CRYSTAL AND MOLECULAR STRUCTURE OF THE TETRACYANATO--BIS(PHENANTHROLINE)COPPER(II) COMPLEX

Kim Tae JIN, Mária KABEŠOVÁ and Josef KOŽÍŠEK

Department of Inorganic Chemistry,
Slovak Technical University, 812 37 Bratislava

Received September 11, 1990
Accepted December 4, 1990

At room temperature, the $[Cu_2(NCO)_4(phen)_2]$ complex possessed monoclinic symmetry, $P2_1/n$, with the unit cell parameters $a = 0{\cdot}7757(3)$ nm, $b = 1{\cdot}3563(5)$ nm, $c = 1{\cdot}1555(4)$ nm, $\beta = 96{\cdot}92(2)°$, $Z = 2$. The central atom is involved in tetragonal pyramidal coordination comprising the CuN_4Cu' chromophor. The nitrogen atoms of the cyanate and phenanthroline ligands are in a square planar arrangement, from which the central copper atom is displaced in the axial direction. Through the Cu–Cu bond (0·320 nm), the $[Cu(NCO)_2(phen)]$ formula units are linked into centrosymmetric units, which in the crystal structure lie in parallel layers. The occurrence of the Cu–Cu bond can account for the fact that only one molecule of the heterocyclic ligand can be coordinated.

During the study of thiocyanatocopper(II) and selenocyanatocopper(II) complexes with phenanthroline (phen), complex compounds of the general formula $[Cu(NCX)_2 . (phen)_2]$ (X = S, Se) were observed to separate from solutions with various Cu/phen concentration ratios[1], the coordination sphere of copper(II) containing two phenanthroline molecules. The central atom in the complexes forms a pseudooctahedral coordination polyhedron involving the CuN_6 chromophor. All the ligands in the coordination sphere are mutually bonded in the *cis* positions. Phenanthroline is simultaneously coordinated through an equatorial and an axial position of the coordination polyhedron. The pseudohalide ligands are coordinated in the equatorial plane in the terminal arrangement, through nitrogen atoms. The complex compounds $[Cu(NCO)_2(phen)]$, with one phenanthroline molecule in the Cu(II) coordination sphere, separate from solutions with various copper(II)-to-phenanthroline ratios. To gain insight into this effect, the crystal structure of the complex is studied in the present work.

EXPERIMENTAL

Aqueous ammoniacal solution of $CuSO_4$ (2 mol l^{-1}) was reacted with ethanolic solution of phenanthroline (1 : 1) and aqueous solution of NH_4NCO (2 mol l^{-1}) to obtain blue needle-shaped crystals. The reaction components were added in the ratio [Cu(II)] : [NH_3] : [phen] :

: [NCO^-] = 1 : 4 : 1 : 2. The crystals were filtered out and washed with 1% aqueous ethanol. For $Cu_2(NCO)_4(N_2C_{12}H_8)_2$ (655·6) calculated: 51·29% C, 2·46% H, 17·09% N, 19·39% Cu; found: 51·26% C, 2·50% H, 17·00% N, 19·40% Cu.

Survey crystallographic data were obtained by the Weissenberg oscillation photographic method. The specific weight of the crystals was determined by the flotation method in a bromoform–methanol mixture. The experiments were performed on a SYNTEX $P2_1$ automatic X-ray diffractometer. The lattice parameters were obtained by refining the positional angles of 18 selected diffractions of a rotational polaroid photograph from the diffractometer, scanned over the range of 2Θ = 0 to 55°. The conditions were as follows: MoK_α radiation (71·069 pm), graphite monochromator, $\Theta - 2\Theta$ scanning technique, scanning rate 4·89 to 29·3° min^{-1}, crystal dimensions 0·1 × 0·1 × 0·5 mm, temperature 20°C; measurement check: intensity measurement of two diffractions after every 98 diffractions, condition for observed diffraction: $I \geqq 2\sigma(I)$, number of observed diffractions 1 143. Standard diffraction fluctuations did not exceed 1%. The observed diffraction intensities were corrected for the Lorentz polarization factor and absorption by measuring the φ scan of selected diffractions.

