Interlayer Inclusion of Tetracyanonickelate Anion and Water Molecules: The Crystal and Molecular Structure of $[\text{-Zn(en)}_2\text{-}\mu\text{-}(NC)_2\text{-Ni-}\mu\text{-}(CN)_2\text{-Zn(en)-}]_n^{2n+}$ $\cdot n[\text{Ni(CN)}_4]^{2-}\cdot 3n\,H_2O$

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Abstract. The crystal structure of $[\text{Zn(en)}_2\text{-}(NC)_2\text{Ni(CN)}_2\text{-Zn(en)}][\text{Ni(CN)}_4]\cdot 3\,H_2O$ consists of infinite positively charged wave-shaped layers of composition $[\text{Zn(en)}_2\text{-}(NC)_2\text{Ni(CN)}_2\text{-Zn(en)}]_n^{2n+}$ with the $[\text{Ni(CN)}_4]^{2-}$ anions and water molecules included between them. Both Ni atoms exhibit square-planar coordination. The chelate bonded en (=ethylenediamine) and N-bonded cyano ligands around two independent zinc atoms form a deformed tetrahedron and a deformed octahedron, respectively. Yellow needles of the complex belong to the orthorhombic space group *Pbcm* with $a = 6.977(1)$, $b = 25.407(4)$, $c = 14.876(2)$Å, $Z = 4$, $D_m = 1.74(1)$ g cm^{-3} and $D_c = 1.739$ g cm^{-3}. The structure was refined to $R = 6.31\%$.

Key words. Crystal structure, disorder, ethylenediamine, inclusion complex, layered structure, tetracyanonickelate, twinning crystals, zinc.

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1. Introduction

The cyano group can act as a monodentate (Ni—C≡N) or bidentate (Ni—C≡N—M) ligand when bonded in the $[\text{Ni(CN)}_4]^{2-}$ anion. This causes great variability in the types of structures formed by tetracyanonickelates(II). These can be ionic, molecular, one-, two- or three-dimensional [1]. Ionic structures are formed if all four cyano groups are bonded as monodentate ligands, e.g. in $[\text{Zn(en)}_3][\text{Ni(CN)}_4]$ [2]. The bidentate character of two out of four of the cyano groups gives rise to molecular structures, e.g. $[\text{Cu(NH}_3)_3\text{Ni(CN)}_4]_4$ [3], or one-dimensional structures, e.g. $\text{Zn(en)}_2\text{Ni(CN)}_4$ [4]. Two- or three-dimensional structures occur in the tetracyanonickelates(II) with four bidentate cyano groups. To this group belong the Hofmann-type and analogous clathrates, e.g.

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$Cd(NH_3)_2Ni(CN)_4\cdot2\,C_6H_6$ (2-dimensional) [5] or $Cd(en)Ni(CN)_4\cdot2\,C_6H_6$ (3-dimensional) [6]. It is interesting to note that no structure with one or three bidentate cyano groups in the $[Ni(CN)_4]^{2-}$ anion has been solved to date, to our knowledge.

This work forms part of our study of the crystallochemistry, spectral and thermal properties of tetracyanonickelates(II) crystallizing from the systems M(II)−en or NH_3-$[Ni(CN)_4]^{2-}$−$H_2O(M(II)$ = Ni, Cu, Zn, Cd). This group of complexes is interesting from a crystallochemical point of view as the materials could be considered as model compounds for the host part of the Hofmann-type and analogous clathrates. In some cases they form inclusion compounds, e.g. $Cd(NH_3)_2Ni(CN)_4\cdot0.5\,H_2O$ [7].

Seven different complexes were prepared from the system Zn−en−$[Ni(CN)_4]^{2-}$−H_2O [8]. The title complex was isolated by using the molar ratio Zn : en = 1 : 2.5. A composition $Zn(en)_{1.5}Ni(CN)_4\cdot1.5\,H_2O$ was found from the results of elemental and thermal analyses, indicating that the correct formula must be doubled. The IR spectrum indicates the presence of terminal as well as bridging cyano groups and non-coordinated water molecules. These water molecules could be removed by heating, but this process is reversible [8]. The aim of this study has been to solve the crystal structure of the prepared complex, to explain its unusual composition and to compare it with the structures of similar complexes. The results obtained from the structure analysis may also be useful for explanation of the thermal properties of the studied complex.

