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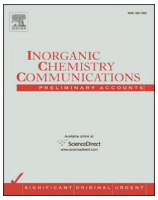

Short communication

Formation of the unprecedented trinuclear $[NiCu_2(CN)_8]^{4-}$ complex anion within the crystal structure of $[Ni(5,5'\text{-}\mathit{dmbpy})_3]_2[NiCu_2(CN)_8]\cdot 6H_2O$

Juraj Černák [a,*], Ivana Kočanová [a], Juraj Kuchár [a], Elizabeth A. Hillard [b,c], Rodolphe Clérac [b,c]

[a] Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Sciences, P. J. Šafárik University in Košice, SK-041 54 Košice, Slovakia
[b] CNRS, CRPP, UMR 5031, 33600 Pessac, France
[c] Univ. Bordeaux, CRPP, UMR 5031, 33600 Pessac, France

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ABSTRACT

From an aqueous-ethanolic solution of $CuCl_2$, 5,5′-*dmbpy* (5,5′-*dmbpy* = 5,5′-dimethyl-2,2′-bipyridine) and $K_2[Ni(CN)_4]$, a novel Cu/Ni heterobimetallic complex $[Ni(5,5'\text{-}\mathit{dmbpy})_3]_2[NiCu_2(CN)_8]\cdot 6H_2O$ was isolated and characterized. Its ionic crystal structure contains the unprecedented Cu(I)/Ni(II,D_{4h}) complex anion $[Cu_2Ni(CN)_8]^{4-}$, along with the rarely structurally characterized $[Ni(5,5'\text{-}\mathit{dmbpy})_3]^{2+}$ complex cation and water solvate molecules. The anions and water molecules are linked by hydrogen bonds, yielding a 1D supramolecular structure. Magnetic measurements performed down to 1.8 K revealed a Curie behavior between 15 and 300 K, while a small zero field splitting effect can be seen below 15 K.

Cyanido complexes, owing to the various bonding possibilities of the cyanido ligand, exhibit high variability with respect to their structure and composition [1–3]. They have been especially studied with respect to their outstanding magnetic properties [4–10], but they have also received interest as hydrogen storage materials [11], sensors [12] and optical materials [13], among others. Cyanido complexes simultaneously containing both nickel and copper ions are often based on the tetracyanidonickellate $[Ni(CN)_4]^{2-}$ anion and various mononuclear, oligomeric or polymeric cyanidocuprate anions $[Cu_x(CN)_y]^{(y-x)-}$, depending upon the reaction conditions and the presence of additional ligands. As examples we can mention $[Cu(\mathit{etim})_4][Ni(CN)_4]$ (*etim* = 1-ethylimidazole) [14], $[Ni(\mathit{en})_3]_6[Cu(CN)_3][Cu_2(CN)_7]_2\cdot 9H_2O$ (*en* = ethylenediamine) [15] and $[Ni(\mathit{tterpy})_2][Cu_6(CN)_8]$ (*tterpy* = 4′-*p*-tolyl-2,2′:6′,2″-terpyridine) [16]. The presence of both Cu(I) and square-planar Ni(II) sites within the same cyanide bridged anion is, to our knowledge, absent in the open databases, although there are few hits in the CSD [17] of Cu(II)/Cu(I)/Ni(II,D_{4h}) heterometallic mixed valence compounds with polymeric structures, e.g. $[Cu(\mathit{en})_2(H_2O)][Cu(\mathit{en})_2Ni_2Cu_2(CN)_{10}]\cdot 2H_2O$ [18], $[\{Cu(\mathit{pn})(H_2O)\}\{NiCu(CN)_5\}]$ (*pn* = 1,2-diaminopropane) [19] and $[Cu(\mathit{dien})CuNi(CN)_5]_n$ (*dien* = diethylenetriamine) [20]. Following our previous studies on cyanido complexes based on copper and nickel [21–24], we have isolated a new complex, $[Ni(5,5'\text{-}\mathit{dmbpy})_3]_2[NiCu_2(CN)_8]\cdot 6H_2O$ (**1**) (5,5′-*dmbpy* = 5,5′-dimethyl-2,2′-bipyridine), containing an unprecedented trinuclear $[NiCu_2(CN)_8]^{4-}$ complex anion. Complex **1** formed from an aqueous-ethanolic system containing $CuCl_2$, 5,5′-*dmbpy*, and $K_2[Ni(CN)_4]$, using a mixture of citric acid and ethanolamine to solubilize the reaction mixture [25]. It is well known from the literature that when solutions containing Cu(II) ions, cyanide anions and N-donor ligands are exposed to air, complex redox equilibria are present, often yielding Cu(I)/Cu(II) mixed-valence compounds [26]. In addition, if the cyanido ligand is introduced in the form of a tetracyanidonickellate anion, as in the present reaction, exchange of the Ni(II) metal ion with another metal ion can also occur [15].

