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Two Different Coordination Polyhedra in the Crystal Structure of $[Cu(bipy)_2NCS]NCS$

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Described $[Cu(bipy)_2NCS]NCS$ (bipy = bipyridine) is triclinic, space group $P\bar{1}$, *with* $a = 10.815(4)$, $b = 14.457(5)$, $c = 16.291(10)$ Å, $\alpha = 110.74(4)$, $\beta = 90.90(4)$, $\gamma = 110.48(3)^\circ$, $Z = 4$. *The final* R *makes 0.068 for 2444 observed independent reflections. The complex compound exhibits two symmetrically independent coordination polyhedra of Cu(II), in which the coordination is quasi-trigonal bipyramidal. The polyhedral differ by the distortion degree of the trigonal bipyramidal arrangement in direction to a tetragonal pyramid.*

Introduction

In the course of the study of the types of coordination polyhedra of Cu(II) complexes and the genesis of their mutual transformations, the crystal structure of $Cu(bipy)_2(NCS)_2$ was also investigated. It is known that for Cu(II) complexes with ligands of the bipyridine type the coordination polyhedra of Cu(II) usually appear as distorted on the transition between trigonal bipyramid – tetragonal pyramid configurations [1]. It was also shown that the distortion degree of such coordination polyhedra being in the crystal structure in the form of cations, depends on the properties of the anion in crystal structure [2]. In connection with the distortion isomerism of Cu(II) complexes [3, 4] such cases were called cationic distortion isomerism [5]. As it will be seen later, the crystal structure of the compound under investigation not only confirms that for the given type of Cu(II) complexes mentioned, distortion of the coordination polyhedra appears to be typical (transition between trigonal bipyramid-tetragonal pyramid), but our results demonstrate the plasticity of Cu(II) coordination polyhedra and in connection with their ability to change their configuration between the tetragonal pyramidal and trigonal bipyramidal arrangement of their ligands in coordination sphere.

Experimental

Preparation

Dark-green prism-shaped crystals of $Cu(bipy)_2(NCS)_2$ were prepared by a reaction of aqueous ammonia solution of $Cu(NO_3)_2$ (1 *M*) with ethanol solution of 2,2'-bipyridine and aqueous solution of KNCS (2 *M*), in the molar ratio of $[Cu(II)]:[NH_3]:[bipy]:[NCS^-] = 1:4:2:2$.

Anal.: Cu, 12.68; N, 17.24; C, 53.94; H, 3.43%. Found: Cu, 12.91; N, 17.08; C, 53.69; H, 3.28%.

Crystal Data

$[Cu(N_2C_{10}H_8)_2(NCS)]NCS$, $M_r = 492.1$, triclinic, $P\bar{1}$, $a = 10.815(4)$, $b = 14.457(5)$, $c = 16.291(10)$ Å, $\alpha = 110.74(4)$, $\beta = 90.90(4)$, $\gamma = 110.48(3)^\circ$, $U = 2206(1)$ Å^3, $Z = 4$, $D_m = 1.50(2)$, $D_x = 1.48$ Mgm^{-3}, Mo-K$_\alpha$ radiation, $\lambda = 0.71069$ Å, μ(Mo-K$_\alpha$) = 1.23 mm^{-1}, $F(000) = 1004$.

The cell parameters were refined with a Syntex $P2_1$ diffractometer by the least-squares method from the angles of 10 selected reflections. The orientation matrix obtained was employed for further intensity measurements carried out within the range of $0 \leqslant 2\theta \leqslant 40^\circ$ using the θ–2θ scanning technique with a variable scan rate ranging from 4.88 to 29.3° min^{-1}. The scan range for each reflection was from 2θ(Mo-K$_{\alpha1}$) – 1° to 2θ(Mo-K$_{\alpha2}$) + 1°. Two standard reflections were re-measured after every 98 reflections. The original total reflections were reduced to 2444 by rejecting reflections with $I < 1.96\sigma(I)$. Intensities were corrected for the Lorentz and polarization factor and experimental absorption effects. The structure was solved by a combination

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TABLE I. Fractional Atomic Coordinates (×10^3) with Estimated Standard Deviations in Parentheses and Equivalent Isotropic Thermal Parameters $B_{(eq)}$.

