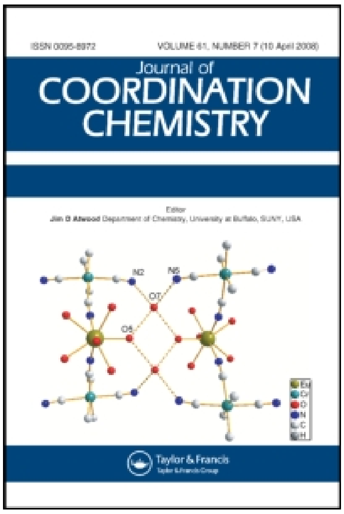

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Crystal Structures of (18-Crown-6)-(2-Hydroxyethylammonium) Tetracyanonickelate(Ii) and 10-Amino-Decylammonium Tetracyanonickeltate(II)

Masato Hashimoto[a]; Toschitake Iwamoto[a]
[a] Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Tokyo, Japan

To cite this Article Hashimoto, Masato and Iwamoto, Toschitake(1991) 'Crystal Structures of (18-Crown-6)-(2-Hydroxyethylammonium) Tetracyanonickelate(Ii) and 10-Amino-Decylammonium Tetracyanonickeltate(II)', Journal of Coordination Chemistry, 23: 1, 269 — 276

To link to this Article: DOI: 10.1080/00958979109408257

URL: http://dx.doi.org/10.1080/00958979109408257

J. Coord. Chem. 1991, Vol. 23, pp. 269–276
Reprints available directly from the publisher
Photocopying permitted by license only

CRYSTAL STRUCTURES OF (18-CROWN-6)-(2-HYDROXYETHYLAMMONIUM) TETRACYANONICKELATE(II) AND 10-AMINODECYLAMMONIUM TETRACYANONICKELTATE(II)

MASATO HASHIMOTO and TOSCHITAKE IWAMOTO*

Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Komaba, Meguro, Tokyo 153, Japan

(Received October 10, 1990)

The crystal structures of the two title tetracyanonickelate(II) salts of organic ammonium ions, (18-crown-6)-(2-hydroxyethylammonium) tetracyanonickelate(II), **I**, and 10-aminodecylammonium tetracyano nickelate(II), **II**, have been analyzed. **I** crystallizes in the monoclinic space group $P2_1/n$ with $a = 10.458(2)$, $b = 8.267(3)$, $c = 24.045(2)$ Å, $\beta = 94.09(1)°$, $V = 2074(1)$ Å^3, $Z = 2$, $R = 0.061$ for 2274 reflections; **II** is triclinic $P\bar{1}$ with $a = 9.437(3)$, $b = 10.094(3)$, $c = 9.205(3)$ Å, $\alpha = 110.16(2)$, $\beta = 112.72(3)$, $\gamma = 69.16(2)°$, $V = 733.7(5)$ Å^3 $Z = 1$, $R = 0.040$ including all the hydrogen atoms refined for 2724 reflections. The square planar tetracyanonickelate(II) anion is in a favourable position to form hydrogen bonds *via N* with the hydroxyl group in **I** and the ammonio group in **II**, respectively.

Keywords: Tetracyanonickelate(II), organic ammonium, X-ray structures

INTRODUCTION

The square planar tetracyanonickelate(II) anion, $[Ni(CN)_4]^{2-}$, is often involved in infinite linkage structures owing to the ambidentate character of the cyanide group; its *N* atoms coordinate to other cations to form one-dimensional chains or two-dimensional networks. Typical examples have been demonstrated in the host structures of the Hofmann-type and analogous series of clathrate compounds, in which the metal-complex hosts have the 2D network of *catena*-[metal(II) tetra-μ-cyano-nickelate(II)] in common.[1] *Cis* and *trans* 1D linkages are also observed in metal-complex host structures we have recently developed.[2–4] The structural features of the tetracyanonickelate(II) ion, based on crystallographic data, have been reviewed recently.[5,6]

During attempts to develop multi-dimensional polymeric cyanometal-complex structures, we have obtained by chance two tetracyanonickelate(II) compounds of considerably bulky organic cations. One is that of (18-crown-6)-(2-hydroxyethyl-ammonium), the other of monoprotonated 1,10-diaminodecane, *i.e.*, 10-aminodecyl-ammonium. This paper describes their crystal structures and hydrogen-bond formation between the tetracyanonickelate(II) anion and the organic cations.

