

THE CRYSTALLOCHEMISTRY OF TETRACYANOCOMPLEXES.  
THE CRYSTAL AND MOLECULAR STRUCTURE OF  
 $\text{Cd}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 0.5 \text{H}_2\text{O}$

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Dedicated to Dr F. Hanic on the occasion of his 60th birthday.

$\text{Cd}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 0.5 \text{H}_2\text{O}$  is orthorhombic, *Imma*, with parameters  $a = 0.7622(4)$ ,  $b = 1.4992(13)$ ,  $c = 0.8961(6)$  nm,  $Z = 4$ ,  $d(\text{exp}) = 2.07(4)$ ,  $d(\text{calc.}) = 2.066 \text{ Mg m}^{-3}$ . The structure, which was refined by the least squares method to  $R = 0.038$  for 1 508 independent reflections, is isostructural with  $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 0.5 \text{H}_2\text{O}$  and consists of infinite layers of the  $[\text{Cd}(\text{NC})_4\text{Ni}]_\infty$  type. Two water molecules in the unit cell occupy 4 equivalent positions between the layers. The shortest intermolecular distances  $0.3023(2)$  ( $\text{H}_2\text{O} \cdots \text{Ni}$ ) and  $0.3371(1)$  nm ( $\text{H}_2\text{O} \cdots \text{NH}_3$ ) indicate zeolitic character of the water molecule.

Solution of the crystal structure of  $\text{Cd}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 0.5 \text{H}_2\text{O}$  (*I*) forms part of our study of the crystallochemistry and other properties of tetracyanonickelates crystallizing in the following systems:  $\text{M}-\text{NH}_3$  or  $\text{en}-[\text{Ni}(\text{CN})_4]^{2-}-\text{H}_2\text{O}$ , where  $\text{M} = \text{Ni}(\text{II})$ ,  $\text{Cu}(\text{II})$ ,  $\text{Zn}(\text{II})$ , and  $\text{Cd}(\text{II})$  (ref.<sup>1</sup>).

Study of the thermal properties of *I* and of  $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 0.5 \text{H}_2\text{O}$  (*II*) has indicated that the loss of water during heating is a reversible process<sup>2</sup>, indicating the zeolitic character of the bonded water. The crystal structure of *II* has been solved<sup>3</sup> (yielding the formula  $\text{Ni}(\text{CN})_2 \cdot \text{NH}_3 \cdot 0.25 \text{H}_2\text{O}$ ), but difficulties in the determination of the crystal structure (data were obtained from only two projections) prevented unambiguous determination of the positions of the  $\text{H}_2\text{O}$  and  $\text{NH}_3$  molecules. This work was carried out to define the positions of these molecules more closely and to explain the reversibility of the dehydration process from a crystallochemical point of view.

## EXPERIMENTAL

Crystals of *I* in a suitable form for X-ray studies were obtained in the following manner: 5 mmol (1.38 g) of freshly prepared  $\text{CdNi}(\text{CN})_4$  were dissolved in a solution of 4 ml of 25% ammonia and 100 ml of an 8% solution of  $\text{NH}_4\text{NO}_3$  in water. Pale yellow platelets crystallized out over

TABLE I  
Crystal data for  $\text{Cd}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 0.5 \text{H}_2\text{O}$

Crystal system	orthorhombic
Unit cell parameters, nm	$a$ 0.7622(4) <sup>a</sup> $b$ 1.4992(13) $c$ 0.8961(6)
Space group	<i>Imma</i>
Volume of a unit cell, nm <sup>3</sup>	1.0240(8)
<i>Z</i>	4
Density, Mgm <sup>-3</sup>	$d_o$ 2.07(4) $d_c$ 2.066
$\mu(\text{MoK}_\alpha)$ , cm <sup>-1</sup>	38.26
$F(000)$	612

<sup>a</sup> The numbers in brackets are the standard deviation.

