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Registry No. $K_4Mo_2Cl_8$, 25448-39-9; $K_4Mo_2Cl_8{\cdot}2H_2O$, 22239-46-9.

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(1) (a) Iowa State University. (b) Texas A&M University. (c) Auburn University.

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(10) It should be kept in mind that there is no evidence to show whether the extent of disordering (7%) found in the crystal used to collect x-ray data for the structure determination will be found in other crystals. If this is the thermodynamic equilibrium value and crystals from other sources are also obtained under equilibrium conditions, the extent of disordering should be the same. We have tentatively assumed this although, provided the value is small, it could be different (not zero, however) without affecting our interpretation of conclusions. The calculation of molar absorptivity (Figure 1) would, of course, be affected.

(11) From Figure 1 it is possible to estimate the oscillator strength of the $\delta \rightarrow \delta^*$ transition. Using the conversion factor given in the caption one obtains 540 ± 135 for ϵ, but account must be taken of the fact that only a fraction (presumably 7%, but see footnote 10) of the molecules are in the correct orientation to absorb. The width at half-height of the peak is about 1600 cm^{-1}. With these data we calculate that $f = (4.6 \times 10^{-9})(\epsilon/0.07)(1600) = (57 \pm 14) \times 10^{-3}$. As is well-known, solutions of $Mo_2Cl_8^{4-}$ are extremely unstable. The nature and kinetics of the decomposition are under study at Texas A&M University by Mr. L. D. Gage. From his data it is possible to obtain by extrapolation the "spectrum at $t = 0$" and this shows a symmetrical band with its maximum at 524 nm, ϵ 1000 ± 50 cm^{-1} M^{-1}, and $\Delta\nu_{1/2} = 2020$ cm^{-1}. From these data we get $f = (4.6 \times 10^{-9})(1000 \pm 50)(2020) = (9.3 \pm 0.5) \times 10^{-3}$. These two results actually agree within a factor of 2 since it is necessary to divide the former by a factor of 3, giving $(19 \pm 4) \times 10^{-3}$, when making the comparison, to account for the random orientation characteristic of the solution.

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Crystal and Molecular Structure of a Mercaptide-Bridged Dinickel(II) Complex: Bis-μ-[2-[(2-pyridylethyl)amino]ethylthiolato]-dinickel(II) Perchlorate

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The crystal structure of bis-μ-[2-[(2-pyridylethyl)amino]ethylthiolato]-dinickel(II) perchlorate, $[Ni(C_9H_{13}N_2S)ClO_4]_2$, was determined by single-crystal x-ray diffraction techniques and was refined by full-matrix least-squares methods to a final conventional *R* index of 0.023. The dark violet crystals form as prisms in space group $P2_12_12$ with $a = 14.896$ (4), $b = 12.861$ (4), and $c = 6.631$ (1) Å at 20 °C. The binuclear molecules of symmetry 2 (C_2 in Schönflies notation) have a mercaptide-bridged structure with a central four-membered $\overline{\mathrm{NiSNiS}}$ ring which is severely folded to 110° at its S^-–S^- diagonal to give a Ni(II)–Ni(II) distance of 2.739 (1) Å. Each Ni(II) ion has distorted square-planar coordination involving an amino nitrogen, a pyridyl nitrogen, and two bridging mercaptide ions.

Introduction

The redox equilibrium between organic disulfide, RSSR, and mercaptide, RS^-, in neutral aqueous solution in the presence of O_2 can be shifted by complexation to Ni(II). (The mercaptide is oxidized slowly by O_2 or more rapidly by H_2O_2.) The direction of the shift depends upon the bidentate R groups studied.[1] When R is 2-[(2-pyridylmethyl)amino]ethyl, the equilibrium shifts to the disulfide, and disulfide complexes of Ni(II) can be isolated.[1] The structures of two of these, chloro[bis[2-[(2-pyridylmethyl)amino]ethyl] disulfide]nickel(II) perchlorate and its isostructural bromide derivative, have been reported.[2,3] In these disulfide complexes, a five-membered chelate ring is formed by each R group with Ni(II). The corresponding six-membered ring does not appear in an isolatable complex and may be considered a disfavoring feature.

When R is 2-[(2-pyridylethyl)amino]ethyl, which is one methylene group larger, the equilibrium favors the mercaptide complex, and a disulfide complex could not be isolated. Apparently a six-membered chelate ring is better accommodated by the mercaptide complex.

This work was undertaken to understand better the dependence of the disulfide–mercaptide Ni(II) complex equilibrium on the chelate ring sizes and orientations and to observe the structural relationship between the disulfide and mercaptide complexes. Perhaps the Ni(II) ion is coordinated to the ligands during the redox process, and a mechanism involving the complexes would be apparent.

