

COMPLEXES WITH NEW CHELATE ANIONIC LIGANDS FORMED BY NUCLEOPHILIC ADDITION IN COPPER(II) COORDINATION SPHERE. III.⁺ THE CRYSTAL STRUCTURES OF (2,2'-BIPYRIDINE-*N,N'*)(CYANATO-*N*)-[METHYL(2-CYANO-2-IMIDOXY ETHANEIMIDATE-*N,N'*)]COPPER(II) AND (2,2'-BIPYRIDINE-*N,N'*)(2-CYANO-2-IMIDOXY ETHANEIMIDATE-*N,N'*)-COPPER(II)

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Crystal structures of Cu(II) compounds with new chelate anionic ligands are presented. The formulae of these compounds are [Cu(bipy)(mcoe)(NCO)] (**1**) and [Cu(bipy)(coe)] (**2**), where bipy is 2,2'-bipyridine, mcoe and coe are the anionic chelate ligands methyl(2-cyano-2-imidoxy ethaneimidate), [(ON)(NC)C-C(NH)(OCH₃)]¹⁻ (**3**), and 2-cyano-2-imidoxy ethaneimidate, [(ON)(NC)C-C(NH)(O)]²⁻ (**4**), respectively, formed by nucleophilic addition of methanol and hydroxide ion to the coordinatively activated β-carbon of the nitroso-dicyanomethanide. Formation of the hydroxide ion from water in the reaction mixture can be explained by protonation of the C(CN)₃⁻ anion. The coordination polyhedra in **1** and **2** are quite different. The coordination polyhedron around the Cu(II) ion in **1** is a distorted trigonal bipyramid and in **2** a distorted square. The Cu(II) ion in **1** is coordinated by four N atoms from two bidentate ligands and one N atom from the NCO⁻ group. The crystal structure consists of discrete molecules with {CuN₅} chromophore. On the other hand, the Cu(II) ion in **2** is coordinated by four N atoms from two bidentate ligands in square coordination and the molecules are linked by weaker contacts between copper and oxygen atoms (Cu-Oⁱ = 2.503(3), Cu-Oⁱⁱ = 2.801(3) Å; i = -x, -y, -z + 1; ii = -x + 1, -y, -z + 1) to infinite chains parallel with *c*. Thus the coordination polyhedron is completed to an elongated tetragonal bipyramid with the {CuN₄O*O*} chromophore. The angle Oⁱ-Cu-Oⁱⁱ is 167.9(1)° and the crystal structure cannot be considered as molecular but consisting of chains running in one direction. Inspection of the bond distances in mcoe and coe indicates strongly delocalized π-bonding systems. This is also supported by the fact that the anions are almost planar with bond angles close to 120°. The calculated Wiberg (bond-order) indices show that due to conjugation, the bonds within the metallocycle in mcoe and coe exhibit partially multiple character.

Key words: Crystal structure determination; Nucleophilic addition; Coordinative activation; Pseudohalogenides; ESR spectroscopy; Copper; Bipyridine complexes; Chelates.

⁺ For Part I and II see ref.³

The general aim of our project is the study of factors leading to "activated states" of individual components of Cu(II) coordination compounds, which may result in:

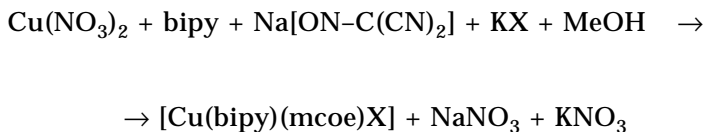
(i) chemical reactions in the coordination sphere of the central atom (addition, exchange, co-ligand, redox reactions), (ii) change in type of the coordination polyhedron and (iii) distortion of the coordination polyhedron.

This work is focused on inorganic synthesis using fine tuning of ligand stereochemical and electronic factors (including solvent) in such a way that they reflect the change in reactivity (activation) of a certain ligand (e.g. nitroso-dicyanomethanide anion, ndcm) under the influence of the central atom and assisting ligands. Such a reaction, using suitable combination of stereochemical and electronic factors, results in model compounds which might be useful for study of bioinorganic systems.