2. Experimental

2.1. PREPARATION

The preparation of the complex **I** in the form of yellow twinning needles has been described previously [8].

2.2. STRUCTURE DETERMINATION

The crystals of **I** were first studied by using a Weissenberg camera (Cu$K\alpha$). The oscillation and Weissenberg photographs taken along the needle axis (a) indicated the presence of twinning. Further studies were made with a diffractometer. By studying different crystals it was found that different twinned crystals contain individuals in different ratios. The two individuals of the twinned crystal (indices 1 and 2 in the following equation) had a common axis **a** and the relation of the two individuals could be expressed by the matrix notation:

$$(\mathbf{a}_1\,\mathbf{b}_1\,\mathbf{c}_1) = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 0.156 & 1.688 \\ 0 & 0.578 & -.156 \end{bmatrix} \times \begin{bmatrix} \mathbf{a}_2 \\ \mathbf{b}_2 \\ \mathbf{c}_2 \end{bmatrix}$$

For the intensity measurements a twinned crystal with one dominating individual was selected with the aim of diminishing the influence of the overlapping of the reflections. The conditions for intensity measurements of the major twin individual are given in Table I. Moreover, about 50 strongest nonoverlapping reflections of the minor twin individual were measured under the same conditions as the major

Table I. Crystallographic data and experimental data

Formula	$C_{14}H_{30}N_{14}O_3Ni_2Zn_2$
Formula weight	690.64
Crystal system	orthorhombic
Space group	$Pbcm$ (No. 57)
Cell parameters, Å	$a = 6.977(1)$
	$b = 25.407(4)$
	$c = 14.876(2)$
V, Å^3	2637.0(8)
Z	4
D_m, g cm^{-3}	1.74(1)
D_c, g cm^{-3}	1.739
Crystal size	$0.2 \times 0.3 \times 0.6$ mm
Diffractometer	Hilger-Watts
$\mu(AgK_\alpha)$, mm^{-1}	3.1
Radiation	AgK_α, $\lambda = 0.5609$ Å
Monochromation	β-filter
Scan mode	$\theta/2\theta$
Measuring method	learned profile method [18]
2θ range, deg	3–44
hkl range	$0 \leqslant h \leqslant 9$, $-33 \leqslant k \leqslant 33$, $0 \leqslant l \leqslant 19$
Reflections collected/unique	6746/3422 ($R_{int} = 0.02$)
Observed reflections	2081 ($F_0 > 4\sigma(F_0)$)
Weighting scheme	$w = k/[\sigma^2(F_0) + 0.0009(F_0)^2]^{-1}$
	($k = 1.9697$)
$F(000)$	1408
$R/R_\omega/S$	6.31/7.45/1.91
$(\Delta/\sigma)_{max}$	0.07
$\Delta\rho$, e Å^{-3}	$\langle -0.64; 0.62 \rangle$

individual to determine the twinning ratio (5.6(3)%). Lp corrections and a correction for twinning were applied to the measured intensities. The precise unit cell parameters were obtained by refining the setting angles of 20 reflections from the range $7.08 \leqslant \theta \leqslant 13.469°$. The observed systematic absences ($0kl: k = 2n + 1$; $h0l: l = 2n + 1$) correspond to the space groups $Pbcm$ and $Pbc2_1$. The centrosymmetric group was selected and then confirmed by structure analysis. The refinement was also carried out in the noncentrosymmetric space group, but correlations between the 'centrosymmetric' parameters were observed.

The positions of the heavy atoms were found from the Patterson map. The remaining non-H atoms were located from the Fourier map. The structure was then subjected to full-matrix least squares refinement. All atoms were refined anisotropically but the disordered C(2) (and C2D) atom was refined isotropically. Owing to the observed disorder in the en and water molecules H atoms were not included in the refinement process.