Experimental Section

Preparation Section. Ethylene monothiocarbonate and 2-(β-aminoethyl)pyridine were obtained from Eastman Kodak Co. and Chemicals Procurement Laboratories, respectively. Reagent grade $NiClO_4{\cdot}6H_2O$ and $NaClO_4$ were obtained from G. Frederich Smith Chemical Co. All other chemicals were of reagent grade quality. The infrared spectrum was obtained using a Beckman IR-10 instrument. Elemental analysis was performed by Galbraith Laboratories.

Preparation of 2-[(2-Pyridylethyl)amino]ethanethiol, $pyCH_2CH_2NHCH_2CH_2SH$. A 43.8-g (0.36 mol) sample of distilled 2-(β-aminoethyl)pyridine was dissolved in 75 mL of toluene (distilled over Na) and brought to reflux. Ethylene monothiocarbonate (18.7 g, 0.18 mol) dissolved in 25 mL of anhydrous toluene was added dropwise with stirring to the refluxing solution. After 2 h of refluxing, an additional 9 g of ethylene monothiocarbonate was added; heating continued for 4 h more at 120 °C, just below reflux temperature. Toluene was distilled away at atmospheric pressure; the remainder was fractionally vacuum distilled. The desired product had a boiling point range of 106–110 °C at 0.15 Torr.

Preparation of Bis-μ-[2-[(2-pyridylethyl)amino]ethylthiolato]-dinickel(II) Perchlorate, $Ni_2(pyCH_2CH_2NHCH_2CH_2S)_2(ClO_4)_2$. Following the procedure of Gavino,[1] a 0.18-g (0.001 mol) sample of $pyCH_2CH_2NHCH_2CH_2SH$, dissolved in 15 mL of acetone was added to an acetone solution of $NiClO_4{\cdot}6H_2O$ (0.37 g or 0.001 mol in 75 mL) containing 1 mL of saturated $NaClO_4$. Dark violet needles formed from the resulting intensely red-brown solution. The infrared spectrum of this complex is identical with that taken by Gavino.[1] Anal. Calcd for $Ni_2C_{18}H_{26}N_4S_2Cl_2O_8$: Ni, 17.30; C, 31.84; H, 3.86; Cl, 10.44. Found: Ni, 17.03; C, 32.21; H, 3.87; Cl, 10.51. Recrystallization by the vapor diffusion method,[4] using acetonitrile and ether as the solvent pair, yielded a single crystal of extreme dimensions 0.11 × 0.14 × 0.50 mm which was used in all subsequent diffraction experiments.

Diffraction Work. A Syntex four-circle computer-controlled diffractometer with graphite-monochromatized Mo Kα radiation (Kα_1, λ 0.709 30 Å; Kα_2, λ 0.713 59 Å) and a pulse-height analyzer was used for preliminary experiments and for the measurement of diffraction intensities. The cell constants and their standard deviations were determined, using $\bar{\lambda}$ 0.710 73 Å, by a least-squares treatment of the angular coordinates of 15 independent reflections with 2θ values between 25 and 34°. The program used was written by R. A. Sparks and is part of the diffractometer program library. The temperature was maintained within 1° of 20 °C throughout. The θ–2θ scan mode was utilized with a constant scan speed of 1° min^{-1}. The total background counting time, equal to the scan time, was equally spent at each end of the scan range, which varied from 2.0° at low 2θ to 2.3° at 50°. The intensities of three reflections, which were remeasured after every 100 during data collection, showed no systematic variations. All reflections ($h00$) for h odd and ($0k0$) for k odd were systematically absent, uniquely defining the space group as $P2_12_12$.

Standard deviations were assigned to individual reflections according to the formula

$$\sigma(I) = [\omega^2(\mathrm{CT} + B_1 + B_2) + (pI)^2]^{1/2}$$

where ω is the scan rate, CT is the total integrated count, B_1 and B_2 are the background counts, and the intensity $I = \omega(\mathrm{CT} - B_1 - B_2)$. A value of 0.02, appropriate to the instrumentation used, was assigned to the empirical parameter p to account for instrument instability. The weights, w, used in least squares were the reciprocal squares of $\sigma(F_o)$. Of the 1345 symmetry independent reflections measured, those for which $2\theta < 50°$, 1205 had intensities larger than three times their standard deviations, and only these were included in the subsequent calculations. The intensities were corrected[5] for Lorentz and polarization effects; the contribution of the monochromator crystal was calculated assuming it to be half perfect and half mosaic in character. An absorption correction[6-8] was made ($\mu = 19.0\ cm^{-1}$); the calculated transmission coefficients ranged from 0.780 to 0.819. Extinction corrections were omitted. The atomic scattering factors[9] for Ni^+, Cl^0, S^0, O^0, N^0, C^0, and H (bonded) were used. The first three were modified to account for the real part of the anomalous dispersion correction.[10]

