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Crystal Structure of [Cu(terpy)(NCSe)$_2$]: a Novel Five-coordinate Copper(II) Complex with Unusual Symmetry

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Terpy (2,2′:6′,2″-terpyridine) as a chelating tridentate ligand allows the obtention of five-coordinate compounds of general formula [Cu(terpy)X$_2$]·nH$_2$O (X = halogen or pseudohalogen anion) [1–4]. In these complexes the copper(II) ions are bonded to three N atoms of the tridentate ligand and the two X$^-$ ions [1,2] or by one X$^-$ and one H$_2$O molecule as in the nitrite complexes [3,4]. In all cases, the copper(II) ion shows a distorted square pyramid geometry with the terpy ligand in the equatorial plane. Recently, we have reported a structural and spectroscopic investigation of two compounds [Cu(terpy)(NCS)$_2$] and [Cu(terpy)Br$_2$] which present an unusual molecular geometry [5]. In the present work, we report the crystal structure and spectroscopic properties of a novel compound of copper(II) with a C_{2v} symmetry for the coordination polyhedron.

Experimental

Synthesis

A diluted solution of CuCl$_2$·2H$_2$O in water and 2,2′:6′,2″-terpyridine in ethanol were mixed in the molar ratio 1:1. The resulting solution was treated with a slight excess of KNCSe to give a green precipitate. It was filtered, washed with water, and recrystallized from a water/methanol solution. *Anal.* Calc. for $C_{15}H_{11}N_3CuN_2C_2Se_2$: C, 40.3; N, 13.8; H, 2.2. Found: C, 39.9; N, 13.6; H, 2.0%.

Structure Determination and Refinement

The diffraction data were obtained from a single crystal of dimensions 0.11 × 0.094 × 0.04 mm. Crystal data: M_r = 506.62, monoclinic, a = 13.892(6), b = 9.613(6), c = 14.45(3) Å, β = 111.42(8)°, V = 1796(7) Å^3, Z = 4, D_m = 1.97(7) (flotation method), D_c = 1.96 Mg m^{-3}, $F(000)$ = 980, Mo Kα radiation, λ = 0.7107 Å, μ(Mo Kα) = 60.4 cm^{-1}. Space group $C2/c$.

Unit cell parameters were obtained from least-squares analyses of 25 reflections ($5° < \theta < 11°$) on an Enraf-Nonius CAD4 computer-controlled diffractometer. Intensity data were recorded on the same instrument using Mo Kα radiation (λ = 0.7107 Å), monochromatized graphite, in the ω–2θ scan mode with a θ range of 1° to 25°.

The stability of the measurement was checked periodically using three standard reflections; no significant variation could be observed during the experiment. Collected intensities were corrected for Lorentz-polarization effects. After averaging equivalent reflections, a set of 1561 independent reflections was obtained, of which 811 reflections with $I \geqslant 2\sigma(I)$ were classified as observed.

The structure was solved using a refinement procedure that began with the atomic position of the isostructural complex [Cu(terpy)(NCS)$_2$] [5] and was carried out by the computer program SHELX 76 [6]. Using anisotropic thermal parameters the structure was refined to the final R value of R = 0.050 and R_ω = 0.055 for all observed reflections.

The final atomic coordinates and equivalent temperature factors for non-H atoms appear in Table I. Selected bond distances and angles for the complex are given in Table II.

TABLE I. Fractional Atomic Coordinates (×10^4) and Equivalent Thermal Parameters[a] for the Non-hydrogen Atoms[b]

Atom	x/a	y/b	z/c	B_{eq}[a] (Å^2)
Cu	0	3702(2)	2500	3.29(1)
N(1)	9242(7)	4084(9)	1036(6)	3.559(6)
N(2)	0	5731(12)	2500	3.53(2)
C(1)	8871(8)	3103(13)	313(8)	3.98(8)
C(2)	8376(9)	3486(14)	−666(9)	4.45(1)
C(3)	8225(10)	4881(14)	−924(10)	5.17(1)
C(4)	8609(9)	5900(13)	−193(9)	4.34(1)
C(5)	9108(8)	5460(11)	779(7)	3.40(1)
C(6)	9556(8)	6384(12)	1635(7)	3.57(1)
C(7)	9538(10)	7848(12)	1593(9)	4.70(3)
C(8)	0	8555(18)	2500	6.33(4)
N(3)	979(8)	2278(10)	2265(7)	4.70(1)
C(9)	1306(9)	1518(13)	1845(7)	3.63(1)
Se	1805(1)	341(1)	1206(1)	5.99(2)

[a] $B_{eq} = 8\pi^2[(U_{11} + U_{22} + U_{33})/3]$. [b] e.s.d.s given in parentheses.

