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Two Polymorphs of Cu(*tn*)Ni(CN)$_4$ Containing Tetracyanonickellate Anions with Triple Bridging Function: Preparation and Crystallographic Characterization

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Summary. Preparation and crystal structures of two polymorphs of Cu(*tn*)Ni(CN)$_4$ (*tn* = 1,3-diaminopropane) are described. The blue polymorph is orthorhombic (space group: Pbca, $Z = 4$, cell dimensions: $a = 9.466(4)$, $b = 12.268(12)$, $c = 19.097(10)$ Å), the violet one monoclinic (space group: I2/c, $Z = 8$, cell parameters: $a = 16.815(16)$, $b = 9.606(3)$, $c = 21.252(20)$ Å, $\beta = 91.75(5)°$). In both polymorphs, a rare case of T-type bridging tetracyanonickellate anion is present. The copper atoms are pentacoordinated by one chelate bonded *tn* molecule and three N atoms from bridging cyano groups. The metallacycles prevail in chair conformation. The polymorphs differ in the dimensionality of the structure: the blue polymorph exhibits a 2D structure, the violet one a 3D arrangement.

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

Zwei Polymorphe von Cu(*tn*)Ni(CN)$_4$ mit Tetracyanonickelatanionen in dreifacher Brückenfunktion: Herstellung und kristallographische Charakterisierung

Zusammenfassung. Herstellung und Kristallstrukturen von zwei Polymorphen des Cu(*tn*)Ni(CN)$_4$ (*tn* = 1,3-Diaminopropan) werden beschrieden. Das blaue Polymorphe ist orthorombisch (Raumgruppe Pbca, $Z = 4$, Zelldimensionen: $a = 9.466(4)$, $b = 12.268(12)$, $c = 19.097(10)$ Å), das violette monoklin (Raumgruppe I2/c, $Z = 8$, Zellparameter: $a = 16.815(16)$, $b = 9.606(3)$, $c = 21.252(20)$ Å, $\beta = 91.72(5)°$). In beiden Fällen liegt der seltene Fall eines überbrückenden Tetracyanonickelatanions vom T-Typ vor. Die Kupferatome werden durch ein chelatisiertes *tn*-Molekül und drei Stickstoffatome der Cyanobrücken fünffach koordiniert. Die Metallacyclen liegen in der Sesselkonformation vor. Die Polymorphen unterscheiden sich voneinander in der Dimensionalität der Struktur: das blaue Polymorphe ist zweidimensional, das violette dreidimensional.

Introduction

The cyano groups in the tetracyanonickellate anion can act as terminal or bridging ligands. Crystal structures containing two or four bridging cyano groups have been

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known for a long time [1]. Only recently, first examples of structures in which one [2] or three bridging cyano groups [3] are present have been reported. The variability of bonding possibilities and the rigidity of the anion renders the tetracyanonickellate anion suitable as a building element (brick and mortar system [4]) in constructing desired types of structures in supramolecular chemistry, chemistry of host-guest systems [1], and low-dimensional magnetic systems [5].

In previous studies we have prepared and characterized tetracyanonickellates containing ammonia, 1,2-diaminoethane (*en*), and 2,2′-bipyridine as ligands bonded to the central atoms in the complex cations [6–8]; some of them behave as low-dimensional magnetic systems at very low temperatures [5, 9]. With the aim to prepare new low-dimensional solids we have extended our series of amine ligands by *tn* (1,3-diaminopropane). Here we report the preparation and crystal structures of two polymorphs of $\mathrm{Cu}(tn)\mathrm{Ni(CN)_4}$, both of them containing three bridging cyano groups in the tetracyanickellate anion.

Results and Discussion

Both polymorphs crystallize from the same solution as a mechanical mixture. Sometimes (in the case of an initial Cu(II):*tn* molar ratio of 1:2), small quantities of bigger violet crystals of $\mathrm{Cu}(tn)_2\mathrm{Ni(CN)_4 \cdot 2H_2O}$ separated. The structure of these crystals is presently under study. It is interesting to note that from the analogous system Cu(II)-*en*-$\mathrm{Ni(CN)_4^{2-}}$–$\mathrm{H_2O}$ only the compound $\mathrm{Cu}(en)_2\mathrm{Ni(CN)_4}$ was isolated [14], which may be a consequence of the high stability of the $\mathrm{Cu}(en)_2^{2+}$ cation.

