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КРАТКИЕ СООБЩЕНИЯ

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BINUCLEAR COMPLEX
[Cu(bappz)(μ-NC)Ni(CN)$_3$]·H$_2$O (bappz = 1,4-BIS(3-AMINOPROPYL)PIPERAZINE)

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The novel bimetallic compound [Cu(bappz)(μ-NC)Ni(CN)$_3$]·H$_2$O (bappz = 1,4-bis(3-aminopropyl)piperazine) is prepared by the reaction of Cu(NO$_3$)$_2$·3H$_2$O, bappz, and K$_2$[Ni(CN)$_4$] in water. The complex is characterized by IR spectroscopy and single crystal X-ray diffraction. The neutral [Cu(bappz)(μ-NC)Ni(CN)$_3$] complex assumes a cyanide-bridged binuclear structure in which the nickel(II) ion is four-coordinated by carbon atoms from four cyano groups (one of them forms a bridge) in a square planar arrangement, whereas the copper(II) ion is five-coordinated by four bappz nitrogen and one cyanide nitrogen atoms in a distorted square-pyramidal geometry.

Keywords: copper(II) complexes, tetracyanonickelates(II), cyano-bridged complexes, X-ray structure analysis.

In general, cyano-bridged homo- and heterometallic complexes continuously attract much attention in coordination chemistry, especially in the context of their fascinating structures with interesting magnetic, electrochemical, magneto-optical, and zeolitic properties [1—6]. For instance, cyanido-bridged tetracyanonickelates^{2-} [Ni(CN)$_4$]$^{2-}$ are suitable model compounds for structural and magnetic studies at low temperatures because the tetracyanonickelate anion may bridge paramagnetic ions partially coordinated with amine ligands, and thus form molecular 1D, 2D, and 3D structures. These complexes can be built by linking the appropriate building blocks by the brick and mortar method [7]. Previously, we have studied the reaction of [Cu(bappz)](ClO$_4$)$_2$ (bappz = 1,4-bis(3-aminopropyl)piperazine) and K$_2$[Ni(CN)$_4$] in water [8]. This reaction leads to two products: prism-like dark blue crystals of the trinuclear complex [Cu(bappz)(μ-NC)Ni(CN)$_2$(μ-CN)Cu(bappz)](ClO$_4$)$_2$ (its crystal structure is described) and blue needle-like crystals of the [Cu(bappz)Ni(CN)$_4$]·H$_2$O compound whose crystal structure has not been solved so far [8]. In this paper, we have continued our study of the [Cu(bappz)Ni(CN)$_4$]·H$_2$O complex and the single crystal X-ray structural analysis revealed that this compound can be formulated as a binuclear [Cu(bappz)(μ-NC)Ni(CN)$_3$]·H$_2$O complex. The number of structural studies on binuclear tetracyanonickelates(2-) of copper(II) is surprisingly low. To date, only three following structural examples of these compounds have been reported: [Cu(dien)(mea)Ni(CN)$_4$]·2H$_2$O (dien = diethylenetriamine, mea = 2-aminoethanol), [Cu(Me$_6$Cy)Ni(CN)$_4$] (Me$_6$Cy = *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane), and [Cu(L)Ni(CN)$_4$]·0.25H$_2$O (L = 1,3,6,8,11,14-hexaazatricyclo[12.2.1.1^{8,11}]octadecane) complexes [9—11].

Experimental. All reagents used in the synthesis were of analytical grade and were used without further modification. The IR spectrum was recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer using a KBr pellet.

Synthesis of the [Cu(bappz)(μ-NC)Ni(CN)$_3$]·H$_2$O complex. The title binuclear compound can be prepared together with [Cu(bappz)(μ-NC)Ni(CN)$_2$(μ-CN)Cu(bappz)](ClO$_4$)$_2$ according to the literature [8].

We have used a new preparative method in order to obtain only the title compound. To a solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.50 g, 2.1 mmol) in water (50 ml) bappz (0.37 ml, 1.8 mmol) was added dropwise with stirring. The resulting solution was filtered and mixed with a solution of $K_2[Ni(CN)_4]$ (0.50 g, 2.1 mmol) in water (20 ml). The reaction mixture was allowed to undergo slow evaporation whereupon a blue crystallic product was obtained. The solid was filtered off, washed with a small amount of water, and dried in air. Yield: 0.24 g, 30 %. Anal. Calc. for $C_{14}H_{26}CuN_8NiO$: C, 37.81; H, 5.89; N, 25.20 %. Found: C, 37.44; H, 6.41; N, 24.92 %. Single crystals of this complex were obtained by slow evaporation from the concentrated ammonia solution.

