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Di-μ-isocyanato-bis[isocyanato(1,10-phenanthroline)copper(II)]

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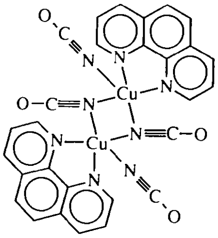
Abstract

The structure of blue $[Cu_2(NCO)_4(C_{12}H_8N_2)_2]$ consists of $[Cu(NCO)_2(phen)]$ subunits (phen is 1,10-phenanthroline) in a distorted planar arrangement, the subunits existing in centrosymmetrically related pairs in the crystal packing. The subunits have a distorted four-coordinate square-planar arrangement of N atoms about the central Cu atom; pairs of these $[Cu(NCO)_2(phen)]$ subunits form dimers by interaction of the fifth position on each Cu center with an N atom of an isocyanate ligand of the associated subunit. The coordination around each Cu atom is best described as distorted square-pyramidal.

Comment

The crystal structure of $[Cu(NCS)_2(phen)]$ (Parker & Breneman, 1993) has been shown to contain an infinite linear chain of NCS^--bridged Cu atoms. It was anticipated that the isocyanate complex (I) might have a similar structure and packing arrangement, and exist as discrete pairs of $[Cu(NCO)_2(phen)]$ subunits. Three related structures have been determined and these exhibit a similar bridging pattern involving the isocyanate ligands. The complexes $[Cu_2(bpm)(NCO)_4]_n$ (Julve, Verdaguer, De Munno, Real & Bruno, 1993), where bpm is bipyrimidine, $[Cu(NCO)_2(diMeen)]_2$ (Mauro, Klein, Saldana, de Simone, Zukerman-Schpector & Castellano, 1990), where diMeen is *N*,*N*-dimethylethylenediamine, and $[Cu_2(apox)(NCO)_2]$ (Lloret, Julve, Faus, Ruiz, Castro, Mollar & Philoche-Levisalles, 1992), where H_2apox is *N*,*N*′-bis(3-aminopropyl)oxamide, have structures that are bridged end-on through the nitrogen ends of the isocyanate ligands.



(I)

An *ORTEP* plot (Johnson, 1965) of (I) is shown in Fig. 1, with the atom-numbering system indicated. A stereoscopic plot of the unit cell is shown in Fig. 2. The title compound consists of discrete $[Cu(NCO)_2(phen)]_2$ pairs which are bridged through isocyanate ligands in an asymmetrical end-on fashion. The subunits have a four-coordinated distorted square-planar arrangement of N atoms about the central Cu atom; pairs of these $[Cu(NCO)_2(phen)]$ subunits form dimers by the interaction of the fifth position on each Cu center with an N atom of a cyanate ligand of the associated subunit. One isocyanate ligand on each Cu center thus serves as a linkage for the dimer, with the other attached through the N atom to only one Cu atom. Each Cu atom has distorted square-pyramidal coordination, with the sixth position unoccupied.

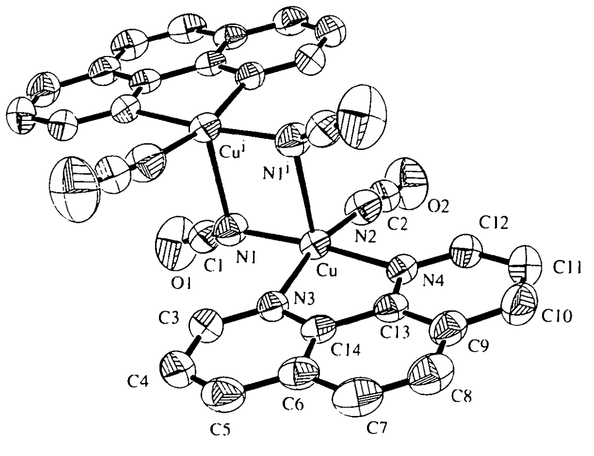


Fig. 1. A displacement ellipsoid plot (50% probability) of $[Cu(NCO)_2(phen)]_2$ showing the atom-numbering scheme.

