

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

XI. [1,9-Bis(diphenylphosphino)-3,7-dithianonane]nickel(II) Diperchlorate

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Abstract

$[\text{Ni}(\text{C}_{31}\text{H}_{34}\text{P}_2\text{S}_2)](\text{ClO}_4)_2$, $\text{C}_{31}\text{H}_{34}\text{NiP}_2\text{S}_2^+ \cdot 2\text{ClO}_4^-$, monoclinic, $P2_1/c$, $a = 13.888$ (4), $b = 16.442$ (4), $c = 15.506$ (5) Å, $\beta = 104.89$ (3)°, $V = 3422$ Å³, $Z = 4$, $D_x = 1.53$, $D_m = 1.53$ Mg m⁻³, $\mu(\text{Cu } K\alpha) = 4.60$ mm⁻¹. 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), acts as a quadridentate ligand with the two P and the two S atoms of one single molecule coordinating Ni, forming a discrete complex ion $[\text{Ni}(\text{C}_{31}\text{H}_{34}\text{P}_2\text{S}_2)]^{2+}$, denoted $[\text{Ni}(\text{pssp})]^{2+}$. Ni is situated in a square plane formed by the four bonded atoms. In the chelate Ni is part of three fused rings: two five-membered, NiPC_2S , and one six-membered, NiSC_3S . The perchlorate ions are not coordinated to Ni. All interatomic distances and angles are normal. The compound is diamagnetic. The final R_w is 0.048 for 1669 reflections.

Introduction

Crystals of the title compound, which were prepared according to Degischer (1968), were provided by the late Professor G. Schwarzenbach, Zürich. A yellow crystal $0.05 \times 0.15 \times 0.15$ mm along a , b and c , respectively, was used for the intensity measurements on a computer-controlled four-circle diffractometer (Enraf-Nonius, CAD-4) with Ni-filtered $\text{Cu } K\alpha$ radiation ($\lambda = 1.54056$ Å) at room temperature. The ω - 2θ scan technique was employed with a peak scan interval $\Delta\omega = (0.85 + 0.40 \tan \theta)^\circ$. Background scans were measured for one quarter of the peak scan time. The intensities of 2304 unique reflections were collected in the interval $3 \leq \theta \leq 40^\circ$ and 4656 in $40 < \theta \leq 70^\circ$. Of these, 1122 and 548 respectively with $I > 2\sigma(I)$, where $\sigma(I)$ was based on counting statistics, were considered significant. In the range $60 < \theta \leq 70^\circ$ there were only 71 reflections with $I > 2\sigma(I)$. Possibly an investigation at lower temperature would have reduced the number of unobserved reflections. The intensities and their e.s.d.'s were corrected for Lorentz-polarization and absorption effects as well as for the

decrease in three standard reflections (about 4%) measured at regular intervals.

The positions of Ni, P and S were determined with *MULTAN* (Germain, Main & Woolfson, 1971) and the Cl, O and C atoms by successive electron-density syntheses. The refinement was performed with *SHELX* (Sheldrick, 1976), minimizing $\sum w_i(|F_o| - |F_c|)^2$; weights were $w_i^{-1} = k\sigma^2(F)$. 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. The C atoms were refined with isotropic and the other non-hydrogen atoms with anisotropic temperature factors. 217 parameters were determined from 1669 reflections, a ratio of 7.7. The final $R = 0.053$ and $R_w = 0.048$ ($R = \sum |F_o| - |F_c| / \sum |F_o|$; $R_w = [\sum w_i(|F_o| - |F_c|)^2 / \sum w_i |F_o|^2]^{1/2}$). The highest residual electron density was $0.5 \text{ e } \text{Å}^{-3}$ in the region of one of the perchlorate ions. The deepest pit was $0.3 \text{ e } \text{Å}^{-3}$. Scattering factors for neutral non-hydrogen atoms were from 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. Final positional and isotropic thermal parameters are given in Table 1.* All calculations were made on the Univac 1100 computer in Lund.

