Inorganica Chimica Acta, *85* (1984) 219–226

The Crystallochemistry of Tetracyanocomplexes. The Crystal and Molecular Structures of Tris(1,2-diaminoethane)zinc(II) Tetracyanoniccolate(II) Monohydrate and Tris(1,2-diaminoethane)zinc(II) Tetracyanoniccolate(II)

J. ČERNÁK, J. CHOMIČ

Department of Inorganic Chemistry, P. J. Šafarik University, Moyzesova 11, 041 67 Košice, Czechoslovakia

M. DUNAJ-JURČO

Department of Inorganic Chemistry, Slovak Technical University, Jánska 1, 812 37 Bratislava, Czechoslovakia

and C. KAPPENSTEIN

Department of Inorganic Chemistry V, University of Poitiers, 40, avenue du Recteur Pineau, 86022 Poitiers Cedex, France

Received July 16, 1983

$C_{10}H_{26}N_{10}ONiZn$, tris(1,2-diaminoethane) zinc(II) tetrakis(cyano)niccolate(II) monohydrate (I), orthorhombic, Pbca, a = *1.1680(4),* b = *1.5844(3),* c = *1.9981(6) nm, Z = 8, d(meas) = 1.54, d(calc) = 1.53 g cm^{-3}. $C_{10}H_{24}N_{10}NiZn$, tris(1,2-diaminoethane) zinc(II) tetrakis(cyano)niccolate(II), (II), monoclinic, $P2_1/n$,* a = *0.7957(2),* b = *1.5170(5),* c = *1.4932(4) nm, β = 96.41(2)°, Z = 4, d(meas) = 1.49, d(calc) = 1.51 g cm^{-3}. Both the structures (I) and (II) have been solved by the heavy atom method and refined by full-matrix least-squares to R(I) = 0.086 for 1890 independent reflections and R(II) = 0.058 for 1689 independent reflections, respectively. In the case of (II) the superlattice structure problem was solved. The crystal structure of (I) consists of $[Zn(en)_3]^{2+}$ cations, $[Ni(CN)_4]^{2-}$ anions and water molecules. Two of the cyano groups in* trans *positions are bonded to water molecules by hydrogen bonds, the distances CN···O being 0.289 and 0.291 nm, respectively. The crystal structure of (II) is constituted by $[Zn(en)_3]^{2+}$ cations and $[Ni(CN)_4]^{2-}$ anions.*

Introduction

The cyano group can act as a monodentate or bidentate ligand [1] when bonded to nickel in the $[Ni(CN)_4]^{2-}$ anion, which causes variability to the bonding possibilities and thus to the structure types present in tetracyanoniccolates(II). These could be ionic, *e.g.* $K_2Ni(CN)_4$ [2], one-dimensional, *e.g.* $Cu(en)_2Ni(CN)_4$ [3] (en = 1,2-diaminoethane), two-dimensional, *e.g.* $Ni(NH_3)_2Ni(CN)_4$ [4], or three-dimensional, *e.g.* $Cd(en)Ni(CN)_4$ [5]. The possibility exists of Hofmann-type clathrate compound formation in the case of two- or three-dimensional structure types, *e.g.* $Cd(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ [6] and $Cd(en)Ni(CN)_4 \cdot 2C_6H_6$ [7], respectively.

Our interests lie in the study of the crystallochemistry, thermal and other properties of the tetracyanoniccolates(II) which crystallize from the following systems: $M-NH_3$ or en–$[Ni(CN)_4]^{2-}-H_2O$, where M = Ni(II), Cu(II), Zn(II), and Cd(II). At first the system with en and M = Zn(II) was studied. The following compounds were prepared: $Zn(en)_3Ni(CN)_4 \cdot H_2O$ (I), $Zn(en)_3Ni(CN)_4$ (II), and $Zn(en)_2Ni(CN)_4$ (III). The thermal behavior of (I) was published recently [8]. The present work deals with the crystal structure determinations of (I) and (II).

Experimental

The preparation of (I) is described elsewhere [8]. The crystals of (II) in a form suitable for X-ray study were prepared in the following way: 5 mmol

0020-1693/84/$3.00

TABLE I. Crystal data for $Zn(en)_3Ni(CN)_4 \cdot H_2O$ and $Zn(en)_3Ni(CN)_4$.

