The four-membered Cu₂O₂ ring lies about an inversion center ($\frac{1}{2}-x, \frac{1}{2}-y, -z$) and the bipyridyl ligand lies on another inversion center ($\frac{1}{2}-x, \frac{3}{2}-y, -z$). The chains run along the *b* axis and stack along a twofold screw axis antiparallel to one another (Fig. 2).

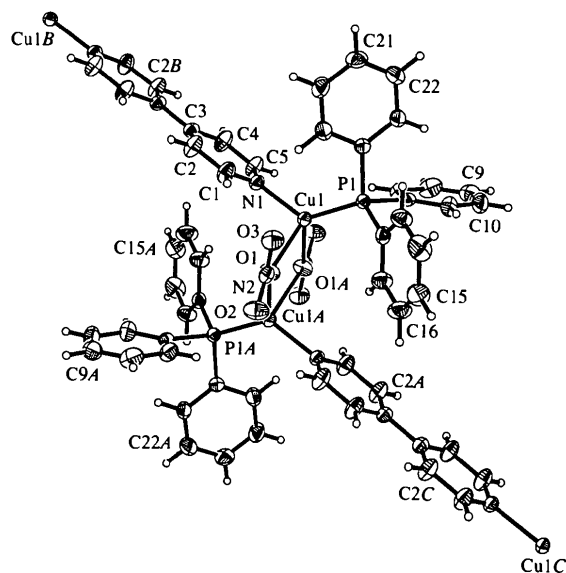


Fig. 1. An ORTEP (Johnson, 1971) view of (I) showing 50% probability displacement ellipsoids for non-H atoms and circles of arbitrary size for H atoms. Symmetrically related equivalent positions for A, B and C are ($\frac{1}{2}-x, \frac{1}{2}-y, -z$), ($\frac{1}{2}-x, \frac{1}{2}-y, -z$) and ($x, y-1, z$), respectively.

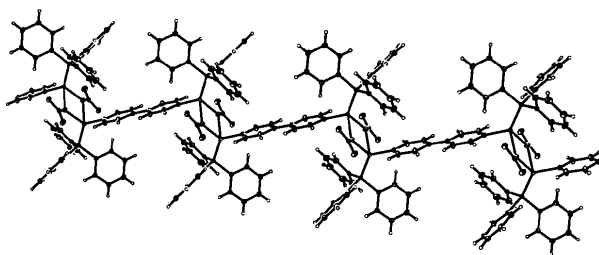


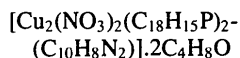
Fig. 2. A one-dimensional polymer with copper(I) centers alternately bridged by nitrate counterions and 4,4'-bipyridine ligands. The triphenylphosphine ligand and nitrate anion bound to copper(I) reduce the dimensionality of the network.

The title structure illustrates that strongly coordinated ancillary ligands and counteranions can affect network topology with respect to 4,4'-bipyridine. Maximum network dimensionality, when each of the tetrahedral sites on the copper(I) are bound to networking 4,4'-bipyridine ligands, is obtained when 4,4'-bipyridine is crystallized with $\text{Cu}^+(\text{CH}_3\text{CN})_4\text{PF}_6$ (MacGillivray, Subramanian & Zaworotko, 1994). This is a result of the non-coordinating propensity of PF_6^- . Yet the network dimensionality of the structure formed by copper(I) and 4,4'-bipyridine in the presence of strongly coordinating triphenylphosphine and nitrate groups is reduced to two-dimensional chains. The dimensionality of network structures therefore depends significantly on the tendency of the counteranions and ancillary ligands to coordinate to the metal.

Experimental

$[\text{Cu}(\text{PPh}_3)_2(\text{NO}_3)]$ was prepared according to the reported procedure of Gysling & Kubas (1979). A solution of 4,4'-bipyridine (0.0194 g, 0.124 mmol) and $[\text{Cu}(\text{PPh}_3)_2(\text{NO}_3)]$ (0.0126 g, 0.019 mmol) in tetrahydrofuran (15 ml) was mixed in a glove box under nitrogen. The resulting clear and colorless solution on standing for four days resulted in light-yellow crystals. The density D_m was measured by flotation in hexane/carbon tetrachloride solution.