Crystal Data. Bis-μ-[2[(2-pyridylethyl)amino]ethylthiolato]-dinickel(II) perchlorate, $[Ni(C_9H_{13}N_2S)ClO_4]_2$ or $Ni_2(pyCH_2CH_2NHCH_2CH_2S)_2(ClO_4)_2$, crystallizes as dark violet prisms in the orthorhombic space group $P2_12_12$ with a = 14.896 (4) Å, b = 12.861 (4) Å, c = 6.631 (1) Å, V = 1270.4 (5) $Å^3$, mol wt = 1204.4 amu, d_{obsd}(flotation) = 1.76 (1) g cm^{-3}, d_{calcd} = 1.774 g cm^{-3}, Z = 2, and $F(000)$ = 696. Figures in parentheses are estimated standard deviations in the units of the least significant digit given.

Structure Determination. The Ni(II) position was learned from an initial three-dimensional Patterson function. All other nonhydrogen atoms were located in successive Fourier syntheses using the fast-Fourier algorithm.[11] Hydrogen atom positions were calculated[12] assuming C–H and N–H distances[13] of 0.95 and 0.87 Å, respectively. All calculated hydrogen atom positions correlated with peaks on a difference Fourier function. Full-matrix least-squares refinement[14] with anisotropic thermal parameters for nonhydrogen atoms and isotropic thermal parameters for hydrogen atoms led to the final error indices $R_1 = \sum(|F_o - |F_c||)/\sum F_o = 0.023$ and $R_2 = [\sum w(F_o - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.025$. The "goodness-of-fit", $[\sum w(F_o - |F_c|)^2/(m - s)]^{1/2}$, is 1.71. The number of observations used in least squares is m (1205), and s (215) is the total number of parameters. The overdetermination ratio (m/s) is 5.6.

In the final cycle of least-squares refinement, all shifts were less than 8 and 15% of their esd's for nonhydrogen and hydrogen atomic parameters, respectively. The two largest peaks on the final difference Fourier function, whose esd was calculated to be 0.04 e $Å^{-3}$, were 0.4 e $Å^{-3}$ in height and were located very close to the Ni or S atoms. The final positional and thermal parameters, together with their standard deviations, are presented in Tables I and II.

Table I. Final Positional Parameters and Their Standard Deviations[a]

	x ($\sigma(x)$)	y ($\sigma(y)$)	z ($\sigma(z)$)
Ni(1)	711.6 (0.4)	674.1 (0.4)	1854.8 (0.8)
S(2)	599.7 (0.8)	−832.0 (0.8)	3303.5 (1.8)
C(3)	1352 (4)	−1569 (4)	1695 (10)
C(4)	1536 (4)	−973 (4)	−202 (8)
N(5)	1730 (3)	129 (4)	291 (7)
C(6)	1989 (4)	737 (5)	−1546 (8)
C(7)	1215 (4)	1372 (5)	−2351 (9)
C(8)	1027 (3)	2279 (4)	−1040 (8)
C(9)	1097 (4)	3316 (5)	−1645 (11)
C(10)	972 (4)	4100 (4)	−316 (13)
C(11)	774 (4)	3877 (4)	1642 (13)
C(12)	705 (4)	2854 (4)	2186 (9)
N(13)	812 (3)	2066 (3)	897 (6)
Cl(14)	3374 (1)	1477 (1)	3761 (2)
O(15)	2949 (3)	474 (3)	3868 (6)
O(16)	3682 (4)	1626 (4)	1764 (8)
O(17)	4059 (4)	1498 (5)	5166 (10)
O(18)	2731 (3)	2259 (4)	4238 (8)
H(3A)	179 (3)	−158 (3)	243 (7)
H(3B)	107 (3)	−222 (4)	147 (7)
H(4A)	203 (4)	−124 (4)	−94 (8)
H(4B)	101 (4)	−95 (4)	−106 (9)
H(5)	198 (4)	21 (4)	114 (8)
H(6A)	247 (3)	122 (4)	−121 (7)
H(6B)	222 (3)	22 (4)	−259 (7)
H(7A)	132 (4)	152 (5)	−361 (10)
H(7B)	61 (4)	90 (5)	−249 (10)
H(9)	116 (3)	342 (4)	−289 (9)
H(10)	98 (4)	482 (5)	−69 (9)
H(11)	71 (4)	433 (4)	242 (9)
H(12)	53 (3)	265 (4)	349 (8)

[a] Values for nonhydrogen atoms are given ×10^4; values for hydrogen atoms are given ×10^3. See Figure 1 or 2 for the identities of the atoms. The esd is in the units of the least significant digit given for the corresponding parameter.