		$Zn(en)_3Ni(CN)_4 \cdot H_2O$	$Zn(en)_3Ni(CN)_4$
Mol. weight		426.48	408.45
Crystallographic system		orthorhombic	monoclinic
Unit cell parameters			
[nm]	*a*	1.1680(4)[a]	0.7957(2)
	b	1.5844(3)	1.5170(5)
	c	1.9981(6)	1.4932(4)
			$\beta = 96.41(2)^\circ$
Space group		*Pbca*	$P2_1/n$
Unit cell volume [nm^3]		3.697(2)	1.7911(5)
Z		8	4
Density [$g\ cm^{-3}$]			
d(meas)		1.54	1.49
d(calc)		1.53	1.51
$\mu(MoK\bar{\alpha})$ [cm^{-1}]		23.7	24.02
F(000)		1776	848

[a] Throughout, the number in parentheses being the standard deviation of the last digit.

TABLE II. Experimental Conditions for Intensity Data Collections.

Compound	$Zn(en)_3Ni(CN)_4 \cdot H_2O$	$Zn(en)_3Ni(CN)_4$
Temperature (K)	293	293
Crystal shape and dimensions (mm)	orthorhombic dipyramid, max 0.6	parallelepiped
Diffractometer	Syntex $P2_1$	Enraf-Nonius CAD-4
Scan technique	$\theta - 2\theta$	ω
Angular width	from $[2\theta(MoK_{\alpha 1}) - 1]^\circ$ to $[2\theta(MoK_{\alpha 2}) + 1]^\circ$	$(1 + 0.35\ tg\theta)^\circ$
Radiation used	MoK_α	MoK_α
λ[nm]	0.071069	0.071069
Monochromatization	graphite	graphite
Scan range of 2θ	0–55°	6–60°
Control of data collection	3 reflexions checked every 100	3 reflexions checked every 97
Number of collected independent reflexions	3099	5613
Condition for observed reflexion	$I_n \geqslant 1.96\ \sigma_I$	$I_n \geqslant 2\sigma_I$
Maximum time for the final scan	variable scan speed 4.88–29.3° min^{-1}	50s, attenuator used
Number of observed reflexions	1890	1689

(1.14 g) of freshly prepared $ZnNi(CN)_4$ were dissolved in 10 ml of 50% 1,2-diaminoethane solution in water. The orange parallelepipeds of (II) crystallized during 48 h at 65 °C.

The crystals of both (I) and (II) were first studied in a Weissenberg camera using CuKα radiation. The photographs of (I) showed the systematic absences hk0, h = 2n + 1; h0l, l = 2n + 1, 0kl, k = 2n + 1, indicating the space group as being *Pbca.* The systematic absences for (II) h0l, h + l = 2n + 1 and 0k0, k = 2n + 1 indicated the space group to be $P2_1/n$.

Least-squares refinement of the values of ten reflections for (I) (Syntex $P2_1$) and fifteen reflections for (II) (CAD-4), respectively, gave the precise unit-cell parameters and their standard deviations. The densities of the crystals were measured

TABLE III. Positional Parameters ($\times 10^4$) for Atoms in Zn(en)$_3$Ni(CN)$_4$·H$_2$O with Standard Deviations.

	x	y	z
Zn	2162(1)	2845(1)	3781(1)
Ni	2595(2)	−122(1)	1238(1)
O	4749(11)	997(7)	3702(7)
N1	2653(12)	4185(7)	3906(6)
N2	1441(11)	3035(8)	2748(6)
N3	1740(12)	1490(8)	3535(7)
N4	2744(11)	2463(8)	4783(7)
N5	3946(10)	2803(8)	3405(7)
N6	517(10)	3007(8)	4306(6)
N11	3632(15)	150(14)	2596(8)
N22	1498(14)	−512(9)	−96(10)
N33	4152(14)	1241(10)	671(8)
N44	1128(14)	−1512(10)	1925(8)
C1	3270(15)	62(13)	2123(9)
C2	1920(17)	−358(11)	462(10)
C3	3559(16)	710(11)	865(7)
C4	1630(17)	−1030(12)	1639(10)
C32	1038(17)	1514(13)	1831(11)
C23	1506(15)	2197(11)	2423(8)
C46	1656(15)	2367(12)	5244(10)
C64	780(15)	3031(10)	5040(11)
C51	4555(12)	3512(9)	3732(10)
C15	3852(15)	4297(10)	3627(9)

by the immersion method in a mixture of acetone and bromoform. Crystal data for both the compounds are summarized in Table I, while the experimental conditions of the intensity data collections are given in Table II. For the crystal structure analysis of (I) 1890 observed independent reflections were used. The intensity data were corrected for Lorentz and polarization factors, but no absorption correction was applied. The heavy atom positions were found from a Patterson map. The subsequent Fourier synthesis revealed the positions of all the other atoms (without H atoms, which were not included in the refinement). The atomic positions were refined by means of full-matrix least-squares methods, the function minimized being $\Sigma w[F_o - |F_c|]^2$ with $w = 1/\sigma$. The refinement with isotropic thermal parameters converged to a conventional R factor 0.099 ($R = \Sigma|[F_o - |F_c|]|/\Sigma|F_o|$). Introducing anisotropic thermal parameters dropped R to 0.086. At this stage the last difference Fourier map was calculated; the maximum peak was 1300 e/nm^3 near to the N3 atom and the next peak was 900 e/nm^3 near to the N1 atom.

