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Structural Investigation of Ni^{II} Complexes. VIII. Structure of Tris(2,4-dimethylpyridine)bis(isothiocyanato)nickel(II)

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Abstract. $[Ni(NCS)_2(C_7H_9N)_3]$, M_r = 496·34, tetragonal, $P4_12_12$, a = 13·44 (1), c = 14·191 (5) Å, Z = 4, V = 2563 (3) Å^3, D_m = 1·285 (6), D_x = 1·29 g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, μ = 9·3 cm^{-1}, F(000) = 1040, room temperature, R = 0·049, wR = 0·056 for 1030 reflections with $I \geq 1·96\sigma(I)$. Five N atoms surround the Ni atom, defining a coordination polyhedron intermediate between trigonal bipyramidal and tetragonal pyramidal. The complex lies on a crystallographic diad axis which passes through the Ni atom and one of the dimethylpyridine ligands which is disordered.

Introduction. Structural studies of $Ni(NCS)_2$(alkylpyridine)$_x$ complexes have shown that there is a direct relationship between the size and position of the pyridine alkyl substituents and the structure of the complex. 4- and 3-alkyl-substituted pyridines form pairs of the pseudo-octahedral complexes of different symmetry [Andreetti, Bocelli & Sgarabotto, 1972; Kerr & Williams, 1977 (4-methylpyridine complexes); Ďurčanská, Jamnický, Koman, Wnęk & Głowiak, 1986 (3-ethylpyridine complexes)] depending on the preparation mode whereas 2-alkyl-substituted pyridines cause a radical change in the coordination number of the Ni^{II} atom, decreasing it from 6 (the usual value) to 4 or 5. The structure determination of $[Ni(NCS)_2$(2,5-dimethylpyridine)$_2]$ (Ďurčanská, Głowiak & Kožíšek, 1982) provides an example of square planar nickel(II) with 2-methylpyridine ligands; the corresponding pentacoordinate nickel(II) species $[Ni(NCS)_2$(2,5-dimethylpyridine)$_3]$ was too unstable for X-ray analysis. Instead we report the structure determination of the title complex. Spectral and magnetic measurements confirmed the pentacoordination of Ni^{II} (Jóna, Jamnický & Šramko, 1978), X-ray analysis now gives a more precise picture of the coordination geometry and of its relationship with the steric properties of the 2-substituted pyridine ligands.

Experimental. Green bipyramids, 0·35 × 0·35 × 0·30 mm; density measured by flotation (CCl_4/acetone). Cell parameters refined on Syntex $P2_1$ diffractometer by least squares from 15 reflections with $4 \leq \theta \leq 17°$. Absorption and extinction ignored. Intensity measurements from θ–2θ scans carried out for $0 \leq 2\theta \leq 55°$. *hkl* range h −17 to 17, k 0 to 17, l 0 to 18. Two standard reflections every 50 measurements, decreased in intensity by 15% during the course of the experiment, 1030 independent reflections with $I \geq 1·96\sigma(I)$ (725 unobserved reflections), $R_{\rm int}$ = 0·032 assuming 4/*mmm* Laue symmetry. Ni atom position from Patterson function; other non-H atoms from Fourier syntheses. The nine H atoms [of the N(2) pyridine ligand] were initially located from a difference map and then refined isotropically; the seven independent H atoms of the disordered N(1) ring were positioned geometrically, full-matrix refinement [except H atoms of N(1) ring] based on F, 173 parameters refined, R = 0·049, wR = 0·056, $w = 1/[\sigma^2(F) + 0·0134\,(F)^2]$, $(\Delta/\sigma)_{\max}$ in final least-squares cycle 0·6 [for C(27)]; $\Delta\rho$ values between 0·27 and −0·32 e Å^{-3}. No attempt was made to determine chirality by refinement in the alternative space group $P4_32_12$. *XTL* program system (Syntex, 1973) and

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Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