Copper(II) complexes with 2,2'-bipyridine have been widely studied¹. Recently we have published several papers dealing with crystal structures of copper(II) compounds with 2,2'-bipyridine and pseudohalogenide anions^{2,3}. In syntheses, we have used a series of "small" anions (CN⁻, NCO⁻, NCS⁻, N(CN)₂⁻) and one of the two "bulky" anions (C(CN)₃⁻ is tricyanomethanide (tcm) and ON-C(CN)₂⁻ is nitrosodicyanomethanide (ndcm)). We have expected the bulky anions to remain outside the coordination sphere. Our aim was to replace a small coordinated anion by a larger one which would induce changes in the coordination polyhedra. Depending on the solvent, two different kinds of compounds were prepared:

A) Five-coordinated compounds of the general formula [Cu(bipy)₂X]Y (bipy is 2,2'-bipyridine, X = CN⁻, NCO⁻, NCS⁻, N(CN)₂⁻ or N(CN)₃⁻, Y = C(CN)₃⁻), using ethanol as a solvent². No compound with Y = ON-C(CN)₂⁻ could be prepared.

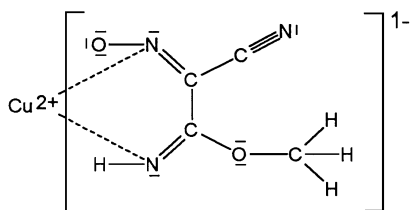
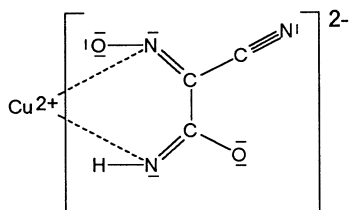
B) Five-coordinated compounds of the general formula [Cu(bipy)(mcoe)X] when replacing ethanol by methanol, where X = N(CN)₂⁻ or ON-C(CN)₂⁻. The bidentate ligand mcoe is methyl(2-cyano-2-imidoxo ethaneimidate) (**3**) formed through the nucleophilic addition of methanol to the coordinated ndcm anion³. After coordinative activation of the (nitrile-carbon in ON-C(CN)₂⁻ consisting in bending the linear N≡C-C fragment (sp-hybridized carbon) via N-coordination and changing the hybridization to sp², the nitrile-carbon becomes susceptible to the nucleophilic attack⁴.



Formation of the mcoe ligand was observed also in $[\text{Cu}(\text{mcoe})_2(\text{H}_2\text{O})_2]$ (ref.⁵). Creation of the ligand has been described also in the presence of Pd^{2+} , Co^{3+} (ref.⁵) and Ni^{2+} (refs^{6,7}). If in the above reaction KOCN ($\text{X} = \text{CNO}^-$) was used the compound **1** was prepared. No compounds containing $\text{X} = \text{C}(\text{CN})_3^-$ anion were formed in these preparations.

Both kinds of five-coordinated compounds (*A*) and (*B*) above) have similar coordination polyhedra with respect to their composition, *i.e.* they have $\{\text{CuN}_5\}$ chromophores ($\{\text{CuN}_4\text{C}\}$ for $\text{X} = \text{CN}^-$), two five-membered metallocycles and one anion X , but their shapes are of different types. According to the trigonality criterion τ (ref.⁸) as well as Harrison and Hathaway criteria⁹, the coordination polyhedra in $[\text{Cu}(\text{bipy})_2\text{X}]Y$ compounds are distorted trigonal bipyramids, while the coordination polyhedra of $[\text{Cu}(\text{bipy})(\text{mcoe})\text{X}]$ compounds are distorted tetragonal pyramids with $\text{X} = \text{N}(\text{CN})_2^-$ or $\text{ON}-\text{C}(\text{CN})_2^-$ bound at the axial position.

