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Dibromobis{ μ -[2-(diphenylphosphino)ethanethiolato]-*P, \mu*-S}-dinickel(II)*

BY KARIN AURIVILLIUS AND GERT-INGE BERTINSSON

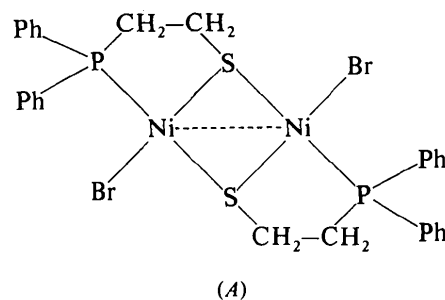
Inorganic Chemistry 1, Chemical Center, University of Lund, PO Box 740, S-220 07 Lund 7, Sweden

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Abstract. $\text{Ni}_2\text{Br}_2(\text{C}_{14}\text{H}_{14}\text{PS})_2$, $\text{C}_{28}\text{H}_{28}\text{Br}_2\text{Ni}_2\text{P}_2\text{S}_2$, $M_r = 767.83$, monoclinic, $C2/c$, $a = 21.748$ (2), $b = 9.289$ (1), $c = 15.473$ (1) Å, $\beta = 108.041$ (5)°, $V = 2972$ Å³, $Z = 4$, $D_m = 1.69$, $D_x = 1.716$ Mg m⁻³, $R = 0.043$ for 2029 observed reflexions. In the complex dibromo{ μ -[2-(diphenylphosphino)ethanethiolato]-*P, \mu*-S}-dinickel(II) the 2-(diphenylphosphino)ethanethiolate ion, $[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{S}]^-$, ps⁻, acts as a bidentate ligand, the P and S atoms forming a five-membered non-planar ring (NiPC₂S). Br is coordinated to Ni *cis* to P. The S atoms bridge two NiBr(ps) units giving a dinuclear uncharged complex. A square plane is formed around each Ni by one Br, one P and two S atoms. The angle between these planes, which are connected by an S–S edge, is 100.7 (2)° giving a short Ni–Ni distance, 2.695 (2) Å, somewhat longer than the metallic Ni–Ni distance of 2.492 (12) Å [Pauling (1960). *The Nature of the Chemical Bond*. New York: Cornell Univ. Press]. All other interatomic distances and angles are normal. The compound is diamagnetic.

Introduction. The title compound (see schematic diagram *A*) in the form of dark-red crystals prepared by the late Professor G. Schwarzenbach (1965) was used for intensity measurements on a four-circle diffractometer (Enraf–Nonius CAD-4) at room temperature.

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



The cell parameters were refined from 49 accurately measured θ values. The space group, determined from Weissenberg photographs, is $C2/c$ or Cc . Data concerning the collection and reduction of the intensities are given in Table 1. Corrections were made for Lorentz–polarization and absorption effects. No systematic change was observed in the three standard reflexions which were measured every second hour. The positions of Br, Ni, P and S were determined with *MULTAN* (Germain, Main & Woolfson, 1971) and the C atoms from electron-density maps, space group $C2/c$ being assumed. The preliminary parameters were refined with *SHELX* (Sheldrick, 1976) minimizing $\sum w(|F_o| - |F_c|)^2$ with $w = K/[\sigma(F) + GF^2]$. The refined value $G = 0.00022$ gave a satisfactory ΔR plot (Abrahams & Keve, 1971). The phenyl rings were treated as rigid groups (C–C 1.395 Å). The positions of the H atoms were geometrically generated at the end

Table 1. Details of the collection and reduction of the intensities and the least-squares refinement

Crystal size (mm) along $a \times b \times c$	0.03 × 0.29 × 0.09
Radiation	Cu K α , $\lambda = 1.54056 \text{ \AA}$ (graphite monochromator)
θ interval ($^\circ$)	4–70
Scan type/width $\Delta\omega$ ($^\circ$)	ω -2 θ /1.0 + 0.50 tan θ
Maximum recording time (min)	3
Control reflexions	826; 113; 221
μ (mm ⁻¹)	7.41
Range of transmission factors	0.40–0.80
Number of reflexions measured	3295
Number of reflexions used in the final refinement [$I > 2\sigma(I)$]	2029
Number of parameters	71
$R = \sum F_o - F_c / \sum F_o $	0.043
$R_w = [\sum w(F_o - F_c)^2 / \sum w F_o ^2]^{1/2}$	0.045

Table 2. Fractional coordinates and isotropic temperature factors for the non-hydrogen atoms

The values for H are deposited. E.s.d.'s are in parentheses. For Br, Ni, S and P the isotropic mean values of U_{ij} are given, calculated according to Willis & Pryor (1975).