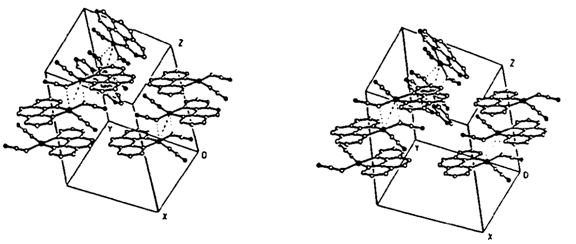


Fig. 2. A stereoscopic drawing of the unit cell of $[Cu(NCO)_2(phen)]_2$.

In (I), the Cu—N_{phen} distances are 2.042 (2) and 2.035 (2) Å, with a N3—Cu—N4 angle of 80.56 (7)°. These values are similar to those found in both $[Cu_2(bpm)(NCO)_4]_n$ (Julve, Verdaguer, De Munno, Real & Bruno, 1993) and $[Cu(NCS)_2(phen)]$ (Parker & Breneman, 1993). The Cu—NCO distances are 1.970 (2) and 1.927 (2) Å, with the isocyanate ligand bridging the two Cu atoms having the longer Cu—N distance. The Cu^i—N1 distance of the fifth position is 2.481 (2) Å [symmetry code: (i) $-x$, $-y$, $2-z$], which compares with 2.456 (7) Å for $[Cu_2(bpm)(NCO)_4]_n$, and 2.346 (5) and 2.466 (5) Å for $[Cu(NCO)_2(diMeen)]_2$. The two Cu and the bridging N atoms of the isocyanate ligands describe a rectangle, with a Cu···Cu^i distance of 3.2373 (5) Å. The Cu···Cu^i distance in $[Cu_2(bpm)(NCO)_4]_n$ is 3.418 (1) Å and in $[Cu(NCO)_2(diMeen)]_2$ 3.2464 (9) Å. In $[Cu(NCO)_2(phen)]_2$, the square-pyramidal coordination of the Cu atom is distorted as the Cu atom lies above the basal plane.

Both the end-on bridging N-coordinated isocyanato and the non-bridging isocyanato ligands are approximately linear, with N—C—O angles of 176.7 (3) and 178.3 (3)°, respectively. In both cases, the C—O distances are longer than the C—N distances, with averages of 1.19 and 1.13 Å, respectively. These angles and distances are very close to those found in both $[Cu_2(bpm)(NCO)_4]_n$ and $[Cu(NCO)_2(diMeen)]_2$.

Experimental

The title compound was prepared by the slow addition of a 25 ml solution of 1,10-phenanthroline monohydrate (1.98 g, 10.0 mmol) in ethanol to a 15 ml solution of $CuCl_2.2H_2O$ (1.71 g, 10.0 mmol) dissolved in water. To the resulting solution, which contained a yellow–green precipitate, solid KOCN (1.66 g, 20.0 mmol) was slowly added with continuous stirring. The product obtained was a pale-blue solid which was dissolved in dimethyl sulfoxide with mild heating. A single crop of bright deep-blue crystals was obtained on evaporation of the solvent.

Crystal data

$[Cu_2(NCO)_4(C_{12}H_8N_2)_2]$
$M_r = 655.58$
Monoclinic
$P2_1/c$
$a = 7.852$ (2) Å
$b = 13.714$ (2) Å
$c = 13.265$ (3) Å
$\beta = 118.98$ (1)°
$V = 1249.6$ (5) Å^3
$Z = 2$
$D_x = 1.743$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 8.93$–22.48°
$\mu = 1.76$ mm^{-1}
$T = 293$ K
Needle
0.70 × 0.20 × 0.10 mm
Blue