The crystal structure was elucidated by using the heavy atom method. The positions of the copper atoms were determined by Patterson synthesis and the positions of the remaining non-hydrogen atoms, by Fourier synthesis. The hydrogen atom positions were calculated by using the sp^2 and sp^3 carbon hybridization concept, and the temperature factor $U = 0{\cdot}06$ was assigned to them. The crystal structure (including all non-hydrogen atoms) was refined using both the isotropic and anisotropic approaches with the full matrix; the least squares method was applied. The final values of $R = 0{\cdot}035$ and $R_w = 0{\cdot}035$ (for $w = 1/\sigma^2(F)$) were attained. The diffraction curves of the neutral atoms were taken from the International Tables[2]. The computations using the programs SHELX'76 (ref.[3]) and PARST (ref.[4]) were carried out on a MINSK-M-4030-1 computer.

RESULTS AND DISCUSSION

The [$Cu_2(NCO)_4(phen)_2$] complex crystallizes in the monoclinic symmetry $P2_1/n$, $Z = 2$. Its crystallographic data are given in Table I. The fractional coordinates of non-hydrogen atoms are given in Table II, bond lengths and angles, in Table III.

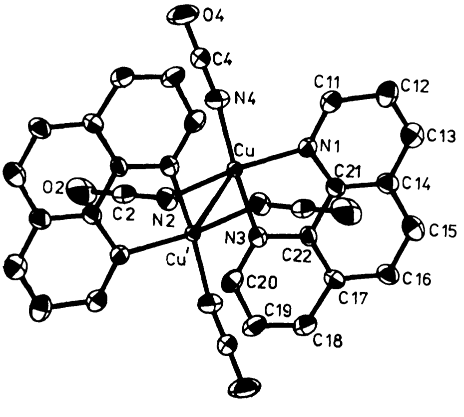

FIG. 1

Schematic representation of the structure of the molecule of the [$Cu_2(NCO)_4(phen)_2$] complex, indicating the atom numbering

TABLE I

Crystallographic data of the $[Cu_2(NCO)_4(phen)_2]$ complex[a]

Crystal system	monoclinic
Space group	$P2_1/n$, $Z = 2$
Elementary cell dimensions:	
a, nm	0·7757(3)
b, nm	1·3563(5)
c, nm	1·1555(4)
β, deg	96·92(2)
V, nm^3	1·2068(8)
Density at room temperature, 10^3 kg m^{-3}	d_c 1·73, d_o 1·72(1)
$\mu(MoK_\alpha)$, mm^{-1}	181
$F(000)$	652

---

[a] Range of diffractions measured: h −9 to 9, k 0 to 17, l 0 to 14; final differential map: $\Delta\zeta_{max}$ and $\Delta\zeta_{min}$ 0·36 and −0·34 e/Å^3, respectively, $(\Delta/\sigma)_{max}$ = 0·03.

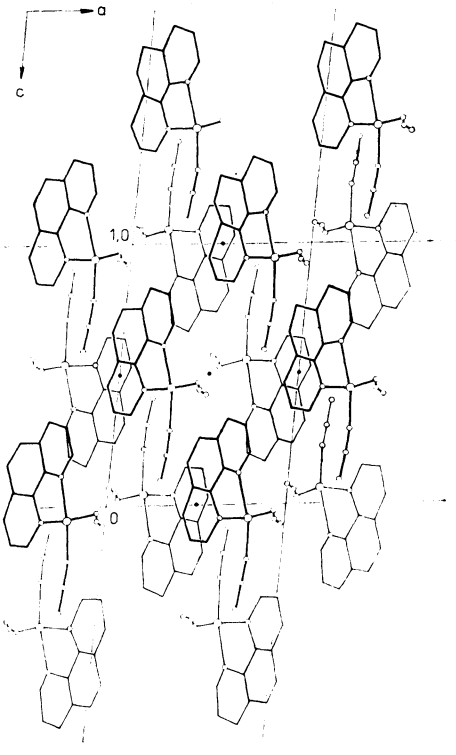

FIG. 2

Orthogonal projection of the crystal structure of the $[Cu_2(NCO)_4(phen)_2]$ complex into the ac plane

