

Three different bonding modes of cyano groups in the coordination polymer $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})][\text{Cu}(\text{en})_2\text{Ni}_2\text{Cu}_2(\text{CN})_{10}]\cdot 2\text{H}_2\text{O}$ (en is 1,2-diaminoethane)

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Received 10 October 2001

Accepted 21 December 2001

Online 20 February 2002

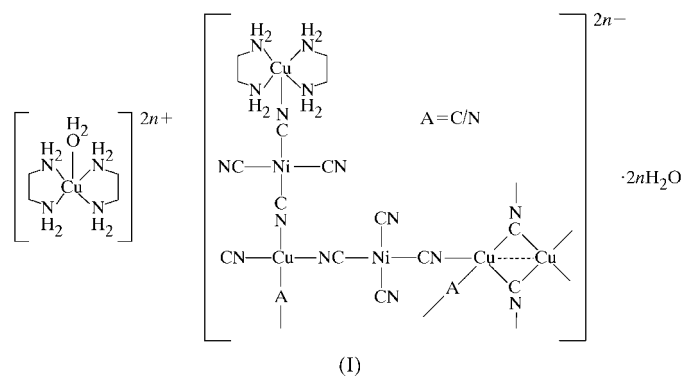
Partial reduction of the Cu^{II} ions in the aqueous system $\text{Cu}^{\text{II}}\text{-en-}[\text{Ni}(\text{CN})_4]^{2-}$ (1/1/1) (en is 1,2-diaminoethane) yields a novel heterobimetallic mixed-valence compound, poly[[aqua-bis(1,2-diaminoethane)copper(II)] [hexa- μ -cyano-tetracyano-bis(1,2-diaminoethane)tricopper(I,II)dinickel(II)] dihydrate], $[\text{Cu}(\text{C}_2\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})][\text{Ni}_2\text{Cu}_3(\text{CN})_{10}(\text{C}_2\text{H}_8\text{N}_2)_2]\cdot 2\text{H}_2\text{O}$ or $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})][\text{Cu}(\text{en})_2\text{Ni}_2\text{Cu}_2(\text{CN})_{10}]\cdot 2\text{H}_2\text{O}$. The structure is formed by a negatively charged two-dimensional array of the cyano complex $[\text{Cu}(\text{en})_2\text{Ni}_2\text{Cu}_2(\text{CN})_{10}]^{2n-}$, $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})]^{2+}$ complex cations and water molecules of crystallization. These last are involved in a complicated hydrogen-bonding system. The cyano groups act as terminal, μ_2 -bridging or μ_3 -bridging ligands.

Comment

Because of the tendency of a cyano group to bridge two metal centres, cyano complexes can be used as building blocks in the construction of compounds possessing varying degrees of dimensionality (Vahrenkamp *et al.*, 1997; Iwamoto, 1996; Verdaguer *et al.*, 1999; Ohba & Okawa, 2000; Černák *et al.*, 2001). Compounds of this type containing paramagnetic central atoms are often the subject of magnetic investigations (Weihe & Güdel, 2000; Verdaguer *et al.*, 1999; Dunbar & Heintz, 1997; Kitazawa *et al.*, 1996; Ma *et al.*, 2001; Trávníček *et al.*, 2001). Such studies may contribute to the understanding of fundamental physical issues, *e.g.* the role of antiferromagnetic spin fluctuations in high-temperature superconductors (Affleck *et al.*, 1987; Khurana, 1988) or the possible practical application of novel molecular devices (Kahn, 1994; Dagotto, 1996).

We are interested in the preparation, crystal structure and magnetic properties of low-dimensional compounds based on