Atom	X	Y	Z	B_{eq}, Å
Cu(1)	2920(0)	2181(1)	3784(0)	4.00
Cu(2)	5805(1)	2290(1)	8857(1)	3.89
S(1)	4481(4)	2380(3)	6564(2)	5.76
S(2)	7352(4)	3081(3)	1834(2)	7.58
S(3)	1543(4)	2187(3)	1179(2)	6.18
S(4)	9793(4)	2889(3)	6195(3)	6.96
N(1)	4619(8)	3365(7)	3920(5)	4.40
N(2)	2210(8)	3315(6)	3653(5)	3.95
N(3)	3054(8)	1172(6)	2541(5)	3.98
N(4)	1198(9)	957(7)	3539(5)	4.31
N(5)	3334(9)	2232(7)	4985(6)	5.33
N(6)	7560(8)	3435(6)	8920(5)	4.10
N(7)	5175(8)	3507(7)	8797(5)	4.02
N(8)	5885(8)	1266(7)	7614(5)	3.59
N(9)	4029(8)	1096(6)	8643(5)	3.84
N(10)	6255(10)	2440(7)	74(6)	5.79
N(11)	1099(10)	2566(8)	9672(7)	6.10
N(12)	8268(10)	2530(8)	4650(7)	6.98
C(1)	5827(11)	3347(9)	4134(7)	5.13
C(2)	7054(13)	4171(10)	4185(8)	6.19
C(3)	6958(12)	5020(10)	3965(8)	6.69
C(4)	4296(12)	4958(8)	6242(8)	5.82
C(5)	4539(12)	4213(8)	3758(6)	4.36
C(6)	3196(10)	4177(8)	3613(6)	3.65
C(7)	2953(13)	5001(9)	3502(7)	5.45
C(8)	1628(15)	4939(10)	3423(8)	6.90
C(9)	608(13)	4062(10)	3465(7)	5.94
C(10)	899(12)	3203(10)	3557(7)	5.61
C(11)	353(12)	892(9)	4141(8)	5.14
C(12)	829(12)	19(9)	6061(8)	5.23
C(13)	1053(12)	890(10)	6866(8)	5.83
C(14)	181(10)	826(8)	7484(8)	4.59
C(15)	960(10)	121(8)	2735(6)	3.71
C(16)	1943(9)	254(7)	2165(6)	2.93
C(17)	8208(11)	456(7)	8710(6)	3.51
C(18)	7120(11)	237(8)	9187(6)	4.09
C(19)	4010(11)	664(9)	1213(8)	4.96
C(20)	4108(11)	1377(9)	2094(8)	4.99
C(21)	3801(11)	2290(9)	5656(7)	4.43
C(22)	8684(11)	3289(9)	9016(8)	5.48
C(23)	−117(11)	4021(10)	8903(8)	6.00
C(24)	9832(12)	4893(9)	8713(8)	6.07
C(25)	8660(10)	5040(8)	8649(7)	4.41
C(26)	7495(10)	4274(8)	8752(6)	3.90
C(27)	6163(10)	4327(8)	8715(6)	3.53
C(28)	4028(12)	4790(8)	1396(7)	4.76
C(29)	5322(13)	4803(10)	1373(8)	6.13
C(30)	3688(14)	4373(11)	8741(11)	7.83
C(31)	3939(11)	3514(9)	8826(7)	4.64
C(32)	3206(9)	1106(9)	9241(7)	3.95
C(33)	1997(11)	211(9)	9081(7)	4.99
C(34)	8304(11)	673(9)	1740(7)	4.79
C(35)	7464(11)	649(8)	2357(7)	4.44
C(36)	3741(10)	264(8)	7861(6)	3.41
C(37)	4700(10)	376(8)	7273(6)	3.71
C(38)	5490(12)	381(9)	3609(7)	4.79
C(39)	4519(13)	234(9)	4120(7)	5.40
C(40)	6714(12)	691(9)	6223(7)	5.10
C(41)	6825(11)	1406(9)	7108(7)	4.32
C(42)	6725(10)	2709(8)	804(7)	3.84
C(43)	1260(10)	2400(8)	296(7)	4.18
C(44)	8908(11)	2691(8)	5280(8)	5.17

