References

Beachley, O. T. & Coates, G. E. (1965). *J. Chem. Soc.* pp. 3324–3326.
Bradford, A. M., Bradley, D. C., Hursthouse, M. G. & Motevalli, M. (1992). *Organometallics*, **11**, 113–115.
Bradley, D. C., Dawes, H. M., Frigo, D. M., Hursthouse, M. G. & Smith, L. M. (1990). *Polyhedron*, **9**, 343–346.
Enraf–Nonius (1989). *CAD-4 Software.* Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Gilmore, C. J. (1983). *MITHRIL. Computer Program for the Automatic Solution of Crystal Structure from X-ray Data.* Department of Chemistry, University of Glasgow, Scotland.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Molecular Structure Corporation (1987). *TEXSAN. TEXRAY Structure Analysis Package.* Revised. MSC, 3200A Research Forest Drive, The Woodlands, TX 77381, USA.
Sun, H.-S., Wang, X.-M., Huang, X.-Y. & You, X.-Z. (1995). *Polyhedron.* In the press.

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mer-Bis[2,6-bis(1-phenyliminoethyl)pyridine-*N*,*N*′,*N*″]copper(II) Diperchlorate

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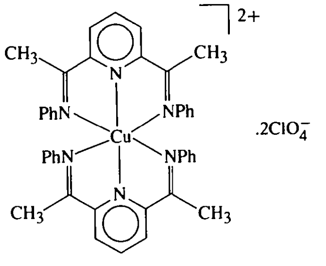
Abstract

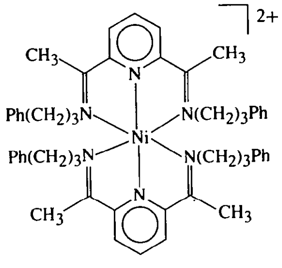
In $[Cu(C_{21}H_{19}N_3)_2](ClO_4)_2$, two tridentate N-donor ligands coordinate to a copper(II) centre to give a distorted octahedral environment. The two ligands are approximately orthogonal, with an angle of 89.7 (2)° between the two CuN_3 planes. One of the ligands lies further from the Cu atom, its Cu—N_{imino} distances (mean 2.31 Å) being 0.21 Å longer than the corresponding distances for the second ligand, an effect which is due to Jahn–Teller distortion.

Comment

In the title compound, *mer*-bis[2,6-bis(1-phenyliminoethyl)pyridine-*N*,*N*′,*N*″]copper(II) diperchlorate, (1), the copper(II) centre lies at the centre of a distorted octahedron of N-donor atoms (Fig. 1). This distortion arises in part from the dimensions, shape and rigidity of the 2,6-bis(1-phenyliminoethyl)pyridine ligand, which also imposes a *mer* configuration on the complex. The two N_3-donor sets are approximately orthogonal, with an angle of 89.7 (2)° between the plane of Cu, N7, N10 and N13 and that of Cu, N7′, N10′ and N13′.



(1)



(2)

The Cu—N distances in compound (1) fall into three groups: approximately 1.95 Å for the pyridyl N atoms, and 2.10 and 2.31 Å for the imino N atoms. A closer

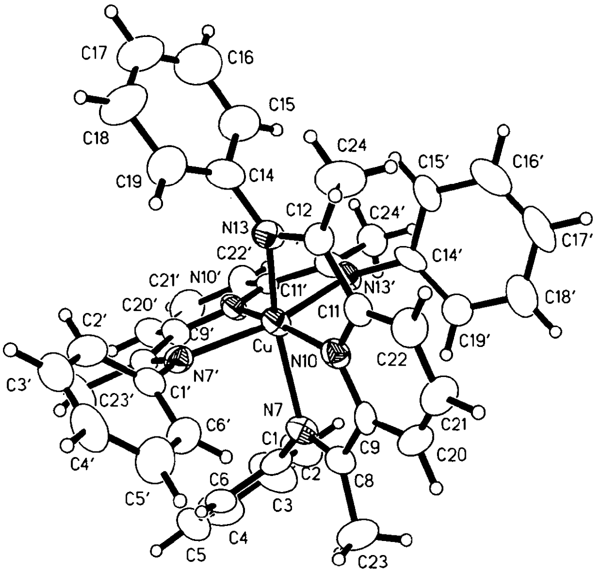


Fig. 1. A view of the title molecule with the atom-numbering scheme. Displacement ellipsoids enclose 30% electron-probability surfaces and H atoms are drawn as small spheres of arbitrary radii. The ligand whose donor set comprises atoms N7, N10 and N13 lies further from the metal centre as a result of a Jahn–Teller elongation of the Cu—N7 and Cu—N13 distances.

