THE CRYSTAL STRUCTURE OF THE COPPER(II) DICYANATO-2,4-LUTIDINE COMPLEX*

F.VALACH, M.DUNAJ-JURČO, J.GARAJ and M.HVASTIJOVÁ

*Department of Inorganic Chemistry,
Slovak Technical University, 880 37 Bratislava*

The [Cu(NCO)$_2$(2,4-lutidine)] crystal structure has been solved by X-ray structural analysis. The complex has a space group of P$\bar{1}$ symmetry and the following lattice parameters: $a = 10·20 \pm 0·03$ Å, $b = 10·08 \pm 0·08$ Å, $c = 10·10 \pm 0·02$ Å, $\alpha = 73·6 \pm 0·2°$, $\beta = 107·5 \pm 0·2°$, $\gamma = 145·8 \pm 0·2°$. The experimental density is $1·58$ g cm^{-3} and the calculated value for $Z = 2$ is $1·52$ g cm^{-3}. The crystal structure consists of infinite polynuclear chains. The approximately square-planar co-ordination around the Cu(II) formed by three nitrogen atoms from OCN groups and one nitrogen atom from a 2,4-lutidine molecule, is completed by one nitrogen atom from an OCN group to form distorted tetragonal pyramidal co-ordination. The co-ordination polyhedron around Cu(II) can be considered a hybrid of a tetragonal pyramid with a trigonal bipyramid. Cyanate groups function as bridges between two copper atoms, through the nitrogen atom, while the oxygen atoms remain free.

The crystal structures of cupric complexes with thiocynate as the ligand are relatively well known[1] and Cu(II) has a co-ordination number of 4 + 2 in them. In contrast to thiocyanate, the cyanate group shows a low tendency to occupy the longer co-ordinate position in the direction of the Z-axis. In general complexes with the cyanate group as the ligand, show an increased tendency towards lowering of the co-ordination number of the central atom during transfer from the thiocyanate or selencyanate ion to the cyanate ion as the ligand. This tendency, due to the poor ability of the cyanate group to form bridges, can be documented well with cobalt(II) complexes of the type CoX$_2$(Py)$_2$ (where X is SeCN, SCN or OCN, and Py is pyridine). While cobalt exhibits octahedral co-ordination in selencyanates or thiocyanates, it shows tetrahedral co-ordination in the cyanate complex[2]. This tendency, as can be seen from the crystal structure of the [Cu(NCO)$_2$(2,4-lut)] complex (lut is lutidine), is also encountered with cupric complexes. The so-far published data on structural investigation point out preferential bonding of the nitrogen atom of the cyanate group to the central atom, while the oxygen atom is usually not bonded to the central atom. Some complex compounds with a metallic ion in a higher oxidation state (Re^{+5}, Re^{+4}, Zr^{4+}, Ti^{4+}, Mo^{3+}) are exceptions[3-5]. King and coworkers[6] correlate in this connection the bridge bonding of the cyanate group in complex compounds with a decrease in the electron density on the central atom. This assumption is in agreement with previous experimental observations. According to the authors[6], the cyanate group can act as the bridge even in the presence of suitable neutral ligands, which have low σ-donor or high π-acceptor ability.

The solution of the crystal structure of the $[Cu(NCO)_2(2,4\text{-lut})]$ complex was initiated by an effort to generalize the crystallo-chemical rules for cupric complexes, in which pseudohalide groups function as ligands, and by the fact that no crystal structure of a cupric compound containing the cyanate group is so far known. This solution has been preceeded by a study of cyanate systems both in solution and in the solid state by indirect physico-chemical methods[7-10].

EXPERIMENTAL AND RESULTS

Space Group and Unit Cell

The crystals with the composition $[Cu(NCO)_2(2,4\text{-lut})]$ are needle-shaped and exhibit triclinic symmetry. The preparation of the crystals has been described in a previous paper[8]. On the basis of the symmetry of the Weissenberg patterns, unconventional space groups, C1 or C$\overline{1}$, were arrived at.

The approximate values of the unit cell parameters from the Weissenberg patterns were refined on the basis of the Guinier diffraction data by the least squares method[11].

The following lattice parameters for the primitive unit cell were obtained:

$$a = 10\cdot20(3) \text{ Å} \qquad b = 10\cdot08(8) \text{ Å} \qquad c = 10\cdot10(2) \text{ Å}$$

$$\alpha = 73\cdot6(2)° \qquad \beta = 107\cdot5(2)° \qquad \gamma = 145\cdot8(2)°$$

The specific mass of the crystals at 25°C, $\varrho_0 = 1\cdot58 \text{ g . cm}^{-3}$, was determined by the flotation method. The specific mass calculated for two formula units in the unit cell ($Z = 2$) is $\varrho_c = 1\cdot52 \text{ g . cm}^{-3}$.