---

* Author for correspondence.

EXPERIMENTAL

Synthesis of $[C_{12}H_{24}O_6 \cdot H_3N(CH_2)_2OH]_2[Ni(CN)_4]$, I

To a 10 cm^3 aqueous solution of 0.46 g $CdCl_2 \cdot 2.5H_2O$ and 0.52 g $K_2[Ni(CN)_4] \cdot H_2O$, 0.63 g of 1,9-diaminononane was added. After the pH was adjusted at *ca* 9.6 with citric acid and 2-aminoethanol (2-hydroxylethylamine), the solution was filtered through a membrane (Millipore, 4 μm) and covered with a 10 cm^3 diethylether solution of 1.0 g of 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane).[7] Orange prismatic crystals, obtained overnight at room temperature, were (18-crown-6)-(2-hydroxylethylammonium) tetracyanonickelate(II). Anal.: Calcd. for $C_{32}H_{63}O_{14}N_6Ni$: C, 47.13; H, 7.91; N, 10.08%. Found: C, 46.42; H, 7.72; N, 10.24%.

Synthesis of $[NH_2(CH_2)_{10}NH_3]_2[Ni(CN)_2]$, *II*

An aqueous solution of $CdCl_2 \cdot 2.5H_2O$, and 1,10-diaminononane was prepared and the pH was adjusted to 9.6 with citric acid and 2-aminoethanol; 10 cm^3 portions of the aqueous solution thus prepared, containing 0.46 g $CdCl_2 \cdot 2.5H_2O$, 0.52 g $K_2[Ni(CN)_4] \cdot H_2O$, and 0.63 g of 1,10-diaminodecane, was covered with neat benzene, toluene, 1-chloronaphthalene, or *o*- or *p*-anisidine in diethyl-ether, or 2,4,6-trimethylaniline in hexane.[7] Orange or wine-red crystals, obtained after one week to one month at room temperature, were 10-aminodecylammonium tetracyanonickelate(II). Anal.: Calcd. for $C_{24}H_{50}N_8Ni$: C, 56.61; H, 9.83; N, 22.02%. Found: C, 55.78; H, 9.73; N, 21.47%.

Structure determination

Table I summarizes the crystallographic and experimental data. All the procedures for refinement of unit cell parameters, collection of intensity data, and structure refinement were carried out using the TEXSAN[8] crystallographic software package installed on the diffractometer system.

The unit cell parameters and the orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 25 carefully centred reflections in the range $27.76° < 2\theta < 36.62°$ for I and $32.70° < 2\theta < 34.95°$ for **II**. Throughout the intensity data collection, intensities of three representative reflections measured after every 200 reflections remained constant for **I** and **II**. For **II**, an empirical absorption correction, based on the azimuthal scans of several reflections, was applied and which resulted in transmission factors ranging from 0.86 to 1.00.

Each structure was solved by a combination of Patterson direct methods using PHASE[9] and DIRDIF.[10] All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares procedure. Atomic scattering factors (neutral), including those for real and imaginary anomalous dispersion corrections for non-hydrogen atoms used were those in the International Tables.[11]

For **I**, the hydrogen atoms of the crown-ring and those of the methylene groups of the 2-hydroxyethylammonium ion were found in a difference Fourier map; their coordinates were fixed at the peak positions but isotropic thermal parameters were refined once before the final stage, in which the parameters were not adjusted but included in the structure factor calculation.[12]

TABLE I
Crystallographic and experimental data.[a]

