

Structures of Complexes between Metal Halides and Phosphinothioethers or Related Ligands.

X. [1,9-Bis(diphenylphosphino)-3,7-dithianonane]monoiodonickel Tetraphenylborate

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(Received 24 September 1979; accepted 5 November 1979)

Abstract

$[\text{Ni}(\text{C}_{31}\text{H}_{34}\text{P}_2\text{S}_2\text{I})][\text{B}(\text{C}_6\text{H}_5)_4]$ is a monoiodonickel(II) complex of the quadridentate ligand $(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_2)_2\text{S}(\text{CH}_2)_3\text{S}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_5)_2$. The structure has been determined by Patterson and Fourier methods and refined to $R = R_w = 0.085$ for 2743 independent counter intensities, the phenyl rings and methylene groups with their attached H atoms being treated as rigid bodies. The crystals are monoclinic, space group Pn , with $a = 14.530(3)$, $b = 10.0546(6)$, $c = 16.647(2)$ Å, $\beta = 94.67(1)^\circ$, $Z = 2$. Ni is five-coordinated, being bonded to one I atom and to the P and S atoms of one single ligand molecule. Ni is situated 0.26 Å outside the plane formed by the two P and the two S atoms. The I atom completes the square-pyramidal coordination of Ni. The structure is built up of discrete $[\text{Ni}(\text{C}_{31}\text{H}_{34}\text{P}_2\text{S}_2\text{I})]^+$ and $[\text{B}(\text{C}_6\text{H}_5)_4]^-$ ions. The positions of the centres of the cations may be described as 000 and $\frac{1}{2}0\frac{1}{2}$ and those of the anions as $\frac{1}{2}\frac{1}{2}0$ and $0\frac{1}{2}\frac{1}{2}$, together giving an approximately face-centred cubic close packing of the bulky molecular ions. At $T > 240$ K the compound exhibits temperature-independent paramagnetism ($\chi_M = 570 \times 10^{-6}$). Extrapolation of μ_{eff} values for different temperatures ($T < 150$ K to 0 K) gives at 0 K $\mu_{\text{eff}} = 0.7$, indicating the presence of a low-spin complex. In the interval 170–240 K the μ_{eff} value increases sharply from 1 to 1.7.

Introduction

The denticity and steric characteristics of ligands are of vital importance for the resulting coordination polyhedron of the acceptor metal atom. The highest symmetry of a five-coordinated Ni^{II} complex is that of a trigonal bipyramid; next highest is the square pyramid (Morassi, Bertini & Sacconi, 1973). Linear open-chain quadridentate ligands tend to form a square pyramid. The complexes can be of high- or low-spin state, the latter being more frequent. The high-spin complexes are generally formed when the ligand donor

atoms are hard, e.g. N, O, Cl, while low-spin complexes are often formed with soft donors, e.g. P, As, S, I.

1,5-Bis(diphenylphosphino)-3-thiapentane, $(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_5)_2$, (psp), forms with NiI_2 a crystalline low-spin complex (Degischer, 1968), in which the open-chain ligand is tridentate. Ni is five-coordinated to one S, two P and two I atoms, the coordination polyhedron being intermediate between a trigonal bipyramid and a square pyramid (Fälth, 1976).

The present work deals with the structure and magnetic properties of a Ni^{II} complex of a related ligand, 1,9-bis(diphenylphosphino)-3,7-dithianonane, $(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_2)_2\text{S}(\text{CH}_2)_3\text{S}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_5)_2$, (pssp) (the abbreviations psp and pssp are according to Degischer, 1968). Compared to psp the ligand pssp offers an additional donor atom; furthermore, the distance between the teeth S–S is longer than between P–S. An increased length of the ligand chain between presumptive donor atoms can force the metal atom upon a constraint coordination, forming dimers or polymers; the first is the case in, for example, $(\text{C}_{29}\text{H}_{30}\text{AgClP}_2)_2$ (Cassel, 1976) and the latter in, for example, $\text{C}_{29}\text{H}_{30}\text{HgI}_2\text{P}_2$ (Aurivillius & Wendel, 1976), both being complexes of the ligand $(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_2)_5\text{P}(\text{C}_6\text{H}_5)_2$. A low-spin complex with square-pyramidal coordination for Ni was expected in the present case at room temperature but instead a temperature-independent paramagnetic complex of approximately the same geometry was found (see below).