of direct methods using the program MULTAN78 [6] and the Fourier synthesis techniques [7], which led to a conventional value of $R = 0.068$ for the 558 parameters varied and 2444 observed reflections used in the refinement. The maximum residual electron density was 0.56 eÅ^{-3}. Neutral-atom scattering factors were obtained from International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, 1975, Vol. 4. The atom coordinates for the non-hydrogen atoms are listed in Table I, while some of the bond lengths and angles are given in Table II. Observed and calculated structure factors, anisotropic temperature factors for all non-hydrogen atoms and all intramolecular distances are in Supplementary Publication No. SUP 00000 (00 pp.).

Results and Discussion

The crystal structure of $Cu(bipy)_2(NCS)_2$ complex consists of two different cations of $[Cu(bipy)_2(NCS)]^+$ and of NCS^- anions (Fig. 1). The cations show in both cases a quasi-trigonal bipyramidal coordination. The bipyridyl ligands are in the coordination polyhedron in a *cis*-position. As chelates they always coordinate one equatorial and one axial position of the coordination polyhedron. The thiocyanate ligand is coordinated in the equatorial plane monodentately, by the nitrogen atom. The electronic spectrum showed (in Nujol suspension) for complex $Cu(bipy)_2(NCS)_2$ a band of the d–d transition at 13050 cm^{-1} with a shoulder at 10000 cm^{-1}. Such a splitting of the absorption band is in agreement with the knowledge of electronic spectra for complex compounds of the analogous type [2, 8–10].

The crystal structure of the complex compound under investigation exhibits two symmetrically independent coordination polyhedra of Cu(II) (Fig. 2). These show negligibly small differences in their interatomic distances; however, significant changes of their bond angles were noted in the equatorial plane. These changes of the bond angles in such coordination polyhedra types indicate, in agreement with the conclusions of [1, 2], a different degree of their distortion, being connected

TABLE II. Selected Bond Lengths (Å) and Angles (°) with Estimated Standard Deviations in Parentheses.

Cu(1)–N(1)	1.967(10)	Cu(2)–N(6)	2.007(9)
Cu(1)–N(2)	2.108(9)	Cu(2)–N(7)	2.126(10)
Cu(1)–N(3)	2.076(8)	Cu(2)–N(8)	2.067(8)
Cu(1)–N(4)	1.982(10)	Cu(2)–N(9)	2.006(9)
Cu(1)–N(5)	1.969(9)	Cu(2)–N(10)	1.951(14)
N(5)–C(21)	1.161(14)	N(10)–C(42)	1.157(14)
C(21)–S(1)	1.584(11)	C(42)–S(2)	1.624(11)
N(1)–Cu(1)–N(2)	79.5(4)	N(6)–Cu(2)–N(7)	78.8(4)
N(1)–Cu(1)–N(3)	96.0(4)	N(6)–Cu(2)–N(8)	93.5(4)
N(1)–Cu(1)–N(4)	175.3(4)	N(6)–Cu(2)–N(9)	173.5(4)
N(1)–Cu(1)–N(5)	92.7(4)	N(6)–Cu(2)–N(10)	92.5(4)
N(2)–Cu(1)–N(3)	110.0(3)	N(7)–Cu(2)–N(8)	112.5(4)
N(2)–Cu(1)–N(4)	99.7(4)	N(7)–Cu(2)–N(9)	100.5(4)
N(2)–Cu(1)–N(5)	118.5(4)	N(7)–Cu(2)–N(10)	112.7(4)
N(3)–Cu(1)–N(4)	79.9(4)	N(8)–Cu(2)–N(9)	80.7(4)
N(3)–Cu(1)–N(5)	131.4(4)	N(8)–Cu(2)–N(10)	134.8(4)
N(4)–Cu(1)–N(5)	91.8(4)	N(9)–Cu(2)–N(10)	93.8(4)
Cu(1)–N(5)–C(21)	168. (1)	Cu(2)–N(10)–C(42)	167. (1)
N(5)–C(21)–S(1)	178. (1)	N(10)–C(42)–S(2)	179. (1)