Because no compounds containing $\text{X} = \text{ON}-\text{C}(\text{CN})_2^-$ anion in $[\text{Cu}(\text{bipy})_2\text{X}]Y$ had been prepared we have decided to perform a synthesis using a 1 : 1 reaction mixture of $\text{ON}-\text{C}(\text{CN})_2^-$ and $\text{C}(\text{CN})_3^-$ in water-ethanol as a solvent. We expected a product of the first kind with the formula $[\text{Cu}(\text{bipy})_2\{\text{ON}-\text{C}(\text{CN})_2\}][\text{C}(\text{CN})_3]$. Elemental analysis of the resulting crystals did not correspond to the expected composition despite the IR spectrum confirmed the presence of both 2,2'-bipyridine and a pseudo-halogenide anion, therefore we determined the crystal structure of the prepared compound. This revealed that the formula of the compound is $[\text{Cu}(\text{bipy})(\text{coe})]$ (**2**), where coe is the anionic chelate ligand 2-cyano-2-imidoxy ethaneimidate **4**. Although the coordination number of $\text{Cu}(\text{II})$ is four, the compound **2** also belongs to the second kind of compounds formed through a nucleophilic addition. Therefore, the crystal structures, ESR spectra and molecular orbital calculations of **1** and **2** are compared and presented here.

**3** = mcoe**4** = coe

EXPERIMENTAL

Synthesis

All chemicals were of analytical grade. Crystals of **1** were prepared by mixing 10 ml of 0.1 M aqueous solution of $\text{Cu}(\text{NO}_3)_2$ with 20 ml of 0.1 M methanolic solution of 2,2'-bipyridine, followed by addition of 10 ml of 0.1 M solution of $\text{Na}[\text{ON}-\text{C}(\text{CN})_2]$ in aqueous methanol (1 : 1) and 10 ml of 0.1 M aqueous solution of KOCN. The resulting dark green solution provided dark green crystals of $[\text{Cu}(\text{bipy})(\text{mcoe})(\text{NCO})]$ (**1**) on standing for 14 weeks.

Crystals of **2** were prepared by mixing 10 ml of 0.1 M aqueous solution of $\text{Cu}(\text{NO}_3)_2$ with 20 ml of 0.1 M ethanolic solution of 2,2'-bipyridine, followed by addition of 10 ml of 0.1 M solution of $\text{Na}[\text{ON}-\text{C}(\text{CN})_2]$ in aqueous ethanol (1 : 1) and 10 ml of 0.1 M solution of $\text{KC}(\text{CN})_3$ in aqueous ethanol (1 : 1). On standing of the resulting dark green solution for 16 weeks, dark green crystals of $[\text{Cu}(\text{bipy})(\text{coe})]$ (**2**) were formed.

X-Ray Structure Determinations

The summary of crystal data and structure refinement for compounds **1** and **2** is presented in Table I. Data collection and cell refinement were performed using Syntex P2₁ software, θ - 2θ scan mode, graphite-monochromated $\text{MoK}\alpha$ radiation. The intensities were corrected for Lorentz and polarization factors and for absorption using XP21 software¹⁰. The structures were solved by direct methods with SHELXS86 (ref.¹¹) and subsequent Fourier syntheses with SHELXL93 (ref.¹²). 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. The hydrogen atom bonded to N3 atom in **2** was included in the refinement in the calculated position with isotropic displacement parameter equal to $1.2 U_{\text{eq}}(\text{N3})$. Geometrical analysis was performed using PARST (ref.¹³) and SHELXL93, ORTEP (ref.¹⁴) was employed to draw the structures. Density of the crystals of **1** and **2** was determined at 21 °C by floatation in a mixture of CCl_4 and benzene, and in a mixture of CCl_4 and CHBr_3 , respectively.

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers **1**: CCDC-115165 and **2**: CCDC-115166. Copies of the data can be obtained free of charge on application to CCDC, e-mail: deposit@ccdc.ca.ac.uk.

ESR Spectrometry

The ESR spectra were recorded on a Bruker SRC-200 D spectrometer operating at X-band, using the 100-kHz field modulation; *g* factors are quoted relative to internal reference standard (diphenylpicrylhydrazyl). The spectra were measured for polycrystalline samples and solutions. Studies on deaerated solutions at 298 K were performed using an aqueous cell, those at 77 K were performed using the solution frozen in quartz tubes and then transferred to a liquid nitrogen Dewar. The magnetic parameters associated with the ESR spectra were determined by computer simulation using programs described elsewhere¹⁵.