In the structure of the blue polymorph, only one set of crystallographically independent copper and nickel atoms is present (Fig. 1). The copper atom is pentacoordinated with one chelate bonded *tn* molecule and three N-bonded bridging cyano groups. The calculated value of $\tau = 46.1$ on the basis of the interbond angles [15] (Table 1) discloses an intermediate coordination type between the trigonal bipyramidal (ideal value: $\tau = 100$) and square pyramidal situation (ideal value: $\tau = 0$). The individual Cu–N bond distances are normal [16]; four of them exhibit almost the same distances within a range of 2.00–2.03 Å, the fifth distance (2.19 Å) to the donor atom in the apical position is somewhat longer (Table 2). The metallacycle involving chelate *tn* ligand exhibits a chair conformation (Fig. 1). The interatomic distances and angles within the chelate ring are normal [17]. The nickel atom is coordinated by four cyano groups in square form with minor deviations of the angles from ideal values. The outstanding feature is that three of four cyano groups are of bridging character. To our knowledge, such T-type bridging has been found only recently in the structure of $[\mathrm{(DMF)_4EuNi(CN)_4}]_\infty$ [3]. The bond distances in the anion are normal [1].

As the building element of the polymeric structure, zigzag chains of the composition $[\text{–Ni–Cl–Nl–Cu–N3–C3–}]_\infty$ which propagate along the *y* axis can be assumed (Fig. 1). The remaining bridging cyano groups (–C2–N2–) link the neighbour chains to double layers giving rise to a 2D structure (Fig. 2). The terminal cyano groups (–C4–N4–) are alternatively directed to the both outer sides of the layers. Due to its lone electron pair, the N4 atom is a candidate for the formation of N···H–N type H-bonds with the *tn* amine groups from the neighbour layers. In this case, literature data indicate for N···N distances in the range of

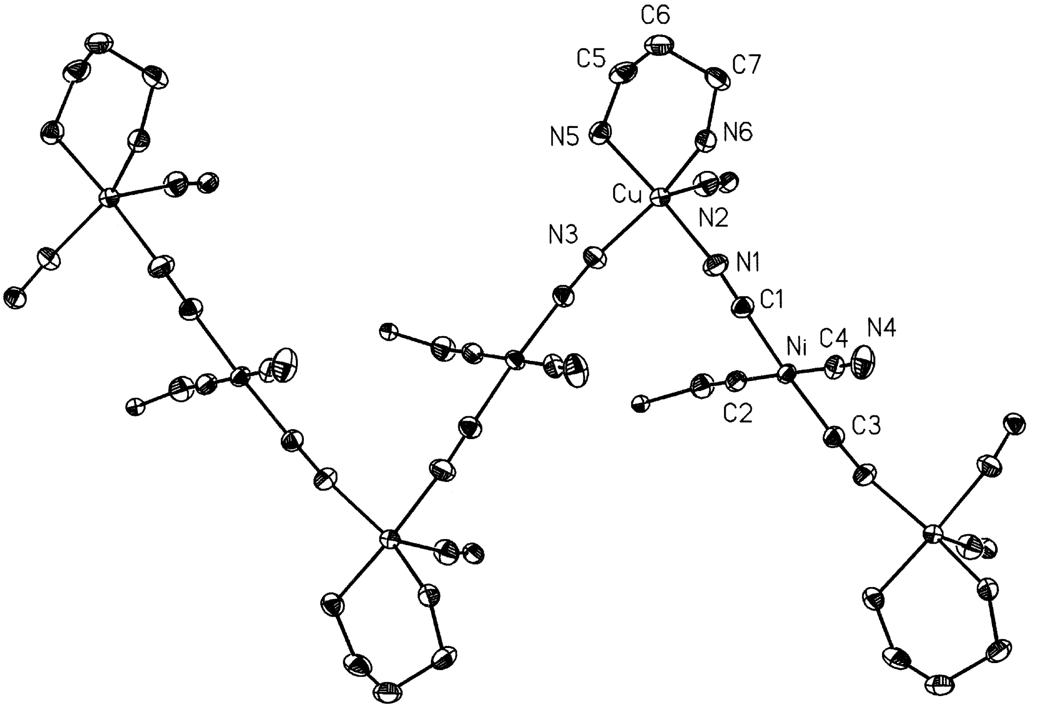

Fig. 1. ZORTEP [22] view of the chain-like fragment in the structure of the blue polymorph displaying the terminal character of one cyano group in the tetracyanonickellate anion; only the atoms of the asymmetric part are labelled; the thermal ellipsoides are drawn at a 40% probability level

2.94–3.35 Å [18]. As can be seen from Table 3a, N4 is involved in two H-bonds, thus contributing to the stability of the whole structure; the third interaction, involving N6 and H6A, can be considered only as a non-bonding contact. All other N5/N6···N distances (except distances within the same coordination polyhedron) are longer than 3.6 Å.

