The present structure represents a new structural type of copper arsine and copper dioximate complex.

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Structural Investigations of Nickel(II) Complexes. IX. Structure of Tetrakis(imidazole)bis(isothiocyanato)nickel(II)

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Abstract. [Ni(NCS)$_2$(C$_3$H$_4$N$_2$)$_4$], $M_r = 447·18$, orthorhombic, *Pbca*, $a = 15·415\,(6)$, $b = 16·422\,(5)$, $c = 15·535\,(4)$ Å, $V = 3932·6\,(2)$ Å^3, $Z = 8$, $D_m = 1·50$, $D_x = 1·510$ g cm^{-3}, $\lambda(\text{Cu } K\alpha) = 1·54178$ Å, $\mu = 34·06$ cm^{-1}, $F(000) = 1840$, room temperature, $R = 0·0486$, $wR = 0·0505$ for 1867 reflections with $I \geq 3\sigma(I)$. The structure consists of isolated molecules of [Ni(NCS)$_2$(Him)$_4$] (Him = imidazole), which contains a distorted octahedral NiN$_6$ chromophore. The NCS ligands are *trans* and four N(imidazole) atoms define an equatorial plane. The mean Ni—N(Him) distance (R_e) is 2·113 (4) and the mean Ni—N(Him) distance (R_a) is 2·080 (3) Å.

Introduction. From the spectral and magnetic data it has been concluded that stereochemical and other properties of Ni^{II} pyridine complexes are influenced by the nature and position of substituents on the pyridine ligands (Jamnický & Jóna, 1984). Furthermore, it was shown by Koman, Jóna & Ďurčanská (1986) that the stereochemistry of [Ni(NCS)$_2L_4$] complexes, where L is a piperidine derivative, depends on the position of methyl substituents in the piperidine ring. When L = piperidine itself, Ni^{II} displays a pseudooctahedral configuration, while the complexes with 3- and 4-methylpiperidine contain pentacoordinated Ni and those with 2-methyl and 2,6-dimethylpiperidine are square planar (Koman, Ďurčanská, Handlovič & Gažo, 1985).

The present paper deals with the structure of tetrakis(imidazole)bis(isothiocyanato)nickel(II). It was expected that exchange of pyridine or piperidine (six-membered-ring heterocyclic ligands) by imidazole which has a five-membered ring might be accompanied by a change in Ni—N bond lengths and by a different type of axial distortion of the metal coordination.

Experimental. Blue prism-shaped crystals, 0·40 × 0·20 × 0·15 mm; density measured by flotation. Syntex $P2_1$ diffractometer, 15 reflections with $5·37 \leq \theta \leq 12·85°$ for determining lattice parameters; absorption and extinction ignored. Intensity measurements from θ–2θ scans carried out for $0 \leq 2\theta \leq 100°$; h, k, l range h 0 to 16, k 0 to 17, l 0 to 16. Two standard reflections re-estimated after every 98 measurements, decreased in intensity by 15% during the course of the experiment. 1867 independent reflections with $I \geq 3\sigma(I)$ (511 unobserved reflections), 308 refined parameters. Ni-atom position from Patterson function, other non-H atoms from Fourier syntheses. H atoms from difference syntheses. Anisotropic full-matrix refinement for non-H atoms (H atoms isotropic refinement) based on F. $R = 0·0486$, $wR = 0·0505$. $w = k[\sigma^2(F_o) + g(F_o)^2]^{-1}$, $k = 2·5456$, $g = 0·000886$, $|\Delta\rho| \leq 0·7$ e Å^{-3}; $(\Delta/\sigma)_{\max} = 0·40$ in final least-squares cycle. Calculations performed with *SHELX76* program system (Sheldrick,

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Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters for non-*H *atoms with e.s.d.'s in parentheses*

