

Preparation and properties of (selenocyanato)bis(2,2'-bipyridine) copper(II) selenocyanate and crystal structure of its α -modification

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Results reported in this paper concern the solving of the crystal structure of α -[Cu(bpy)₂NCSe]NCSe. The structural unit consists of a complex cation and a selenocyanate anion. Coordination polyhedron of the central atom is trigonal bipyramidal in shape, with a square-pyramidal distortion. The selenocyanate group is coordinated as a unidentate ligand through the nitrogen atom in the equatorial plane of the coordination polyhedron. In the complex under investigation, existence of two different kinds of selenocyanate groups has also been proved by means of infrared spectra. The distortion of the trigonal bipyramidal coordination polyhedron of the Cu(II) central atom has also been registered as a splitting of ligand field absorption bands. This result confirms a suggestion about a possible correlation between the type of coordination polyhedra of Cu(II) and the shape of ligand field band in electronic absorption spectra. Two different forms of the above-mentioned compound have been prepared under various conditions of preparation. They are preliminarily regarded as distortion isomers which are intermediates between a trigonal bipyramid and a tetragonal pyramid.

В работе приведены результаты исследования кристаллической структуры α -[Cu(bpy)₂NCSe]NCSe. Структурная единица состоит из комплексного катиона и селеноцианатного аниона. Координационный полиэдр центрального атома в комплексном катионе представляет собой тригональную бипирамиду с квадратно-пирамидальной деформацией. Селеноизоцианатный лиганд координирован в экваториальной плоскости координационного полиэдра. В исследуемом комплексе с помощью ИК-спектроскопии подтверждено наличие двух видов селеноизоцианатных групп. Деформация тригонально-бипирамидальной координации центрального атома Cu(II) проявилась и в расщеплении полос лигандного поля. Этот результат подтверждает предположение о возможной корреляции между типом координационных полиэдров Cu(II) и формой адсорбционных полос поля лигандов в электронных спектрах. Исследуемое соединение

было получено в двух разных формах, которые мы предварительно считаем дисторсионными изомерами с координационными полиэдрами, являющимися промежуточными между тригональной бипирамидой и тетрагональной пирамидой.

Pseudohalides as ligands, namely cyanates, thiocyanates, and selenocyanates may be bonded to the central atom in various modes [1—4]. It has been found that the mode how a thiocyanate ligand is bonded in heterogeneous Cu(II) complexes is affected by mutual influence of ligands in the coordination sphere of the central atom [3—5]. In order to learn other factors which had influence on structural properties of Cu(II) complexes of the mentioned type, thiocyanate and selenocyanate Cu(II) complexes with 1,10-phenantroline ligand were studied in paper [6].

In this paper, a complex of a summary formula $\text{Cu}(\text{bpy})_2(\text{NCSe})_2$ where $\text{bpy} = 2,2'$ -bipyridine has been studied. Since in complexes of the type of $\text{Cu}(\text{bpy})_2(\text{NCX})_2$ ($X = \text{S}, \text{Se}$) a pentacoordination or a hexacoordination of Cu(II) central atom was expected, it seemed to be interesting to determine the type of coordination polyhedron in the complex by means of single crystal X-ray structure analysis and to bring the results into correlation with those obtained for ligand field bands in electronic absorption spectra. Considering stereochemical peculiarities of coordination polyhedra of Cu(II), namely their plasticity [7], it was worthy to investigate the possibilities of such structural states which would represent a transition between a trigonal bipyramid and tetragonal pyramid, *i.e.* the occurrence of distortion isomers of the given type [8—10].

Experimental

Preparation of $\alpha\text{-Cu}(\text{bpy})_2(\text{NCSe})_2$

When an aqueous solution of $\text{Cu}(\text{NO}_3)_2$ (5 cm^3) with a concentration of 1 mol dm^{-3} was mixed with a 0.125 M ethanolic solution of $2,2'$ -bipyridine (100 cm^3) and a 2 M aqueous solution of KNCSe in a mole ratio of $\text{Cu(II)}:\text{bpy}:\text{NCSe}^- = 1:2.5:2$, dark green crystals crystallized from the solution. The crystalline product contained as a by-product white needle-like crystals, probably of KNO_3 , which were removed by washing with water (*i.e.* by a different method when compared with that given in paper [11]). The dark green crystals were then washed with ethanol and finally dried with ether.