In the structure of the violet polymorph, two crystallographically independent copper and two crystallographically independent nickel atoms are present (Fig. 3). Both copper atoms exhibit the same type of coordination as was found in the blue polymorph. The chair conformation of metallacycles involving the *tn* ligand and the copper central atoms are preserved. The calculated τ values in the respective copper coordination spheres are 19.7 (Cu1) and 8.0 (Cu2), disclosing nearly square pyramidal coordination [15]. The respective copper atoms Cu1 and Cu2 are displaced from the mean plane formed by the nitrogen atoms in the basal plane towards the apical ligand by 0.264(2) Å (apical donor atom N2) and 0.332(3) Å (N6), respectively.

The Cu1–N distances are similar to those found in the blue polymorph, whereas the Cu2–N distances display some deviations: the apical bond Cu2–N6 (2.47 Å) is longer, and the basal Cu2–N bonds cover a larger interval (1.96–2.05 Å). Here, the fact that the Cu2 atom along with the *tn* chelate ring is disordered by the two-fold axis must be taken into account. The obtained results do not allow to decide if this

Table 1. Fractional atomic coordinates and equivalent thermal parameters
a) Blue polymorph

Atom	x	y	z	U_{eq}
Cu	0.15476(3)	0.18695(2)	0.13579(2)	0.0256(1)
Ni	−0.26794(4)	0.41868(3)	0.13940(2)	0.0259(1)
N1	−0.0102(2)	0.2827(2)	0.1114(1)	0.0398(4)
N2	0.2016(2)	0.2917(2)	0.2257(1)	0.0414(5)
N3	0.0140(2)	0.0701(2)	0.1642(1)	0.0372(4)
N4	−0.2424(3)	0.5109(2)	−0.0065(1)	0.0457(5)
N5	0.3123(2)	0.0811(2)	0.1558(1)	0.0347(4)
N6	0.2720(2)	0.2549(2)	0.0586(1)	0.0310(4)
C1	−0.1094(2)	0.3336(2)	0.1201(1)	0.0318(4)
C2	−0.2862(2)	0.3452(2)	0.2249(1)	0.0322(4)
C3	−0.4211(2)	0.5105(2)	0.1573(1)	0.0301(4)
C4	−0.2533(2)	0.4791(2)	0.0496(1)	0.0316(4)
C5	0.4580(2)	0.1254(2)	0.1613(1)	0.0427(6)
C6	0.5045(2)	0.1800(2)	0.0943(2)	0.0426(5)
C7	0.4207(3)	0.2813(2)	0.0759(2)	0.0424(6)

b) Violet polymorph

Atom	x	y	z	U_{eq}
Cu1	0.51962(5)	−0.1450(1)	0.34156(4)	0.0279(2)
Cu2	0.2600(2)	0.6742(2)	0.51387(9)	0.0270(5)
Ni1	0.43455(6)	0.3082(1)	0.42720(5)	0.0288(3)
Ni2	0.2500	−0.2500	0.2500	0.0314(4)
N1	0.5020(3)	0.0546(7)	0.3667(3)	0.040(1)
N2	0.5198(4)	−0.2185(7)	0.4405(3)	0.044(2)
N3	0.3967(5)	0.4260(9)	0.2990(3)	0.068(2)
N4	0.3291(5)	0.5289(7)	0.4797(4)	0.070(3)
N5	0.4051(3)	−0.1612(7)	0.3119(3)	0.038(1)
N6	0.1880(5)	−0.2561(12)	0.3810(4)	0.090(4)
N7	0.5344(3)	−0.3326(6)	0.3021(3)	0.039(1)
N8	0.6383(3)	−0.1109(7)	0.3374(3)	0.039(1)
N9	0.1712(4)	0.8130(7)	0.5248(3)	0.043(2)
C1	0.4826(4)	0.1550(8)	0.3901(3)	0.032(1)
C2	0.4633(4)	0.2479(7)	0.5087(3)	0.032(1)
C3	0.4101(4)	0.3791(8)	0.3472(3)	0.040(2)
C4	0.3722(5)	0.4472(8)	0.4606(4)	0.049(2)
C5	0.3464(4)	−0.1932(8)	0.2875(3)	0.037(2)
C6	0.2083(4)	−0.2551(10)	0.3313(3)	0.048(2)
C7	0.5998(5)	−0.4232(9)	0.3282(4)	0.047(2)
C8	0.6946(4)	−0.2250(9)	0.3571(4)	0.052(2)
C9	0.6799(4)	−0.3560(9)	0.3188(4)	0.053(2)
C10	0.1935(12)	0.9598(20)	0.5359(9)	0.049(4)
C11	0.2500	1.0213(12)	0.5000	0.063(4)
C12	0.3328(11)	0.9564(20)	0.4930(8)	0.047(4)

