Table 1. *Selected geometric parameters (Å, °)*

Mg—O1	2.083 (2)	Mg—O6	2.059 (3)
Mg—O2	2.098 (3)	S—O11	1.469 (3)
Mg—O3	2.096 (3)	S—O12	1.455 (3)
Mg—O4	2.043 (3)	S—O13	1.462 (3)
Mg—O5	2.092 (2)	S—O14	1.472 (3)
Mg—O1—C1	135.1 (2)	Mg—O4—C4	143.8 (2)
Mg—O2—C2	131.7 (2)	Mg—O5—C5	135.4 (2)
Mg—O3—C3	131.7 (2)	Mg—O6—C6	138.0 (2)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	H···*A*	*D*···*A*	*D*—H···*A*
O*W*—H*W*1···O13^{i}	2.07	2.987 (3)	160
N12—H121···O11	2.15	3.050 (4)	157
N12—H122···O5^{ii}	2.00	2.945 (4)	175
N21—H211···O12^{iii}	2.00	2.839 (4)	146
N21—H212···O4	2.06	2.901 (4)	147
N22—H221···O14^{iii}	2.02	2.968 (4)	176
N22—H222···O*W*^{iv}	2.16	3.086 (4)	166
N31—H311···O14^{v}	2.10	2.991 (4)	156
N41—H411···O11^{vi}	1.89	2.829 (5)	170
N42—H421···O13^{vi}	2.06	2.990 (5)	167
N61—H611···O12^{vii}	1.90	2.814 (4)	160
N61—H612···O2	2.02	2.871 (4)	147

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $\frac{1}{2}-x, y, \frac{1}{2}+z$; (iii) $-x, 1-y, -z$; (iv) $\frac{1}{2}-x, y, z-\frac{1}{2}$; (v) $\frac{1}{2}-x, \frac{3}{2}-y, z$; (vi) $x, \frac{3}{2}-y, z-\frac{1}{2}$; (vii) $\frac{1}{2}+x, 1-y, \frac{1}{2}-z$.

A decay correction was applied. For calculation of the positions of the water H atoms, the most appropriate acceptor atoms of hydrogen bonds, *A*1 and *A*2, were first determined exploring the geometry surrounding O*W*, as well as the valence sums (Brown & Altermatt, 1985) of the atoms constituting this geometry. H atoms were thus calculated to lie in the O*W*/*A*1/*A*2 plane, with the geometrical constraints O*W*—H = 0.95 Å and H1—O*W*—H2 = 109.5°. Amino H atoms were placed in calculated positions (N—H = 0.95 Å). All H atoms were refined in a riding geometry, with fixed U_{iso} = 0.0506 Å^2.

Data collection: *CAD*-4 *Manual* (Enraf–Nonius, 1988). Data reduction: *SDP*/*PDP* (Enraf–Nonius, 1985). Program(s) used to solve structure: *MULTAN*11/82 (Main *et al.*, 1982). Program(s) used to refine structure: *SDP*/*PDP*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *KAPPA* (Macíček, 1992).

This work has been supported by the Bulgarian Academy of Sciences and the Bulgarian National Science Fund (projects Ch-402 and Ch-651).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1345). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 1760–1763

Bis(2,2′-bipyridine-*N*,*N*′)(isothiocyanato-*N*)-copper(II) Tricyanomethanide

IVAN POTOČŇÁK,[a] MICHAL DUNAJ-JURČO,[a] DUŠAN MIKLOŠ[a] AND LOTHAR JÄGER[b]

[a]*Department of Inorganic Chemistry, Slovak Technical University, Radlinského 9, 812 37 Bratislava, Slovakia, and* [b]*Institute of Inorganic Chemistry, Martin-Luther-University, Halle-Wittenberg, Weinbergweg 16, 06120 Halle/Saale, Germany. E-mail: potocnak@cvtstu.cvt.stuba.sk*

