42901-32-6; [(en)$_2$Co(SeCH$_2$CH$_2$NH$_2$)]$^{2+}$, 58866-01-6; [(en)$_2$Co(S(O)CH$_2$CH$_2$NH$_2$)]$^{2+}$, 68645-75-0; [(en)$_2$Co(S(O)$_2$CH$_2$CH$_2$NH$_2$)]$^{2+}$, 75249-42-2; [(en)$_2$Co(S(CH$_2$CO$_2$H)CH$_2$CH$_2$NH$_2$)]$^{3+}$, 94090-13-8; [(en)$_2$Co(S(CH(CO$_2$H)CH$_2$CO$_2$H)CH$_2$CH$_2$NH$_2$)]$^{3+}$, 85782-08-7; [(en)$_2$Co(S(CH$_2$COCH$_3$)CH$_2$CH$_2$NH$_2$)]$^{3+}$, 94090-14-9; [(en)$_2$Co(S((CH$_2$)$_2$COCH$_3$)CH$_2$CH$_2$NH$_2$)]$^{3+}$, 85781-93-7; [(en)$_2$Co(S((CH$_2$)$_2$CHO)CH$_2$CH$_2$NH$_2$)]$^{3+}$, 85782-04-3; [(en)$_2$Co(S((CH$_2$)$_2$CN)CH$_2$CH$_2$NH$_2$)]$^{3+}$, 85782-05-4; [(en)$_2$Co(S((CH$_2$)$_2$CONH$_2$)CH$_2$CH$_2$NH$_2$)]$^{3+}$, 85781-97-1; [(en)Co(S(CH$_2$C(CH$_3$)=N(CH$_2$)$_2$NH$_2$)CH$_2$CH$_2$NH$_2$)]$^{3+}$, 94090-15-0.

Supplementary Material Available: Tables A and B, giving observed pseudo-first-order and derived second-order rate constants (10 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
University of Michigan, Ann Arbor, Michigan 48109

Synthesis and Reactions of Binary Metal Sulfides. Structural Characterization of the $[(S_4)_2Zn]^{2-}$, $[(S_4)_2Ni]^{2-}$, $[(S_5)Mn(S_6)]^{2-}$, and $[(CS_4)_2Ni]^{2-}$ Anions

D. COUCOUVANIS,* P. R. PATIL, M. G. KANATZIDIS, B. DETERING, and N. C. BAENZIGER

Received June 26, 1984

A general procedure for the synthesis of the polysulfido, $[M(S_x)_2]^{2-}$, complexes ($M = Zn$, $x = 4$–6; $M = Cd$, $x = 5$; $M = Ni$, $x = 4$; $M = Mn$, $x = 5, 6$) is described. These complexes and the mixed thiophenolate polysulfido complexes, $[M(SPh)_2(S_x)_2]^{2-}$ ($M = Zn$, $x = 4, 5$; $M = Cd$, $x = 5$), are obtained by the oxidation of all or two of the thiophenolate ligands in the $[M(SPh)_4]^{2-}$ complexes by dibenzyl trisulfide with the concomitant generation of the polysulfide dianions. The diamagnetic $[Ni(S_4)_2]^{2-}$ and high-spin $[Mn(S_x)_2]^{2-}$ complexes react readily with CS_2 to give the corresponding perthiocarbonate complexes $[Ni(CS_4)_2]^{2-}$, $[Mn(CS_4)_2]^{2-}$, and $[Mn(S_6)(CS_4)]^{2-}$. The structures of the tetraethylammonium salts of $[Zn(S_4)_2]^{2-}$ (I) and $[Ni(S_4)_2]^{2-}$ (II) and of the tetraphenylphosphonium salts of $[Ni(CS_4)_2]^{2-}$ (III) and $[MnS_{11}]^{2-}$ (IV) have been determined by X-ray crystallography. Lattice parameters and space group information are as follows: for I, $a = 12.410$ (3) Å, $b = 16.350$ (1) Å, $c = 13.906$ (2) Å, $\alpha = 90.00°$, $\beta = 95.73$ (1)°, $\gamma = 90.00°$, monoclinic, $P2_1/c$ ($Z = 4$); for II, $a = 10.475$ (2) Å, $b = 10.452$ (2) Å, $c = 12.738$ (2) Å, $\alpha = \beta = \gamma = 90.00°$, orthorhombic, $Pnn2$ ($Z = 2$); for III, $a = 9.231$ (3) Å, $b = 10.156$ (3) Å, $c = 13.694$ (4) Å, $\alpha = 82.48$ (1)°, $\beta = 72.12$ (1)°, $\gamma = 85.51$ (1)°, triclinic, $P\bar{1}$ ($Z = 1$); for IV, $a = 23.266$ (5) Å, $b = 20.390$ (3) Å, $c = 23.894$ (5) Å, $\alpha = 90.00°$, $\beta = 118.03$ (1)°, $\gamma = 90.00°$, monoclinic, $P2_1/n$ ($Z = 8$). Diffraction data (Mo Kα radiation, $2\theta_{max} = 50, 45, 40, 45$, respectively, for I–IV) were collected by either a Picker FACS-I (I) or a Nicolet P3F automatic diffractometer (II–IV). The structures were solved and refined by direct methods and full-matrix least-squares procedures to R values of 0.062, 0.041, 0.030, and 0.121, respectively, for I–IV from 2481, 831, 1971, and 6495 reflections on 244, 149, 280 and 277 variables, respectively, for I–IV. The anion in I contains the Zn tetrahedrally coordinated by two bidentate S_4^{2-} chelates, $\overline{Zn–S} = 2.351$ Å. In II the coordination of the two S_4^{2-} chelates around the Ni(II) ion gives a square-planar complex, Ni–S = 2.179 Å. The anion in III is planar, and in the two bidentate CS_4^{2-} chelates the C=S groups are located trans to each other, $\overline{Ni–S} = 2.170$ Å. The $[(S_5)Mn(S_6)]^{2-}$ and $[(S_5)Mn(S_5)]^{2-}$ anions both occupy the anion sites in IV where the Mn(II) is tetrahedrally coordinated by the S_x^{2-} chelates $\overline{Mn–S} = 2.425$ Å. A discussion of S–S bonding in the S_4^{2-} and CS_4^{2-} chelates is presented.