Atomic scattering factors for all the atoms were taken from [9]. No correction for anomalous dispersion was applied. All the calculations were carried out by means of the XTL program package on the

TABLE IV. Anisotropic Thermal Parameters ($\times 10^4$ nm) for Atoms in Zn(en)$_3$Ni(CN)$_4$·H$_2$O.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zn	2.73(10)	3.01(10)	2.31(10)	0.07(11)	0.08(11)	−0.08(8)
Ni	3.66(12)	3.12(12)	2.19(11)	0.14(12)	−0.14(12)	−0.61(10)
O	8.9(1.0)	3.6(7)	5.0(9)	1.4(8)	0.5(9)	−1.0(7)
N1	4.3(9)	2.7(7)	3.1(9)	−0.2(6)	0.1(7)	0.1(6)
N2	4.7(9)	2.7(8)	1.7(8)	−0.1(6)	−0.6(7)	0.5(7)
N3	5.6(1.1)	2.4(8)	4.3(1.0)	0.1(7)	−0.7(8)	−1.4(7)
N4	2.2(9)	3.5(8)	3.9(9)	1.2(6)	−0.1(7)	0.4(6)
N5	2.0(8)	3.4(8)	4.3(9)	0.3(8)	0.7(6)	−0.5(7)
N6	3.7(8)	4.4(9)	0.7(7)	0.7(6)	0.5(6)	0.6(7)
N11	9.4(1.4)	12.0(1.8)	1.3(1.0)	1.5(1.1)	−3.6(1.0)	−5.1(1.3)
N22	6.4(1.3)	4.5(1.0)	5.8(1.3)	−1.1(1.0)	0.8(1.0)	−1.2(9)
N33	6.3(1.2)	7.0(1.3)	3.0(1.0)	2.6(9)	−0.3(9)	−1.6(1.0)
N44	5.6(1.3)	5.2(1.2)	4.8(1.2)	1.8(9)	1.8(9)	2.5(9)
C1	4.2(1.2)	5.8(1.3)	3.5(1.2)	2.5(1.1)	−0.7(1.0)	−3.5(1.1)
C2	5.2(1.4)	4.0(1.2)	4.5(1.4)	1.1(9)	−0.3(1.1)	−1.7(9)
C3	5.8(1.3)	3.9(1.2)	−0.2(9)	0.1(8)	−1.0(8)	−0.7(1.0)
C4	4.2(1.3)	4.3(1.3)	5.0(1.4)	−0.3(1.1)	3.0(1.1)	−2.5(1.0)
C32	5.6(1.5)	6.3(1.6)	5.8(1.5)	−1.5(1.2)	−1.1(1.2)	−0.6(1.1)
C23	5.7(1.2)	3.3(1.1)	0.4(8)	0.1(8)	−0.3(8)	−0.4(1.0)
C46	3.3(1.1)	4.8(1.3)	5.5(1.4)	−1.2(1.0)	−0.4(1.0)	0.4(9)
C64	4.0(1.1)	2.4(1.0)	6.9(1.4)	−0.3(1.0)	1.2(1.0)	1.0(9)
C51	2.7(1.0)	2.7(9)	6.1(1.3)	1.3(1.2)	0.4(1.1)	−0.8(7)
C15	4.5(1.2)	3.2(1.0)	5.1(1.5)	0.3(9)	−0.6(1.0)	−0.5(8)

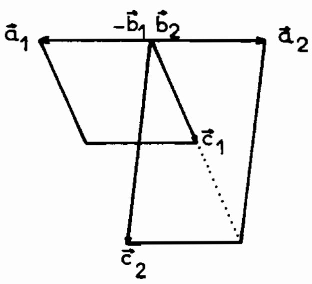

Fig. 1. Relation between the original cell ($P2_1/n$) and the reduced one ($P2_1/m$).

computer attached to the diffractometer. The atomic positions with thermal parameters are given in Tables III and IV. 1689 observed reflections of the crystal (II) were corrected for Lorentz and polarization factors. No absorption correction was made. Scattering factors for all the atoms were taken from [10] and were corrected for anomalous dispersion. All calculations were performed with SHELX'76 [11] on an IBM 370 computer.