cyano complexes, which are used as bridges in linking paramagnetic centres (Černák *et al.*, 2001). To date, starting from the aqueous system $\text{Cu}^{\text{II}}\text{-en-}[\text{Ni}(\text{CN})_4]^{2-}$, only one product has been isolated, with composition $\text{Cu}(\text{en})_2\text{Ni}(\text{CN})_4$ (Dunaj-Jurčo *et al.*, 1976). This compound possesses a one-dimensional crystal structure (Lokaj *et al.*, 1991; Seitz *et al.*, 2001), but its spins behave as a two-dimensional magnet at low temperatures (Orendáč *et al.*, 1995). On the other hand, numerous compounds have been isolated from the analogous systems containing Ni^{II} , Zn^{II} or Cd^{II} , (Černák *et al.*, 1989, 1993). In addition, the compound $\text{Cu}(\text{H}_2\text{O})_2(\text{en})\text{SO}_4$ was reported to be one-dimensional, with $[\text{Cu}(\text{en})(\text{H}_2\text{O})_2]^{2+}$ cations linked by bridging sulfate anions (Healy *et al.*, 1978). For the work reported here, our goal was to examine the possibility of replacing the sulfate group with a tetracyanonickelate anion. From the above-mentioned system with a Cu-en ratio of 1:1, we isolated the title mixed valence coordination polymeric compound, $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})][\text{Cu}(\text{en})_2\text{Ni}_2\text{Cu}_2(\text{CN})_{10}]\cdot 2\text{H}_2\text{O}$, (I).



The formation of (I) from the aqueous system $\text{Cu}^{\text{II}}\text{-en-}[\text{Ni}(\text{CN})_4]^{2-}$ required partial reduction of Cu^{II} to Cu^{I} by the cyano groups present in the initial solution in the form of the tetracyanonickelate anion (see *Experimental*). The formation of a $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ redox equilibrium is often observed in systems containing Cu^{II} , cyano groups and *N*-donor ligands (Dunaj-Jurčo *et al.*, 1988). The fact that the first crystals appeared in the mother liquor after a week supports the synthetic route presented here and suggests that the equilibrium is achieved slowly.

The structure of (I) is formed by a negatively charged two-dimensional cyano complex array, $[\text{Cu}(\text{en})_2\text{Ni}_2\text{Cu}_2(\text{CN})_{10}]^{2n-}$, $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})]^{2+}$ complex cations and water molecules of crystallization (Fig. 1). In the complicated two-dimensional array can be distinguished a core and side arms, which are directed to the upper and lower sides of the core (Fig. 2). The core is built up of Cu^{I} and Ni^{II} atoms linked by bridging cyano groups, while the side arms exhibit the composition $-\mu\text{-NC-Ni}^{\text{II}}(\text{CN})_2-\mu\text{-CN-Cu}(\text{en})_2$ and are linked to the core *via* bridging cyano groups. The packing of neighbouring two-dimensional arrays leads to channels parallel to [010]. Enclosed in the channels are the $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})]^{2+}$ complex cations and water molecules of crystallization. Therefore, this structure can also be viewed as a host-guest system, with complex cations and water mol-

ecules as the guests placed between the host layers. This structure is unique among cyano complexes.

Atoms Ni1 and Ni2 are both coordinated by four cyano groups. They exhibit square-planar geometry and are thus diamagnetic. Two of the cyano groups, in *trans* positions in each anion, exhibit bridging character. The Ni—C (1.854–1.891 Å) and C≡N (1.132–1.156 Å) distances are close to the ideal values of 1.86 and 1.15 Å, respectively (Sharpe, 1976). The Ni—C—N angles deviate only slightly from linearity (maximum deviation 4.6°). On the other hand, the C11—N11—Cu3 angle from the bridging cyano group is bent considerably [135.2(4)°], but such a situation is not uncommon for a bridging cyano group (Vahrenkamp *et al.*, 1997; Janiak *et al.*, 1999).

Atoms Cu1 and Cu2, as indicated by their distorted tetrahedral coordination geometry and charge balance, are in oxidation state I, and consequently they are diamagnetic. Atom Cu1 is coordinated by three ordered N-oriented bridging cyano groups (mean distance 1.994 Å). The fourth cyano group is disordered, as imposed by the symmetry, and is at the somewhat shorter distance of 1.963 Å. One of the cyano groups, C25—N25, acts as an unsymmetrical μ_3 -cyano ligand, >CN⁻; the N atom coordinates to Cu1, while the C atom coordinates unsymmetrically (2.044 *versus* 2.142 Å) to two different Cu2 atoms related by a symmetry centre. Consequently, these are close together [2.444(1) Å]. A similar situation was found in some cyano-cuprate complexes, *e.g.* [Cu₅(CN)₆(dmf)₄] (dmf is dimethylformamide; Peng & Liaw, 1986) or [Zn(NH₃)_{0.7}(H₂O)_{0.3}Cu(CN)₃] (Černák *et al.*, 1998).