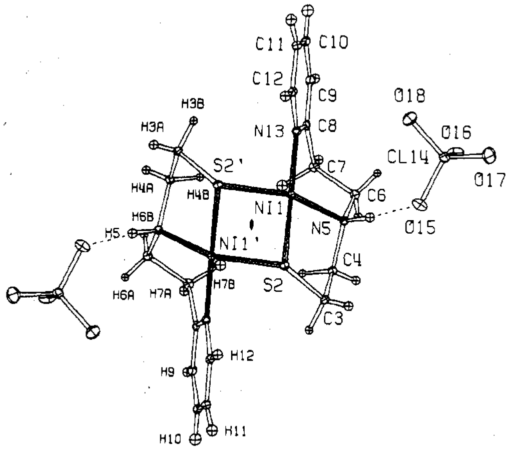

Figure 1. $[Ni(pyCH_2CH_2NHCH_2CH_2S)(ClO_4)]_2$ molecule shown[15] with ellipsoids of 5% probability. The twofold axis of molecular symmetry is indicated. The hydrogen bond between H(5) and O(15) is noted by a dashed line.

Discussion

The Ni(II) ion is four-coordinate, in a near square-planar N_2S_2 environment. Its ligands are one amino nitrogen atom, one pyridyl nitrogen atom, one mercaptide ion all from the same parent ligand, and one mercaptide ion of another ligand (see Figure 1). The distortion of the Ni coordination sphere from square-planar geometry is indicated by the deviation of angles (79.58 (5) to 97.3 (1)°) about Ni(II) from 90° (see Table III) and by the displacement of N(5) and N(13) by −0.33 and 0.26 Å, respectively, from the Ni(1), S(2), S(2′), N(5), N(13) plane (see Table IV). Wei and Einstein[16] expect

Table II. Thermal Vibration Parameters and Their Standard Deviations[a]

1. Nonhydrogen Atoms

$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni(1)	32.5 (0.3)	35.9 (0.3)	124.2 (1.3)	1.3 (0.3)	0.2 (0.6)	0.8 (0.6)
S(2)	38.8 (0.6)	39.9 (0.6)	141.9 (2.5)	4.3 (0.5)	−4.6 (1.2)	9.5 (1.2)
C(3)	37 (3)	49 (3)	251 (15)	7 (2)	−10 (6)	5 (7)
C(4)	37 (2)	55 (3)	203 (14)	4 (2)	−6 (5)	−19 (6)
N(5)	36 (2)	52 (3)	139 (10)	−1 (2)	0 (4)	−7 (5)
C(6)	47 (3)	64 (4)	198 (14)	1 (3)	30 (5)	5 (7)
C(7)	48 (3)	83 (5)	135 (13)	−5 (3)	1 (5)	15 (6)
C(8)	31 (2)	62 (3)	203 (13)	−8 (2)	−17 (5)	35 (6)
C(9)	47 (3)	74 (5)	284 (20)	−2 (3)	3 (6)	76 (8)
C(10)	48 (3)	45 (4)	476 (26)	−3 (3)	11 (7)	43 (8)
C(11)	45 (3)	43 (3)	410 (22)	7 (3)	−8 (9)	−7 (8)
C(12)	46 (3)	48 (3)	258 (15)	3 (3)	−5 (7)	5 (6)
N(13)	31 (2)	38 (2)	180 (10)	0 (2)	−5 (4)	6 (4)
Cl(14)	48 (1)	64 (1)	193 (3)	−7 (1)	2 (1)	−27 (1)
O(15)	98 (3)	82 (3)	289 (12)	−32 (3)	−5 (6)	−2 (5)
O(16)	150 (5)	84 (3)	336 (15)	5 (4)	114 (7)	28 (7)
O(17)	90 (3)	152 (5)	646 (24)	−6 (4)	−125 (8)	−90 (11)
O(18)	83 (3)	103 (4)	467 (18)	28 (3)	42 (6)	−38 (7)

2. Hydrogen Atoms

	B, Å^2		B, Å^2		B, Å^2		B, Å^2
H(3A)	2 (1)	H(5)	3 (1)	H(7A)	7 (2)	H(10)	5 (4)
H(3B)	2 (1)	H(6A)	3 (1)	H(7B)	7 (2)	H(11)	5 (2)
H(4A)	4 (1)	H(6B)	4 (1)	H(9)	4 (1)	H(12)	3 (1)
H(4B)	5 (1)						

[a] The β's are ×10^4. See Figure 1 or 2 for the identities of the atoms. The esd is in the units of the least significant digit given for the corresponding parameter.