$\beta\text{-Cu}(\text{bpy})_2(\text{NCSe})_2$ was obtained as dark green precipitate when the same procedure was employed but dried acetonetic solutions were used.

For $\alpha\text{-Cu}(\text{bpy})_2(\text{NCSe})_2$ calculated: 10.85% Cu, 45.10% C, 14.34% N, 2.76% H; found: 10.64% Cu, 44.81% C, 14.25% N, 2.80% H.

For $\beta\text{-Cu}(\text{bpy})_2(\text{NCSe})_2$ calculated: 10.85% Cu, 45.10% C, 14.34% N, 2.76% H; found: 10.62% Cu, 44.51% C, 14.21% N, 2.73% H.

Content of copper was determined complexometrically, while that of carbon, nitrogen, and hydrogen was found by elemental analysis.

Equipment

Magnetic susceptibility was measured by the Gouy method at room temperature with an equipment made in our laboratory. Intensities of magnetic field were in the range 280—520 kAm⁻¹. The value of magnetic moment was calculated according to the relation

$$\mu_{\text{eff}} = 798 \sqrt{\chi'_m T}.$$

E. p. r. spectra of powdered samples were taken with a spectrophotometer Varian E-3.

Infrared spectra were recorded with a spectrophotometer Perkin—Elmer 225 both in KBr pellets in the range 400—4000 cm⁻¹ and in nujol mulls in the range 200—400 cm⁻¹.

Electronic absorption spectra were measured in nujol mulls with a spectrophotometer Specord UV VIS in the range 14 500—30 000 cm⁻¹ as well as with Unicam SP 700 in the range 7000—15 000 cm⁻¹.

In solving the crystal structure, a set of diffraction data collected in the form of integral intensities was measured with an automatic four-circle diffractometer Syntex P2₁ employing 2θ method, MoK_α radiation, and a graphite monochromator.

Procedure of solving the crystal structure

Intensities of 1863 independent reflections were corrected both for Lorentz and polarization factors, as well as for absorption. All intensities were transformed to absolute scale using the Wilson method ($B = 0.322 \text{ nm}^2$). The crystal structure was solved by the Patterson and Fourier method and the refinement was carried out by full-matrix least squares method up to the final value of $R = 0.094$. The phase of structure factors for the first Fourier synthesis was calculated for one atom of copper and two selenium atoms, localized from Patterson synthesis. After the last cycle of refinement, the values of changes for all position parameters were smaller than 0.1 σ and those for temperature parameters smaller than 0.2 σ . All computing was done with a computer Nova 1200 XTL — modul of Syntex P2₁.

Results and discussion

In solving the crystal structure of $\alpha\text{-Cu}(\text{bpy})_2(\text{NCSe})_2$, the following results have been obtained:

The basic crystallographic data for the above compound are as follows: $a = 1.7176$ (3) nm; $b = 0.8257$ (3) nm; $c = 1.8331$ (5) nm; $\beta = 123.31$ (2)°; $Z = 4$; space group $P2_1/c$; $\rho_{\text{obsd}} 1.73$ (2) g cm⁻³, $\rho_{\text{calc}} = 1.74$ g cm⁻³. Atomic coordinates, interatomic distances as well as bond angles in a structural unit are given in Tables 1 and 2. The structure of a cation of $[\text{Cu}(\text{bpy})_2\text{NCSe}]^+$ is shown in Fig. 1.