The crystal structure of $[Ni(5,5'\text{-}\mathit{dmbpy})_3]_2[NiCu_2(CN)_8]\cdot 6H_2O$ is ionic and consists of $[Ni(5,5'\text{-}\mathit{dmbpy})_3]^{2+}$ complex cations, the trinuclear $[NiCu_2(CN)_8]^{4-}$ complex anion and solvate water molecules (Fig. 1). The central Ni(II) atom of the cation is hexacoordinated by three chelating 5,5′-*dmbpy* ligands. It is interesting to note that while the complexes containing the $[Ni(\mathit{bpy})_3]^{2+}$ unit are rather common [27–29], with more than 100 hits in CSD [17], the 5,5′-dimethylated analogue $[Ni(5,5'\text{-}\mathit{dmbpy})_3]^{2+}$ was only recently structurally reported, e.g. in $[Ni(5,5'\text{-}\mathit{dmbpy})_3]_2VW_{12}O_{40}$ [30]. The Ni—N bond distances range from 2.0860(15) to 2.1053(14) Å, while the values of the N—Ni—N bite angles vary between 78.58(6) and 79.13(6)°; these values are close to those reported for $[Ni(5,5'\text{-}\mathit{dmbpy})_2(N_3)_2]\cdot H_2O$ [31] (Table S2).

The outstanding feature of the present structure is the formation of the unprecedented trinuclear Cu(I)/Ni(II) heterobimetallic anion $[Cu_2Ni(CN)_8]^{4-}$, which is composed of a central tetracyanidonickelate

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[*] Corresponding author.
E-mail address: juraj.cernak@upjs.sk (J. Černák).

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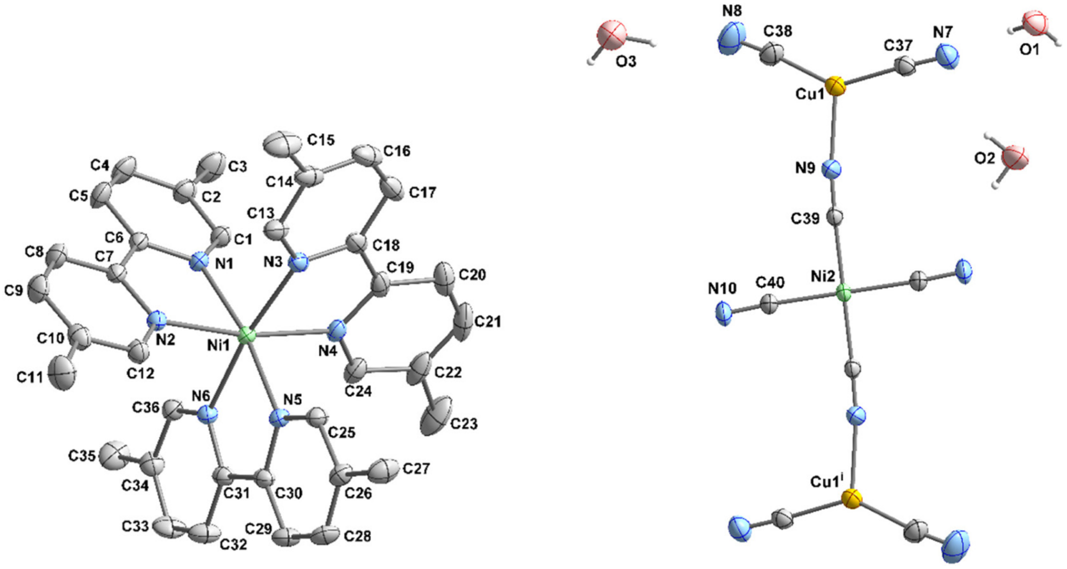

Fig. 1. Molecular structure of **1** with the cation on the left, and the anion and solvate water molecules on the right. The hydrogen atoms within the complex cation are omitted for clarity. The thermal ellipsoids were drawn at the 30% probability level. Symmetry code: i: 1 − x, 1 − y, −z.

