BIS(1,10-PHENANTHROLINE)COPPER(II) COMPLEXES. REFINEMENT OF THE CRYSTAL STRUCTURE OF THE DITHIOCYANATO-BIS(1,10-PHENANTHROLINE)COPPER(II) COMPLEX

Mária KABEŠOVÁ and Zlatica KOŽÍŠKOVÁ

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

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$[Cu(NCS)_2(phen)_2]$ possesses the orthorhombic structure *Pbcn* at room temperature; the elementary cell parameters are $a = 1{\cdot}3029(21)$, $b = 0{\cdot}9900(15)$, $c = 1{\cdot}7256(23$ nm, $Z = 4$. The central atom has the pseudooctahedral CuN_6 coordination. The thiocyanate ligands are coordinated by the nitrogen atom in the equatorial plane of the coordination polyhedron. Each phenanthroline ligand in the coordination polyhedron coordinates one equatorial and one axial position. All the coordinating ligands possess the *cis* arrangement in the coordination sphere. The experimental results are correlated with published data of other bis(phenanthroline)copper(II) crystal structures.

The objective of the present work was refinement of the crystal structure of the $[Cu(NCS)_2(phen)_2]$ complex, established in ref.[1], with particular emphasis on verification of the unusual structural motif of the substance. The results of the structural analysis are compared with published data of crystal structures of other bis(phenanthroline)copper(II) complexes.

EXPERIMENTAL

The substance under study was obtained in the form of green needle-shaped crystals by reacting an aqueous-ammoniacal solution of $Cu(NO_3)_3$ (1 mol l^{-1}) with an ethanolic solution of phenanthroline (1 : 1) and with an aqueous solution of KNCS (2 mol l^{-1}). The reaction components were added in the ratio of Cu(II) : NH_3 : phen : NCS^- = 1 : 4 : 2 : 2. The crystals were separated from the mother liquor by filtration and rinsed with 1% aqueous ethanol. For $C_{26}H_{16}CuN_6S_2$ (540·1) calculated: 57·82% C, 2·99% H, 11·76% Cu, 15·56% N; found: 57·34% C, 3·10% H, 11·80% Cu, 15·56% N.

Crude crystallographic data were obtained by the Weissenberg method. The photographs, however, indicated that the substance exhibits poor diffraction properties. Since attempts to prepare better single crystals failed, the photographs were taken even though the precision of the results was poorer (a relatively high number of unobserved diffractions, high standard deviations of the interatomic distances and angles). The specific weight of the crystals was determined by the flotation method in a bromoform–methanol mixture at room temperature. The experimental data

were measured on a SYNTEX $P2_1$ four-ring X-ray diffractometer. The lattice parameters were obtained by refining the 20 positional angles for selected diffractions of a rotational Polaroid photograph from the diffractometer. The positions of all the diffractions were scanned over the angular region of $2\theta = 0$ to 55°. The intensity measurement conditions were as follows: MoK_α radiation (71·069 pm), graphite monochromator, $\theta - 2\theta$ scanning technique, scan rate 4·89 to 29·3° min^{-1}, crystal size 0·1 × 0·15 × 0·4 mm, temperature 20°C; the measurements were checked by intensity measurement of two diffractions after each 98 diffractions, conditions for observed diffractions: $I \geq 2\sigma(I)$, number of observed diffractions: 668 (number of measured diffractions 1 215). The intensity variations of standard diffractions did not exceed 2%. The experimental diffraction intensities were corrected for the Lorentz polarization factor and for absorption by measuring the Ψ scan of selected diffractions.

The crystal structure* was elucidated by using the heavy atom method. The position of the copper atoms was determined by Patterson synthesis, and the positions of the remaining non-

TABLE I

Crystallographic data of the $[Cu(NCS)_2(phen)_2]$ complex and some experimental parameters

Crystallographic system	orthorhombic
Space group	*Pbcn*, $Z = 4$
Elementary cell dimensions:	
a, nm	1·3029(21)
b, nm	0·9900(15)
c, nm	1·7256(23)
V, nm	2·225 80(5·75)
Density at room temperature:	
$d_o \cdot 10^3$, kg m^{-3}	1·62(1)
$d_c \cdot 10^3$, kg m^{-3}	1·61
$\mu(MoK_\alpha)$, mm^{-1}	119·12
F(000)	1 036
R, R_w	0·044, 0·041
Range of diffractions measured:	
h	0 to 13
k	0 to 17
l	0 to 23
Final differential map:	
$\Delta\varrho_{max} \cdot 10^4$, e/$nm^3$	0·30
$\Delta\varrho_{min} \cdot 10^4$, e/$nm^3$	−0·36
$(\Delta/\sigma)_{max}$	0·2