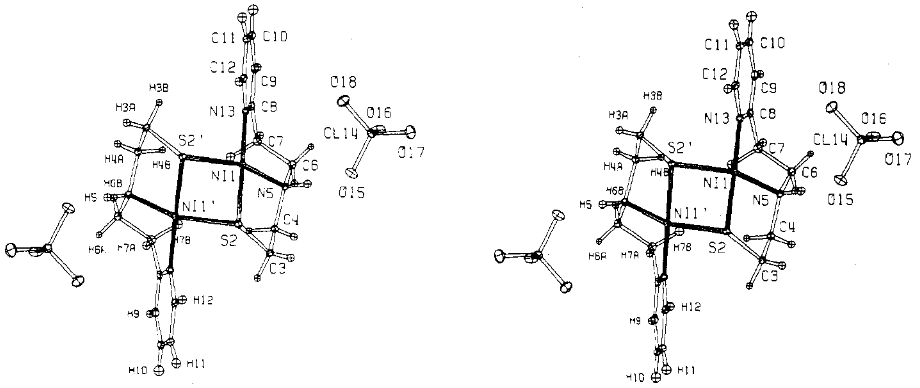

Figure 2. Stereoview[15] of $[Ni(C_9H_{13}N_2S)ClO_4]_2$ using ellipsoids of 5% probability.

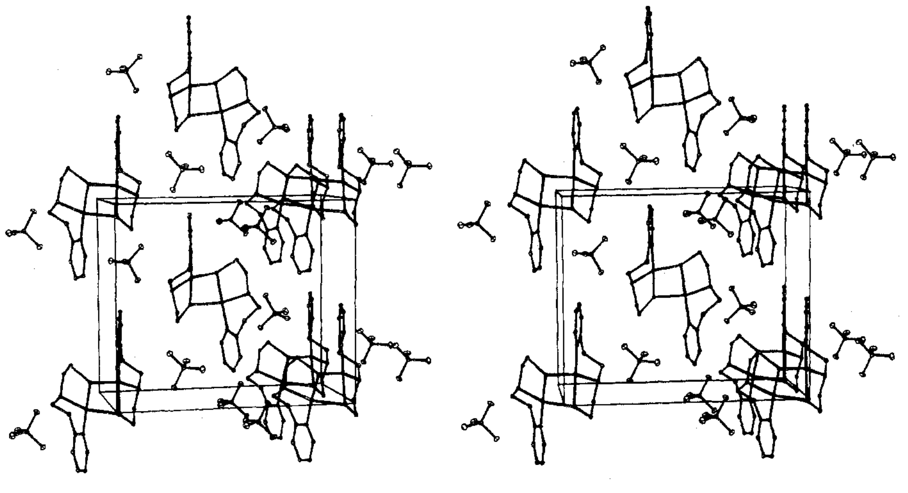

Figure 3. Stereoview[15] illustrating the packing of the molecules in the crystal. The view is approximately into *c* with *a* horizontal and *b* vertical in the plane of the paper. Ellipsoids of 5% probability are used.

Table III. Molecular Dimensions and Esd's[a]

1. Bond Lengths, Å

Ni(1)–S(2)	2.169 (1)	C(7)–C(8)	1.481 (8)	Cl(14)–O(17)	1.382 (6)	C(7)–H(7A)	0.87 (7)
Ni(1)–S(2′)[b]	2.186 (1)	C(8)–C(9)	1.397 (8)	Cl(14)–O(18)	1.424 (5)	C(7)–H(7B)	1.09 (7)
Ni(1)–N(5)	1.967 (4)	C(9)–C(10)	1.353 (10)	C(3)–H(3A)	0.81 (4)	C(9)–H(9)	0.84 (6)
Ni(1)–N(13)	1.905 (4)	C(10)–C(11)	1.362 (12)	C(3)–H(3B)	0.95 (5)	C(10)–H(10)	0.96 (6)
S(2)–C(3)	1.815 (7)	C(11)–C(12)	1.368 (8)	C(4)–H(4A)	0.96 (5)	C(11)–H(11)	0.78 (6)
C(3)–C(4)	1.499 (8)	C(12)–N(13)	1.335 (7)	C(4)–H(4B)	0.98 (6)	C(12)–H(12)	0.94 (7)
C(4)–N(5)	1.483 (7)	N(13)–C(8)	1.352 (7)	N(5)–H(5)	0.68 (5)	O(15)–H(5)[c]	2.34 (5)
N(5)–C(6)	1.498 (7)	Cl(14)–O(15)	1.439 (5)	C(6)–H(6A)	0.97 (5)		
C(6)–C(7)	1.510 (8)	Cl(14)–O(16)	1.414 (6)	C(6)–H(6B)	1.02 (5)		

