Ni(en)₂Ni(CN)₄.nH₂O (n = 2·16): Structure and Molecular-Mechanics Investigation of Hydrogen Bonding

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Abstract. *catena*-Poly[bis(ethylenediamine)nickel]-μ-(cyano-*N*:*C*)-[bis(cyano-*C*)nickel]-μ-(cyano-*C*:*N*)] 2·16 hydrate, [Ni(C₂H₈N₂)₂(μ-NC)Ni(CN)₂(μ-CN)].-2·16H₂O, $M_r = 380·60$, orthorhombic, *Pnna*, $a = 28·107\,(3)$, $b = 8·399\,(3)$, $c = 14·571\,(4)$ Å, $V = 3440\,(2)$ Å³, $Z = 8$, $D_m = 1·49\,(1)$, $D_x = 1·47$ Mg m⁻³, λ(Cu $K\bar{\alpha}) = 1·54178$ Å, $\mu = 2·830$ mm⁻¹, $F(000) = 1580·8$, $T = 293$ K, $R = 0·0679$ for 1191 reflections. The structure consists of infinite zigzag chains parallel to the *x* axis. The chains are formed by *trans*-Ni(en)₂-μ-(NC)₂, *cis*-μ-(NC)₂Ni(CN)₂ and *cis*-μ-(CN)₂Ni(en)₂ groups, the Ni coordination numbers being six, four and six, respectively (en = 1,2-diaminoethane). Four water molecules are not part of the coordination sphere of Ni, but they constitute a network of hydrogen bonds. Their positions are only partially occupied. The possible full occupancy corresponds to $n = 3$. Molecular-mechanics investigation describes the hydrogen-bond contact scheme. This complex is the first known case of a structure in which *cis*- as well as *trans*-[Ni(en)₂*X*₂] complexes are present.

Introduction. During studies relating to the preparation, thermal properties and crystallochemistry of tetracyanoniccolates(II) seven different complexes of the type Ni(en)ₓNi(CN)₄.nH₂O (en = 1,2-diaminoethane, $x = 1–3$, $n = 0–2·5$) were prepared from the system Niᴵᴵ–en–[Ni(CN)₄]²⁻–H₂O. The anhydrous complexes as well as the complexes with $x = 1$ or 2 could be prepared by thermal decomposition reactions of hydrates or complexes with $x = 3$ (Čerňák, Chomič & Potočňák, 1989). This group of complexes provides a good opportunity to study the structure changes occurring during heating.

By using the molar ratio Niᴵᴵ: en = 1:2·5 during the preparation, two crystalline products of composition Ni(en)₂Ni(CN)₄ (very good X-ray quality) and Ni(en)₂Ni(CN)₄.2·5H₂O (poor X-ray quality) were isolated. Ni(en)₂Ni(CN)₄ has a chain structure in which the bridging cyano groups are in *trans* positions not only in the complex cation but also in the complex anion (Čerňák, Chomič, Baloghová & Dunaj-Jurčo, 1988). The IR spectrum and the measured magnetic moment of Ni(en)₂Ni(CN)₄.2·5H₂O show that it is paramagnetic, contains terminal as well as bridging cyano groups and the water molecules are not coordinated to the central atoms. At the same time the X-ray diffraction pattern of the product obtained by dehydration of Ni(en)₂Ni(CN)₄.2·5H₂O shows that it differs from the anhydrous complex, the structure of which was solved (Čerňák, Chomič & Potočňák, 1989). The aim of this study has been to solve the crystal structure of Ni(en)₂Ni(CN)₄.2·5H₂O and to elucidate the role of the water molecules in this structure by using X-ray structure analysis and molecular mechanics.