This investigation is part of a more general one on complexes between transition-metal halides and substituted phosphines or related ligands.

Experimental

Crystals of the title compound in the form of dark-red plates were kindly supplied by the late Professor G. Schwarzenbach, Zürich. A single crystal 0.19, 0.27 and 0.08 mm along *a*, *b* and *c*, respectively, was used for data collection on a computer-controlled four-circle diffractometer (Enraf–Nonius, CAD-4) with graphite-monochromatized $\text{Mo } K\alpha$ radiation ($\lambda = 0.71069$ Å) at

Table 1. *Crystal data*

[Ni(C₃H_{3.4}P₂S₂)I][B(C₆H₅)₄], $M_r = 1037.5$, monoclinic, Pn , $a = 14.530$ (3), $b = 10.0546$ (6), $c = 16.647$ (2) Å, $\beta = 94.67$ (1)°, $V = 2424$ Å³, $Z = 2$, $D_m = 1.4$ (by flotation), $D_x = 1.42$ Mg m⁻³, $\mu(\text{Mo K}\alpha) = 1.23$ mm⁻¹.

room temperature. The cell data showed monoclinic symmetry with systematic absences $h0l$ for $h + l \neq 2n$, indicating space group $P2/n$ or Pn . The ω - 2θ -scan technique was used with a scan interval $\Delta\omega = (0.80 + 0.50 \tan \theta)^\circ$. The background was measured for one quarter of the scan time at each end of the interval. Three standard reflections were measured at regular intervals. No systematic variation was detected. The intensities of 4658 unique reflections were collected in the interval $3^\circ \leq \theta \leq 25^\circ$. Of these, 1915 with $I < 2\sigma(I)$, where $\sigma(I)$ was based on counting statistics, were considered unobserved and deleted. The remaining 2743 reflections were corrected for Lorentz-polarization and absorption effects. The transmission factors, evaluated by numerical integration, varied between 0.82–0.92. The cell dimensions were determined by least-squares analysis from θ values of 60 reflections in the interval $4^\circ \leq \theta \leq 12^\circ$. The magnetic-susceptibility measurements were performed in the temperature interval 85–340 K with a Faraday balance (Blom & Hörlin, 1977). Fig. 1 gives μ_{eff}^2 as a function of T . The data are corrected for the underlying diamagnetism. Above 240 K the compound exhibits temperature-independent paramagnetism ($\chi_M = 570 \times 10^{-6}$). In the interval 170–240 K the μ_{eff} value increases sharply from 1 to 1.7. Extrapolation of μ_{eff} values for different temperatures ($T < 150$ K to 0 K) gives at 0 K $\mu_{\text{eff}} = 0.7$, indicating the presence of a low-spin complex. Structural investigations are in progress at 225 and 125 K to study the structures corresponding to the magnetic states at these temperatures. At ~ 150

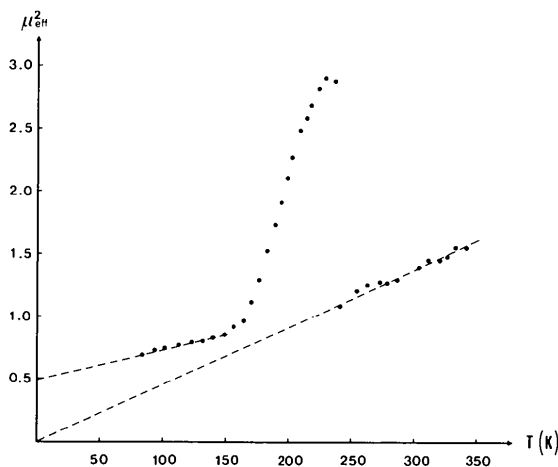


Fig. 1. μ_{eff}^2 as a function of T (μ_{eff} is the number of Bohr magnetons). The values were calculated from $\mu_{\text{eff}}^2 = 8\chi_M T$. The extrapolations to 0 K of the linear parts of the curve at $T > 240$ K and $T < 150$ K are shown by dashed lines.