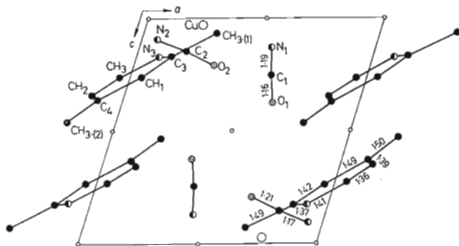
FIG. 1

The Projection of the $[Cu(NCO)_2(2,4\text{-lut})]$ Crystal Structure on the (010) Plane

Solution of the Crystal Structure

The patterns of the crystals were obtained by the Weissenberg equiinclination method, using the CuK_α radiation at room temperature. The crystal used with dimensions of $0\cdot2 \cdot 0\cdot25 \cdot 0\cdot7$ mm was irradiated in the direction of 1st growth axis — the b-axis — and five layers were taken, while zero layers were taken in the direction of the other two axes.

The intensities of the diffracted radiation were measured photometrically and corrected for non-linearity, $K_{\alpha 1}$, $K_{\alpha 2}$ splitting, and the Lorentz polarization factor. The effect of absorption was neglected ($\mu R = 0\cdot62$).

The crystal structure was solved using 1087 independent non-zero reflections in the $C\bar{1}$ or $C1$ space group. The position of the heavy atom was determined on the basis of the three-dimensional Patterson synthesis. A centre-symmetrical space group was obtained by interpretation of the values of the Patterson function and by localization of the other atoms. The positions of the other atoms were found by the method of progressive approximations. The structural parameters were refined by the least squares method down to the R-value of $0\cdot165$ ($R = \sum \|F_0| - |F_c\| / \sum |F_0|$). The Cruickshank weighed scheme[12], $w = (A + F_0 + CF_0^2)^{-1/2}$, where $(\Delta w)^2 = $ const and $A = 4\cdot0$ and $C = 0\cdot04$, was used. The values of the atomic factors are in agreement with those of Cromer and Waber[13]. The accuracy of the refinement of the structure was verified by the Fourier synthesis and calculation of the differential Fourier synthesis. The maximum value of the electron density in the differential Fourier synthesis is $1\cdot73$ e/Å^3, the maximum value of the electron density in the normal Fourier synthesis being equal to $59\cdot94$ e/Å^3. The relatively high value of the R-factor is probably caused by the fact that the crystal had been decomposing slowly during taking of the patterns. The refined fraction co-ordinates of the atoms, the isotropic coefficients of the thermal vibrations and the anisotropic coefficients of the thermal vibrations of the copper atom are given in Table I. The values of the calculated and observed structural factors are at disposal with the authors. All computations were carried out on the CDC3300 computer.
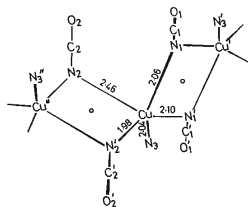

FIG. 2

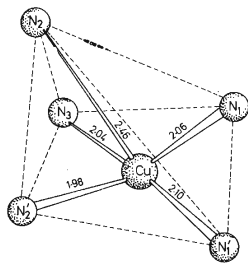One Part of the Infinite Chain in the [Cu(NCO)₂(2,4-lut)] Crystal Structure

FIG. 3

The Co-ordination Polyhedron around Cu(II) in the [Cu(NCO)₂(2,4-lut)] Crystal Structure

TABLE I

The Refined Fraction Co-Ordinates and Coefficients of Thermal Vibrations of the Atoms in the [Cu(NCO)$_2$ (2,4-lut)] Crystal Structure