Introduction

An ever-increasing interest in the synthesis and reactivity of polysulfido–metal complexes and derivatives has been stimulated by the recognized importance of metal–sulfide complexes in both industrial and enzymatic catalysis. The catalytic hydrodesulfurization (HDS) of fossil fuels,[1] biological nitrogen fixation,[2] and biological electron transfer[3] are among processes that are facilitated by metal–sulfide compounds.

Numerous metal–sulfide complexes are known to contain $(S_x)^{2-}$ chelating ligands ($x = 4$–9). In these complexes the MS_x metallocycles have been characterized by X-ray crystallography in the structures of $(C_5H_5)_2MS_5$ ($M = Ti$,[4,5] V[5]), $[(S_5)Fe_2S_2(S_5)]^{2-}$,[6] $[(S_5)FeMS_4]^{2-}$ (M = Mo, W),[7] $[(S_6)FeMoS_4]^{2-}$,[7] $(C_5H_5)Co(S_5)PMe_3$,[8] $Os_2(Et_2Dtc)(Et_2DtcS)(\mu\text{-}S_5)$,[9] $[PdS_{11}]^{2-}$,[10] $[PtS_{15}]^{2-}$,[11] NH_4CuS_4,[12] $Pt(S_4)(PPh_3)_2$,[13] $(C_5H_5)_2MS_4$ (M = Mo,[14] W[15]), $[Cu_3(S_6)_3]^{3-}$,[16] $[MoS_9]^{2-}$,[17] $[Mo_2S_{10}]^{2-}$,[17,18] $[(Mo)_2(NO)_2(S_2)_3(S_5)OH]^{3-}$,[19] $[Hg(S_6)_2]^{2-}$,[20] $[Cu_6S_{17}]^{2-}$,[21] and $[AuS_9]^{-}$.[22]

The unusual reactivity characteristics of the coordinated polysulfido ligands in either binary or organometallic polysulfido complexes have become apparent in recent years. Examples of this reactivity include the addition of disubstituted acetylenes, RC≡CR (R = COOCH$_3$), to MoS_9^{2-},[23] $[Fe_2S_{12}]^{2-}$,[24] $(Cp)_2M(S_5)$

---

(1) Weisser, O.; Landa, S. In "Sulphide Catalysts: Their Properties and Applications"; Pergamon Press: London, 1973.

(2) Orme-Johnson, W. H.; Davis, L. C. In "Iron-Sulfur Proteins"; Lovenberg, W., Ed. Academic Press: New York, 1977; Vol. 3, Chapter 2.