Data of the observed and calculated structure factors, anisotropic temperature factors, and fractional coordinates of hydrogen atoms can be obtained from the authors on request.

In the $[Cu_2(NCO)_4(phen)_2]$ crystal structure (Fig. 1), each copper atom has a CuN_4Cu' chromophor, and the coordinating atoms are arranged in a tetragonal pyramid. The nitrogen atoms from the phenanthroline and cyanate ligands form a slightly distorted square planar arrangement. The copper atoms are 0·008 nm displaced from this plane in the axial direction. Through the fifth coordination site, the $[Cu(NCO)_2(phen)]$ formula units are linked by the Cu—Cu′ bond (0·320 nm) into centrosymmetric dimeric structural units, which in the crystal structure are arranged in layers mutually bonded by van der Waals forces (Fig. 2).

From the point of view of its steric bonding situation, the coordination of phenanthroline in the equatorial plane of the coordination polyhedron with a tetragonal

TABLE II

Fractional coordinates of non-hydrogen atoms (.10^4) and their temperature factors $B_{eq} = (8/3).\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$ (standard deviations are given in parentheses)

Atom	x/a	y/b	z/c	B_{eq} . 10^{-4} nm^2
Cu	2018(1)	840(1)	481(1)	2·24(2)
N1	2674(6)	32(5)	−1146(5)	3·4(1)
N2	1911(8)	123(6)	2101(5)	4·8(2)
N3	3612(7)	1259(4)	553(5)	3·3(1)
N4	559(8)	−1064(4)	197(5)	4·1(2)
C2	1987(9)	−25(6)	3066(6)	4·1(2)
O2	2076(10)	−172(6)	4079(4)	8·2(3)
C4	362(10)	−1860(6)	486(6)	4·0(2)
O4	81(10)	−2697(4)	736(6)	8·0(3)
C11	2202(10)	−596(5)	−1993(6)	4·2(4)
C12	2678(11)	−503(6)	−3095(7)	4·8(2)
C13	3628(10)	283(6)	−3353(6)	4·3(2)
C14	4144(8)	982(5)	−2490(6)	3·5(2)
C15	5135(10)	1833(6)	−2666(6)	4·4(2)
C16	5590(10)	2468(6)	−1778(7)	4·6(3)
C17	5097(10)	2311(5)	−657(6)	4·0(2)
C18	5543(10)	2945(6)	270(7)	4·8(3)
C19	5055(11)	2708(6)	1318(8)	4·9(2)
C20	4076(10)	1850(6)	1443(6)	4·1(2)
C21	3634(8)	8150(5)	−1398(6)	3·2(2)
C22	4142(4)	1480(5)	−477(6)	3·4(2)

