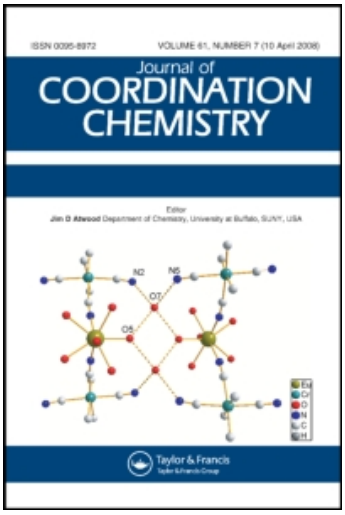

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Synthesis and crystal structure of bis(dicyclohexylammonium) Tetracyanonickel(II)

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SYNTHESIS AND CRYSTAL STRUCTURE OF BIS(DICYCLOHEXYLAMMONIUM) TETRACYANONICKEL(II)

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A novel, one-dimensional nickel(II) complex, $[(C_6H_{11})_2NH_2]_2[Ni(CN)_4]$, has been synthesized and structurally characterized by X-ray single crystallographic methods. The complex crystallizes in the triclinic, space group $P\bar{1}$ with $a=9.237(1)$, $b=9.576(2)$, $c=9.689(3)$ Å, $\alpha=61.51(2)$, $\beta=85.69(3)$, $\gamma=74.27(2)^\circ$, $V=723.6(3)$ Å^3, $Z=1$. The square-planar Ni(II) centre of the cyanonickellate anion is four coordinated by cyanide ligands. The dicyclohexylammonium cation occupies a bridging position by hydrogen bonding to the cyanide ligand nitrogen atoms of adjacent anions.

Keywords: Cyanonickellate(II) complex; Dicyclohexylamine; Hydrogen bonding; Crystal structure

INTRODUCTION

Supramolecular and molecular architecture by crystal engineering are of great interest in different areas such as chemistry, solid-state physics and biology, because of their possible application in material science, catalysis and metallo-biochemistry [1–4]. As a part of strategies to design novel supramolecular frameworks of cyanometallate systems, Iwamoto [5] and co-workers have used various complementary ligands, such as NH_3, H_2O, unidentate aliphatic and aromatic amines, ambidentate α,ω-diaminoalkanes, etc., to stabilize supramolecular frameworks. They obtained many types of supramolecular structures, including one-dimensional chains, two-dimensional layers and three-dimensional networks using aliphatic or aromatic amines.

In a previous paper [6], it was noted that the introduction of complementary ligands into the host structure gives rise to a change in the $[Cd(CN)_2]_n$ framework. The cyclohexylamine ligand appears to play two roles in building the host framework [7]: one is to occupy the channel space and the other is to block coordination sites of the Cd atom. Therefore, suitable combinations of central metal ions, complementary

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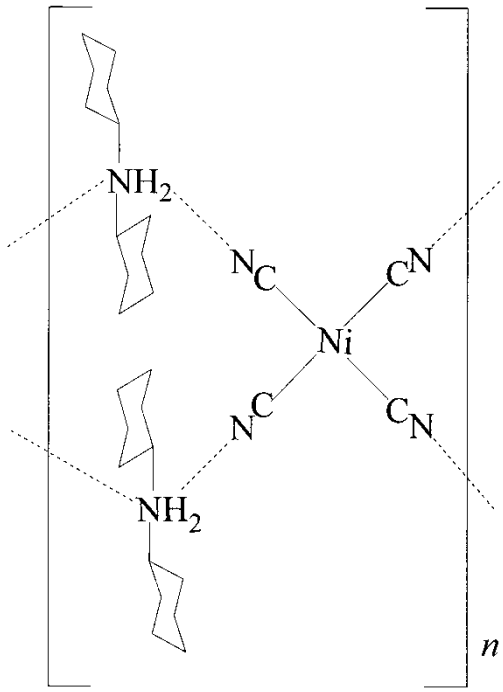

FIGURE 1 Structural diagram of $[(C_6H_{11})_2NH_2]_2[Ni(CN)_4]$.

ligands and guest molecules can lead to a variety of $[Cd(CN)_2]_n$ host frameworks. However, a supramolecular structure with the cyclic amine as a complementary ligand has not yet been explored in detail in comparison with the aliphatic or aromatic amines.