Experimental. The plate shaped light-violet microcrystals were twinned along the plane (100) and cracked along the plane (010). D_m by flotation. The monocrystal (0·03 × 0·17 × 0·30 mm), sealed in a glass capillary in order to prevent the escape of the water molecules, was mounted on a Siemens AED diffractometer (nickel-filtered Cu $K\bar{\alpha}$ radiation, $\lambda = 1·54178$ Å) controlled by a computer. The crystallographic system and space group are according to analysis; lattice parameters were from angle values of 23 reflections (19·21 ≤ θ ≤ 39·19°); data were collected at laboratory temperature by θ–2θ technique; a check reflection was measured after 50 measurements without significant change; Lorentz and polarization corrections were applied, data were adjusted to a consistent scale. Absorption corrections were applied following the method of Walker & Stuart (1983) by using the program *ABSORB* (Ugozzoli, 1987). The absorption coefficients calculated in the polar angles of the incident and diffrac-

ted beam range from 1·254 to 0·799. 3362 reflections were collected; of these, 2943 were unique; 1191 reflections were observed [$F_o \geq 3\sigma(F_o)$] ($3\cdot0 \leq \theta \leq 65\cdot0°$, $0 \leq h \leq 33$, $0 \leq k \leq 9$, $0 \leq l \leq 17$). *SHELXS*86 (Sheldrick, 1986) was used for localization of the heavy atoms, other non-H atoms were found from a difference Fourier map. The site occupation factors of the O atoms were estimated from the difference Fourier map, following the method of Hanic (1989). The electron densities corresponding to the O atoms were summed and then normalized. It must be noted that the electron densities for atoms O(3) and O(4) had a considerably more dispersed shape in comparision with the electron densities for atoms O(1) and O(2), which manifests itself in the high thermal parameters of these atoms. The anisotropic refinement was performed with a full matrix by using the least-squares method and *SHELX*76 (Sheldrick, 1976). From the difference map calculated at the end of the refinement only some of the H atoms of en could be seen and the attempt at their positional refinement failed. Thus the H atoms of en where placed in calculated positions. The weighting scheme $w = [\sigma^2(F_o)]^{-1}$ in the last cycles was changed to $w = k/[\sigma^2(F_o) + 0\cdot0007F_o^2]$ ($k = 0\cdot8231$), which showed no systematic shifts as a function of F_o. Final $R = 0\cdot0679$, $S = 1\cdot13$ (198 parameters varied), $wR = 0\cdot0682$; $(\Delta/\sigma)_{max} = 0\cdot08$; empirical extinction parameter $g = 9$ (2) $\times 10^{-8}$; remaining electron density was within the range $-0\cdot54$ to $0\cdot51$ e Å^{-3}; atomic scattering factors and corrections for dispersion were taken from *SHELX*76 (Sheldrick, 1976) (for C, H, N, O) and *International Tables for X-ray Crystallography* (1974, Vol. IV) (Ni). The geometrical analysis was performed with the program *PARST* (Nardelli, 1983) and calculated on the Gould computer in the CNR centre in Parma and the EC 1045 computer at the Technical University in Košice. The molecular-mechanics calculations were performed using the original code *ALTAMIRA* (Ori, 1987) on an IBM-RT machine. The experimental dehydration energy was measured on a Perkin-Elmer DSC 2a.

Discussion. The fractional coordinates of the atoms are given in Table 1 while the values of the bond lengths and angles are in Table 2.*

The structure consists of infinite zigzag chains parallel with the x axis, and non-coordinated water molecules (Fig. 1). In the chain there are three crystallographically and stereochemically non-equivalent atoms of Ni and two of them, Ni(1) and

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53107 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (Å$^2 \times 10^2$) for non-H atoms, with e.s.d.'s in parentheses*