The diffraction intensities inspection showed that the intensities of 315 reflections following the condition $h + l = 2n + 1$ are systematically weaker. There was in the Patterson map a very high peak (86% of

TABLE V. Positional Parameters ($\times 10^4$) for Atoms in $Zn(en)_3Ni(CN)_4$ with Standard Deviations.

	x	y	z
Zn	9327(1)	2464(1)	6899(1)
Ni(1)	0	0	0
Ni(2)	0	5000	0
N1	8728(8)	2502(5)	8311(4)
N2	8360(8)	1120(5)	6576(4)
N3	6703(9)	2996(4)	6665(4)
N4	0622(8)	3776(5)	7049(4)
N5	1663(8)	1727(5)	7320(4)
N6	9956(7)	2353(4)	5491(4)
C13	7216(14)	3108(6)	8318(6)
C31	5987(10)	2965(5)	7542(8)
C46	1662(10)	3842(5)	6256(8)
C64	627(11)	3554(6)	5407(6)
C25	9921(13)	574(5)	6456(5)
C52	1284(10)	755(6)	7250(5)
C1	−797(12)	3951(7)	464(7)
C2	6089(14)	3995(7)	4645(7)
C3	3363(14)	4857(6)	4009(7)
C4	1515(14)	4332(7)	−595(8)
N11	−1206(11)	3292(6)	736(6)
N22	6785(13)	3402(6)	4414(6)
N33	2393(11)	4775(6)	3990(6)
N44	2424(12)	3922(6)	−943(7)

TABLE VI. Anisotropic Thermal Parameters ($\times 10^4$ nm) for Atoms in $Zn(en)_3Ni(CN)_4$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zn	3.15(5)	3.11(6)	2.77(5)	0.07(9)	0.32(4)	0.21(9)
Ni1	4.83(18)	2.86(13)	2.47(15)	−0.10(10)	0.08(12)	−0.27(11)
Ni2	4.22(17)	4.38(15)	3.55(17)	0.56(12)	0.02(13)	−0.80(12)
N1	5.0(5)	5.5(5)	3.1(4)	−1.2(7)	0.05(30)	1.1(7)
N2	4.3(5)	3.4(5)	4.6(5)	0.2(4)	0.0(4)	0.1(4)
N3	4.1(5)	3.6(5)	3.4(4)	0.7(4)	0.3(4)	0.3(4)
N4	3.5(5)	5.8(6)	3.1(4)	0.1(4)	0.1(4)	−0.7(4)
N5	3.0(5)	4.4(5)	2.8(4)	0.5(4)	0.1(3)	0.4(4)
N6	3.7(4)	3.6(6)	3.2(4)	−0.3(4)	0.7(4)	−0.3(4)
C13	6.9(9)	13.8(1.3)	4.2(7)	0.3(8)	1.9(6)	4.9(9)
C31	3.7(7)	11.5(1.1)	6.1(8)	−1.3(8)	1.1(6)	0.9(7)
C46	5.0(7)	5.3(7)	7.7(8)	−0.3(7)	2.0(6)	−2.0(6)
C64	6.4(8)	6.9(8)	4.1(6)	1.2(6)	0.6(6)	−1.7(7)
C25	6.6(8)	3.3(6)	4.2(6)	−0.4(5)	2.1(5)	−0.3(5)
C52	3.4(6)	5.0(7)	5.1(7)	0.8(6)	−0.3(5)	0.2(5)
C1	3.6(6)	3.6(6)	4.2(6)	0.2(5)	1.1(5)	−0.2(5)
C2	5.6(8)	4.1(7)	3.4(6)	0.1(6)	−0.6(6)	−0.8(6)
C3	5.6(7)	1.8(5)	4.3(6)	−0.1(4)	1.4(5)	0.2(5)
C4	4.3(7)	4.0(7)	4.2(7)	0.9(6)	−0.0(5)	−0.8(6)
N11	4.8(6)	4.8(6)	6.3(6)	1.1(5)	2.6(5)	−0.1(5)
N22	6.6(7)	5.9(7)	4.7(6)	−1.7(6)	−2.3(5)	1.8(6)
N33	6.2(6)	5.1(6)	3.5(5)	−0.9(4)	−1.0(5)	1.0(5)
N44	6.7(8)	4.8(7)	6.7(7)	1.0(6)	2.4(6)	−1.0(6)

TABLE VII. H Atom Positions ($\times 10^4$) with U_{iso} ($\times 10^4$ nm)[a] for $Zn(en)_3Ni(CN)_4$.

	x	y	z	U_{iso}
H1I	9772	2766	8747	56
H1II	8400	1859	8533	56
H2I	7520	1126	5971	47
H2II	7750	862	7128	47
H3I	5956	2591	6179	48
H3II	6733	3661	6431	48
H4I	1417	3807	7674	52
H4II	9696	4294	7006	52
H5I	2099	1884	8009	47
H5II	2604	1889	6889	47
H6I	8835	2574	5032	41
H6II	904	2186	5354	41
H13I	7611	3796	8304	82
H13II	6607	3007	8929	82
H31I	5437	2315	7634	76
H31II	5000	3454	7550	76
H46I	2760	3407	6377	58
H46II	2109	4511	6204	58
H64I	9598	4035	5275	65
H64II	1413	3598	4860	65
H25I	9571	–120	6436	54
H25II	382	746	5823	54
H52I	2433	402	7140	53
H52II	850	522	7868	53

