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Structural Investigations of Ni^{II} Complexes. V. Preparation, Properties and Structure of Bis(2,6-dimethylpiperidine)di(thiocyanato-*N*)nickel(II)–Benzene, $[Ni(NCS)_2(C_7H_{15}N)_2].C_6H_6$

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Abstract. $M_r = 479{\cdot}40$, triclinic, $P\bar{1}$, $a = 11{\cdot}859$ (4), $b = 8{\cdot}494$ (3), $c = 7{\cdot}365$ (3) Å, $\alpha = 103{\cdot}98$ (3), $\beta = 112{\cdot}00$ (2), $\gamma = 102{\cdot}59$ (3)°, $V = 627{\cdot}0$ (5) Å^3, $Z = 1$, $D_m = 1{\cdot}274$, $D_x = 1{\cdot}270$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 9{\cdot}5$ cm^{-1}, $F(000) = 256$, $T = 293$ K, $R = 5{\cdot}5\%$, 1611 reflections. The Ni^{II} atom has a square-planar coordination sphere: $Ni(N_{NCS})_2(N_{pip})_2$ (N_{NCS}: N atoms of the NCS groups; N_{pip}: N atoms of the piperidine ligands). The bond lengths are: Ni—N_{NCS} 1·849 (7) and Ni—N_{pip} 1·984 (7) Å. The bond angle N_{NCS}—Ni—N_{pip} is 88·59 (3)°. The plane of the benzene molecule forms a dihedral angle of 51 (3)° with the coordination plane of Ni^{II}, while the C(11)C(13)-C(15)C(16) plane is nearly perpendicular to the coordination plane [81·5 (3)°], forming with the benzene plane an angle of 49 (3)°. The shortest intermolecular distances between $Ni(NCS)_2(2,6\text{-}Me_2pip)_2$ and benzene are 3·64 (4) and 3·66 (8) Å. The NCS groups are terminally bonded through the N atom.

Introduction. The X-ray crystal structure determination of $Ni(NCS)_2L_4$ pseudo-octahedral complexes [where L is an N-heterocyclic ligand such as pyridine (py) or piperidine (pip) and their derivatives] has shown the influence of the exchange of py (unsaturated bonds) by pip (saturated bonds) on the Ni—N distances [*e.g.* $Ni(NCS)_2py_4$ (Valach, Sivý & Koreň, 1984) compared with $Ni(NCS)_2pip_4$ (Koman, Handlovič, Ďurčanská & Gažo, 1983)]. The crystal structure determination of the title complex was undertaken to study the influence of the analogous exchange for square-planar $Ni(NCS)_2L_2$ complexes. The title compound was found to have clathrate character: it is formed by $Ni(NCS)_2(2,6\text{-}Me_2pip)_2$ complex molecules and by benzene molecules held together by weak van der Waals bonds with the shortest contacts between the methyl groups of the Me_2pip ligands and the benzene molecules. Similar host–guest interactions were found in other Ni^{II} isothiocyanate complexes with N-heterocyclic ligands (Andreetti, Cavalca & Sgarabotto, 1970).

Experimental. 1·80 g $Ni(NCS)_2$ was mixed with 40 cm^3 benzene and 14 cm^3 2,6-Me_2pip, brought to the boil under reflux and continuously stirred for 3 h; the hot solution was filtered and left to crystallize. Within 48 h red crystals were formed. From the analysis (experimental: Ni 12·24, N 11·68, C 54·64, H 7·56%; calculated: Ni 12·51, N 11·68, C 54·64, H 7·51%) the title formula was determined. The electronic absorption spectrum showed a band with maximum at 19 000 cm^{-1}, typical for Ni^{II} square-planar complexes. From the IR spectrum the bands at 2070, 852 and 483 cm^{-1} indicated terminal bonding of the NCS groups through the N atom.