* The values of the observed and calculated structural factors, anisotropic temperature factors and fractional coordinates of hydrogen atoms can be obtained from the authors on request.

hydrogen atoms were determined by Fourier synthesis. The positions of hydrogen atoms were calculated by differential Fourier synthesis, and an isotropic temperature factor value of $U_{iso} = 0{\cdot}1$ was assigned to them. The crystal structure refinement was made using the least squares method for the isotropic and anisotropic refinement with the full matrix. The final value obtained is $R = 0{\cdot}044$; the weighted value is $Rw = 0{\cdot}041$ at $w = 0{\cdot}5399/[\sigma^2(F_o) + 0{\cdot}0001(F_o)^2]$. The dispersion curves of the neutral atoms were taken from the International Tables[2]. Calculations were made on a MINSK-M-4030-1 computer using the programs SHELX'76 (ref.[3]) and PARST (ref.[4]).

RESULTS AND DISCUSSION

The crystallographic data of the $[Cu(NCS)_2(phen)_2]$ complex are given in Table I. The fractional coordinates of non-hydrogen atoms are given in Table II and the interatomic distances and angles are summarized in Table III.

The crystal structure of $[Cu(NCS)_2(phen)_2]$ (Fig. 1) is composed of structural units in which the Cu(II) atom has the CuN_6 chromophor and the coordinating ligands possess the pseudo-octahedral arrangement.

TABLE II

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

Atom	x/a	y/b	z/c	$B_{eq} \cdot 10^{-4}$ nm^2
Cu	0	1596(2)	2500	3·53(5)
S	−1393(3)	4730(3)	4227(2)	6·4(1)
Ni	−340(6)	3002(9)	3303(6)	4·9(3)
N2	1629(6)	1289(8)	2771(4)	3·3(3)
N3	−58(9)	87(9)	3375(6)	4·3(3)
C1	−791(9)	3726(12)	3698(7)	4·2(4)
C2	2420(9)	1866(10)	2446(7)	4·6(4)
C3	3419(8)	1540(12)	2659(7)	4·8(4)
C4	3577(10)	586(12)	3193(8)	4·9(5)
C5	2749(8)	−62(11)	3543(6)	3·5(4)
C6	1768(9)	314(10)	3303(6)	3·5(3)
C7	871(10)	−271(13)	3623(7)	3·4(4)
C8	1020(9)	−1248(14)	4178(8)	4·2(4)
C9	154(13)	−1835(12)	4520(7)	5·8(5)
C10	−780(11)	−1427(16)	4269(9)	5·5(5)
C11	−908(11)	−461(16)	3712(9)	5·3(5)
C12	2813(10)	−1074(13)	4097(8)	4·9(5)
C13	2003(10)	−1636(13)	4420(7)	4·9(4)

The thiocyanate ligands are coordinated in the equatorial plane of the coordination polyhedron by the nitrogen atom. Each phenanthroline ligand coordinates one equatorial and one axial position of the coordination polyhedron of Cu(II), and possesses the *cis* arrangement in the coordination sphere. The observed lengths of the axial and equatorial bonds of the phenanthroline ligands at Cu(II) are not beyond the region of interatomic distances in known crystal structures (Table IV).

TABLE III

Interatomic distances and angles in $[Cu(NCS)_2(phen)_2]$

Atoms	Distance, nm	Atoms	Distance, nm
Cu—N1	0·2013(10)	C5—C12	0·1387(17)
Cu—N2	0·2195(9)	C4—C5	0·1593(17)
Cu—N3	0·2125(10)	C5—C6	0·1394(16)
N1—C1	0·1151(15)	C6—C7	0·1416(17)
N2—C2	0·1305(14)	C7—C8	0·1375(19)
N2—C6	0·1344(13)	C8—C9	0·1400(19)
N3—C7	0·1332(17)	C8—C13	0·1401(17)
N3—C11	0·1363(19)	C9—C10	0·1353(20)
C3—C4	0·1336(17)	C10—C11	0·1367(20)
C2—C3	0·1391(16)	C12—C13	0·1317(18)
Atoms	**Angle, deg**	**Atoms**	**Angle, deg**
N1—Cu—N1′	92·9(7)	N2—C6—C7	116·7(1·0)
N2—Cu—N3	89·3(6)	C4—C5—C12	125·8(1·1)
N3—Cu—N3′	90·7(6)	C4—C5—C6	117·3(1·0)
N1—Cu—N3	169·3(4)	C5—C6—C7	122·1(1·0)
N1—Cu—N2	91·7(3)	C6—C7—C8	116·3(1·2)
Cu—N1—C1	162·0(9)	N3—C7—C8	122·6(1·2)
Cu—N2—C6	112·0(7)	C7—C8—C13	122·0(1·3)
Cu—N2—C2	127·7(7)	C7—C8—C9	118·2(1·3)
C2—N2—C6	120·1(9)	C9—C8—C13	119·9(1·2)
Cu—N3—C11	127·7(9)	C8—C9—C10	117·8(1·3)
Cu—N3—C7	112·5(8)	C9—C10—C11	123·0(1·3)
C7—N3—C11	119·7(1·2)	N3—C11—C10	118·7(1·3)
N2—C2—C3	121·6(1·0)	C5—C12—C13	123·3(1·2)
C2—C3—C4	119·4(1·1)	C8—C13—C12	119·4(1·2)
C3—C4—C5	120·4(1·2)	C6—C5—C12	116·9(1·0)
N2—C6—C5	121·2(1·0)		