[a] $U_{iso}(H_x) = U_{iso}(X) + 0.01$; atom H_x is bonded to the atom X.

the peak-origin) with the coordinates 0.5, 0, 0.5, which corresponds to the pseudotranslation $\vec{a}/2 + \vec{c}/2$, and we were unsuccessful in solving the Patterson map. These facts show a superlattice structure problem. This problem was solved in the following way: the 315 above mentioned reflections were rejected. In this manner, an elementary cell was obtained in this way with half the volume of the original one, the parameters and symmetry of the lattice being: $a = 0.7957$, $b = 1.5170$, $c = 0.8058$ nm, $\beta = 112.97°$, $Z = 2$, $P2_1/m$ (Fig. 1). The Patterson map calculated in this reduced lattice allowed the location of heavy atoms in special positions (zinc in (2e) and nickel in (2a)). A difference Fourier map then also revealed the remaining non-hydrogen atoms and images. The positions of the atoms (without images) in the original lattice were obtained after atomic position re-transformations by introducing the 315 above mentioned reflections, which determined the original lattice.

The structure refinement by means of full-matrix least squares technique with all non-hydrogen atoms and isotropic thermal parameters led to an R factor of 0.080. The R factor dropped to 0.058 by introducing the anisotropic thermal parameters for all non-hydrogen atoms and the calculated H atom positions. The value of Rw was 0.055, the weight being $w = 1/\sigma_{(F_o)}^2$ and $Rw = [\Sigma w(F_o - |F_c|)^2/\Sigma wF_o^2]^{1/2}$.

The residual Fourier map was featureless and showed a maximum of 600 e/nm³. The final atomic positions with thermal parameters are given in Tables V–VII.

Results and Discussion

The crystal structure of (I) is built up from $[Zn(en)_3]^{2+}$ complex cations, $[Ni(CN)_4]^{2-}$ complex

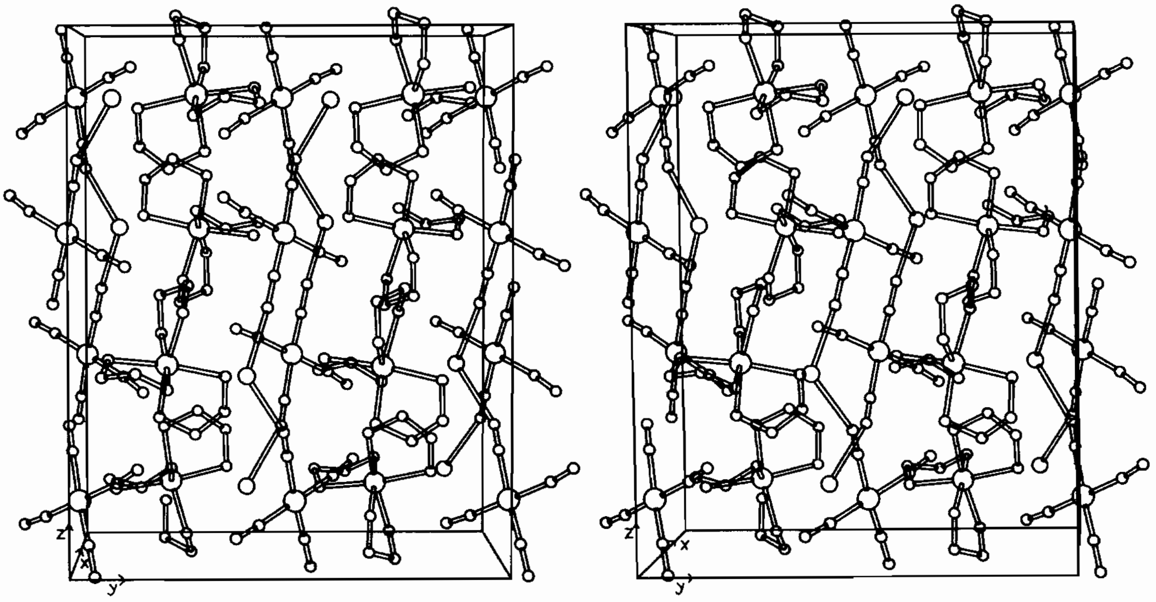

Fig. 2. A stereoview of the unit cell of $Zn(en)_3Ni(CN)_4 \cdot H_2O$.