TABLE II  
Experimental conditions for intensity measurements

Temperature, K	293
Crystal shape and size, mm	platelets, 0.44 × 0.32 × 0.07
Diffractometer	Enraf-Nonius CAD-4
Scanning technique	$\omega - 2\theta$
Angle width	(2.4 + 0.35 tg $\theta$ )°
Radiation, nm	MoK $\alpha$ , 0.071069
Monochromatization	graphite
Scanning range of 2 $\theta$	0–90°
Control of intensity measurement	3 reflections ( $2\bar{4}4$ , $\bar{4}40$ , 523) remeasured after each 97 reflections
Number of measured reflections	2 264
Conditions for observed reflection	$I \geq 4 \sigma_I$
Number of observed reflections	1 508

several days. Their composition was controlled by CHN analysis using a Hewlett-Packard 185 CHN Analyzer. For  $C_4H_7CdN_6NiO_{0.5}$  (318.2) calculated: 15.10% C, 2.22% H, 26.41% N; found: 15.19% C, 2.06% H, 26.98% N.

The crystals were subjected to preliminary study using a precession camera and a retigraph with  $CuK_{\alpha}$  radiation. The observed systematic extinctions were in agreement with the *Imma* space group in which the crystal structure of *II* was solved. The noncentrosymmetric space group *Ima2* was also tested during the refining. In this space group, the *R* value did not change and a correlation was observed between the parameters of atoms "connected through the centre of symmetry". Thus, further refinement was carried out in the centrosymmetric space group.

The precise lattice parameters with their standard deviations were obtained using the Tournarie program<sup>4</sup> from the diffractometric positions of 15 reflections, with a  $\theta$  value in the range  $11.01^\circ < \theta < 18.84^\circ$ . The crystal density was determined by the immersion method in a mixture of acetone and bromoform. The crystallographic data are given in Table I and the experimental conditions for the intensity measurements are given in Table II.

A total of 1 508 independent observed reflections were employed for analysis of the crystal structure of *I*. The intensities were corrected for the Lorentz and polarization factors and correction was carried out for absorption. The crystal used for the intensity measurements was defined by the following planes (the numbers in brackets are the distances in mm of the crystal planes from the origin inside the crystal):  $\pm 001$  (0.031),  $\pm 120$  (0.160),  $\pm 100$  (0.255),  $\pm 010$  (0.191),  $\pm \bar{1}20$  (0.218).

The positions of the Ni atoms in *II* were used as an initial model. The Fourier map obtained was employed to obtain the positions of all the other atoms (except for the hydrogen atoms which were not included in the refinement). The positions of the atoms were refined by the least squares method, where the function  $\sum w(F_o - |F_c|)^2$  was minimized for  $w = 1$ . Refinement from the isotropic temperature factors converged to  $R = 0.169$ . Introduction of the coefficients of the anisotropic temperature factors (symmetry limitation was obtained from the literature (ref.<sup>5</sup>)) for the Cd and Ni atoms decreased the *R* factor to a value of 0.052 and to a value of  $R = 0.038$  for all the refined atoms. The value of the weighted *R* factor was  $R_w = 0.045$  for  $w = [\sigma(F_o)]^{-2}$ . The shift in all the parameters was less than  $0.007\sigma$  in the last refinement cycle. At this stage in the refinement, the calculated differential Fourier map exhibited an anomalous maximum ( $1\ 800\ e\ nm^{-3}$ ) and minimum ( $-1\ 500\ e\ nm^{-3}$ ) around the Cd atom. An analogous anomalous situation was found around the Ni atom, where the maximum had a value of  $1\ 250\ e\ .\ nm^{-3}$ . No explanation was found for these observations.

The atomic factors were taken from ref.<sup>6</sup>. Correction was made for anomalous scattering. All the calculations were carried out using the SHELX '76 program (ref.<sup>7</sup>) in the computer centre at the University of Poitiers (CICUP) and Orsay (CIRCE). Tables of the observed and calculated values of the structure factors can be obtained on request from the authors.

