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Bis-(*bis*-(1,3-diaminopropane)-copper(II) Tetracyanonickellate(II)) Tetrahydrate: Preparation, Characterization, and Crystal Structure of a Novel Molecular Tetracyanonickellate

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Summary. $[Cu(tn)_2Ni(CN)_4]_2 \cdot 4H_2O$ and $Cu(tn)_2Ni(CN)_4$ ($tn = $ 1,3-diaminopropane) were prepared and characterized. The hydrate is unstable on air and readily dehydrates to $Cu(tn)_2Ni(CN)_4$. Crystal structure analysis of the hydrate at 150 K revealed a novel tetranuclear molecular structure of the tetracyanonickellate. The building elements are two $[Cu(tn)_2]^{2+}$ cations (coordination numbers of Cu: 5 and 6, respectively), two $[Ni(CN)_4]^{2-}$ anions, and crystal water. The two cations are linked by one tetracyanonickellate anion *via* bridging cyano groups placed in *cis* positions. The second anion is bound weakly ($Cu\text{-}N = 2.82$ Å) *via* one μ_2-bridging cyano ligand. The tetranuclear molecules and pairs of solvate water molecules are linked by strong hydrogen bonds, thus forming infinite planes which are linked in the third dimension by considerably weaker hydrogen bonds.

Keywords. Hydrogen bonds; Tetracyanonickellate; Crystal structure; 1,3-Diaminopropane; Copper.

Introduction

Due to the diversity of the formed crystal structures and their interesting properties, especially in the context of their magnetic behaviour, cyanocomplexes unceasingly keep attracting high attention within coordination chemistry [1–10]. The tetracyanonickellates $Ni(en)_2Ni(CN)_4$ ($en = $ 1,2-diaminoethane, *NENC*) [11] and $Cu(en)_2Ni(CN)_4$ (*CENC*) [12] contain paramagnetic central atoms in the cation and exhibit one-dimensional crystal structures. Magnetic studies have revealed different magnetic behaviour of these compounds: *NENC* shows 1D magnetic character [13], whereas *CENC* can be considered as a 2D magnet due to the presence of hydrogen bonds which serve as additional exchange paths between paramagnetic centres [14].

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It is known that the shape and the composition of the paramagnetic central atom coordination sphere can greatly affect the formed crystal structure and consequently the magnetic properties of a compound [15]. In order to extend our structural studies of this class of substances, we decided to modify the copper coordination sphere in *CENC* by replacement of the *en* ligand by the somewhat larger *tn* (1,3-diaminopropane) moiety. From the aqueous system Cu(II)-*tn*-$Ni(CN)_4^{2-}$ we have isolated two polymorphs of Cu(*tn*)$Ni(CN)_4$ (blue and violet, *CTCB* and *CTCV*) [16] at low Cu:*tn* ratio, whereas $[Cu(tn)_2Ni(CN)_4]_2 \cdot 4H_2O$ (*CTNCH*) has been formed at higher Cu:*tn* ratios. The anhydrous complex $Cu(tn)_2Ni(CN)_4$ (*CTNC*) is formed after dehydration of *CTNCH*. Here we report the preparation and characterization of *CTNC* and *CTNCH* along with the results of the crystal structure analysis of *CTNCH*.

Results and Discussion

The synthetic strategy of new low-dimensional cyanocomplexes can be based on the 'brick and mortar' procedure [15, 21], where the complex cations function as bricks and the cyanocomplex anions linking the cations work as mortar. In our case, $Cu(tn)_2^{2+}$ cations and $Ni(CN)_4^{2-}$ anions were present in the mother liquor at the beginning of crystallization leading to the tetranuclear product *CTNCH*. From the same system, but with lower *tn* concentration and thus containing presumably $Cu(tn)_{aq}^{2+}$ cations, two polymorphs of Cu(*tn*)$Ni(CN)_4$ were formed. From the analogous system with *en* only one product (*CENC*) was isolated [22].