Single crystal X-ray diffraction analysis. Diffraction data for the studied compound were collected on a Bruker APEX-II CCD diffractometer at 150(2) K using graphite monochromated MoK_α radiation. The structure was solved by direct methods using the SHELXS97 program [12] and refined by full matrix least squares on F^2 with SHELXL97 [12]. The hydrogen atoms were included in the calculated positions and treated as riding atoms using the SHELXL97 default parameters. All non-hydrogen atoms were refined anisotropically. An empirical absorption correction was applied using SADABS [13]. The crystallographic data for the studied compound have also been deposited with the Cambridge Crystallographic Data Centre as supplementary material with the deposition number: CCDC 937907. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk). The resulting crystal data and details concerning the data collection and refinement are quoted in Table 1. Selected bond distances and angles are listed in Table 2.

Results and discussion. In the studied binuclear Cu(II)—Ni(II) complex the central atoms are bridged by the cyano anion (Fig. 1). The copper atom is five-coordinated by four nitrogen atoms from 1,4-bis(3-aminopropyl)piperazine and one nitrogen atom from the cyano bridge in a distorted square-pyramidal arrangement with four bappz nitrogen atoms bonded in the basal plane and one cyano nitro-

Table 1

Crystal data and structure refinements for [Cu(bappz)(μ-NC)Ni(CN)$_3$]·H$_2$O

Formula weight, g/mol	444.68
Crystal system	Monoclinic
Space group	$P2_1/c$
a, *b*, *c*, Å	11.0560(2), 9.7979(2), 18.2263(4)
β, deg.	106.7500(10)
V, Å^3	1890.60(7)
Z; D_c, g/cm^3	4; 1.562
Absorption coefficient, mm^{-1}	2.140
F(000)	924
Crystal size, mm	0.32×0.28×0.19
θ range for data collection, deg.	2.33—27.59
Index ranges	$-14 \le h \le 14$, $-12 \le k \le 12$, $-23 \le l \le 23$
Reflection collected / unique	36647 / 4374 [*R*(int) = 0.0203]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4374 / 44 / 226
Goodness-of-fit on F^2	1.052
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0177$, $wR2 = 0.0458$
R indices (all data)	$R1 = 0.0195$, $wR2 = 0.0466$
Largest diff. peak and hole, e/Å^3	0.338 and –0.331

Table 2

Selected bond distances (Å) *and angles* (deg.) *for* [Cu(bappz)(μ-NC)Ni(CN)$_3$]·H$_2$O

Ni(1)—C(3)	1.8664(13)	C(3)—Ni(1)—C(1)	175.89(6)	N(8)—Cu(1)—N(7)	94.39(4)
Ni(1)—C(1)	1.8669(13)	C(3)—Ni(1)—C(4)	90.40(5)	N(5)—Cu(1)—N(6)	95.73(4)
Ni(1)—C(4)	1.8703(13)	C(1)—Ni(1)—C(4)	91.16(5)	N(8)—Cu(1)—N(6)	152.88(4)
Ni(1)—C(2)	1.8720(13)	C(3)—Ni(1)—C(2)	89.87(5)	N(7)—Cu(1)—N(6)	73.20(4)
Cu(1)—N(5)	2.0122(11)	C(1)—Ni(1)—C(2)	88.63(5)	N(5)—Cu(1)—N(3)	92.32(4)
Cu(1)—N(8)	2.0141(11)	C(4)—Ni(1)—C(2)	179.08(6)	N(8)—Cu(1)—N(3)	103.09(5)
Cu(1)—N(7)	2.0500(10)	N(5)—Cu(1)—N(8)	90.75(4)	N(7)—Cu(1)—N(3)	100.97(4)
Cu(1)—N(6)	2.0776(11)	N(5)—Cu(1)—N(7	164.25(4)	N(7)—Cu(1)—N(3)	102.93(4)
Cu(1)—N(3)	2.1838(11)				

gen atom as the apical ligand. The in-plane Cu—N bond lengths are ranging from 2.0122(11) Å to 2.0766(11) Å and the axial Cu—N bond distance of 2.1838(11) Å is significantly longer than the in-plane Cu—N bond lengths. The N(7)—Cu(1)—N(6) angle (73.20(4)°) is smaller than the ideal value of 90° because this angle is part of a five-membered chelate. The value of the τ parameter (0.19) confirms the square-pyramidal geometry of the coordination polyhedron (the ideal τ value for the square-pyramidal coordination sphere is 0 and for the trigonal bipyramidal arrangement it should be 1) [14]. The nickel atom is four-coordinated by four carbon atoms from cyano groups (one of them forms a bridge) with a slightly distorted square-planar arrangement, and the mean bond lengths of Ni—C (1.87 Å) and C—N (1.15 Å) in the Ni(CN)$_4$ moiety are in good accordance with the reported values for similar compounds [8—11, 15]. As usually, the Ni(CN)$_4$ fragment exhibits a planar structure. The bridging cyano group coordinates to copper in a bent fashion with the C—N—Cu bond angle of 138.69(10)°. The intramolecular Ni···Cu distance is 4.846 Å.

The Cu(II)—Ni(II) units are joined together through the intermolecular H-bonding between the crystallization water molecule and the secondary amine hydrogen atom of the bappz ligand and two terminal cyano groups in the [Ni(CN)$_4$]$^{2-}$ moiety, resulting in a 2D supramolecular network structure (Fig. 2). These H bonds with distances and angles ranging from 2.86 Å to 2.91 Å and from 164° to 173° respectively, fall to the interval of values typical of medium strength hydrogen bonds (D···A ≈ 2.5—3.2 Å and angle NHO ≈ 130—180°) [16]. Detailes of the H-bonding are presented in Table 3.