Table 2. Bond distances (Å) and angles (°) for Cu(*tn*)Ni(CN)$_4$ with e.s.d.s in parentheses

a) Blue polymorph

Cu–N1	2.009(2)	Cu–N2	2.191(2)
Cu–N3	2.031(2)	Cu–N5	2.014(2)
Cu–N6	2.025(2)	N5–C5	1.486(3)
C5–C6	1.510(4)	C6–C7	1.515(4)
N6–C7	1.481(3)		
Ni–C1	1.865(2)	Ni–C2	1.873(2)
Ni–C3	1.868(2)	Ni–C4	1.874(2)
C1–N1	1.139(3)	C2–N2	1.155(3)
C3–N3	1.151(3)	C4–N4	1.144(3)
N1–Cu–N2	89.75(9)	N1–Cu–N3	88.0(1)
N1–Cu–N5	175.31(9)	N1–Cu–N6	90.95(9)
N2–Cu–N3	109.74(9)	N2–Cu–N5	94.57(9)
N2–Cu–N6	102.60(9)	N3–Cu–N5	88.9(1)
N3–Cu–N6	147.64(8)	N5–Cu–N6	89.88(9)
C1–Ni–C2	88.7(1)	C1–Ni–C3	176.9(1)
C1–Ni–C4	89.9(1)	C2–Ni–C3	93.4(1)
C2–Ni–C4	174.40(9)	C3–Ni–C4	89.21(9)
Ni–C1–N1	176.7(2)	Ni–C2–N2	174.0(2)
Ni–C3–N3	175.6(2)	Ni–C4–N4	176.6(2)
Cu–N1–C1	158.0(2)	Cu–N2–C2	173.8(2)
Cu–N3–C3	156.8(2)	Cu–N5–C5	117.7(2)
N5–C5–C6	111.9(2)	C5–C6–C7	114.0(2)
N6–C7–C6	111.8(2)	Cu–N6–C7	116.6(2)

b) Violet polymorph

Cu1–N1	2.015(6)	Cu1–N2	2.217(6)
Cu1–N5	2.015(6)	Cu1–N7	2.006(6)
Cu1–N8	2.027(6)		
N7–C7	1.497(9)	N8–C8	1.499(9)
C7–C9	1.51(1)	C8–C9	1.52(1)
Cu2–N4	1.969(7)	Cu2–N4[a]	2.054(8)
Cu2–N9	2.020(6)	Cu2–N9[a]	1.962(7)
Cu2–N6[b]	2.47(1)		
N9–C1O	1.48(2)	N9–C12[a]	1.43(2)
C1O–C11	1.37(2)	C11–C12	1.54(2)
Ni1–C1	1.865(7)	Ni1–C2	1.877(7)
Ni1–C3	1.866(8)	Ni1–C4	1.853(8)
C1–N1	1.138(9)	C2–N2[c]	1.144(8)
C3–N3	1.135(9)	C4–N4	1.150(9)
Ni2–C5	1.866(7)	Ni2–C6	1.884(8)
N5–C5	1.143(9)	N6–C6	1.12(1)
N1–Cu1–N2	92.8(3)	N1–Cu1–N5	90.6(3)
N1–Cu1–N7	170.6(3)	N1–Cu1–N8	90.6(2)
N2–Cu1–N5	104.3(2)	N2–Cu1–N7	96.5(3)
N2–Cu1–N8	96.9(2)	N5–Cu1–N7	85.9(2)
N5–Cu1–N8	158.8(2)	N7–Cu1–N8	89.6(2)
N7–C7–C9	110.5(7)	N8–C8–C9	111.5(6)
C7–C9–C8	114.5(6)		

Table 2 (*continued*)

C1–N1–Cu1	165.7(9)	C2^{c}–N2–Cu1	165.1(6)
C5–N5–Cu1	165.3(6)	C7–N7–Cu1	117.8(4)
C8–N5–Cu1	119.0(5)		
N4–Cu2–N4^{a}	89.0(5)	N4–Cu2–N6^{b}	109.2(4)
N4–Cu2–N9	163.1(4)	N4–Cu2–N9^{a}	88.0(3)
N4^{a}–Cu2–N6^{b}	111.3(4)	N4^{a}–Cu2–N9	84.2(3)
N4^{a}–Cu2–N9^{a}	158.4(3)	N9–Cu2–N6^{b}	87.7(3)
N9–Cu2–N9^{a}	92.7(4)	N9^{a}–Cu2–N6^{b}	89.9(3)
C6–N6–Cu2^{d}	138.3(9)	C4–N4–Cu2	177.1(8)
Cu2–N9–C10	117.6(8)	N9–C10–C11	121(2)
C10–C11–C12	122(1)	C11–C12–N9^{a}	112(1)
C12–N9^{a}–Cu2	124.6(8)		
C1–Ni1–C2	92.5(3)	C1–Ni1–C3	89.3(3)
C4–Ni1–C2	90.1(3)	C4–Ni1–C3	88.6(4)
N1–C1–Ni1	171.0(6)	N2^{c}–C2–Ni1	176.2(7)
N3–C3–Ni1	177.7(8)	N4–C4–Ni1	175.4(9)
C5–Ni2–C6	87.6(3)		
N5–C5–Ni2	178.0(7)	N6–C6–Ni2	175.8(7)

