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## 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)

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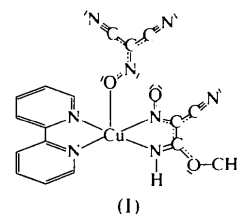
### Abstract

A new ligand formation was observed in the title complex, (bipyridine-*N,N'*)(dicyanonitrosomethanido-*O*)(3-imino-3-methoxy-2-nitrosoacrylonitrilato-*N*<sup>2</sup>,*N*<sup>3</sup>)-copper(II), [Cu(C<sub>4</sub>H<sub>4</sub>N<sub>3</sub>O<sub>2</sub>)(C<sub>3</sub>N<sub>3</sub>O)(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)], as a result of the nucleophilic addition reaction between a dicyanonitrosomethanide anion (ndcm), [ONC(CN)<sub>2</sub>]<sup>-</sup>, and a methanol molecule, CH<sub>3</sub>OH, in the inner coordination sphere of the Cu<sup>II</sup> atom. This new ligand, the methyl(2-cyano-2-hydroxyimino)ethanimidate

anion (mcoe), [ONC(CN)C(NH)OCH<sub>3</sub>]<sup>-</sup>, is coordinated as a chelate, forming a five-membered metalocycle with the Cu<sup>II</sup> atom. Thus, the distorted tetragonal-pyramidal coordination of the Cu<sup>II</sup> 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 metalocycles form the base and a fifth atom, an O atom of the ndcm anion, forms the apex of the tetragonal pyramid, creating a {CuN<sub>4</sub>O} 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, [Cu(bipy)<sub>2</sub>]<sup>2+</sup>/<sup>-</sup>[Cu(bipy)]<sup>2+</sup> or [Cu(phen)<sub>2</sub>]<sup>2+</sup>/<sup>-</sup>[Cu(phen)]<sup>2+</sup>, and a variable anionic part with a slim (*X*<sup>-</sup>) and a bulky (*Y*<sup>-</sup>) pseudohalide anion coupled in an *XY*-pair [*X*<sup>-</sup> = CN<sup>-</sup>, NCO<sup>-</sup>, NCS<sup>-</sup> or N(CN)<sub>2</sub><sup>-</sup>; *Y*<sup>-</sup> = C(CN)<sub>3</sub><sup>-</sup> or ONC(CN)<sub>2</sub><sup>-</sup>].



Both the ONC(CN)<sub>2</sub><sup>-</sup> and C(CN)<sub>3</sub><sup>-</sup> 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 [Cu(phen)<sub>2</sub>{ONC(CN)<sub>2</sub>}(H<sub>2</sub>O)][ONC(CN)<sub>2</sub>] [(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 [Cu(bipy)<sub>2</sub>*X*]<sup>+</sup> cation, the Cu<sup>II</sup> atom is five-coordinated, and the slim anions enter the inner and the bulky anions the outer coordination sphere; [Cu(bipy)<sub>2</sub>(NCO)][C(CN)<sub>3</sub>] [(III);

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

Potočňák *et al.*, 1998a] and [Cu(bipy)<sub>2</sub>(NCS)][C(CN)<sub>3</sub>] [(IV); Potočňák *et al.*, 1998b]. In compounds containing the [Cu(bipy)<sub>2</sub>Y]<sup>+</sup> cation, the Cu<sup>II</sup> atom is five-coordinated by two bipyridine molecules and one bulky anion forming a distorted trigonal bipyramid having the {CuN<sub>5</sub>} chromophore; [Cu(bipy)<sub>2</sub>{C(CN)<sub>3</sub>}] [C(CN)<sub>3</sub>] [(V); Potočňák *et al.*, 1997]. The solvent molecule does not enter the coordination sphere to take up a sixth coordination position as happened in the case of the phenanthroline complex (II) described above.