Symmetry code: N1′, N3′: $-x, y, 0{\cdot}5 - z$.

TABLE IV

A survey of some published structural data of bis(phenanthroline)copper(II) complexes $[Cu(phen)_2Z$

Z[a]	Chromophor	Coordination polyhedron[b]	Phenanthroline ligand $(Cu—N)_{ax,eq}$ bond lengths nm	Equatorial bond angles deg α_1 α_2 α_3	Ref.[c]
Cl]$NO_3.H_2O$	CuN_4Cl	D TR B	$0{\cdot}1989(4)_{ax}$	119·2(1)	5
			$0{\cdot}1988(4)_{ax}$	135·8(1)	
I			$0{\cdot}2132(1)_{eq}$	105·0(1)	
			$0{\cdot}2091(2)_{eq}$		
Cl]ClO_4	CuN_4Cl	D TR B	$0{\cdot}2004(6)_{ax}$	*)	6
			$0{\cdot}1986(6)_{ax}$		
II			$0{\cdot}2136(6)_{eq}$		
			$0{\cdot}2077(6)_{eq}$		
Cl]Cl.3 H_2O.acetone	CuN_4Cl	D TR B	$0{\cdot}1993(4)_{ax}$	120·6(1)	7
			$0{\cdot}1990(4)_{ax}$	133·0(1)	
(solvate)			$0{\cdot}2151(4)_{eq}$	106·4(1)	
III			$0{\cdot}2108(2)_{eq}$		
	CuN_4Cl	DTR B	$0{\cdot}1955(3)_{ax}$	129·6(1)	7
			$0{\cdot}19999(4)_{ax}$	130·4(1)	
			$0{\cdot}2138(3)_{eq}$	100·0(1)	
			$0{\cdot}2126(3)_{eq}$		
I].S_8	CuN_4I	D TR B	$0{\cdot}200(1)_{ax}$	125·3(3)	8
			$0{\cdot}210(1)_{eq}$	125·3(3)	
IV				109·4(3)	
(thio)]$ClO_4.H_2O$	CuN_4S	D TR B	$0{\cdot}1983(5)_{ax}$	120·2(1)	9
			$0{\cdot}2003(5)_{ax}$	123·2(1)	
			$0{\cdot}2080(4)_{eq}$	116·6(1)	
V			$0{\cdot}2087(5)_{eq}$		
(CN)]$NO_3.H_2O$	CuN_4C	D TR B	$0{\cdot}2001(10)_{ax}$	129·0(3)	10
			$0{\cdot}2014(10)_{ax}$	132·4(3)	
			$0{\cdot}2102(6)_{eq}$	98·6(2)	
VI			$0{\cdot}2123(6)_{eq}$		
$(H_2O)]BF_4$	CuN_4O	D TR B	$0{\cdot}1985(6)_{ax}$	111·7(3)	11
			$0{\cdot}2041(7)_{eq}$	136·6(3)	
VII				111·7(3)	

TABLE IV
(*Continued*)