	x	y	z	U_{eq}*	k†
Ni(1)	0	5000	0	3·7 (1)	0·50
Ni(2)	2500	5000	1187 (2)	3·9 (1)	0·50
Ni(3)	969 (1)	4498 (2)	2866 (1)	3·8 (1)	
O(1)	1038 (4)	5893 (13)	6193 (9)	7·3 (5)	0·83
O(2)	1595 (7)	7500	7500	10·5 (1·1)	0·36
O(3)	2156 (11)	4977 (45)	8141 (17)	20·2 (2·0)	0·50
O(4)	1867 (10)	3104 (49)	6616 (29)	23·8 (2·6)	0·47
N(11)	271 (4)	2803 (13)	−432 (7)	4·4 (4)	
N(12)	448 (4)	5879 (12)	−1036 (7)	4·2 (5)	
N(21)	3045 (4)	4813 (15)	201 (6)	5·1 (5)	
N(22)	2509 (4)	2487 (13)	1094 (6)	4·9 (4)	
N(31)	1382 (4)	3519 (17)	4687 (8)	6·5 (6)	
N(32)	−36 (4)	4342 (14)	3508 (8)	6·6 (5)	
N(33)	551 (3)	5174 (14)	1019 (7)	4·6 (4)	
N(34)	1956 (4)	4914 (14)	2161 (7)	5·0 (4)	
C(11)	503 (6)	3040 (21)	−1315 (11)	7·2 (8)	
C(12)	760 (5)	4566 (21)	−1323 (10)	6·9 (7)	
C(21)	3188 (6)	3149 (22)	184 (12)	8·4 (8)	
C(22)	2801 (6)	2059 (19)	298 (11)	7·3 (7)	
C(31)	1216 (4)	3917 (19)	4002 (10)	5·1 (6)	
C(32)	356 (5)	4367 (17)	3276 (9)	4·9 (5)	
C(33)	725 (4)	4951 (19)	1717 (9)	4·4 (5)	
C(34)	1577 (4)	4758 (17)	2441 (19)	4·4 (5)	

*$U_{eq} = (U_{11} + U_{22} + U_{33})/3$.
†Site occupation factor, given if different from unity.

Table 2. *Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses*

Ni(1)—N(11)	2·093 (11)	Ni(2)—N(21)	2·106 (10)
Ni(1)—N(12)	2·100 (11)	Ni(2)—N(22)	2·115 (11)
Ni(1)—N(33)	2·150 (9)	Ni(2)—N(34)	2·087 (11)
Ni(3)—C(31)	1·860 (14)	Ni(3)—C(32)	1·827 (14)
Ni(3)—C(33)	1·849 (13)	Ni(3)—C(34)	1·831 (12)

N(11)—Ni(1)—N(12)	82·9 (4)	N(21)—Ni(2)—N(22)	82·7 (4)
N(11)—Ni(1)—N(33)	90·3 (4)	N(21)—Ni(2)—N(34)^i	86·2 (4)
N(12)—Ni(1)—N(33)	92·3 (4)	N(22)—Ni(2)—N(34)	91·0 (4)
		N(34)—Ni(2)—N(34)^i	94·4 (4)
C(31)—Ni(3)—C(32)	92·6 (6)	C(31)—Ni(3)—C(33)	176·6 (7)
C(31)—Ni(3)—C(34)	89·1 (5)	C(32)—Ni(3)—C(33)	87·6 (6)
C(32)—Ni(3)—C(34)	176·5 (6)	C(33)—Ni(3)—C(34)	90·9 (5)

N(11)—C(11)	1·46 (2)	N(21)—C(21)	1·45 (2)
C(11)—C(12)	1·47 (2)	C(21)—C(22)	1·43 (2)
C(12)—N(12)	1·47 (2)	C(22)—N(22)	1·47 (2)
C(31)—N(31)	1·15 (2)	C(32)—N(32)	1·15 (2)
C(33)—N(33)	1·14 (2)	C(34)—N(34)	1·15 (2)

Ni(1)—N(11)—C(11)	108·0 (9)	Ni(2)—N(21)—C(21)	106·5 (9)
N(11)—C(11)—C(12)	110 (1)	N(21)—C(21)—C(22)	114 (1)
C(11)—C(12)—N(12)	111 (1)	C(21)—C(22)—N(22)	111 (1)
C(12)—N(12)—Ni(1)	107·4 (9)	C(22)—N(22)—Ni(2)	107·6 (9)
Ni(3)—C(31)—N(31)	177 (1)	Ni(3)—C(32)—N(32)	177 (1)
Ni(3)—C(33)—N(33)	176 (1)	Ni(3)—C(34)—N(34)	179 (1)
C(33)—N(33)—Ni(1)	155·6 (9)	C(34)—N(34)—Ni(2)	158 (1)

Symmetry code: (i) $0\cdot5 - x$, $1 - y$, z.