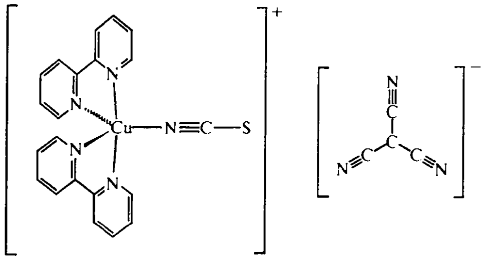
(*Received 30 January 1998; accepted 5 June 1998*)

Abstract

The crystal structure of $[Cu(NCS)(C_{10}H_8N_2)_2][C(CN)_3]$ is composed of discrete $[Cu(bipy)_2(NCS)]^+$ cations (bipy is 2,2′-bipyridine) and $[C(CN)_3]^-$ anions. The coordination polyhedron of Cu^{II} is a distorted trigonal bipyramid with a $\{CuN_5\}$ chromophore.

Comment

Recently, we published the crystal structures of two $[Cu(bipy)_2X][C(CN)_3]$ compounds [X = $C(CN)_3^-$ and OCN^-; Potočňák, Dunaj-Jurčo, Mikloš & Jäger, 1997; Potočňák *et al.*, 1998]. The coordination polyhedra around the five-coordinated Cu^{II} atoms in these two compounds can be described as trigonal bipyramidal with some degree of distortion towards tetragonal pyramidal. In comparison with these compounds, the coordination polyhedra in related $[Cu(phen)_2X][C(CN)_3]$ compounds [phen is 1,10-phenanthroline; X = CN^-, NCS^- and $N(CN)_2^-$] show a smaller degree of distortion towards the tetragonal-pyramidal arrangement (Potočňák *et al.*, 1996*a*,*b*,*c*). As the pseudohalogenide anions (*X*) are different in the bipy and phen compounds, we have not been able to discover whether the coordination polyhedra are influenced essentially by different neutral ligands or by different anionic ligands. In order to settle this point, we decided to prepare a compound with the bipy ligand and the NCS$^-$ anion, which was already used in the phen compound. The result is the title compound, [Cu(bipy)$_2$(NCS)][C(CN)$_3$], (I), whose preparation and crystal structure are presented here.



(I)

One formula unit together with the labelling scheme is shown in Fig. 1. The coordination polyhedron around the Cu atom is a distorted trigonal bipyramid. The Cu atom is five-coordinated by four N atoms of the two bipy molecules and by one N atom of the NCS$^-$ ligand. The tcm$^-$ anion [tcm$^-$ is C(CN)$_3^-$] does not enter the inner coordination sphere.

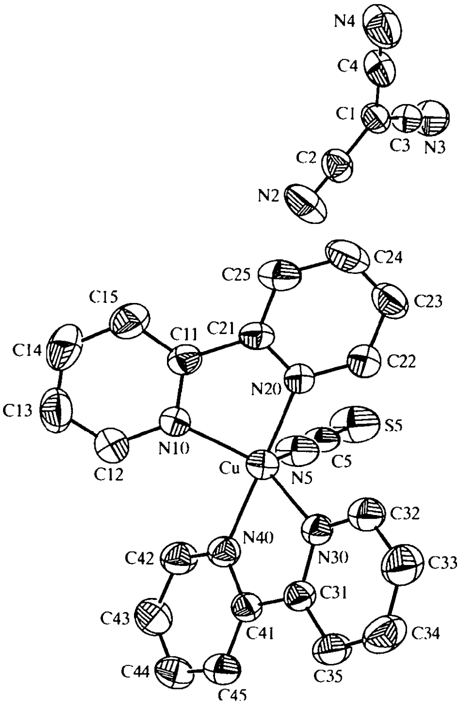


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the formula unit of (I) showing the labelling of atoms. Displacement ellipsoids are plotted at the 40% probability level.

The two out-of-plane Cu—N20 and Cu—N40 bonds in (I) have practically the same length and are almost collinear [N20—Cu—N40 174.21 (12)°]. The two in-plane Cu—N10 and Cu—N30 bonds have similar values also, but they are longer on average than the out-of-plane Cu—N distances by 0.105 Å. The third in-plane bond, Cu—N5 (N from the NCS$^-$ ligand), is significantly shorter then the other two and is the same length as the out-of-plane bonds. The out-of-plane angles lie within the range 79.61 (12)–97.53 (12)°. All mentioned values of bond distances and angles are comparable with those of the earlier published phen and bipy compounds.