K the colour of the substance changed to light-brown. Some crystal data are given in Table 1.

Structure determination and refinement

From a vector map the positions of the I and Ni atoms were found. As $Z = 2$ and as the atomic positions of the two heavy atoms were not in accordance with the special twofold ones in $P2/n$, the space group must be Pn . Least-squares refinement based on the deduced parameters and followed by difference syntheses revealed the positions of all the other non-hydrogen atoms. The positions of the H atoms were found by geometrical considerations with C–H = 1.00 Å. A least-squares refinement including the I, Ni, S and P atoms with anisotropic, the B, C and H atoms with isotropic, temperature factors converged at $R = \sum |F_o| - |F_c| / \sum |F_o| = 0.084$ and $R_w = [\sum w_i (|F_o| - |F_c|)^2 / \sum w_i |F_o|^2]^{1/2} = 0.120$ for 2743 reflections. The H atoms had fixed positional and thermal parameters ($B = 4.0$ Å²). The function minimized was $\sum w_i (|F_o| - |F_c|)^2$ where the weights w_i were calculated from $w_i^{-1} = \sigma_i^2 (|F_o|^2) / 4|F_o|^2 + C^2 |F_o|^2$. C was adjusted so as to give the most constant averages of $w_i (|F_o| - |F_c|)^2$ over ranges of $|F|$ and $\sin \theta$. The value of $S = [\sum w_i (|F_o| - |F_c|)^2 / (m - n)]^{1/2}$ was 1.37, where m is the number of observations and n ($= 278$) the number of parameters varied.

The result of the structure determination looked to be quite accurate as far as e.s.d.'s in interatomic distances and angles were concerned. Some of the phenyl rings deviated from planarity, however, and therefore a new refinement was performed with *SHELX* (Sheldrick, 1976). In this procedure the phenyl rings and the methylene groups were treated as rigid groups with C–C 1.395, C–H 1.080 Å; C–C–C, H–C–C 120, H–C–H 109.5°. The H atoms were geometrically generated at the end of the refinement of the non-hydrogen atoms. 183 parameters were determined from 2743 intensities, a ratio of 1:15. Unit weights were used and the final $R = R_w = 0.085$ for 2743 reflections. The highest residual electron density was $0.77 \text{ e } \text{Å}^{-3}$ in the region of Ni in the difference map. The deepest pit was $0.80 \text{ e } \text{Å}^{-3}$. Scattering factors for neutral I, Ni, S, P, C and B were according to Doyle & Turner (1968) and for neutral H from Stewart, Davidson & Simpson (1965). Corrections for anomalous dispersion (Cromer & Liberman, 1970) but not for extinction were included. No efforts were made to determine the absolute configuration of the single crystal actually used. Final positional and isotropic thermal parameters are given in Table 2.* The

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34971 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Fractional coordinates ($\times 10^4$) and isotropic temperature factors ($\times 10^4$, $\times 10^3$ for B, C and H) with e.s.d.'s in parentheses

For I, Ni, P and S the isotropic mean values of U_{ij} are given.