Symmetry codes: $^{a}0.5-x, y, 1-z$; $^{b}0.5-x, y+1, 1-z$; $^{c}1-x, -y, 1-z$; $^{d}0.5-x, y-1, 1-z$

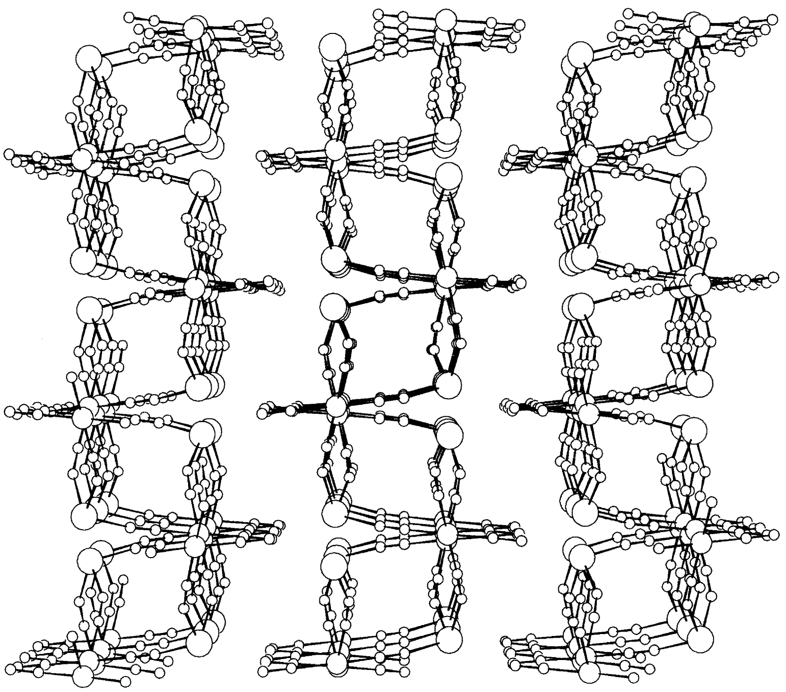

Fig. 2. MOLDRAW [23] packing diagram of the 2D structure of the blue polymorph (big balls = copper, medium balls = nickel, small balls = nitrogen and carbon); the chelate bonded diamine molecules are omitted for the sake of clarity

Table 3. Possible hydrogen bonds (Å)

a) Blue polymorph

D–H	*D*···*A*	H···*A*	*D*–H···*A*
N5–H5B	N5···N4^{a}	H5B···N4^{a}	N5–H5B···N4^{a}
0.97(3)	3.110(3)	2.25(3)	146(3)
N6–H6A	N6···N4^{a}	H6A···N4^{a}	N6–H6A···N4^{a}
0.85(3)	3.413(4)	2.76(1)	135(3)
N6–H6B	N6···N4^{b}	H6B···N4^{b}	N6–H6B···N4^{b}
0.78(3)	3.052(4)	2.34(3)	153(3)

Equivalent positions: $^{a}x+1/2,\ 1/2-y,\ -z$; $^{b}-x,\ 1-y,\ -z$

a) Violet polymorph

D–H	*D*···*A*	H···*A*	*D*–H···*A*
N7–H7A	N7···N3^{a}	H7A···N3^{a}	N7–H7A···N3^{a}
0.90	3.28(1)	2.42(1)	158.6(7)
N8–H8A	N8···N3^{b}	H8A···N3^{b}	N8–H8A···N3^{b}
0.90	2.962(9)	2.169(9)	146.4(7)
N9^{d}–H9D^{d}	N9^{d}···N6^{c}	H9D^{d}···N6^{c}	N9^{d}–H9D^{d}···N6^{c}
0.90	3.13(1)	2.49(1)	127.8(8)
N9–H9A	N9–N6^{c}	H9A···N6^{c}	N9–H9A···N6^{c}
0.90	3.15(1)	2.56(1)	123.3(8)

Equivalent positions: $^{a}x,\ y-1,\ z$; $^{b}1-x,\ y-1/2,\ 1/2-z$; $^{c}x,\ y+1,\ z$; $^{d}1/2-x,\ y,\ 1-z$

disorder reflects a statistical distribution of two different orientations of the square pyramid or if it is a consequence of a dynamic process.