TABLE I
Summary of crystal data and structure refinement for **1** and **2**

	1	2
Empirical formula	C ₁₅ H ₁₂ N ₆ O ₃ Cu	C ₁₃ H ₉ N ₅ O ₂ Cu
Formula weight	387.85	330.79
Crystal system	monoclinic	monoclinic
Space group	<i>C2/c</i>	<i>P2₁/c</i>
Unit cell dimensions		
<i>a</i> , Å	25.685(8)	7.806(2)
<i>b</i> , Å	7.299(2)	17.622(5)
<i>c</i> , Å	17.984(6)	9.393(3)
β, °	110.23(2)	104.58(2)
Volume, Å ³	3 164(2)	1 250.5(6)
<i>Z</i>	8	4
Density calculated, mg m ⁻³	1.629	1.757
Density measured, mg m ⁻³	1.59(1)	1.73(1)
Absorption coefficient, mm ⁻¹	1.410	1.759
<i>F</i> (000)	1 576	668
Crystal size, mm	0.3 × 0.2 × 0.05	0.4 × 0.25 × 0.15
Temperature, K	293(2)	293(2)
Absorption correction	Ψ scan (ref. ²⁴)	Ψ scan (ref. ²⁴)
Max. and min. transition coefficients	0.875 and 0.730	0.997 and 0.765
Radiation	Mo- <i>K</i> α (λ = 0.71073 Å)	Mo- <i>K</i> α (λ = 0.71073 Å)
θ range for data collection, °	1.69 to 26.25	2.31 to 27.79
Index ranges	0 ≤ <i>h</i> ≤ 32, -9 ≤ <i>k</i> ≤ 9, -22 ≤ <i>l</i> ≤ 21	0 ≤ <i>h</i> ≤ 10, -23 ≤ <i>k</i> ≤ 23, -12 ≤ <i>l</i> ≤ 11
Standard reflections	3, collected every 100 refl.	3, collected every 100refl.
Reflections collected	3 879	3 678
Independent reflections	3 187 [<i>R</i> (int) = 0.0891]	2 911 [<i>R</i> (int) = 0.0589]
Solution	direct methods	direct methods
Refinement method	full-matrix least-squares on <i>F</i> ²	full-matrix least-squares on <i>F</i> ²
Data/Restraints/Parameters	3 160/0/274	2 911/0/220
Goodness-of-fit on <i>F</i> ² all, obs.	0.796, 0.891	0.798, 1.021
Final <i>R</i> indices (<i>I</i> > 2θ(<i>I</i>))	<i>RI</i> = 0.0552, <i>wRI</i> = 0.1221	<i>RI</i> = 0.0381, <i>wRI</i> = 0.0801
<i>R</i> indices (all data)	<i>RI</i> = 0.1609, <i>wRI</i> = 0.1674	<i>RI</i> = 0.1385, <i>wRI</i> = 0.0963
Hydrogen atoms	refined	refined
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.1069P)^2]$; $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0329P)^2]$; $P = (F_o^2 + 2F_c^2)/3$
Largest diff. peak and hole, e Å ⁻³	0.507 and -0.811	0.356 and -0.475

MO Calculations

The MO-LCAO-SCF calculations were done by the quasirelativistic INDO/1 method^{16,17} which is of an approximate, but semiempirical ZDO-type.

RESULTS AND DISCUSSION

Crystal Structures

Selected intramolecular bond lengths and angles for **1** and **2** are presented in Table II. The labelling schemes of formula units are shown in Figs 1 and 2. In compound **1**, the Cu(II) ion is five-coordinated by one bidentate bipy molecule, one *N,N'*-bidentate mcoe and one *N*-bonded NCO⁻ anion. The Cu-N distances in both metallocycles are quite normal³ and lie within the interval from 1.991(6) to 2.031(4) Å. The coordination polyhedron is completed to a distorted trigonal bipyramid by a cyanate anion at a Cu-N4 distance of 2.046(6) Å. The trigonality criterion τ is 64.8 ($\tau = 100$ for ideal trigonal bipyramid and $\tau = 0$ for ideal tetragonal pyramid). There are two anionic ligands, mcoe and NCO, with (1-) negative charge in the structure. A comparison of the interatomic distances N-C (1.150(9) Å) and C-O (1.212(8) Å) in NCO with data for covalent radii from¹⁸ suggests that the multiplicity of the respective bonds should be 3 and 2. The crystal structure of **1** is molecular, formed by discrete molecules which are connected by the hydrogen bonds N3-H3...O3ⁱ (H3...O3ⁱ = 2.290(60) Å; *i* = *x*, *y* + 1, *z*) into infinite chains. These chains are separated at van der Waals distances.