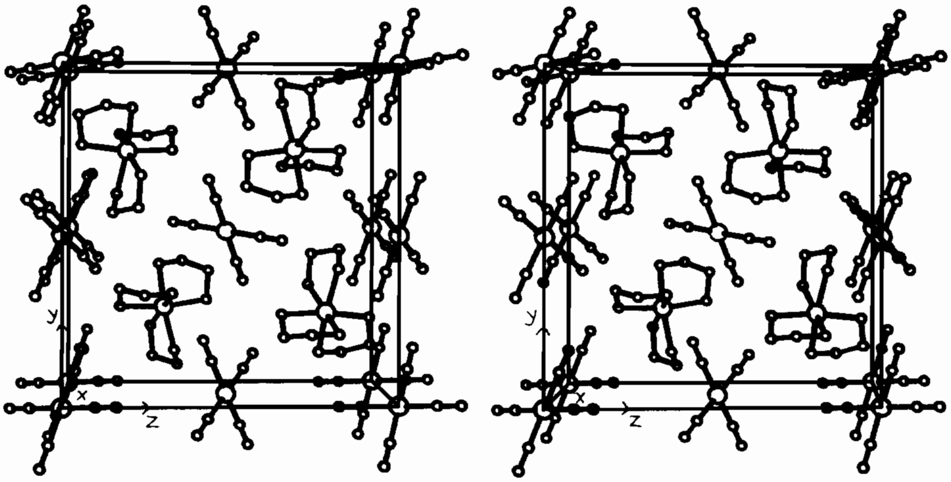

Fig. 3. A stereoview of the unit cell of $Zn(en)_3Ni(CN)_4$.

TABLE VIII. Interatomic Distances (nm) and Angles (°) for $Zn(en)_3Ni(CN)_4 \cdot H_2O$.

Zn octahedron					
Zn–N1	0.2213(11)	N1–Zn–N2	94.2(5)	N2–Zn–N5	92.6(5)
Zn–N2	0.2250(13)	N1–Zn–N3	173.5(5)	N2–Zn–N6	95.5(5)
Zn–N3	0.2257(13)	N1–Zn–N4	94.7(5)	N3–Zn–N4	90.2(5)
Zn–N4	0.2200(13)	N1–Zn–N5	79.8(5)	N3–Zn–N5	96.0(5)
Zn–N5	0.2216(12)	Ni–Zn–N6	93.5(5)	N3–Zn–N6	93.4(5)
Zn–N6	0.2204(12)	N2–Zn–N3	81.1(5)	N4–Zn–N5	90.6(5)
		N2–Zn–N4	171.1(5)	N4–Zn–N6	82.4(5)
				N5–Zn–N6	169.9(5)
1,2-diaminoethane rings					
N1–C15	0.1517(22)	Zn–N1–C15	108.1(9)		
C15–C51	0.1506(22)	N1–C15–C51	110.8(1.3)		
C51–N5	0.1480(20)	C15–C51–N5	107.6(1.3)		
		C51–N5–Zn	106.2(9)		
N2–C23	0.1480(21)	Zn–N2–C23	105.3(9)		
C23–C32	0.1460(26)	N2–C23–C32	113.6(1.4)		
C32–N3	0.1629(25)	C23–C32–N3	108.1(1.5)		
		C32–N3–Zn	106.0(1.0)		
N4–C46	0.1577(22)	Zn–N4–C46	108.0(9)		
C46–C64	0.1523(25)	N4–C46–C64	108.5(1.4)		
C64–N6	0.1496(25)	C46–C64–N6	112.5(1.4)		
		C64–N6–Zn	106.9(1.0)		
Ni square-plane					
Ni–C1	0.1959(18)	C1–Ni–C2	175.4(8)	C2–Ni–C4	87.1(8)
Ni–C2	0.1779(20)	C1–Ni–C3	90.7(8)	C3–Ni–C4	177.7(8)
Ni–C3	0.1888(17)	C1–Ni–C4	88.4(8)		
Ni–C4	0.1995(20)	C2–Ni–C3	93.9(8)		
CN^- ions					
C1–N11	0.1046(24)	Ni–C1–N11	179.1(1.9)		
C2–N22	0.1243(27)	Ni–C2–N22	176.9(1.7)		
C3–N33	0.1155(24)	Ni–C3–N33	176.3(1.6)		
C4–N44	0.1120(25)	Ni–C4–N44	173.0(1.8)		

TABLE IX. Interatomic Distances (nm) and Angles (°) for $Zn(en)_3Ni(CN)_4$.