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan
$T_{min} = 0.870$, $T_{max} = 0.997$
2303 measured reflections
2085 independent reflections

1814 observed reflections [$I > 3\sigma(I)$]
$R_{int} = 0.018$
$\theta_{max} = 25.0°$
$h = -9 \rightarrow 8$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 15$
1 standard reflection
frequency: 167 min
intensity decay: 0.80%

Refinement

Refinement on F
$R = 0.028$
$wR = 0.036$
$S = 1.44$
1814 reflections
222 parameters
H atoms refined as riding
$w = 1/[\sigma^2(F) + 0.0004F^2]$
$(\Delta/\sigma)_{max} = 0.03$

$\Delta\rho_{max} = 0.57$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from Cromer & Mann (1968) and *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}
Cu	0.15358 (3)	0.00811 (2)	0.95188 (2)	2.900 (6)
O1	0.0654 (3)	−0.2688 (2)	0.9251 (2)	7.38 (7)
O2	−0.2023 (4)	−0.0172 (2)	0.5922 (2)	7.92 (8)
N1	0.0354 (3)	−0.1078 (1)	0.9807 (2)	3.69 (4)
N2	−0.0221 (3)	0.0117 (2)	0.7883 (2)	4.37 (5)
N3	0.3831 (2)	0.0039 (1)	1.1146 (1)	2.99 (4)
N4	0.3058 (2)	0.1260 (1)	0.9443 (1)	3.04 (4)
C1	−0.0133 (3)	−0.1864 (2)	0.9512 (2)	3.66 (5)
C2	−0.1083 (4)	−0.0034 (2)	0.6937 (2)	3.82 (6)
C3	0.4204 (3)	−0.0600 (2)	1.1981 (2)	3.72 (5)
C4	0.5767 (3)	−0.0496 (2)	1.3088 (2)	4.34 (6)
C5	0.6988 (3)	0.0286 (2)	1.3350 (2)	4.17 (6)
C6	0.6630 (3)	0.0982 (2)	1.2489 (2)	3.51 (5)
C7	0.7790 (3)	0.1837 (2)	1.2661 (2)	4.33 (6)
C8	0.7367 (3)	0.2469 (2)	1.1795 (2)	4.38 (6)
C9	0.5773 (3)	0.2309 (2)	1.0666 (2)	3.65 (5)
C10	0.5250 (3)	0.2935 (2)	0.9723 (2)	4.59 (6)
C11	0.3711 (3)	0.2696 (2)	0.8682 (2)	4.78 (6)
C12	0.2650 (3)	0.1857 (2)	0.8564 (2)	3.75 (5)
C13	0.4612 (3)	0.1484 (2)	1.0481 (2)	2.93 (5)
C14	0.5041 (3)	0.0815 (2)	1.1400 (2)	2.95 (4)

Table 2. *Selected geometric parameters (Å, °)*

Cu···Cu^i	3.2373 (5)	N4—C13	1.360 (3)
Cu—N1	1.970 (2)	C3—C4	1.391 (4)
Cu—N2	1.927 (2)	C4—C5	1.366 (4)