Discussion

Selected interatomic distances and angles are given in Fig. 1 and Table 2. A stereoscopic view of the atomic arrangement of the $[\text{Ni}(\text{pssp})]^{2+}$ ion is shown in Fig. 2 and the content of the unit cell is shown in Fig. 3.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35551 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates ($\times 10^4$) and isotropic temperature factors ($\times 10^3$) with e.s.d.'s in parentheses

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

| | <i>x</i> | <i>y</i> | <i>z</i> | U (Å ²) |
|-------|-----------|----------|-----------|-----------------------|
| Ni | 6485 (1) | 5032 (1) | 1876 (1) | 40 (1) |
| Cl(1) | 7686 (3) | 1718 (3) | 3079 (3) | 62 (2) |
| Cl(2) | 5908 (4) | 7741 (3) | 895 (3) | 71 (2) |
| S(1) | 5607 (2) | 4266 (2) | 775 (2) | 46 (1) |
| S(2) | 5026 (2) | 5495 (2) | 1977 (2) | 45 (1) |
| P(1) | 7833 (2) | 4584 (2) | 1539 (2) | 41 (1) |
| P(2) | 7134 (2) | 5668 (2) | 3120 (2) | 40 (1) |
| O(1) | 7982 (13) | 1883 (8) | 3950 (9) | 210 (11) |
| O(2) | 8541 (9) | 1701 (8) | 2812 (11) | 189 (10) |
| O(3) | 7040 (7) | 2330 (6) | 2624 (7) | 112 (6) |
| O(4) | 7248 (8) | 977 (7) | 2909 (10) | 172 (8) |
| O(5) | 5521 (10) | 8004 (6) | 40 (8) | 157 (8) |
| O(6) | 5845 (8) | 6875 (6) | 936 (7) | 114 (6) |
| O(7) | 5276 (12) | 7995 (9) | 1416 (9) | 203 (10) |
| O(8) | 6839 (8) | 7974 (7) | 1341 (11) | 192 (9) |
| C(1) | 7485 (8) | 3592 (6) | 1032 (8) | 44 (4) |
| H(1A) | 7453 (8) | 3156 (6) | 1545 (8) | 47 (4) |
| H(1B) | 8036 (8) | 3400 (6) | 693 (8) | |
| C(2) | 6488 (8) | 3642 (7) | 370 (8) | 49 (4) |
| H(2A) | 6582 (8) | 3902 (7) | -243 (8) | 50 (4) |
| H(2B) | 6188 (8) | 3035 (7) | 243 (8) | |
| C(3) | 5071 (8) | 3548 (7) | 1438 (8) | 51 (4) |
| H(3A) | 5630 (8) | 3384 (7) | 2036 (8) | 52 (4) |
| H(3B) | 4815 (8) | 3008 (7) | 1051 (8) | |
| C(4) | 4197 (9) | 3960 (7) | 1692 (8) | 59 (4) |
| H(4A) | 3787 (9) | 3496 (7) | 1941 (8) | 50 (4) |
| H(4B) | 3727 (9) | 4222 (7) | 1091 (8) | |
| C(5) | 4449 (9) | 4626 (6) | 2384 (8) | 56 (4) |
| H(5A) | 3772 (9) | 4825 (6) | 2541 (8) | 46 (4) |
| H(5B) | 4958 (9) | 4390 (6) | 2979 (8) | |
| C(6) | 5226 (8) | 6168 (7) | 2956 (8) | 53 (4) |
| H(6A) | 5132 (8) | 5826 (7) | 3523 (8) | 54 (4) |
| H(6B) | 4693 (8) | 6660 (7) | 2816 (8) | |
| C(7) | 6284 (8) | 6513 (7) | 3161 (8) | 46 (4) |
| H(7A) | 6333 (8) | 6967 (7) | 2671 (8) | 52 (4) |
| H(7B) | 6477 (8) | 6785 (7) | 3818 (8) | |
| C(13) | 7890 (5) | 6048 (5) | 671 (5) | 66 (4) |
| C(12) | 8133 (5) | 6548 (5) | 31 (5) | 97 (5) |
| C(11) | 8576 (5) | 6215 (5) | -600 (5) | 87 (5) |
| C(10) | 8777 (5) | 5383 (5) | -591 (5) | 104 (6) |
| C(9) | 8534 (5) | 4884 (5) | 49 (5) | 80 (5) |
| C(8) | 8091 (5) | 5217 (5) | 680 (5) | 47 (4) |
| H(13) | 7546 (5) | 6306 (5) | 1160 (5) | 126 (10) |
| H(12) | 7977 (5) | 7192 (5) | 24 (5) | |
| H(11) | 8764 (5) | 6602 (5) | -1096 (5) | |
| H(10) | 9121 (5) | 5126 (5) | -1080 (5) | |
| H(9) | 8690 (5) | 4240 (5) | 56 (5) | |
| C(19) | 9830 (6) | 4916 (4) | 2343 (5) | 50 (4) |
| C(18) | 10760 (6) | 4738 (4) | 2912 (5) | 64 (4) |
| C(17) | 10875 (6) | 4063 (4) | 3474 (5) | 62 (4) |
| C(16) | 10060 (6) | 3566 (4) | 3468 (5) | 56 (4) |
| C(15) | 9129 (6) | 3743 (4) | 2900 (5) | 48 (4) |
| C(14) | 9014 (6) | 4418 (4) | 2337 (5) | 35 (3) |
| H(19) | 9741 (6) | 5438 (4) | 1908 (5) | 126 (10) |
| H(18) | 11391 (6) | 5123 (4) | 2916 (5) | |
| H(17) | 11595 (6) | 3926 (4) | 3914 (5) | |
| H(16) | 10148 (6) | 3043 (4) | 3903 (5) | |
| H(15) | 8498 (6) | 3358 (4) | 2895 (5) | |
| C(25) | 8560 (5) | 6771 (5) | 2925 (4) | 57 (4) |
| C(24) | 9508 (5) | 7119 (5) | 3121 (4) | 73 (5) |
| C(23) | 10264 (5) | 6810 (5) | 3818 (4) | 67 (4) |
| C(22) | 10073 (5) | 6154 (5) | 4319 (4) | 62 (4) |