Compound[b]	I	II
Empirical formula	$NiO_{14}N_6C_{32}H_{64}$	$NiN_8C_{24}H_{50}$
Formula weight	815.59	509.41
Crystal colour, habit	yellow, prisms	wine-red, plates
Crystal dimensions (mm)	0.30 × 0.30 × 0.20	0.55 × 0.55 × 0.25
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a/Å	10.458(2)	9.437(3)
b/Å	8.267(3)	10.094(3)
c/Å	24.045(2)	9.205(3)
α/°	90	110.16(2)
β/°	94.09(1)	112.72(3)
γ/°	90	69.16(2)
V/Å^3	2074(1)	733.7(5)
Z	2	1
D_m/D_x	1.30(1)/1.306	1.16(1)/1.15
$F(000)$	876	278
μ(MoKα)/cm^{-1}	5.33	6.87
Scan type	ω	ω-2θ
Scan rate, S/° min^{-1}	8.0	16.0
Scan width/°	$0.71 + 0.30\tan\theta$	$0.76 + 0.30\tan\theta$
$2\theta_{max}$/°	55.1	55.1
Number of reflections		
total	5399	3598
unique	5129	3389
used, N_o	2274 ($I > 1.5\sigma(I)$)	2724 ($I > 3\sigma(I)$)
Systematic absences	$h0l$: $h + l \neq 2n$ $0k0$: $k \neq 2n$	none
Corrections	Lp	Lp, absorption
No. of variables, N_v	241	251
R; R_w; GOF[c]	0.061; 0.064; 41.37	0.040; 0.044; 1.42
p-factor[c]	0.05	0.03
Max shift/error[c]	0.00	0.09
Maximum peak/e$^-$Å^{-3} [d]	0.47	0.55
Minimum peak/e$^-$Å^{-3} [d]	−0.28	−0.16

[a] The following conditions are in common for I and II. Rigaku AFC5R diffractometer; graphite monochromated MoKα radiation ($\lambda = 0.71059$ Å); 12 kW rotating anode generator; 25°C; Ni foil attenuators with factors 3.7, 13.6, and 49.6; take-off angle 6°; detector aperture 6.0 mm both horizontal and vertical; crystal to detector distance 40 mm. [b]I = $[C_{12}H_{24}O_6{\cdot}NH_3(CH_2)_2OH]_2[Ni(CN)_4]$; II = $[NH_2(CH_2)_{10}NH_3]_2[Ni(CN)_4]$. [c] Function minimized: $\sum w(|F_o| - |F_c|)^2$; $w = 4F_o^2/[\sigma(F_o)]^2$; $[\sigma(F_o)]^2 = [S^2(C + R^2B) + (pF_o^2)^2]$, where C is total integrated peak count, R = ratio of scan time to background counting time, B total background count, and Lp Lorentz-polarization factor; GOF = $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$. [d] Those values in the final difference Fourier map.

All the hydrogen atoms in II appeared as peaks of electron density; their positional and isotropic thermal parameters were refined along with the anisotropic non-hydrogen atoms in the final stage.[12]

TABLE II
Atomic coordinates and equivalent thermal parameters for I.

atom	x/a	y/b	z/c	$B_{eq}/Å^{2}$ [a]
Ni	0.5000	0.5000	0.5000	3.50(4)
O11	0.3798(3)	0.2428(5)	0.1537(1)	5.7(2)
O21	0.5005(3)	0.4868(5)	0.2774(1)	4.9(2)
O22	0.7715(3)	0.4887(4)	0.2717(1)	4.6(2)
O23	0.8740(3)	0.4781(5)	0.1669(2)	5.3(2)
O24	0.7352(4)	0.6368(5)	0.0812(1)	5.2(2)
O25	0.4693(4)	0.6835(5)	0.0873(1)	5.3(2)
O26	0.3645(3)	0.6637(4)	0.1924(1)	4.8(2)
N1	0.7456(4)	0.6127(6)	0.4548(2)	5.3(2)
N2	0.3437(4)	0.6993(7)	0.4161(2)	5.8(3)
N11	0.5976(3)	0.4705(4)	0.1680(1)	3.0(2)
C1	0.6516(5)	0.5703(7)	0.4716(2)	4.0(2)
C2	0.4040(5)	0.6244(7)	0.4477(2)	4.1(3)
C11	0.4762(5)	0.2561(6)	0.1163(2)	4.6(3)
C12	0.5996(5)	0.3019(6)	0.1464(2)	4.4(3)
C21	0.5885(6)	0.5070(8)	0.3246(2)	5.5(3)
C22	0.7064(7)	0.4150(7)	0.3156(2)	5.7(3)
C23	0.8872(6)	0.4056(8)	0.2630(3)	6.0(3)
C24	0.9515(5)	0.4868(8)	0.2174(3)	6.6(3)
C25	0.9336(6)	0.5412(8)	0.1202(4)	7.3(4)
C26	0.8421(7)	0.5414(8)	0.0703(3)	6.9(4)
C27	0.6481(7)	0.659(1)	0.0335(2)	6.7(4)
C28	0.5419(7)	0.7654(8)	0.0488(2)	6.4(3)
C29	0.3607(6)	0.7726(8)	0.1023(3)	6.4(3)
C30	0.2903(5)	0.6743(8)	0.1415(3)	5.9(3)
C31	0.3036(5)	0.5673(8)	0.2324(3)	5.6(3)
C32	0.3825(6)	0.5679(7)	0.2852(2)	5.5(3)