Prism-shaped crystal, 0·4 × 0·3 × 0·2 mm, mounted inside a glass capillary. D_m measured by flotation. Syntex $P2_1$ diffractometer. 10 reflections with $8 \leq \theta \leq 17°$ for measuring lattice parameters. Absorption and extinction ignored. $0 < 2\theta < 45°$. *hkl* range 0,–8,–7 to 11,8,7. Two standard reflections after every 98, no significant intensity variation. 1611 independent reflections with $I > 2\sigma(I)$. Ni and S positions from Patterson map; other non-H atoms from Fourier map. H atoms of methyl groups from difference Fourier map, the remainder in calculated positions. Anisotropic full-matrix refinement (except H atoms) based on F. $w = 1/\sigma^2(F)$. $wR = 0{\cdot}061$, $R = 0{\cdot}055$; $(\Delta/\sigma)_{max}$ in final least-squares cycle 0·20. $\Delta\rho \leq |0{\cdot}5|$ e Å^{-3}. Calculations performed on a NOVA 1200 computer, with the *XTL* system supplied by Syntex corporation.

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Discussion. Atomic coordinates are listed in Table 1;* Table 2 gives the bond distances and angles. The crystal structure consists of $\mathrm{Ni(NCS)_2(2,6\text{-}Me_2pip)_2}$ and benzene molecules (Fig. 1). The $\mathrm{Ni^{II}}$ atom has a centrosymmetric square-planar coordination involving four N atoms. The interatomic distances $\mathrm{Ni{-}N_{NCS}}$ and $\mathrm{Ni{-}N_{pip}}$ are 1·849 (7) and 1·984 (7) Å, respectively. These values should be compared with those found for $\mathrm{Ni(NCS)_2(2,6\text{-}Me_2py)_2}$ in order to consider the influence of the exchange of the saturated pip ligand by the unsaturated py ligand in $\mathrm{Ni^{II}}$ square-planar complexes. As the crystal structure of $\mathrm{Ni(NCS)_2(2,6\text{-}Me_2py)_2}$ is not known, the comparison must be made with the known structure of $\mathrm{Ni(NCS)_2(2,5\text{-}Me_2py)_2}$, where $\mathrm{Ni{-}N_{NCS}} = 1{\cdot}865\ (8)$ and $\mathrm{Ni{-}N_{py}} = 1{\cdot}910\ (7)$ Å (Ďurčanská, Głowiak & Kožíšek, 1982). Coordination bond lengths in both compounds correspond well to the average interatomic Ni—N distances found for other square-planar $\mathrm{Ni^{II}}$ complexes, which are in the range 1·80 to 1·96 Å (Bowers, Banks & Jacobson, 1972; Chang, Park & Li, 1968; Hanic, Pavelčík & Gyepesová, 1972; Stromberg, 1969), and there is no significant difference in Ni—N distances in both $\mathrm{Ni(NCS)_2}L_2$ complexes. The same change of ligands in pseudo-octahedral $\mathrm{Ni(NCS)_2}L_4$ complexes produces quite evident changes of interatomic distances in the coordination sphere. The average $\mathrm{Ni{-}N_{NCS}}$ distances (for axial bonds) have been found in the range 2·05 to 2·15 Å, and the $\mathrm{Ni{-}N}_L$ (equatorial bonds) in the range 2·03 to 2·17 Å (Jóna, 1980). The distances found for $\mathrm{Ni(NCS)_2py_4}$ are: $\mathrm{Ni{-}N_{NCS}}$ 2·062 (8), and $\mathrm{Ni{-}N_{py}}$ 2·169 (31) and 2·151 (8) Å (Valach, Sivý & Koreň, 1984), while for $\mathrm{Ni(NCS)_2pip_4}$ the $\mathrm{Ni{-}N_{NCS}}$ distance is 2·00 (1) Å and $\mathrm{Ni{-}N_{pip}}$ distances are 2·28 (2) and 2·36 (3) Å (Koman, Handlovič, Ďurčanská & Gažo, 1983). These values show that the exchange of py by pip σ-donor ligands causes a significant elongation of the equatorial and shortening of the axial interatomic distances. Similar dependences were observed also for $\mathrm{Cu^{II}}$ complexes and were explained using the concept of equatorial–axial interactions (Gažo, Boča, Jóna, Kabešová, Macášková & Šima, 1982).

