C(14)—C(15)—C(16)	127.0 (3)	N—C(16)—C(15)	122.8 (3)
N—C(16)—C(17)	120.6 (3)	C(15)—C(16)—C(17)	116.5 (3)
N—C(18)—C(19)	122.4 (2)	N—C(18)—C(23)	118.0 (2)
C(19)—C(18)—C(23)	119.2 (2)	C(18)—C(19)—C(20)	120.7 (3)
C(19)—C(20)—C(21)	120.4 (3)	C(20)—C(21)—C(22)	119.6 (3)
C(21)—C(22)—C(23)	121.2 (3)	S—C(23)—C(18)	120.9 (2)
S—C(23)—C(22)	120.3 (2)	C(18)—C(23)—C(22)	118.8 (2)

The density was measured by flotation in a mixture of chloroform and bromoform. The data were collected using a variable scan speed of 5.33–29.3° min^{-1} in ω. The structure was solved by direct methods and refined by full-matrix least squares. *SHELXTL/PC* was used for all calculations.

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Lists of structure factors, anisotropic thermal parameters, and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55478 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1015]

References

Sheldrick, G. M. (1990). *SHELXTL/PC*. Release 4.1. Siemens Crystallographic Research Systems, Madison, Wisconsin, USA.

Teo, S. B., Teoh, S. G., Okechukwu, R. C. & Wei, C. (1992). *J. Coord. Chem.* In the press.

Yeap, G. Y., Fun, H. K., Teo, S. B. & Teoh, S. G. (1992). *Acta Cryst.* C**48**, 1109–1110.

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Structure of $[Cu(CN)(py)_2]$

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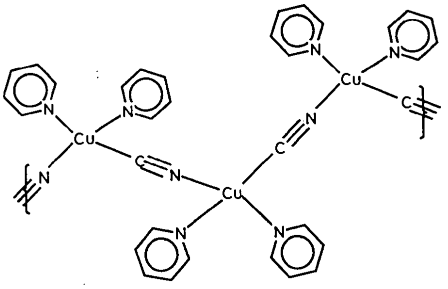
Abstract

catena-Poly[{bis(pyridine-*N*)copper(I)}-μ-cyano-*N*:*C*] crystallizes with two independent polymeric chains in the structure. The chains are propagated by —CN— groups that are N-bound and C-bound to Cu^I centres with no apparent disorder. Each Cu is bound to two pyridines, the N atom of one CN and the C atom of another. The coordination geometry is distorted tetrahedral with particularly wide angles involving the cyanide groups.

Comment

Although the compound $[Cu(CN)(py)_2]$ probably has been known since before the turn of the century, its structure never appears to have been reported. Werner (1897) understood that it was probably not monomeric, based on solubility considerations. The polymeric nature of a related structure, [Cu(CN)(bpy)], was deduced by Cooper & Plane (1966) based on solubility and IR considerations. However, the considerable variety found in the structures and stoichiometries of copper(I) cyanides (Roof, Larson & Cromer, 1968; Cromer & Larson, 1962; Cromer, 1957) and of their Lewis-base adducts (Cromer, Larson & Roof, 1965, 1966; Williams, Cromer & Larson 1971; Goher & Drátovski, 1976) is ample proof that a crystal structure determination is necessary to know the structure with certainty.

Recently, the compound $[Cu(CN)(py)_2]$ (1) was reported to be a product in the reaction between metallic copper, oxygen and nitromethane in pyridine (Gargano, Ravasio, Rossi, Tiripicchio & Camellini, 1989), as well as from heating a mixture of copper(II) acetate, acetic anhydride and formamide in pyridine (Connor, Gibson & Price, 1986, 1987). Evidently its synthesis can be approached from any of the common oxidation states of copper. In the present case it was formed from the decomposition of tetracyanoethylene during the reaction of metallic copper and tetracyanoethylene in pyridine.



(1)

The structure of $[Cu(CN)(py)_2]$ consists of two separate polymeric spiral chains of [—C—N—Cu(py)$_2$—C—N—Cu(py)$_2$—]. A portion of these chains in depicted in Fig. 1. Although the geometry at copper can best be described as tetrahedral, there is a significant widening of the angle involving the cyanides. At Cu(1) this N—Cu—C angle is 131.3 (2)° while at Cu(2) it is 128.3 (2)°. The spiral chain motif with wide N—Cu—C angles of *ca* 133° is common to

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a number of structures, important representatives being found in $KCu_2(CN)_3.H_2O$ (Cromer & Larson, 1962) and $KCu(CN)_2$ (Cromer, 1957). The Cu—N bonds to the pyridine N atoms are longer (average 2.139 Å) than those to cyanide (average 1.954 Å), and the Cu—C bonds are still shorter at an average distance of 1.890 Å. Non-bonded interactions between the chains are only minor; the closest of note are between the Cu and pyridine H atoms. For Cu(1), there are two hydrogen interactions at 2.93 and 3.17 Å, and for Cu(2) there are two at 3.17 and 3.18 Å. Fig. 2 illustrates the packing of the structure in the unit cell.