For solving and refining of the structure the programme package SDS was used [9]. The last cycles of refinement were performed by using the programme SHELX'76 [10]. Geometrical analysis was performed using the programme PARST [11]. The figures were obtained using the ORTEP program [12]. The final atomic parameters along with the equivalent/isotropic thermal parameters are listed in

Table II.   Final fractional atomic coordinates and equivalent isotropic thermal parameters B_{eq} (esds in parentheses). $B_{eq} = \frac{8}{3}\pi^2 \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$

atom	x/a	y/b	z/c	$B_{eq}(\text{Å}^2)$	K^*
Zn(1)	0.0	0.0	0.0	2.77(3)	0.5
Zn(2)	0.3148(2)	0.25	0.5	2.92(3)	0.5
Ni(1)	0.0763(2)	0.14198(5)	0.25	2.17(3)	0.5
Ni(2)	0.5292(2)	0.10110(1)	0.25	2.75(3)	0.5
O(1)	0.3987(17)	−0.1275(4)	0.2310(12)	4.4(5)	0.5
O(2)	0.1008(16)	−0.1997(4)	0.2327(11)	4.0(4)	0.5
O(3)	−0.3004(15)	−0.1956(3)	0.25	5.1(3)	0.5
N(1)	0.2513(12)	0.0324(3)	−0.0581(5)	4.6(2)	
N(2)	−0.1421(13)	0.0572(3)	−0.0787(5)	5.0(3)	
N(3)	0.5261(11)	0.2043(3)	0.5536(5)	4.0(2)	
N(11)	0.0150(11)	0.0579(3)	0.1118(4)	3.6(2)	
N(12)	0.1699(11)	0.2139(3)	0.4050(4)	3.4(2)	
N(21)	0.5325(12)	0.1011(3)	0.4528(5)	4.4(2)	
N(22)	0.4418(18)	−0.0146(4)	0.25	5.1(4)	0.5
N(23)	0.6106(20)	0.2172(4)	0.25	5.5(4)	0.5
C(1)	0.1921(22)	0.0730(7)	−0.1196(10)	9.0(6)	
C(2)	0.0408(23)	0.0987(6)	−0.0961(11)	5.1(4)	0.70(3)
C(2D)	−0.0335(53)	0.0750(14)	−0.1443(27)	5(1)	0.30(3)
C(3)	0.7098(15)	0.2221(4)	0.5110(9)	6.2(4)	
C(11)	0.0342(11)	0.0905(3)	0.1644(5)	2.6(2)	
C(12)	0.1288(11)	0.1887(3)	0.3444(5)	2.7(2)	
C(21)	0.5288(12)	0.1004(3)	0.3761(6)	3.3(2)	
C(22)	0.4736(19)	0.0294(4)	0.25	3.5(3)	0.5
C(23)	0.5788(19)	0.1729(4)	0.25	3.5(3)	0.5

$^*K$, site occupation factor given if different from unity

Table II. Tables of anisotropic thermal parameters and structure factors have been deposited.

3. Results and Discussion

The structure is illustrated in Figures 1 and 2. Bond distances and angles are given in Table III while the possible hydrogen bonds are given in Table IV.