As can be seen from Fig. 1, the structure of the title compound can be considered as molecular with solvate water molecules. Molecular structures are rather rare among tetracyanonickellates; as examples, we can mention Cu(*dien*)(*mea*)$Ni(CN)_4 \cdot 2H_2O$ (*dien* = N-(2-aminoethyl)-1,2-ethane-diamine, *mea* = 2-aminoethanol) [23] and [(Ni(*dien*))$_2$(*ox*)$Ni(CN)_4$] (*ox* = oxalato) [24]. The tetranuclear molecule of the title compound is formed from two stereochemically and crystalographically different $Cu(tn)_2^{2+}$ cations and two crystallographically different $Ni(CN)_4^{2-}$ anions. The cations are linked by one tetracyanonickellate anion *via* two bridging cyano groups (N11 and N12) located in *cis* positions in the anion. The second tetracyanonickellate anion is bound to Cu2 only weakly through one bridging cyano group (N21). The remaining three cyano groups in this anion are terminal ligands (the shortest Cu···N distance is 3.591(4) Å); thus, only one out of four cyano groups exerts a bridging function. Recently, such type of coordination has been observed in the molecular structure of Cu(*dien*)(*mea*)$Ni(CN)_4 \cdot 2H_2O$, but with stronger coordination of the tetracyanonickellate anion represented by a Cu–N bond length of 2.474(4) Å and a C≡N–Cu angle of 143.6(3)° [23]. The tetranuclear unit of the title compound, except the atoms of the *tn* ligands, is almost planar; the largest deviation from the mean plane through the unit is 0.226(4) Å (N23).

Cu1 and Cu2 are located in different coordination polyhedra. Cu1 is clearly penta coordinated. The value of the parameter τ (18.9) [25] discloses a square-pyramidal shape of the coordination polyhedron. The basal plane is occupied by two N-bonded chelate *tn* molecules with an average Cu–N distance of 2.02(1) Å. Almost the same values for the Cu–N bonds have been observed in $Cu(tn)_2SO_4 \cdot H_2O$ [26]. The N11 atom from the bridging cyano group is placed in the apical position at a

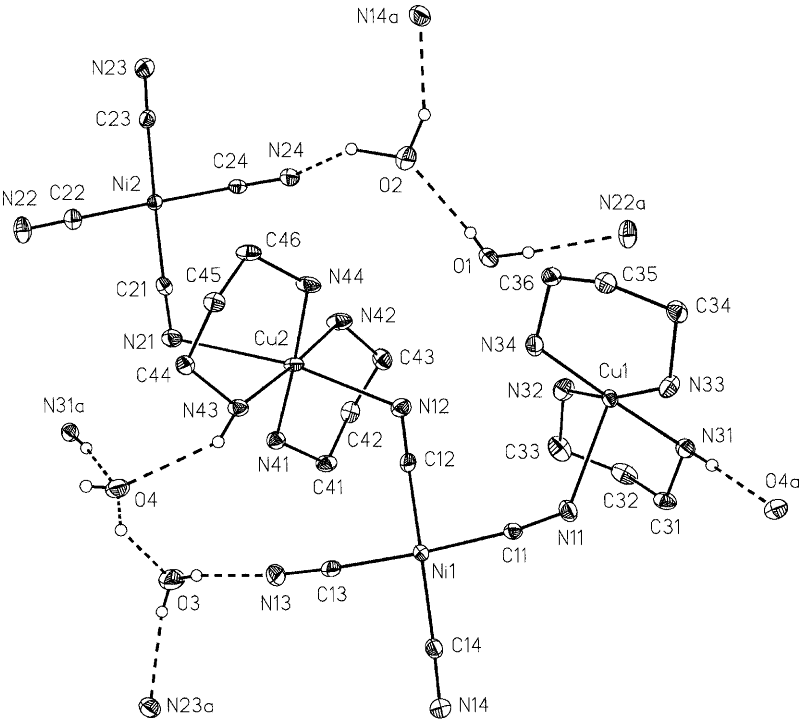

Fig. 1. ORTEP [33] view of the tetranuclear molecule of $[Cu(tn)_2Ni(CN)_4]_2 \cdot 4H_2O$; hydrogen bonds are represented by dashed lines; the thermal ellipsoids are drawn at 40% probability level

larger distance of 2.444(4), Å, exerting a sufficiently strong interaction to displace the copper atom by 0.122(4) Å toward the apical ligand from the mean plane formed by four N donor atoms.