Ni(2), occupy special positions. The Ni atoms are joined to one another by bridging cyano groups (Fig. 2). The coordination numbers of Ni(1) (symmetry of position: $\bar{1}$) and Ni(2) (symmetry of position: 2) atoms are both six. Four positions are occupied by two chelate-bonded en molecules and two positions by two N-bonded bridging cyano groups. The difference in the coordination polyhedra of atoms

Ni(1) and Ni(2) involves the fact that the bridging cyano groups are linked in *trans* positions to Ni(1), as similarly observed for the anhydrous complex, while they are linked in *cis* positions to Ni(2). According to the Cambridge Structural Database (Allen, Bellard, Brice, Cartwright, Doubleday, Higgs, Hummelink, Hummelink-Peters, Kennard, Motherwell, Rodgers & Watson, 1988), this is the first known case of a complex Ni(en)$_2X_2$ containing
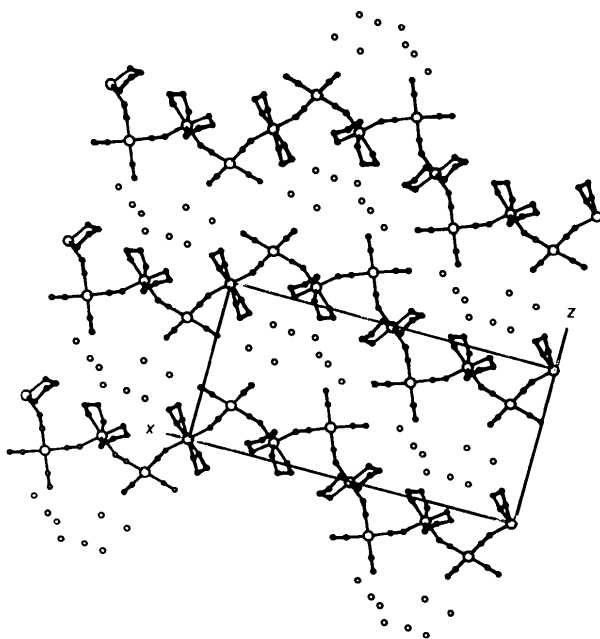

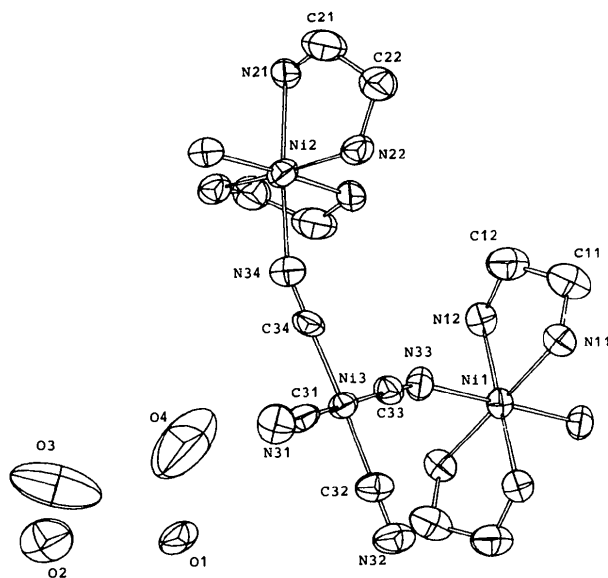Fig. 1. A projection of the structure (*PLUTO*; Motherwell, 1976).

Fig. 2. *ORTEP* diagram (Johnson, 1965) with atom-numbering scheme showing the coordination of the Ni atoms. H atoms have been omitted for clarity.

en in which both *cis* and *trans* isomers are present in a single structure. The linkage of bridging cyano groups in the *cis* position in a complex cation was observed in tetracyanoniccolates(II) only for Cd(en)$_2$Ni(CN)$_4$ (Jameson, Bachmann, Oswald & Dubler, 1981).