| | x | y | z | $U(\text{\AA}^2)$ |
|-------|------------|------------|------------|-------------------|
| I | -610 (3) | -696 (3) | -1465 (2) | 374 (5) |
| Ni | 0 | 99 (3) | 0 | 77 (4) |
| P(1) | 1245 (4) | 1016 (6) | -452 (3) | 90 (9) |
| P(2) | 558 (4) | -1892 (6) | 342 (3) | 98 (9) |
| S(1) | -564 (5) | 2184 (6) | 50 (4) | 151 (10) |
| S(2) | -1196 (4) | -488 (7) | 686 (4) | 144 (10) |
| B | 6135 (18) | 5586 (29) | 903 (16) | 25 (6) |
| C(1) | 767 (16) | 2410 (23) | -1054 (13) | 23 (5) |
| C(2) | 147 (21) | 3215 (30) | -564 (18) | 48 (8) |
| C(3) | -1679 (18) | 2078 (29) | -518 (16) | 39 (7) |
| C(4) | -2390 (21) | 1309 (31) | -43 (18) | 50 (8) |
| C(5) | -2234 (19) | -96 (29) | 17 (16) | 43 (7) |
| C(6) | -1166 (19) | -2341 (26) | 737 (16) | 38 (6) |
| C(7) | -453 (19) | -2901 (30) | 224 (17) | 46 (7) |
| C(8) | 2070 (10) | 240 (17) | -1084 (7) | 20 (5) |
| C(9) | 1785 | -89 | -1880 | 37 (6) |
| C(10) | 2421 | -588 | -2387 | 50 (7) |
| C(11) | 3342 | -758 | -2098 | 47 (7) |
| C(12) | 3627 | -429 | -1303 | 48 (8) |
| C(13) | 2991 | 70 | -796 | 34 (6) |
| C(14) | 2009 (12) | 1748 (14) | 371 (8) | 21 (5) |
| C(15) | 2254 | 955 | 1042 | 26 (5) |
| C(16) | 2844 | 1453 | 1674 | 37 (6) |
| C(17) | 3189 | 2744 | 1635 | 34 (6) |
| C(18) | 2944 | 3537 | 964 | 57 (9) |
| C(19) | 2354 | 3039 | 332 | 33 (6) |
| C(20) | 884 (12) | -2187 (12) | 1417 (9) | 22 (5) |
| C(21) | 1168 | -3465 | 1651 | 45 (7) |
| C(22) | 1359 | -3763 | 2466 | 45 (7) |
| C(23) | 1267 | -2784 | 3047 | 40 (7) |
| C(24) | 983 | -1506 | 2814 | 45 (7) |
| C(25) | 792 | -1207 | 1999 | 41 (7) |
| C(26) | 1453 (12) | -2711 (19) | -175 (9) | 32 (6) |
| C(27) | 1272 | -3273 | -937 | 51 (8) |
| C(28) | 1979 | -3888 | -1317 | 59 (9) |
| C(29) | 2869 | -3941 | -934 | 80 (11) |
| C(30) | 3051 | -3378 | -172 | 56 (8) |
| C(31) | 2343 | -2763 | 208 | 50 (8) |
| C(32) | 5307 (10) | 6390 (11) | 1355 (9) | 20 (5) |
| C(33) | 4715 | 5650 | 1799 | 25 (5) |
| C(34) | 4021 | 6286 | 2187 | 36 (6) |
| C(35) | 3920 | 7664 | 2129 | 31 (6) |
| C(36) | 4512 | 8404 | 1685 | 38 (7) |
| C(37) | 5205 | 7768 | 1298 | 33 (6) |
| C(38) | 7133 (11) | 5588 (14) | 1547 (9) | 27 (6) |
| C(39) | 7835 | 4660 | 1471 | 38 (6) |
| C(40) | 8661 | 4761 | 1957 | 40 (7) |
| C(41) | 8785 | 5788 | 2518 | 38 (6) |
| C(42) | 8083 | 6716 | 2594 | 39 (7) |
| C(43) | 7257 | 6615 | 2109 | 27 (6) |
| C(44) | 5783 (11) | 3992 (14) | 708 (7) | 24 (5) |
| C(45) | 5912 | 3012 | 1300 | 34 (6) |
| C(46) | 5564 | 1734 | 1152 | 25 (5) |
| C(47) | 5087 | 1436 | 413 | 37 (6) |
| C(48) | 4957 | 2416 | -179 | 44 (7) |
| C(49) | 5305 | 3694 | -31 | 26 (5) |
| C(50) | 6361 (10) | 6261 (16) | -16 (9) | 26 (5) |
| C(51) | 5706 | 7056 | -446 | 46 (7) |
| C(52) | 5868 | 7517 | -1212 | 47 (8) |
| C(53) | 6685 | 7183 | -1549 | 45 (7) |
| C(54) | 7341 | 6388 | -1119 | 36 (6) |
| C(55) | 7178 | 5927 | -353 | 31 (6) |

Table 2 (cont.)