Table 1 (cont.)

| | <i>x</i> | <i>y</i> | <i>z</i> | U (Å ²) |
|-------|-----------|----------|----------|-----------------------|
| C(21) | 9125 (5) | 5806 (5) | 4123 (4) | 55 (4) |
| C(20) | 8369 (5) | 6115 (5) | 3426 (4) | 39 (3) |
| H(25) | 7975 (5) | 7011 (5) | 2385 (4) | 126 (10) |
| H(24) | 9656 (5) | 7627 (5) | 2733 (4) | |
| H(23) | 10998 (5) | 7079 (5) | 3970 (4) | |
| H(22) | 10658 (5) | 5915 (5) | 4859 (4) | |
| H(21) | 8977 (5) | 5298 (5) | 4511 (4) | |
| C(31) | 6908 (5) | 5302 (3) | 4803 (5) | 56 (4) |
| C(30) | 6832 (5) | 4773 (3) | 5486 (5) | 66 (4) |
| C(29) | 6891 (5) | 3935 (3) | 5371 (5) | 59 (4) |
| C(28) | 7025 (5) | 3625 (3) | 4573 (5) | 52 (4) |
| C(27) | 7100 (5) | 4153 (3) | 3889 (5) | 44 (3) |
| C(26) | 7042 (5) | 4991 (3) | 4004 (5) | 34 (3) |
| H(31) | 6862 (5) | 5951 (3) | 4892 (5) | 126 (10) |
| H(30) | 6728 (5) | 5013 (3) | 6104 (5) | |
| H(29) | 6832 (5) | 3526 (3) | 5901 (5) | |
| H(28) | 7070 (5) | 2976 (3) | 4484 (5) | |
| H(27) | 7204 (5) | 3913 (3) | 3271 (5) | |