Z[a]	Chromophor	Coordination polyhedron[b]	Phenanthroline ligand $(Cu—N)_{ax,eq}$ bond lengths nm	Equatorial bond angles deg α_1 α_2 α_3	Ref.[c]
$(H_2O)]NO_3$	CuN_4O	D TR B	$0{\cdot}199(1)_{ax}$ $0{\cdot}203(1)_{eq}$	110·0(4) 140·0(4) 110·0(4)	12
VIII					
(3,5-diMepy)]$(ClO_4)_2$	CuN_4N'	D TE P	$0{\cdot}2134(13)_{ax}$ $0{\cdot}2009(10)_{eq}$ $0{\cdot}2010(10)_{eq}$ $0{\cdot}2036(10)_{eq}$	81·3(5) 93·4(4) 92·7(4)	13
IX					
$(H_2O)]$quan.9 H_2O	CuN_4O	D TE P	$0{\cdot}1987(8)_{ax}$ $0{\cdot}1991(7)_{eq}$	83·2(3) 101·5(3)	14
X					
$(CH_3CO_2)]ClO_4.2\ H_2O$	CuN_4OO^*	D TE B	$0{\cdot}1999(2)_{ax}$ $0{\cdot}2122(2)_{eq}$	150·2(2) 95·9(2) 113·4(2)	15
XI					
$(CH_3CO_2)]NO_3.2\ H_2O$	CuN_4OO^*	D TE B	$0{\cdot}2000(3)_{ax}$ $0{\cdot}2170(3)_{eq}$	157·7(2) 97·6(1) 104·3(1)	15
XII					
$(CH_3CO_2)]BF_4.2\ H_2O$	CuN_4OO^*	D TE B	$0{\cdot}2000(4)_{ax}$ $0{\cdot}2123(4)_{eq}$	149·5(2) 95·4(2) 114·7(2)	15
XIII					
$(CH_3CO_2)]ClO_4$	CuN_4OO^* (298 K)	D TE B	$0{\cdot}2006(4)_{ax}$ $0{\cdot}1994(4)_{ax}$ $0{\cdot}2130(4)_{eq}$ $0{\cdot}2098(4)_{eq}$	157·5(2) 91·1(1) 114·1(2)	16
	CuN_4OO^* (173 K)	D TE B	$0{\cdot}2012(4)_{ax}$ $0{\cdot}2002(3)_{ax}$ $0{\cdot}2141(3)_{eq}$ $0{\cdot}2097(2)_{eq}$	154·9(2) 91·3(1) 113·6(1)	16
XIV					
$(CH_3CO_2)]BF_4$	CuN_4OO^*	D TE B	$0{\cdot}2010(2)_{ax}$ $0{\cdot}2025(2)_{ax}$ $0{\cdot}2062(2)_{eq}$ $0{\cdot}2218(2)_{eq}$	160·5(1) 95·7(1) 103·5(1)	15
XV					

TABLE IV
(*Continued*)

Z[a]	Chromophor	Coordination polyhedron[b]	Phenanthroline ligand $(Cu—N)_{ax,eq}$ bond lengths nm	Equatorial bond angles deg α_1 α_2 α_3	Ref.[c]
$(NO_2)]BF_4$	CuN_4OO^*	D TE B	$0{\cdot}1999(4)_{ax}$	154·5(1)	17
			$0{\cdot}2019(3)_{ax}$	93·2(1)	
			$0{\cdot}2049_{eq}$	89·1(1)	
XVI			$0{\cdot}2167_{eq}$		
$(CO_2)]ClO_4$	CuN_4OO^*	D TE B	$0{\cdot}1985(3)_{ax}$	148·1(1)	18
			$0{\cdot}2111(3)_{eq}$	97·0(1)	
XVII				114·9(1)	
$(im)PF_6]$	$CuN_4N'F$	D TE B	$0{\cdot}2219(7)_{ax}$	92·6(3)	19
			$0{\cdot}2042(5)_{eq}$	93·0(2)	
			$0{\cdot}2008(6)_{eq}$	81·9(3)	
XVIII			$0{\cdot}2034(6)_{eq}$		
$(NCS)_2]$	CuN_6	D TE B	$0{\cdot}2195(9)_{ax}$	89·2(6)	**
XIX			$0{\cdot}2125(10)_{eq}$	90·7(6)	
				92·9(7)	
$(NCSe)_2]$	CuN_6	D TE B	$0{\cdot}2183(11)_{ax}$	91·3(5)	1
			$0{\cdot}2127(11)_{eq}$	91·7(4)	
XX				92·9(7)	

[a] thio thiourea, phen 1,10-phenanthroline, 3,5-diMepy 3,5-dimethylpyridine, quan quanosine, im imidazole; [b] D TR B distorted trigonal bipyramid, D TE P distorted tetragonal pyramid, D TE B distorted tetragonal bipyramid; O* is a semicordinated oxygen atom; [c] ** this work, *) bond angles are not reported in the source (ref.[6]).

The carbon and nitrogen atoms forming heterocyclic rings of the phenanthroline ligand are not coplanar.