| | x | y | z | $U(\text{\AA}^2)$ |
|-------|------------|------------|------------|-------------------|
| H(1A) | 365 (16) | 2034 (23) | -1579 (13) | 50 (5) |
| H(1B) | 1323 (16) | 3020 (23) | -1241 (13) | |
| H(2A) | 579 (21) | 3841 (30) | -163 (18) | 48 (8) |
| H(2B) | -296 (21) | 3830 (30) | -962 (18) | |
| H(3A) | -1596 (18) | 1545 (29) | -1070 (16) | 50 (7) |
| H(3B) | -1920 (18) | 3074 (29) | -657 (16) | |
| H(4A) | -3060 (21) | 1460 (31) | -360 (18) | 50 (8) |
| H(4B) | -2384 (21) | 1730 (31) | 554 (18) | |
| H(5A) | -2823 (19) | -563 (29) | 256 (16) | 50 (7) |
| H(5B) | -2144 (19) | -494 (29) | -574 (16) | |
| H(6A) | -1841 (19) | -2725 (26) | 539 (16) | 51 (7) |
| H(6B) | -988 (19) | -2639 (26) | 1354 (16) | |
| H(7A) | -291 (19) | -3913 (30) | 400 (17) | 49 (8) |
| H(7B) | -727 (19) | -2882 (30) | -399 (17) | |
| H(9) | 1072 (10) | 42 (17) | -2103 (7) | 65 (15) |
| H(10) | 2200 | -843 | -3003 | |
| H(11) | 3834 | -1144 | -2491 | |
| H(12) | 4340 | -560 | -1079 | |
| H(13) | 3211 | 325 | -180 | |
| H(15) | 1987 (12) | -45 (14) | 1072 (8) | 65 (15) |
| H(16) | 3034 | 839 | 2193 | |
| H(17) | 3646 | 3129 | 2124 | |
| H(18) | 3211 | 4536 | 933 | |
| H(19) | 2164 | 3653 | -188 | |
| H(21) | 1239 (12) | -4223 (12) | 1201 (9) | 65 (15) |
| H(22) | 1579 | -4753 | 2646 | |
| H(23) | 1415 | -3015 | 3678 | |
| H(24) | 912 | -748 | 3264 | |
| H(25) | 572 | -218 | 1818 | |
| H(27) | 583 (12) | -3233 (19) | -1233 (9) | 65 (15) |
| H(28) | 1839 | -4324 | -1907 | |
| H(29) | 3417 | -4417 | -1228 | |
| H(30) | 3740 | -3419 | 125 | |
| H(31) | 2484 | -2328 | 798 | |
| H(33) | 4793 (10) | 4583 (11) | 1844 (9) | 65 (15) |
| H(34) | 3563 | 5713 | 2531 | |
| H(35) | 3383 | 8156 | 2429 | |
| H(36) | 4434 | 9470 | 1641 | |
| H(37) | 5664 | 8341 | 953 | |
| H(39) | 7738 (11) | 3865 (14) | 1037 (9) | 65 (15) |
| H(40) | 9204 | 4043 | 1898 | |
| H(41) | 9425 | 5866 | 2894 | |
| H(42) | 8180 | 7511 | 3029 | |
| H(43) | 6714 | 7333 | 2167 | |
| H(45) | 6282 (11) | 3243 (14) | 1872 (7) | 65 (15) |
| H(46) | 5664 | 976 | 1611 | |
| H(47) | 4817 | 447 | 299 | |
| H(48) | 4587 | 2185 | -751 | |
| H(49) | 5205 | 4452 | -489 | |
| H(51) | 5073 (10) | 7315 (16) | -185 (9) | 65 (15) |
| H(52) | 5361 | 8133 | -1545 | |
| H(53) | 6811 | 7539 | -2142 | |
| H(54) | 7974 | 6129 | -1379 | |
| H(55) | 7685 | 5311 | -20 | |

calculations were made on the Univac 1108 computer in Lund, Sweden, and at the NEUCC Computing Center, Copenhagen, Denmark.