As in [NiI(pssp)][B(C₆H₅)₄] (Aurivillius & Bertinsson, 1980) the fundamental building elements of [Ni(pssp)](ClO₄)₂ are complex cations, where the ligand (C₆H₅)₂P(CH₂)₂S(CH₂)₃S(CH₂)₂P(C₆H₅)₂, (pssp), is quadridentate with the two P and the two S atoms of one single molecule coordinating Ni. The coordination of Ni in [Ni(pssp)]²⁺ (Fig. 2) is square planar with the metal atom in the middle of the plane formed by the P and the S atoms (Table 3) in contrast to [NiI(pssp)][B(C₆H₅)₄], where Ni is five-coordinated in the form of a square pyramid, (NiP₂S₂I). The distances Ni—P [2.175 (4), 2.196 (4) Å] and Ni—S [2.208 (4), 2.218 (4) Å] are in good agreement with corresponding distances [Ni—P 2.185 (3), Ni—S 2.210 (4) Å] given by Gastaldi, Porta & Tomlinson (1974) for an approximately square-planar coordination (NiS₂PA_s) in [1-(diphenylarsino)-2-(diphenylphosphino)ethane](*O*-methylphosphorodithioato)nickel(II) benzene (2/1), [Ni(C₂₆H₂₄AsP)(CH₃O₂PS₂)]·½C₆H₆. As expected the present Ni—P and Ni—S distances are some-

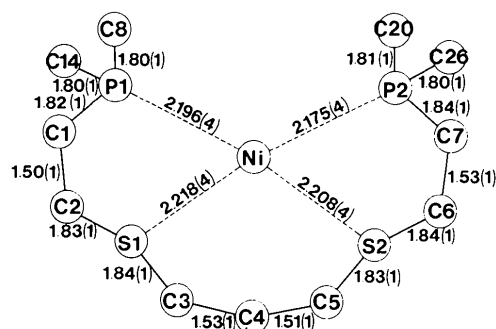


Fig. 1. Selected interatomic distances (Å) in the complex ion [Ni(C₃H₃₄P₂S₂)]²⁺. The C—C distances in the phenyl rings (omitted in the drawing) are assumed to be 1.395 Å. The bonds of the ligand chain are drawn with heavy lines, those in the coordination polyhedron of Ni with dashed lines.

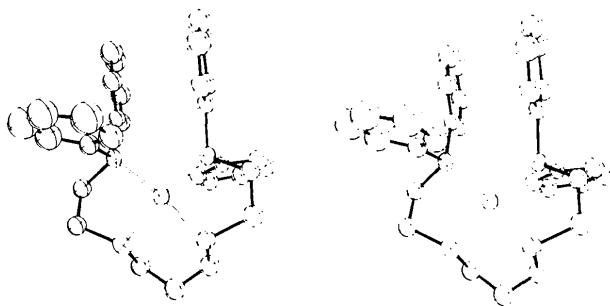


Fig. 2. A stereoview of the complex ion $[\text{Ni}(\text{C}_{31}\text{H}_{34}\text{P}_2\text{S}_2)]^{2+}$. The bonds of the ligand molecule $(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_2)_2\text{S}(\text{CH}_2)_3\text{S}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_5)_2$ are drawn with heavy lines, those in the coordination polyhedron of Ni with double lines. The H atoms are omitted. The ellipsoids are drawn to enclose 50% probability.

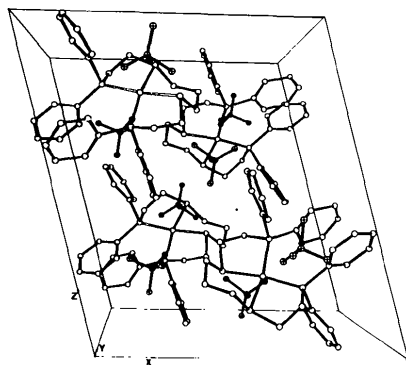


Fig. 3. A view of the content of one unit cell of $[\text{Ni}(\text{C}_{31}\text{H}_{34}\text{P}_2\text{S}_2)](\text{ClO}_4)_2$. The H atoms are omitted.