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comparison shows that the ligand containing atoms N7, N10 and N13 is the more loosely bound, as it possesses the longest Cu—N distances [1.975 (9), 2.299 (9) and 2.320 (9) Å compared with 1.934 (8), 2.100 (9) and 2.103 (8) Å for the other ligand]. It also exhibits a narrower *trans* N—Cu—N angle [149.4 (3) *versus* 157.0 (4)°]. There is no indication from the molecular geometry around the imino N atoms that any have undergone reduction and we attribute the inequivalent Cu—N_{imino} distances to a Jahn–Teller elongation of the Cu—N7 and Cu—N13 distances.

In contrast to this effect observed at the d^9 Cu^{II} centre in compound (1), the two ligands around the d^8 Ni^{II} centre in bis{2,6-bis[1-(3-phenylpropylimino)ethyl]-pyridine-*N*,*N*′,*N*″}nickel(II) bis(tetrafluoroborate), (2) (Blake, Lavery, Hyde & Schröder, 1989), are equivalent. Although the nickel coordination sphere is also distorted octahedral, the Ni—N_{imine} separations [2.121 (7), 2.135 (7), 2.142 (7) and 2.160 (7) Å; mean 2.140 (14) Å] occupy a narrow range. The Ni—$N_{pyridyl}$ distances in compound (2) are 1.981 (7) and 1.989 (7) Å.

Experimental

The title compound, *mer*-bis[2,6-bis(1-phenyliminoethyl)-pyridine-*N*,*N*′,*N*″]copper(II) diperchlorate, was obtained by reaction of copper(II) nitrate with 2,6-bis(1-phenyliminoethyl)-pyridine in ethanol, followed by addition of 70% perchloric acid and recrystallization from ethanol.

Crystal data

$[Cu(C_{21}H_{19}N_3)_2](ClO_4)_2$
$M_r = 889.22$
Monoclinic
$P2_1/n$
$a = 20.960 (13)$ Å
$b = 13.809 (13)$ Å
$c = 14.503 (8)$ Å
$\beta = 94.151 (14)°$
$V = 4187 (5)$ Å^3
$Z = 4$
$D_x = 1.411$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 8 reflections
$\theta = 3.5–7.5°$
$\mu = 0.709$ mm^{-1}
$T = 293 (2)$ K
Lath
0.68 × 0.12 × 0.04 mm
Bright green

Data collection

Stoe Stadi-2 two-circle diffractometer
ω scans
Absorption correction: none
5714 measured reflections
5484 independent reflections
1990 observed reflections [$I > 2\sigma(I)$]

$R_{int} = 0.0550$
$\theta_{max} = 24.98°$
$h = -24 \rightarrow 24$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 17$
Standard reflections: see *Experimental* text below

Refinement

Refinement on F^2
$R(F) = 0.0943$
$wR(F^2) = 0.2258$
$S = 0.894$
5479 reflections
484 parameters
H atoms were included in calculated positions