Crystal data



$M_r = 538.02$

Monoclinic

$C2/c$

$a = 29.282(6) \text{ \AA}$

$b = 12.478(2) \text{ \AA}$

$c = 14.476(3) \text{ \AA}$

$\beta = 107.43(3)^\circ$

$V = 5046.4(17) \text{ \AA}^3$

$Z = 8$

$D_x = 1.416 \text{ Mg m}^{-3}$

$D_m = 1.38 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 9.61\text{--}11.81^\circ$

$\mu = 0.965 \text{ mm}^{-1}$

$T = 198(2) \text{ K}$

Rectangular

$0.34 \times 0.32 \times 0.14 \text{ mm}$

Transparent yellow

Data collection

Enraf-Nonius CAD-4 diffractometer

ω - θ scans

Absorption correction:

by integration from crystal shape (Sheldrick, 1990)

$T_{\min} = 0.749$, $T_{\max} = 0.881$

4128 measured reflections

3945 independent reflections

3049 observed reflections

$[I > 2\sigma(I)]$

$R_{\text{int}} = 0.0341$

$\theta_{\text{max}} = 23.97^\circ$

$h = -31 \rightarrow 33$

$k = 0 \rightarrow 14$

$l = -16 \rightarrow 0$

3 standard reflections

monitored every 97

reflections

frequency: 90 min

intensity decay: 0.6%

Refinement

Refinement on F^2

$R(F) = 0.0379$

$wR(F^2) = 0.1042$

$S = 1.069$

3945 reflections

362 parameters

H-atom parameters refined as riding

$w = 1/[\sigma^2(F_o^2) + (0.0569P)^2 + 7.293P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.066$

$\Delta\rho_{\text{max}} = 0.604 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.254 \text{ e \AA}^{-3}$

Extinction correction: none

Atomic scattering factors

from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

	x	y	z	U_{eq}
Cu1	0.300723 (13)	0.32025 (3)	0.06257 (3)	0.02616 (14)
P1	0.36473 (3)	0.25297 (6)	0.16305 (6)	0.0228 (2)
N2	0.22888 (9)	0.2396 (2)	0.1572 (2)	0.0262 (6)
O1	0.23326 (8)	0.2566 (2)	0.07334 (15)	0.0310 (5)
O2	0.19715 (10)	0.1796 (2)	0.1656 (2)	0.0455 (7)
O3	0.25656 (9)	0.2871 (2)	0.2267 (2)	0.0385 (6)
N1	0.28133 (9)	0.4747 (2)	0.0360 (2)	0.0272 (6)
C1	0.25996 (13)	0.5262 (3)	0.0923 (3)	0.0385 (9)
C2	0.24707 (14)	0.6330 (3)	0.0802 (3)	0.0387 (9)
C3	0.25643 (11)	0.6927 (2)	0.0080 (2)	0.0252 (7)
C4	0.27914 (14)	0.6387 (3)	-0.0500 (3)	0.0369 (9)
C5	0.29062 (14)	0.5317 (3)	-0.0338 (2)	0.0357 (8)
C6	0.40950 (11)	0.2024 (2)	0.1084 (2)	0.0248 (7)
C7	0.41132 (13)	0.2485 (3)	0.0227 (3)	0.0365 (8)
C8	0.4455 (2)	0.2160 (3)	-0.0194 (3)	0.0467 (10)
C9	0.47777 (14)	0.1367 (3)	0.0229 (3)	0.0441 (10)
C10	0.47520 (13)	0.0888 (3)	0.1062 (3)	0.0440 (10)
C11	0.44113 (12)	0.1210 (3)	0.1491 (2)	0.0345 (8)
C12	0.35735 (11)	0.1411 (3)	0.2382 (2)	0.0263 (7)
C13	0.38138 (13)	0.1332 (3)	0.3369 (3)	0.0380 (9)
C14	0.37587 (14)	0.0435 (3)	0.3884 (3)	0.0491 (10)
C15	0.34646 (14)	-0.0384 (3)	0.3433 (3)	0.0492 (10)
C16	0.32249 (14)	-0.0318 (3)	0.2461 (3)	0.0479 (10)
C17	0.32753 (13)	0.0582 (3)	0.1940 (3)	0.0364 (8)
C18	0.39801 (11)	0.3506 (2)	0.2512 (2)	0.0249 (7)
C19	0.37226 (12)	0.4292 (3)	0.2825 (3)	0.0355 (8)
C20	0.39570 (13)	0.5042 (3)	0.3504 (3)	0.0408 (9)
C21	0.44478 (13)	0.5034 (3)	0.3870 (3)	0.0402 (9)
C22	0.47051 (13)	0.4269 (3)	0.3554 (3)	0.0411 (9)
C23	0.44735 (12)	0.3503 (3)	0.2892 (3)	0.0339 (8)
O4C†	0.5473 (9)	0.2079 (19)	-0.1200 (20)	0.112 (6)
C25C†	0.5673 (11)	0.3019 (19)	-0.0677 (16)	0.100 (7)
C26C†	0.5841 (10)	0.3615 (15)	-0.1416 (16)	0.097 (7)
C27C†	0.6061 (9)	0.2711 (19)	-0.1827 (16)	0.096 (5)
C28C†	0.5716 (10)	0.1823 (19)	-0.1872 (17)	0.113 (7)