what shorter than those found for the five-coordinated Ni atom in the $[\text{NiI}(\text{pssp})]^+$ ion $[\text{Ni}-\text{P} 2.216(6), \text{Ni}-\text{S} 2.245(5) \text{ \AA}]$ in $[\text{Ni}(\text{C}_{31}\text{H}_{34}\text{P}_2\text{S}_2)\text{I}][\text{B}(\text{C}_6\text{H}_5)_4]$. In the square-planar coordination (NiP_2S_2), the angles $\text{P}-\text{Ni}-\text{S}$ and $\text{S}-\text{Ni}-\text{S}$ (neighbouring atoms) vary between 85.2 and 87.7° . The angle $\text{P}-\text{Ni}-\text{P}$ is larger, 100.8° , probably because of steric requirements of the four phenyl rings.

In $[\text{NiI}(\text{pssp})]^+$ and $[\text{Ni}(\text{pssp})]^{2+}$ Ni is part of three fused rings, two five-membered (NiPC_2S) and one six-membered (NiSC_3S). The NiSC_3S rings are in chair forms in both structures.

The perchlorate O atom nearest to Ni is at $3.38(1) \text{ \AA}$, implying no bonding.

In the structure there are four unique phenyl rings and two by two are approximately parallel at an average distance of 3.3 \AA .

As expected P is tetrahedrally coordinated although in a distorted way. Five of the bond angles around the P atoms vary between 105 and 109° ; the sixth [the angles $\text{Ni}-\text{P}-\text{C}(\text{phenyl})$ of the mutually parallel phenyl groups] is in both cases 125° . The deviations from tetrahedral geometry are certainly due to steric requirements of the phenyl rings. Mean values of the

Table 2. Distances (\AA) and angles ($^\circ$) in the ClO_4^- ions and angles ($^\circ$) 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. 1 and Table 1.

| | | | |
|--|------------|---|------------|
| $\text{Cl}(1)-\text{O}(1)$ | 1.334 (12) | $\text{Cl}(2)-\text{O}(5)$ | 1.365 (11) |
| $-\text{O}(2)$ | 1.354 (10) | $-\text{O}(6)$ | 1.429 (10) |
| $-\text{O}(3)$ | 1.411 (9) | $-\text{O}(7)$ | 1.401 (14) |
| $-\text{O}(4)$ | 1.358 (10) | $-\text{O}(8)$ | 1.355 (10) |
| $\text{O}(1)-\text{Cl}(1)-\text{O}(2)$ | 104.3 (10) | $\text{O}(5)-\text{Cl}(2)-\text{O}(6)$ | 110.2 (7) |
| $\text{O}(1)-\text{Cl}(1)-\text{O}(3)$ | 110.6 (8) | $\text{O}(5)-\text{Cl}(2)-\text{O}(7)$ | 108.5 (9) |
| $\text{O}(1)-\text{Cl}(1)-\text{O}(4)$ | 112.7 (10) | $\text{O}(5)-\text{Cl}(2)-\text{O}(8)$ | 119.5 (9) |
| $\text{O}(2)-\text{Cl}(1)-\text{O}(3)$ | 110.9 (8) | $\text{O}(6)-\text{Cl}(2)-\text{O}(7)$ | 102.4 (9) |
| $\text{O}(2)-\text{Cl}(1)-\text{O}(4)$ | 107.8 (9) | $\text{O}(6)-\text{Cl}(2)-\text{O}(8)$ | 108.7 (7) |
| $\text{O}(3)-\text{Cl}(1)-\text{O}(4)$ | 110.3 (7) | $\text{O}(7)-\text{Cl}(2)-\text{O}(8)$ | 106.2 (10) |
| $\text{P}(1)-\text{Ni}-\text{P}(2)$ | 100.8 (1) | | |
| $\text{P}(1)-\text{Ni}-\text{S}(1)$ | 87.7 (1) | | |
| $\text{S}(1)-\text{Ni}-\text{S}(2)$ | 85.2 (1) | | |
| $\text{S}(2)-\text{Ni}-\text{P}(2)$ | 87.2 (1) | | |
| $\text{P}(1)-\text{Ni}-\text{S}(2)$ | 170.6 (2) | | |
| $\text{P}(2)-\text{Ni}-\text{S}(1)$ | 167.4 (2) | | |
| $\text{Ni}-\text{P}(1)-\text{C}(1)$ | 104.8 (4) | $\text{Ni}-\text{P}(2)-\text{C}(7)$ | 105.8 (4) |
| $\text{Ni}-\text{P}(1)-\text{C}(8)$ | 109.0 (3) | $\text{Ni}-\text{P}(2)-\text{C}(20)$ | 125.1 (3) |
| $\text{Ni}-\text{P}(1)-\text{C}(14)$ | 124.6 (3) | $\text{Ni}-\text{P}(2)-\text{C}(26)$ | 106.5 (3) |
| $\text{C}(1)-\text{P}(1)-\text{C}(8)$ | 106.2 (5) | $\text{C}(7)-\text{P}(2)-\text{C}(20)$ | 104.9 (4) |
| $\text{C}(1)-\text{P}(1)-\text{C}(14)$ | 104.8 (4) | $\text{C}(7)-\text{P}(2)-\text{C}(26)$ | 105.7 (4) |
| $\text{C}(8)-\text{P}(1)-\text{C}(14)$ | 106.1 (3) | $\text{C}(20)-\text{P}(2)-\text{C}(26)$ | 107.4 (3) |
| $\text{Ni}-\text{S}(1)-\text{C}(2)$ | 107.4 (4) | $\text{Ni}-\text{S}(2)-\text{C}(5)$ | 104.3 (4) |
| $\text{Ni}-\text{S}(1)-\text{C}(3)$ | 99.0 (4) | $\text{Ni}-\text{S}(2)-\text{C}(6)$ | 108.6 (4) |
| $\text{C}(2)-\text{S}(1)-\text{C}(3)$ | 103.5 (5) | $\text{C}(5)-\text{S}(2)-\text{C}(6)$ | 99.9 (5) |