$w = 1/[\sigma^2(F_o^2) + (0.084P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.037$
$\Delta\rho_{max} = 0.41$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}
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 isotropic or equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}/U_{iso}
Cu	0.03524 (6)	0.21370 (11)	0.20494 (8)	0.0573 (5)
N7	0.1182 (4)	0.3111 (7)	0.1664 (6)	0.057 (3)
N10	0.0526 (4)	0.2922 (7)	0.3178 (6)	0.055 (2)
N13	−0.0242 (4)	0.1461 (8)	0.3174 (6)	0.062 (3)
C2	0.1250 (4)	0.3470 (6)	0.0053 (7)	0.099 (5)
C3	0.1532 (5)	0.3316 (8)	−0.0773 (5)	0.126 (6)
C4	0.2075 (5)	0.2740 (8)	−0.0787 (6)	0.121 (6)
C5	0.2336 (3)	0.2318 (6)	0.0025 (8)	0.095 (4)
C6	0.2054 (4)	0.2471 (6)	0.0851 (6)	0.069 (4)
C1	0.1511 (4)	0.3048 (6)	0.0865 (5)	0.059 (3)
C8	0.1359 (5)	0.3668 (9)	0.2339 (9)	0.056 (3)
C23	0.1945 (6)	0.4265 (10)	0.2404 (8)	0.099 (4)
C9	0.0978 (5)	0.3635 (8)	0.3189 (7)	0.049 (3)
C11	0.0160 (5)	0.2883 (9)	0.3899 (7)	0.055 (3)
C12	−0.0296 (5)	0.2048 (9)	0.3841 (7)	0.059 (3)
C24	−0.0749 (6)	0.1935 (11)	0.4581 (7)	0.110 (5)
C15	−0.1172 (5)	0.0577 (8)	0.2579 (6)	0.090 (4)
C16	−0.1537 (4)	−0.0264 (10)	0.2521 (7)	0.144 (7)
C17	−0.1337 (6)	−0.1079 (8)	0.3025 (8)	0.117 (6)
C18	−0.0771 (6)	−0.1053 (7)	0.3587 (7)	0.118 (5)
C19	−0.0406 (4)	−0.0212 (9)	0.3645 (5)	0.094 (4)
C14	−0.0606 (4)	0.0603 (7)	0.3141 (6)	0.068 (4)
C20	0.1056 (5)	0.4247 (9)	0.3908 (8)	0.067 (3)
C21	0.0679 (6)	0.4177 (10)	0.4637 (8)	0.075 (4)
C22	0.0227 (6)	0.3484 (10)	0.4648 (8)	0.077 (4)
N7′	0.1023 (4)	0.1005 (6)	0.2152 (7)	0.058 (3)
N10′	0.0248 (4)	0.1625 (7)	0.0807 (6)	0.053 (2)
N13′	−0.0393 (4)	0.2992 (6)	0.1438 (6)	0.053 (2)
C2′	0.1328 (4)	−0.0293 (7)	0.3219 (7)	0.081 (4)
C3′	0.1651 (5)	−0.0614 (5)	0.4032 (8)	0.094 (5)
C4′	0.2017 (4)	0.0029 (8)	0.4585 (5)	0.089 (5)
C5′	0.2060 (3)	0.0994 (7)	0.4324 (5)	0.093 (4)
C6′	0.1737 (4)	0.1316 (5)	0.3511 (6)	0.074 (4)
C1′	0.1371 (3)	0.0672 (8)	0.2958 (5)	0.060 (3)
C8′	0.1103 (5)	0.0614 (8)	0.1371 (8)	0.054 (3)
C23′	0.1588 (5)	−0.0116 (10)	0.1158 (7)	0.095 (5)
C9′	0.0662 (5)	0.0966 (9)	0.0574 (8)	0.058 (3)
C11′	−0.0161 (5)	0.2055 (8)	0.0166 (8)	0.052 (3)
C12′	−0.0535 (5)	0.2796 (9)	0.0567 (8)	0.057 (3)
C24′	−0.1006 (5)	0.3377 (9)	−0.0037 (7)	0.075 (4)
C15′	−0.1301 (4)	0.3513 (6)	0.2263 (6)	0.088 (4)
C16′	−0.1586 (3)	0.4211 (8)	0.2788 (6)	0.098 (5)
C17′	−0.1275 (5)	0.5083 (7)	0.2985 (5)	0.103 (5)
C18′	−0.0679 (5)	0.5258 (6)	0.2657 (6)	0.092 (5)
C19′	−0.0393 (3)	0.4560 (7)	0.2132 (5)	0.071 (4)
C14′	−0.0704 (4)	0.3687 (6)	0.1935 (4)	0.052 (3)
C20′	0.0681 (6)	0.0703 (10)	−0.0349 (9)	0.079 (4)
C21′	0.0251 (7)	0.1127 (11)	−0.1000 (8)	0.085 (4)
C22′	−0.0176 (6)	0.1811 (10)	−0.0751 (8)	0.077 (4)
Cl1	0.7403 (2)	0.6427 (3)	0.4458 (3)	0.1060 (13)
O11	0.7570 (5)	0.5451 (7)	0.4412 (7)	0.131 (4)
O12	0.6713 (5)	0.6532 (9)	0.4338 (7)	0.154 (4)
O13	0.7576 (5)	0.6783 (9)	0.5403 (9)	0.167 (5)
O14	0.7580 (9)	0.6934 (12)	0.3683 (14)	0.150†
O14′	0.798 (3)	0.699 (3)	0.424 (3)	0.150†
Cl2	0.1014 (2)	0.6847 (3)	0.2900 (3)	0.0994 (13)
O21	0.0821 (5)	0.6057 (8)	0.2294 (6)	0.126 (4)
O22	0.151 (3)	0.656 (2)	0.363 (2)	0.150†

O22′	0.114 (2)	0.6534 (18)	0.3793 (18)	0.150†
O23	0.0483 (6)	0.7425 (11)	0.3076 (8)	0.192 (6)
O24	0.1415 (6)	0.7435 (9)	0.2435 (8)	0.172 (5)

† Fixed U_{iso}.