The structure exhibits a two-dimensional character. The basis of the structure are infinite layers of the $[Zn(en)_2\text{-}(NC)_2Ni(CN)_2\text{-}Zn(en)]_n^{2n+}$ type which run parallel with the bc plane. It could be said that the layers are built up of NiC_4 squares, ZnN_6 octahedra and ZnN_4 tetrahedra connected via $C\equiv N$ bonds. The positive charge of these layers is counterbalanced by the isolated tetracyanonickelate(II) anions which are included in the free space between the layers. The water molecules do not enter into the coordination sphere of the central atoms. They occupy the remaining free space between the layers. These layers exhibit a wavy shape and are bent at the Zn(2) atoms. Though the layered structure type is very common for the group of tetracyanonickelates(II), e.g. in the Hofmann-type clathrates [13], the solved structure represents a novel, previously unreported layered structure type
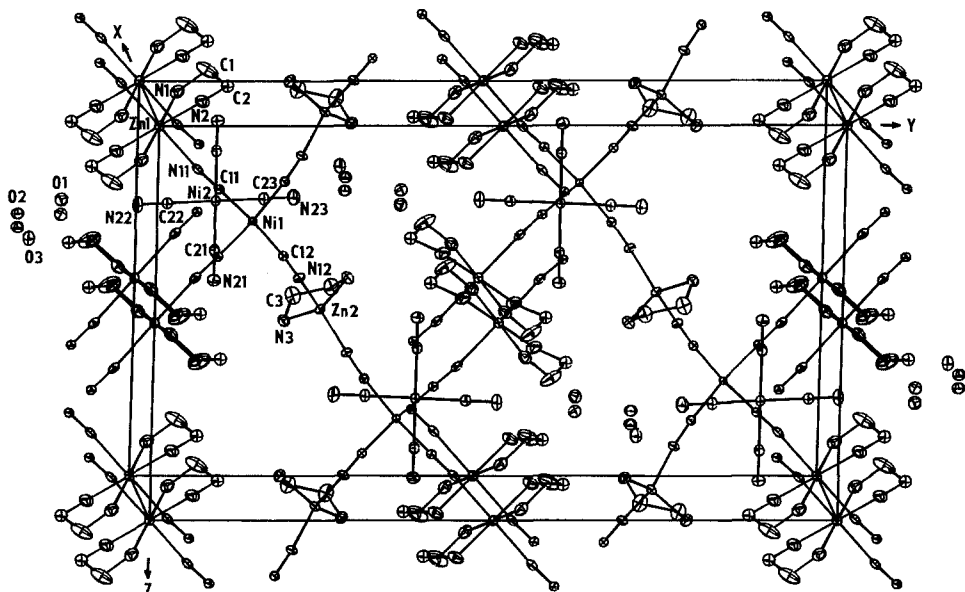
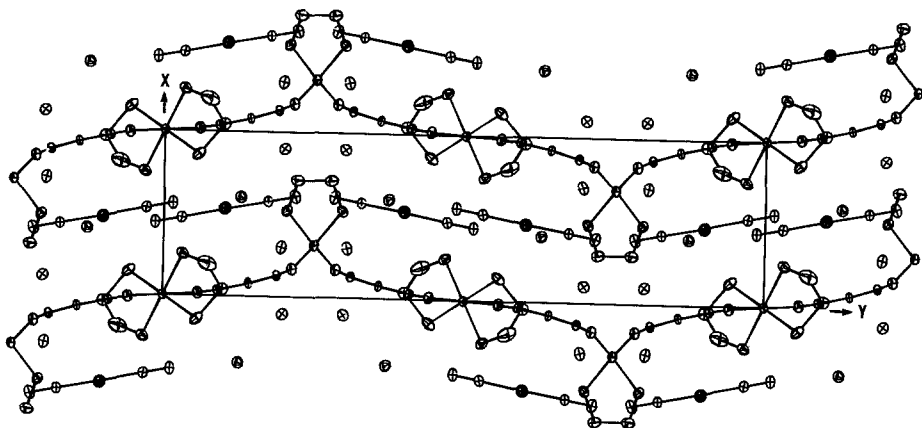Fig. 1.   ORTEP view of the unit cell along with atom numbering scheme.

Fig. 2.   View of the structure along the z axis (ORTEP) showing the packing of the layers.

among the series of tetracyanonickelates(II). In principle, the present structure is related to the structure of $[Zn(en)_2NCAgCN][Ag(CN)_2]$ which is built up of positively charged chains $[-Zn(en)_2-NC-Ag-CN-]_n^{n+}$ and isolated $[Ag(CN)_2]^-$ anions [14].