We have introduced dicyclohexylamine as a complementary cyclic amine ligand to develop a new type of supramolecular structure. In this paper, we report the preparation and crystal structure of the one-dimensional nickel(II) complex $[(C_6H_{11})_2NH_2]_2$-$[Ni(CN)_4]$, with the dicyclohexylamine ligand arranged as shown in Fig. 1.

EXPERIMENTAL

Synthesis and Analysis of $[(C_6H_{11})_2NH_2]_2[Ni(CN)_4]$

Dicyclohexylamine (5 cm^3, 20 mmol) was added to an aqueous solution (30 cm^3) of $K_2[Ni(CN)_4]$ (2.4 g, 10 mmol). The pH of the mixture was adjusted to 9 by adding 2-aminoethanol and citric acid. After a small amount of the precipitate was filtered off, the aqueous solution was allowed to stand in a refrigerator at 278 K. After a few weeks, pale yellow crystals were obtained.

IR spectra of the product were recorded on a BioRad Digilab FTS-165 infrared spectrophotometer using KBr wafers. The strong peak at 2150 cm^{-1} was assigned to CN stretching, and dicyclohexylamine was assigned by relevant IR absorption bands [8]. EDS spectra obtained on Philips XL-30S FEG scanning electron microscope/EDAX Phoenix energy dispersive X-ray spectrometer showed the presence of C, N and Ni elements. Carbon, hydrogen and nitrogen were determined by a CE EA-1110 elemental

analyzer. Ni was determined by a Jobin-Yvon Ultima-C inductively coupled plasma emission spectrometer. The composition of the product was deduced from the elemental analyses; the formula of $[(C_6H_{11})_2NH_2]_2[Ni(CN)_4]$ is consistent with the results of single-crystal X-ray diffraction analysis. Yield: *ca* 70%. Anal Calcd. for $C_{28}H_{48}N_6Ni$ (%): C, 63.76; H, 9.17; N, 15.93; Ni, 11.13. Found: C, 63.53; H, 9.31; N, 15.91; Ni, 11.30.

X-ray Crystallography

A pale yellow, blocky crystal of the title compound was coated with epoxy glue to prevent spontaneous liberation of dicyclohexylamine from the specimen under ambient conditions. The epoxy-coated crystal was then mounted on a Siemens P4 four-circle X-ray diffractometer and intensity data were collected in the θ–2θ scan mode using graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å). Unit cell parameters and an orientation matrix were determined from the least-squares fit of 88 accurately centred reflections with a θ range 4.39–23.62°. Three standard reflections were monitored every 97 reflections; no decay was observed during the data collection. Lorentz and polarization corrections were applied to the intensity data, and a semi-empirical absorption correction based on psi-scans was applied [9].

All calculations in the structural solution and refinement were performed using the Siemens SHELXTL crystallographic software package [10]. The space group was assigned based on systematic absences and intensity statistics, and confirmed by successful refinement. The structure was solved by direct methods [11] and refined by successive full-matrix least-squares methods followed by difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically; the hydrogen atoms were placed in calculated positions and assigned isotropic thermal parameters. Final difference maps

TABLE I Crystal data and structure refinement details for $[(C_6H_{11})_2NH_2]_2$ $[Ni(CN)_4]$

Chemical formula	$C_{28}H_{48}N_6Ni$
Formula weight	527.43
Temperature (K)	293(2)
Crystal system	Triclinic
Space group	*P*1
Unit cell dimensions	
a (Å)	9.237(1)
b (Å)	9.576(2)
c (Å)	9.689(3)
α (°)	61.51(2)
β (°)	85.69(3)
γ (°)	74.27(2)
V (Å^3)	723.6(3)
Z	1
Density (calculated) (g cm^{-3})	1.210
μ(MoKα) (mm^{-1})	0.696
F(000)	286
θ range for data collection (°)	2.3–27.7
Index range	$-1 \le h \le 11$, $-10 \le k \le 10$, $-12 \le l \le 12$
Reflections measured	3425
Independent reflections	3425 ($R_{int} = 0.0000$)
Data/restraints/parameters	3425/3/316
Goodness of fit on F^2	1.090
Final *R* indices [$I > 2\sigma(I)$]	0.0291, 0.0799
R indices (all data)	0.0296, 0.0811

contained no significant features. Further details concerning crystallographic and experimental data are given in Table I.