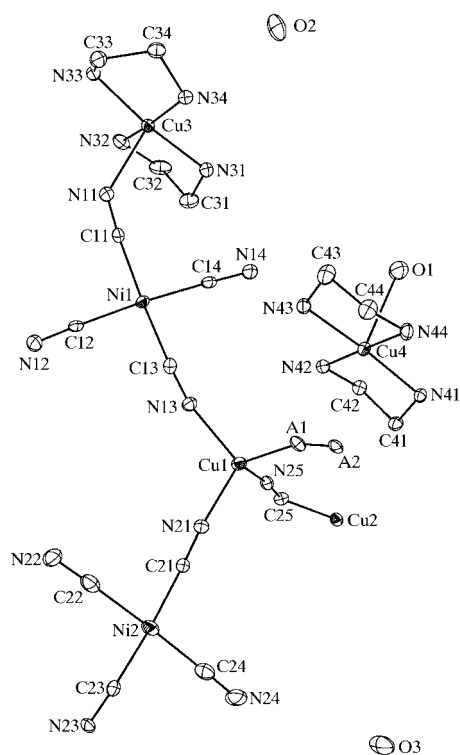


Figure 1
The asymmetric unit of (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity.

The geometric parameters are similar to those found in the above-mentioned examples.

Two different paramagnetic Cu centres are present in the structure of (I) and both are pentacoordinated. The calculated values of the τ parameters (Adison *et al.*, 1984) are 9.2% for Cu3 and 5.3% for Cu4, indicating an almost ideal square-pyramidal form (ideal value $\tau = 0$) of the coordination polyhedron. Atom Cu3 is linked to the anionic array by the bridging cyano group and exhibits a CuN₄N chromophore, with four N atoms from two chelate-bonded en ligands in the basal plane (mean Cu—N 2.012 Å) and an N atom from the bridging cyano group in the apical position, with a longer Cu—N distance of 2.325(5) Å. The central Cu atom is displaced from the mean plane of the four atoms N31, N32, N34 and N34 toward atom N11 by 0.159(2) Å.

An interesting situation is observed around atom Cu4. This atom (chromophore CuN₄O) is coordinated in the basal plane with two chelate-type en ligands, with four short Cu—N distances (mean 2.010 Å). The apical O atom from the water molecule is at a longer distance of 2.547(4) Å. In the sixth direction of a very distorted tetragonal bipyramid is placed, almost perpendicularly, the disordered cyano group A1—A2, at a distance of 2.94(2) Å to the middle of the cyano group. Moreover, the displacement of atom Cu4 toward the apical atom O1 from the mean plane formed by N41, N42, N43 and N44 is significantly smaller than that for Cu3 at 0.055(2) Å. Molecular-orbital quantum chemical calculations for [Cu(NH₃)₄Cu₄(CN)₆] indicated the existence of a weak π -bonding interaction between Cu²⁺ and the triple bond, with a distance of 2.97(1) Å (Dunaj-Jurčo & Boča, 1983). A similar weak π -bonding interaction can be assumed in the present case. The geometric parameters in the chelate rings of both cations are close to those found in similar compounds (Williams *et al.*, 1972; Lokaj *et al.*, 1991).

Hydrogen bonds may play an important role in Cu^{II} compounds as possible exchange paths for magnetic interac-

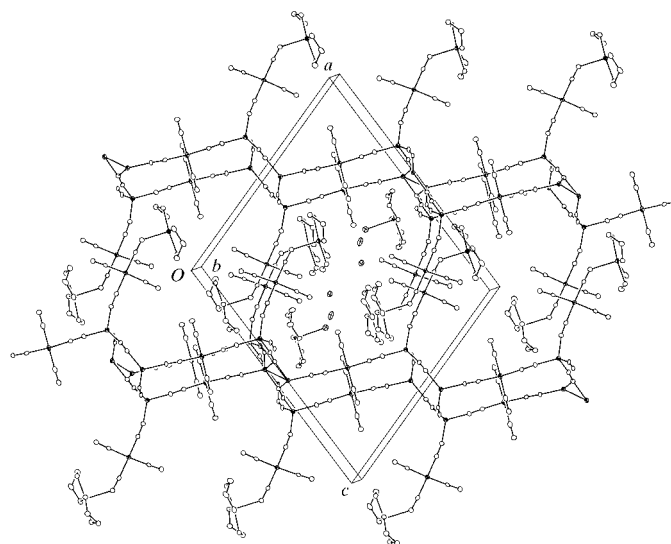


Figure 2
A packing diagram for (I) viewed approximately along the *b* axis. The [Cu(en)₂(H₂O)]²⁺ complex cations and water molecules are shown only in the central channel. H atoms have been omitted for clarity.

tions. In compound (I), several hydrogen bonds are possible, of the types O—H···O, O—H···N, N—H···O and N—H···N(C), with participation of water molecules, terminal cyano groups and amine groups from the [Cu(en)₂]²⁺ and [Cu(H₂O)(en)₂]²⁺ paramagnetic cations. Details of the most important hydrogen bonds are given in Table 2.