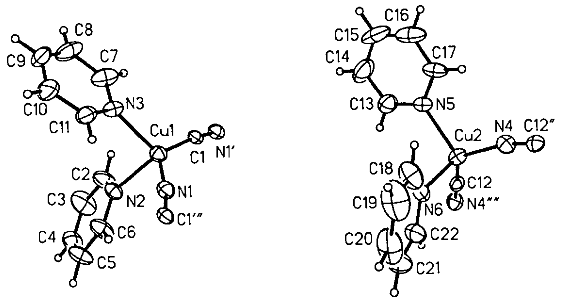

Fig. 1. A depiction of the asymmetric unit, comprised of portions of two $[Cu(CN)(py)_2]$ chains, and the atom-numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

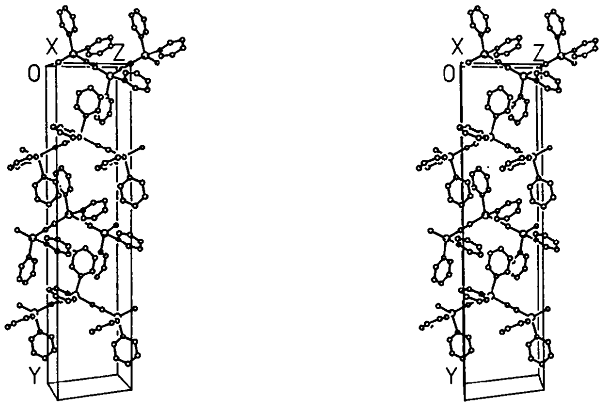

Fig. 2. A stereoview of the crystal packing. H atoms are omitted for clarity.

Experimental

Crystal data

$[Cu(C_5H_5N)_2(CN)]$
$M_r = 247.8$
Monoclinic
Cc
$a = 9.082$ (2) Å
$b = 31.835$ (7) Å
$c = 9.000$ (2) Å
$\beta = 119.44$ (1)°
$V = 2266$ (1) Å^3
$Z = 8$

$D_x = 1.45$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 42 reflections
$\theta = 9–18°$
$\mu = 1.90$ mm^{-1}
$T = 130$ K
0.60 × 0.50 × 0.50 mm

Data collection

Syntex $P2_1$ diffractometer
Absorption correction: empirical
$T_{min} = 0.33$, $T_{max} = 0.45$
5533 measured reflections
2782 independent reflections
2695 observed reflections $[F>4.0\sigma(F)]$
$R_{int} = 0.025$

$\theta_{max} = 55.0°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 40$
$l = -11 \rightarrow 10$
3 standard reflections monitored every 197 reflections
intensity variation: 1.4%

Refinement

Refinement on *F*
Final $R = 0.032$
$wR = 0.035$
$S = 1.60$
2695 reflections
269 parameters
$w = [\sigma^2(F)+0.0003F^2]^{-1}$

$(\Delta/\sigma)_{max} = 0.055$
$\Delta\rho_{max} = 0.41$ e Å^{-3}
$\Delta\rho_{min} = -0.65$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$U_{eq} = 1/3$(trace of the orthogonalized U_{ij} tensor).