Table 1

Atomic coordinates ($\times 10^4$) and coefficients of anisotropic temperature factor [10^{-20} m^2]

Atom	<i>X/a</i>	<i>Y/b</i>	<i>Z/c</i>	<i>B</i> ₁₁	<i>B</i> ₂₂	<i>B</i> ₃₃	<i>B</i> ₁₂	<i>B</i> ₁₃	<i>B</i> ₂₃
Cu	7331 (2)	0208 (3)	0649 (2)	2.31 (12)	2.50 (13)	3.90 (14)	0.38 (11)	1.93 (11)	−0.04 (11)
Se1	2394 (2)	1126 (3)	2294 (2)	4.04 (13)	3.76 (13)	6.16 (16)	−0.73 (11)	3.21 (12)	−1.75 (11)
N1	2407 (12)	3538 (21)	3420 (10)	3.71 (98)	5.68 (120)	2.40 (96)	−1.36 (84)	2.20 (81)	−1.08 (79)
N3	6258 (11)	4736 (18)	4390 (11)	3.28 (93)	1.58 (77)	5.15 (109)	0.35 (69)	3.00 (86)	−0.63 (73)
N4	6382 (10)	1407 (17)	0766 (11)	1.18 (77)	2.18 (82)	4.21 (100)	−0.24 (63)	1.77 (77)	−0.07 (73)
N5	1722 (11)	4137 (19)	4480 (10)	3.58 (95)	2.53 (87)	4.04 (98)	−0.29 (72)	3.09 (84)	−0.24 (70)
N6	8390 (10)	2017 (18)	1192 (10)	1.81 (84)	2.64 (86)	3.76 (95)	−0.32 (66)	1.83 (74)	−0.39 (69)
C1	2399 (15)	2601 (27)	2997 (12)	5.93 (140)	5.28 (133)	3.02 (119)	−0.74 (111)	4.97 (115)	0.33 (103)
C3	3814 (15)	0387 (21)	1306 (14)	5.11 (135)	1.77 (97)	3.72 (120)	−0.71 (88)	3.72 (115)	−0.27 (86)
C4	4589 (16)	0218 (24)	2146 (14)	3.61 (121)	2.60 (111)	4.47 (137)	−0.49 (98)	1.77 (107)	1.59 (99)
C5	4626 (15)	4349 (25)	2722 (14)	3.24 (125)	3.63 (128)	3.61 (133)	1.05 (98)	1.39 (110)	−0.46 (95)
C6	4682 (14)	3632 (24)	3400 (13)	3.61 (116)	3.15 (123)	1.77 (106)	1.08 (92)	0.46 (97)	−0.47 (89)
C7	5475 (14)	3867 (23)	4244 (13)	3.00 (115)	2.11 (99)	3.57 (123)	0.58 (90)	2.45 (103)	0.06 (89)
C8	5593 (13)	3227 (20)	5011 (13)	1.85 (104)	1.45 (91)	2.99 (110)	0.76 (74)	1.34 (93)	0.15 (78)
C9	4881 (13)	2722 (23)	0000 (14)	2.11 (108)	2.26 (107)	6.19 (145)	−0.70 (83)	2.89 (107)	−0.70 (100)
C10	5093 (18)	3234 (23)	0808 (18)	6.41 (163)	1.23 (103)	8.45 (190)	−1.64 (105)	5.59 (155)	−1.38 (113)
C11	5890 (16)	2794 (23)	1579 (15)	3.77 (125)	2.00 (107)	6.31 (150)	0.50 (95)	3.41 (119)	0.82 (100)
C12	6552 (12)	1865 (23)	1519 (12)	1.65 (100)	3.05 (107)	2.34 (105)	−1.04 (79)	0.83 (86)	−1.05 (82)
C13	1859 (16)	2613 (25)	4821 (12)	6.52 (152)	2.95 (121)	2.67 (110)	0.05 (106)	2.54 (109)	0.39 (92)
C14	1154 (14)	1890 (23)	4902 (13)	2.64 (114)	2.09 (105)	5.82 (140)	0.07 (88)	2.66 (109)	0.78 (91)
C15	0326 (16)	2680 (26)	4589 (14)	4.69 (144)	3.37 (127)	5.81 (145)	−0.79 (107)	3.72 (123)	−0.28 (107)
C16	0170 (14)	4298 (25)	4193 (14)	2.73 (115)	4.05 (134)	4.89 (134)	−0.76 (92)	2.55 (104)	0.06 (96)
C17	0899 (13)	4964 (24)	4196 (12)	1.20 (93)	3.23 (117)	4.43 (119)	0.08 (89)	1.59 (88)	−0.26 (94)
C18	9182 (15)	1582 (23)	1202 (13)	3.52 (124)	2.08 (107)	4.47 (130)	0.98 (91)	2.55 (108)	0.32 (88)
C19	9940 (15)	2572 (27)	1487 (14)	3.02 (116)	3.33 (129)	4.82 (132)	−1.50 (97)	1.83 (102)	−0.16 (99)
C20	9912 (16)	4077 (29)	1840 (14)	3.49 (128)	4.17 (135)	4.84 (142)	−0.82 (104)	1.94 (113)	−0.56 (105)