Table 3. The coordination of Ni: distances (\AA) and angles ($^\circ$) in the square plane and deviations (\AA) from the least-squares plane

P and S were used for calculation of the plane. E.s.d.'s are in parentheses.

| | | | |
|---------------------------|-----------|---------------------------------------|-----------|
| $\text{P}(1)-\text{P}(2)$ | 3.369 (4) | $\text{S}(1)-\text{P}(1)-\text{P}(2)$ | 85.5 (1) |
| $\text{P}(1)-\text{S}(1)$ | 3.058 (4) | $\text{P}(1)-\text{P}(2)-\text{S}(2)$ | 86.6 (1) |
| $\text{P}(2)-\text{S}(2)$ | 3.021 (4) | $\text{P}(2)-\text{S}(2)-\text{S}(1)$ | 93.1 (1) |
| $\text{S}(1)-\text{S}(2)$ | 2.997 (4) | $\text{S}(2)-\text{S}(1)-\text{P}(1)$ | 92.9 (1) |
| Ni | 0.04 (1) | S(1) | -0.15 (1) |
| P(1) | 0.14 (1) | S(2) | 0.15 (1) |
| P(2) | -0.14 (1) | | |

distances $\text{P}-\text{C}(\text{phenyl})$ and $\text{P}-\text{C}(\text{methylene})$ are $1.80(1)$ and $1.83(1) \text{ \AA}$ compared to the corresponding values of $1.83(2)$ and $1.81(2) \text{ \AA}$ in $[\text{NiI}(\text{pssp})][\text{B}(\text{C}_6\text{H}_5)_4]$.

S is also sp^3 hybridized, one position being occupied by the lone pair of electrons. The angles around S vary from 99 to 109° (Table 2). The mean $\text{S}-\text{C}$ (methylene) distance is $1.84(1) \text{ \AA}$, in good agreement with the corresponding value, $1.84(1) \text{ \AA}$, in $[\text{NiI}(\text{pssp})][\text{B}(\text{C}_6\text{H}_5)_4]$.

