Table 6. *The* $(NR_4)[Ni(dmit)_2]$ *compounds*

	$R = CH_3$	$R = C_2H_5$	$R = n\text{-}C_3H_7$	$R = n\text{-}C_4H_9$
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P2_1/c$
Side/side (a) or face/face (b)	$a + b$	b	b	a
Ni—S distance (Å)	2·158	2·157	2·160	2·156
Variations in S—S contacts (Å)	3·23–3·71	3·51–3·71	3·50–3·70	3·40–3·61
σ(S cm⁻¹)	5×10^{-6}	4×10^{-5}	6×10^{-8}	5×10^{-9}

orbital overlap can be formed by the S5—S5 contacts (3·231 Å, Table 5) and probably the S9—S10 contacts (3·691 Å). The second pathway is a zigzag interaction between both molecules (Table 5) with contacts mainly along the x axis. These pathways may explain the relatively high single-crystal conductivity at room temperature found for this compound (5×10^{-6} S cm⁻¹), compared to the related $(NBu_4)[Ni(dmit)_2]$ (5×10^{-9} S cm⁻¹) (Groeneveld, Schuller, Kramer, Haasnoot & Reedijk, 1986). The single-crystal conductivity of $(NPr_4)[Ni(dmit)_2]$, 6×10^{-8} S cm⁻¹, is of the same order of magnitude as the conductivity of $(NBu_4)[Ni(dmit)_2]$. The 'isolated character' of the anionic part of $(NPr_4)[Ni(dmit)_2]$ and (NBu_4)-$[Ni(dmit)_2]$ may cause the relatively low conductivity.

In Table 6 the main differences between the $(NR_4)[Ni(dmit)_2]$ compounds ($R = CH_3$, C_2H_5, $n\text{-}C_3H_7$ and $n\text{-}C_4H_9$) are summarized.

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Structure of *catena*-Poly[bis(ethylenediamine)nickel(II)-μ-cyano-dicyanonickel(II)-μ-cyano]

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Abstract. $Ni(en)_2Ni(CN)_4$, $M_r = 341\cdot67$, monoclinic, $P2_1/n$, $a = 7\cdot104$ (3), $b = 10\cdot671$ (3), $c = 9\cdot940$ (2) Å, $\beta = 114\cdot68$ (2)°, $V = 684\cdot7$ (4) Å³, $Z = 2$, $D_m = 1\cdot68$ (1), $D_x = 1\cdot66$ Mg m⁻³, $\lambda(\text{Mo } K\bar{\alpha}) = 0\cdot71069$ Å, $\mu = 2\cdot70$ mm⁻¹, $F(000) = 352$, $T = 295$ K, $R = 0\cdot0487$ for 1137 unique reflections. The structure is built up of infinite electroneutral $[-Ni(en)_2-NC-Ni(CN)_2-CN-]_\infty$ chains parallel to the c axis. The Ni(1) atom is square-planar coordinated by four cyano groups. The *trans*-coordinated cyano groups form bridges to two

different Ni(2) atoms. The distorted octahedral coordination of Ni(2) is completed by two chelate ethylenediamine molecules bonded in the equatorial plane. The carbon atoms in the ethylenediamine ligand are disordered in two positions.

Introduction. Among the series of complexes $M(en)_2Ni(CN)_4$ (M = Ni, Cu, Zn, Cd) the crystal structures of $Cu(en)_2Ni(CN)_4$ and $Cd(en)_2Ni(CN)_4$ have been determined by the single-crystal diffraction method. In $Cu(en)_2Ni(CN)_4$ (Dunaj-Jurčo, Garaj, Chomič, Haluška & Valach, 1976) copper is octahedrally coordinated by two chelating ethylenediamine (en) molecules in the equatorial plane and the bridging cyano groups are linked in axial positions. On the other hand, in the $Cd(en)_2Ni(CN)_4$ complex (Jameson, Bachmann, Oswald & Dubler, 1981) the bridging cyano groups are bonded in *cis* positions in the distorted CdN_6 octahedron. The present structure determination is part of our study on the crystal chemistry of tetracyanoniccolates and our aim is to study the effect of the replacement of the atom M by Ni on the mode of coordination and the structure type.

