

0.01. Maximum and minimum peak heights in the final difference Fourier synthesis were 0.48 and  $-0.46 \text{ e } \text{Å}^{-3}$ . Final atomic coordinates and  $B_{\text{eq}}$  values are reported in Table 1.\*

**Related literature.** Unindexed powder diffraction data for  $\text{Na}_2\text{AlH}_3(\text{P}_2\text{O}_7)_2$  were reported previously by two independent groups (Pintard-Scrépel, Dorémieux-Morin & d'Yvoire, 1981; Grunze & Grunze, 1984). The results of the first group are in accord with those reported here whereas Grunze & Grunze described polymorphs of a compound they believed to be  $\text{NaAlH}_4(\text{P}_2\text{O}_7)_2$ . However, the lattice spacings for one of these match fairly well those of our compound. Doubt remains whether the second structure found by Grunze & Grunze is a polymorphic phase of  $\text{NaAlH}_3(\text{P}_2\text{O}_7)_2$ ; it may correspond to a different compound with the composition attributed to it by these authors.

The atomic arrangement of  $\text{Na}_2\text{AlH}_3(\text{P}_2\text{O}_7)_2$  projected along the  $c$  axis is shown in Fig. 1. Distorted  $\text{O}_6$  octahedra about Al share two opposite edges [O(2)—O(3)] with two diphosphate anions. These octahedra are connected by two symmetry related P(1) tetrahedra, forming a chain parallel to [001].

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55081 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU0258]

The chains are held together by the three hydrogen bonds in directions [100], [010] and [110].

Table 2 reports the main interatomic distances and bond angles. The diphosphate anion shows the expected features: the average P—O bond length is 1.532 Å and the P(1)—O(4)—P(2) angle is 133.3°. The  $\text{Na}^+$  ions lie in tunnel cavities parallel to [001], with seven O-atom neighbours at distances shorter than 3 Å. The mean Na—O distance [2.570 Å] is very similar to the values encountered in other ionic Na conductors.

We thank the staff of Servei de Microscopia Electrònica, University of Barcelona, for microanalysis and scanning electron microscopy facilities.

#### References

- BEURSKENS, P. T., BOSMAN, W. P., DOESBURG, H. M., GOULD, R. O., VAN DEN HARK, TH. E. M., PRICK, P. A. J., NOORDIK, J. H., BEURSKENS, G. & PARTHASARATHI, V. (1981). *DIRDIF*. Tech. Rep. 1981/2. Crystallography Laboratory, Toernooiveld, 6525 ED Nijmegen, The Netherlands.
- GRUNZE, I. & GRUNZE, H. (1984). *Anorg. Allg. Chem.* **512**, 39–41.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P., & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
- PINTARD-SCRÉPEL, M., DORÉMIEUX-MORIN, C. & D'YVOIRE, F. (1981). *J. Solid State Chem.* **37**, 85–94.
- SHELDRIK, G. M. *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

*Acta Cryst.* (1992). **C48**, 1652–1654

## Structural Investigations of Nickel(II) Complexes. X. Tris(3,5-dimethylpiperidine)-bis(isothiocyanato)nickel(II), $[\text{Ni}(\text{NCS})_2(3,5\text{-diMepip})_3]$

BY M. KOMAN, E. JÓNA AND E. ĎURČANSKÁ

*Department of Inorganic Chemistry, Slovak Technical University, CS-81237 Bratislava, Czechoslovakia*

(Received 19 March 1991; accepted 13 January 1992)

**Abstract.**  $[\text{Ni}(\text{NCS})_2(\text{C}_7\text{H}_{15}\text{N})_3]$ ,  $M_r = 514.5$ , triclinic,  $P\bar{1}$ ,  $a = 10.41$  (1),  $b = 10.63$  (2),  $c = 13.63$  (2) Å,  $\alpha = 81.8$  (1),  $\beta = 76.6$  (1),  $\gamma = 69.8$  (1)°,  $V = 1373.7$  (4.1) Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.19$ ,  $D_x = 1.24 \text{ g cm}^{-3}$ ,  $\lambda(\text{Mo } K\alpha) = 0.71070$  Å,  $\mu = 8.7 \text{ cm}^{-1}$ ,  $F(000) = 556$ , room temperature,  $R = 0.0568$ ,  $wR = 0.0567$  for 975 reflections with  $I \geq 3\sigma(I)$ . The crystal is formed by monomeric units of  $[\text{Ni}(\text{NCS})_2(3,5\text{-diMepip})_3]$ . The two N atoms of two NCS groups and three 3,5-diMepip ligands define a tetragonal pyramid about the Ni atom. The axial site contains a 3,5-diMepip

ligand and the basal plane pairs of *trans* NCS<sup>−</sup> and 3,5-diMepip ligands.