In the IR spectrum, the characteristic vibrations ν(C≡N) were assigned. The presence of the cyano bridge is shown by the splitting of the ν(C≡N) stretching band which appears at about 2000—2200 cm^{-1} for cyano complexes [17]. According to the literature, the formation of the cyano bridge shifts ν(C≡N) towards higher frequencies [18]. In the present complex the strong band at 2152 cm^{-1} may be attributed to ν(C≡N) of the bridging cyanide; another (2124 cm^{-1}) is due to the terminal one. The band at 3153 cm^{-1} belongs to the N—H stretching vibration and the broad band around 3600 cm^{-1} can be assigned to the O—H stretching vibration.

The magnetic properties of this binuclear μ-cyano compound have not been studied. Because of the diamagnetism of the nitroprusside anion there is no possibility of the intramolecular interaction between the copper and iron centres *via* the cyanido group, only the copper(II) ion (S = 1/2) is paramagnetic.

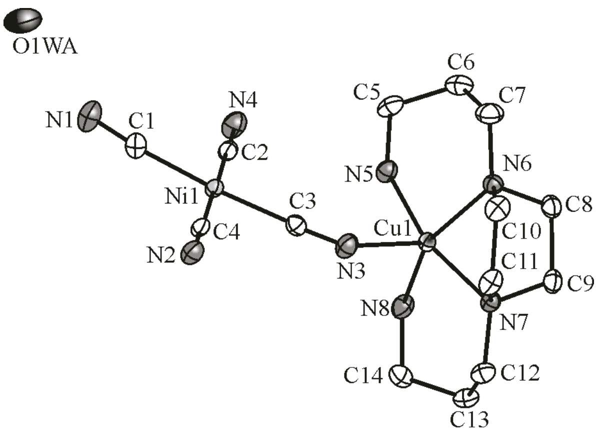

Fig. 1. Molecular structure of [Cu(bappz)(μ-NC)·Ni(CN)$_3$]·H$_2$O with the atom numbering scheme. Hydrogen atoms are omitted for clarity. Displacement ellipsoids are drawn at the 50 % probability level

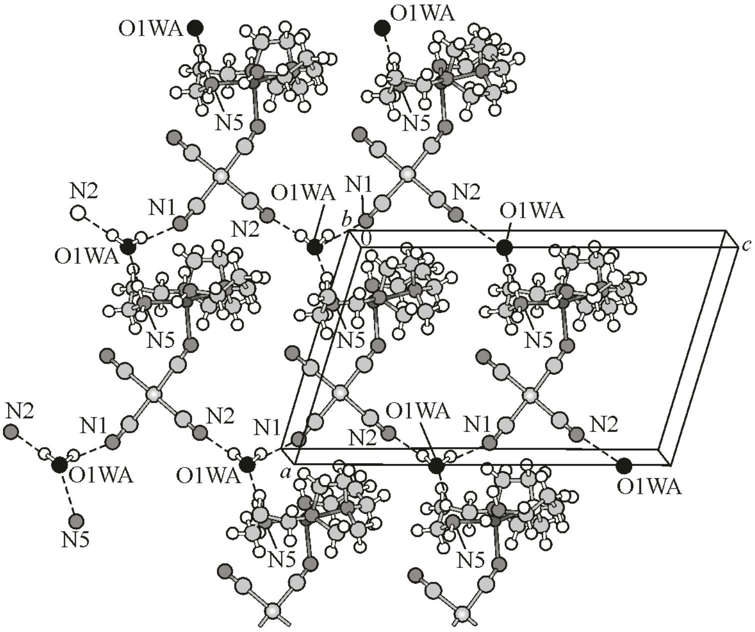

Fig. 2. A view of the crystal structure of $[\mathrm{Cu(bappz)}(\mu\text{-NC})\mathrm{Ni(CN)_3}]\cdot\mathrm{H_2O}$ down the *b* axis. Dashed lines indicate possible hydrogen bonds

Table 3

Selected H *bond lengths* (Å) *and angles* (deg.) *for* $[\mathrm{Cu(bappz)}(\mu\text{-NC})\mathrm{Ni(CN)_3}]\cdot\mathrm{H_2O}$

Donor—H···Acceptor	*d*(D—H)	*d*(H···A)	*d*(A···D)	∠(D—H···A)
N(5)—H(5A)···O(1WA)#1	0.92	1.96	2.8565(15)	163.8
O(1WA)—H(1WA)···N(1)	0.86	2.07	2.9087(17)	164.5
O(1WA)—H(2WA)···N(2)#2	0.85	2.02	2.8603(16)	172.6

Symmetry transformations used to generate equivalent atoms: #1 $x-1, y, z$; #2 $x, -y+3/2, z-1/2$.

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