	x	*y*	*z*	U_{eq}
Cu(1)	0.7565	0.21950 (1)	0.3526	0.029 (1)
N(1)	0.9299 (5)	0.2464 (1)	0.5604 (5)	0.030 (1)
N(2)	0.9070 (5)	0.2065 (1)	0.2267 (5)	0.031 (1)
N(3)	0.7614 (5)	0.1570 (1)	0.4278 (5)	0.031 (1)
C(1)	0.5474 (5)	0.2395 (1)	0.1772 (6)	0.025 (2)
C(2)	0.8341 (8)	0.1914 (2)	0.0734 (8)	0.051 (2)
C(3)	0.9107 (9)	0.1879 (3)	−0.0269 (9)	0.064 (3)
C(4)	1.0731 (8)	0.2035 (2)	.0398 (8)	0.050 (3)
C(5)	1.1515 (8)	0.2196 (2)	0.1998 (9)	0.053 (3)
C(6)	1.0640 (7)	0.2206 (2)	0.2891 (7)	0.046 (2)
C(7)	0.6448 (8)	0.1294 (2)	0.3243 (7)	0.047 (2)
C(8)	0.6628 (10)	0.0859 (2)	0.3551 (9)	0.059 (4)
C(9)	0.8001 (10)	0.0718 (2)	0.4955 (12)	0.065 (4)
C(10)	0.9212 (9)	0.0993 (2)	0.6039 (12)	0.070 (4)
C(11)	0.8942 (7)	0.1419 (2)	0.5657 (8)	0.044 (2)
Cu(2)	0.0769 (1)	0.4671 (1)	0.2960 (1)	0.035 (1)
N(4)	0.0383 (5)	0.4896 (1)	0.4762 (5)	0.035 (2)
N(5)	−0.0169 (5)	0.4058 (1)	0.2586 (5)	0.032 (1)
N(6)	0.3432 (5)	0.4522 (1)	0.4527 (6)	0.038 (2)
C(12)	0.0442 (6)	0.4941 (1)	0.0947 (6)	0.029 (2)
C(13)	0.0020 (8)	0.3794 (2)	0.1542 (8)	0.047 (3)
C(14)	−0.0498 (10)	0.3378 (2)	0.1361 (11)	0.068 (4)
C(15)	−0.1295 (9)	0.3233 (2)	0.2252 (10)	0.067 (3)
C(16)	−0.1457 (8)	0.3498 (2)	0.3292 (8)	0.060 (3)
C(17)	−0.0896 (6)	0.3912 (2)	0.3473 (7)	0.042 (2)
C(18)	0.3939 (9)	0.4276 (2)	0.5911 (8)	0.061 (3)
C(19)	0.5581 (12)	0.4247 (3)	0.7181 (11)	0.061 (3)
C(20)	0.6799 (10)	0.4478 (3)	0.7002 (16)	0.118 (6)
C(21)	0.6306 (10)	0.4724 (3)	0.5503 (17)	0.100 (6)
C(22)	0.4651 (9)	0.4732 (2)	0.4455 (11)	0.062 (3)

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

Cu(1)—N(1)	1.953 (3)	N(4)—C(12)	1.162 (7)
Cu(1)—N(3)	2.096 (4)	Cu(1)—N(2)	2.201 (5)
N(1)—C(1)	1.159 (5)	Cu(1)—C(1)	1.886 (4)
Cu(2)—N(4)	1.956 (5)	Cu(2)—N(5)	2.090 (4)
Cu(2)—N(6)	2.170 (4)	Cu(2)—C(12)	1.893 (5)
N(1)—Cu(1)—N(2)	99.4 (2)	N(1)—Cu(1)—N(3)	103.1 (1)
N(2)—Cu(1)—N(3)	93.9 (2)	N(1)—Cu(1)—C(1)	131.3 (2)
N(2)—Cu(1)—C(1)	104.9 (2)	N(3)—Cu(1)—C(1)	116.3 (2)
Cu(1)—N(1)—C(1)	171.1 (5)	Cu(1)—C(1)—N(1)	171.7 (5)
N(4)—Cu(2)—N(5)	104.5 (2)	N(4)—Cu(2)—N(6)	97.9 (2)
N(5)—Cu(2)—N(6)	97.8 (1)	N(4)—Cu(2)—C(12)	128.3 (2)
N(5)—Cu(2)—C(12)	114.2 (2)	N(6)—Cu(2)—C(12)	108.8 (2)
Cu(2)—N(4)—C(12)	167.8 (4)	Cu(2)—C(12)—N(4)	174.4 (4)

[Cu(CN)(py)$_2$], RN 102499-39-8, was obtained from tetracyanoethylene (0.516 g, 4.03 mmol) dissolved in pyridine (10 ml) and stirred with copper powder (0.51 g, 8.02 mmol) under argon at room temperature for 0.5 h. The originally brown solution became dark red and as the slightly exothermic reaction proceeded the copper metal dissolved to give a clear solution. On standing overnight pale-yellow crystals separated (yield 0.73 g, 39% based on copper). The crystals are stable under an inert atmosphere but are hygroscopic in air [m.p. > 573 K; v(CN) 2100 cm^{-1} (KBr)].

The space group was found to be *Cc* not *C*2/*c* by successful solution of the structure in *Cc* by direct methods. The coordinates of x and z for Cu(1) were held to fix the origin during refinement. H atoms were treated as riding on bonded atoms (C—H 0.96 Å, $U_{\rm iso} = 1.2 \times U_{\rm eq}$ of the bonded C atom). The absorption correction was applied using *XABS*, a program which provides an empirical correction based on F_o and F_c differences (Hope & Moezzi, 1987).