**Experimental.** Green prism-shaped crystals of poor quality,  $0.51 \times 0.31 \times 0.23 \text{ mm}$ ; density measured by flotation. A Syntex  $P2_1$  four-circle diffractometer with graphite-monochromated Mo  $K\alpha$  radiation was used for data collection. 15 reflections with  $4.91 \leq \theta \leq 12.72^\circ$  were used for determination of the lattice parameters. Absorption and extinction were ignored. Intensity measurements from  $\theta$ – $2\theta$  scans were made

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2$ ) for non-H atoms with *e.s.d.*'s in parentheses

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

	x	y	z	$U_{\text{eq}}$
Ni	0.1140 (3)	0.4805 (2)	0.2285 (2)	0.066 (2)
N1	0.1515 (15)	0.4159 (16)	0.0925 (11)	0.088 (13)
C1	0.1575 (17)	0.3443 (18)	0.0329 (15)	0.076 (14)
S1	0.1797 (6)	0.2424 (5)	-0.0494 (4)	0.096 (4)
N2	0.1513 (15)	0.5381 (15)	0.3456 (12)	0.067 (13)
C2	0.1835 (19)	0.6093 (20)	0.3854 (14)	0.076 (16)
S2	0.2229 (6)	0.7094 (5)	0.4374 (4)	0.096 (5)
N3	0.1795 (18)	0.2832 (13)	0.2815 (12)	0.072 (11)
C31	0.1448 (17)	0.2318 (18)	0.3845 (13)	0.061 (13)
C32	0.1982 (26)	0.0890 (18)	0.4099 (16)	0.084 (16)
C33	0.3575 (26)	0.0374 (16)	0.3721 (18)	0.088 (15)
C34	0.3910 (25)	0.0882 (25)	0.2648 (18)	0.092 (19)
C35	0.3286 (24)	0.2383 (18)	0.2500 (12)	0.066 (16)
C36	0.1629 (19)	0.0552 (17)	0.5217 (16)	0.082 (14)
C37	0.5473 (29)	0.0380 (21)	0.2348 (16)	0.122 (18)
N4	-0.0975 (13)	0.5249 (14)	0.2573 (11)	0.055 (10)
C41	-0.1712 (23)	0.5891 (17)	0.3521 (12)	0.062 (14)
C42	-0.3276 (26)	0.6319 (21)	0.3560 (14)	0.096 (18)
C43	-0.3779 (19)	0.5252 (22)	0.3371 (18)	0.094 (17)
C44	-0.3028 (26)	0.4696 (21)	0.2376 (21)	0.074 (17)
C45	-0.1480 (25)	0.4205 (16)	0.2355 (11)	0.073 (14)
C46	-0.3942 (19)	0.6867 (18)	0.4561 (16)	0.099 (15)
C47	-0.3460 (21)	0.3626 (23)	0.2164 (18)	0.147 (21)
N5	0.1271 (20)	0.6629 (14)	0.1518 (10)	0.065 (11)
C51	0.2749 (21)	0.6531 (20)	0.1243 (12)	0.072 (17)
C52	0.3006 (25)	0.7699 (24)	0.0629 (13)	0.082 (18)
C53	0.2109 (27)	0.8945 (19)	0.1131 (14)	0.077 (16)
C54	0.0605 (22)	0.9045 (18)	0.1328 (14)	0.075 (16)
C55	0.0406 (18)	0.7853 (22)	0.1960 (12)	0.065 (14)
C56	-0.0394 (21)	0.0417 (19)	0.1901 (13)	0.103 (16)
C57	0.4516 (26)	0.7528 (22)	0.0508 (16)	0.128 (21)

Table 2. Interatomic distances ( $\text{\AA}$ ) and selected bond angles ( $^\circ$ ) with *e.s.d.*'s in parentheses

Ni—N1	1.97 (2)	N4—C41	1.47 (2)
Ni—N2	1.95 (2)	C41—C42	1.52 (2)
Ni—N3	2.05 (1)	C42—C43	1.48 (3)
Ni—N4	2.04 (1)	C43—C44	1.49 (3)
Ni—N5	2.10 (1)	C44—C45	1.51 (3)
N1—C1	1.15 (2)	C45—N4	1.47 (2)
C1—S1	1.61 (2)	C42—C46	1.48 (3)
N2—C2	1.16 (2)	C42—C46	1.48 (3)
C2—S2	1.56 (2)	C44—C47	1.45 (3)
N3—C31	1.44 (2)	N5—C51	1.47 (2)
C31—C32	1.45 (2)	C51—C52	1.47 (2)
C32—C33	1.54 (3)	C52—C53	1.49 (3)
C33—C34	1.49 (3)	C53—C54	1.50 (3)
C34—C35	1.50 (3)	C54—C55	1.48 (2)
C35—N3	1.44 (2)	C55—N5	1.43 (2)
C32—C36	1.50 (3)	C52—C57	1.49 (3)
C34—C37	1.50 (3)	C54—C56	1.65 (2)
N1—Ni—N2	158.2 (7)	N1—Ni—N3	87.4 (7)
N1—Ni—N5	85.5 (4)	N2—Ni—N3	91.5 (6)
N2—Ni—N5	87.7 (6)	N3—Ni—N5	158.5 (6)
N4—Ni—N1	97.4 (7)	N4—Ni—N2	104.1 (7)
N4—Ni—N3	102.1 (7)	N4—Ni—N5	98.9 (6)
Ni—N1—C1	157.2 (8)	N1—C1—S1	175.0 (8)
Ni—N2—C2	153.0 (9)	N2—C2—S2	178.0 (9)