core unit {Ni(CN)$_4$} and two {Cu(CN)$_2$} arms linked to the Ni(II) center in a *trans* orientation by μ-bridging cyanido ligands. The trinuclear anion is centrosymmetric (the Ni(II) ion is on an inversion center), but is not planar; the angle between the least squares plane formed by the NiC$_4$ chromophore and the least squares plane through the two CuC$_2$N chromophores is 16.23(9)°. The reason for the deviation from planarity, other than possible steric effects, may be the effort to maximize the formation of hydrogen bonds (see below). On the other hand, the Cu—NC—Ni—CN—Cu arrangement deviates only slightly from linearity; the highest deviation is represented by the value of 172.85(18)° for Cu1—N9—C39 (Table S2). The observed geometric parameters associated with this anion indicate square coordination of the central Ni(II) ion with Ni—C bond distances of 1.861(2) and 1.869(2) Å and a C39—Ni2—C40 angle of 92.05(8)°; these values are comparable with the corresponding ones found for example in [Cu(*bpy*)$_2$(CN)]$_2$[Ni(CN)$_4$]·4H$_2$O [22]. The coordination of the Cu(I) ion can be described as rather deformed trigonal with an NC$_2$ donor set. The highest deviation from the ideal values for trigonal coordination is represented by the C37—Cu1—C38 angle of 140.81(11)° (Fig. 1, Table S2). The Cu1—N9 bond exhibits a value of 2.024(2) Å, while both crystallographically independent Cu—C bond distances exhibit a value of 1.915(3) Å× (Table S3). In the analogous [{Cu(*pn*)(H$_2$O)}{NiCu(CN)$_5$}] compound containing the Cu^{I}CN$_2$ chromophore, somewhat shorter values were reported for the Cu—N (1.954(3) and 1.988(3) Å) and Cu—C bonds (1.894(4) Å) [19].

The crystal structure of the title complex is stabilized by hydrogen bonds of the O—H···O and O—H···N types, linking the complex anions and water solvate molecules in a one-dimensional (1D) hydrogen bonded supramolecular structure running along the *b* axis (Fig. 2, Table S4). Within the supramolecular structure three ring patterns, ***R1–R3***, are formed, and these can be described by the descriptors $R_2^2(11)$ (***R1***), $R_4^3(8)$ (***R2***) and $R_6^6(26)$ (***R3***), respectively. The hydrophobic complex cations [Ni(5,5′-*dmbpy*)$_3$]$^{2+}$ are situated between the hydrophilic hydrogen bonded chains (Fig. S3). The complex cation interacts

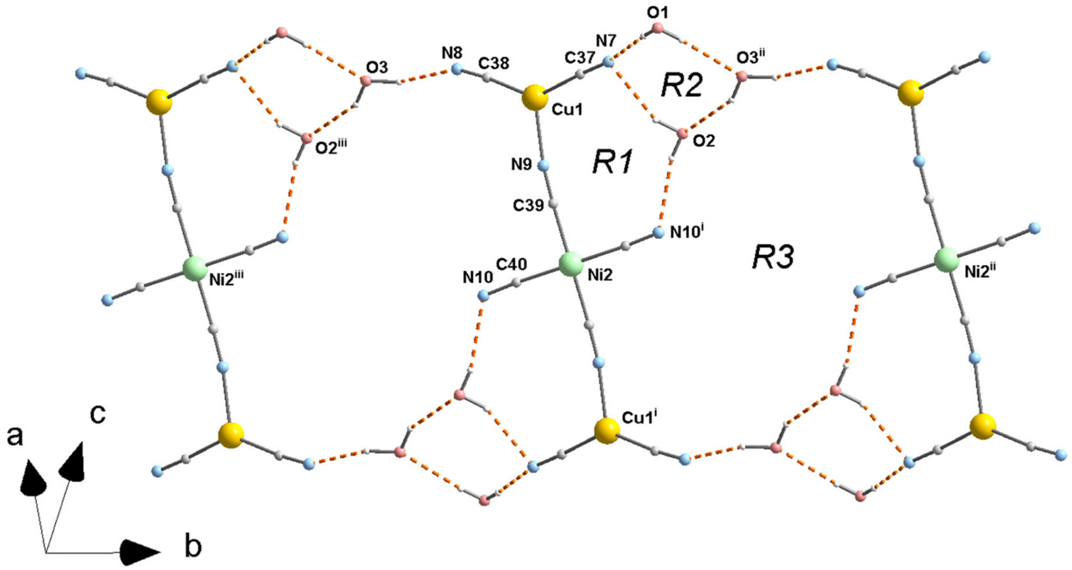

Fig. 2. Chain-like hydrogen bonded supramolecular network in **1**. Possible hydrogen bonds are depicted by orange dashed lines. *R1*, *R2* and *R3* are the formed supramolecular ring systems. For further information see the text. Symmetry codes: i: 1 − x, 1 − y, −z; ii: x, 1 + y, z; iii: x, y − 1, z.