The en molecules in both coordination polyhedra are in the *gauche* conformation. The angle between the planes N(11)—Ni(1)—N(12) and C(11)–Ni(1)–C(12) is 25·6 (7)° while this value is 24·1 (8)° for planes N(21)—Ni(2)—N(22) and C(21)–Ni(2)–C(22). These values are comparable with the value of 29·6 (3)° found for the anhydrous complex (Černák, Chomič, Baloghová & Dunaj-Jurčo, 1988).

The atom Ni(3) is square coordinated by four cyano groups of which two are bridging and in the *cis* position in contrast to the anhydrous complex in which the bridging cyano groups are in *trans* positions.

There are four crystallographically non-equivalent water molecules in the structure. They are not coordinated to the central atoms and function as solvent molecules. Atoms O(1) and O(4) occupy general positions, atom O(2) is in a special position (symmetry 2) and atom O(3) is disordered in two positions which are joined by a 2 axis. The distance between these two positions is 1·93 (4) Å. The O atom positions are partially occupied. At the possible full occupancy the complex should behave as a trihydrate. The value $n = 2·5$ was found by thermal analysis, which is comparable with the value obtained by summing the estimated site occupation factors ($n = 2·16$). As can be seen from Fig. 3 and Table 3 there is a possibility for the formation of four hydrogen bonds in the case of the O(1) and O(2) water molecules. On the other hand, although four contacts in the range 2·77 to 3·14 Å were observed in the case of the O(3) and O(4) water molecules, from a stereochemical point of view the formation of only three hydrogen bonds can be expected. These observations suggest the presence of a hydrogen-bond system, which could contribute to the stabilization of the structure formed. The formation of a hydrogen-bond system was confirmed by the observation of a typical broadening of the ν(OH) peak in the region 3630–3000 cm^{-1} in the IR spectrum of the complex studied (Černák, Chomič & Potočňák, 1989).

Besides the contacts reported in Table 3 there are only two contacts shorter than 3·4 Å. The first is the contact N(12)···N(32) [3·20 (2) Å] and the second is N(11)···N(32) [3·36 (2) Å], but the observed values of the angles N—H···N [115·0 (6) and 124·6 (6)°] do not indicate the presence of hydrogen bonds.
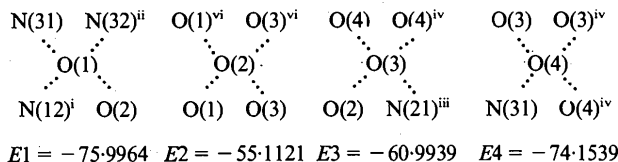
The observed values of bond lengths and angles are comparable with the values obtained for the anhydrous complex Ni(en)$_2$Ni(CN)$_4$ (Černák, Chomič, Baloghová & Dunaj-Jurčo, 1988). As for

intermolecular contacts, we have to mention the relatively short distance between atoms Ni(3) and Ni(3)^i [symmetry code: (i) x, $0.5-y$, $0.5-z$] 3·522 (3) Å. However, this value is too high to represent a bond interaction.

In order to explain the physical behaviour of the water molecules, using the technique of molecular mechanics, the interaction energy between the four water molecules and the polymeric chains has been derived.

With the usual structural constraints [d(O—H) = 0·958 Å and H—O—H angle of 105°] imposed on the four water molecules, the potential energy of the system has been calculated taking into account van der Waals and Pauli forces, described by the Lennard–Jones 6–12 formula. The N$\cdots$H and O$\cdots$H hydrogen-bond (HB) contributions have been introduced employing a reparametrized Morse function $U_{HB}(r) = D\{1 - \exp[\ln 2(r - r_0)/(r_1 - r_0)]\}^2 - D$ where D is the coupling constant, r is the distance between the interacting atoms, r_0 is the equilibrium distance and r_1 is the distance at which $U_{HB}(r_1) = 0$. In the present work the following values have been adopted: $D = 16.75$ kJ mol^{-1}; $r_0 = 1.8$, $r_1 = 1.5$ Å. The calculations have been performed allowing the water molecules to rotate freely (with the specified geometry) in order to minimize the system potential energy.