Atom	x/a	y/b	z/c	B, Å^2
Cu	0·2307(4)	−0·2081(4)	0·0265(2)	
N(1)	0·5601(31)	0·0131(31)	0·1347(16)	3·487(284)
C(1)	0·5884(36)	−0·0164(36)	0·2561(19)	2·447(296)
O(1)	0·6375(42)	−0·0295(42)	0·3732(24)	7·163(498)
N(2)	0·0760(34)	−0·5702(34)	0·0911(18)	2·962(318)
C(2)	0·2053(33)	−0·5569(33)	0·1427(16)	1·850(261)
O(2)	0·3398(34)	−0·5396(34)	0·2053(19)	5·463(377)
N(3)	0·0964(30)	−0·2474(30)	0·1705(15)	2·482(248)
C(3)	0·1479(36)	−0·0713(36)	0·1665(18)	2·612(314)
CH(1)	0·0556(40)	−0·1006(40)	0·2689(21)	3·324(364)
C(4)	−0·1102(36)	−0·3146(36)	0·3649(19)	2·718(317)
CH(2)	−0·1366(42)	−0·4708(42)	0·3591(23)	3·809(403)
CH(3)	−0·0389(38)	−0·4425(38)	0·2686(20)	2·927(339)
CH$_3$(1)	0·3041(46)	0·1339(46)	0·0636(25)	4·274(434)
CH$_3$(2)	−0·2116(53)	−0·3380(53)	0·4647(28)	5·214(531)

Atom	B_{11}, 10^{-2} Å	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	0·0024(1)	0·0082(10)	0·0060(2)	−0·0008(3)	0·0041(2)	0·0010(7)

TABLE II

The Bond Lengths (Å) and Valence Angles (°) in the [Cu(NCO)$_2$ (2,4-lut)] Crystal Structure

Bond	Bond length	Bond	Bond length	Atoms	Angle
Cu—N(1)	2·056(20)	N(3)—C(3)	1·374(23)	N(1)—Cu—N(3)	96·3(0·7)°
Cu—N(1′)	2·100(19)	C(3)—CH(1)	1·421(27)	N(2′)—Cu—N(3)	90·9(0·7)°
Cu—N(2)	2·458(18)	CH(1)—C(4)	1·488(30)	N(2)—Cu—N(3)	98·9(0·6)°
Cu—N(2′)	1·975(18)	C(4)—CH(2)	1·388(28)	N(1′)—Cu—N(1)	78·4(0·8)°
Cu—N(3)	2·043(15)	CH(2)—CH(3)	1·361(29)	N(2′)—Cu—N(2)	80·2(0·7)°
N(1)—O(1)	1·187(25)	CH(3)—N(3)	1·409(26)	N(2′)—Cu—N(1)	172·4(0·6)°
C(1)—O(1)	1·158(29)	CH$_3$(1)—C(3)	1·490(33)	N(2)—Cu—N(1)	96·0(0·7)°
N(2)—O(2)	1·169(22)	CH$_3$(2)—C(4)	1·502(33)	N(1′)—Cu—N(2)	109·3(0·6)°
C(2)—O(2)	1·209(24)			N(3)—Cu—N(1′)	151·6(0·7)°
				N(2′)—Cu—N(1′)	96·5(0·4)°
				N(1)—C(1)—O(1)	173·7(2·4)°
				N(2)—C(2)—O(2)	175·0(1·8)°
				N(3)—C(3)—CH(1)	115·0(1·7)°

DISCUSION

The $\left[\text{Cu(NCO)}_2(2,4\text{-lut})\right]$ crystal structure consists of infinite polynuclear chains, mutually bonded by van der Waals bonds. The distance between the copper atoms in the chains is 3·22 and 3·44 Å, from which a weak Cu—Cu interaction may be presumed. The projection of the crystal structure into the (010) plane is shown in Fig. 1.

TABLE III

The Deviations from the Planes (Å) of the Atoms of the [Cu(NCO)₂ (2,4-lut)] Crystal Structure

Equatorial plane (1)		Plane of 2,4-lutidine (2)			
Atom	deviation	atom	deviation	atom	deviation
N(3)	0·237	N(3)	0·032	CH(2)	−0·011
N(1)	−0·321	C(3)	0·019	CH(3)	−0·027
N(2′)	−0·245	CH(1)	−0·064	CH₃(1)	0·003
N(1′)	0·329	C(4)	0·030	CH₃(2)	0·018

The nitrogen atoms in the cyanate groups fulfill the function of bridges between the copper atoms, while the oxygen atoms remain free. One part of the infinite chain in the crystal structure is represented in Fig. 2.

The approximately square planar co-ordination around the Cu(II) central atom, formed by the nitrogen atoms of the cyanate groups, N(1), N(1′), N(2), and by the 2,4-nitrogen atom, N(3), is completed by the N(2) nitrogen atom of the cyanate group, to a deformed tetragonal pyramidal co-ordination (Fig. 3). The co-ordination polyhedron around Cu(II) can also be assumed to be a hybrid of a tetragonal pyramid with a trigonal bipyramid. The equatorial plane of the trigonal bipyramid is formed by atoms N(1′), N(2), and N(3), and atoms N(1) and N(2′) are in the axial positions.