Zn octahedron					
Zn–N1	0.2215(6)	Ni–Zn–N2	97.2(2)	N2–Zn–N5	81.7(3)
Zn–N2	0.2214(7)	Ni–Zn–N3	80.9(2)	N1–Zn–N6	91.3(2)
Zn–N3	0.2229(7)	N1–Zn–N4	91.5(2)	N3–Zn–N4	96.1(2)
Zn–N4	0.2242(7)	N1–Zn–N5	90.3(2)	N3–Zn–N5	167.3(2)
Zn–N5	0.2200(6)	N1–Zn–N6	171.1(3)	N3–Zn–N6	96.3(2)
Zn–N6	0.2232(6)	N2–Zn–N3	90.1(2)	N4–Zn–N5	93.4(3)
		N2–Zn–N4	170.0(2)	N4–Zn–N6	90.3(2)
				N5–Zn–N6	93.6(2)
1,2-diaminoethane rings					
N1–C13	0.1515(12)	Zn–N1–C13	106.1(5)		
C13–C31	0.1447(14)	N1–C13–C31	111.7(7)		
C31–N3	0.1486(14)	C13–C31–N3	114.2(8)		
		C31–N3–Zn	107.1(5)		
N2–C25	0.1519(12)	Zn–N2–C25	105.0(5)		
C25–C52	0.1539(11)	N2–C25–C52	109.2(6)		
C52–N5	0.1506(12)	C25–C52–N5	110.3(6)		
		C52–N5–Zn	108.7(4)		
N4–C46	0.1510(13)	Zn–N4–C46	105.4(4)		
C46–C64	0.1509(13)	N4–C46–C64	110.2(6)		
C64–N6	0.1478(12)	C46–C64–N6	111.3(7)		
		C64–N6–Zn	108.6(5)		
Ni square-planes					
Ni–C1	0.1875(10)	C1–Ni–C4	88.7(5)		
Ni–C4	0.1874(11)				
Ni–C2	0.1860(10)	C2–Ni–C3	89.2(5)		
Ni–C3	0.1872(11)				
CN^- ions					
C1–N11	0.1140(14)	N1–C1–N11	176.4(9)		
C4–N44	0.1123(15)	Ni–C4–N44	179.1(1.0)		
C2–N22	0.1130(15)	Ni–C2–N22	180.0(1.0)		
C3–N33	0.1143(13)	Ni–C3–N33	177.0(1.0)		

anions and water molecules. The complex cations are situated in the planes y = 0.25 and 0.75 and the complex anions are situated in the planes y = 0.0 and 0.5, appproximately. The coordination number of both the cations and anions is equal to eight; the packing of the ions in the unit cell corresponds to a distorted CsCl structure type. The water molecules are not bonded directly to the central metal atoms. Each water molecule forms two hydrogen bonds with the nitrogen atoms of the cyanogroups, which are from different $[Ni(CN)_4]^{2-}$ anions, and chains of H_2O... $[Ni(CN)_4]^{2-}$ ...H_2O, along the *c*-direction, could be observed as a consequence of hydrogen bonds (Fig. 2).

The crystal structure of (II) is likewise ionic and consists of $[Zn(en)_3]^{2+}$ complex cations and $[Ni(CN)_4]^{2-}$ complex anions. Two crystallographically-independent complex anions are in special positions (2a) and (2c) (symmetry center). Similarly as was found in (I), the complex cations are in the planes y = 0.25 and 0.75 (approximately) and complex anions are in the planes y = 0.0 and 0.5 (accurately). The similarity in the packing of the ions in both the structures (I) and (II) is in agreement with the close values of the cell parameters, *b* being in (I) 1.5844 and in (II) 1.5170 nm. The coordination number of the ions is six. The anions are placed in the octahedral cavities of the closest packed structure formed by cations, the coordination polyhedron about the cation being trigonal-prism. This method of packing corresponds to the NiAs structure (Fig. 3).

In both the compounds (I) and (II) the zinc atoms are distorted octahedra coordinated by three en molecules bonded as chelates. The en molecules exhibit gauche conformation, as was found in other $[M(en)_3]^{2+}$ cations [12]. The ranges of the Zn–N bond lengths are 0.220–0.226 (I) and 0.220–0.224 nm (II), respectively (Tables VIII and IX). A somewhat longer bond length for Zn–N (0.228 nm) was found in this cation in a water solution, which could be explained by the lack of crystal packing forces [13].

The C–N bond distances in en molecules in both compounds are within the range 0.148–0.152 nm, except for two bond distances in (I) – 0.158 and 0.163 nm. Similar deviations were found in the case of the dimeric complex $Zn(en)_2I(C_2O_4)_{0.5}$ [14]. For C–C bond distances in chelate bonded en molecules the reported values range from 0.141 [15] to 0.157 nm [14]. The values found in (I) and (II) lie within this interval.