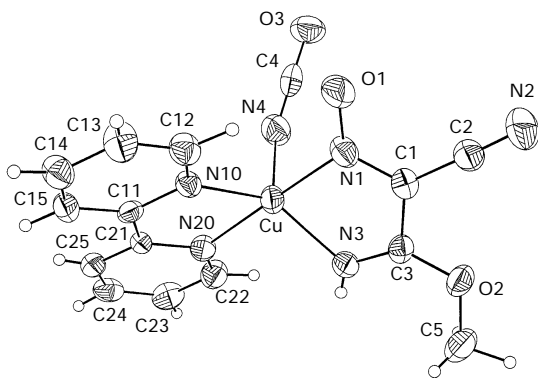


FIG. 1

ORTEP drawing of the formula unit of **1** and labelling of atoms. Displacement ellipsoids are plotted at the 40% probability level

TABLE II
Selected bond lengths (Å) and angles (°) for **1** and **2**

	1		2				
Cu-N1	2.003(5)	N4-C4	1.150(9)	Cu-N10	1.985(3)	C1-C3	1.479(50)
Cu-N3	1.991(6)	C3-O2	1.323(7)	Cu-N20	1.983(3)	C3-O2	1.237(4)
Cu-N20	2.007(5)	C3-C1	1.456(8)	Cu-N1	1.987(3)	N3-C3	1.253(5)
Cu-N10	2.031(4)	O2-C5	1.431(9)	Cu-N3	1.922(2)	N1-C1	1.306(4)
Cu-N4	2.046(6)	C4-O3	1.212(8)	Cu-O1 ⁱ	2.503(3)	C1-C2	1.421(6)
N3-C3	1.258(8)	C1-C2	1.417(8)	Cu-O2 ⁱⁱ	2.801(3)	C2-N2	1.135(5)
N1-O1	1.264(6)	N2-C2	1.127(8)	N1-O1	1.264(6)		
N1-C1	1.316(7)						
N1-Cu-N3	80.2(2)	O1-N1-Cu	125.4(4)	N3-Cu-N10	169.18(11)	C1-N1-Cu	110.3(3)
N1-Cu-N20	175.7(2)	C1-N1-Cu	113.6(4)	N10-Cu-N20	81.79(13)	N3-C3-C1	113.9(3)
N3-Cu-N20	99.0(2)	C4-N4-Cu	147.6(6)	N10-Cu-N20	102.48(13)	N1-C1-C2	121.1(4)
N1-Cu-N10	98.0(2)	N3-C3-O2	129.9(6)	N3-Cu-N20	93.85(12)	C2-C1-C3	122.3(3)
N3-Cu-N10	136.8(2)	N3-C3-C1	117.5(6)	N20-Cu-N1	175.25(12)	O2-C3-N3	127.8(4)
N20-Cu-N10	79.6(2)	O2-C3-C1	112.5(5)	N3-Cu-N1	82.29(12)	O1-N1-C1	121.8(3)
N1-Cu-N4	91.9(2)	C3-O2-C5	117.5(5)	O1 ⁱ -Cu-O2 ⁱⁱ	167.9(1)	N1-C1-C3	116.6(4)
N3-Cu-N4	113.0(2)	O3-C4-N4	177.7(7)	C3-N3-Cu	115.8(2)	N2-C2-C1	178.5(4)
N20-Cu-N4	92.3(2)	N1-C1-C2	122.9(6)	O1-N1-Cu	127.8(2)	O2-C3-C1	118.3(4)
N10-Cu-N4	110.2(2)	N1-C1-C3	113.9(5)				
C3-N3-Cu	114.4(5)	C2-C1-C3	123.2(5)				
O1-N1-C1	120.9(5)	N2-C2-C1	176.7(8)				

Symmetry transformations: i = -x, -y, -z + 1; ii = -x + 1, -y, -z + 1

In compound **2**, the first coordination environment of the Cu atom is a distorted N_4 -square. The copper atom is coordinated by four N atoms forming two five-membered metallocycles. The crystal structure of **2** consists of discrete molecules which are connected by weak contacts between copper and oxygen atoms to infinite chains parallel with c ($Cu-O1^i = 2.503(3)$ Å, $Cu-O2^{ii} = 2.801(3)$ Å; $i = -x, -y, -z + 1$; $ii = -x + 1, -y, -z + 1$) shown in Fig. 3. In this respect the coordination polyhedron might be considered as an elongated tetragonal bipyramid with the angle $O1^i-Cu-O2^{ii} = 167.9(1)^\circ$.