The bond angles in the equatorial plane of (I) differ considerably from the ideal trigonal angle of 120°, with one large angle (α_1 = N5—Cu—N10) and two small angles (α_2 = N5—Cu—N30 and α_3 = N10—Cu—N30). Thus, the α_3 angle is smaller than the ideal angle of 120° by 4.16°, and there is a difference of 8.38° between α_1 and α_2. All these values are closer to the values found in the aforementioned three phen compounds rather than the two bipy compounds. According to the criteria of Harrison & Hathaway (1980), the coordination polyhedron around the Cu atom in (I) can be best described as trigonal bipyramidal with near C_{2v} symmetry, as for phen compounds. On the other hand, according to the values of the angles α_1, α_2 and α_3 for the bipy compounds, their coordination polyhedra are best described as distorted trigonal bipyramidal with square-pyramidal distortion shown by one elongated Cu—N in-plane bond. It can be concluded that the shape of the coordination polyhedron in the copper compounds with related neutral ligands (phen and bipy) is influenced especially by different anionic ligands (*X*) rather than by different neutral ligands. We believe that one of the reasons for this is the different volume of the coordinated pseudohalogenide anions (*X*) and their different bonding mode to the Cu atom (Potočňák, Dunaj-Jurčo & Mikloš, 1997).

The sum of the bond angles in the equatorial plane of the title compound (360°) indicates coplanarity of the Cu atom with the three equatorial atoms [the deviation of the Cu atom from the N5/N10/N30 plane is 0.009 (2) Å towards the N40 atom].

Owing to steric considerations in the trigonal-bipyramidal polyhedron, the N atoms of the bipy molecules are coordinated both in equatorial and axial positions. Both bipy molecules are nearly planar [the largest deviation of atoms from the mean planes is 0.079 (7) Å]. The mean planes of the two bipy molecules are inclined at 114.91 (8)° with respect to one another. The bond distances and angles of both bipy molecules are quite normal.

The bonding mode of the isothiocyanato anion can be considered as linear [C5—N5—Cu 171.3 (3)°]. Both the bond distances and angles in the isothiocyanato anion correspond to the values found in other compounds

(Tyagi & Hathaway, 1981; Manríquez *et al.*, 1988). In the similar structure of $[Cu(bipy)_2(NCO)][C(CN)_3]$ (Potočňák *et al.*, 1998), the bonding mode of the NCO^- anion is angular [146.3 (4)°] and, therefore, the two compounds cannot be considered as isometric.

The tcm^- anion is almost planar [the largest deviation of atoms from the mean plane is 0.045 (5) Å]. The mode of bonding in the tcm^- anion can be described as a largely delocalized π-bonding system (Golub *et al.*, 1986). According to this model, the C—C lengths around the central C1 atom have similar values and they are considerably shorter than single Csp^2—Csp bonds (1.440 Å). Although the triple C≡N bond lengths are the same within 1σ, contrary to the above model, they are just about 3σ shorter than normal C≡N triple-bond lengths (1.153 Å). The angles around the central C atom are close to the ideal value of 120°, while the C1—C*n*≡N*n* (*n* = 2,3,4) fragments are almost linear.

Experimental

Crystals of (I) were prepared by mixing 10 ml of a 0.1 *M* water solution of $Cu(NO_3)_2$ with 20 ml of a 0.1 *M* ethanol solution of bipyridine, followed by addition of 10 ml of a 0.1 *M* water solution of KNCS and 10 ml of a 0.1 *M* ethanol solution of $KC(CN)_3$. The resulting green precipitate was dissolved by adding 15 ml of concentrated ammonia solution. Light-green crystals of the title complex appeared over a period of several days.

