for example, in large-ring *cyclo*-poly(phosphazenes) such as $N_6P_6(NMe_2)_{12}$ (Wagner & Vos, 1968). The PNC_2 units are coplanar to within ±0·02 Å.

In contrast, the coordination of the phosphazane-ring N atoms N(1) and N(2) is appreciably pyramidal, each N atom lying 0·21 Å from the plane defined by adjacent P and C atoms. Despite the statement of Peterson & Wagner (1973), which has been widely accepted by other authors (*e.g.* Cameron *et al.*, 1977), planar coordination appears to be the exception rather than the rule for phosphazane N atoms: thus in *cis*- and *trans*-[PhP(S)NEt]$_2$ the N atoms are displaced by up to 0·24 Å from the P_2C planes (Bullen & Tucker, 1973; Bullen, Rutherford & Tucker, 1973) and values of 0·14 and 0·28 Å are reported for similar displacements in *trans*-[PhP(S)NMe]$_2$ (Cameron *et al.*, 1975) and *trans*-[ClP(O)NBu^t]$_2$ (Manojlović-Muir & Muir, 1974); only in *trans*-[PhP(S)NPh]$_2$ (Peterson & Wagner, 1973) does an accurately planar phosphazane-N environment occur. It should be noted that these variations in the degree of planarity of the bonds from phosphazane N atoms are achieved with relatively minor alterations in valency angles. Corresponding angles at N in *trans*-[PhP(S)NPh]$_2$ disagree by no more than 2·5° with those found here. It is also worth emphasizing that the sum of the valency angles at N is a poor test of the coplanarity of the valencies. The sums of angles at N(1), and N(2), respectively 354 and 355°, do not differ substantially from 360°. To summarize, the available results on *cyclo*-di(phosphazanes) indicate that a range of N coordinations can occur with little change in bond lengths or valency angles. This view conflicts with that of Cameron, Howlett & Prout (1977), who attempt to explain unusually long P–N ring distances in $[C_{15}H_{15}N_2PS]_2$ in terms of the non-planarity of the bonds to the ring N atoms.

The N–CMe_3 distance of 1·497 (3) Å found here agrees with the corresponding distance of 1·507 (5) Å in *trans*-[ClP(O)NBu^t]$_2$ (Manojlović-Muir & Muir, 1974). It appears to be significantly longer than the N–CH_3 and N–Et distances in [PhP(S)N*R*]$_2$, *R* = Me, Et, all of which are close to 1·46 Å.

It is a pleasure to thank Dr R. Keat for gifts of crystals and, with Dr Lj. Manojlović-Muir, for helpful discussions.

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α-Tetrakis(4-methylpyridine)diisothiocyanatonickel(II)

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(*Received* 19 *May* 1977; *accepted* 14 *July* 1977)

Abstract. $C_{26}H_{28}N_6S_2Ni$, $M_r = 547·4$, monoclinic, $P2_1/c$, $a = 19·205$ (1), $b = 9·768$ (1), $c = 16·765$ (1) Å, $\beta = 113·544$ (3)°, $U = 2883$ Å^3, $Z = 4$, $D_x = 1·261$ g cm^{-3}, $F(000) = 1144$, μ(Cu $K\alpha$, $\lambda = 1·5418$ Å) = 25·7 cm^{-1}. The structure was refined to $R = 0·042$. It consists of discrete propeller-shaped molecules, with the pitch of the four pyridine blades ranging from 49 to 60°. Ni is octahedrally coordinated to the N atoms of

two *trans*-coordinated isothiocyanate and four pyridine ligands at average distances of 2·068 (4) and 2·128 (6) Å respectively.

Introduction. α-(4-Methylpyridine)$_4$Ni(NCS)$_2$ belongs to a group of complexes of the type P_4MX_2, (where P is a pyridine derivative, M a divalent transiton metal and X a halide or thiocyanate) which form clathrates with suitable guests (Schaeffer, Dorsey, Skinner & Christian, 1957; Belitskus, Jeffrey, McMullan & Stephenson, 1963). Some exhibit zeolitic properties permitting desorption without the host lattice collapsing (Allison & Barrer, 1969). Following Hart & Smith (1962), whose mode of preparation was used, we call the unsolvated phase α and the solvated β.

Crystals of a size suitable for X-ray analysis were produced by the procedure of Kemula, Lipkowski & Sybilska (1974): rapid evaporation of a hot solution of the complex in nitromethane produced large deep-blue rhombs. A crystal 0·25 × 0·15 × 0·3 mm was mounted along **c**. To prevent deterioration in air, it was coated with picture varnish.