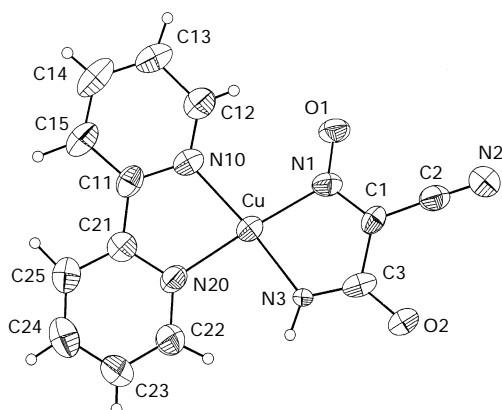


FIG. 2

ORTEP drawing of the formula unit of **2** and labelling of atoms. Displacement ellipsoids are plotted at the 40% probability level

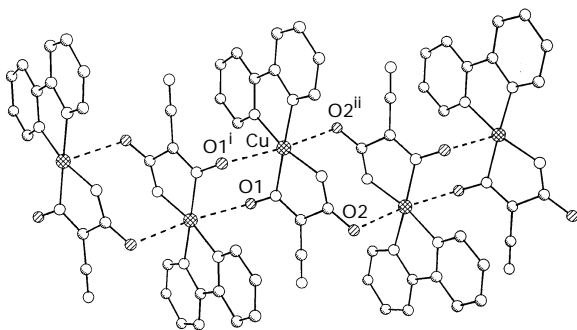


FIG. 3

A fragment of the polymeric chain in **2** parallel with the c axis (symmetry transformations: $i = -x, -y, -z + 1$; $ii = -x + 1, -y, -z + 1$)

Inspection of the bond distances in the anionic ligands mcoe and coe (Figs 4 and 5) shows that C1–C3, C1–C2, C3–O2 (mcoe), C5–O2 (mcoe), and C2–N2 bonds can be considered as single and triple, respectively. The values of all the other C–O, C–N and N–O bonds lie between the values expected for single and double bonds, indicating a strongly delocalized π -bonding system which is in agreement with the bonding mode of the original ndcm anion¹⁹. This is also supported by the fact that the anions are almost planar (the largest deviation of atoms from the mean planes being 0.072(6) Å for mcoe (except for the methyl group) and 0.096(4) Å for coe) and the values of bond angles are in the range from 113 to 130°.

ESR Spectra

The ESR spectra for the polycrystalline sample of **1** at 298 and 77 K are almost identical. The g values ($g_{\parallel} = 2.051$; $g_{\perp} = 2.155$), obeying the relation $g_{\perp} > g_{\parallel}$, indicate the d_{z^2} ground state typical for the trigonal bipyramidal copper(II)

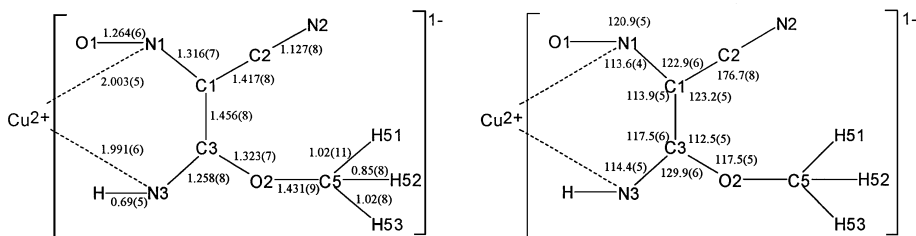


FIG. 4

Schematic drawing of mcoe **3** with bond distances (Å) and angles (°)