Experimental. Violet parallelepipeds of $Ni(en)_2$-$Ni(CN)_4$ were obtained together with light-violet microcrystals of $Ni(en)_2Ni(CN)_4.2.5H_2O$ from the system $Ni^{II}-en-[Ni(CN)_4]^{2-}-H_2O$. Details of preparation and identification of the products are described elsewhere (Černák, Chomič & Potočňák, 1988). D_m by flotation in a mixture of bromoform and acetone. Crystal: $0.2 \times 0.3 \times 0.4$ mm. Preliminary Weissenberg photographs reveal space group $P2_1/n$ and isostructurality with $Ni(en)_2Pd(CN)_4$ (Rüegg & Ludi, 1971). Data collection: Syntex $P2_1$ diffractometer, graphite-monochromated Mo $K\bar{\alpha}$ radiation, unit-cell parameters from 15 reflections with $3.01 \leq \theta \leq 13.95°$. $\theta-2\theta$ scan technique, scan angle from $[2\theta(Mo\ K\alpha_1)-1]°$ to $[2\theta(Mo\ K\alpha_2)+1]°$. 2005 unique reflections ($0 \leq h \leq 10, 0 \leq k \leq 14, -13 \leq l \leq 13$) with $0 < \theta < 30°$; of these, 1137 had $F_o > 3.92\sigma(F_o)$ according to the condition for 'observed' reflections used in the *GECOR* procedure (*XTL/E-XTL Structure Determination System*, 1976) from which the program *XP*21 (Pavelčik, 1986) was derived and were used in the refinement process. Standard reflections 120 and 35$\bar{4}$ used for orientation and intensity control every 100 reflections, intensities corrected for the variation ($\pm5\%$ of mean values) observed with the standard reflections together with Lp corrections using the program *XP*21 (Pavelčik, 1986). No absorption corrections. As an initial model the atomic positions from $Ni(en)_2$-$Pd(CN)_4$ (Rüegg & Ludi, 1971) were taken. Full-matrix least-squares refinement of non-H atoms. High U values of the carbon atoms (from en), short C—C distance and two peaks ($\simeq1.8$ e Å^{-3}) in the difference map indicate the presence of disorder. The disordered C atoms were

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

K, the site-occupation factor, is given when it is different from unity.

$$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U/U_{eq}	K
Ni(1)	0	0	0	2.72 (5)	
Ni(2)	0	0	5000	2.68 (5)	
N(1)	−796 (8)	339 (5)	2719 (5)	3.6 (2)	
N(2)	4078 (9)	−1034 (6)	2205 (6)	5.5 (4)	
N(3)	1197 (7)	1813 (4)	5514 (5)	3.7 (3)	
N(4)	−2744 (7)	873 (4)	4845 (5)	3.6 (3)	
C(1)	−597 (9)	277 (5)	1637 (6)	3.0 (3)	
C(2)	2556 (9)	−647 (5)	1332 (6)	3.5 (3)	
C(3)	−300 (14)	2530 (9)	5865 (10)	5.3 (2)	0.77 (4)
C(33)	−526 (35)	2739 (21)	5142 (24)	2.5 (4)	0.23 (4)
C(4)	−2440 (14)	2223 (9)	4761 (10)	5.3 (2)	0.77 (4)
C(44)	−2108 (39)	2174 (24)	5567 (27)	3.3 (5)	0.23 (4)

treated isotropically and their site-occupation factors were fixed in the subsequent cycles of refinement. H-atom positions calculated. $w(\Delta F)^2$ minimized, weighting scheme $w = k/\sigma^2(F_o)$ in the last cycles changed to $w = k/[\sigma^2(F_o) + gF_o^2]$ ($k = 0.5557$ and $g = 0.0005$) which showed no systematic shifts as a function of F_o. Final $R = 0.049$, $wR = 0.070$, $S = 1.53$ (83 parameters varied), $(\Delta/\sigma)_{max} = 0.005$. The final difference map shows two peaks of 0.96 and 0.92 e Å^3 near the two nickel atoms, elsewhere $-0.54 \leq \Delta\rho \leq 0.62$ e Å^3. Scattering factors from *International Tables for X-ray Crystallography* (1974) and *SHELX*76 (Sheldrick, 1976) which was used for all calculations on the EC 1045 computer in the Institute of Calculations of the Technical University of Košice. Angles between the planes in the en ligand were calculated by the program *PARST* (Nardelli, 1983). Program *PLUTO* (Motherwell, 1976) was used for drawing Fig. 1.