The perchlorate ions exhibit the expected tetrahedral geometry, though somewhat deformed. They display a

feature often found among perchlorates of bulky organic cations, namely large vibrational thermal motion. The average Cl—O distances, corrected or uncorrected for thermal motion, for the two ions are rather short, 1.36 (1) and 1.39 (1) Å. The largest deviations for the two ions from the tetrahedral angle (109.5°) amount to 5.2 and 10.0°, which are about 5 and 10 times the e.s.d.'s. The difference maps did not give any further information about the state of these ions.

Some rather short O...H and C...H contacts exist between the perchlorate O and methylene H atoms [O(3)...H(1A), O(4)...H(5A), O(5)...H(3B), 2.34 (1) (3×) Å] and the phenyl C and H atoms of different rings [C(16)...H(24), 2.53 (1) Å]. The van der Waals values for O—H and C—H are 2.4 and 2.5 Å, respectively (Gieren & Dederer, 1977; Baur, 1972). The H atoms were, however, located by geometrical methods, the phenyl and methylene groups assumed to be rigid bodies.

The packing of the ions is shown in Fig. 3. The two perchlorate ions, not bonded to Ni, are situated one on each side of the complex cation.

Magnetic-susceptibility measurements were performed at room temperature with a Faraday balance (Blom & Hörlin, 1977). As expected the compound is diamagnetic.

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References

- AURIVILLIUS, K. & BERTINSSON, G.-I. (1980). *Acta Cryst.* B36, 790–794.
 BAUR, W. H. (1972). *Acta Cryst.* B28, 1456–1465.
 BLOM, B. & HÖRLIN, T. (1977). *Chem. Commun. Univ. Stockholm*, No. 5.
 CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* 53, 1891–1892.
 DEGISCHER, G. (1968). Dissertation No. 4163, ETH, Zürich, Switzerland.
 DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* A24, 390–397.
 GASTALDI, L., PORTA, P. & TOMLINSON, A. A. G. (1974). *J. Chem. Soc. Dalton Trans.* pp. 1424–1429.
 GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A27, 368–376.
 GIENEN, A. & DEDERER, B. (1977). *Acta Cryst.* B33, 3296–3303.
 SHELDRIK, G. M. (1976). *SHELX*. Program for crystal structure determination. Univ. of Cambridge, England.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175–3187.

Acta Cryst. (1981). B37, 75–79

Studies on the Metal—Amide Bond.

III.* The Structure of the Copper(II) Deprotonated Complex of *N,N'*-Ethylenedi-2-pyridinecarboxamide

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Abstract

Aqua(*N,N'*-ethylenedi-2-pyridinecarboxamido)copper(II) monohydrate, [Cu(C₁₄H₁₂N₄O₂)(H₂O)].H₂O, C₁₄H₁₄CuN₄O₃.H₂O, is monoclinic, space group *P*2₁/*c*, with *a* = 17.298 (15), *b* = 13.505 (9), *c* = 14.119 (22) Å, β = 115.8 (2)°, *Z* = 8. The structure was refined to *R* = 0.099 for 3112 non-zero photographic reflexions. The crystal contains two distinct geometric isomers. In each the ligand acts

as an approximately planar N₄ quadridentate ligand, coordinating the Cu atom [Cu—N(amide) average 1.920 (7), Cu—N(pyridine) average 2.053 (7) Å, N(amide)—Cu—N(amide) average 82.5 (3), N(pyridine)—Cu—N(pyridine) 110.8 (3), 112.7 (3)°], with a water molecule occupying the apex of a distorted square pyramid [Cu—O 2.361 (8) and 2.317 (8) Å]. The Cu atoms are 0.22 and 0.28 Å above the N₄ planes. The two isomers differ in the degree and nature of folding of the quadridentate ligands from planarity. The molecules pack in a series of planes parallel to (10 $\bar{1}$) with the coordinated and lattice water molecules

* Part II: Chapman, Stephens & Vagg (1980).