RESULTS AND DISCUSSION

Refined atomic parameters and selected bond lengths and angles for $[(C_6H_{11})_2NH_2]_2[Ni(CN)_4]$ are listed in Tables II and III, respectively. An ORTEP drawing and a crystal packing diagram of $[(C_6H_{11})_2NH_2]_2[Ni(CH)_4]$ are shown in Figs. 2 and 3, respectively.

As shown in Fig. 2, the crystal structure consists of negatively charged $[Ni(CN)_4]^{2-}$ and positively charged $[(C_6H_{11})_2NH_2]^+$ ions in a 1 : 2 ratio. In the asymmetric unit there is one independent anion and two independent cations. The tetracyanonickellate(II) is not bridged to another Ni(II) centre via cyano N atoms and is

TABLE II Atomic coordinates and equivalent thermal parameters for $[(C_6H_{11})_2NH_2]_2[Ni(CN)_4]$

Atom	*x/a*	*y/b*	*z/c*	U_{eq} (Å^2)[a]
Ni	0.5763(1)	0.9546(1)	0.9422(1)	0.031(1)
C(1)	0.6783(6)	0.8097(7)	1.1425(6)	0.034(1)
N(1)	0.7282(7)	0.7337(8)	1.2652(7)	0.055(2)
C(2)	0.4702(6)	1.0879(7)	1.0256(7)	0.036(1)
N(2)	0.4082(8)	1.1697(6)	1.0819(8)	0.051(2)
C(3)	0.4814(7)	1.0930(8)	0.7457(7)	0.042(1)
N(3)	0.4217(7)	1.1835(8)	0.6172(7)	0.051(2)
C(4)	0.6856(7)	0.8184(7)	0.8589(7)	0.039(2)
N(4)	0.7426(7)	0.7469(7)	0.7971(7)	0.050(2)
N(10)	0.6884(5)	0.6207(5)	0.5946(6)	0.030(1)
C(11)	0.7943(7)	0.4429(7)	0.6838(7)	0.033(1)
C(12)	0.7658(8)	0.3316(7)	0.6264(9)	0.046(2)
C(13)	0.8727(8)	0.1600(8)	0.7211(10)	0.055(2)
C(14)	1.0439(8)	0.1604(10)	0.7249(12)	0.060(2)
C(15)	1.0639(9)	0.2896(10)	0.7578(13)	0.062(2)
C(16)	0.9503(7)	0.4566(8)	0.6705(9)	0.044(1)
C(21)	0.5224(7)	0.6427(7)	0.5888(6)	0.034(1)
C(22)	0.4642(6)	0.5468(7)	0.7541(7)	0.035(1)
C(23)	0.2935(7)	0.5824(9)	0.7444(9)	0.051(2)
C(24)	0.2180(8)	0.7592(9)	0.6782(8)	0.051(2)
C(25)	0.2691(8)	0.8537(10)	0.5121(10)	0.058(2)
C(26)	0.4459(8)	0.8241(9)	0.5162(9)	0.050(2)
N(20)	0.4607(5)	0.2957(6)	0.2868(6)	0.033(1)
C(31)	0.6312(7)	0.2744(7)	0.2919(8)	0.035(1)
C(32)	0.6830(7)	0.3624(9)	0.1327(8)	0.043(1)
C(33)	0.8559(7)	0.3273(8)	0.1446(8)	0.048(2)
C(34)	0.9297(7)	0.1378(9)	0.2166(10)	0.060(2)
C(35)	0.8750(8)	0.0454(9)	0.3751(9)	0.055(2)
C(36)	0.7075(7)	0.0861(8)	0.3713(8)	0.043(2)
C(41)	0.3625(6)	0.4610(7)	0.1968(7)	0.031(1)
C(42)	0.1952(6)	0.4526(8)	0.2093(9)	0.042(1)
C(43)	0.0912(9)	0.6270(9)	0.1095(11)	0.049(1)
C(44)	0.1190(9)	0.7416(9)	0.1743(12)	0.066(2)
C(45)	0.2747(8)	0.7525(9)	0.1514(11)	0.059(2)
C(46)	0.3798(7)	0.5815(9)	0.2533(9)	0.048(2)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

TABLE III Selected bond lengths (Å) and angles (°) for $[(C_6H_{11})_2NH_2]_2$-$[Ni(CN)_4]$

