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Structure of Bis[(bipyridyl)dicyanatocopper(II)](*Cu–Cu*)

BY M. KABEŠOVÁ, V. JORÍK AND M. DUNAJ-JURČO

Department of Inorganic Chemistry, Slovak Technical University, 81237 Bratislava, Czechoslovakia

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Abstract. [$Cu_2(NCO)_4(C_{10}H_8N_2)_2$], $M_r = 607.5$, triclinic, $P\bar{1}$, $a = 6.62$ (1), $b = 9.99$ (1), $c = 10.40$ (1) Å, $\alpha = 118.4$ (1), $\beta = 95.3$ (1), $\gamma = 102.8$ (1)°, $V = 574.1$ (19) Å^3, $Z = 1$, $D_m = 1.74$, $D_x = 1.757$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 1.98$ mm^{-1}, $F(000) = 306$, room temperature, $R = 0.0490$, $wR = 0.0471$ for 1652 reflections with $I \geq 2\sigma(I)$. Each Cu atom is involved in tetragonal pyramidal coordination and has an N_4Cu donor set. The N atoms of the cyanate and bipyridyl ligands define a square plane from which the central Cu atom is slightly displaced in the axial direction. An axial Cu—Cu bond (3.375 Å) links the [$Cu(NCO)_2(bpy)$] units into centrosymmetric dimers which lie in parallel layers in the crystal structure. The occurrence of the Cu—Cu bond may explain why only one bipyridyl ligand can be accommodated in the coordination sphere of each Cu^{II} ion.

Experimental. Blue prism-shaped crystals of poor quality; density measured by flotation, dimensions 0.45 × 0.1 × 0.065 mm. A Syntex $P2_1$ four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation was used for data collection. 20 reflections with $4.91 \leq \theta \leq 12.72°$ were used for determination of the lattice parameters. Extinction was ignored. Intensity measurements from ω–2θ scans were made for $0 \leq 2\theta \leq 55°$; h −8 to 8, k −7 to 7, l 0 to 14. Two standard reflections monitored every 98 measurements; intensity fluctuations did not exceed 1% during the course of the experiment; corrections for decomposition were therefore not applied. 1652 independent reflections with $I \geq 2\sigma(I)$ were collected (925 unobserved reflections). 196 parameters were refined. The position of the Cu atom was obtained from the Patterson function, positions of the other atoms (including H atoms) from Fourier syntheses. Anisotropic full-matrix refinement on F for non-H atoms. H atoms were assigned a fixed isotropic displacement parameter $U = 0.1$ Å^2 and only their fractional coordinates were refined. $R = 0.0490$, $wR = 0.0471$, $w = k/[\sigma^2(F_o) + g(F_o)^2]$, $k = 1.0464$, $g = 0.001010$, $\Delta\rho_{\max} = 0.52$, $\Delta\rho_{\min} = -0.31$ e Å^{-3}. $(\Delta/\sigma)_{\max}$ in the final least-squares cycle was 0.120 for non-H atoms and 0.350 for H atoms. Calculations were performed with *SHELX*76 (Sheldrick, 1976); scattering factors were obtained from *International Tables for X-ray Crystallography* (1974, Vol. IV). Positional and equivalent isotropic thermal parameters for non-H atoms are in Table 1.* Table 2 gives selected interatomic distances and bond angles.

Related literature. In the crystal structure of [$Cu_2(NCO)_4(bpy)_2$] (Fig. 1) the Cu atom has tetragonal pyramidal coordination. N atoms from the bipyridyl and cyanate ligands form a slightly distorted square plane and there is another Cu atom, Cu′, in the axial position, at a distance of 3.375 (6) Å. The coordination of bipyridyl in the equatorial plane of a Cu^{II} coordination polyhedron is uncommon. The cyanate ligands are terminally bound and virtually linear. The copper coordination closely resembles that observed in [$Cu_2(NCO)_4(phen)_2$] (phen = 1,10-phenanthroline) (Jin, Kabešová & Kožíšek, 1991) and is in agreement with the maximum found *ca* 16000 cm^{-1} in the absorption spectrum of the complex.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55843 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1023]

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Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for non*-H *atoms with e.s.d.'s in parentheses*