2949 independent reflections were measured (to $\theta = 50°$) on a Siemens off-line four-circle diffractometer with Ni-filtered Cu $K\alpha$ radiation (Allen, Rogers & Troughton, 1971). 417 had $I \leq 2{\cdot}58\sigma(I)$ and were classed as unobserved. The net count of the 460 reflection, measured as a reference every 50 reflections, showed, during the data collection (*ca* 4½ days), a steady decay (as did other periodically monitored reflections) amounting to *ca* 30%. The data were brought to a uniform arbitrary scale by the use of this reflection (Allen *et al.*, 1971). Lorentz and polarization corrections were applied; no correction for absorption was made.

The structure was solved by the heavy-atom method and the non-hydrogen atoms were refined anisotropically by full-matrix least squares to $R = 0{\cdot}083$. A difference map revealed the positions of all the H atoms which, for subsequent refinement, were fixed at optimized positions 1 Å from their atoms. The H atoms of the methyl groups have two orientations and were fixed at half weight in six equally staggered positions. Six reflections were suspected of being affected by extinction and were removed from the least-squares calculations. Subsequent refinement, with allowance for anomalous scattering by the Ni and S atoms, reduced R to 0·042.* The maximum residual electron density in the final difference map was, with one exception, <0·2 e Å^{-3}. The exception was an unexplained peak of 0·4 e Å^{-3}, 1·53 Å from C(2) and 1·14 Å from S(2).

Unit weights were used. Scattering factors were from Doyle & Turner (1968), or from Stewart, Davidson & Simpson (1965) for H. Anomalous scattering factors were from Cromer (1965). Calculations were performed with the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

Discussion. The final atomic parameters for the non-hydrogen atoms are listed in Table 1, those for the H atoms in Table 2. Fig. 1 is a stereoview of the molecule (*ORTEP*, Johnson, 1965) and indicates the numbering scheme. Fig. 2 shows the bond lengths and angles around the Ni atom including the isothiocyanate ligands; Table 3 gives the values for the rest of the structure.

The molecule adopts a very similar configuration to that reported for the desorbed β phase (Andreetti, Bocelli & Sgarabotto, 1972). The Ni is octahedrally coordinated to the N atoms of the isothiocyanate and four pyridine ligands at average distances of 2·068 (4) and 2·128 (6) Å respectively, a significant difference. Angles subtended at Ni are all within 1·5° of 90° (Fig.

Table 1. *Fractional coordinates* (×10^4) *for the non-hydrogen atoms, with estimated standard deviations in parentheses*

	x	y	z
Ni	2507 (0)	2742 (1)	2722 (0)
N(1)	3277 (2)	1167 (4)	2922 (2)
C(1)	3598 (3)	164 (5)	3128 (3)
S(1)	4063 (1)	-1270 (2)	3428 (1)
N(2)	1729 (2)	4311 (4)	2513 (2)
C(2)	1497 (3)	5384 (6)	2358 (3)
S(2)	1180 (1)	6956 (2)	2136 (2)
N(11)	1822 (2)	1859 (4)	1493 (2)
C(12)	1776 (3)	507 (5)	1363 (3)
C(13)	1342 (3)	−82 (5)	570 (3)
C(14)	926 (3)	723 (5)	−136 (3)
C(15)	958 (3)	2103 (6)	9 (3)
C(16)	1407 (3)	2629 (5)	810 (3)
C(17)	454 (3)	138 (6)	−1013 (3)
N(21)	1910 (2)	1533 (4)	3294 (2)
C(22)	2259 (3)	713 (5)	3975 (3)
C(23)	1869 (3)	−148 (5)	4309 (3)
C(24)	1094 (3)	−197 (5)	3937 (3)
C(25)	738 (3)	638 (6)	3236 (3)
C(26)	1156 (2)	1484 (5)	2945 (3)
C(27)	652 (4)	−1105 (7)	4282 (4)
N(31)	3203 (2)	3559 (4)	3958 (2)
C(32)	3959 (2)	3358 (5)	4300 (3)
C(33)	4431 (2)	3750 (5)	5122 (3)
C(34)	4139 (3)	4401 (5)	5649 (3)
C(35)	3370 (3)	4639 (5)	5304 (3)
C(36)	2923 (2)	4203 (5)	4468 (3)
C(37)	4636 (3)	4786 (6)	6568 (3)
N(41)	3088 (2)	3951 (4)	2122 (2)
C(42)	3418 (3)	3355 (5)	1641 (3)
C(43)	3777 (3)	4083 (5)	1212 (3)
C(44)	3813 (3)	5486 (5)	1254 (3)
C(45)	3476 (3)	6090 (5)	1757 (3)
C(46)	3133 (3)	5321 (5)	2181 (3)
C(47)	4210 (4)	6295 (6)	799 (4)