The coordination polyhedron of Cu2 can be described as an unsymmetrically deformed octahedron (4+1+1 form). Copper coordination in the 4+1+1 form is not uncommon and has already been observed in *e.g.* $[Cu_3(bep)_2(\mu\text{-}N_3)_6]$ (*bep* = 2-benzoylpyridine; longer axial bond: 2.627(9)Å) [27]. In the Cu2 polyhedron, the equatorial positions are occupied by four nitrogen atoms of two chelate *tn* molecules with Cu–N distances in the range of 2.009(3)–2.047(3) Å. The shorter axial Cu2–N12 bond amounts to 2.458(3) Å, whereas the second axial donor atom N21 is positioned at a distance of 2.828(4) Å. The Cu2 atom is displaced from the mean equatorial plane by 0.061(1) Å toward the closer axial ligand (N12). At the same time, both Cu2–N≡C angles exhibit values close to 120°: 122.1(3) and 115.3(3)°. These are among the lowest values found in cyanocomplexes. The observations suggest that the distance of 2.828(4) Å (Cu–N21) corresponds only to a weak bonding interaction and probably, as suggested by the low angle value, this interaction can be of partial ionic character. The Cu-*tn* metallocycles in both coordination polyhedra adopt a chair conformation like in $Cu(tn)Ni(CN)_4$. Bond distances and angles within these metallocycles exhibit usual values [26, 28].

There are four crystallographically different solvate water molecules in the structure forming two pairs (O1/O2 and O3/O4). Within these pairs, the water molecules are fixed by strong hydrogen bonds (Fig. 1, Table 4). O1 and O2 connect three neighbouring tetracyanonickellate anions: Ni2, Ni2a (symmetry code: x, $1+y$, z) and Ni1a ($x+1/2$, $1-y$, $z-1/2$) *via* O–H$\cdots$N($\equiv$C) contacts. Moreover, they participate in weaker N–H$\cdots$O interactions. O3 is involved in three hydrogen bonds. Two of them are of the O–H$\cdots$N($\equiv$C) type and connect the Ni2 and Ni1c ($x+1/2$, $-y$, $z-1/2$) tetracyanonickellate anions. In the third one (O3$\cdots$H–O4), O3 acts as an acceptor. O4 oxygen atom is also involved in bridges of the N–H$\cdots$O type with the neighbouring cations Cu2c ($x+1/2$, $-y$, $z-1/2$) and Cu1a ($x+1/2$, $1-y$, $z-1/2$), respectively. Summing up, all tetranuclear units are linked by hydrogen bonds to form infinite planes which are further connected in the third dimension through two further weak interactions of the N–H$\cdots$N($\equiv$C) type (Table 4). There is another short contact of 2.858(4) Å between O4 and O1d from neighbouring planes ($d: x$, $1/2-y$, $z-1/2$), but the angle at H42 (103(2)°) is unfavourable for an O4–H42$\cdots$O1d hydrogen bond.

Finally, there are three other contacts of the N–H$\cdots$N($\equiv$C) type including N12 and N21 atoms from bridging cyano groups. All are located in the same above mentioned plane; two of them are intramolecular, one is intermolecular (Table 4). Usually, the X–H$\cdots$N bonds ($X=$ O, N) to the nitrogen atom of the bridging cyano group are not considered as hydrogen bonds because the free electron pair of the nitrogen atom is used for coordination; they can be considered as interactions of pure electrostatic character.