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

	x	y	z	U_{eq}
Ni*	0·7749 (2)	0·7749	0	0·053 (1)
N	0·7489 (6)	0·7509 (7)	0·1365 (6)	0·079 (5)
C	0·7309 (8)	0·7360 (8)	0·2134 (6)	0·070 (5)
S	0·7064 (3)	0·7258 (3)	0·3248 (2)	0·107 (2)
N(2)	0·8780 (5)	0·6518 (5)	−0·0034 (6)	0·061 (4)
C(21)	0·8473 (7)	0·5577 (6)	−0·0027 (8)	0·062 (5)
C(22)	0·9119 (9)	0·4775 (7)	−0·0041 (7)	0·070 (5)
C(23)	1·0131 (8)	0·4920 (6)	−0·0074 (8)	0·064 (5)
C(24)	1·0443 (8)	0·5898 (8)	−0·0089 (8)	0·073 (6)
C(25)	0·9760 (7)	0·6646 (7)	−0·0078 (8)	0·064 (6)
C(26)	0·7341 (9)	0·5401 (8)	0·0014 (14)	0·092 (8)
C(27)	1·0856 (12)	0·4086 (10)	−0·0039 (12)	0·095 (8)
N(1)*	0·8846 (6)	0·8846	0	0·100 (8)
C(11)	0·9404 (9)	0·9005 (8)	0·0764 (12)	0·098 (8)
C(12)	1·0181 (11)	0·9727 (12)	0·0766 (15)	0·153 (15)
C(13)*	1·0300 (8)	1·0300	0	0·172 (15)
C(14)*	1·1100 (9)	1·1100	0	0·309 (23)
C(15)†	0·9527 (22)	0·8470 (18)	0·1643 (21)	0·198 (21)

* On diad axis x, x, 0.

† Site-occupation factor is 0·5.

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

Ni—N	1·995 (9)	N—C	1·136 (12)
Ni—N(1)	2·085 (3)	C—S	1·621 (9)
Ni—N(2)	2·159 (7)		
N—Ni—N(1)	103·8 (3)	Ni—N—C	177·6 (9)
N—Ni—N(2)	90·6 (3)	N—C—S	175·0 (1)
N(1)—Ni—N(2)	95·1 (2)	N(2)—Ni—N(2′)	169·9 (3)
N—Ni—N′	152·4 (4)	N—Ni—N(2′)	87·0 (3)

A prime indicates the transformation y, x, $-z$.

*SHELX*76 (Sheldrick, 1976), *PARST* (Nardelli, 1983), scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. Positional and equivalent isotropic thermal parameters are given in Table 1,* main interatomic distances and bond angles in Table 2. The crystal structure consists of mononuclear complex molecules having C_2 symmetry [the Ni—N(1) lies on the twofold axis]. The molecular drawing with the atom-numbering scheme is given in Fig. 1 and the crystal packing is shown in Fig. 2. The coordination geometry was first studied by spectral and magnetic measurements. The magnetic moment, 3·29 BM ($1\text{BM} \equiv 9{\cdot}27 \times 10^{-24}$ J T^{-1}), and the electronic absorption spectra with five absorption maxima at $\tilde{\nu}$ = 6700, 10400, 14800, 24500 and 28150 cm^{-1} (Jóna, Jamnický & Šramko, 1978) show that the Ni^{II} atom is five coordinate. However, the symmetry and the geometry of the coordination polyhedron could only be determined by the X-ray analysis.

The coordination polyhedron around the Ni^{II} atom can be described as tetragonal pyramidal [having two N and two N(2) atoms in basal positions and N(1) in the apical position] strongly distorted towards trigonal bipyramidal [with N(1) and two N(NCS) atoms forming the equatorial plane, the apical positions being occupied by N(2) atoms]. The degree of distortion can by seen from comparison of the bond angles for regular tetragonal pyramidal and the trigonal bipyramidal coordination (Addison, Nageswara Rao, Reedijk, van Rijn & Verschoor, 1984) with those found for the title complex (Table 2).

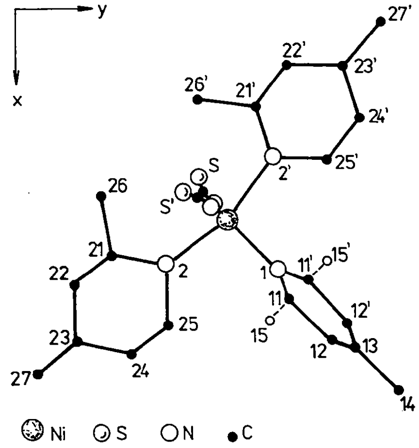

Fig. 1. The molecular drawing with atom numbering.

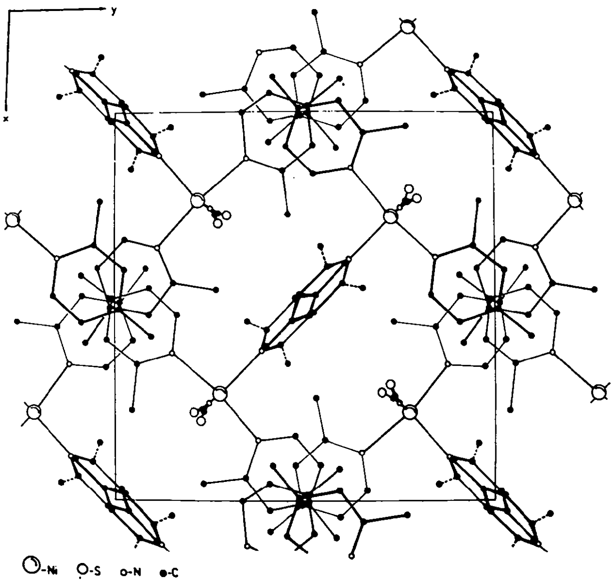

Fig. 2. Projection of the structure along **c**.