There are two crystallochemically different nickel atoms in the structure. Both of them occupy special positions. The difference between the Ni atoms lies in the fact that the cyano groups bonded to the Ni(1) atom behave as bidentate ligands while the cyano groups bonded to the Ni(2) atoms are monodentate. This gives an explanation for the observation of two strong peaks at 2120 and 2156 cm^{-1} in the

Table III.   Bond distances [Å] and angles [deg]

Zn octahedron			
Zn(1)—N(1)	2.121(8)	N(1)—Zn(1)—N(2)	84.0(3)
Zn(1)—N(2)	2.113(8)	N(1)—Zn(1)—N(11)	90.5(3)
ZN(1)—N(11)	2.223(7)	N(2)—Zn(1)—N(11)	88.9(3)
N(1)—C(1)	1.44(2)	Zn(1)—N(1)—C(1)	107.5(8)
N(2)—C(2)	1.68(2)	N(1)—C(1)—C(2)	115(1)
N(2)—C(2D)	1.32(4)	N(1)—C(1)—C(2D)	117(2)
C(1)—C(2D)	1.62(4)	C(1)—C(2)—N(2)	110(1)
C(1)—C(2)	1.29(2)	C(2)—N(2)—Zn(1)	99.3(7)
		C(1)—C(2D)—N(2)	112(3)
		C(2D)—N(2)—Zn(1)	112(2)
		Zn(1)—N(11)—C(11)	173.5(6)
Zn tetrahedron			
Zn(2)—N(3)	2.039(8)	N(3)—Zn(2)—N(12)	112.8(3)
Zn(2)—N(12)	1.965(7)	N(3)—Zn(2)—N(12)^i	110.9(3)
N(3)—C(3)	1.50(1)	N(12)—Zn(2)—N(12)^i	118.1(3)
C(3)—C(3)^i	1.46(1)	N(3)—Zn(2)—N(3)^i	87.4(3)
		Zn(2)—N(3)—C(3)	106.3(6)
		N(3)—C(3)—C(3)^i	112.9(9)
		Zn(2)—N(12)—C(12)	163.4(7)
$[Ni(CN)_4]^{2-}$ *anions*			
Ni(1)—C(11)	1.849(8)	Ni(1)—C(11)—N(11)	177.4(7)
Ni(1)—C(12)	1.875(8)	Ni(1)—C(12)—N(12)	174.3(7)
N(11)—C(11)	1.147(10)	C(11)—Ni(1)—C(12)	171.4(3)
N(12)—C(12)	1.142(10)	C(11)—Ni(1)—C(11)^{ii}	87.1(3)
		C(11)—Ni(1)—C(12)^{ii}	87.9(3)
		C(12)—Ni(1)—C(12)^{ii}	97.0(3)
Ni(2)—C(21)	1.876(9)	Ni(2)—C(21)—N(21)	178.0(8)
Ni(2)—C(22)	1.863(10)	Ni(2)—C(22)—N22	179.2(9)
Ni(2)—C(23)	1.857(10)	Ni(2)—C(23)—N23	179.6(9)
N(21)—C(21)	1.141(12)	C(22)—Ni(2)—C(23)	178.7(3)
N(22)—C(22)	1.140(15)	C(21)—Ni(2)—C(23)	90.6(2)
N(23)—C(23)	1.147(15)	C(21)—Ni(2)—C(22)	89.5(2)
		C(21)—Ni(2)—C(21)^{ii}	178.9(3)

Symmetry codes: ^{i}: $x, 0.5 - y, 1 - z$; ^{ii}: $x, y, 0.5 - z$

Table IV.   Possible hydrogen bonds [Å]

O(1)···O(2)	2.77(2)	O(1)···O(2)^i	2.82(2)
O(1)···N(22)	2.90(1)	O(1)···O(3)^{ii}	2.74(1)
O(1)···N(2)^{iii}	3.40(2)	O(1)···N(3)^{iv}	3.32(2)
O(2)···O(3)	2.81(2)	O(2)···N(23)^v	2.93(2)
O(3)···N(3)^{vi}	3.326(9)	O(3)···N(3)^{vii}	3.326(9)
O(3)···N(23)^{viii}	3.10(2)	N(1)···N(21)^i	3.06(1)
N(2)···N(21)^{ix}	3.15(1)	N(2)···N(22)^{iii}	3.47(1)