TABLE III

Interatomic distances and angles in $[Cu_2(NCO)_4(phen)_2]$

Atoms	Distance nm	Atoms	Distance nm	Atoms	Angle deg
Cu—N1	0·201(1)	C12—C13	0·135(1)	N3—Cu—N4	172·2(3)
Cu—N2	0·188(1)	C13—C14	0·140(1)	N2—Cu—N4	95·5(3)
Cu—N3	0·201(1)	C14—C15	0·142(1)	N2—Cu—N3	92·2(3)
Cu—N4	0·193(1)	C14—C21	0·139(1)	N1—Cu—N4	91·4(3)
Cu—Cu′[a]	0·320(0)	C15—C16	0·135(1)	N1—Cu—N3	80·9(2)
N1—Cu11	0·132(1)	C16—C17	0·142(1)	N1—Cu—N2	167·9(3)
N1—C21	0·135(1)	C17—C18	0·138(1)	Cu—N1—C21	112·6(4)
N2—C2	0·113(1)	C17—C22	0·138(1)	Cu1—N1—C11	129·7(5)
N3—C20	0·132(1)	C18—C19	0·135(1)	Cu2—N2—C2	166·9(7)
N3—C22	0·134(1)	C19—C20	0·141(1)	Cu—N3—C22	113·3(5)
N4—C4	0·115(1)	C21—C22	0·141(1)	Cu—N3—C20	128·5(5)
C2—O2	0·118(1)	—	—	Cu—N4—C4	143·9(6)
C4—O2	0·120(1)	—	—	N2—C2—O2	179·4(9)
C11—C12	0·137(1)	—	—	N4—C4—O4	176·2(9)

[a] Symmetry code for Cu′ is $-x$, $-y$, $-z$.

TABLE IV

Calculated departures D ($.10^{-4}$ nm) of atoms from planes formed by phenanthroline rings in $[Cu_2(NCO)_4(phen)_2]$. Standard deviations S are given in parentheses

Plane 1

Atom	N3	C20	C19	C18	C17	C22
D	10(6)	−10(8)	−8(9)	14(8)	−3(8)	−9(7)

$\sum(D/S)^2 = 0{\cdot}104$. Plane equation: $-0{\cdot}82x + 0{\cdot}52y - 0{\cdot}24z = -1{\cdot}51$

Plane 2

Atom	C22	C17	C16	C15	C14	C21
D	−8(7)	5(8)	1(8)	−1(8)	−4(7)	8(7)

$\sum(D/S)^2 = 0{\cdot}0378$. Plane equation: $-0{\cdot}82x + 0{\cdot}52y - 0{\cdot}25z = -1{\cdot}49$

Plane 3

Atom	N1	C11	C12	C13	C14	C21
D	−3(6)	1(8)	−10(9)	−1(8)	5(7)	3(7)

$\sum(D/S)^2 = 0{\cdot}0467$. Plane equation: $-0{\cdot}81x + 0{\cdot}52y - 0{\cdot}26z = -1{\cdot}43$

pyramidal shape is rather unusual. It gives rise to a lowering of the N1—Cu—N3 angle to 80·9° (Table III) and distortion of one phenanthroline ring (N3—N17—C18—C19—C20—C22) resulting in a departure of the atoms from planarity (Table IV).

The cyanide ligands in the complex compound are monofunctional and virtually linear.

The concept of pentacoordinated coordination polyhedra occurring about Cu(II) in the crystal structure of $[Cu_2(NCO)_4(phen)_2]$ is consistent with the observed position of the maximum of the ligand field band at about 16 000 cm^{-1}.

In conclusion, the X-ray analysis performed suggests that the fact that a single phenanthroline molecule is coordinated to copper in the cyanatocopper(II) complexes is related with the blocking of a coordination site in the coordination sphere of copper by the Cu—Cu bond. Actually, no analogous metal–metal bond has been found in thiocyanatocopper(II) and selenocyanatocopper(II) complexes.

REFERENCES

1. Sedov A., Kabešová M., Dunaj-Jurčo M., Gažo J., Garaj J.: Koord. Khim. *8*, 1062 (1982).
2. *International Tables for X-Ray Crystallography*, Vol. IV. Kynoch Press, Birmingham 1974.
3. Sheldrick G. M.: *SHELX-76. A Program for Crystal Structure Determination.* University of Cambridge, Cambridge (U.K.) 1976.
4. Nardelli M.: *PARST. A Program for Crystal Structure Determination.* Comput. Chem. *7*, 95 (1983).

Translated by P. Adámek.