For the (mono)bipyridine complexes, we have shown that the nucleophilic addition reaction takes place between the coordinated bulky ndcm anion and the solvent (methanol) molecule, creating a new mcoe ligand. The Cu<sup>II</sup> atom is five-coordinate in the [Cu(bipy)(mcoe)X] complex, forming a distorted tetragonal-pyramidal {CuN<sub>5</sub>} chromophore; [Cu(bipy)(mcoe){N(CN)<sub>2</sub>}] [(VI); Dunaj-Jurčo *et al.*, 1996]. The same reaction between the above-discussed reactants was also described in the presence of Ni<sup>II</sup>; [Ni(mcoe)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] [(VII); Hvastijová *et al.*, 1995]. Replacement of X in complex (VI) by Y resulted in the title compound, [Cu(bipy)(mcoe)(ndcm)], (I).

The crystal structure of the title compound is molecular, formed by discrete molecules which are held together by van der Waals forces (Fig. 1).

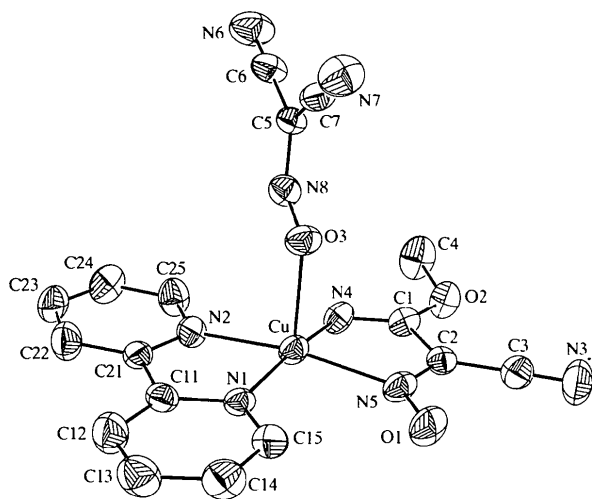


Fig. 1. ORTEP (Johnson, 1976) drawing showing the formula unit and the atom labeling. Displacement ellipsoids are plotted at the 40% probability level.

The Cu<sup>II</sup> atom is five-coordinated by one bipy molecule, one mcoe and one ndcm anion. The bipy and mcoe ligands form two five-membered metallocycles with the Cu<sup>II</sup> atom. The Cu—N distances in both metallocycles are quite normal and lie within the interval from 1.947 (4) to 2.053 (3) Å. The distorted

tetragonal-pyramidal coordination is completed by one end-*O*-bonded ndcm anion, with a Cu—O<sub>3</sub> distance of 2.200 (2) Å. The trigonality criterion ( $\tau$ ), which gives values of 100 and 0 for an ideal trigonal bipyramid and a tetragonal pyramid, respectively (Addison *et al.*, 1984), is 3.4 for (I), 18.7 for (VI) and 69.2 for [Cu(phen)<sub>2</sub>N(CN)<sub>2</sub>][C(CN)<sub>3</sub>] [(VIII); Potočňák *et al.*, 1996]. Both pentacoordinated units in (VI) and (VIII) are very similar with respect to their composition, *i.e.* they have {CuN<sub>5</sub>} chromophores, two five-membered metallocycles and one end-bonded [N(CN)<sub>2</sub>]<sup>-</sup> anion, but the coordination polyhedra are of different types; in (VI), it is a distorted tetragonal pyramid, and in (VIII), it is a distorted trigonal bipyramid. In (I), the pentacoordinated unit also contains two five-membered metallocycles and one end-*O*-bonded [ONC(CN)<sub>2</sub>]<sup>-</sup> anion, but in an almost ideal tetragonal-pyramidal coordination. This difference between coordination polyhedra in (VIII) on one hand, and (VI) and (I) on the other hand, is caused by the rigidity of the phenanthroline molecule and the flexibility of the bipyridine molecule.