The *cis*-coordination of two phenanthroline ligands in the coordination sphere of Cu(II) is usual and is present in the majority of known crystal structures. Their occurrence in the coordination sphere stimulates the coordination of ligands in the shape of a compressed trigonal bipyramid about Cu(II). The ligands at the fifth (and/or sixth) coordination site can, through a change in the bond angles (or dis-

tances), cause a distortion of the coordination sphere. This can be oriented in several directions:

A – distortion corresponding to transition between the trigonal bipyramid and the tetragonal pyramid, with the coordination number 5 (complexes *I* to *X* in Table IV).

B – distortion corresponding to transition between the trigonal bipyramid and the tetragonal bipyramid, with the coordination number 5 and with additional equatorial bonds (complexes *XI* to *XVIII* in Table IV).

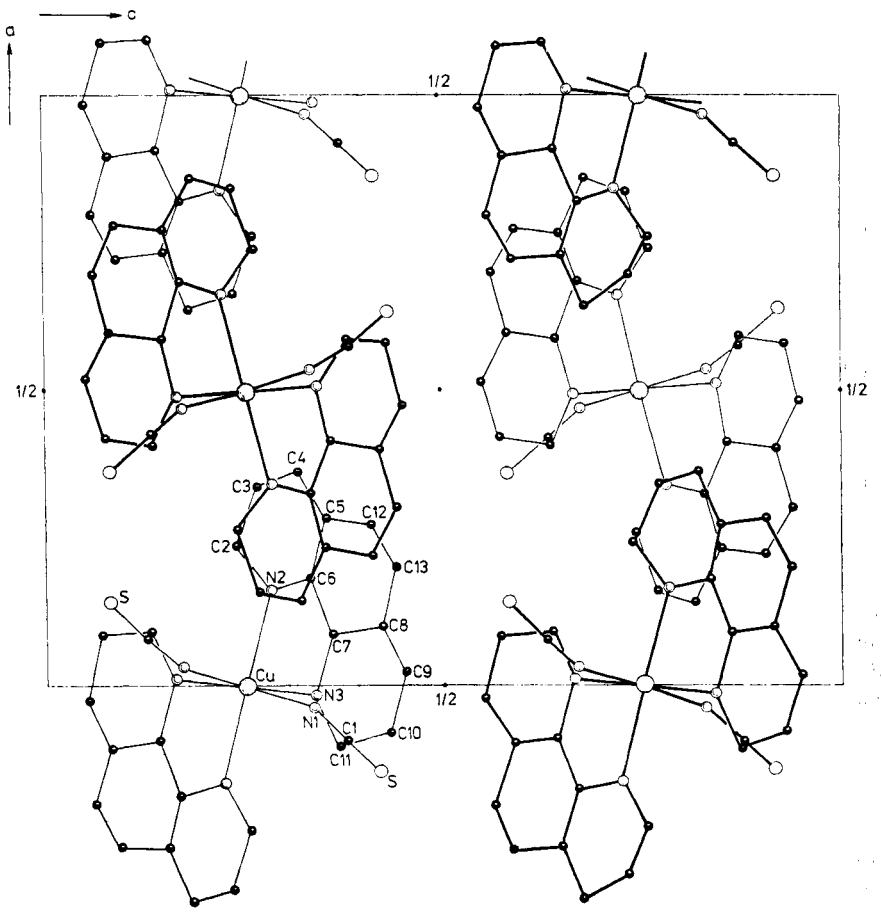

FIG. 1

Schematic picture of the crystal structure of the $[Cu(NCS)_2(phen)_2]$ complex in the *xy* projection, with atom numbering

C – distortion corresponding to transition between the tetragonal bipyramid and the square-planar arrangement, with the coordination number 8 (complexes *XVIII* to *XX* in Table IV).

Data of known crystal structures in Table IV suggest that distortion of *A* type is observed if the bis(phenanthroline)copper(II) complex contains monofunctional ligands, e.g. Cl^-, I^-, CN^-, H_2O, $CS(NH_2)_2$, 3,5-diMepy. If the complex contains bidentate ligands such as $CH_3CO_2^-$, CO_2^-, NO_2^-, *B* type distortion occurs, whereas *C* type distortion is observed if the complex involves two monofunctional ligands in the coordination sphere.

Structural analysis gave evidence that $[Cu(NCS)_2(phen)_2]$, and apparently also its isostructural form, viz. complex *XX*, deviates from the hitherto known facts as described above in its slightly distorted octahedral coordination on the one hand and, particularly, in the coordination of two monofunctional anionic ligands in the equatorial plane on the other hand. In this connection it is noteworthy that for this complex an anomaly has also been observed in the electronic spectra, particularly with respect to the predicted and observed number of ligand field bands[20].

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