2. Bond Angles, Deg

S(2)–Ni(1)–S(2′)[b]	79.61 (6)	C(7)–C(8)–N(13)	116.3 (5)	S(2)–C(3)–H(3B)	106 (3)	H(6A)–C(6)–C(7)	107 (3)
S(2)–Ni(1)–N(5)	88.5 (1)	C(8)–C(9)–C(10)	121.0 (6)	H(3A)–C(3)–H(3B)	116 (4)	H(6B)–C(6)–C(7)	112 (3)
S(2′)–Ni(1)–N(13)[b]	97.4 (1)	C(9)–C(10)–C(11)	119.6 (6)	H(3A)–C(3)–C(4)	111 (3)	C(6)–C(7)–H(7A)	108 (4)
N(5)–Ni(1)–N(13)	95.7 (2)	C(10)–C(11)–C(12)	118.1 (6)	H(3B)–C(3)–C(4)	114 (3)	C(6)–C(7)–H(7B)	111 (4)
Ni(1)–S(2)–Ni(1′)[b]	77.94 (5)	C(11)–C(12)–N(13)	123.5 (6)	C(3)–C(4)–H(4A)	113 (3)	H(7A)–C(7)–H(7B)	101 (6)
Ni(1)–S(2)–C(3)	99.1 (2)	C(12)–N(13)–Ni(1)	119.4 (3)	C(3)–C(4)–H(4B)	111 (4)	H(7A)–C(7)–C(8)	115 (4)
Ni(1′)–S(2)–C(3)[b]	110.0 (2)	C(8)–N(13)–C(12)	118.9 (4)	H(4A)–C(4)–H(4B)	110 (5)	H(7B)–C(7)–C(8)	110 (4)
S(2)–C(3)–C(4)	109.8 (4)	C(8)–N(13)–Ni(1)	121.7 (3)	H(4A)–C(4)–N(5)	108 (3)	C(8)–C(9)–H(9)	116 (4)
C(3)–C(4)–N(5)	109.8 (5)	O(15)–Cl(14)–O(16)	108.1 (3)	H(4B)–C(4)–N(5)	105 (3)	H(9)–C(9)–C(10)	123 (4)
C(4)–N(5)–C(6)	111.7 (4)	O(15)–Cl(14)–O(17)	108.0 (3)	Ni(1)–N(5)–H(5)	86 (4)	C(9)–C(10)–H(10)	123 (4)
C(4)–N(5)–Ni(1)	107.8 (3)	O(15)–Cl(14)–O(18)	109.1 (3)	C(4)–N(5)–H(5)	115 (4)	H(10)–C(10)–C(11)	117 (4)
Ni(1)–N(5)–C(6)	116.2 (3)	O(16)–Cl(14)–O(17)	112.9 (4)	H(5)–N(5)–C(6)	117 (5)	C(10)–C(11)–H(11)	120 (4)
N(5)–C(6)–C(7)	111.9 (4)	O(16)–Cl(14)–O(18)	109.3 (3)	N(5)–C(6)–H(6A)	110 (3)	H(11)–C(11)–C(12)	122 (4)
C(6)–C(7)–C(8)	111.3 (5)	O(17)–Cl(14)–O(18)	109.4 (4)	N(5)–C(6)–H(6B)	108 (3)	H(12)–C(12)–N(13)	114 (3)
C(7)–C(8)–C(9)	124.7 (5)	S(2)–C(3)–H(3A)	99 (3)	H(6A)–C(6)–H(6B)	109 (4)	N(5)–H(5)–O(15)[c]	175 (6)

3. Selected Torsion Angles, Deg

Ni(1)–N(5)–C(6)–C(7)	24	Ni(1)–S(2)–Ni(1′)–S(2′)	48	S(2′)–Ni(1)–N(13)–C(12)	53	S(2′)–Ni(1)–S(2)–Ni(1′)	47
Ni(1)–N(13)–C(8)–C(7)	2						

[a] The esd is in the units of the least significant digit given for the corresponding parameter. [b] The coordinates of the primed atoms are related to those given in Table I by the intramolecular twofold axis illustrated in Figures 1 and 2. [c] Hydrogen bond.