for  $0 \leq 2\theta \leq 55^\circ$ ;  $h, k, l$  range  $h$  0 to 13,  $k$  - 14 to 14,  $l$  - 17 to 17. Two standard reflections monitored every 98 measurements decreased in intensity by 15% during the course of the experiment; corrections for the decomposition were not applied. 975 independent reflections with  $I \geq 3\sigma(I)$  were collected (2341 unobserved reflections). 280 parameters were refined. The Ni-atom position was obtained from the Patterson function, positions of other non-H atoms from Fourier syntheses. The positions of H atoms were calculated. Anisotropic full-matrix refinement

for non-H atoms was based on  $F_o$ .  $R = 0.0568$ ,  $wR = 0.0567$   $\{w = k/[\sigma^2(F_o) + g(F_o)^2]$ ,  $k = 1.0895$ ,  $g = -0.001967\}$ .  $|\Delta\rho| \leq 0.30 \text{ e \AA}^{-3}$ ;  $(\Delta/\sigma)_{\text{max}}$  in the final least-squares cycle was 0.456. Calculations were performed with the *SHELX76* program system (Sheldrick, 1976); scattering factors were obtained from *International Tables for X-ray Crystallography* (1974, Vol. IV). Positional and equivalent isotropic thermal parameters are given in Table 1; \* Table 2 gives the interatomic distances and main bond angles.

**Related literature.** The crystal structure consists of  $[\text{Ni}(\text{NCS})_2(3,5\text{-diMepip})_3]$  molecules (see Fig. 1). Spectroscopic and magnetic measurements were consistent with the presence of a five-coordinate Ni atom in the title complex but did not discriminate between square pyramidal and trigonal bipyramidal coordination (Koman, Jóna & Đurčanská, 1986). Our results now show that the coordination polyhedron around  $\text{Ni}^{\text{II}}$  is a nearly regular tetragonal pyramid [ $\tau = 0.5\%$  (Addison, Rao, Reedijk, van Rijn & Verschoor, 1984)]. The basal plane contains *trans* pairs of 3,5-diMepip ligands coordinated through N and the apical position is occupied by the N atom of the third 3,5-diMepip ligand. In  $[\text{Ni}(\text{NCS})_2(2,4\text{-diMepy})_3]$  (2,4-diMepy = 2,4-dimethylpyridine) the  $\tau$  parameter (29.17%) shows the coordination geometry to be tetragonal pyramidal but strongly distorted towards trigonal bipyramidal (Đurčanská, Koman & Jamnický, 1991) and the Ni—N distances [ $\text{Ni—N}(\text{NCS}) = 1.995$  (9),  $\text{N—N1}(2,4\text{-diMepy}) = 2.085$  (3) and  $\text{Ni—N2}(2,4\text{-diMepy}) = 2.159$  (7)  $\text{\AA}$ ] are rather longer than the corresponding values found here (Table 2). The opposite trend is shown by pseudo-octahedral  $\text{Ni}(\text{NCS})_2\text{L}_4$  complexes (Gažo,

\* 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 55058 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU0254]

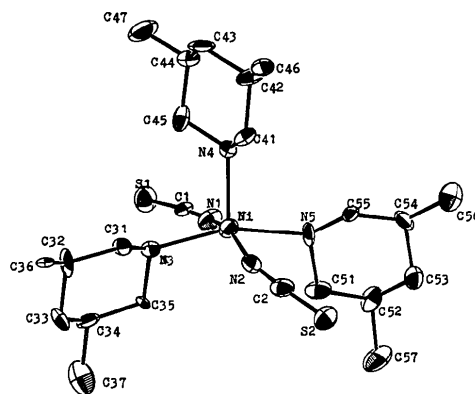


Fig. 1. The molecular structure of  $[\text{Ni}(\text{NCS})_2(3,5\text{-diMepip})_3]$ .

Boča, Jóna, Kabešová, Macašková, Šima, Pelikán & Valach, 1982) where Ni—N(pip) > Ni—N(py).