Description and discussion

Interatomic distances and angles are given in Fig. 2 and Table 3; the labelling of the atoms is according to Fig. 2

and Table 2. The present ligand, $(C_6H_5)_2P(CH_2)_2S(CH_2)_3S(CH_2)_2P(C_6H_5)_2$, (pssp), is potentially quadridentate. The investigation has shown that, in the title compound $[Ni(pssp)][BPh_4]$, Ni^{II} besides being coordinated to one I atom is bonded to the two P and the two S atoms of one single ligand molecule, which hereby has adopted a suitable conformation. Ni is situated 0.26 Å outside the plane formed by the P and the S atoms (Table 4) in the direction of I and its coordination polyhedron is a square pyramid, the I atom forming the apex. It may be regarded as a semi-square-planar coordination (Hathaway & Billing, 1970). The mean values of the Ni–P and Ni–S distances, 2.216 (6) and 2.245 (5) Å, respectively, are somewhat longer than the corresponding values of 2.189 (2) and 2.190 (3) Å in $C_{28}H_{28}I_2NiP_2S_2$, $[Ni_2(psp)]$ (Fälth, 1976). In the resulting chelate, Ni takes part in three fused rings – two five-membered, $NiPC_2S$, and one six-membered, $NiSC_3S$ – together with the I atom and the phenyl groups forming the complex ion $[Ni(C_{31}H_{34}P_2S_2)I]^+$, $[NiI(pssp)]^+$, shown in Fig. 3. The Ni–I distance, 2.649 (3) Å, lies between the 2.542 (2) and 2.794 (5) Å given for $[Ni_2(psp)]$ and is longer than the 2.514 (5) and 2.567 (5) Å for the square-pyramidal coordination of Ni in $[Ni(dsp)I_2]$ [$dsp = bis(o\text{-methylthiophenyl})phenylphosphine$] (Meek & Ibers, 1969). All Ni–I, Ni–S and Ni–P bonds seem to be somewhat longer than the corresponding distances in low-spin $[Ni_2(psp)]$ and $[Ni(dsp)I_2]$. The angles of the square pyramid around Ni are, in the present compound, in good agreement with angles in the same coordination polyhedron of similar Ni complexes, e.g. $C_{28}H_{28}Br_2NNiP_2$, $[NiBr_2(pnp)]$ (Orioli & Ghilardi, 1970) and $[Ni(dsp)I_2]$. The angles P–Ni–P, P–Ni–S and S–Ni–S (neighbouring atoms) vary between 85.0 (2) and 99.9 (2)°, the P–Ni–P angle having the largest value, probably depending on the bulky phenyl groups. A square-pyramidal arrangement with angles between the

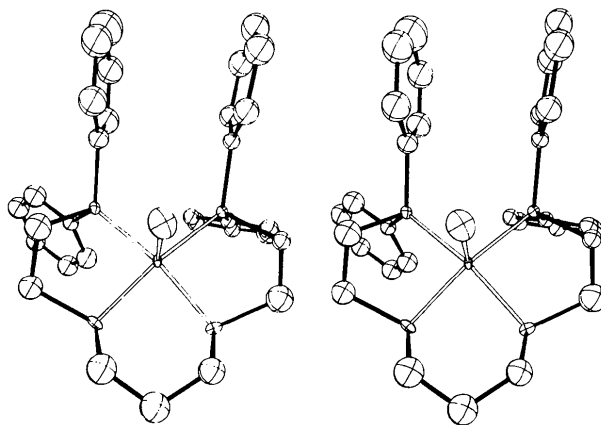


Fig. 3. A stereoview of the complex ion $[Ni(C_{31}H_{34}P_2S_2)I]^+$. The bonds of the ligand molecule $(C_6H_5)_2P(CH_2)_2S(CH_2)_3S(CH_2)_2P(C_6H_5)_2$ are drawn with heavy lines, those in the coordination polyhedron of Ni with double lines. The H atoms are omitted. The ellipsoids are drawn to enclose 50% probability.