The resulting following map shows the HB network which affects the four water molecules and the global lattice–molecule interaction energies (kJ mol^{-1}) (see Fig. 3. for symmetry code):

N(31) N(32)^{ii} O(1)^{vi} O(3)^{vi} O(4) O(4)^{iv} O(3) O(3)^{iv}

    O(1)   O(2)   O(3)   O(4)

N(12)^i O(2)   O(1) O(3)   O(2) N(21)^{iii} N(31) O(4)^{iv}

$E1 = -75.9964$ $E2 = -55.1121$ $E3 = -60.9939$ $E4 = -74.1539$

It is remarkable that the O(2) water molecule exhibits resonant behaviour between two geometrical arrangements where a pair of O(2)$\cdots$O(1) and O(2)$\cdots$O(3) HB's have a high energy (-14.5884 and -12.8121 kJ mol^{-1}, respectively) whereas the remaining two HB's are low energy contacts (-2.5410 and -3.3693 kJ mol^{-1}, respectively). In the minimum-system-energy configuration one of the O(3)$\cdots$O(4) and the O(1)$\cdots$N(31) HB's are very weak. This energetic investigation confirms the HB scheme previously proposed on the basis of the structural analysis (see Table 3 and Fig. 3).

The four water molecules are guests in the large crystalline channel (see Fig. 1) and therefore, from a topological point of view, they have the ability to leave the host lattice. Moreover, it is reasonable to expect that the intrawater HB's suffer the destabilizing action of the high temperature more than the O$\cdots$N HB's. So as a result the O(1) water is the best candidate for higher occupancy as a consequence of it having both the strongest interactions and two strong HB's with framework N atoms. The remaining molecules, showing weaker interactions and almost three interwater contacts, tend therefore to have lower occupation factors. Initial evidence for the validity of these considerations arises from the fact that the calculated energy sequence $-E_1 > -E_4 > -E_3 > -E_2$ is in good agreement with the experimental occupation coefficients (see Table 1), $K_1 > K_3 \geq K_4 > K_2$ suggesting that the crystal prefers to release the water molecules, less destabilizing its structure. The E_i ($i = 1...4$) quantities have been obtained for a structure with complete water occupancy [that means $K_i = 1$, except in the O(3) case which exhibits a short O(3)$\cdots$O(3) contact implying $K_3 = 0.5$]. A more realistic analysis of the behaviour of the water molecules must take into account the effects due to the experimental K_i factors. The absence of a water
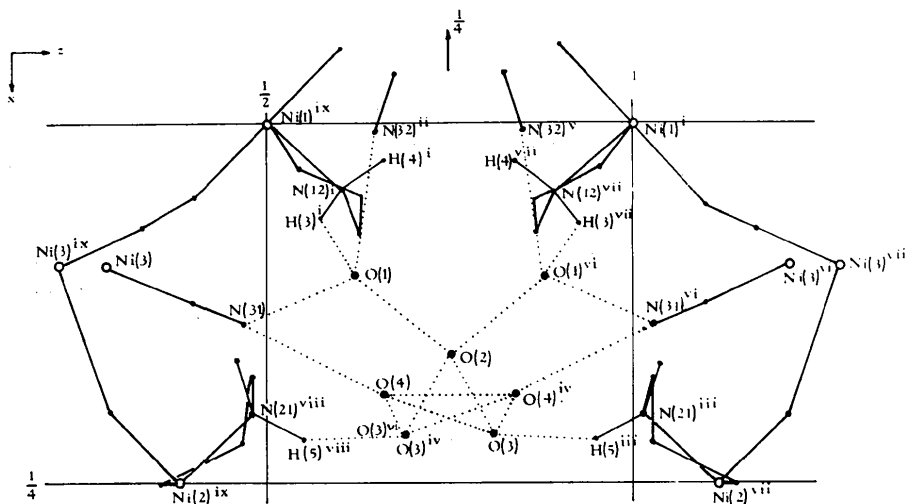