The absolute configuration was determined by *SHELXTL-Plus* (Sheldrick, 1989). This method is similar to that suggested by Rogers (1981).

Redundant data were collected and merged after determination of hand and application of the absorption correction.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55499 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1021]

References

Connor, J. A., Gibson, D. & Price, R. (1986). *J. Chem. Soc. Dalton Trans.* p. 347.

Connor, J. A., Gibson, D. & Price, R. (1987). *J. Chem. Soc. Perkin Trans.* 1, pp. 619–621.

Cooper, D. & Plane, R. A. (1966). *Inorg. Chem.* **5**, 2209–2212.

Cromer, D. T. (1957). *J. Phys. Chem.* **61**, 1388–1392.

Cromer, D. T. & Larson, A. C. (1962). *Acta Cryst.* **15**, 397–403.

Cromer, D. T., Larson, A. C. & Roof, R. B. Jr (1965). *Acta Cryst.* **19**, 192–197.

Cromer, D. T., Larson, A. C. & Roof, R. B. Jr (1966). *Acta Cryst.* **20**, 279–282.

Gargano, M., Ravasio, N., Rossi, M., Tiripicchio, A. & Camellini, M. T. (1989). *J. Chem. Soc. Dalton Trans.* pp. 921–925.

Goher, M. A. S. & Drátovski, M. (1976). *Collect. Czech. Chem. Commun.* **41**, 3213–3218.

Hope, H. & Moezzi, B. (1987). Chemistry Department, University of California, Davis, USA.

Rogers, D. (1981). *Acta Cryst.* A**37**, 734–741.

Roof, R. B. Jr, Larson, A. C. & Cromer, D. T. (1968). *Acta Cryst.* B**24**, 269–273.

Sheldrick, G. M. (1989). *SHELXTL-Plus.* Program for crystal structure determination. Siemens Analytical X-ray Instruments, Madison, Wisconsin, USA.

Werner, A. (1897). *Z. Anorg. Chem.* **15**, 1–40.

Williams, R. J., Cromer, D. T. & Larson, A. C. (1971). *Acta Cryst.* B**27**, 1701–1706.

Acta Cryst. (1993). C**49**, 372–374

Structure of Aquabis(2,2′-bipyridyl)zinc(II) Diperchlorate

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Abstract

The Zn atom is pentacoordinated involving four N atoms of the bipyridyl ligands and an O atom in nearly trigonal bipyrimidal arrangement. The 2,2′-bipyridyl groups are planar and make an angle of 115.2° with each other. Hydrogen bonding exists involving O(9) of the cation and O(5) of a perchlorate anion.

Comment

The final atomic coordinates are given in Table 1. The bond lengths and angles involving the Zn atom are given in Table 2. An *ORTEP*II (Johnson, 1976) drawing of the structure is shown in Fig. 1. The atoms of the bidentate ligand 2,2′-bipyridyl (bpy) occupy *cis* positions in the pentacoordinated Zn complex. The Zn—N(2) and Zn—N(3) bonds are long and collinear, while the Zn—N(1) and Zn—N(4) bonds are short and non-collinear. The Zn—N distances are in close agreement with those found in bis(2,2′-bipyridyl)mononitritozinc(II) nitrate (Walsh, Walsh, Murphy & Hathaway, 1981). The bond distances and angles in the bipyridyl groups have normal values (Stephens, 1969) except

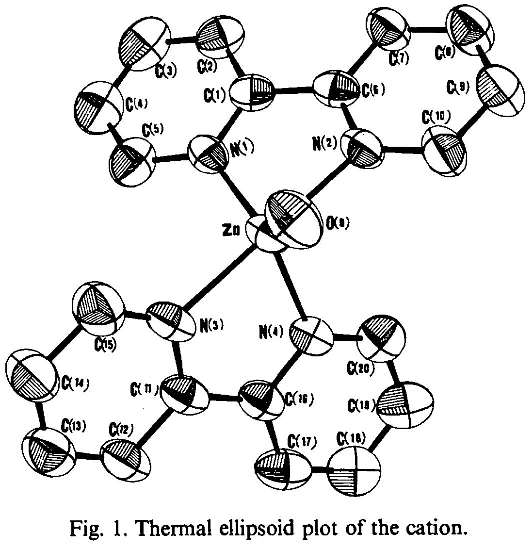

Fig. 1. Thermal ellipsoid plot of the cation.