As *CTNCH* dehydrates rapidly, only the characteristic features of its IR spectrum will be discussed and compared with the spectrum of *CTNC*. The presence of the water molecules in the structure of *CTNCH* is represented by a medium absorption band arising from the ν(OH) vibration at 3430 cm^{-1}. Its broad shape and position (shift to lower wavenumbers) is in line with the participation of water molecules in hydrogen bonds. This absorption band along with those at 1640wsh (δ(OH$_2$)), 896m, and 690m (ρ(H$_2$O)) cm^{-1} are missing in the spectrum of the dehydrated compound *CTNC*.

Two absorption bands observed in the hydrate at 2136ssh and 2112vs cm^{-1} due to ν(CN) stretching vibrations of the cyano groups are very characteristic. The first one can be assigned to the stretching vibrations of the bridging cyano groups, the second to the stretching vibrations of the terminal cyano groups; their relative intensities qualitatively correspond to the presence of 3 bridging and 5 terminal cyano groups in the structure. The anhydrous sample exhibits in this region only one peak at 2112 cm^{-1}. This low value usually characterizes terminal bonding of the cyano groups. The IR spectrum of the similar *CENC* compound [22] displays only one absorption band at 2120 cm^{-1}, too, despite the presence of two bridging cyano groups in the structure: two *trans* positioned cyano groups are clearly terminal and involved in hydrogen bonding, whereas the remaining two are bridging with longer Cu–N distances of 2.534(5) Å (twice). These observations along with the known crystal structure of the hydrate suggest that the presence of the water molecules stabilizes the tetranuclear molecule in the present form in the structure of the hydrate, and that the anhydrous *CTNC* compound may exhibit a similar structure to that found for *CENC* with terminal as well as weakly bonded bridging cyano groups.

The coordinated *tn* ligands manifest themselves by a large number of absorption bands. These are at almost the same positions in the hydrate as well as

Table 1. Selected absorption bands (cm^{-1}) in the IR spectra of *CTNCH* and *CTNC*

	CTNCH	*CTNC*
ν(OH)	3430m	
ν(NH)	3328vs	3328vs
	3290ssh	
	3264vs	3264vs
	3230ssh	
	3140msh	3140wsh
$\nu(C{\equiv}N)$	2136ssh	
	2112vs	2112vs
$\delta(OH_2)$	1640wsh	
$\delta(NH_2)$	1588s	1588s
$\rho(H_2O)$	896m	
	690wsh	
$\rho(NH_2)$	656m	656m
δ(chelate ring)	488m	488m
δ(NiCN)	416s	412s

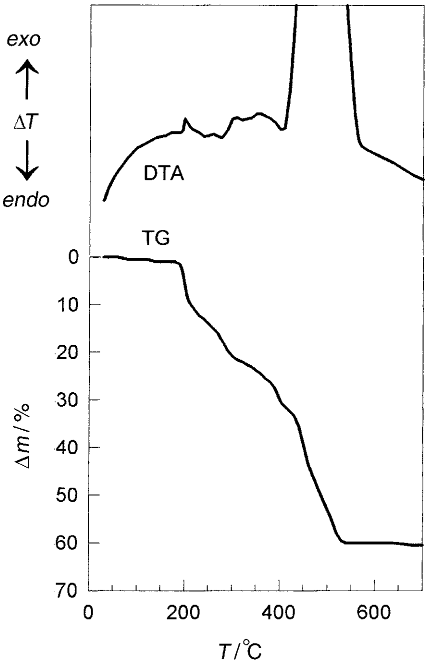

Fig. 2. Thermal curves for *CTNC*

in the anhydrous compound, indicating chelate bonding of the *tn* ligand in *CTNC*. Bridging coordination of the *tn* ligands was found in $Cd(tn)_2Ni(CN)_4$ [29]. The relevant data are collected in Table 1, and their assignment was performed using literature data on similar compounds [30–31].