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TABLE II. Some Selected Bond Lengths (Å) and Angles (°)[a]

Cu–N(1)	2.02(9)	Cu–N(2)	1.95(1)
Cu–N(3)	2.04(2)	N(1)–C(1)	1.36(3)
Se–C(9)	1.75(3)	N(1)–C(5)	1.36(1)
N(2)–C(6)	1.33(5)	N(3)–C(9)	1.14(3)
C(5)–C(6)	1.46(4)		
N(1)–Cu–N(2)	79.5(2)		
Cu–N(2)–C(6)	118.1(6)		
N(1)–C(5)–C(6)	112.5(8)		
Cu–N(1)–C(5)	115.2(6)		
Cu–N(1)–C(1)	125.6(7)		
N(1)–Cu–N(1)^i	159.0(4)		
N(2)–Cu–N(3)	132.0(3)		
N(1)–Cu–N(3)	94.1(3)		
Se–C(9)–N(3)	179(1)		
N(3)–Cu–N(3)^i	95.8(4)		
Cu–N(3)–C(9)	158.9(8)		

[a]e.s.d.s given in parentheses. Symmetry code: ^{i} $-x, y, \frac{1}{2}-z$.

Physical Measurements

A Brucker ER 200tt spectrometer equipped with a standard low-temperature device, operating at X-band calibrated by an NMR probe for the magnetic field and an HP 5342A frequency counter for the microwave frequency, was used to record the EPR powder spectra of the complex at different temperatures.

Results and Discussion

The unit cell contents comprise discrete molecules of the complex [Cu(terpy)(NCSe)$_2$] in which the copper(II) ion is five-coordinated by the three N atoms of the terpyridine molecule [Cu–N(1), N(2) = 2.02(9), 1.95(1) Å] and the two N atoms of the selenocyanate groups [Cu–N(3) = 2.04(2) Å] (Fig. 1). These distances are similar to those observed in the thiocyanate complex [Cu–N(1),N(2) = 2.021(5), 1.937(7) Å and Cu–N(3) = 2.020(7) Å for the tridentate and NCS ligands, respectively] [5]. Each molecule lies astride a crystallographic two-fold axis [through C(8)–N(2)–Cu], so that only one half of it is crystallographically independent. The ligand plane, including the copper(II) ion, lies parallel to the *b* axis. The angle formed by the two N(3) atoms of the selenocyanate groups and the Cu^{2+} ion in the title complex is 95.8(4)°. It is slightly lower than the analogous one in the [Cu(terpy)(NCS)$_2$] compound [98.1(3)°] [5].

The coordination polyhedron |CuN$_3$N$_2$| exhibits a C_{2v} symmetry. The distortion of this one has been determined using Muetterties model [7], considering the trigonal bipyramid and regular square pyramid as limit geometries (Table III). The value obtained shows a deviation (Δ) of 31% to the trigonal bipyramid, and a topology close to 'reverse geometry' (SP$_r$) defined by Reinen *et al.* [5].

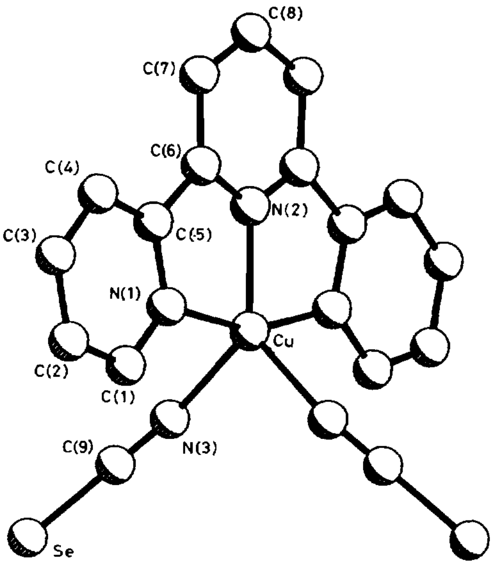


Fig. 1. View of the complex showing the copper coordination and the atomic numbering.