Table 1 (Continued)

Atom	<i>X/a</i>	<i>Y/b</i>	<i>Z/c</i>	<i>B</i> ₁₁	<i>B</i> ₂₂	<i>B</i> ₃₃	<i>B</i> ₁₂	<i>B</i> ₁₃	<i>B</i> ₂₃
C21	9145 (16)	4558 (25)	1849 (13)	2.64 (112)	3.62 (126)	4.12 (128)	0.07 (99)	0.73 (99)	0.47 (94)
C22	8410 (14)	3444 (25)	1542 (13)	3.27 (118)	3.15 (119)	4.21 (126)	0.43 (95)	2.26 (103)	-0.98 (95)
Se2	7832 (2)	2277 (3)	3887 (2)	4.74 (14)	4.64 (15)	5.56 (15)	-0.11 (11)	3.09 (13)	0.28 (12)
N2	6693 (15)	0643 (23)	4378 (14)	5.34 (142)	4.13 (128)	7.56 (151)	-1.09 (96)	3.24 (120)	-0.39 (95)
C2	7105 (15)	1280 (27)	4184 (16)	1.82 (116)	2.61 (125)	7.25 (167)	-0.13 (94)	1.94 (111)	-0.91 (113)

Table 2

Interatomic distances and bond angles in a structural unit
of α -[Cu(bpy)₂NCSe]NCSe

Atoms	Interatomic distance [nm]
Cu—N1	0.2075(17)
Cu—N3	0.2040(17)
Cu—N4	0.2021(20)
Cu—N5	0.1983(21)
Cu—N6	0.2123(17)
N1—C1	0.1107(29)
C1—Se1	0.1799(23)
N2—C2	0.1096(40)
C2—Se2	0.1825(29)

	Bond angle [°]
N1—Cu—N3 (α_1)	129.0 (7)
N1—Cu—N6 (α_2)	109.6 (7)
N3—Cu—N6 (α_3)	121.4 (7)
N4—Cu—N5	177.1 (7)
N1—Cu—N4	92.3 (7)
N1—Cu—N5	90.2 (8)
N3—Cu—N4	81.7 (7)
N3—Cu—N5	97.9 (7)
N4—Cu—N6	97.4 (7)
N5—Cu—N6	80.4 (7)
Cu—N1—C1	170.1(19)
N1—C1—Se1	178.2(22)
N2—C2—Se2	177.5(25)

The structural unit consists of the complex cation [Cu(bpy)₂NCSe]⁺ and an anion of NCSe⁻. The shortest interatomic distance found between the central atom and the selenocyanate anion (Cu—N = 0.39 nm and Cu—Se = 0.43 nm) excludes the possibility that the selenocyanate group would be in the coordination sphere of the central atom. The above-mentioned anion has a linear structure. Interatomic distances between the individual atoms in the selenocyanate anion are in agreement with those published previously [12].

The cation [Cu(bpy)₂NCSe]⁺ contains a chromophore CuN₅. When comparing values of α_1 , α_2 , and α_3 (Fig. 1), its arrangement in space can be described as a trigonal bipyramid showing a square-pyramidal distortion in direction B or, according to [13], in direction C. The equatorial plane is formed by the nitrogen atom of an NCSe group and two nitrogen atoms of bipyridine ligands. The other two nitrogen atoms of bipyridine ligands are bonded to Cu(II) in axial positions.