The best way to describe the mode of bonding in the mcoe and ndcm ligands is to compare the corresponding average values found in the structures with expected values for bonds with multiplicities of 1, 1.5, 2 and 3, which are, respectively (in Å): C—C 1.54, 1.44, 1.34, 1.20; C—N 1.47, 1.37, 1.27, 1.15; C—O 1.43, 1.33, 1.22, 1.13; N—O 1.36, 1.26, 1.15, 1.08 (Jolly, 1984).

A comparison of interatomic distances for mcoe ligands found in structures (I) and (VI) shows that they may be considered to be the same within 3 $\sigma$ , except for O1—N5, where the interval is 4 $\sigma$ . The mode of bonding in the mcoe ligand can be derived from a comparison of the corresponding average values found in (I) and (VI) with the expected values for the multiplicity of 1.5 (given in parentheses) for some selected bonds: N5—O1 1.25 (1.26), C2—C3 1.42 (1.44), C1—C2 1.44 (1.44) and C1—O2 1.32 Å (1.33 Å). Because the differences between these values are in a range of 0.03 Å, one can say that the multiplicity of these bonds in mcoe is 1.5. The N5—C2 distance of 1.32 Å is adequate for a multiplicity higher than 1.5 (1.37 Å) and the N4—C1 distance of 1.27 Å corresponds exactly to a double bond (1.27 Å). The peripheral N3—C3 bond of 1.14 Å (1.15 Å) is a triple and O2—C4 of 1.43 Å (1.43 Å) a single bond. This situation is illustrated by the canonical formula in the drawing of (I) shown in the Scheme above.

The mode of bonding in the ndcm ligand can be described in a similar manner. Inspection of the bond distances indicates a strongly delocalized  $\pi$ -bonding system. Higher multiplicity of the methanide C—N bonds is also supported by the fact that the complete ndcm ligand is planar in both (I) and (II) [largest deviation of atoms from the mean plane being 0.025 (4) for (I) and 0.037 (6) Å for (II)]. The peripheral bonds C7—N7 of 1.12 (1.15) and C6—N6 of 1.13 Å (1.15 Å)

are triple bonds. The canonical formula given in drawing (I) corresponds to the former results.

According to Golub *et al.* (1986), the bonding mode of ndcm to the Cu<sup>II</sup> atom can be considered as angular [Cu—O3—N8 110.6 (2) for (I) and 120.2 (2)° for (II)].

## Experimental

Crystals of (I) were prepared by mixing 10 ml of a 0.1 M water solution of Cu(NO<sub>3</sub>)<sub>2</sub> with 20 ml of a 0.1 M methanol solution of bipy and 20 ml of a 0.1 M water solution of NaONC(CN)<sub>2</sub> (ratio Cu:bipy:ndcm = 1:2:2). Dark-green prismatic crystals of (I) appeared after eight months.

### Crystal data

[Cu(C<sub>4</sub>H<sub>4</sub>N<sub>3</sub>O<sub>2</sub>)(C<sub>3</sub>N<sub>3</sub>O)-  
(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)]  
M<sub>r</sub> = 439.89  
Monoclinic  
C2/c  
a = 20.118 (4) Å  
b = 8.358 (2) Å  
c = 23.444 (5) Å  
β = 114.02 (3)°  
V = 3600.7 (14) Å<sup>3</sup>  
Z = 8  
D<sub>x</sub> = 1.623 Mg m<sup>-3</sup>  
D<sub>m</sub> = 1.59 (1) Mg m<sup>-3</sup>  
D<sub>m</sub> measured by flotation in  
benzene/CCl<sub>4</sub>

Mo Kα radiation  
λ = 0.71073 Å  
Cell parameters from 21  
reflections  
θ = 2.24–7.83°  
μ = 1.253 mm<sup>-1</sup>  
T = 293 (2) K  
Prism  
0.70 × 0.25 × 0.10 mm  
Dark green