Table 3. Distances (Å) and angles (°) in the $B(C_6H_5)_4^-$ ion and angles (°) in the coordination polyhedra of Ni, P(1), P(2), S(1) and S(2)

E.s.d.'s are given in parentheses. For labelling of the atoms, see Fig. 2 and Table 2.

| | | | |
|-----------------|------------|------------------|------------|
| B–C(32) | 1.68 (3) | B–C(44) | 1.71 (3) |
| B–C(38) | 1.73 (3) | B–C(50) | 1.73 (3) |
| C(32)–B–C(38) | 108.5 (16) | C(38)–B–C(44) | 110.0 (17) |
| C(32)–B–C(44) | 108.9 (16) | C(38)–B–C(50) | 109.7 (16) |
| C(32)–B–C(50) | 113.7 (17) | C(44)–B–C(50) | 106.0 (16) |
| I–Ni–P(1) | 92.0 (2) | P(1)–Ni–S(1) | 86.3 (3) |
| I–Ni–P(2) | 93.0 (2) | S(1)–Ni–S(2) | 85.8 (3) |
| I–Ni–S(1) | 102.7 (2) | P(2)–Ni–S(2) | 85.0 (2) |
| I–Ni–S(2) | 100.1 (2) | P(1)–Ni–S(2) | 166.8 (3) |
| P(1)–Ni–P(2) | 99.9 (2) | P(2)–Ni–S(1) | 163.1 (2) |
| Ni–P(1)–C(1) | 102.8 (8) | Ni–P(2)–C(7) | 101.8 (10) |
| Ni–P(1)–C(8) | 127.5 (6) | Ni–P(2)–C(20) | 117.1 (5) |
| Ni–P(1)–C(14) | 111.9 (5) | Ni–P(2)–C(26) | 123.3 (6) |
| C(1)–P(1)–C(8) | 104.4 (9) | C(7)–P(2)–C(20) | 99.2 (11) |
| C(1)–P(1)–C(14) | 106.3 (9) | C(7)–P(2)–C(26) | 107.8 (11) |
| C(8)–P(1)–C(14) | 102.4 (7) | C(20)–P(2)–C(26) | 104.5 (8) |
| Ni–S(1)–C(2) | 106.4 (10) | Ni–S(2)–C(5) | 105.5 (9) |
| Ni–S(1)–C(3) | 103.8 (10) | Ni–S(2)–C(6) | 105.7 (9) |
| C(2)–S(1)–C(3) | 105.3 (13) | C(5)–S(2)–C(6) | 104.8 (13) |

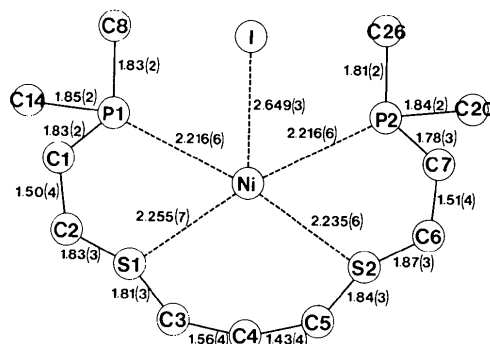


Fig. 2. Selected interatomic distances (Å) in the complex ion $[Ni(C_{31}H_{34}P_2S_2)I]^+$. The C–C distances in the phenyl rings (omitted in the drawing) are assumed to be 1.395 Å. The bonds of the ligand chain are drawn with heavy lines, those in the coordination polyhedron of Ni with dashed lines.

axial and equatorial bonds of about 100° is not much less stable than that of the trigonal bipyramid (Gillespie, 1963; Sacconi, 1972). The angles I–Ni–P are 92.0 (2) and 93.0 (2)° and I–Ni–S 100.1 (2) and 102.7 (2)°; thus the average value of the apical angle is less than 100°, indicating a trend from semi- to ordinary square-planar coordination.