As can be seen from Fig. 2, the anhydrous compound is stable till 180°C. At this temperature a multistage decomposition begins with an exothermic process

(DTA_{max} at 200°C). At this temperature a colour change from blue to brown was observed under the microscope of the heating block. The further decomposition is a complicated process as shown by the successive appearance of two weak endothermic and two weak exothermic peaks on the DTA curve. On the TG curve, a three-step process can be seen in this temperature region (weight losses; 12.5, 8.5, and 11%) which may correspond to decomposition of the *tn* ligands. Strong exothermic decomposition accompanied with a weight loss of 28% was observed within the temperature range of 420–520°C. This can be attributed to the decomposition of the cyano groups with simultaneous formation of oxides. The final product of the thermal decomposition (observed weight loss 60%) consists of a mixture of CuO (tenorite) and NiO (calculated 58.8%) as was shown by its powder X-ray diffractogram recorded with CuK_α radiation. The mean features of this thermal decomposition process (dehydration, deamination, decomposition of cyano groups, final formation of oxides) are the same as were found in similar tetracyanonickellates with diamines [32].

Experimental

Preparation

Copper sulfate pentahydrate (*p.a.*) was purchased from Lachema Brno (Czech Republic), *tn* (>99%) from Aldrich, and $K_2[Ni(CN)_4] \cdot H_2O$ was prepared from nickel sulfate heptahydrate and KCN (both *p.a.*, Lachema Brno) according to Ref. [17]. To the violet solution formed by mixing 20 cm^3 of a 0.1 *M* solution of $CuSO_4 \cdot 5H_2O$ (2 mmol) and 0.498 cm^3 of *tn* (6 mmol), 20 cm^3 of a 0.1 *M* solution of $K_2[Ni(CN)_4] \cdot H_2O$ (2 mmol) were added. The formed solution was filtered and left aside for crystallization. The first crystals appeared next day. The large (up to 2 mm) violet crystals of *CTNCH* were filtered off after a week. These crystals were unstable on air due to rapid dehydration (within one hour), yielding the blue anhydrous *CTNC*. Found: C 32.53, H 5.37, N 29.75%; calcd. for $C_{10}H_{20}CuN_8Ni$ ($M_r = 374.56$): C 32.07, H 5.38, N 29.91%; yield: 55%.

Analytical methods

Elemental analyses were performed with a Carlo Erba EA 1108 instrument. IR spectra were recorded on a Specord M80 (Carl Zeiss Jena) IR spectrometer in the region from 4000 to 200 cm^{-1} (KBr pellets). The IR spectrum of a few *CTNCH* crystals was measured immediately after isolating them from the mother liquor in order to prevent dehydration. For thermal analyses, a Derivatograph OD-102 device (MOM Budapest) was used. TG, DTG, and DTA curves were recorded under the following experimental conditions: TG = 100 mg, DTG = 1/5, DTA = 1/5, air, ceramic crucibles, heating rate 10°/min, $t_{max} = 1000$°C.

Crystallography

The X-ray study of *CTNCH* was performed at 150 K with a single crystal placed in a capillary in the presence of the mother liquor. For data collection a CAD4 (Enraf-Nonius) diffractometer was used with graphite-monochromatized MoK_α radiation ($\lambda = 0.7108$ Å). Crystal data: monoclinic, *Cc*, $a = 15.251(5)$, $b = 13.002(5)$, $c = 18.282(7)$ Å, $\beta = 107.73(3)°$, $V = 3453(2)$ $Å^3$, $Z = 4$, $D_c = 1.580$ Mg/m^3, 5183 independent reflections, 4792 observed reflections, 422 parameters used for refinement. For the sake of comparison, we give also the cell parameters measured on the same crystal at 295 K: $a = 15.461(3)$, $b = 13.080(4)$, $c = 18.355(14)$ Å, $\beta = 107.74(5)°$.