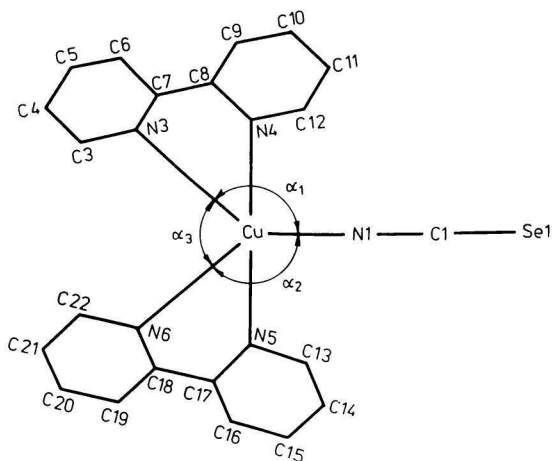


Fig. 1. Schematic representation of the structure of cation $[\text{Cu}(\text{bpy})_2\text{NCSe}]^+$.

The interatomic distance of Cu—N in axial direction of the coordination polyhedron is slightly shorter than that in the equatorial plane. However, such data are common for trigonal bipyramidal complexes of Cu(II).

According to [11], a trigonal bipyramidal arrangement of ligands was supposed to occur in $\text{Cu}(\text{bpy})_2(\text{NCS})_2$ as well as in $\text{Cu}(\text{bpy})_2(\text{NCSe})_2$. For $\text{Cu}(\text{bpy})_2(\text{NCS})_2$, however, a "symmetric" or a bridging coordination of the thiocyanate ligand and consequently, a distorted *cis* octahedral arrangement of ligands in the coordination polyhedron of Cu(II) has also been expected [14]. An X-ray structure analysis performed in our department for analogous complexes with phenantroline as ligand confirmed the *cis* arrangement, pseudohalide ligands having been found to be bonded through their nitrogen atoms as terminal groups [6, 15].

The selenocyanate ligand is coordinated to Cu(II) as a unidentate ligand through the nitrogen atom. This phenomenon cannot be unambiguously explained by the π -bond hypothesis [2, 5], since it is known that pseudohalide ligands in the equatorial plane of a coordination polyhedron of Cu(II) can be bonded exclusively *via* their nitrogen atoms [2, 3, 5]. Bipyridine ligands in α - $[\text{Cu}(\text{bpy})_2\text{NCSe}]\text{NCSe}$ exhibit a typical plane arrangement [16] with angles between pyridine circles N3, C3—C7 and N4, C8—C12; N5, C13—C17 and N6, C18—C22 equal to 3.77° and 2.53°, respectively. The angle between the bipyridine ligands is close to 60°. Interatomic distances and bond angles in the bipyridine ligands are in a good agreement with those already published [10, 13].

Magnetic moment for α - $[\text{Cu}(\text{bpy})_2\text{NCSe}]\text{NCSe}$ was found to be equal to 2.02 B.M. According to [11], the latter was found to be 2.0 B.M. The difference

between the found value and the calculated pure spin value (1.73 B.M.) can be explained by a spin-orbital interaction. The complex under investigation belongs to a group of magnetically diluted complexes in which interatomic distances of Cu—Cu in their crystal structure should be greater than 0.5 nm [17]. In the case of α -[Cu(bpy)₂NCSe]NCSe, the above distance is approximately equal to 0.7 nm.

E.p.r. spectrum of α -[Cu(bpy)₂NCSe]NCSe is of isotropic type with a value of $g = 2.115$. This value is similar to that recorded for phenantroline complexes [6] but different from data given in paper [11] where a spectrum of axial type was observed with values of $g_{\parallel} = 2.023$ and $g_{\perp} = 2.220$. Although e.p.r. spectral data do not make it possible to draw any conclusions on the basic state of the complex under investigation, nevertheless, the results of the X-ray structure analysis give support to the assumption that d_x^2 state is the basic one [17].