[a] $B_{eq} = 4\,[\sum_i \sum_j B_{ij} a_i a_j]/3$.

RESULTS AND DISCUSSION

The positional parameters refined for I and II are listed in Tables II and III, respectively; the structures are illustrated in Figures 1 and 2 with atomic notations.

Structure of I

The crown-ring is little distorted; the skeletal O–C–C angles ranging from 108.7(4) to 110.4(5)° give an average of 109.2(6)°, and C–O–C angles ranging from 110.9(4) to 113.8(5)° average 112(1)°. No abnormal values were observed for the bond distances. The *H*-ammonium fragment of the 2-hydroxyethylammonium cation (meaH) is trapped by the crown-ring through hydrogen bonds; three of the six N–O distances between N11 of the ammonium ion and the crown-O atoms, 2.891(5) (N11–O21), 2.893(5) (N11–O23), and 2.880(5) Å (N11–O25), are slightly shorter than the other three, 2.984(5) (N11–O22), 2.957 (N11–O24), and 3.008(5) Å (N11–O26). The skeleton of the cation takes a *gauche* configuration with no abnormal bond distances and angles. The crown-ammonium complex looks like a pot lid with a twisted handle.

TABLE III

Atomic coordinates and equivalent thermal parameters for **II**.

atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{eq}/Å^{2} [a]
Ni	0.5000	0.5000	0.5000	2.80(2)
N1	0.5820(3)	0.6265(3)	0.2996(3)	4.9(1)
N2	0.1522(2)	0.5824(3)	0.3192(3)	5.0(1)
N11	0.1824(2)	0.3955(3)	−0.1522(3)	3.5(1)
N12	1.2193(3)	−0.3283(3)	1.0412(3)	4.6(1)
C1	0.5502(3)	0.5790(3)	0.3762(3)	3.4(1)
C2	0.2843(3)	0.5521(3)	0.3874(3)	3.5(1)
C11	0.2121(3)	0.2956(3)	−0.0509(3)	3.3(1)
C12	0.3848(3)	0.2566(3)	0.0476(3)	3.0(1)
C13	0.4124(3)	0.1675(3)	0.1635(3)	3.1(1)
C14	0.5849(3)	0.1250(3)	0.2640(3)	3.2(1)
C15	0.6127(3)	0.0413(3)	0.3852(3)	3.4(1)
C16	0.7853(3)	0.0028(3)	0.4878(3)	3.8(1)
C17	0.8147(3)	−0.0781(4)	0.6119(4)	4.0(1)
C18	0.9876(3)	−0.1161(4)	0.7129(4)	4.1(1)
C19	1.0196(3)	−0.2015(4)	0.8341(4)	4.2(1)
C20	1.1916(3)	−0.2357(4)	0.9348(4)	4.2(1)
H1	0.177(3)	0.209(3)	−0.124(3)	3.6(5)
H2	0.141(3)	0.347(3)	0.017(3)	4.0(6)
H3	0.454(3)	0.201(2)	−0.026(3)	3.3(5)
H4	0.414(3)	0.345(3)	0.106(3)	3.6(5)
H5	0.375(3)	0.078(3)	0.100(3)	3.1(5)
H6	0.346(3)	0.229(3)	0.237(3)	3.7(5)
H7	0.652(3)	0.062(3)	0.193(3)	3.5(5)
H8	0.619(3)	0.214(3)	0.321(3)	4.2(6)
H9	0.577(3)	−0.048(3)	0.330(3)	3.9(6)
H10	0.544(3)	0.103(3)	0.454(3)	4.3(6)
H11	0.853(3)	−0.057(3)	0.423(3)	4.5(6)
H12	0.816(3)	0.091(3)	0.542(3)	4.5(6)
H13	0.748(3)	−0.012(3)	0.680(3)	5.4(7)
H14	0.787(3)	−0.170(3)	0.560(3)	5.6(7)
H15	1.053(3)	−0.178(3)	0.642(3)	5.1(7)
H16	1.016(3)	−0.019(3)	0.774(3)	5.7(7)
H17	0.993(3)	−0.297(3)	0.772(4)	5.8(7)
H18	0.953(4)	−0.139(3)	0.911(4)	6.0(7)
H19	1.223(3)	−0.138(3)	1.000(3)	5.7(7)
H20	1.258(4)	−0.297(3)	0.862(4)	5.8(8)
H21	0.256(3)	0.361(3)	−0.211(3)	4.9(7)
H22	0.086(3)	0.408(3)	−0.221(3)	4.5(6)
H23	0.188(3)	0.492(4)	−0.089(4)	5.5(7)
H24	1.304(4)	−0.340(4)	1.092(4)	6(1)
H25	1.139(5)	−0.263(5)	1.118(5)	11(1)