## RESULTS AND DISCUSSION

The final fractional coordinates of the atoms and coefficients of the anisotropic temperature factors are listed in Table III. The crystal structure of compound *I* consists of infinite layers of the  $[Cd(NC)_4Ni]_{\infty}$  type deformed into a wave shape (Fig. 1). A similar deformation has been observed (in addition to the structure of compound *II*) in inclusion compounds  $Cd(NH_2C_2H_4OH)_2Ni(CN)_{4.2}C_4H_4NH$  (ref.<sup>8</sup>),  $Cd(NH(CH_3)_2)_2Ni(CN)_4 \cdot G$  ( $G = o, m, p\text{-}CH_3C_6H_4NH_2$ ) (ref.<sup>9</sup>), and  $Cd \cdot (NH(CH_3)_2)_2Ni(CN)_4 \cdot 0.5\ C_6H_6$  (ref.<sup>10</sup>), where the above described layers are

TABLE III

Fractional coordinates ( $\cdot 10^4$ ) and coefficients of anisotropic temperature factors ( $\cdot 10^4 \text{ nm}^2$ ) of the atoms in  $\text{Cd}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 0.5 \text{ H}_2\text{O}$ .  
The temperature factor is in the form  $T = \exp [-2\pi^2(U_{11}a^{*2}h^2 + \dots + 2U_{12}a^*b^*hk)]$

Atom	Wyckoff positional notation	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Cd	4(a)	0	0	0	1.53(1)	1.87(1)	3.90(2)	0.13(1)	0	0
Ni	4(e)	5 000	2 500	425(1)	1.29(2)	1.40(2)	5.22(4)	0	0	0
N1	16(j)	2 215(3)	1 081(2)	304(3)	2.63(9)	2.98(9)	6.60(18)	-0.13(10)	0.04(9)	-1.02(8)
C	16(j)	3 266(3)	1 626(1)	379(3)	1.86(7)	1.94(8)	5.39(15)	-0.11(8)	0.07(8)	-0.12(6)
N2	8(h)	0	-271(3)	2 545(18)	3.94(18)	6.15(22)	3.90(19)	0.70(19)	0	0
O <sup>a</sup>	4(e)	0	2 500	7 949(19)	10(1)	6.0(8)	10(1)	0	0	0

<sup>a</sup> The occupation factor for the oxygen atom is 1/2.

present in various arrangements. On the other hand, it was found for other compounds that layers of the  $[M(CN)_4Ni]_{\infty}$  type are coplanar, for example in a clathrate of the Hofmann type,  $Cd(NH_3)_2Ni(CN)_4 \cdot 2 C_6H_6$  (ref.<sup>11</sup>) or in  $Ni(NH_3)_2Ni(CN)_4$

TABLE IV

Interatomic distances (in nm) and angles (in°) in  $Cd(NH_3)_2Ni(CN)_4 \cdot 0.5 H_2O$

Cd octahedral		Ni square planar		CN <sup>-</sup> group	
Cd—N1	0.2356(2)	Ni—C	0.1862(2)	C—N	0.1146(3)
Cd—N2	0.2316(4)	C—Ni—C''	89.5(1)	Ni—C—N1	177.7(3)
N1—Cd—N1'	88.5(1)			Cd—N1—C	176.3(3)
N1—Cd—N2	89.6(1)				

Symmetry codes: '  $\bar{x}, \bar{y}, \bar{z}$ ; "  $x, \frac{1}{2} - y, z$ .