Ni–C(1)	1.891(5)	Ni–C(2)	1.851(6)
Ni–C(3)	1.833(3)	Ni–C(4)	1.881(6)
C(1)–N(1)	1.109(9)	C(2)–N(2)	1.165(9)
C(3)–N(3)	1.192(9)	C(4)–N(4)	1.120(9)
N(10)–C(11)	1.556(7)	N(10)–C(21)	1.491(8)
C(11)–C(12)	1.502(9)	C(12)–C(13)	1.528(1)
C(13)–C(14)	1.586(1)	C(14)–C(15)	1.476(1)
C(15)–C(16)	1.519(1)	C(16)–C(11)	1.472(9)
C(21)–C(22)	1.560(7)	C(22)–C(23)	1.521(8)
C(23)–C(24)	1.486(1)	C(24)–C(25)	1.536(1)
C(25)–C(26)	1.580(1)	C(26)–C(21)	1.501(9)
N(20)–C(31)	1.534(8)	N(20)–C(41)	1.453(8)
C(31)–C(32)	1.479(9)	C(32)–C(33)	1.541(9)
C(33)–C(34)	1.561(1)	C(34)–C(35)	1.492(1)
C(35)–C(36)	1.489(1)	C(36)–C(31)	1.553(9)
C(41)–C(42)	1.562(8)	C(42)–C(43)	1.541(9)
C(43)–C(44)	1.581(1)	C(44)–C(45)	1.464(1)
C(45)–C(46)	1.529(1)	C(46)–C(41)	1.540(9)
C(1)–Ni–C(2)	87.9(3)	C(1)–Ni–C(3)	178.5(4)
C(1)–Ni–C(4)	91.6(2)	C(2)–Ni–C(3)	93.5(3)
C(2)–Ni–C(4)	179.5(3)	C(3)–Ni–C(4)	87.0(3)
Ni–C(1)–N(1)	173.1(6)	Ni–C(2)–N(2)	177.4(6)
Ni–C(3)–N(3)	179.0(6)	Ni–C(4)–N(4)	173.7(6)
C(11)–N(10)–C(21)	118.7(5)	N(10)–C(11)–C(12)	111.8(5)
N(10)–C(11)–C(16)	107.5(5)	C(11)–C(12)–C(13)	108.4(6)
C(12)–C(13)–C(14)	113.6(7)	C(13)–C(14)–C(15)	112.6(6)
C(14)–C(15)–C(16)	115.1(8)	C(15)–C(16)–C(11)	112.0(6)
C(16)–C(11)–C(12)	114.0(6)	N(10)–C(21)–C(22)	112.6(5)
N(10)–C(21)–C(26)	108.1(6)	C(21)–C(22)–C(23)	110.8(5)
C(22)–C(23)–C(24)	112.3(6)	C(23)–C(24)–C(25)	109.9(6)
C(24)–C(25)–C(26)	110.6(7)	C(25)–C(26)–C(21)	110.0(7)
C(26)–C(21)–C(22)	111.0(5)	C(31)–N(20)–C(41)	118.2(5)
N(20)–C(31)–C(32)	111.4(5)	N(20)–C(31)–C(36)	106.6(5)
C(31)–C(32)–C(33)	108.9(6)	C(32)–C(33)–C(34)	109.7(6)
C(33)–C(34)–C(35)	111.3(7)	C(34)–C(35)–C(36)	111.7(6)
C(35)–C(36)–C(31)	113.1(6)	C(36)–C(31)–C(32)	112.0(6)
N(20)–C(41)–C(42)	109.1(5)	N(20)–C(41)–C(46)	113.0(5)
C(41)–C(42)–C(43)	109.2(5)	C(42)–C(43)–C(44)	107.7(7)
C(43)–C(44)–C(45)	109.2(7)	C(44)–C(45)–C(46)	108.4(6)
C(45)–C(46)–C(41)	109.7(6)	C(46)–C(41)–C(42)	108.8(5)

square planar. Two dicyclohexylammonium cations are arranged in inverse positions. The anion has four C–Ni–C angles from 87.0(3) to 93.5(3)° and two C–Ni–C angles of 178.5(4), 179.5(3)° with the Ni–C distance ranging from 1.833(3) to 1.891(5) Å. Individual cations in the asymmetric unit have two C–N–C angles of 118.7(5), 118.2(5)° with N–C distances ranging from 1.453(8) to 1.556(7) Å. The cyclohexyl rings of the dicyclohexylammonium cations have the chair conformation. Bond lengths and angles related to the dicyclohexylammonium cation are not unusual.