The nickel atoms in both the complexes (I) and (II) exhibit the classical square-planar coordination. Bond distances and angles in $[Ni(CN)_4]^{2-}$ anions of (II) are nearly equal to those found in the other tetracyanoniccolate(II) complexes [1, 4, 6, 7]. However, this is not the case for some values found in complex (I). The most significant deviations were found in bond distances of two cyano groups: 0.105 and 0.124 nm. These cyano groups are connected with water molecules by hydrogen bonds (0.289 and 0.291 nm) which cause the non-equivalency of the cyano groups.

The shortest contact between water molecules and the ions in (I) is 0.307 nm (with N from en), all the other contacts being longer than 0.315 nm. The shortest contacts between the ions in (II) are in the range from 0.306 to 0.312 nm, indicating very weak hydrogen bonds.

From the results of the crystal structure analysis of (I) and (II) it could be concluded that during the first step of the thermal decomposition of (I) forming (II) [8]

$$Zn(en)_3Ni(CN)_4\cdot H_2O \xrightarrow[\text{at } 90\,^\circ C]{\text{max DTA}} Zn(en)_3Ni(CN)_4 + H_2O$$

dehydratation causes the change in packing of the mode complex ions, which could be described as a structure change from CsCl to NiAs, but does not cause changes in the type of the coordination polyhedra of the central atoms.

In the second step of the thermal decomposition of (I) one of the three en molecules is evolved [8]:

$$Zn(en)_3Ni(CN)_4 \xrightarrow[\text{at } 210\,^\circ C]{\text{max DTA}} Zn(en)_2Ni(CN)_4 + en$$

forming the compound (III), which could be prepared as twinned yellow needles by lowering the en concentration in the solution used for preparation of (I). The crystal structure of (III) is under examination.

Some results indicate that in the system with M = Ni and en, analogous crystalline complexes are formed, *e.g.* the IR spectra, thermal behavior and diffraction patterns of $Ni(en)_3Ni(CN)_4\cdot H_2O$ are similar to that of (I) [8]. On the other hand in the system with M = Cd(II), although there is a report about the preparation of $Cd(en)_3Ni(CN)_4\cdot H_2O$ [16], our results and those of others [5, 17] suggest the formation of $Cd(en)_3Ni(CN)_4$ under analogous conditions of preparation as in the case of (I). In the system with M = Cu(II) under similar conditions the compound $Cu(en)_2Ni(CN)_4$ was prepared, and exhibited one-dimensional structure [3].

References

1 A. G. Sharpe, 'The Chemistry of the Cyano Complexes of the Transition Metals', Academic Press, London (1976).

2 N. G. Vannerberg, *Acta Chem. Scand., 18,* 2385 (1964).

3 M. Dunaj-Jurčo, J. Garaj, J. Chomič, V. Haluška and F. Valach, *Proc. Conf. Coord. Chem., 6,* 45 (1976); *CA, 90,* 64844 U.

4 A. I. Rae and E. N. Maslen, *Z. Krist., 123,* 391 (1966).

5 G. B. Jameson, W. Bachmann, H. R. Oswald and E. Dubler, *Acta Cryst., A35, Suppl.,* C88 (1981).

6 Y. Sasaki, *Bull. Chem. Soc. Japan, 42,* 2412 (1969).

7 T. Miyoshi, T. Iwamoto and Y. Sasaki, *Inorg. Chim. Acta, 6,* 59 (1972).

8 A. Sopková, J. Černák, M. Šingliar, J. Bubanec and P. Kralik, *Pol. J. Chem.,* in press.

9 P. A. Doyle and P. S. Turner, *Acta Cryst., A24,* 390 (1968).

10 International Tables for X-ray Crystallography, Vol. IV, Kynoch Press, Birmingham (1974).

11 G. M. Sheldrick (1976), SHELX'76, Program for crystal structure determination, Univ. of Cambridge, England.

12 a) D. L. Cullen and C. Lingafelter, *Inorg. Chem., 9,* 1858 (1970).
b) M. U. Haque, C. N. Caughlan and K. Emerson, *Inorg. Chem., 9,* 2421 (1970).

13 T. Fujita, T. Yamaguchi and H. Ohtaki, *Bull. Chem. Soc. Japan., 52,* 3539 (1979).

14 I. F. Burshtejn, A. E. Shvelashvili and B. M. Shchedrin, 'Kristallochimija neorganicheskih sojedinenij', Izd. Shtiinca, Kishinev (1976).

15 R. J. Williams, A. C. Larson and D. T. Cromer, *Acta Cryst., B28,* 858 (1972).

16 M. Rüegg and A. Ludi, *Theoret. Chim. Acta, 20,* 193 (1971).

17 W. Bachmann, J. R. Günter and H. R. Oswald, Experientia, Suppl. 37, 36 (1979).