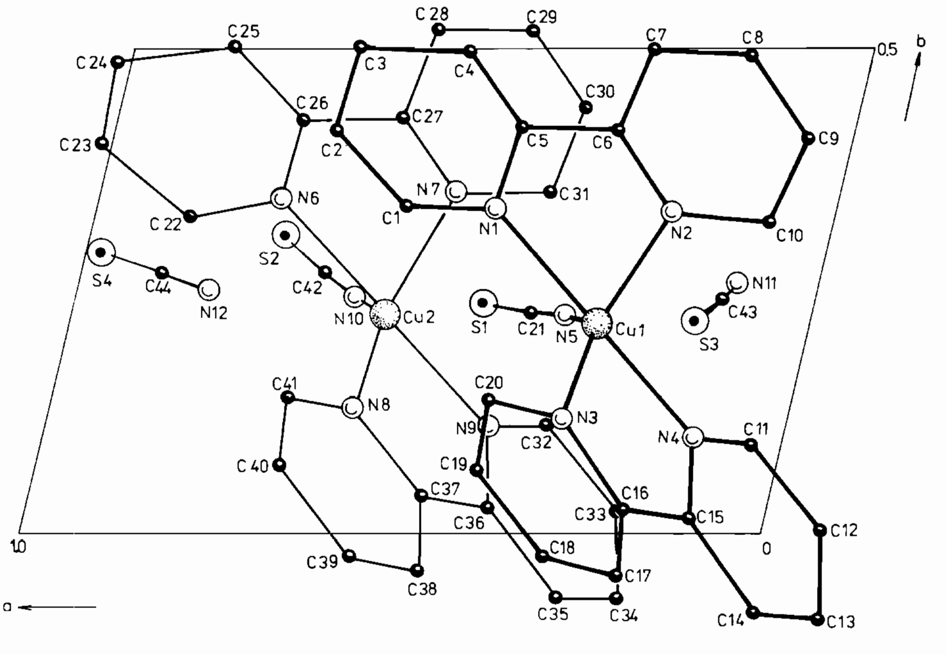

Fig. 1. Projection along *c* in the unit cell in crystals of $Cu(bipy)_2(NCS)_2$.

with their transition from a trigonal bipyramidal to a tetragonal pyramidal coordination.

In the crystal structure of $[Cu(edp)(H_2O)]H_2O$ [11] also two symmetrically independent pentacoordinated coordination polyhedra of Cu(II) were observed: they showed however the shape of a tetragonal pyramid. Similarly, as in the above case, the differences in the interatomic distances are negligibly small, while the bond angles in the equatorial plane show significant changes. It seems that in connection with the knowledge of the genesis of mutual transitions for the different types of Cu(II) coordination polyhedra, the above example may be also understood as a different distortion degree of the coordination polyhedron (on the transition from tetragonal pyramid to trigonal bipyramid).