$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$

	x	y	z	U_{eq} (Å^2)
Ni1	0·0090 (1)	0·7512 (1)	−0·1185 (1)	0·0491 (3)
S1	0·1835 (1)	0·5498 (1)	0·0049 (1)	0·0617 (5)
S2	−0·1497 (1)	0·9790 (1)	−0·2546 (1)	0·0752 (6)
N1	0·0723 (2)	0·6633 (2)	−0·0682 (3)	0·0452 (12)
N2	−0·0897 (2)	0·8424 (2)	−0·1678 (3)	0·0451 (13)
C1	0·1177 (3)	0·6161 (3)	−0·0376 (3)	0·0362 (13)
C2	−0·1153 (3)	0·8988 (3)	−0·2027 (3)	0·0389 (14)
N3	−0·0726 (2)	0·6652 (2)	−0·1979 (2)	0·0410 (12)
C3	−0·0996 (3)	0·6757 (3)	−0·2796 (3)	0·0521 (23)
N4	−0·1493 (4)	0·5603 (3)	−0·2378 (4)	0·0822 (23)
C4	−0·1458 (5)	0·6127 (4)	−0·3050 (5)	0·0576 (19)
C5	−0·1029 (5)	0·5936 (4)	−0·1748 (5)	0·0783 (26)
N5	−0·0977 (2)	0·7245 (2)	−0·0188 (2)	0·0400 (12)
C6	−0·0986 (4)	0·6608 (3)	0·0324 (4)	0·0518 (18)
N6	−0·1713 (3)	0·6563 (3)	0·0761 (3)	0·0569 (16)
C7	−0·2213 (4)	0·7187 (4)	0·0544 (4)	0·0595 (20)
C8	−0·1752 (3)	0·7622 (3)	−0·0049 (3)	0·0463 (17)
N7	0·0496 (2)	0·8412 (2)	−0·0409 (3)	0·0405 (12)
C9	0·0629 (4)	0·8383 (4)	0·0411 (4)	0·0600 (20)
N8	0·0954 (4)	0·9077 (4)	0·0702 (4)	0·0658 (20)
C10	0·1050 (4)	0·9570 (4)	0·0051 (5)	0·0787 (23)
C11	0·0768 (4)	0·9178 (3)	−0·0648 (4)	0·0664 (22)
N9	0·0797 (2)	0·7720 (2)	−0·2192 (2)	0·0394 (11)
C12	0·0863 (4)	0·8331 (3)	−0·2741 (4)	0·0526 (18)
N10	0·1552 (4)	0·8255 (4)	−0·3248 (4)	0·0621 (16)
C13	0·1961 (4)	0·7576 (4)	−0·3017 (4)	0·0627 (24)
C14	0·1501 (3)	0·7246 (4)	−0·2371 (3)	0·0491 (18)

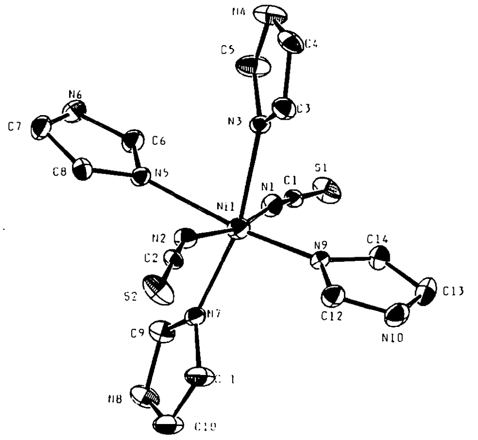

Fig. 1. The molecular structure of [Ni(NCS)$_2$(Him)$_4$].

1976); scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. The final coordinates for the non-H atoms are listed in Table 1 and selected distances and angles are in Table 2.* The molecular structure and atomic numbering are shown in Fig. 1.

Table 2. *Interatomic distances* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

Ni1—N1	2·066 (3)	Ni1—N2	2·094 (3)
Ni1—N3	2·119 (3)	Ni1—N5	2·114 (3)
Ni1—N7	2·111 (3)	Ni1—N9	2·106 (3)
N1—C1	1·148 (5)	C1—S1	1·629 (4)
N2—C2	1·143 (5)	C2—S2	1·634 (4)
N3—C3	1·345 (5)	C3—C4	1·318 (7)
C4—N4	1·355 (7)	N4—C5	1·330 (6)
C5—N3	1·315 (6)	N5—C6	1·313 (5)
C6—N6	1·312 (6)	N6—C7	1·326 (7)
C7—C8	1·365 (7)	C8—N5	1·365 (5)
N7—C9	1·292 (6)	C9—N8	1·326 (7)
N8—C10	1·305 (7)	C10—C11	1·336 (7)
C11—N7	1·378 (6)	N9—C12	1·321 (5)
C12—N10	1·331 (7)	N10—C13	1·329 (7)
C13—C14	1·343 (7)	C14—N9	1·364 (5)
N1—Ni1—N2	178·7 (1)	N3—Ni1—N5	89·2 (1)
N1—Ni1—N3	91·9 (1)	N3—Ni1—N7	177·1 (1)
N1—Ni1—N5	88·2 (1)	N3—Ni1—N9	88·6 (1)
N1—Ni1—N7	90·9 (1)	N5—Ni1—N7	90·3 (1)
N1—Ni1—N9	90·0 (1)	N5—Ni1—N9	177·2 (1)
N2—Ni1—N3	89·4 (1)	N7—Ni1—N9	91·9 (1)
N2—Ni1—N5	91·9 (1)	Ni1—N1—C1	177·5 (3)
N2—Ni1—N7	87·8 (1)	Ni1—N2—C2	163·4 (3)
N2—Ni1—N9	89·9 (1)	N1—C1—S1	179·1 (4)
N2—C2—S2	178·4 (4)		

Table 3. *Values of* R_e, R_a (Å) *and* R_e/R_a *ratios in trans-*[Ni(NCS)$_2L_4$] *complexes with* NiN$_6$ *chromophores*

R_a is the mean axial Ni—N(NCS) bond length and R_e is the mean equatorial Ni—N(L) distance, Him - imidazole (title complex), py - pyridine (Valach, Sivý & Koreň, 1984), pip - piperidine (Koman, Handlovič, Ďurčanská & Gažo, 1983).