[a] $B_{eq} = 4\,[\sum_i \sum_j B_{ij} a_i a_j]/3$; the values for hydrogen atoms are for B_{iso}.

The tetracyanonickelate(II) ion is also little distorted from square planar configuration with Ni–C1 and Ni–C2 distances of 1.863(2) and 1.865(2) Å, and central bond angles deviating ±1.1(1)° from 90°; Ni–C1–N1 and Ni–C2–N2 angles are 179.4(2) and 179.0(2)°. However, one of the two crystallographically independent N atoms of

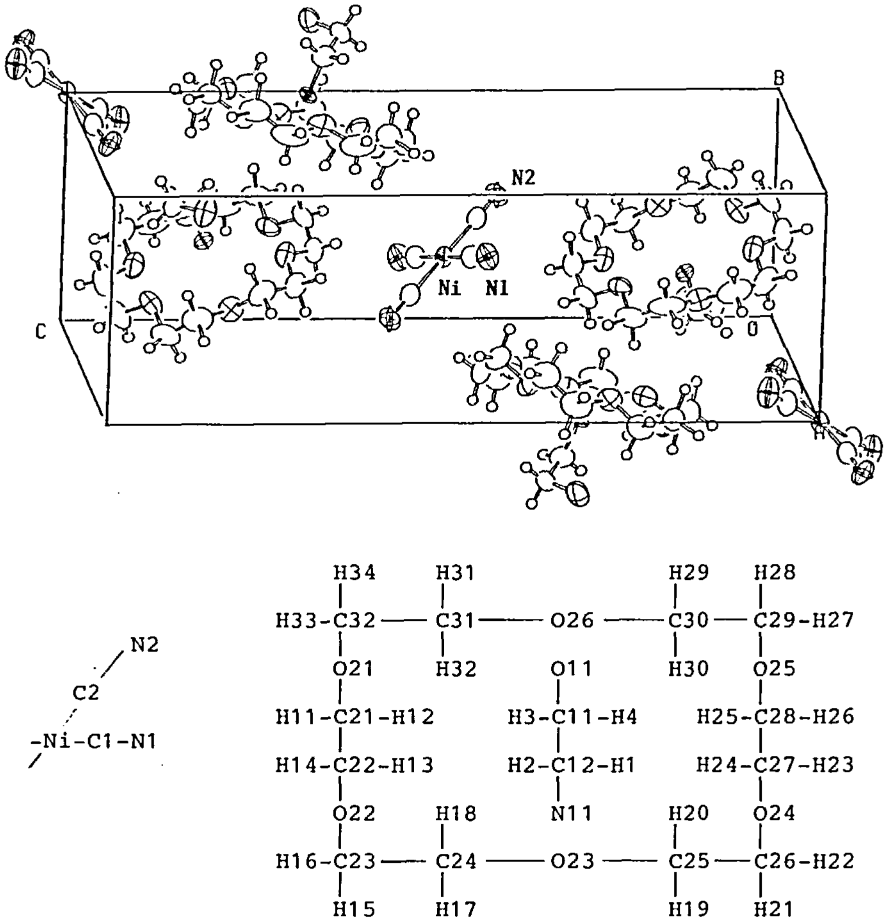

FIGURE 1 A perspective view of the unit cell for (18-crown-6) (2-hydroxyethylammonium) tetracyano-nickelate(II) (above) and the atomic notations (below).

the cyanide groups, N2, is at a hydrogen-bond distance of 2.801(6) Å from O11′ (generated by the symmetry operation $1/2-x$, $1/2+y$, $1/2-z$) of meaH; the other N atom, N1, is more than 4 Å far from any hydroxyl oxygens. Since the Ni atom is at the centre of inversion, the anion spans a pair of meaH-crown cations by the hydrogen bonds.