Crystal data

$[Cu(NCS)(C_{10}H_8N_2)_2](C_4N_3)$
$M_r = 524.06$
Triclinic
$P\overline{1}$
$a = 8.291 (3)$ Å
$b = 11.303 (6)$ Å
$c = 13.967 (5)$ Å
$\alpha = 90.12 (4)°$
$\beta = 98.17 (3)°$
$\gamma = 111.83 (3)°$
$V = 1200.5 (9)$ Å^3
$Z = 2$
$D_x = 1.450$ Mg m^{-3}
$D_m = 1.42 (1)$ Mg m^{-3}
D_m measured by flotation in CCl_4–benzene

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 22 reflections
$\theta = 3.82–11.32°$
$\mu = 1.027$ mm^{-1}
$T = 293 (2)$ K
Prism
0.35 × 0.30 × 0.20 mm
Light green

Data collection

Syntex $P2_1$ diffractometer
$\theta/2\theta$ scans
Absorption correction:
ψ scan (North *et al.*, 1968)
$T_{min} = 0.699$, $T_{max} = 0.814$
4240 measured reflections
4240 independent reflections

2227 reflections with $I > 2\sigma(I)$
$\theta_{max} = 25°$
$h = 0 \rightarrow 10$
$k = -14 \rightarrow 13$
$l = -18 \rightarrow 17$
3 standard reflections every 100 reflections
intensity decay: <2.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.078$
$S = 0.740$
4237 reflections
380 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0619P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.004$
$\Delta\rho_{max} = 0.150$ e Å^{-3}
$\Delta\rho_{min} = -0.225$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Cu—N20	1.970 (3)	C1—C2	1.395 (5)
Cu—N40	1.979 (3)	C1—C4	1.378 (6)
Cu—N5	1.978 (4)	C1—C3	1.405 (5)
Cu—N10	2.064 (3)	C2—N2	1.137 (5)
Cu—N30	2.094 (3)	C3—N3	1.139 (5)
S5—C5	1.596 (4)	C4—N4	1.138 (5)
C5—N5	1.144 (4)		
N20—Cu—N40	174.21 (12)	N10—Cu—N30	115.84 (11)
N20—Cu—N5	93.10 (13)	N5—C5—S5	179.7 (4)
N40—Cu—N5	92.58 (13)	C5—N5—Cu	171.3 (3)
N20—Cu—N10	79.98 (12)	C2—C1—C4	120.2 (4)
N40—Cu—N10	97.53 (12)	C2—C1—C3	119.2 (4)
N5—Cu—N10	126.27 (12)	C4—C1—C3	120.4 (3)
N20—Cu—N30	96.70 (12)	N2—C2—C1	179.3 (5)
N40—Cu—N30	79.61 (12)	N3—C3—C1	179.1 (4)
N5—Cu—N30	117.89 (13)	N4—C4—C1	178.9 (5)

Intensities were corrected for Lorentz and polarization effects using *XP*21 (Pavelčík, 1993). Anisotropic displacement parameters were refined for all non-H atoms. All H atoms were located from the difference Fourier map and refined with free isotropic displacement parameters. Geometrical analysis was performed using *PARST* (Nardelli, 1983) and *SHELXL*93 (Sheldrick, 1993).

Data collection: Syntex $P2_1$ software. Cell refinement: Syntex $P2_1$ software. Data reduction: *XP*21. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and the Ministry of Education, Slovak Republik (grant No. 1/1412/94).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1277). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 1763–1765

Dicyanonitrosomethanide as a Subject of Nucleophilic Addition of Methanol and as an End-*O*-Coordinated Ligand in the Same Copper(II) Complex. II.† (Bipyridine)(dicyanonitrosomethanido)[methyl(2-cyano-2-hydroxyimino)ethanimidato]copper(II)

MICHAL DUNAJ-JURČO,[a] DUŠAN MIKLOŠ,[a] IVAN POTOČŇÁK[a] AND LOTHAR JÄGER[b]

[a]*Department of Inorganic Chemistry, Slovak Technical University, Radlinského 9, 812 37 Bratislava, Slovakia, and* [b]*Institute of Inorganic Chemistry, Martin-Luther-University, Halle-Wittenberg, Weinbergweg 16, 06120 Halle/Saale, Germany. E-mail: dunaj@cvtstu.cvt.stuba.sk*