	x	y	z	U (\AA^2)
Br	0.35132 (3)	0.20696 (8)	0.63610 (4)	0.0617 (3)
Ni	0.43724 (4)	0.30700 (8)	0.74618 (5)	0.0356 (3)
S	0.51575 (6)	0.41900 (13)	0.84446 (9)	0.0372 (4)
P	0.42082 (6)	0.19251 (14)	0.85829 (9)	0.0369 (4)
C(1)	0.5332 (2)	0.3291 (5)	0.9549 (3)	0.040 (1)
C(2)	0.5012 (2)	0.1835 (6)	0.9441 (3)	0.042 (1)
C(3)	0.3659 (1)	0.2832 (4)	0.9074 (2)	0.039 (1)
C(4)	0.3075 (1)	0.3313 (4)	0.8473 (2)	0.054 (2)
C(5)	0.2640 (1)	0.4071 (4)	0.8801 (2)	0.065 (2)
C(6)	0.2789 (1)	0.4347 (4)	0.9730 (2)	0.060 (2)
C(7)	0.3373 (1)	0.3865 (4)	1.0330 (2)	0.062 (2)
C(8)	0.3808 (1)	0.3107 (4)	1.0002 (2)	0.058 (2)
C(9)	0.3948 (2)	0.0064 (4)	0.8420 (3)	0.041 (1)
C(10)	0.3472 (2)	-0.0499 (4)	0.8754 (3)	0.051 (1)
C(11)	0.3312 (2)	-0.1956 (4)	0.8637 (3)	0.063 (2)
C(12)	0.3629 (2)	-0.2850 (4)	0.8187 (3)	0.069 (2)
C(13)	0.4105 (2)	-0.2286 (4)	0.7853 (3)	0.074 (2)
C(14)	0.4265 (2)	-0.0829 (4)	0.7969 (3)	0.061 (2)

of each cycle of the refinement of the non-hydrogen atoms (C–H 1.080 \AA). The C and H atoms were given isotropic and the other atoms anisotropic temperature factors. A correction was made for anomalous dispersion (Cromer & Liberman, 1970) but not for extinction, since the intensities showed no indication of the latter.

The highest residual electron density and the deepest trough were 0.9 and 0.5 $e \text{ \AA}^{-3}$, respectively. Scattering factors for neutral non-hydrogen atoms were from Doyle & Turner (1968) and for neutral H from Stewart, Davidson & Simpson (1965). Final positional parameters are given in Table 2.* As the refinement

* Lists of structure factors, anisotropic thermal parameters, and fractional coordinates and isotropic temperature factors for the H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36553 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

was satisfactory in space group $C2/c$, Cc was not considered.

A magnetic susceptibility measurement with a Faraday balance (Blom & Hörlin, 1977) showed the compound to be diamagnetic. A Univac 1100 at Lund's Data Center was used for the computer work.

Discussion. Selected interatomic distances and angles are given in Fig. 1 and Table 3. A view of the atomic arrangement of Ni₂Br₂(ps)₂ and a stereoview of the contents of the unit cell are given in Figs. 2 and 3 (Johnson, 1965). The structure of complexes between Ni^{II} and disubstituted β -mercaptoethylamines and phosphines are dependent, among other things, on the steric requirements of the substituents. Ligands with limited steric demands form the trinuclear sulphur-bridged cation $\text{Ni}[\text{NiL}_2]_2^{2+}$ whereas bulky ligands mostly form dimers $\text{Ni}_2\text{L}_2\text{X}_2$ ($\text{X} = \text{halide ion}$) (Root & Busch, 1968; Wei & Dahl, 1970). The present X-ray study of the title compound has shown that a dimeric complex is formed. The dinuclear molecule of symmetry 2 has a thiolate-bridged structure with a central four-membered NiSnS ring, which is folded to 100.7 (2) $^\circ$ along the S–S diagonal. Each Ni is coordinated, in addition to the two thiolate S of the ps⁻ groups, to one P and one Br atom in a square-planar arrangement. Thus a five-membered non-planar ring (NiPC₂S) is formed, *cf.* Table 4. The Ni atom is situated 0.055 (2) \AA from the least-squares plane formed by its ligand atoms Br, P and S (Table 4). The folding of the complex brings the two Ni atoms close together [2.695 (2) \AA], indicating the possibility of a weak metal–metal interaction of the same order [Ni–Ni 2.739 (1) \AA] as found in, for example, bis- $\{\mu$ -[2-(2-pyridylethylamino)ethanethiolato]- N, μ -S}-dinickel(II) perchlorate, $[\text{Ni}(\text{C}_9\text{H}_{13}\text{N}_2\text{S})_2]_2[\text{ClO}_4]_2$ (Vance, Warner & Seff, 1977).