In cyano complexes, the absorption bands due to the $\nu(\text{CN})$ stretching vibrations of the cyano groups, which can be found in the wavenumber range 2000–2200 cm⁻¹ (Sharpe, 1976), are very characteristic. There are three absorption bands at 2152 (*m*), 2128 (*s*) and 2096 (*s*) cm⁻¹ in the spectrum of (I). The absorption bands at 2128 and 2152 cm⁻¹ can be ascribed to the stretching vibrations of terminal and bridging cyano groups, respectively, of the tetracyanonickelate anion, while the remaining absorption band at 2096 cm⁻¹ may be due to the presence of bridging cyano groups linking two Cu^I atoms. The presence of the en ligands manifests itself by various absorption bands due to $\nu(\text{NH}_2)$, $\nu(\text{CH}_2)$, $\delta(\text{NH}_2)$ and other vibrations. These are presented in the *Experimental* section. Only one broad absorption band due to $\nu(\text{OH})$ vibrations is present in the spectrum, at 3416 (*m*) cm⁻¹, accompanied by a shoulder at 3390 (*msh*) cm⁻¹; their position and shape are in line with the presence of the hydrogen-bonding system. The presence of water molecules is also shown by weak absorption bands at 1664 (*w*) and 1650 (*wsh*) cm⁻¹, due to a deformation vibration, $\delta(\text{H}_2\text{O})$.

The thermodynamic and magnetic properties of (I) are being studied (Kajňáková *et al.*, 2002).

Experimental

In a typical preparation procedure, a 0.1 M solution of CuSO₄ (20 ml, 2 mmol) was added to a 0.1 M solution of K₂[Ni(CN)₄] (20 ml, 2 mmol) and water (60 ml). The resultant precipitate redissolved upon the addition of solid citric acid (1.8 g) and ethanolamine (1.6 ml). Finally, 1,2-ethanediamine (0.135 ml) was added. This solution was filtered and placed in a refrigerator for crystallization *via* slow evaporation. Within a week, blue-violet needles of (I) (approximate dimensions: 0.1 mm in diameter and 5 mm in length) appeared, and these were separated by filtration and dried in air (yield 35%). Spectroscopic analyses were carried out using a Carlo Erba EA1108 and a Specord M40 spectrometer. Analysis calculated for C₁₈H₃₈Cu₄N₁₈Ni₂O₃ (*M_r* = 926.24): C 23.34, H 4.14, N 27.22%; found: C 23.82, H 3.90, N 26.50%; IR (cm⁻¹, KBr disc): $\nu(\text{OH})$: 3416 (*m*), 3390 (*msh*); $\nu(\text{NH}_2)$: 3328 (*s*), 3272 (*s*); $\nu(\text{CH}_2)$: 2980 (*wsh*), 2968 (*w*), 2896 (*w*); $\nu(\text{CN})$: 2152 (*m*), 2128 (*s*), 2096 (*s*); $\delta(\text{OH}_2)$: 1664 (*w*), 1650 (*wsh*); $\delta(\text{NH}_2)$: 1610 (*msh*), 1588 (*s*); $\nu(\text{C—N})$: 1040 (*vs*); $\rho(\text{NH}_2)$: 696 (*m*); $\delta(\text{NCCN})$: 420 (*m*); $\delta(\text{Ni—CN})$: 404 (*m*).

Crystal data

[Cu(C₂H₈N₂)₂(H₂O)][Ni₂Cu₃(CN)₁₀(C₂H₈N₂)₂·2H₂O]
M_r = 926.24
 Monoclinic, *P*₂₁/*n*
a = 19.476 (2) Å
b = 8.2737 (4) Å
c = 21.786 (2) Å
 β = 107.583 (2)°
V = 3346.4 (3) Å³
Z = 4

D_x = 1.838 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 80 reflections
 θ = 2.0–28.0°
 μ = 3.65 mm⁻¹
T = 173 (2) K
 Needle, blue
 0.24 × 0.23 × 0.11 mm

Table 1

Selected geometric parameters (Å, °).