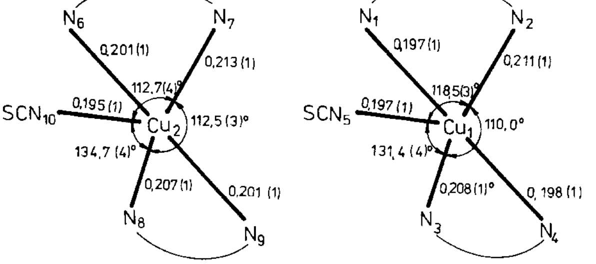

Fig. 2. Schematic illustration of two symmetrical independent coordination polyhedra of $[Cu(bipy)_2(NCS)]^+$.

The interactomic distances of Cu–N (of the bipyridine ligand) in both the coordination polyhedra of cations $[Cu(bipy)_2(NCS)]^+$ are considerably shorter in axial direction compared with the equatorial plane, as observed also for other complexes of this type [10]. In accordance with literature data also the interatomic distance of Cu–N (thiocyanate ligand) was determined, *viz.* 1.963(7) and 1.925(8) Å, respectively, being, however, shorter than the other Cu–N distances in the equatorial plane [10]. The found interatomic distances and the bond angles in bipyridine and thiocyanate ligands (as also in the thiocyanate anion) are within the limits of the published values [8, 10, 12].

As already mentioned it was found that the phenomenon of a cationic distortion isomerism for Cu(II) complexes occurs at a change of the anion in the coordination compound [2, 5]. A similar phenomenon was also observed for Cu(II) complexes, occurring, however, on the transition of tetrahedral to a square-planar coordination of Cu(II) for the $[CuCl_4]^{2-}$ anion in dependence on the cation properties [13, 14]. In the crystal structure of $[Cu(bipy)_2(NCS)_2]$ two differently distorted coordination polyhedra of the complex cation of Cu(II) were found, though with the same anion. This fact allows us to suppose that the plasticity of the coordination sphere of such complex cations is their intrinsic characteristic property.

As it was already said the determination of the crystal structure of the $Cu(bipy)_2(NCS)_2$ complex had the aim to contribute to knowledge of known types of Cu(II) coordination polyhedra [3]. On the basis of our results and of literature data the possible (as also the observed) mutual transitions between the types of Cu(II) coordination polyhedra are marked in the scheme (Fig. 3). With arrows and full lines are marked those transitions that were realised experimentally. Arrows with full lines and the symbol *x* characterize such transitions of coordination polyhedra, which were also theoretically interpreted (based on the theory of vibronic interactions of degenerated or pseudo-degenerated electronic states [3]). Arrows with dotted lines characterize changes of coordination polyhedra, that may be supposed on the basis of structure data allowing to choose alternatively the coordination polyhedron type. The results of this work contributes to the data of the genesis of mutual conversions of Cu(II) coordination polyhedra by a possible transition between the trigonal bipyramidal and a tetragonal configuration of the Cu(II) coordination polyhedra.

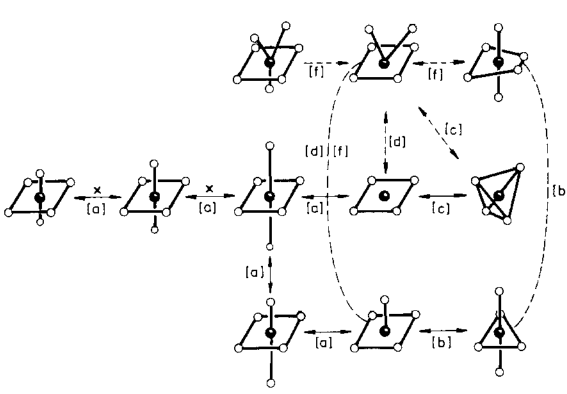

Fig. 3. Types of Cu(II) coordination polyhedra: (a) ref. [3]; (b) ref. [1]; (c) ref. [14]; (d) ref. [15]; (f) ref. [16].

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