Discussion. Final atomic positional parameters are given in Table 1.* The structure consists of infinite electroneutral [−Ni(en)$_2$−NC−Ni(CN)$_2$−CN−]$_\cdot$ chains running parallel to the c axis (Fig. 1), as was found in the isostructural complex $Ni(en)_2Pd(CN)_4$ (Rüegg & Ludi, 1971). However, the chains are significantly bent at the N(1) atom |155.6 (4)° compared with the 165.7 (1.1)° calculated from the given atomic positions in the Pd analogue], but this is less than the bending found in the $Cu(en)_2Ni(CN)_4$ complex, 123.1 (5)° (Dunaj-Jurčo, Garaj, Chomič, Haluška & Valach, 1976).

Ni(1) exhibits the classical slightly deformed square-planar coordination and the bond distances and angles

(Fig. 2) in the [Ni(CN)₄]²⁻ anion are nearly equal to those found in other tetracyanoniccolate(II) complexes (Sharpe, 1976).
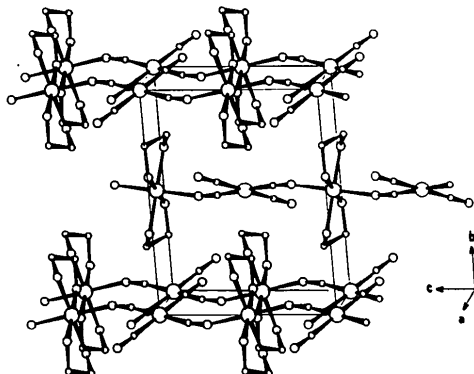

Fig. 1. Crystal-packing diagram. H atoms and disordered C atoms omitted for clarity.
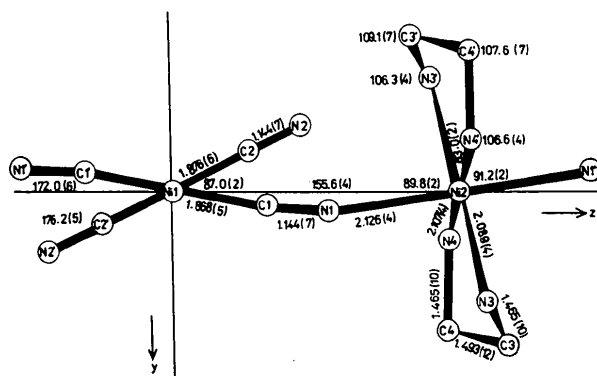

Fig. 2. Bond distances (Å), angles (°) and atom-numbering scheme for Ni(en)₂Ni(CN)₄ shown in the x-axis projection. E.s.d.'s in parentheses. The bond distances and bond angles in the en ring with disordered C atoms are: N(3)—C(33) 1·49 (2), C(33)—C(44) 1·48 (3), C(44)—N(4) 1·54 (3) Å, Ni(2)—N(3)—C(33) 110 (1), N(3)—C(33)—C(44) 108 (2), C(33)—C(44)—N(4) 117 (2), C(44)—N(4)—Ni(2) 106 (1)°.

The coordination geometry of Ni(2) is deformed octahedral. In the equatorial plane two chelating en molecules are coordinated. In the axial positions two bidentate cyano groups from different [Ni(CN)₄]²⁻ anions are linked. Thus, the coordination geometry and the structure type are similar to those found in Cu(en)₂Ni(CN)₄ (Dunaj-Jurčo, Garaj, Chomič, Haluška & Valach, 1976) and is different from that of Cd(en)₂Ni(CN)₄ (Jameson, Bachmann, Oswald & Dubler, 1981). From these results it seems that the difference in the coordination mode of the Cd^{II} cation is due to its considerably greater ionic radius (0·97 Å) when compared with the ionic radii of Ni^{II} (0·72 Å) and Cu^{II} (0·69 Å).

The en ligand in both disordered positions has a *gauche* conformation. C(3) and C(4) are displaced by 0·37 (1) Å on opposite sides with respect to the plane through Ni(2), N(3), N(4), while C(33) is displaced by 0·33 (2) Å on one side and C(44) by 0·36 (2) Å on the other with respect to the same plane. The angle between the planes through Ni(2),N(3),N(4) and Ni(2),C(3),C(4) is 29·6 (3)° and that between the planes through Ni(2),N(3),N(4) and Ni(2),C(33),C(44) is 28 (1)°; these values are normal (Raymond, Corfield & Ibers, 1968). Similarly, disorder in the en ligand was also observed for the Cu(en)₂Cu₂Cl₄ complex, but with one C and one N atom disordered (Simonsen & Toftlund, 1987).