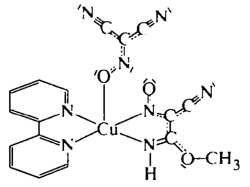
(*Received 17 March 1998; accepted 5 June 1998*)

Abstract

A new ligand formation was observed in the title complex, (bipyridine-*N*,*N*′)(dicyanonitrosomethanido-*O*)(3-imino-3-methoxy-2-nitrosoacrylonitrilato-N^2,N^3)-copper(II), $[\mathrm{Cu(C_4H_4N_3O_2)(C_3N_3O)(C_{10}H_8N_2)}]$, as a result of the nucleophilic addition reaction between a dicyanonitrosomethanide anion (ndcm), $[\mathrm{ONC(CN)_2}]^-$, and a methanol molecule, $\mathrm{CH_3OH}$, in the inner coordination sphere of the $\mathrm{Cu^{II}}$ atom. This new ligand, the methyl(2-cyano-2-hydroxyimino)ethanimidate anion (mcoe), $[\mathrm{ONC(CN)C(NH)OCH_3}]^-$, is coordinated as a chelate, forming a five-membered metallocycle with the $\mathrm{Cu^{II}}$ atom. Thus, the distorted tetragonal-pyramidal coordination of the $\mathrm{Cu^{II}}$ atom is formed by one chelate-coordinated molecule of 2,2′-bipyridine (bipy), one chelate-coordinated mcoe ligand and one end-*O*-coordinated ndcm. Four N atoms of the two metallocycles form the base and a fifth atom, an O atom of the ndcm anion, forms the apex of the tetragonal pyramid, creating a $\{\mathrm{CuN_4O}\}$ chromophore. The structure of [Cu(bipy)(mcoe)(ndcm)] consists of discrete molecules and is the first example of a compound in which one ndcm anion is the subject of a nucleophilic addition reaction and another is an end-*O*-coordinated ligand.

Comment

The title compound, (I), was prepared and its crystal structure solved as part of our study of the synthesis, crystal chemistry and properties of copper compounds containing a constant cationic part, $[\mathrm{Cu(bipy)_2}]^{2+}$/$[\mathrm{Cu(bipy)}]^{2+}$ or $[\mathrm{Cu(phen)_2}]^{2+}$/$[\mathrm{Cu(phen)}]^{2+}$, and a variable anionic part with a slim (X^-) and a bulky (Y^-) pseudohalide anion coupled in an *XY*-pair [X^- = $\mathrm{CN^-}$, $\mathrm{NCO^-}$, $\mathrm{NCS^-}$ or $\mathrm{N(CN)_2^-}$; Y^- = $\mathrm{C(CN)_3^-}$ or $\mathrm{ONC(CN)_2^-}$].



(I)

Both the $\mathrm{ONC(CN)_2^-}$ and $\mathrm{C(CN)_3^-}$ anions are known to have quite good coordination abilities (Golub *et al.*, 1986). A dicyanonitrosomethanide anion (ndcm) can be bonded to the central atom as an end-*O*-bonded, an end-*N*-bonded or, after the nucleophilic addition reaction, as an mcoe *N*,*N*′-chelate-bonded ligand. It can also be bonded in the outer coordination sphere. Compound (I) and $[\mathrm{Cu(phen)_2\{ONC(CN)_2\}(H_2O)}][\mathrm{ONC(CN)_2}]$ [(II); Mikloš *et al.*, 1998] are the first known examples where two ndcm anions are bonded to the central atom but in different modes: (i) only in the inner coordination sphere as end-*O*-bonded and as part of the mcoe ligand in (I); (ii) in the outer coordination sphere as an uncoordinated anion and in the inner coordination sphere as an end-*O*-bonded ligand in (II).

We have shown for the bis(bipyridine) complexes that in compounds containing the $[\mathrm{Cu(bipy)_2}X]^+$ cation, the $\mathrm{Cu^{II}}$ atom is five-coordinated, and the slim anions enter the inner and the bulky anions the outer coordination sphere; $[\mathrm{Cu(bipy)_2(NCO)}][\mathrm{C(CN)_3}]$ [(III);

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† Part I: Dunaj-Jurčo *et al.* (1996).