Complex	R_e	R_a	R_e/R_a
Ni(NCS)$_2$(Him)$_4$	2·113 (4)	2·080 (3)	1·016
Ni(NCS)$_2$(py)$_4$	2·160 (10)	2·062 (8)	1·048
Ni(NCS)$_2$(pip)$_4$	2·260 (11)	1·987 (9)	1·137

The Ni^{II} atom exhibits an axially distorted octahedral coordination with *trans*-N-bonded thiocyanate ligands. The equatorial plane of the complex is formed by four Ni—N(imadazole) bonds with lengths between 2·106 (3) and 2·119 (3) Å, and the axial positions are occupied by two N-bonded NCS groups [Ni—N(NCS) = 2·066 (3) and 2·094 (3) Å]. Comparison of Ni—N distances and of the R_e/R_a ratios which measure the relative tetragonal distortion (Procter, Hathaway & Nicholls, 1968) in [Ni(NCS)$_2L_4$] complexes (L = Him, pyridine = py, piperidine = pip) shows the influence of the ligand properties (electronic and steric) on the coordination polyhedra (Table 3). In [Ni(NCS)$_2$(Him)$_4$] the tetragonal distortion is smallest, possibly reflecting the smaller size of the Him ring compared with those of py and pip.

From Table 3 it is apparent that the tetragonal distortion increases along the series Him, py, pip, with R_e also increasing along the series while R_a decreases. Thus, the metal—axial ligand distances

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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 53835 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

depend on the metal—equatorial ligand distances. This is in agreement with the concept of the equatorial—axial interactions of the ligands (Gažo, Boča, Jóna, Kabešová, Macašková, Šima, Pelikán & Valach, 1982).

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Structure of Tetramethylammonium Tribromocadmate in the Ferroelectric Phase

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Abstract. [$N(CH_3)_4$][$CdBr_3$], M_r = 426·2, hexagonal, $P6_1$, a = 9·257 (4), c = 20·900 (5) Å, V = 1551 (1) Å^3, Z = 6, D_x = 2·738 g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, μ = 135·27 cm^{-1}, $F(000)$ = 1176, T = 133 K, final R = 0·041 for 1610 independent reflections. The cell dimension is tripled along the c axis in comparison with the structure in the room-temperature phase. $N(CH_3)_4$ groups are ordered. H-atom positions were not determined.

Introduction. $N(CH_3)_4MX_3$-type compounds (M = Mn, Ni, Cd, ...; X = Cl, Br, I) have been widely studied as quasi-one-dimensional magnetic systems. $N(CH_3)_4CdBr_3$ is the only compound which has been known to exhibit ferroelectric activity; spontaneous polarization along the c axis is observed below 156 K (Gesi, 1990). The crystal structure at room temperature (space group $P6_3/m$; Z = 2) consists of infinite linear chains formed by face-shared $CdBr_6$ octahedra and of orientationally disordered $N(CH_3)_4$ groups (Asahi, Hasebe & Gesi, 1990). Most $N(CH_3)_4MX_3$-type compounds have such a structure at room temperature (Morosin & Graeber, 1967; Morosin, 1972). The ferroelectric phase is expected to be an ordered phase as suggested by several authors (Daoud, 1976; Venu, Sastry & Ramakrishna, 1987). The present paper reports the structure in the ferroelectric phase at 133 K.

Experimental. Single crystals were grown by the evaporation method from aqueous solution. D_m not measured. Spherical specimen with radius 0·10 mm, Rigaku AFC-5 diffractometer, graphite-monochromated Mo $K\alpha$ radiation; scan mode θ–2θ, scan speed 10° min^{-1} in θ, scan width (1·5 + 0·5tanθ)°; cell dimensions from 24 reflections, 7·7 < θ < 8·9°; Lorentz and polarization corrections; absorption corrections, min. and max. transmission coefficients 0·154 and 0·197; $\sin\theta/\lambda$ < 0·904 Å^{-1} ($0 \le h \le 16$, $0 \le k \le 16$, $0 \le l \le 37$ and $-16 \le h \le 0$, $-16 \le k \le 0$, $0 \le l \le 37$); four standard reflections ($\bar{2}16$, 026, 0,0,12, 231) monitored every 150 reflections, no significant variation; 7430 reflections measured, 3293 unique reflections [$R_{\rm int}$ = 0·042 based on F for 1871 unique reflections with $F > \sigma(F)$], of which 1613 with $F > 3\sigma(F)$ were used in refinement. The positional parameters of Cd, Br and N atoms in the room-temperature phase (Asahi *et al.*, 1990) were used as the starting parameters; C atoms found by Fourier synthesis; atomic scattering factors for Cd^{2+}, Br$^-$, N and C and dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV); full-matrix least-squares refinement with anisotropic thermal parameters (total of 81 parameters varied). At the final stage of refinement, three reflections (230, 0,0,12 and 203) were removed because of the possibility of extinction effects. R = 0·041, wR =

0108-2701/91/061208-03$03.00