Structure of II

The 10-aminodecylammonium ion, *i.e.*, monoprotonated 1,10-diaminodecane (dadcnH), in **II** takes in all-*trans* skeletal configuration. The C–C distances, from 1.508(3) to 1.520(3) Å, and the C–C–C angles, from 111.8(2) to 113.9(2)°, give averages 1.515(4) Å and 113.3(7)°, respectively. The C–H distances, and the H–C–H and H–C–C angles, from 0.96(3) to 1.04(3) Å, from 106(2) to 114(2)°, and from

104(2) to 112(2)°, respectively, give averages 0.99(2) Å, 110(3)°, and 109(2)°, respectively. An imbalance between the N-H distances, 0.75(3) Å for N12–H24 and 1.12(5) Å for N12–H25, in the amino group is in contrast with the well-balanced ammonio group, with respective N-H distances of 0.88(3), 0.94(3), and 0.96(3) Å for N11–H22, -H21, and -H23. Except for this distortion in the amino group, the dadcnH has the molecular structure of a typical aliphatic chain.

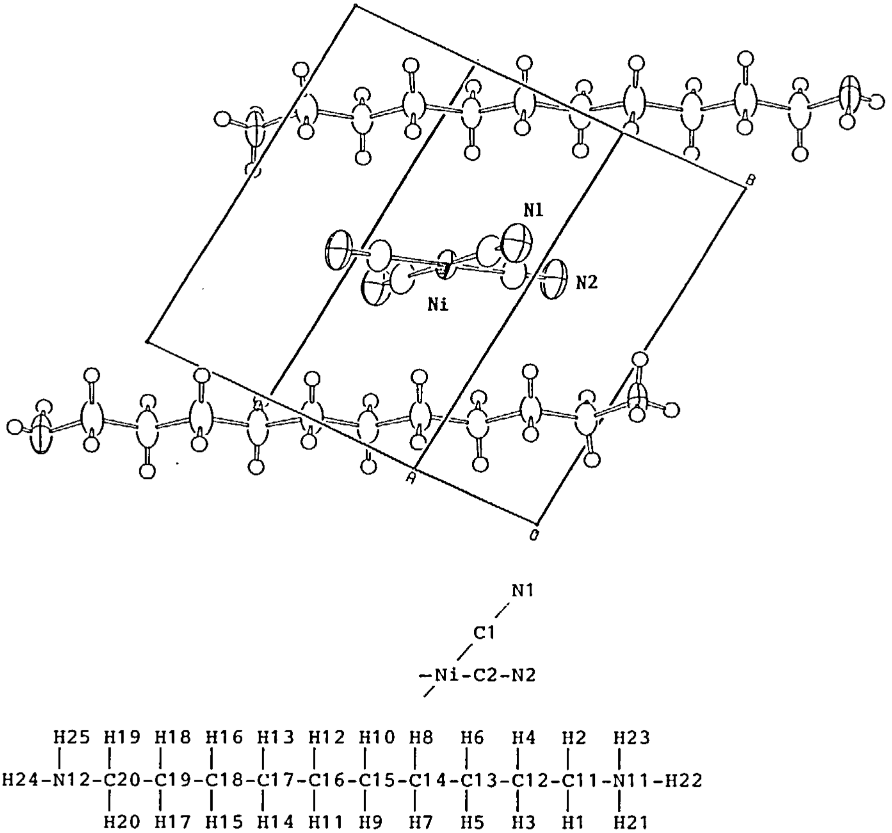

FIGURE 2 A perspective view of the unit cell for 10-aminodecylammonium tetracyanonickelate(II) (above) and the atomic notations (below).