The benzene molecule lies at a center of symmetry. In the packing process its plane forms an angle of

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

$B_{\mathrm{eq}} = \frac{1}{3}(B_{11} + B_{22} + B_{33})$; B_{ij} orthogonalized.

	x	y	z	B_{eq}(Å^2)
Ni	0	0	0	2·9 (1)
N(1)	−0·0627 (6)	0·1526 (8)	−0·1139 (10)	3·6 (2)
C(1)	−0·1140 (7)	0·2466 (10)	−0·1558 (13)	3·4 (3)
S(1)	−0·1927 (2)	0·3749 (3)	−0·2221 (4)	5·5 (1)
N(11)	0·1238 (5)	0·1992 (7)	0·2603 (10)	3·3 (2)
C(11)	0·0856 (8)	0·1997 (11)	0·4366 (13)	4·1 (3)
C(12)	−0·0538 (8)	0·2033 (12)	0·3593 (15)	5·3 (4)
C(13)	0·1783 (9)	0·3551 (11)	0·6359 (14)	5·0 (3)
C(14)	0·3188 (9)	0·3600 (12)	0·7094 (15)	5·5 (4)
C(15)	0·3572 (8)	0·3661 (11)	0·5310 (15)	4·9 (3)
C(16)	0·2656 (7)	0·2107 (11)	0·3254 (15)	4·3 (3)
C(17)	0·2967 (8)	0·2291 (11)	0·1451 (15)	4·8 (3)
C(21)	0·5866 (42)	0·1352 (32)	0·0001 (112)	7·9 (5)
C(22)	0·6005 (23)	0·1156 (51)	0·1765 (73)	7·9 (5)
C(23)	0·5182 (69)	−0·0151 (92)	0·1944 (73)	7·8 (6)

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

C(12′) is at $x+1, y, z$; C(21′) is at $1-x, \bar{y}, \bar{z}$.

Ni—N(1)	1·849 (7)	C(15)—C(16)	1·55 (1)
Ni—N(11)	1·984 (7)	C(16)—C(17)	1·54 (1)
Ni—C(1)	1·14 (1)	C(16)—N(11)	1·54 (1)
C(1)—S(1)	1·63 (1)	C(21)—C(22)	1·30 (8)
N(11)—C(11)	1·53 (1)	C(22)—C(25)	1·38 (9)
C(11)—C(12)	1·54 (1)	C(23)—C(21′)	1·43 (9)
C(11)—C(13)	1·53 (1)		
C(13)—C(14)	1·53 (2)	C(12′)···C(22)	3·64 (4)
C(14)—C(15)	1·55 (1)	C(17)···C(23)	3·66 (8)
N(1)—Ni—N(11)	88·59 (3)	C(11)—C(13)—C(14)	111·70 (8)
Ni—N(1)—C(1)	164·95 (7)	C(13)—C(14)—C(15)	108·64 (8)
N(1)—C(1)—S(1)	177·72 (8)	C(14)—C(15)—C(16)	111·84 (8)
Ni—N(11)—C(11)	110·77 (5)	C(15)—C(16)—N(11)	110·57 (7)
Ni—N(11)—C(16)	112·93 (5)	C(15)—C(16)—C(17)	110·94 (8)
C(11)—N(11)—C(16)	112·52 (6)	C(17)—C(16)—N(11)	107·66 (7)
N(11)—C(11)—C(13)	111·14 (7)	C(22)—C(21)—C(23)	120·62 (56)
N(11)—C(11)—C(12)	107·63 (7)	C(21′)—C(23)—C(22)	118·29 (43)
C(12)—C(11)—C(13)	110·65 (8)		