### Data collection

Syntex P2<sub>1</sub> diffractometer  
θ/2θ scans  
Absorption correction:  
ψ scan (North *et al.*,  
1968)  
T<sub>min</sub> = 0.603, T<sub>max</sub> = 0.882  
4915 measured reflections  
4092 independent reflections  
1588 reflections with  
I > 2σ(I)

R<sub>int</sub> = 0.061  
θ<sub>max</sub> = 27.56°  
h = 0 → 24  
k = -10 → 9  
l = -30 → 27  
3 standard reflections  
every 100 reflections  
intensity decay: none

### Refinement

Refinement on F<sup>2</sup>  
R[F<sup>2</sup> > 2σ(F<sup>2</sup>)] = 0.037  
wR(F<sup>2</sup>) = 0.065  
S = 0.957  
4092 reflections  
310 parameters  
All H atoms refined  
w = 1/[σ<sup>2</sup>(F<sub>o</sub><sup>2</sup>) + (0.0161P)<sup>2</sup>]  
where P = (F<sub>o</sub><sup>2</sup> + 2F<sub>c</sub><sup>2</sup>)/3

(Δ/σ)<sub>max</sub> = 0.005  
Δρ<sub>max</sub> = 0.293 e Å<sup>-3</sup>  
Δρ<sub>min</sub> = -0.341 e Å<sup>-3</sup>  
Extinction correction: none  
Scattering factors from  
*International Tables for  
Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Cu—N4	1.947 (4)	C1—C2	1.441 (5)
Cu—N1	1.982 (3)	C2—N5	1.327 (4)
Cu—N2	2.012 (3)	C2—C3	1.421 (5)
Cu—N5	2.053 (3)	C5—N8	1.325 (4)
Cu—O3	2.200 (2)	C5—C7	1.402 (6)
O1—N5	1.245 (3)	C5—C6	1.418 (5)

O2—C1	1.310 (4)	C3—N3	1.128 (5)
O2—C4	1.437 (6)	C6—N6	1.129 (4)
O3—N8	1.287 (3)	C7—N7	1.121 (5)
C1—N4	1.273 (5)		
N4—Cu—N1	170.98 (15)	N5—C2—C3	122.9 (4)
N4—Cu—N2	98.0 (2)	N5—C2—C1	114.7 (4)
N1—Cu—N2	80.41 (13)	C3—C2—C1	122.4 (4)
N4—Cu—N5	80.0 (2)	C1—N4—Cu	115.8 (3)
N1—Cu—N5	99.91 (14)	N8—C5—C7	123.3 (3)
N2—Cu—N5	168.94 (12)	N8—C5—C6	116.1 (4)
N4—Cu—O3	94.30 (13)	C7—C5—C6	120.5 (4)
N1—Cu—O3	94.66 (10)	O1—N5—C2	119.8 (3)
N2—Cu—O3	93.49 (10)	O1—N5—Cu	128.5 (3)
N5—Cu—O3	97.49 (10)	C2—N5—Cu	111.5 (3)
C1—O2—C4	118.4 (4)	N3—C3—C2	178.3 (6)
N8—O3—Cu	110.6 (2)	N6—C6—C5	179.5 (4)
N4—C1—O2	130.3 (4)	N7—C7—C5	179.1 (5)
N4—C1—C2	116.9 (4)	O3—N8—C5	114.6 (3)
O2—C1—C2	112.7 (4)		

Intensities were corrected for Lorentz and polarization factors using XP21 (Pavelčík, 1993). Anisotropic displacement parameters were refined for all non-H atoms. All H atoms were found in the difference map and then refined isotropically. Geometrical analysis was performed using PARST (Nardelli, 1983) and SHELXL93 (Sheldrick, 1993).

Data collection: Syntex P2<sub>1</sub> software. Cell refinement: Syntex P2<sub>1</sub> software. Data reduction: XP21. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93. Molecular graphics: ORTEPII (Johnson, 1976). Software used to prepare material for publication: SHELXL93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1284). Services for accessing these data are described at the back of the journal.

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