The bond lengths and their standard deviations are given in Table II. The equation of the plane, defined by atoms N(1), N(1′), N(2′), N(3) (1), and by atoms of 2,4 lutidine molecule (2) in the C$\bar{1}$ space group, calculated by the least squares method are (in Å)

$$-0.8221x + 0.4852y - 0.2980z = -3.2641 , \qquad (1)$$

$$0.3337x + 0.6653y + 0.6978z = 1.7705 . \qquad (2)$$

The deviations from the plane of the atoms forming the equatorial plane of the tetragonal pyramid as a co-ordination polyhedron around Cu(II) and the atoms of the

2,4-lutidine molecule, are given in Table III. The perpendicular distance of the copper atom from the plane defined by atoms N(3), N(1), N(2′), and N(1′) is 0·209 Å (in the direction towards the fifth nitrogen atom). The cyanate groups have the valence angle, N—C—O, values, 173·67° or 174·99°, which represents a small deviation from the linearity of the NCO group, in comparison with HNCO (ref.[14]) and AgNCO (ref.[15]).

The N—C and C—O bond lengths in the cyanate groups are approximately equal to the analogous lengths in the other cyanates with known crystal structures (Table IV).

TABLE IV

The N—C and C—O Bond Lengths in the AgNCO, HNCO and $[Cu(NCO)_2 (2,4-lut)]$ Crystal Structures

Bond	Bond length, Å	Compound	Reference
N—C	1·195(11)	AgNCO	15
	1·180(20)	HNCO	14
	1·187(25)	$[Cu(NCO)_2 (2,4-lut)]$	this paper
	1·169(22)	$[Cu(NCO)_2 (2,4-lut)]$	this paper
C—O	1·180(11)	AgNCO	15
	1·180(20)	HNCO	14
	1·158(29)	$[Cu(NCO)_2 (2,4-lut)]$	this paper
	1·209(24)	$[Cu(NCO)_2 (2,4-lut)]$	this paper

Each cyanate group is approximately coplanar with two copper atoms, between which it functions as a bridge, through the nitrogen atom. An approximate sp^2 hybridization may be assumed at the nitrogen atoms of the cyanate groups (the sum of the bond angles on the nitrogen atoms of the cyanate groups is 358·34° or 355·77°, and the value of the Cu—N—Cu bond angles is 101·55° or 99·76°).

The unusually large values of the isotropic thermal vibration coefficients for the oxygen atoms (Table I) are in agreement with the fact that these atoms do not function as bridges and form contacts with other atoms of the crystal structure, corresponding to a van der Waals effect. The relatively large values of the isotropic thermal vibration coefficients for the carbon atom in the CH_3 group can be explained similarly.

REFERENCES

1. Garaj J., Dunaj-Jurčo M., Lindgren O.: This Journal 36, 3863 (1971).
2. Nelson S. M.: Proc. Chem. Soc. 1961, 372.
3. Bailey R. A., Kozak S. L.: J. Inorg. Nucl. Chem. 31, 1587 (1964).
4. Burmeister J. L., Daedorff E. A., Van Dike C. E.: Inorg. Chem. 8, 170 (1969).

5. Coutts R. S. P., Wailes P. C.: Australian J. Chem. *19*, 2069 (1966).
6. King H. C. A., Körös E., Nelson S. M.: Nature *196*, 572 (1962).
7. Kohout J., Quastlerová M., Kohútová M.: Z. Naturforsch. *24b*, 134 (1969).
8. Kohout J., Quastlerová-Hvastijová M., Kohútová M., Gažo J.: Monatsh. *102*, 350 (1971).
9. Kohout J., Quastlerová-Hvastijová M., Gažo J.: This Journal *36*, 4026 (1971).
10. Kohout J., Quastlerová M.: Chem. zvesti *22*, 776 (1968).
11. Lindquist O., Wengelin F.: Arkiv Kemi *28*, 179 (1967).
12. Cruikshank D. W. J., Pilling D. E., Sujosa A., Lovell F. M., Trutter M. R.: *Computing Methods and the Phase Problem in X-Ray Analysis*, Symposium Publications Division, p. 32. Pergamon Press, New York 1961.
13. Cromer D. T., Waber J. T.: Acta Cryst. *18*, 104 (1965).
14. Dohlen W. C., Carpenter G. B.: Acta Cryst. *8*, 646 (1955).
15. Britton D., Dunitz J. D.: Acta Cryst. *18*, 426 (1965).

Translated by M. Štulíková.