Cu—N3	2.035 (2)	C5—C6	1.409 (4)
Cu—N4	2.042 (2)	C6—C7	1.434 (4)
O1—C1	1.193 (3)	C6—C14	1.396 (3)
Cu^{i}—N1	2.481 (2)	C7—C8	1.346 (4)
O2—C2	1.196 (4)	C8—C9	1.428 (4)
N1—C1	1.147 (3)	C9—C10	1.405 (4)
N2—C2	1.119 (4)	C9—C13	1.398 (3)
N3—C3	1.329 (3)	C10—C11	1.363 (4)
N3—C14	1.356 (3)	C11—C12	1.385 (4)
N4—C12	1.330 (3)	C13—C14	1.430 (3)
N1—Cu—N2	95.27 (9)	C7—C6—C14	118.6 (2)
N1—Cu—N3	91.70 (8)	C6—C7—C8	121.1 (2)
N1—Cu—N4	172.26 (8)	C7—C8—C9	121.6 (2)
N2—Cu—N3	167.98 (9)	C8—C9—C10	124.6 (2)
N2—Cu—N4	92.35 (9)	C8—C9—C13	118.3 (2)
N3—Cu—N4	80.56 (7)	C10—C9—C13	117.0 (2)
Cu—N1—C1	143.3 (2)	C9—C10—C11	119.2 (3)
Cu—N2—C2	166.3 (2)	C10—C11—C12	120.3 (3)
Cu—N3—C3	128.8 (2)	N4—C12—C11	122.4 (3)
Cu—N3—C14	113.3 (2)	N4—C13—C9	123.3 (2)
C3—N3—C14	117.8 (2)	N4—C13—C14	116.3 (2)
Cu—N4—C12	129.2 (2)	C9—C13—C14	120.4 (2)
Cu—N4—C13	112.8 (1)	N3—C14—C6	123.6 (2)
C12—N4—C13	117.7 (2)	N3—C14—C13	116.4 (2)
O1—C1—N1	176.7 (3)	C6—C14—C13	120.0 (2)
O2—C2—N2	178.3 (3)	Cu^{i}—N1—Cu	92.59 (8)
N3—C3—C4	122.5 (2)	Cu^{i}—N1—C1	118.9 (2)
C3—C4—C5	120.0 (2)	N1^{i}—Cu—N1	87.41 (8)
C4—C5—C6	119.1 (2)	N1^{i}—Cu—N2	99.49 (9)
C5—C6—C14	117.0 (2)	N1^{i}—Cu—N3	90.58 (8)
C5—C6—C7	124.3 (2)	N1^{i}—Cu—N4	92.73 (7)

Symmetry code: (i) $-x, -y, 2 - z$.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MolEN*. Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP* (Johnson, 1965) in *SHELXTL/PC* (Sheldrick, 1990). Software used to prepare material for publication: *MolEN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PT1036). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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cis-(*R*,*S*)-Bis(benzyl methyl sulfoxide)dichloroplatinum(II)

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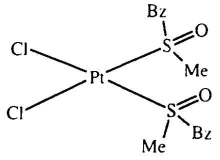
Abstract

The coordination around the Pt atom in the title compound, $[PtCl_2(C_8H_{10}OS)_2]$, is pyramidally distorted from *cis* square-planar; two chloride ions form Pt—Cl bonds of 2.310 (3) and 2.307 (3) Å and two benzyl methyl sulfoxide groups form Pt—S bonds of 2.241 (2) and 2.233 (2) Å.

Comment

There should be three isomers of the complex *cis*-bis(benzyl methyl sulfoxide)dichloroplatinum(II): the (*S*,*S*), (*R*,*R*) and *meso* forms. The crystal structure of the (*S*,*S*) form as a methanol solvate have been determined by X-ray methods (Antolini, Folli, Iarossi, Schenetti & Taddei, 1991). We have crystallized and determined the structure of the *meso* form, (I).



(I)

The title compound is composed of neutral *cis*-$[PtCl_2(MeBzSO)_2]$ complexes (Fig. 1). The closest Pt···Pt distance is 7.274 (1) Å. Both the benzyl methyl sulfoxide molecules are bonded *via* their chiral S atoms. The structure analysis reveals that the two S atoms have different chiralities, *R* and *S*, giving the *meso* form of the platinum complex. The S atoms are in approximately tetrahedral environments with angles ranging from 100.1 (5) (C—S—C) to 117.1 (3)° (Pt—S—O). The S—O and S—C bond distances are close to those found in other sulfoxides (Almeida, Hubbard & Farrell, 1992; Antolini *et al.*, 1991; Melanson & Rochon, 1975, 1987; Melanson, Chevrotire & Rochon, 1985).