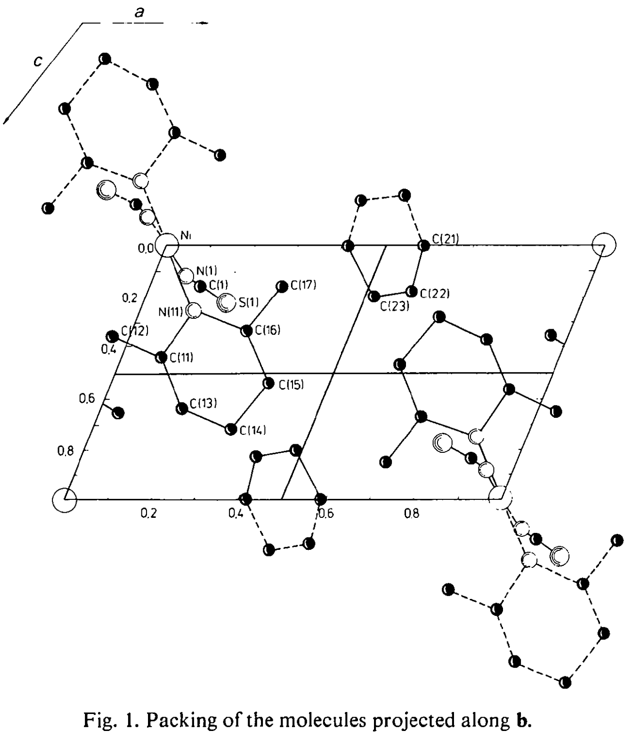

Fig. 1. Packing of the molecules projected along **b**.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42266 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

51 (3)° with the plane of $NiN_{NCS}N_{pip}$ [plane (1)], and an angle of 49 (3)° with the plane of four C atoms of the 2,6-Me_2pip ligand [C(11)C(13)C(15)C(16)] [plane (2)]; planes (1) and (2) form an angle of 81·5 (3)°. The benzene molecule is thus trapped in the cage formed by four 2,6-Me_2pip ligands of two adjacent complex molecules. The two pairs of methyl groups are directed towards benzene molecules with contacts C(17)···C(23) 3·66 (8) and C(12′)···C(22) 3·64 (4) Å (Table 2), close to the van der Waals contact distance of 3·7 Å calculated as the sum of 2·0 Å for the methyl radius and 1·7 Å for the benzene half-thickness. The weak intermolecular bonding of the benzene in the crystal structure explains the rather high values of the temperature-factor coefficients of the benzene atoms (Table 1).

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Structure of Bis(triphenylphosphine)iminium* Bis(cyano)(phthalocyaninato)ferrate(III), $[N\{P(C_6H_5)_3\}_2][Fe(CN)_2(C_{32}H_{16}N_8)]$, at 180 K

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Abstract. $M_r = 1159{\cdot}0$, triclinic, $P\bar{1}$, $a = 12{\cdot}940$ (4), $b = 12{\cdot}320$ (2), $c = 10{\cdot}322$ (3) Å, $\alpha = 65{\cdot}22$ (8), $\beta = 68{\cdot}24$ (15), $\gamma = 76{\cdot}34$ (9)°, $V = 1381{\cdot}2$ Å^3, $Z = 1$, $D_x = 1{\cdot}393$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 3{\cdot}83$ cm^{-1}, $F(000) = 599$, $T = 180$ K. $R = 4{\cdot}7\%$ for 3023 independent observed reflexions. The Fe^{III}-bis(cyano)phthalocyanine anion and the bis(triphenylphosphine)iminium cation are in special positions, site symmetry $\bar{1}$. Thus, the P—N—P skeleton is in the very seldom observed linear configuration. The Fe—C—N arrangement is essentially linear with Fe—C = 1·974 (4) Å, angle Fe—C—N = 176·7 (3)°, in distinct contrast to the 'bent' geometry found in cyanoheme proteins.

Introduction. The study of metallophthalocyanines has been and continues to be of interest because of their close structural relationship to naturally occurring oxygen carriers, their catalytic activity, and their electrical properties. Special attention is focused on the iron(III) phthalocyanines. Synthesis and spectroscopical properties of bis(cyano)(phthalocyaninato)ferrates(III), $[Fe(CN)_2Pc(2-)]^-$, isolated as the bis(triphenylphosphine)iminium (PNP) salt, have been reported by Kalz, Homborg, Küppers, Kennedy & Murray (1984). In this paper, the structural characterization is presented.

Experimental. [PNP] $[Fe(CN)_2Pc]$ was crystallized by slow diffusion of HCN-containing CH_2Cl_2 into a CH_2Cl_2 solution of $[PNP][Fe(OH)_2Pc]$. The bis(hydroxo) complex was synthesized according to the procedure of Kalz & Homborg (1983). Crystal approximately isometric with edges *ca* 0·25 mm; sample temperature 180 K, Philips PW 1100 diffractometer, θ–2θ scans, Mo $K\alpha$ radiation; 3406 reflexions measured in θ range 2–25°, 3023 unique; $R_{int} = 0{\cdot}035$; index range $h \pm 13$, $k -12/13$, l 0/9; lattice parameters by

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* Bis(triphenylphosphoranediyl)ammonium.