The atoms labelled A represents a C or N atom of the disordered cyano group.

Cu1—A1	1.963 (5)	Cu4—N41	2.019 (4)
Cu1—N21	1.984 (5)	Cu4—N43	2.022 (4)
Cu1—N25	1.992 (4)	N11—C11	1.142 (6)
Cu1—N13	2.005 (4)	N12—C12	1.149 (6)
Ni1—C12	1.858 (5)	N13—C13	1.145 (6)
Ni1—C13	1.860 (5)	N14—C14	1.155 (6)
Ni1—C14	1.860 (5)	A1—A2	1.153 (6)
Ni1—C11	1.881 (5)	N21—C21	1.146 (6)
Ni2—C21	1.855 (6)	C22—N22	1.132 (7)
Ni2—C23	1.856 (6)	N23—C23	1.146 (6)
Ni2—C24	1.858 (6)	C24—N24	1.147 (7)
Ni2—C22	1.891 (6)	N25—C25	1.156 (6)
Cu2—A2 ⁱ	1.962 (5)	N31—C31	1.486 (7)
Cu2—N23 ⁱⁱ	1.991 (4)	C31—C32	1.503 (8)
Cu2—C25	2.044 (5)	N32—C32	1.485 (7)
Cu2—C25 ⁱⁱⁱ	2.142 (5)	N33—C33	1.481 (7)
Cu2—Cu2 ⁱⁱⁱ	2.4440 (12)	C33—C34	1.507 (7)
Cu3—N33	2.007 (4)	N34—C34	1.487 (6)
Cu3—N31	2.007 (4)	N41—C41	1.494 (6)
Cu3—N34	2.013 (4)	C41—C42	1.501 (7)
Cu3—N32	2.022 (5)	N42—C42	1.486 (6)
Cu3—N11	2.325 (5)	N43—C43	1.482 (7)
Cu4—N44	1.998 (4)	C43—C44	1.479 (7)
Cu4—N42	2.000 (4)	N44—C44	1.483 (6)
A1—Cu1—N21	108.33 (19)	N34—Cu3—N11	97.78 (18)
A1—Cu1—N25	111.00 (18)	N32—Cu3—N11	94.47 (18)
N21—Cu1—N25	107.66 (18)	N44—Cu4—N41	94.93 (16)
A1—Cu1—N13	112.30 (19)	N42—Cu4—N41	85.08 (16)
N21—Cu1—N13	112.27 (17)	N44—Cu4—N43	84.84 (16)
N25—Cu1—N13	105.18 (17)	N42—Cu4—N43	95.06 (16)
C12—Ni1—C13	88.9 (2)	C11—N11—Cu3	135.2 (4)
C13—Ni1—C14	88.2 (2)	N11—C11—Ni1	175.8 (5)
C12—Ni1—C11	93.3 (2)	N12—C12—Ni1	172.5 (5)
C14—Ni1—C11	89.8 (2)	C13—N13—Cu1	167.1 (4)
C21—Ni2—C24	92.8 (2)	N13—C13—Ni1	175.4 (5)
C23—Ni2—C24	91.8 (2)	N14—C14—Ni1	178.0 (5)
C21—Ni2—C22	87.2 (2)	A2—A1—Cu1	161.5 (4)
C23—Ni2—C22	88.3 (2)	A1—A2—Cu2 ⁱ	156.6 (4)
A2 ⁱ —Cu2—N23 ⁱⁱ	106.80 (18)	C21—N21—Cu1	174.9 (4)
A2 ⁱ —Cu2—C25	109.49 (19)	N21—C21—Ni2	177.3 (5)
N23 ⁱⁱ —Cu2—C25	114.76 (18)	N22—C22—Ni2	177.6 (6)
C25—Cu2—C25 ⁱⁱⁱ	108.60 (16)	C23—N23—Cu2 ^{iv}	170.2 (4)
N33—Cu3—N34	84.68 (17)	N23—C23—Ni2	177.2 (4)
N31—Cu3—N34	93.27 (17)	N24—C24—Ni2	175.4 (6)
N33—Cu3—N32	95.87 (18)	C25—N25—Cu1	172.9 (4)
N31—Cu3—N32	84.74 (18)	N25—C25—Cu2	152.5 (4)
N33—Cu3—N11	95.24 (17)	N25—C25—Cu2 ⁱⁱⁱ	134.7 (4)
N31—Cu3—N11	91.51 (17)	Cu2—C25—Cu2 ⁱⁱⁱ	71.40 (16)