The P atoms show the expected tetrahedral stereochemistry, although large deviations occur due to steric requirements. Mean values of the distances

Table 4. *The square pyramid of Ni; distances (Å) and angles (°) in the square plane and deviations (Å) from the least-squares plane*

Only the P and S atoms were used for the calculation of the least-squares plane. E.s.d.'s are in parentheses.

| | | | |
|-----------|-----------|----------------|-----------|
| P(1)–P(2) | 3.392 (8) | S(1)–P(1)–P(2) | 86.4 (3) |
| P(1)–S(1) | 3.057 (9) | P(1)–P(2)–S(2) | 87.2 (3) |
| P(2)–S(2) | 3.009 (8) | P(2)–S(2)–S(1) | 93.6 (3) |
| S(1)–S(2) | 3.056 (9) | S(2)–S(1)–P(1) | 92.7 (3) |
| Ni | 0.26 (1) | S(1) | –0.04 (1) |
| P(1) | 0.03 (1) | S(2) | 0.04 (1) |
| P(2) | –0.03 (1) | | |

P–C(phenyl) and P–C(methylene) are 1.833 (8) and 1.81 (2) Å compared to the corresponding values of 1.822 (5) and 1.83 (1) Å in [NiI₂(psp)]. The angles around P vary between 99.2 and 127.5° (Table 3).

S is also tetrahedrally coordinated, the fourth position occupied by the lone pair of electrons. The mean S–C distance is 1.84 (1) Å, compared to 1.82 (1) Å in [NiI₂(psp)]. The angles around S vary from 103.8 to 106.4° (Table 3).

The methylene C–C distances in the ligand chain are also normal, the mean value being 1.50 (2) Å compared to 1.52 (2) Å in [AgCl(psp)] (Aurivillius, Cassel & Fälth, 1974).

The geometry of the negative counter ion BPh₄[–] is normal. The mean B–C distance of 1.71 (2) Å is in good agreement with, for example, the corresponding value of 1.67 (4) Å in [CoCl(qp)][BPh₄] [qp = tris(*o*-diphenylphosphinophenylphosphine) (Blundell & Powell, 1971)]. The angles around B vary between 106.0 and 113.7° (Table 3).

In the structure there are eight independent phenyl rings. Two groups of two rings, the atoms C(8)–C(13), C(26)–C(31) and C(14)–C(19), C(44)–C(49), respectively, have their planes mutually parallel at average distances of 3.58 and 3.62 Å, compared to the minimum distance between aromatic rings of 3.40 Å (Pauling, 1960). The packing of the ions in the unit cell is shown in a stereoview (Fig. 4). The bulky molecular ions approximate face-centred cubic close-packing; the

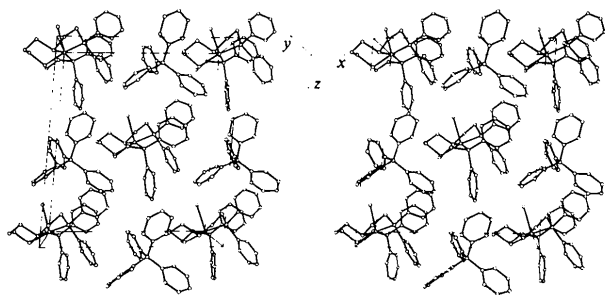


Fig. 4. A stereoview of the contents of one unit cell of [Ni(C₃₁H₃₄P₂S₂)I][B(C₆H₅)₄]. The H atoms are omitted.

positions of the centres of the cations may be described as 000 and $\frac{1}{2}0\frac{1}{2}$ and those of the anions as $\frac{1}{2}\frac{1}{2}0$ and $0\frac{1}{2}\frac{1}{2}$.

A short intermolecular contact I–H of 2.9 Å to the phenyl H atom H(16) was found. Furthermore, four rather short C–H contacts varying from 2.4 to 2.6 Å exist between the complex positive and negative ions. The van der Waals values for I–H and C–H are reported to be 3.35 and 2.7 Å, respectively (Pauling, 1960). With the radius 1.00 Å for H (Baur, 1972) the value I–H is still short, about 0.3 Å shorter than the sum of the van der Waals radii. In this connection it is worth mentioning that the H atoms were found by geometrical methods, with the phenyl and methylene groups assumed to be rigid bodies.

In partial agreement with the general rule that low-spin complexes are formed with soft donors such as I, P and S the compound is of low-spin type at $T < 240$ K, but it exhibits temperature-independent paramagnetism at $T > 240$ K.

The authors thank Professors S. Fronaeus and R. Norrestam and Drs B. Blom, M. Nygren and Å. Oskarsson for valuable discussions. This investigation is part of a research programme financially supported by the Swedish Natural Science Research Council.

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