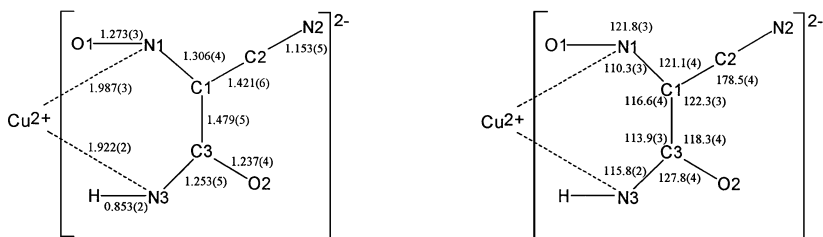


FIG. 5

Schematic drawing of coe **4** with bond distances (Å) and angles (°)

complexes²⁰. The ESR spectrum of **1** in frozen dimethyl sulfoxide (DMSO) consists of two mutually overlapped signals with $g_{\parallel} > g_{\perp}$. The first signal exhibits axial symmetry ($g_{\parallel} \approx 2.17$; $g_{\perp} \approx 2.055$) without any resolved hyperfine structure. For the second signal, only the $m_1 = -3/2$ component of the hyperfine structure in parallel region of the spectrum was clearly resolved and the other features were overlapped by the first signal. After addition of pyridine (5% v/v of pyridine) to the DMSO solution of **1**, the ESR spectrum became better resolved and showed one signal attributable to one species in the solution. The spectrum exhibits axial symmetry with resolved hyperfine structure in its parallel region ($g_{\parallel} = 2.246$; $g_{\perp} = 2.056$; $|A_{\parallel}^{\text{Cu}}| = 550$ MHz; $|A_{\perp}^{\text{Cu}}| = 30$ MHz). The change in the relation of the g -factors ($g_{\perp} > g_{\parallel}$ in the solid state, $g_{\parallel} > g_{\perp}$ in frozen solutions) indicates that the trigonal bipyramidal coordination of **1** does not longer exist in the solution, and most likely the square pyramidal coordination is preferred. As a consequence, the vacant sixth coordination position is more easily accessible to a solvent or base molecule (dmsO, py). Therefore, the presence of the two signals in DMSO frozen solution ESR spectrum of **1** may be attributed to both partial solvent coordination and molecular aggregation (formation of "dimeric" species) in frozen solution. Closer inspection of the spectrum revealed a low intense half-field transition at ≈ 1 560 G ($\Delta m_s = \pm 2$ transition). In the presence of pyridine in DMSO solution, the aggregation is more difficult and pyridine coordination takes place.

The spectra of the complex **2** in polycrystalline state at 298 and 77 K exhibit axial symmetry ($g_{\parallel} = 2.188$; $g_{\perp} = 2.058$). The lines are very broad without any resolved hyperfine structure. The frozen DMSO solution ESR spectrum of **2** shows three of four low-field parallel components of the copper hyperfine structure which are well separated from the much stronger perpendicular portion of the spectrum. The perpendicular part of the spectrum is more complex. This is due not only to nitrogen superhyperfine structure (eight of nine lines observed), but also to the presence of an overshoot line²¹. The spin Hamiltonian parameters were calculated to be $g_{\parallel} = 2.236$; $g_{\perp} = 2.058$; $A_{\parallel}^{\text{Cu}} = 565$ MHz; $A_{\perp}^{\text{Cu}} = 15$ MHz; $A_{\perp}^{\text{N}} = 47$ MHz, matching well with those found for square planar copper(II) complexes with four donor nitrogen atoms²². The fluid-solution ESR spectra of complexes **1** and **2** were poorly resolved and the spectral parameters could not be determined.

There is only one anionic ligand in the structure of **2**. It must bear either a negative charge of -2 and the copper oxidation state must be II, or a negative charge of -1 and Cu(II) must be reduced to Cu(I). No maxima which might be assigned to H atoms around O2 and N3 atoms were found in the difference electron density map. Therefore, it was not possible to decide un-

ambiguously whether the nucleophilic addition of water or hydroxide ion to the ndcm took place during the synthesis. According to the ESR spectra of **2**, it can be concluded that the nitrile-carbon of ndcm is attacked by the hydroxide, resulting in a dianion.