Symmetry codes: (i) 2 - x, -y, 1 - z; (ii) $\frac{1}{2} + x, -\frac{1}{2} - y, \frac{1}{2} + z$; (iii) 2 - x, -1 - y, 1 - z; (iv) $x - \frac{1}{2}, -\frac{1}{2} - y, z - \frac{1}{2}$.

Data collection

Bruker SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: analytical, based on measured indexed crystal faces (SHELXTL; Sheldrick, 1997)
T_{min} = 0.532, *T_{max}* = 0.930

20 433 measured reflections
 7643 independent reflections
 4511 reflections with *I* > 2 σ (*I*)
R_{int} = 0.068
 θ_{max} = 27.5°
h = -25 → 24
k = -10 → 10
l = -28 → 25

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.044
wR(*F*²) = 0.108
S = 0.92
 7643 reflections
 429 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0492P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 2.14 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -1.35 \text{ e } \text{Å}^{-3}$

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1A...N24 ⁱ	0.83 (3)	2.16 (5)	2.898 (7)	148 (7)
O1—H1B...O2 ⁱⁱ	0.82 (3)	2.14 (3)	2.942 (7)	165 (8)
O2—H2A...N14 ⁱⁱ	0.88 (3)	1.96 (3)	2.835 (6)	174 (8)
O2—H2B...O3 ⁱⁱ	0.87 (3)	2.72 (8)	3.37 (5)	132 (7)
O3—H3A...O1 ⁱ	0.87 (3)	2.62 (12)	2.803 (7)	93 (8)
O3—H3B...N12 ⁱⁱⁱ	0.85 (3)	1.99 (3)	2.843 (7)	174 (9)
N31—H31A...O3 ^{iv}	0.92	1.96	2.841 (7)	160
N31—H31A...O3 ^{iv}	0.92	2.04	2.90 (4)	155
N34—H34B...O2	0.92	2.19	3.026 (7)	151

 Symmetry codes: (i) $2 - x, -y, 1 - z$; (ii) $3 - x, -y, 1 - z$; (iii) $x - \frac{1}{2}, -\frac{1}{2} - y, \frac{1}{2} + z$; (iv) $1 + x, y, z$.

The atoms labelled A represents a C or N atom of the disordered cyano group. The site-occupancy factors for atoms A1 and A2 were obtained by refining the relative contributions of the C and N atom (a common isotropic displacement parameter was used at this stage). The site-occupancy factors were then fixed and both atoms A1 and A2 were refined anisotropically. The disordered cyano group (A1—A2) could also be modelled by two different cyano groups with site-occupancy factors of 0.41 (4) and 0.59 (1), but the cyano groups in this case exhibited unusual bond distances of 1.04 and 1.20 Å. The largest peak in the final difference map is 0.92 Å from Ni2. During the localization and refinement of the O atoms of the water molecules, a peak was present in the difference map; at the same time, the displacement parameter of atom O3 was high. It was possible to interpret and refine the observed peak as a second position of the disordered water oxygen O3. The minor position was refined isotropically and its H atoms were not located. A riding model was used for the H atoms bound to C and N atoms. The H atoms of the water molecules were found from a difference map and were refined freely, with O—H distances restrained to 0.84 Å and H...H to 1.33 Å. Full data collection details are in the relevant _special_details section of the archived CIF and are also reported elsewhere (Abboud *et al.*, 1997).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART* and *SAINT* (Bruker, 1998); data reduction: *SHELXTL* (Sheldrick, 1997); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

This work was supported, in part, by the Slovak Grant Agency (VEGA 1/7426/20), by the National Science Foundation (NSF INT-9722935) and by the University of Florida Center for Ultralow Temperature Research (CULTR). JC is grateful to Mrs Heinrichová for assistance in the synthetic work. KAA wishes to acknowledge the National Science Foundation and the University of Florida for funding the purchase of the X-ray equipment. We have benefited from discussions with M. W. Meisel, who reviewed the manuscript.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1484). Services for accessing these data are described at the back of the journal.

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