The Ni(2)—N (from en) bond distances are shorter than Ni(2)—N (from cyano group). The opposite is true for Ni(en)₂Pd(CN)₄ (Rüegg & Ludi, 1971). At the same time the distances Ni(2)—N (from en) are a little shorter than the bond distances of the same type in some tris(en) complexes (Table 2). This means that the en ligands in bis(en) complexes quoted in Table 2 are bonded more strongly than in tris(en) complexes. The other bond distances and angles in the chelate rings are comparable (within the e.s.d.'s) with those found in analogous complexes. The only exception is the

Table 2. *Relevant bond distances* (Å) *in some bis(en) and tris(en) complexes*

Complex	Ni—N(en)	Ni—N(CN)	C—N	C—C	Reference
Ni(en)₃(NO₃)₂	2·120 (13)		1·500 (25)	1·498 (28)	(1)
Ni(en)₃SO₄	2·124 (6)		1·476 (9)	1·544 (9)	(2)
Ni(en)₃Ag₂(CN)₄	2·144 (4)		1·460 (7)	1·532 (12)	(3)
	2·133 (4)		1·475 (7)	1·523 (8)	
	2·130 (4)		1·487 (8)		
Ni(en)₂Pd(CN)₄	2·101 (8)	2·054 (11)	1·466 (16)	1·458 (16)	(4)
	2·110 (6)		1·490 (11)		
Ni(en)₂Ni(CN)₄	2·089 (4)	2·126 (4)	1·465 (10)	1·493 (12)	(5)
	2·107 (4)		1·465 (10)		
			1·49 (2)*	1·48 (3)*	
			1·54 (3)*		

References: (1) Swink & Atoji (1960). (2) Haque, Caughlan & Emerson (1970). (3) Kappenstein, Ouali, Guerin, Černák & Chomič (1988). (4) Rüegg & Ludi (1971). (5) This work.

* Bond distances of the disordered en molecule.

C(44)—N(4) bond distance of 1·54 (3) Å, and this could be the consequence of some error due to the observed disorder.

We thank Professor P. Domiano for help in preparing Fig. 1.

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Structure of {4-[2-(2-Aminoethylamino)ethylimino]pentan-2-onato-N,N',N'',O}copper(II) Perchlorate Monohydrate

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Abstract. $[Cu(C_9H_{18}N_3O)]ClO_4.H_2O$, $M_r = 365·3$, triclinic, $P\bar{1}$, $a = 8·603$ (2), $b = 9·666$ (2), $c = 9·993$ (3) Å, $\alpha = 77·41$ (2), $\beta = 67·59$ (2), $\gamma = 80·94$ (2)°, $V = 747·2$ (3) Å^3, $Z = 2$, $D_m = 1·64$ (2), $D_x = 1·623$ (1) Mg m^{-3}, $\lambda(Mo\ K\alpha) = 0·70926$ Å, $\mu = 1·72$ mm^{-1}, $F(000) = 378$, $T = 293$ K, $R = 0·040$, 4375 unique reflections. The structure consists of $[CuC_9H_{18}N_3O]^+$ complex cations and perchlorate anions. The coordination polyhedron around Cu is a distorted square with the $C_9H_{18}N_3O^-$ ligand tetradentate to the metal through one O and three N atoms.

Introduction. The study of the title compound was undertaken as part of an investigation of complexes with unsymmetrical tetradentate Schiff bases (Podlahová, Knížek, Loub & Hašek, 1988).

Experimental. The complex was prepared from copper(II) perchlorate, diethylenetriamine and acetylacetone (2,5-pentanedione) in methanolic solution in stoichiometric ratio. The solution was allowed to stand in air for a few days. Dark violet crystals were obtained, stable in air and to X-rays. Density determined by flotation method (mixture of diiodomethane and tetrachloromethane). A spherical crystal of $r = 0·13$ mm was used for the measurements. Syntex $P2_1$ diffractometer, graphite monochromator, 15 reflections with 2θ from 8 to 26° for measuring lattice parameters; ω–2θ scan; absorption ignored; max. $(\sin\theta)/\lambda = 0·69$ Å^{-1}; $h\ 0{\rightarrow}12$, $k\ -13{\rightarrow}13$, $l\ -13{\rightarrow}13$; three standard reflections after 97 reflections with variation <2%; 4645 measured reflections, 4375 unique reflections, 3838 reflections used with $I \geq 1·96\sigma(I)$; heavy-atom method; F magnitudes in full-matrix least-squares refinement; H atoms [except $H_2O(6)$] localized in theoretical positions; all positional parameters were refined with the

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