Both nickel atoms exhibit slightly deformed square coordination. The Ni1 tetracyanonickellate anion clearly contains three bridging and one terminal cyano ligands. A somewhat different situation occurs in the case of the second anion (Ni2) due to the above mentioned disorder involving the Cu2 atom. In one disordered position (site occupancy: 0.5), the Cu–N(6) bonding distance is 2.47(1) Å, whereas in the second disordered position the calculated distance of 3.112(9) Å can be assumed as non-bonding. As a consequence, on the average three of four cyano groups are bridging ligands and one is a terminal ligand. The geometrical parameters in both anions are normal [1]; worth noting is the high bending (138.3(9)°) of the C6–N6–Cu2 angle, but similar values have already been found in other structures of tetracyanonickellates, *e.g.* in Cu(*en*)$_2$Ni(CN)$_4$ (123.1(5)°) [14].

Two Cu(1)(*tn*)$^{2+}$ cations and two Ni(1)(CN)$_4^{2-}$ anions form a centrosymmetric ring with the composition [-μ–NC–Ni(CN)(μ–CN)–μ–CN–Cu(*tn*)(–μ–NC)$_2$–]$_2$ (Fig. 3). A similar ring has been observed in the molecular tetrameric structure of [Cu(NH$_3$)$_3$Ni(CN)$_4$]$_4$ [19]. The formed rings are linked together in two different ways (Fig. 4): (*i*) by the second tetracyanonickellate anion (Ni2) forming a chain-like arrangement running alternatively in the directions [111] and [11–1] (body diagonals of the unit cell), and (*ii*) by the Cu2(*tn*)$^{2+}$ cations forming connections parallel to the [010] direction. Further linking comes into operation between the

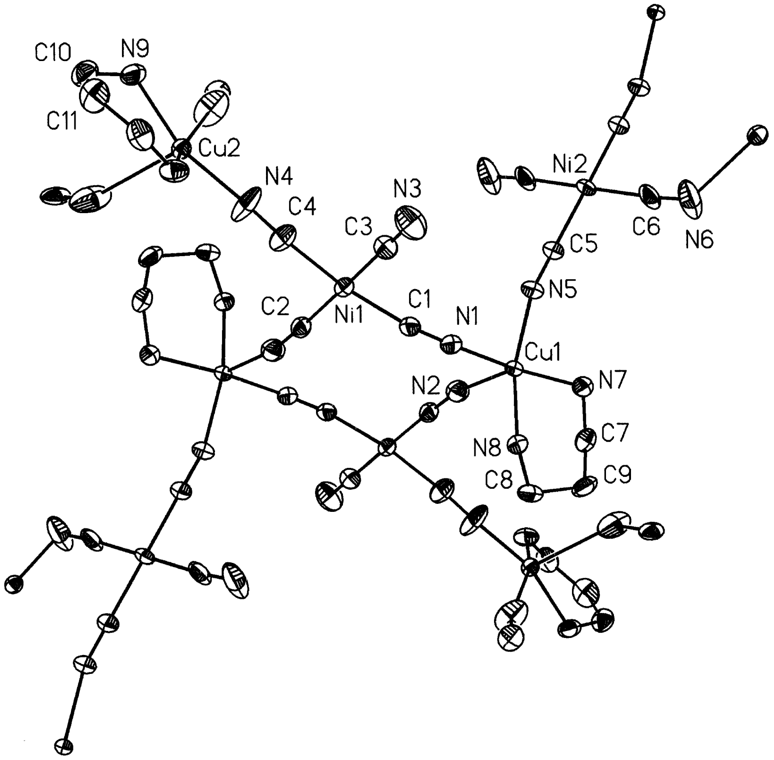

Fig. 3. ZORTEP [22] view of the ring shape fragment in the violet polymorph displaying coordination polyhedra of the central atoms; the Cu2 atom and the corresponding chelate ring are displayed in one of the disordered positions. Atoms of the asymmetric part are labelled, and thermal ellipsoides are drawn at a 40% probability level

anions and cations not forming the ring by N6–Cu2 coordination bonds. As a result, a 3D supramolecular framework is formed.

The potential energy of the structure may be lowered by H-bonds of the CN···H–N type between free terminal cyano group (N3 atom) with the amine groups (N7, N8) from *tn*. The observed N···N distances (Table 3b) are within the above given range for H-bonds. There exist two further interactions involving N6 atom with suitable N···N distances. These may lead only to very weak H-bonds as the corresponding N–H···N angles are close of 120° (Table 4b).