#### References

ADDISON, A. W., RAO, T. N., REEDIJK, J., VAN RIJN, J. & VERSCHOOR, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.

ĐURČANSKÁ, E., KOMAN, M. & JAMNICKÝ, M. (1991). *Acta Cryst.* C47, 1191–1193.

GAŽO, J., BOČA, R., JÓNA, E., KABEŠOVÁ, M., MACAŠKOVÁ, L., ŠIMA, J., PELIKÁN, P. & VALACH, F. (1982). *Coord. Chem. Rev.* 43, 87–131.

KOMAN, M., JÓNA, E. & ĐURČANSKÁ, E. (1986). *Inorg. Chim. Acta*, 121, 47–51.

SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

*Acta Cryst.* (1992). C48, 1654–1655

## Structure of a Dinuclear Nickel Compound, Ni<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(SC<sub>3</sub>H<sub>6</sub>S)<sub>2</sub>

BY RONG CAO, ZHIYING HUANG, XINJIAN LEI, BEISHENG KANG, MAOCHUN HONG AND HANQIN LIU

Fuzhou Laboratory of Structural Chemistry and Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China

(Received 15 May 1991; accepted 13 January 1992)

**Abstract.** Bis(1,2-propanedithiolato-1:2κ<sup>2</sup>S',2κS<sup>2</sup>)bis-(triphenylphosphine)dinickel, [Ni<sub>2</sub>(C<sub>3</sub>H<sub>6</sub>S<sub>2</sub>)<sub>2</sub>·{(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P}₂], *M<sub>r</sub>* = 854.43, monoclinic, *C2/c*, *a* = 26.499 (13), *b* = 9.037 (6), *c* = 17.419 (7) Å, β = 107.33 (3)°, *V* = 3982.1 Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.43 g cm<sup>-3</sup>, λ(Mo *Kα*) = 0.71069 Å, μ = 12.6 cm<sup>-1</sup>, *F*(000) = 1776, *T* = 296 K, *R* = 0.053 and *wR* = 0.059 for 2575 reflections with *I* > 3σ(*I*). The complex is a dimer, where each Ni atom is four-coordinated by one P and three S atoms with square-planar geometry. The average Ni—S and Ni—P bond lengths are 2.190 and 2.193 Å, respectively.

**Experimental.** The title complex was prepared by reaction of Na, H<sub>2</sub>pdt, PPh<sub>3</sub> and NiCl<sub>2</sub>·6H<sub>2</sub>O in MeOH solution and a crystal suitable for the X-ray analysis was grown in a solution of 1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>/MeOH.

A crystal of dimensions 0.8 × 0.5 × 0.2 mm was used for the X-ray analysis. Cell parameters were obtained from least-squares refinement of 20 strong reflections within the 2θ range 12–14°, measured on a Rigaku AFC-5R four-circle diffractometer with Mo *Kα* radiation. Integrated intensities were measured at room temperature in the 2θ range within 50° (0 < *h* < 31, 0 < *k* < 10, -20 < *l* < 20) by the θ/2θ scan mode. Among 3852 reflections, 2575 with *I* > 3σ(*I*) were used for structure determination. The data were corrected for anisotropic decay (between 0.966 and 1.034), Lp effects, and empirical absorption based on a series of ψ scans (between 0.608 and 1.000). An empirical absorption correction was made by the program *DIFABS* (Walker & Stuart, 1983)

after structure refinement with isotropic thermal parameters; the maximum and minimum absorption corrections were 1.054 and 0.705, respectively.

All calculations were performed on a VAX 785 computer with the *SDP* program package (Frenz, 1978). The coordinates of all metal atoms were determined by direct methods and the remaining non-H atoms were located from successive difference Fourier maps. H atoms were not included. Full-matrix least-squares refinement with anisotropic temperature factors for all non-H atoms led to convergence with *R* = 0.053 and *wR* = 0.059. The function minimized was Σw(|*F<sub>o</sub>*| - |*F<sub>c</sub>*|)<sup>2</sup>, where *w* = 1/[σ<sup>2</sup>(*F*) + 0.0001*F*<sup>2</sup> + 1.0] (Killeen & Lawrence, 1969). Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The final cycle of refinement included 226 variable parameters. The goodness of fit (*S*) was 2.45. The largest Δ/σ was 0.80 while the extreme peaks in the difference electron density map were 1.01 and -0.62 e Å<sup>-3</sup>. Final positional parameters are given in Table 1 and selected bond distances and angles are listed in Table 2.\* The structure of the molecule is depicted in Fig. 1.

**Related literature.** The structures of [Ni(PPh<sub>3</sub>)<sub>2</sub>(SCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>S)] (Cao, Lei, Huang, Hong &

\* Lists of anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55048 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS0501]