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for *CTNCH*; U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U_{eq}
Cu1	8631(1)	7655(1)	3437(1)	20(1)
Cu2	8931(1)	2673(1)	3299(1)	22(1)
N31	8960(2)	8763(2)	4263(2)	26(1)
C31	9132(2)	8424(3)	5067(2)	30(1)
C32	9954(3)	7704(4)	5320(2)	38(1)
C33	9823(3)	6684(3)	4917(2)	38(1)
N32	9714(2)	6806(3)	4075(2)	32(1)
N33	7772(2)	8623(2)	2697(2)	28(1)
C34	7908(3)	8742(3)	1923(2)	29(1)
C35	7707(2)	7750(3)	1480(2)	26(1)
C36	8360(2)	6883(3)	1825(2)	26(1)
N34	8310(2)	6590(2)	2597(2)	28(1)
N41	9107(2)	2189(2)	4400(2)	26(1)
C41	9616(3)	2838(3)	5051(2)	29(1)
C42	10588(3)	3063(3)	5034(2)	29(1)
C43	10651(3)	3672(3)	4356(2)	31(1)
N42	10268(2)	3110(3)	3623(2)	34(1)
N43	7628(2)	2121(2)	2965(2)	24(1)
C44	7338(2)	1478(3)	2264(2)	26(1)
C45	7394(2)	2028(3)	1558(2)	25(1)
C46	8364(2)	2327(3)	1585(2)	28(1)
N44	8761(2)	3083(3)	2205(2)	31(1)
Ni1	7079(1)	4904(1)	4308(1)	19(1)
C13	6994(2)	3500(3)	4485(2)	26(1)
N13	6963(3)	2627(3)	4574(2)	37(1)
C12	7933(2)	4612(2)	3805(2)	23(1)
N12	8483(2)	4439(2)	3506(2)	29(1)
C11	7256(2)	6295(3)	4127(2)	21(1)
N11	7422(2)	7113(2)	3976(2)	29(1)
C14	6273(2)	5175(3)	4884(2)	24(1)
N14	5782(2)	5315(3)	5243(2)	36(1)
Ni2	10696(1)	84(1)	2395(1)	19(1)
N21	9374(2)	563(3)	3286(2)	29(1)
C21	9883(2)	360(3)	2955(2)	23(1)
C22	10590(2)	−1322(3)	2552(2)	25(1)
N22	10510(2)	−2194(3)	2642(2)	36(1)
C23	11487(2)	−150(3)	1814(2)	24(1)
N23	11979(3)	−262(3)	1454(2)	36(1)
C24	10763(2)	1496(3)	2234(2)	21(1)
N24	10801(2)	2369(3)	2141(2)	29(1)
O1	10348(2)	5613(2)	2844(2)	37(1)
O2	10302(3)	4410(3)	1620(3)	67(1)
O3	12619(3)	−682(3)	197(2)	53(1)
O4	12209(2)	−176(2)	−1281(2)	39(1)

Table 3. Selected bond lengths (Å) and angles (°) for *CTNCH*

Cu1–N33	2.013(3)	Cu2–N44	2.009(3)
Cu1–N34	2.014(3)	Cu2–N42	2.023(3)
Cu1–N31	2.036(3)	Cu2–N43	2.024(3)
Cu1–N32	2.033(3)	Cu2–N41	2.047(3)
Cu1–N11	2.444(4)	Cu2–N12	2.458(3)
		Cu2–N21	2.828(3)
Ni1–C12	1.849(4)	Ni2–C23	1.859(4)
Ni1–C13	1.865(4)	Ni2–C22	1.865(4)
Ni1–C11	1.873(3)	Ni2–C24	1.867(3)
Ni1–C14	1.879(4)	Ni2–C21	1.867(4)
N31–Cu1–N32	89.2(1)	N42–Cu2–N41	88.9(1)
N33–Cu1–N34	87.7(1)	N44–Cu2–N43	88.6(1)
N33–Cu1–N11	91.9(1)	N21–Cu2–N12	170.5(1)
N34–Cu1–N11	94.1(1)	C11–N11–Cu1	127.9(3)
N31–Cu1–N11	87.2(1)	C12–N12–Cu2	122.1(3)
N32–Cu1–N11	101.1(1)	C21–N21–Cu2	115.3(3)
C11–Ni1–C14	94.1(2)	C23–Ni2–C24	89.7(2)
C12–Ni1–C13	89.0(2)	C22–Ni2–C21	90.0(2)
C12–Ni1–C11	87.1(2)	C24–Ni2–C21	88.6(2)
C13–Ni1–C14	89.7(2)	C23–Ni2–C22	91.7(2)