Fig. 3. A projection of the structure into the plane xz showing the hydrogen bonds and other contacts (dotted lines) less than 3·5 Å. Symmetry code: (i) $x, 1.5 - y, 0.5 - z$; (ii) $-x, 1 - y, 1 - z$; (iii) $0.5 - x, 1 - y, 1 + z$; (iv) $x, 0.5 - y, 1.5 - z$; (v) $-x, 0.5 + y, 0.5 + z$; (vi) $x, 1.5 - y, 1.5 - z$; (vii) $x, y, 1 + z$; (viii) $0.5 - x, 0.5 + y, 0.5 - z$; (ix) $x, 0.5 + y, 0.5 - z$.

Table 3. *Hydrogen bonds and interatomic contacts* (Å) *less than* 3·4 Å, *and hydrogen bond angles* (°)

O(1)···O(2)	2·81 (2)	O(2)···O(1)	2·81 (2)
···N(31)	3·12 (2)	···O(3)	2·80 (4)
···N(32)^{ii}	2·86 (2)	···O(1)^{vi}	2·81 (2)
···N(12)^i	3·19 (2)	···O(3)^{vi}	2·80 (4)

N(12)—H(3)···O(1) 141·3 (6)

O(3)···O(4)	2·84 (5)	O(4)···O(3)	2·84 (5)
···O(4)^{iv}	2·74 (5)	···O(3)^{iv}	2·74 (5)
···O(2)	2·80 (4)	···O(4)^{iv}	2·77 (6)
···N(21)^{iii}	3·06 (3)	···N(31)	3·14 (4)

N(21)—H(5)···O(3) 157 (1)

Symmetry code: (i) $x,1·5-y,0·5-z$; (ii) $-x,1-y,1-z$; (iii) $0·5-x,1-y,1+z$; (iv) $x,0·5-y,1·5-z$; (vi) $x,1·5-y,1·5-z$.

molecule implies generally a rearrangement in the energy E_w of the water molecules set according to $E_w = (e_1 + H_{12}K_2)K_1 + [e_2 + H_{12}^{vi}K_1 + (H_{23} + H_{23}^{vi})K_3]K_2 + [e_3 + (H_{34} + H_{34}^{iv})K_4]K_3 + (e_4 + H_{43}^{iv}K_3 + H_{44}^{iv}K_4)K_4$ where: H_{ij} are the contributions to E_i arising from the HB's between i and j water molecules and e_i are the remaining parts of E_i. In this expression the K_i coefficients are coupled, affecting with their mutual influence both the single molecule energy and the global energy E_w. By making the approximation that $-E_w$ corresponds to the dehydration energy, employing the occupation coefficients of Table 1, and deriving from the E_i quantities the e_i and H_{ij} values, one obtains $-E_w = 284$ J g^{-1} which is in very good agreement with the experimental value of 279 J g^{-1}. This last computation supports the accuracy of the crystallographic work and the efficiency of the computational model (Ori, 1987).

On the basis of the known crystal structure of Ni(en)$_2$Ni(CN)$_4$ (Černák, Chomič, Baloghová & Dunaj-Jurčo, 1988) and the results obtained in this

work we may draw the conclusion that two different kinds of chains are formed in the synthesis under equivalent experimental conditions and the solvating water molecules are likely to play an important part in the stabilization of one type of chain.

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Azoles. 28. Structure of the Molecular Complex of 3,5-Dinitroindazole with Pyrrolidine (1/1)

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Abstract. 3,5-Dinitro-1*H*-indazole–pyrrolidine (1/1), (C$_7$H$_4$N$_4$O$_4$.C$_4$H$_9$N)$_2$, $M_r = 558·51$, monoclinic,

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$P2_1/n$, $a = 19·917$ (3), $b = 9·751$ (1), $c = 6·703$ (1) Å, $\beta = 90·90$ (1)°, $V = 1301·6$ (3) Å^3, $Z = 2$, $D_m = 1·42$ (1), $D_x = 1·425$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 0·846$ mm^{-1}, $F(000) = 584$, room