As shown in Fig. 3, the dicyclohexylammonium cation occupies a bridging position by hydrogen bonding to cyanide nitrogen atoms of adjacent $[Ni(CN)_4]^{2-}$ anions. All N_{CN} atoms and N–H groups are involved in hydrogen bonding. The strongest H-bonds are N(10)−H(10a)···N(4) 2.881(8) Å, 162.3°; N(10)−H(10b)···

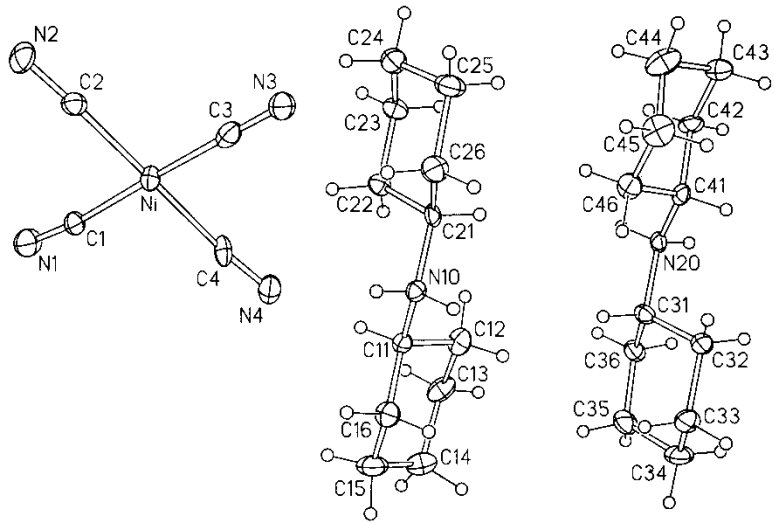

FIGURE 2 ORTEP drawing of $[(C_6H_{11})_2NH_2]_2[Ni(CN)_4]$ with the atom – numbering scheme. Thermal ellipsoids are drawn at the 30% probability level.

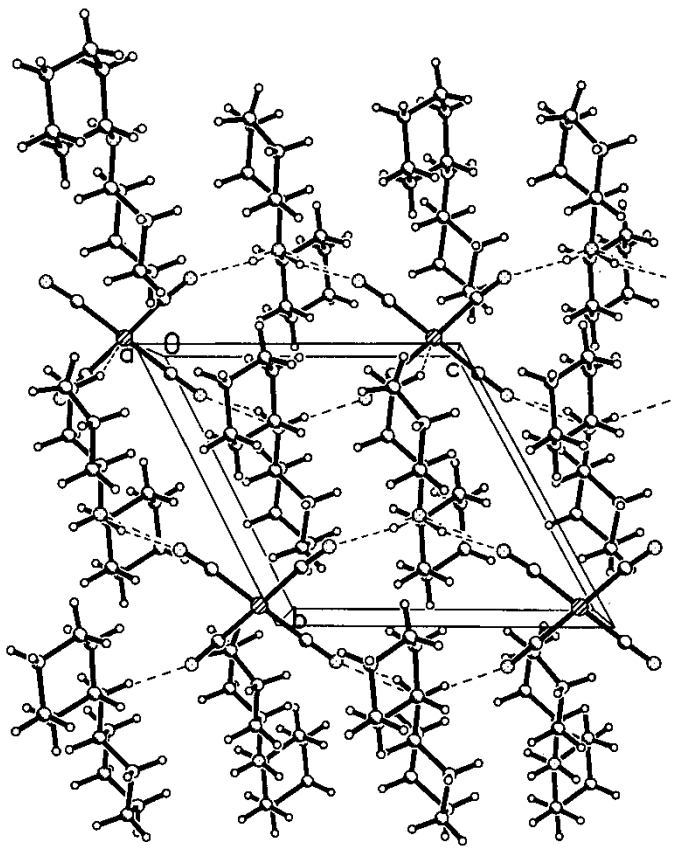

FIGURE 3 Crystal packing diagram of $[(C_6H_{11})_2NH_2]_2[Ni(CN)_4]$ viewed along the *a* axis.

N(1) 2.870(9) Å, 161.3°; N(20)−H(20a)···N(2) 2.895(8) Å, 157.8° and N(20)−H(20b)···N(3) 2.879(8) Å, 163.4°. This complex provides a one-dimensional infinite hydrogen-bonded chain structure.

Acknowledgments

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Supplementary Material

Full lists of crystallographic data are available from the authors upon request.

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