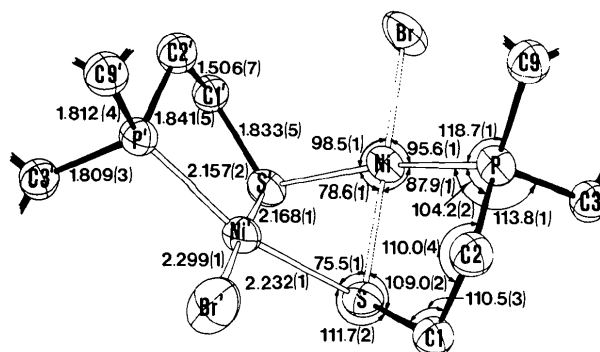


Fig. 1. A drawing of the complex molecule Ni₂Br₂(ps)₂ showing interatomic distances (\AA) and the angles ($^\circ$); for clarity some angles are given in Table 3. The C–C distances in the phenyl rings (omitted in the drawing) are assumed to be 1.395 \AA . The bonds in the ligand are drawn with heavy lines and those in the coordination polyhedra of Ni with double lines.

Table 3. Angles (°) not given in Fig. 1, in the coordination polyhedra of Ni and P

E.s.d.'s are given in parentheses. For labelling, see Fig. 1 and Table 2.

Br—Ni—S	175.1 (1)	C(2)—P—C(3)	108.7 (2)
P—Ni—S'	163.2 (1)	C(2)—P—C(9)	104.1 (2)
		C(3)—P—C(9)	106.5 (2)

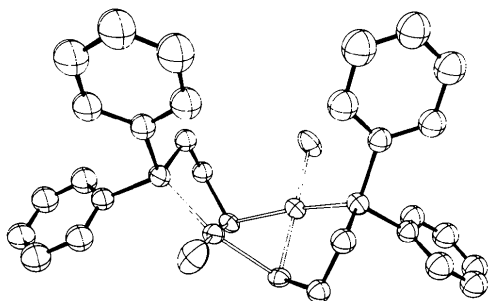


Fig. 2. A view of the complex Ni₂Br₂(ps)₂. The bonds of the ligand, ps, are drawn with heavy lines and those in the coordination polyhedra of Ni with double lines. The H atoms are omitted. The ellipsoids are drawn to enclose 50% probability.

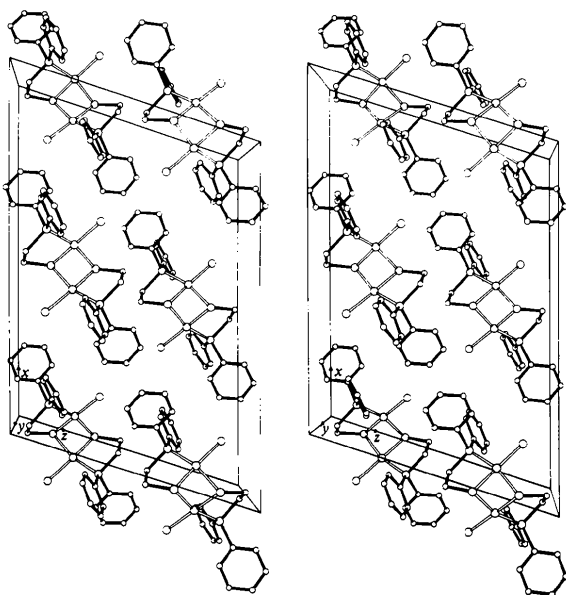


Fig. 3. A stereoview of the packing of Ni₂Br₂(ps)₂ in the unit cell. The H atoms are omitted.

The two Ni—S distances are significantly different, 2.232 (1) and 2.168 (1) Å. Similar differences in Ni—S distances are reported for other dinuclear thiolate-bridged Ni complexes, e.g. 2.186 (1) and 2.169 (1) Å in bis{μ-[2-(2-pyridylethylamino)ethanethiolato]-N,μ-S}-dinickel(II) perchlorate and 2.219 (4), mean, and 2.183 (4) Å, mean, in bis{μ-[2,2'-thiobis(ethylthio)]-S,S',μ-S''}-nickel(II) (Barclay, McPartlin & Stephenson, 1969).

Table 4. The planarities of the coordination figure of Ni and the chelate ring NiPC₂S with e.s.d.'s in parentheses

Br, S, S' and P were used for the calculation of the square plane and all atoms were used for the ring. Deviations in Å.

Square plane		Chelate ring	
Ni	-0.055 (2)	Ni	0.051 (1)
Br	-0.119 (2)	S	-0.073 (1)
S	-0.135 (2)	P	-0.124 (1)
S'	0.135 (2)	C(1)	0.114 (5)
P	0.118 (2)	C(2)	0.637 (5)

The Ni—P distance 2.157 (2) Å is somewhat shorter than 2.196 (4) and 2.175 (4) Å found for Ni—P in [1,9-bis(diphenylphosphino)-3,7-dithianonane]nickel(II) diperchlorate, [Ni(pssp)](ClO₄)₂ (Aurivillius & Bertinsson, 1981). The difference may be due to the *trans* coordinating atom, which is a thiolate S in the present compound and a thioether S in the cited structure.