For α -[Cu(bpy)₂NCSe]NCSe, an asymmetric absorption band is observed in its electronic absorption spectrum in the spectral region of ligand field bands. A maximum of the band is registered at $12\,400\text{ cm}^{-1}$ while a shoulder is shown at $10\,700\text{ cm}^{-1}$. In papers [10, 18], a possibility is suggested how to predict the type of a coordination polyhedron of Cu(II) on the basis of electronic absorption spectra. According to the above papers, undistorted trigonal bipyramidal complexes exhibit a symmetric $d-d$ absorption band while those with a tetragonal pyramidal distortion are expected to show a split band. Results obtained for α -[Cu(bpy)₂NCSe]NCSe are in a full agreement with the above-mentioned suggestion [10]. The X-ray structure analysis results have shown that there exists a distortion of trigonal bipyramidal coordination of the Cu(II) central atom and, at the same time, a splitting of the corresponding $d-d$ absorption band was also registered. However, a symmetrical and unsplit $d-d$ absorption band has been observed in electronic absorption spectrum of analogous phenantroline Cu(II) complexes which were investigated in our laboratory, although X-ray structure analysis results unexpectedly proved a *cis* pseudoctahedral arrangement of ligands [6, 10, 15]. The results have shown that the possibilities for identification of the type of coordination polyhedron in Cu(II) complexes, based on electronic absorption spectra only, are limited [8].

Infrared spectra of α -[Cu(bpy)₂NCSe]NCSe and bipyridine (anal. grade) were also measured. In comparing both spectra, absorption bands could be identified which are assigned to the vibrations of selenocyanate groups. A split band showing maxima at 2055 and 2070 cm^{-1} has been assigned to the stretching vibration of $\tilde{\nu}(\text{CN})$. The corresponding band is unsplit in infrared spectra of analogous phenantroline complexes and X-ray structure analysis results have shown that both selenocyanate groups are bonded in the complexes through the nitrogen atoms as unidentate ligands [6]. Taking into account also papers [2, 19], the splitting observed for α -[Cu(bpy)₂NCSe]NCSe may be explained by occurrence of one coordinated selenocyanate group and the other one which is uncoordinated. In

accordance with paper [2], the bands at 646, 450, and 420 cm^{-1} have been assigned to a stretching vibration $\bar{\nu}(\text{CSe})$ and deformation vibration $\delta(\text{NCSe})$ of the coordinated selenocyanate group, and deformation vibration $\delta(\text{NCSe})$ of the uncoordinated NCSe group, respectively. A band at 285 cm^{-1} may probably be assigned to a stretching vibration $\bar{\nu}(\text{Cu—N})$ of the bipyridine ligand.

When preparing the complex of $\text{Cu}(\text{bpy})_2(\text{NCSe})_2$ under various conditions, two modifications of the compound have been obtained differing in several physicochemical properties. The differences have been observed in X-ray powder diffractograms, as well as in e.p.r. and electronic spectra. The α -modification gives, for example, an isotropic e.p.r. spectrum with a value of $g = 2.115$ while the β -modification shows a spectrum of axial type, g_{\parallel} being equal to 2.004 and $g_{\perp} = 2.181$. Electronic absorption spectra of both modifications differ in splitting of the absorption bands assigned to $d-d$ transitions. A band with a maximum at 12 400 cm^{-1} and a shoulder at 10 700 cm^{-1} is observed in the spectrum of the α -modification while the β -modification exhibits a band at 12 400 cm^{-1} with a shoulder at 10 300 cm^{-1} . Such a difference may be elucidated by a different degree of distortion of the coordination polyhedron on transition from a trigonal bipyramid to a tetragonal pyramid [10]. If it is true, then the modifications may be regarded as distortion isomers with coordination polyhedra which are intermediates between a trigonal bipyramid and a tetragonal pyramid [7, 10, 13].

A similar phenomenon was observed for complexes of $[\text{Cu}(\text{bpy})_2\text{X}]\text{Y}$ [10, 13] where for the same X but different Y, "cationic distortion isomers" occur with a various degree of distortion of chromophore CuN_4X in the direction from a trigonal bipyramid to a tetragonal pyramid. The above phenomenon is in paper [13] described as an illustration for plasticity of Cu(II) complexes and it is explained by different Van der Waals forces as well as by effects in crystal structure. In our case, composition of the complex is unchanged and distortion isomers with chromophore CuN_5 have been obtained by changed conditions in preparation of the complex. This knowledge may serve as an example for another manifestation of plasticity of Cu(II) coordination polyhedra [7, 13] as well as for further possibilities of formation of Cu(II) distortion isomers [9]. In paper [7], any connection between the plasticity of coordination polyhedra and the existence of distortion isomerism of the above type in the case of Cu(II) complexes, was not analyzed.

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