Table IV[a]

	Plane no.				
	1	2	3	4	5
Deviations of Atoms from Least-Squares Planes, Å × 10³					
Ni(1)	*−480*	*49*	*0*	25	−581
Ni(1′)[b]	−480		−1856		
S(2)	*480*	*38*	*0*		−1152
S(2′)[b]	*480*	*−13*	−479		
C(3)		−645	−345		
C(4)		−1252	−844		−1019
N(5)		*−335*	*0*		*−55*
C(6)		−852	−396		*104*
C(7)		−1521		112	−703
C(8)		−525		*10*	*−92*
C(9)				*−4*	396
C(10)				*−8*	
C(11)				*2*	
C(12)		1246		*8*	681
N(13)		*261*		*−8*	*43*
Other Parameters					
q_a	0	4661	6289	9743	8143
q_b	0	3654	3013	−201	4221
q_c	10000	8058	7167	2244	3983
D	1.711	1.753	1.809	1.266	2.300
δ	480	192	0	7	78

[a] Italic deviations indicate the atoms used to define the least-squares plane. A negative deviation from a plane indicates that the atom with the coordinates given in Table I lies between that plane and the origin. The direction cosines (×10⁴), q, are with respect to orthogonalized axes. D is the distance (in Å) from the plane to the origin. The root-mean-square deviation (Å × 10³) of the boldface atoms from the plane is δ. [b] The coordinates of the primed atoms are related to those given in Table I by the intramolecular twofold axis illustrated in Figure 1.

such square-planar geometry for highly covalent Ni(II)–ligand bonds. Apparently, the steric requirements of the $pyCH_2CH_2NHCH_2CH_2S^-$ ligands are primarily responsible for the minor distortions observed in this work.

The Ni_2S_2 ring is folded at the S^-–S^- line to 110° into the syn–endo form.[17] This folding results in a Ni–Ni distance of 2.739 (1) Å, much less than a distance of 3.079 Å calculated for a square-planar Ni_2S_2 ring using the average Ni–S bond length observed, 2.177 Å. The Ni–Ni distance is within the 2.647–2.92 Å range observed in the six previously determined structures of sulfide-bridged multinuclear Ni(II) complexes (see the recent reviews by Fackler[17] and references therein). A Ni–Ni interaction involving the overlap of the vacant 4p and the filled $3d_{z^2}$ orbitals of both Ni atoms has been discussed.[17-19] The S–S distance of 2.786 (2) Å is much shorter than a typical nonbonded S–S distance of ~3.2 Å and, with the acute S–Ni–S angle of 79.61 (6)°, suggests a S–S interaction also;[17,20] however, this may merely be a geometric consequence of a Ni(II)–Ni(II) interaction. Additional Ni_2S_2 ring parameters include a Ni–S–Ni bond angle of 77.94 (5)° and Ni–S and Ni–S′ bond distances of 2.169 (1) and 2.186 (1) Å, respectively.

The five-membered $\overline{\text{CNNiNC}}$ chelate ring retains nearly the same conformation as observed in the corresponding ring in chloro[bis(2-((2-pyridylmethyl)amino)ethyl) disulfide]-nickel(II) perchlorate.[2]

The six-membered $\overline{\text{CNNiNCC}}$ chelate ring adopts a boat configuration where Ni(1) and C(7) are −0.58 and −0.71 Å from the least-squares plane of the remaining four atoms. Gavino's prediction[1] that this six-membered ring is less strained than the corresponding five-membered ring in the Ni(II) complex of $(pyCH_2NHCH_2CH_2S)_2$[2] is supported by the observations that the (amino N)–Ni(II)–(pyridyl N) angle is closer to 90° (95.7 (1) vs. 80.4 (6)°), and the Ni(II)–(pyridyl N)–(pyridyl C) angle is closer to 120° (121.5 (3) vs. 114 (1)°).

Hydrogen bonding occurs between O(15) of the perchlorate anion and H(5), at a distance of 2.25 (5) Å; the O(15)–N(5) distance is 3.016 (5) Å. The O(15)–H(5)–N(5) bond angle is 173 (5)°, and Cl(14)–O(15)–H(5) is 111 (1)°. O(16) seems to participate in a weak interaction with H(10) on the pyridyl ring at 2.50 (5) Å with C(10)–H(10)–O(16) = 170 (4)° and Cl(14)–O(16)–H(10) = 102 (1)°.

The structure of this mercaptide complex is quite different from that of the disulfide complexes of Ni(II), in which each half ligand is one methylene group shorter. A simple redox mechanism utilizing Ni(II) is not apparent for either ligand system.