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32859 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Fractional coordinates* ($\times 10^4$) *for the hydrogen atoms*

$U = 0{\cdot}082$ Å^2 for methyl H atoms and $0{\cdot}070$ Å^2 for the rest.

	x	y	z
H(12)	2076	−119	1854
H(13)	1343	−1103	508
H(15)	639	2735	−472
H(16)	1439	3644	883
*H(171)	185	904	−1428
*H(172)	770	−385	−1248
*H(173)	48	−486	−969
*H(174)	489	−881	−1004
*H(175)	−102	398	−1179
*H(176)	617	517	−1462
H(22)	2835	708	4255
H(23)	2177	−730	4839
H(25)	162	618	2932
H(26)	877	2095	2437
*H(271)	87	−986	3906
*H(272)	786	−2084	4250
*H(273)	745	−852	4889
*H(274)	992	−1640	4785
*H(275)	299	−530	4455
*H(276)	327	−1753	3805
H(32)	4188	2898	3928
H(33)	4993	3563	5338
H(35)	3117	5136	5643
H(36)	2358	4392	4228
*H(371)	4336	5244	6856
*H(372)	4884	3937	6910
*H(373)	5055	5420	6576
*H(374)	5184	4523	6699
*H(375)	4617	5792	6657
*H(376)	4474	4286	6986
H(42)	3391	2333	1581
H(43)	4023	3587	874
H(45)	3472	7111	1801
H(46)	2905	5803	2546
*H(471)	4178	7298	913
*H(472)	4765	6024	1043
*H(473)	3979	6112	168
*H(474)	4421	5661	486
*H(475)	3854	6955	388
*H(476)	4647	6819	1250

* These atoms have half occupancy.

2). The four pyridine nitrogens and the Ni deviate only slightly from planarity ($\Delta_{\max} = 0{\cdot}018$ Å) and form a suitable reference plane from which the angles of pitch of the pyridine rings are measured. These (Table 4) range from 49·7 (ring 2) to 59·9° (ring 3) (*cf.* 49·6 and 57·7° for the *β* phase; from Andreetti's data). Although individual pyridine rings are planar to within 0·01 Å,

Table 3. *Distances* (Å) *and angles* (°) *in the four pyridine rings*

	$R = 1$	$R = 2$	$R = 3$	$R = 4$
N(*R*1)–C(*R*2)	1·335 (6)	1·335 (5)	1·344 (5)	1·341 (7)
C(*R*2)–C(*R*3)	1·382 (6)	1·385 (8)	1·368 (6)	1·378 (8)
C(*R*3)–C(*R*4)	1·378 (6)	1·364 (7)	1·377 (8)	1·372 (7)
C(*R*4)–C(*R*5)	1·366 (8)	1·369 (7)	1·373 (7)	1·383 (8)
C(*R*5)–C(*R*6)	1·374 (6)	1·370 (8)	1·387 (6)	1·371 (8)
C(*R*6)–N(*R*1)	1·335 (5)	1·330 (5)	1·336 (6)	1·342 (6)
C(*R*4)–C(*R*7)	1·499 (6)	1·495 (10)	1·501 (6)	1·502 (9)
Ni–N(*R*1)–C(*R*2)	122·1 (3)	123·0 (3)	120·8 (3)	120·3 (3)
Ni–N(*R*1)–C(*R*6)	121·8 (3)	120·8 (3)	122·9 (3)	123·2 (4)
C(*R*6)–N(*R*1)–C(*R*2)	116·1 (3)	116·1 (4)	116·1 (3)	116·5 (4)
N(*R*1)–C(*R*2)–C(*R*3)	122·9 (4)	122·9 (4)	123·8 (5)	123·1 (4)
C(*R*2)–C(*R*3)–C(*R*4)	120·6 (5)	120·2 (4)	120·0 (4)	120·8 (5)
C(*R*3)–C(*R*4)–C(*R*5)	116·2 (4)	116·8 (5)	116·9 (4)	115·6 (5)
C(*R*4)–C(*R*5)–C(*R*6)	120·6 (4)	120·2 (4)	120·1 (5)	121·4 (5)
C(*R*5)–C(*R*6)–N(*R*1)	123·6 (4)	123·8 (4)	123·1 (4)	122·6 (5)
C(*R*3)–C(*R*4)–C(*R*7)	122·7 (5)	121·9 (5)	121·3 (4)	121·6 (5)
C(*R*5)–C(*R*4)–C(*R*7)	121·1 (4)	121·3 (5)	121·8 (5)	122·8 (5)

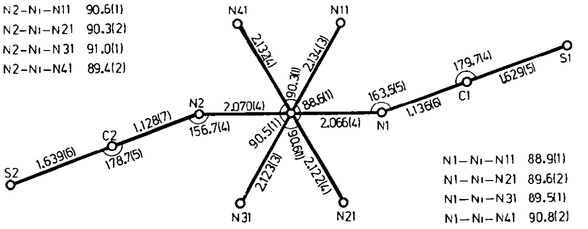

Fig. 2. The environment of the Ni atom including the isothiocyanate ligands. Distances (Å) and angles (°) are shown.