Bonding Characteristics of Anions

The Wiberg (bond-order) index²³ $W_{\text{Cu-N4}} = 0.78$ shows that the coordination bond of the NCO^- anion to the copper atom in **1** is weaker than a single bond, while the other bonds of the anion are multiple in character ($W_{\text{C4-O3}} = 1.71$ and $W_{\text{N4-C4}} = 2.18$). The bond distance C4–O3 of 1.212(8) Å corresponds according to Jolly¹⁸ to a double bond (1.22 Å) which is in agreement with $W_{\text{C4-O3}} = 1.71$. On the other hand, the bond distance N4–C4 of 1.150(9) Å corresponds according to Jolly¹⁸ to a triple bond (1.15 Å) which does not agree with $W_{\text{N4-C4}} = 2.18$. From the chemical point of view only the double bond is acceptable which is supported also by the bonding mode angle Cu–N4–C4 of 147.6(6)°, and the angle N4–C4–O3 of 177.7(7)°.

Both coordination bonds in mcoe are weaker than single bonds ($W_{\text{Cu-N1}} = 0.58$ and $W_{\text{Cu-N3}} = 0.60$). On the other hand, there is only one coordination bond weaker than a single bond in coe ($W_{\text{Cu-N1}} = 0.69$). Due to the conjugation, the C–N ($W_{\text{C1-N1}} = 1.31$ (1.42) and $W_{\text{C3-N3}} = 1.52$ (1.25)), N–O ($W_{\text{N1-O1}} = 1.52$ (1.38)) and C–O ($W_{\text{C3-O2}} = 1.57$ in coe) bonds exhibit partially multiple character (data for coe are given in parentheses). The other bonds in the anions are single and the C2–N2 bond is triple.

The most negative charges in anions are on oxygen atoms; the O3 atom of NCO^- in **1** (–0.46) and the O1 and O2 atoms in **2** possess the most negative charges (–0.47 and –0.52, respectively), while the C3 atoms bear the most positive charges ($Q_{\text{C3}} = +0.51$ (+0.53)). The N–H bonds are polar as $Q_{\text{N3}} = -0.33$ (–0.32) and $Q_{\text{H3}} = +0.19$ (+0.16) (data for coe are given in parentheses). This might be a consequence of the short N3–H3 bond (0.69(5) Å) in mcoe, which could be an artefact of the X-ray structure determination reflecting the positions of the electron density maxima rather than internuclear distances (if the N–H bond is strongly polar or the H atom bears a high positive charge). The d-orbital populations of $d^{9.20}$ ($d^{9.34}$) confirm the behaviour corresponding to a Cu(II) system.

Referring to the introductory classification of possible effects of the factors influencing formation of the above Cu(II) coordination compounds, we may conclude the following:

As far as (i) is concerned, creation of mcoe or coe ligands depends on the character of the mother solution. If methanol–water mother solution is used, mcoe is created (**1**). If ethanol–water mother solution is used, coe is created (**2**). According to (ii), the change caused by removing the methyl group from the mcoe ligand and thus transforming mcoe into coe caused great stereochemical and crystallochemical changes in the above structures. The coordination polyhedra in **1** and **2** are quite different. The coordination polyhedron around the Cu atom in **1** is a distorted trigonal bipyramid and in **2** a distorted square completed subsequently to a tetragonal bipyramid. The crystal structure of **1** consists of discrete molecules. On the other hand, the crystal structure of **2** can be considered a structure with polymeric chains in one direction. As far as (iii) is concerned, we have shown³ that, according to the trigonality criterion τ , the coordination polyhedra in $[\text{Cu}(\text{bipy})(\text{mcoe})\text{X}]$ compounds ($\text{X} = \text{N}(\text{CN})_2^-$ or $\text{ON}-\text{C}(\text{CN})_2^-$) may be considered as tetragonal pyramids ($\tau = 18.8$ and 3.4 , respectively) with relatively small differences in corresponding angles and distances within the Cu(II) coordination sphere. On the other hand, the trigonality criterion τ (64.8) for **1** indicates substantial distortion of the coordination polyhedron towards trigonal bipyramid. The above mentioned hydrogen bonds could support the change in the coordination polyhedron, observed in $[\text{Cu}(\text{bipy})(\text{mcoe})\text{X}]$ compounds ($\text{X} = \text{N}(\text{CN})_2^-$ or $\text{ON}-\text{C}(\text{CN})_2^-$), where no hydrogen bonds were found, from tetragonal pyramid to trigonal bipyramid in **1**.

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