$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$

	x	y	z	U_{eq}
Cu	0.2216 (1)	0.1536 (1)	0.0546 (1)	0.0377 (4)
O1	0.3352 (8)	−0.0342 (5)	−0.3642 (5)	0.0765 (38)
O2	0.3234 (7)	−0.2747 (5)	−0.1578 (5)	0.0644 (30)
N1	0.2547 (8)	0.1251 (6)	−0.1362 (6)	0.0592 (35)
N2	0.1966 (7)	−0.0660 (5)	−0.0032 (6)	0.0477 (28)
N3	0.2396 (6)	0.3822 (5)	0.1376 (5)	0.0408 (26)
N4	0.2246 (6)	0.2195 (5)	0.2674 (4)	0.0364 (24)
C1	0.2941 (9)	0.0443 (6)	−0.2483 (7)	0.0485 (34)
C2	0.2627 (8)	−0.1664 (5)	−0.0786 (5)	0.0375 (29)
C31	0.2536 (10)	0.4577 (7)	0.0616 (8)	0.0608 (42)
C32	0.2694 (12)	0.6172 (9)	0.1303 (11)	0.0746 (66)
C33	0.2675 (10)	0.6991 (8)	0.2764 (10)	0.0687 (64)
C34	0.2506 (9)	0.6233 (6)	0.3556 (8)	0.0488 (41)
C35	0.2372 (7)	0.4638 (6)	0.2827 (6)	0.0374 (31)
C41	0.2217 (9)	0.1274 (7)	0.3260 (7)	0.0498 (34)
C42	0.2212 (10)	0.1816 (9)	0.4735 (8)	0.0641 (46)
C43	0.2253 (10)	0.3341 (9)	0.5643 (7)	0.0571 (47)
C44	0.2290 (9)	0.4313 (7)	0.5064 (6)	0.0472 (35)
C45	0.2283 (7)	0.3712 (6)	0.3577 (5)	0.0322 (26)

Table 2. *Selected interatomic distances* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

Cu—N1	1.907 (5)	C33—C34	1.356 (10)
Cu—N2	1.942 (5)	C34—C35	1.377 (7)
Cu—N3	1.991 (4)	C35—N3	1.335 (6)
Cu—N4	1.983 (4)	C35—C45	1.463 (8)
N1—C1	1.155 (7)	N4—C41	1.321 (7)
C1—O1	1.183 (6)	C41—C42	1.363 (8)
N2—C2	1.151 (6)	C42—C43	1.350 (10)
C2—O2	1.191 (6)	C43—C44	1.362 (10)
N3—C31	1.323 (8)	C44—C45	1.366 (7)
C31—C32	1.375 (9)	C45—N4	1.344 (6)
C32—C33	1.343 (11)	Cu—Cu^{i}	3.375 (6)
N1—Cu—N4	170.1 (2)	N2—Cu—N1	94.5 (4)
N2—Cu—N3	172.9 (2)	N2—C2—O2	177.3 (6)
N3—Cu—N4	79.9 (2)	N1—C1—O1	176.7 (7)
N3—Cu—N1	92.5 (2)	Cu—N2—C2	138.9 (5)
N2—Cu—N4	93.1 (2)	Cu—N1—C1	145.2 (5)

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

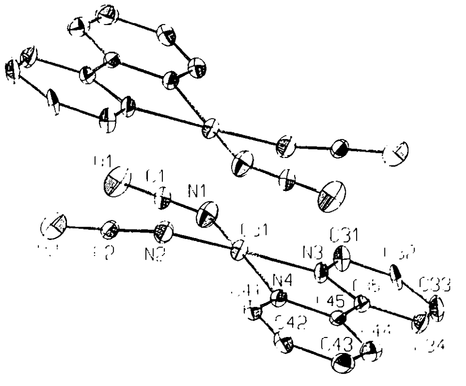

Fig. 1. Schematic representation of the structure of $[Cu_2(NCO)_4(bpy)_2]$ indicating the atom-numbering scheme.

The presence of Cu—Cu bonds in $[Cu_2(NCO)_4(phen)_2]$ and $[Cu_2(NCO)_4(bpy)_2]$ may explain why each Cu^{II} ion is associated with only one phen or bpy ligand. In the analogous NCS$^-$ and NCSe$^-$ complexes the Cu^{II} ions remain pentacoordinate but adopt trigonal bipyramidal coordinations involving two heterocyclic ligands and Cu—Cu bonding interactions do not occur (Sedov, Kabešová, Dunaj-Jurčo, Gažo & Garaj, 1983; Sedov Kožíšek, Kabešová, Dunaj-Jurčo, Gažo & Garaj, 1983).

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Bis[bis(triphenylphosphine)iminium] Dodecacarbonylhexanickelate

BY ROBERT E. BACHMAN AND KENTON H. WHITMIRE*

Department of Chemistry, Rice University, PO Box 1892, *Houston, Texas* 77251, *USA*

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Abstract. $[Ni_6(CO)_{12}][C_{36}H_{30}NP_2]_2$, $M_r = 1765.5$, triclinic, $P\overline{1}$, $a = 13.299$ (4), $b = 13.343$ (4), $c = 13.051$ (5) Å, $\alpha = 106.24$ (3), $\beta = 119.04$ (2), $\gamma = 81.41$ (3)°, $V = 1943$ (1) Å^3, $Z = 1$, $D_x = 1.508$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 15.7$ cm^{-1}, $F(000) = 902$, $T = 296$ K. Final conventional $R = 0.033$ for 5134 observed reflections and 487 variables. The title compound has already been reported with Me_4N as the counter-cation. This sample employs bis(triphenylphosphine)iminium

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* Author to whom correspondence should be addressed.

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