Symmetry codes:
^{i}: $x, y, 0.5 - z$; ^{ii}: $1 + x, y, z$;
^{iii}: $-x, -y, -z$; ^{iv}: $1 - x, -y, z - 0.5$;
^{v}: $1 - x, y - 0.5, z$; ^{vi}: $-x, -y, 1 - z$;
^{vii}: $-x, -y, z - 0.5$; ^{viii}: $-x, y - 0.5, z$;
^{ix}: $x - 1, y, 0.5 - z$;

IR spectrum of the studied complex. A similar situation was found in the structure of [-Zn(en)$_2$NC-Ag-CN-][Ag(CN)$_2$] where two different kinds of [Ag(CN)$_2$]$^-$ anions were found [14]. Both nickel atoms exhibit classical square coordination. The Ni(1)C$_4$ square is not exactly planar. The Ni(1) atom is displaced 0.51(2) Å from the plane formed by four carbon atoms. This could be explained by the fact that these atoms are part of the polymeric network. On the other hand, in the isolated [Ni(CN)$_4$]$^{2-}$ anion the Ni(2)C$_4$ square does not significantly deviate from planarity. The Ni—C and C≡N distances and angles in the anions are normal [1]. It is interesting to note that, as was expected, the deviations of the angles from the ideal values of 90 and 180°, respectively, are greater in the anion bonded in the layer.

Two zinc atoms occupy special positions. They are different from the crystallochemical as well as the geometrical points of view. The Zn(1) atom exhibits deformed octahedral coordination. Two chelate bonded en molecules are placed in the equatorial plane, the axial positions being occupied by N-bonded cyano groups. The same type of coordination was found in the structure of Zn(en)$_2$Ni(CN)$_4$ [4]. The coordination number of the Zn(2) atom is equal to 4 and the coordination is deformed tetrahedral formed by one chelate bonded en molecule and two N-bonded cyano groups. This coordination number and type of coordination is very common for the Zn complexes but, surprisingly, this is the first example of this coordination number for the Zn atom in the structures of tetracyanonickelates(II). The Zn(1)—N bond distances are normal [4, 14–5]. Zn(2)—N bond distances are shorter than the Zn(1)—N distances due to the lower coordination number of the Zn(2) atom. The mean value of 2.03 Å is in agreement with the value of 2.037(5) Å found for the Zn—N bond in Zn(CN)$_2$ [16].

There are two crystallochemically different en molecules in the structure. Both are bonded as chelating ligands. The observed bond distances and angles in the en molecule bonded to the Zn(2) atom are comparable with those found in other similar complexes [2, 4, 14, 15]. On the other hand, the observed bond distances and angles in the en molecules bonded to the Zn(1) atom strongly deviate from the normal values. This could be explained by the observed disorder. While the C(2) atom is disordered in two positions with the ratio 7:3, the C(1) atom is located, but its thermal parameter is unusually large ($B_{eq} = 9$ Å) indicating some disorder in its position. A disorder of the en molecules was also observed in the structures of Zn(en)$_2$Ni(CN)$_4$ [4] and Cu(en)$_2$Cu$_2$Cl$_4$ [17].

The water molecules are placed in the cavities formed between the layers. One oxygen atom (O(3)) lies on a special position (mirror plane) the remaining two are disordered by the mirror plane. The interatomic distances of the O···O, O···N(≡C), O···N(en) and (C≡)N···N(en) types indicate the presence of hydrogen bonds (Table IV). The water molecules could be removed from the structure by heating [8]. From the results of structure analysis if follows that this process requires only breaking of relatively weak bonds (hydrogen bonds). However, the anhydrous structure formed is not stable in the presence of air humidity and rehydration takes place [8]. The reversibility of dehydration indicates that the structure of the dehydrated complex will be closely related to the structure of the hydrate and that the layered host structure is conserved during dehydration.

4. Conclusion

From the results of this structure analysis it can be concluded that a novel structure type among the series of tetracyanonickelates(II) was prepared. This is the first example of the layered structure type for the tetracyanonickelates(II) with chelate bonded en molecules. The presented structure could be considered as an inclusion compound with included $[Ni(CN)_4]^{2-}$ anions and water molecules between the layers which form the host part of the structure.

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