The complex of Ni(II) with 2-[(2-pyridylmethyl)amino]ethyl mercaptide, the parent ligand of the disulfide complexes,[2,3] has been prepared. Its stoichiometry, $\mathrm{NiLClO_4{\cdot}H_2O}$, coupled with preliminary diffraction results which indicate an unusually large asymmetric unit, suggest that it is a large cluster compound, perhaps containing a central $\mathrm{Ni_4S_4}$ "cube", quite a different structure again from that herein reported. Difficulty in obtaining a suitable single crystal has prevented further progress.

The apparent absence of simple structure relationships in these systems suggests that redox processes occur through intermediate states quite dissimilar to these complexes, which form afterwards according to their structural stabilities.

The absolute configuration of the structure was not successfully determined. Beginning with the model refined to convergence with $\Delta f''$ values set equal to zero, the R_2 values calculated without further refinement were 0.031 62 for the structure shown in the figures, and 0.031 65, an insignificantly different value, for the enantiomorphic structure. Subsequent refinement to convergence with nonzero $\Delta f''$ values[21] for Ni (0.285), Cl (0.132), and S (0.110) did not appreciably change the difference between the two R_2 values, 0.030 00 and 0.030 07, respectively. Repetition of this procedure with an entirely independent full-matrix least-squares program, FMLS,[22] verified this result. A comparison of the 51 reflections for which $|F_{c,R} - F_{c,S}| > 2$ with the F_o values did not suggest that one chirality (*R* or *S*) is more likely than the other.

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Registry No. $\mathrm{Ni_2(pyCH_2CH_2NHCH_2CH_2S)_2(ClO_4)_2}$, 62882-90-0; $\mathrm{pyCH_2CH_2NHCH_2CH_2SH}$, 49850-74-0; 2-($\beta$-aminoethyl)pyridine, 2706-56-1; ethylene monothiocarbonate, 20628-59-5.

Supplementary Material Available: A listing of structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of $[\mathrm{N}(n\text{-}\mathrm{C_4H_9})_4]^+[\mathrm{Fe(CO)_4B_7H_{12}}]^-$

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The crystal and molecular structure of $[\mathrm{N}(n\text{-}\mathrm{C_4H_9})_4]^+[\mathrm{Fe(CO)_4B_7H_{12}}]^-$ has been determined. Three-dimensional x-ray data were collected on an automated diffractometer with monochromatized Mo Kα radiation. The structure was solved in the space group $P2_1/c$ with four molecules in the unit cell for which a = 10.840 (5) Å, b = 11.629 (6) Å, c = 23.698 (10) Å, and β = 90.15 (3)°. The calculated density is 1.10 g/cm^3. The structure was solved by the heavy atom method and was refined by block-diagonal least squares to a final conventional R index of 0.068 and a weighted R index of 0.075 for 2685 independent reflections for which $I \geq 3\sigma(I)$. The anion $\mathrm{Fe(CO)_4B_7H_{12}}^-$ consists of a pentagonal-pyramidal, $\mathrm{B_6H_9}$ structure into which a $\mathrm{BH_3}$ and an $\mathrm{Fe(CO)_4}$ group are inserted into nonadjacent basal boron–boron bond sites to form apparent three-center bonds. The $\mathrm{Fe(CO)_4}$ and $\mathrm{BH_3}$ groups are located at bridge sites beneath the pentagonal-basal plane of the $\mathrm{B_6}$ framework. The structural data favor a hybridization of iron which more closely approximates dsp^3 than d^{2}sp^3. The closest distance of Fe to a terminal B–H hydrogen is 2.82 (5) Å, thereby suggesting little interaction in terms of Fe–H–B bonding. For the inserted $\mathrm{BH_3}$ group, one of the B–H hydrogens is positioned so as to form a "pseudo" B–H–B bridge with a $\mathrm{B_6H_9}$ framework boron, but the distance of this hydrogen, 1.68 (8) Å, to the framework boron is significantly longer than is observed for normal B–H distances, 1.3 Å, in B–H–B bonds. The $\mathrm{N}(n\text{-}\mathrm{C_4H_9})_4^+$ ion has the trans configuration. The δ carbon of the fourth branch is badly disordered. Bond distances and bond angles within the $\mathrm{B_6H_9}$ group and the $\mathrm{N}(n\text{-}\mathrm{C_4H_9})^+$ ion appear to be normal.

Introduction

The hexaborane(10) molecule is a pentagonal pyramid which can be represented by the valence structure shown below.[1] Hexaborane(10) possesses acidic[2] and basic character.[3] It functions as a Bronsted acid through removal of a bridging proton to yield $\mathrm{B_6H_9}^-$, and it functions as a Bronsted