Two of the three hydrogen atoms in the ammonio group of dadcnH appear to participate in hydrogen bond formation with the N atoms of the tetracyanonickelate(II) ion; both the N1–H21′ $(-x-1, -y, -z)$ and N2–H22″ $(-x, -1-y, -z)$ distances are 2.05(3) Å. In other words, all the N atoms of the tetracyanonickelate(II) ion are at 2.05(3) Å from the ammonium hydrogens. The last hydrogen of the ammonio group, H23, forms another hydrogen bond with an adjacent amino group of dadcnH; the N12–H23* $(x+1, y-1, z+1)$ distance of 1.85(3) Å supports this.

The tetracyanonickelate(II) ion shows an almost regular square planar configuration again, with Ni–C1 and Ni–C2 distances of 1.863(5) and 1.861(5) Å and the central bond angles deviating ±0.7(2)° from 90°; Ni–C1–N1 and Ni–C2–N2 angles are 178.9(4) and 179.0(5)°, respectively. In the unit cell the square planar bivalent tetracyanonickelate(II) anion at the centre of inversion is sandwiched by two rod-like univalent dadcnH cations whose protonated surfaces are shifted nearer to the inversion centre than the non-protonated surfaces. The hydrogen bonds, however, are formed with the ammonio groups of four dadcnH ions other than the two in the unit cell. A trend in thermal parameters has been observed for the atoms of the methylene group in dadcnH; the greater the distance from the $-NH_3^+$ group, the greater the parameter becomes.

The structure of **II** would be one of the rather rare cases in which the long aliphatic chain, including all the aliphatic hydrogen atoms located experimentally, was demonstrated with acceptable precision. Although the demonstrated structure is not unreasonable, the wine-red colouration of the crystal should be noted. The colour of the crystals prepared by the procedures described in Experimental is orange, as is usual for tetracyanonickelate(II) compounds, when the crystals are grown from the solutions. Then, the colour turns gradually wine-red irrespective of whether the compound is kept in or removed from the solution, or whether in the dark or the light. Photo-induced decomposition of the aliphatic diamine appears implausible. There are no unusually short contacts between the tetracyanonickelate(II) and dadcnH; the distances to the aliphatic hydrogen atoms are longer than 3 Å. The electronic state of the tetracyanonickelate(II) should be investigated in order to solve the above colour problem, although we have not yet explored this.

Analogous ω-aminoalkylammonium tetracyanonickelates(II) have not yet been obtained for 1,8-diaminooctane and 1,9-diaminononane.

REFERENCES

1. T. Iwamoto, "Inclusion Compounds" (eds. J.L. Atwood, J.E.D. Davies and D.D. MacNicol), Vol. I (Academic Press, London, 1984) pp. 29–57.
2. M. Hashimoto and T. Iwamoto, *Chem. Lett.*, 1387 (1989).
3. M. Hashimoto and T. Iwamoto, *Chem. Lett.*, 1531 (1990).
4. M. Hashimoto and T. Iwamoto, in preparation.
5. J. Cernak, M. Dunaj-Juroo, M. Melnik, J. Chomic and J. Skorsepa, *Rev. Inorg. Chem.*, 9, 259 (1988).
6. T. Iwamoto, "Inclusion Compounds" (eds J.L. Atwood, J.E.D. Davies and D.D. MacNicol), Vol. 5 (Oxford University Press, Oxford, in press).
7. These procedures were applied in attempt to obtain inclusion compounds of the respective organic molecules in cadmium-α,ω-diaminoalkane-tetracyanonickelate(II) metal-complex hosts.
8. TEXSAN–TEXRAY Structure Analysis Package, Molecular Structure Corporation (1985).
9. J.C. Calbrese, PHASE—Patterson Heavy Atom Solution Extractor, University of Wisconsin-Madison Ph.D. Thesis (1972).
10. P.T. Beurskens, DIRDIF: Direct Methods for Difference Structures—an automatic procedure for phase extension and refinement of difference structure factors. Technical Report 1984. 1, Crystallography Laboratory, Toerenooiveld, 6525 Ed Nijmegen, Netherlands.
11. "International Tables for X-ray Crystallography" Vol. IV (Kynoch Press, Birmingham, 1974), Tables 2.2A and 2.3.1.
12. Tables of bond lengths and angles, structure factors, anisotropic thermal parameters for I and II, and atomic parameters for the hydrogen atoms for I are available from the authors.