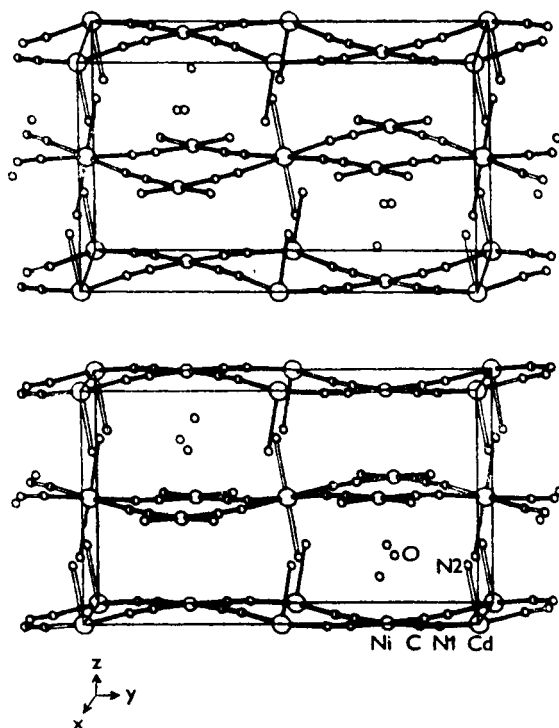


FIG. 1

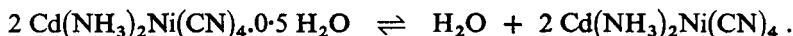
Stereoscopic view of the structure of  $Cd(NH_3)_2Ni(CN)_4 \cdot 0.5 H_2O$

(ref.<sup>12</sup>). Layers of the  $[\text{Cd}(\text{NC})_4\text{Ni}]_\infty$  type are located perpendicular to the  $c$ -axis so that the  $\text{NH}_3$  molecules bonded to the Cd atom are oriented into the centre of the square cavities in the neighbouring layer.

The Ni atom has square coordination. Four  $\mu$ -cyano groups are bonded through their N(N1) atoms to 4 different Cd atoms. The coordination polyhedron of the Cd atom is completed by two  $\text{NH}_3$ (N2) molecules bonded in the axial positions. The  $\text{CdN}_6$  octahedron is slightly flattened so that the Cd—N2 bond is shorter than the Cd—N1 bond (Table IV).

The bonding distances and bond angles have the usual values found in similar compounds, for example, in  $\text{Cd}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2 \text{C}_6\text{H}_6$  (ref.<sup>11</sup>). The values obtained are more precise than those for compound II, for example (in brackets are the values for II):  $\text{C}\equiv\text{N}$  0.1146(3) (0.115(3)) nm, Ni—C 0.1862(2) (0.186(4)) nm.

The positions of the  $\text{H}_2\text{O}$  molecules were found unambiguously. Two water molecules occupy four equivalent positions (4e) in the unit cell. They are located between the layers and produce deformation of these layers. The shortest observed distances Ni $\cdots$ OH<sub>2</sub> 0.3023(2) nm and NH<sub>3</sub> $\cdots$ H<sub>2</sub>O 0.3371(1) nm confirm the absence of valence bonds between the H<sub>2</sub>O molecule and an atom in the layers. The distance of 0.3371(1) nm between the H<sub>2</sub>O and NH<sub>3</sub> molecules is too long for this to be considered as a hydrogen bond. These results confirm the zeolitic character of the water molecules and explain the reversibility of the process



The reversibility of this process indicates that the layers do not change during this process. Similar layer retention was observed for the thermal decomposition of  $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2 \text{C}_6\text{H}_6$ , with loss of the guest molecule<sup>13</sup>.

It can be seen from Table III that coefficients  $U_{33}$  of the atoms forming the layers are 2–3 times larger than the values of  $U_{11}$  and  $U_{22}$ . This can be explained on the basis of large anisotropy of thermal motion; the  $x$  and  $y$  directions define layers where strong bonds are present, the  $z$  direction remains relatively free during thermal motion. Large  $U_{ii}$  values were expected for the oxygen atom because of the zeolitic character of the water molecule and the presence of only van der Waals forces. The large anisotropy of thermal motion can be the reason for the relatively large value of the  $R$  factor for isotropic refinement of the crystal structure.

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