The Ni—Br distance 2.299 (1) Å is in good agreement with 2.305 (3) Å found in dibromobis(benzyl-diphenylphosphine)nickel(II) (square) (Kilbourn & Powell, 1970). The angles between neighbouring atoms subtended at Ni in the square-planar arrangement vary from 78.6 (1) to 98.5 (1)°, the S—Ni—S' angle being the smallest.

The distance between the bridging sulphur atoms, 2.788 (3) Å, is much shorter than that reported for [Ni(pssp)](ClO₄)₂, 2.977 (4) Å, involving no S—S interaction. The angles around S vary from 75.5 (1) to 111.7 (2)° (Fig. 1). The distortion of the angle S—Ni—S' (78.6°), the S—S distance and the bond angles of the pyramidally (*sp*³ hybridized) coordinated S atom are typical for this type of compound and probably result from the stereochemical requirements of the ligand in the formation of the dimer (Barclay, McPartlin & Stephenson, 1969).

The P atom is *sp*³ hybridized as expected although the configuration about P is distorted (Fig. 1 and Table 3). The angles are between 104.1 (2) and 118.7 (1)°. The deviations from tetrahedral geometry are certainly due to steric requirements of the phenyl rings. In [Ni(pssp)](ClO₄)₂ the corresponding angles around P vary from 104.8 (4) to 125.1 (3)°.

The P—C(phenyl), 1.810 (3) Å, mean, and the P—C(methylene), 1.841 (5) Å, as well as the S—C, 1.833 (5) Å, and the C—C, 1.506 (7) Å, distances (Fig. 1) are in good agreement with analogous values reported in the literature.

The packing of the molecules is shown in Fig. 3. The shortest intermolecular distances are Br—H(5), 2.99 (4) Å, and C(11)—H(1B), 2.73 (1) Å. The H atoms have, however, been generated geometrically.

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Sodium Cytosine-5-methylenesulfonate Trihydrate*

BY CHARLES, L. BARNES† AND STUART W. HAWKINSON

Department of Biochemistry, The University of Tennessee, Knoxville, Tennessee 37916, USA

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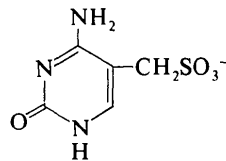
Abstract. C₅H₆N₃O₄S⁻.Na⁺.3H₂O, *P*2₁/*c*, *a* = 5.235 (1), *b* = 22.843 (5), *c* = 9.141 (2) Å, β = 90.93 (1)°, *Z* = 4, *D*_c = 1.709, *D*_o = 1.70 Mg m⁻³, *V* = 1092.8 Å³, *M*_r = 281.2, λ(Mo *K*α₁) = 0.70926 Å, *T* = 299 ± 1 K, *F*(000) = 584. The intensity data were collected on an automated diffractometer and the structure was solved by direct methods. Full-matrix least-squares refinement, with the temperature factors of the non-H atoms allowed to refine anisotropically, yielded an *R* of 0.038 for the 2160 significant data. The anions are packed as pairs of columns linked by N–N hydrogen bonds and bridged by solvent interactions.

Introduction. Bisulfite has been shown to be mutagenic in a number of microbial systems (see, for example, Hayatsu, 1976; Shapiro, 1977). Because bisulfite catalyzes the deamination of cytosine by reversibly adding across the C(5)–C(6) double bond, and because most mutations attributed to bisulfite have been characterized as guanine–cytosine (G–C) to adenine–thymine (A–T) transitions, cytosine deamina-

tion has been proposed as the mechanism of bisulfite mutagenesis.

One system in which bisulfite-mediated mutations have been observed, and characterized as G–C to A–T transitions, is the *rII* system of T4 bacteriophage (Summer & Drake, 1971). However, bacteriophage T4, as do other T-even bacteriophages, contains hydroxymethylcytosine in place of cytosine in its genome. A deaminated product of the reaction of bisulfite with hydroxymethylcytosine has been suggested as the ultimate mutagen in the T4 system (Shapiro, 1977).

It has recently been shown that the major product of the reaction of bisulfite with hydroxymethylcytosine under conditions similar to those employed for the modification of cytosine, namely acid pH and high bisulfite concentration, is cytosine-5-methylenesulfonate



rather than a C(6) substituted dihydropyrimidine sulfonate (Hayatsu & Shiragami, 1979).

* Sodium 4-amino-2(1*H*)-oxo-5-pyrimidinylmethanesulfonate.

† Present address: Department of Chemistry, The University of Oklahoma, Norman, Oklahoma 73019, USA.