Structure solution was accomplished by the SHELXS-86 program [18]; for the refinement, the program SHELXL-93 was used [19]. Hydrogen atoms of the *tn* ligands were put into calculated positions and refined along with the isotropic thermal parameters of the parent carbon and nitrogen atoms. The water hydrogen atoms were taken from difference maps and refined as above. Due to the small dimensions of the single crystal used for data collection no absorption correction was applied. $R = 3.21\%$, and $wR = 8.58\%$, $S = 1.009$, $\Delta\rho = (-0.805\text{–}1.294\,\mathrm{e\AA^{-3}})$. For geometric calculations the program PARST was used [20]. The fractional coordinates of atoms are given in Table 2, selected bond distances and angles in Table 3, possible hydrogen bonds in Table 4.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication (CCDC 146457). Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

Conclusions

Using $\mathrm{Cu}(tn)_2^{2+}$ cations as bricks and $\mathrm{Ni(CN)}_4^{2-}$ anions as mortar, the new tetranuclear molecular compound *CTNCH* was prepared. It was characterized, and its structure was solved. The obtained results show that the replacement of *en* with the larger *tn* ligand in the similar synthetic procedure did not lead to the desired 1D product analogous to *CENC* [12, 22]. We suggest that the shape and size of the respective cations, and so the effectiveness of space filling, may play an important role in this context. The study of magnetic and thermodynamic properties of the anhydrous compound *CTNC* is planned.

Table 4. Selected (shorter than 3.15 Å) possible hydrogen bonds in *CTNCH* (Å, °); the full list has been deposited (cf. Experimental)

D–H	*D*···*A*	H···*A*	*D*–H···*A*
N32–H32C	N32···O1	H32C···O1	N32–H32C···O1
0.88(3)	3.119(5)	2.52(2)	126(1)
O1–H11	O1···O2	H11···O2	O1–H11···O2
0.73(3)	2.713(6)	2.01(3)	160(2)
O2–H22	O2···N24	H22···N24	O2–H22···N24
1.20(5)	2.844(5)	1.77(4)	146.3(5)
O3–H32	O3···N23	H32···N23	O3–H32···N23
0.73(3)	2.810(6)	2.09(3)	171(1)
O4–H41	O4···O3	H41···O3	O4–H41···O3
0.91(4)	2.664(5)	1.89(4)	142.3(6)
N31–H31C	N31···N21^{a}	H31C···N21^{a}	N31–H31C···N21^{a}
0.8(3)	3.122(5)	2.61(1)	124(1)
O1–H12	O1···N22^{a}	H12···N22^{a}	O1–H12···N22^{a}
0.82(4)	2.896(5)	2.08(4)	173(1)
N33–H33D	N33···O4^{b}	H33D···O4^{b}	H33–H33D···O4^{b}
0.76(3)	3.046(5)	2.41(2)	141(1)
N31–H31D	N31···O4^{b}	H31D···O4^{b}	N31–H31D···O4^{b}
0.80(2)	3.143(4)	2.35(2)	170(1)
N43–H43C	N43···O4^{c}	H43C···O4^{c}	N43–H43C···O4^{c}
0.83(2)	3.041(5)	2.32(2)	146(2)
O2–H21	O2···N14^{d}	H21···N14^{d}	O2–H21···N14^{d}
1.04(4)	2.850(7)	1.94(4)	144(2)
O3–H31	O3···N13^{e}	H31···N13^{e}	O3–H31···N13^{e}
0.88(3)	2.830(5)	1.98(3)	162(2)

Superscripts denote equivalent positions; ^{a} $x, y+1, z$; ^{b} $x-1/2, 1-y, z+1/2$; ^{c} $x-1/2, -y, z+1/2$; ^{d} $x+1/2, 1-y, z-1/2$; ^{e} $x+1/2, -y, z-1/2$

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