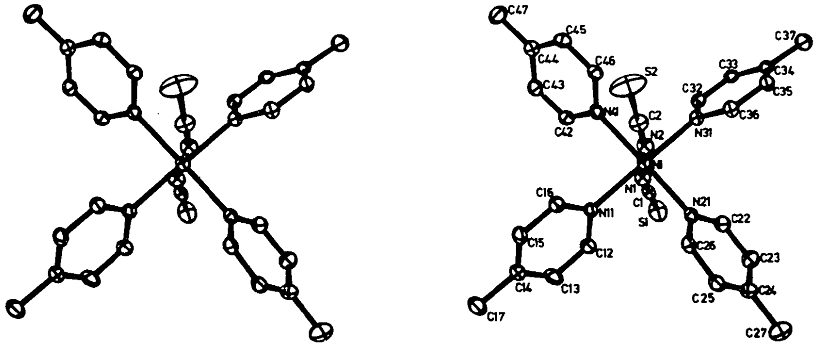

Fig. 1. Stereoscopic view of the molecule, showing the numbering scheme.

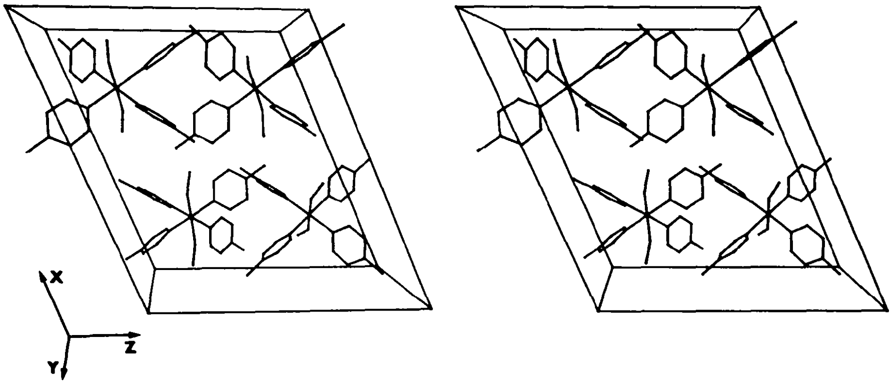

Fig. 3. Stereoscopic packing diagram with the unit cell outlined.

Table 4. *Angles* (°) *between the planes of the pyridine rings and the plane through* N(11), N(21), N(31) *and* N(41)

Ring	1	2	3	4
Angle	56·2	49·7	59·9	56·2

Table 5. *Shortest intermolecular distances* (Å)

$C(33)-C(33)^{i}$	3·408	$S(1)-C(45)^{iv}$	3·640
$C(24)-C(15)^{ii}$	3·581	$C(35)-C(42)^{ii}$	3·663
$C(25)-C(17)^{iii}$	3·586	$C(34)-C(43)^{ii}$	3·672
$C(15)-C(25)^{ii}$	3·592	$C(37)-C(44)^{i}$	3·681

Symmetry code

(i) $1-x, 1-y, 1-z$ (ii) $x, \frac{1}{2}-y, \frac{1}{2}+z$
(iii) $\bar{x},\bar{y},\bar{z}$ (iv) $x, 1+y, z$

the Ni deviates by as much as 0·2 Å from these planes. An asymmetric feature of the molecule is a significant difference of 6·8° between the angles at the N in the isothiocyanate groups. The packing of the molecules (Fig. 3) produces no sizeable voids. Contacts between molecules are consistent with van der Waals interactions and the eight shortest are given in Table 5.

This complex differs from those studied by Nardelli, Gasparri, Musatti & Manfredotti (1966) and Capacchi, Gasparri, Nardelli & Pelizzi (1968) where a thiocyanate ligand forms bridges between the Ni atoms of adjacent molecules. The absence of such chains in the present study, leading to the possibility of clathrate formation, must be due to the full coordination of the Ni. Greater similarity is found with the structure of $(thiourea)_2Ni(NCS)_2$ (Nardelli, Gasparri, Battistini & Domiano, 1966) where the isothiocyanates are terminal; the reported Ni–N distance [1·992 (7) Å] is significantly shorter than that found here (2·068 Å), but the reported NiN(CS) angle (162·2°) is close to the larger of the two values found here (163·5°, Fig. 2).

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