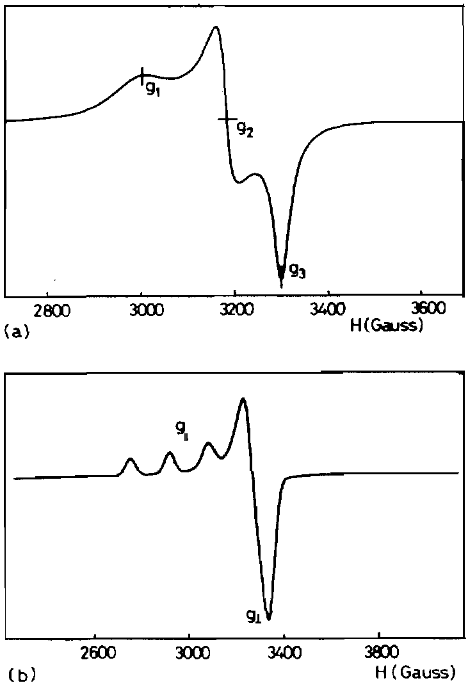


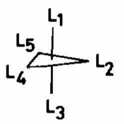
Fig. 2. X-band EPR spectra of [Cu(terpy)(NCSe)$_2$]: (a) powder at room temperature; (b) frozen DMSO solution at 115 K.

The powder EPR spectrum of the complex at 300 K is orthorhombic, with $g_1 = 2.247$, $g_2 = 2.119$, $g_3 = 2.041$ (Fig. 2a), in good agreement with the structural results. The *g* values are not modified

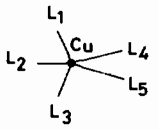
TABLE III. Distortion of the Coordination Polyhedron for the $[Cu(terpy)(NCSe)_2]$ Compound and for the Ideal Geometries[a]

Designation	TBP	$\overline{SP}_r$	$[Cu(terpy)$-$(NCSe)_2]$	SP_r
δa_1	101.5	119.2	119.5	121.8
δa_3	101.5	94.8	97.5	121.8
δa_4	101.5	119.2	119.5	121.8
δa_6	101.5	94.8	92.8	121.8
δa_2	101.5	94.8	92.8	73.9
δa_5	101.5	94.8	97.5	73.9
δe_1	53.1	37.5	36.6	73.9
δe_2	53.1	82.1	82.4	73.9
δe_3	53.1	37.5	36.6	0.0
Δ	0.0	0.28	0.31	1.0

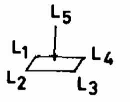
$$\Delta = \left[\frac{(\delta a_1 + \delta a_3 + \delta a_4 + \delta a_6) - 406.0}{182.7}\right] + \left[\frac{(\delta a_2 + \delta a_5) - 203.0}{248.4}\right] + \left[\frac{(\delta e_1 + \delta e_2) - 106.2}{187.2}\right] + \left[\frac{(53.1 - \delta e_3)}{477.9}\right]$$



TBP



$\overline{SP}_r$



SP_r

[a] TBP = trigonal bipyramid; $\overline{SP}_r$ = 'reverse geometry' (L_1-CuL_3 = 172.5°, L_4CuL_5 = 97.5°); SP_r = regular square pyramid (L_1CuL_3 = L_2CuL_4 = 165°).

at 115 K ($g_1 = 2.250$, $g_2 = 2.118$, $g_3 = 2.037$). The EPR frozen solution spectrum (DMSO at 115 K) (Fig. 2b) shows a clear resolution of the 'g' tensor in parallel and perpendicular components: $g_\parallel = 2.254$ and $g_\perp = 2.036$, with a hyperfine splitting ($A_\parallel = 157 \times 10^{-4}$ cm^{-1} and $A_\perp = 0$). These results are indicative of a distorted square pyramidal geometry for the $|CuN_3N_2|$ chromophore. The average g values for polycrystalline samples are slightly larger than those found for the frozen solution. The change of topology in the complex suggests a small energy difference between the solid state and the frozen solution geometries. Hence, it is apparently possible to stabilize a 'reverse geometry' ($\overline{SP}_r$) as in the $[Cu(terpy)X_2]$ (X = NCS, Br) compounds [5], when the steric ligand strains and packing in the unit cell are additionally present.

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