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

Cu—N7	2.299 (9)	Cu—N7′	2.100 (9)
Cu—N10	1.975 (9)	Cu—N10′	1.934 (8)
Cu—N13	2.320 (9)	Cu—N13′	2.103 (8)
N7—C1	1.394 (9)	N7′—C1′	1.410 (10)
N7—C8	1.278 (12)	N7′—C8′	1.277 (12)
N10—C9	1.365 (12)	N10′—C9′	1.318 (12)
N10—C11	1.343 (11)	N10′—C11′	1.355 (12)
N13—C12	1.274 (12)	N13′—C12′	1.305 (11)
N13—C14	1.408 (11)	N13′—C14′	1.391 (9)
N7—Cu—N10	77.4 (4)	N10—Cu—N13′	97.3 (3)
N7—Cu—N13	149.4 (3)	N13—Cu—N10′	118.5 (4)
N7—Cu—N7′	86.5 (3)	N13—Cu—N7′	92.4 (3)
N7—Cu—N10′	91.4 (3)	N13—Cu—N13′	95.8 (3)
N7—Cu—N13′	97.0 (3)	N7′—Cu—N10′	79.8 (4)
N10—Cu—N13	73.4 (4)	N7′—Cu—N13′	157.0 (4)
N10—Cu—N7′	105.5 (3)	N10′—Cu—N13′	77.4 (4)
N10—Cu—N10′	167.1 (4)		

The high value for the conventional *R* factor is attributed to poor crystal quality, as indicated by preliminary oscillation and Weissenberg photography. It was particularly noticeable that relatively few reflections appeared at higher angles. Several axial and zero-layer reflections were checked intermittently as a means of detecting possible crystal movement. They gave no sign of crystal decay. Disorder in the perchlorate counteranions was originally modelled by allowing all O atoms to refine with anisotropic displacement parameters, but the extreme thermal motion observed for atoms O14 and O22 required each of these atoms to be modelled by two components and O14′ and O22′ were introduced into the model to accomplish this. All four disorder components were refined with a fixed U_{iso} of 0.15 Å^2.

Data collection: local programs. Cell refinement: local programs. Data reduction: local programs. Program(s) used to solve structure: *SHELX*76 (Sheldrick, 1976). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1992). Software used to prepare material for publication: *SHELXL*93 (Sheldrick, 1993).

The authors thank the SERC for support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1197). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Blake, A. J., Lavery, A. J., Hyde, T. I. & Schröder, M. (1989). *J. Chem. Soc. Dalton Trans.* pp. 965–970.

Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination.* University of Cambridge, England.

Sheldrick, G. M. (1992). *SHELXTL/PC.* Version 4.3. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

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cis-Diisothiocyanatobis(1,10-phenanthroline)copper(II), [Cu(NCS)$_2$(C$_{12}$H$_8$N$_2$)$_2$]

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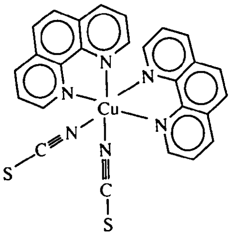
Abstract

The crystal and molecular structure of green *cis*-[Cu(NCS)$_2$(phen)$_2$] (phen = 1,10-phenanthroline) containing a distorted octahedral [Cu^{II}N$_6$] core is reported. The structure of [Cu(NCS)$_2$(phen)$_2$] consists of discrete molecules in which the six-coordinate Cu atom sits on a twofold rotation axis with the thiocyanates coordinating through the N atom. The Cu—N$_{NCS}$ distances are 2.020 (7) Å, while the Cu—N$_{phen}$ distances are 2.132 (5) Å *trans* to NCS and 2.217 (5) Å *trans* to N$_{phen}$. The geometry is distorted from octahedral stereochemistry because of the 76.9 (2)° N—Cu—N bite angle of each 1,10-phenanthroline and because of a slight elongation of the *trans* positions that are occupied by an N atom from each phenanthroline ligand. The thiocyanate ions are linear [N—C—S = 178.9 (6)°] and are at an angle of 161.0 (6)° to the Cu atom.

Comment

The title compound, (I), is an analog of [Fe(NCS)$_2$(phen)$_2$] and [Mn(NCS)$_2$(phen)$_2$]. The iron complex is the archetype of a series of complexes that exhibit a spin-state crossover between the high-spin ($^5T_2$) and low-spin ($^1A_1$) states (Konig & Madega, 1967; Konig, Madeja & Watson, 1968; Ganguli, Gütlich & Müller, 1981). The manganese complex has a distorted octahedral [Mn^{II}N$_6$] core (Holleman, Parker & Breneman, 1994). Here, we report the crystal and molecular structure of the copper complex *cis*-[Cu(NCS)$_2$(phen)$_2$], (I).



(I)

The structure of [Cu(NCSe)$_2$(phen)$_2$] shows a similar *trans* distortion and similar bond distances (Sedov, Dunaj-Jurco, Kabesova, Gazo & Garat, 1982). In this