Conclusions

The results of the structure analysis have shown that two different supramolecular structures are formed for the same stoichiometric composition of Cu(*tn*)$Ni(CN)_4$. Cu(*tn*)$^{2+}$ cations and $Ni(CN)_4^{2-}$ anions are used as building elements, and both of them exhibit a threefold connectivity. The blue polymorph exhibits a 2D structure which is more dense than the 3D structure of the violet polymorph. The reason may be that in the 2D structure very compact layers are formed which are placed close together due to hydrogen bonds; on the other hand, in the 3D structure a lower

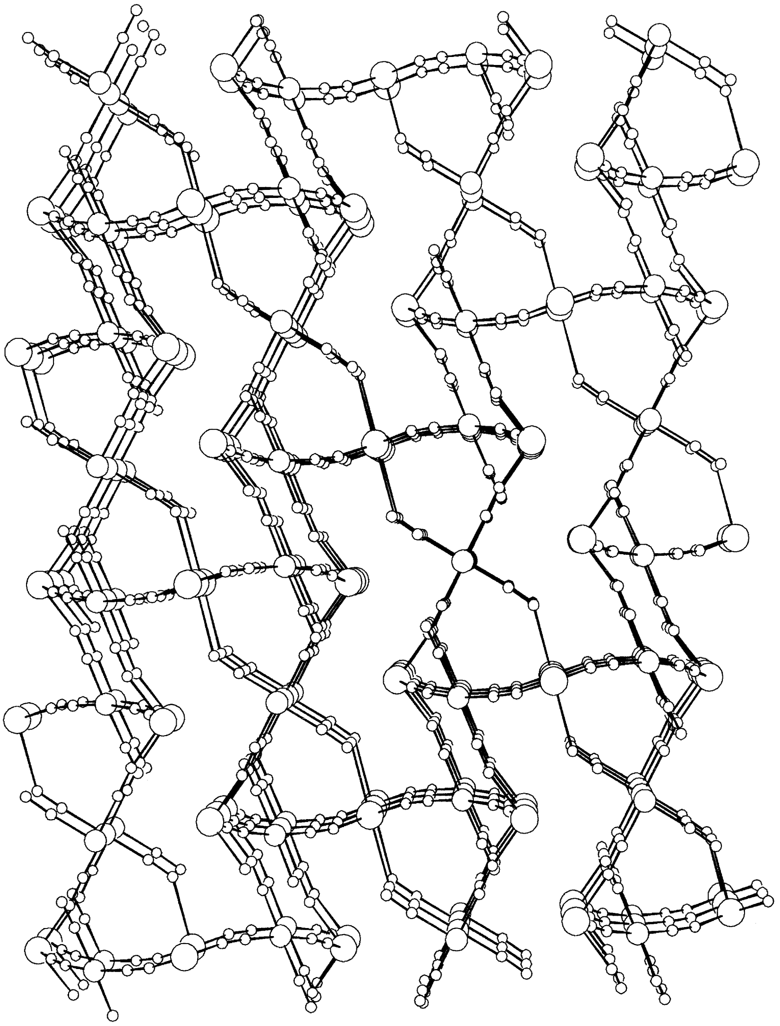

Fig. 4. MOLDRAW [23] packing view of the 3D structure of the violet polymorph displaying the linking modes of the ring-shape fragments (big balls = copper, medium balls = nickel, small balls = nitrogen and carbon); diamine chelate rings are omitted for clarity; both coordination possibilities of the Cu2 atoms by N6 are shown

efficiency of space filling can be deduced from the observed disorder around Cu2 and the Cu–N6 coordination bonds. We may only speculate about the reasons of the formation of two different structures, but the plasticity of the copper coordination sphere due to the *Jahn-Teller* effect may play some role.

2D and 3D structures are very common among tetracyanonickellates, and usually all four cyano groups are involved in formation of infinite planar or wave-shape deformed layers of the composition $[ML_2\text{–}(NC)_4\text{–}Ni]_\infty$. These can be present without direct chemical bonds, like in the *Hofmann*-type clathate $Cu(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ [20], or they are pillared by an appropriate bridging ligand, *e.g. tn* in Cd(*tn*)Ni(CN)$_4$ $\cdot$ 1/2(*m*–ClC$_6$H$_4$NH$_2$) [21] turning the structure to

3D. The structure types of the studied compounds are different and are rather distinct ones among the series of tetracyanonickellates.

The outstanding feature of both polymorphs is the presence of T-type bridging of the tetracyanonickellate anion. Literature data show that also onefold coordination of the tetracyanonickellate anion is possible by tuning the number of free coordination sites on the cationic central atom [2]. In our case, the preference of copper to pentacoordination and occupation of two coordination sites by *tn* lead to T-type coordination of the anion. The present results and data from the literature on the crystal structures of tetracyanonickellates indicate a strong tendency of the tetracyanonickellate anion of coordinate also *via* the nitrogen atoms of the cyano groups. We suggest that the number of coordinated cyano groups may be controlled by the use of appropriate multi-N-donor ligands or by combination of ligands leaving the desired number of coordination sites on the cationic central atom free for N-end cyano coordination.