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* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles including those for H atoms and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53857 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The arrangement of donor atoms around the central atom is influenced by the steric properties of the 2,4-dimethylpyridine ligand: the 2-methyl substituents, *i.e.* the pairs of diad-related C(26) and C(15) methyl groups, block further coordination of the Ni atom; the intramolecular distances Ni···C(26) and Ni···C(15) are 3·20 (1) and 3·48 (3) Å, respectively. Two C(26) methyl groups lie approximately in the position *trans* to N(1), while the two disordered C(15) methyl groups occupy the space between the N(1) atom and the N atoms of the NCS groups.

The N(1) pyridine atoms N(1), C(13) and C(14) lie on a crystallographic twofold axis, with consequent disordering of both methyl substituents. The high U_{eq} values for some of the C atoms of this ring (Table 1) may also reflect the disorder.

The N(2) pyridine ring is planar, the N(1) pyridine atoms deviate significantly from planarity [C(11) and C(12) atoms by 0·02 (1) and 0·03 (2) Å, respectively]; their average planes form a dihedral angle of 71·1 (6)°.

The shortest contacts were found between the S and H atoms [H atoms bonded to the C(24) and C(12) atoms] of the adjacent complex molecules; further contacts were found between 2,4-dimethylpyridine ligands of adjacent molecules. Intermolecular contacts correspond to the sum of the van der Waals radii of the atoms involved.

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Synthesis and Structure of Bis(tetraphenylphosphonium) Bis(tetratellurido)palladate Dimethylformamide Solvate

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Abstract. $[P(C_6H_5)_4]_2[Pd(Te_4)_2].C_3H_7NO$ (I), M_r = 1806, orthorhombic, *Pbca*, a = 29·611 (10), b = 16·291 (6), c = 23·325 (9) Å, V = 11251·8 Å^3, Z = 8, D_x = 2·17, D_m = 2·20 (1) g cm^{-3} (by flotation in $CHBr_3$/heptane), Mo $K\alpha$, λ = 0·71069 Å, μ = 44·9 cm^{-1}, $F(000)$ = 6680, T = 296 K, final R = 0·044, wR = 0·049 for 4453 reflections with $F_o^2 > 3\sigma(F_o^2)$. The structure is composed of Ph_4P^+ cations, $[Pd(Te_4)_2]^{2-}$ anions and DMF molecules. The $[Pd(Te_4)_2]^{2-}$ complex features a nearly square-planar Pd^{2+} atom chelated by two Te_4^{2-} ligands. The $PdTe_4$ five-membered rings are puckered forming an envelope conformation. The mean Pd—Te bond distance is 2·587 (2) Å. The mean Te—Te bond distance is 2·74 (3) Å.

Introduction. Transition-metal polytelluride chemistry is relatively little explored. Recently reports of some remarkable species $[Hg_4Te_{12}]^{4-}$ and $[Hg_2Te_5]^{2-}$ (Haushalter, 1985*a*), $[NbTe_{10}]^{3-}$ (Flomer & Kolis, 1988), $[Mo_4Te_{16}(en)_4]^{2-}$ (Eichhorn, Haushalter, Cotton & Wilson, 1988), $[Fe_2(CO)_6Te_3]^{2-}$ (Eichhorn & Haushalter, 1990), $[Cr(CO)_2(Te_2)_2]^{2-}$ (Flomer, O'Neal, Kolis, Jeter & Cordes, 1988), $[Au_2Te_2]^{2-}$ (Haushalter, 1985*b*), and $[KAu_9Te_7]^{4-}$ and $[K_2Au_4Te_4(solv)_4]^{2-}$ (Haushalter, 1985*c*) indicate that polytelluride chemistry will produce new compounds, not quite analogous to S or even Se. As part of our synthetic efforts in this area we synthesized and structurally characterized $[Pd(Te_4)_2]^{2-}$ as the Ph_4P^+ salt. While our work was in progress (Kanatzidis, 1988), the structure of $(Ph_4P)_2[Pd(Te_4)_2]$ was reported (Adams, Wolfe, Eichhorn & Haushalter, 1989). Interestingly, although the molecular structure of Haushalter's $[Pd(Te_4)_2]^{2-}$ is essentially the same as ours, the space groups in the two varieties are different. Our complex (I) is a dimethylformamide (DMF) solvate and has an orthorhombic crystal system, whereas Haushalter's compound (II) is unsolvated and is triclinic. Since (I) is different, we wish to

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