O4D‡	0.5590 (7)	0.1900 (11)	-0.1014 (16)	0.112 (5)
C25D‡	0.5498 (6)	0.3052 (12)	-0.1053 (15)	0.094 (5)
C26D‡	0.5933 (6)	0.3475 (11)	-0.1157 (16)	0.107 (6)
C27D‡	0.6144 (6)	0.2610 (16)	-0.1601 (16)	0.123 (6)
C28D‡	0.5874 (7)	0.1710 (11)	-0.1596 (15)	0.121 (5)

† Occupancy of 0.40 (2). ‡ Occupancy of 0.60 (2).

Table 2. Selected geometric parameters (Å, °)

Cu1—N1	2.013 (3)	Cu1—O1	2.177 (2)
Cu1—O1 ⁱ	2.147 (2)	C3—C3 ⁱⁱ	1.480 (6)
Cu1—P1	2.1680 (11)		
N1—Cu1—O1 ⁱ	103.05 (10)	N1—Cu1—O1	98.77 (10)
N1—Cu1—P1	129.54 (8)	O1 ⁱ —Cu1—O1	73.82 (9)
O1 ⁱ —Cu1—P1	120.80 (7)	P1—Cu1—O1	115.56 (7)

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} - y, -z$; (ii) $\frac{1}{2} - x, \frac{3}{2} - y, -z$.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *CAD-4 Software*, *PROFILE* (Blessing, Coppens & Becker, 1974). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1971). Software used to prepare material for publication: *CIFTAB* in *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: FG1111). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(Cyclohexylamine-*N*){2-[(2-thiophenyl)iminomethyl]phenolato-*O,N,S*}nickel(II)

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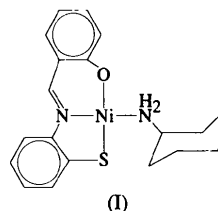
(Received 28 November 1995; accepted 13 May 1996)

Abstract

The crystal of the title compound is composed of discrete neutral [Ni(C₁₃H₉NOS)(C₆H₁₃N)] molecules. The Ni ion has a distorted square-planar coordination. The bond distances between the Ni atom and the donor N2, S1, N1 and O1 atoms are 1.948 (5), 2.148 (2), 1.874 (5) and 1.845 (5) Å, respectively. Although the bond angles around the Ni atom range from 83.4 (2) to 96.1 (2)°, their sum is 360.1°. The cyclohexyl ring is disordered.

Comment

N-(2-Hydroxyphenyl)salicylaldimine and its thio derivatives are interesting tridentate ligands. With metals of the first transition series such as Fe²⁺, Ni²⁺, Cu²⁺ and Co²⁺, these ligands form bridged dimeric complexes which have been the subject of attention from coordination chemists. If amine is present in the reaction, Ni²⁺ alone of these ions has a tendency to form mononuclear square-planar complexes instead of dimers. The crystal structures of Ni²⁺-Schiff base complexes with different ligands and amines have been reported previously (Elerman, Fuess & Paulus, 1991; Soriano-García, Toscano, Valdés-Martínez & Fernández-G., 1985; Elerman, Paulus & Fuess, 1991; Kabak, Elerman, Özbey & Atakol, 1995). We report here a new mononuclear Ni²⁺ complex, (cyclohexylamine-*N*){2-[(2-thiophenyl)iminomethyl]phenolato-*O,N,S*}nickel(II), (I).



The structure consists of discrete [Ni(C₁₃H₉NOS)-(C₆H₁₃N)] molecules (Fig. 1). The Ni²⁺ ion is located in a slightly distorted square-planar environment.