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 (p.a., Lachema Brno) following the procedure given in Ref. [10]. $20\,cm^3$ of a $0.1\,M$ solution of $CuSO_4 \cdot 5H_2O$ (2 mmol) were mixed with $20\,cm^3$ of a $0.1\,M$ solution of $K_2[Ni(CN)_4] \cdot H_2O$ (2 mmol). The formed blue-green precipitate was added to a solution $0.332\,cm^3$ of *tn* (4 mmol) in $20\,cm^3$ H_2O. A violet solution formed from which almost instantaneously a microcrystalline precipitate separated. This was filtered off, and the solution was left aside by crystallization at 5°C. Within some days, a mixture of small blue and violet crystals suitable for single crystal X-ray diffraction were obtained. These were filtered off, washed with small portions of water and ethanol, and dried on air (yield: 10%). The mixture of crystals gave satisfactory results of CHN analysis for the composition $C_7H_{10}CuN_6Ni$ ($M = 300.45$; calcd.: C 27.97, H 3.35, N 27.97; found C 28.09, H 3.50, N 27.59).

Crystallography

Experimental parameters for the two compounds under study are presented in Table 4. For data collection a CAD4 (Enraf-Nonius) diffractometer was used (CuKα radiation, $\lambda = 1.54178$ Å). Structure solution was performed by the SHELXS-86 program [11]; for structure refinement, the program SHELXL-93 was used [12]. In the blue polymorph, the positions of the hydrogen atoms were refined along with common isotropic thermal parameters for H(C) and H(N) type atoms. The refinement of the violet polymorph showed that the Cu2 atom is disordered (Cu2···Cu2 distance: 0.670(3) Å). A similar disorder was detected during anisotropic refinement in the case of C10 (the refined site occupation factors for these two disordered positions were the same within experiment error: 0.45(5) for C10 and 0.55(5) for C12^i (*i*: 1/2-*x*, *y*, 1-*z*; the notation of the atoms corresponds Table 2). Therefore, 4 possible arrangements of the *tn* chelate ring occur. Best interbonding angles within the ring were found for the model defined by atoms Cu2–N9–C10–C11–C12–N9^i (*i*: 1/2-*x*, *y*, 1-*z*). The hydrogen atoms in the disordered chelate ring were placed in the calculated positions and then refined as a rigid methylene type groups along with their common group (H(C) and H(N)) isotropic thermal parameters as for other hydrogen atoms. The positional parameters of other hydrogen atoms were fixed with the positions of the parent atoms. For geometric calculations, the program PARST was used [13].

Table 4. Experimental crystallographic data

	Cu(*tn*)Ni(CN)$_4$ (blue)	Cu(*tn*)Ni(CN)$_4$ (violet)
Colour	blue	violet
Crystal system	orthorhombic	monoclinic
Space group	Pbca	I2/c
Cell dimensions		
a (Å)	9.466(4)	16.815(16)
b (Å)	12.268(12)	9.606(3)
c (Å)	19.097(10)	21.252(20)
β (°)	90	91.72(5)
V (Å)^3	2218(3)	3431(5)
Z	4	8
D_o (g · cm^{-3})	1.79	1.79
D_c (g · cm^{-3})	1.80	1.74
2θ range	$9 \leq 2\theta \leq 143$	$4 \leq 2\theta \leq 152$
hkl range	$0 \leq h \leq 11$	$-21 \leq h \leq 0$
	$0 \leq k \leq 15$	$0 \leq k \leq 12$
	$0 \leq l \leq 22$	$-26 \leq l \leq 26$
No. of reflections collected	4075	3844
unique	2131	3508
observed ($I_o \geq 2\sigma_I$)	1863	2380
No. of parameters	169	236
μ (mm^{-1})	4.29	4.16
R_1	0.0276	0.0642
wR_2	0.0716	0.1463
wR_2 (all)	0.0745	0.1696
w	$1/(\sigma^2(F_o^2)+(0.0463P)^2+0.5026P)$ $P=(F_o^2+2F_c^2)/3$	$1/(\sigma^2(F_o^2)+(0.0761P)^2+2.5458P)$ $P=(F_o^2+2F_c^2)/3$
S	1.118	1.034
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e · Å^{-3})	−0.4(1), 0.4 (1)	−0.9(1), 0.8(1)

The fractional coordinates of both polymorphs are given in Table 1, bond distances and angles in Table 2, and possible hydrogen bonds are displayed in Table 3.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 114098 (violet polymorph) and 114099 (blue polymorph), respectively. 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).

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