(3) Holm, R. H.; Ibers, J. A. In "Iron-Sulfur Proteins"; Lovenberg, W., Ed.; Academic Press: New York, 1977; Vol. 3, Chapter 7.

(4) Epstein, E. F.; Bernal, I. *J. Organomet. Chem.* **1971**, *26*, 229.

(5) Müller, K. G.; Petersen, J. L.; Dahl, L. F. *J. Organomet. Chem.*, **1976**, *111*, 91.

(6) Coucouvanis, D.; Swenson, D.; Stremple, P.; Baenziger, N. C. *J. Am. Chem. Soc.* **1979**, *101*, 3392.

(7) Coucouvanis, D.; Stremple, P.; Simhon, E. D.; Swenson, D.; Baenziger, N. C.; Draganjac, M.; Chan, L. T.; Simopoulos, A.; Papaefthymion, V.; Kostikas, A.; Petrouleas, V. *Inorg. Chem.* **1983**, *22*, 293.

(8) Burschka, C.; Leonard, H. *Z. Anorg. Allg. Chem.* **1980**, *464*, 30.

(9) Maheu, L. J.; Pignolet, L. H. *J. Am. Chem. Soc.* **1980**, *102*, 6346.

(10) Haradem, P. S.; Cronin, J. L.; Krause, R. A.; Katz, L. *Inorg. Chim. Acta* **1977**, *25*, 173.

(11) (a) Jones, P. E.; Katz, L. *J. Chem. Soc., Chem. Commun.* **1967**, 842. (b) Spangenberg, M.; Bronger, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 482.

(12) Burschka, C. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35B*, 1511.

(13) (a) Wickenden, A. E.; Krause, R. A. *Inorg. Chem.* **1969**, *8*, 779. (b) Schmidt, M.; Hoffman, G. G. *Z. Anorg. Allg. Chem.* **1979**, *452*, 112. (c) Dudis, D.; Fackler, J. P. *Inorg. Chem.* **1982**, *21*, 3578.

(14) Block, H. D.; Allman, R. *Cryst. Struct. Commun.* **1975**, *4*, 53.

(15) Davis, B. R.; Bernal, I.; Köpf, H. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 921.

(16) Müller, A.; Schimanski, U. *Inorg. Chim. Acta* **1983**, *77*, L187.

(17) Draganjac, M.; Simhon, E.; Chan, L. T.; Kanatzidis, M.; Baenziger, N. C.; Coucouvanis, D. *Inorg. Chem.* **1982**, *21*, 3321.

(18) Clegg, W.; Christou, G.; Garner, C. D.; Sheldrick, G. M. *Inorg. Chem.* **1981**, *20*, 1562.

(19) Müller, A.; Eltzner, W.; Bögge, H.; Krickemeyer, E. *Angew. Chem.* **1983**, *95*, 905.

(20) Müller, A.; Schimanski, J.; Schimanski, U. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 159.

(21) Müller, A.; Römer, M.; Bögge, H.; Krickemeyer, E.; Bergmann, D. *J. Chem. Soc., Chem. Commun.* **1984**, 348.

(22) Marbach, G.; Strahle, J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 246.

(23) Draganjac, M.; Coucouvanis, D. *J. Am. Chem. Soc.* **1983**, *105*, 139.

(24) Kanatzidis, M. G.; Coucouvanis, D. *Inorg. Chem.* **1984**, *23*, 403.

0020-1669/85/1324-0024$01.50/0

(M = Ti,[25] V[26]), and $[Mo_2S_6O_2]^{2-}$[27] with formation of the $[Mo(L)_3]^{2-}$, $[[FeL_2]_2]^{2-}$, $(Cp)_2ML$, and $[Mo_2O_2S_2(L')_2]^{2-}$ complexes (L = 1,2-dicarbomethoxydithiolene; L' = $(S_2C_2(CO_2CH_3)_2)^{2-}$, "vinyl disulfide" ligand). In these complexes the dithiolene ligands (L) are S,S chelated to the metals, with the exception of the $[Mo_2O_2S_2(L')_2]^{2-}$ complex in which the L' vinyl disulfide ligands are C,S chelated to the molybdenum to form the five-membered metalla-2,3-dithiacyclopent-4-ene rings. The reactivity of the S_x^{2-} ligands toward electrophiles is demonstrated further in the reactions of MoS_9^{2-} and $Mo_2S_{10}^{2-}$ with CS_2 and the synthesis of the perthiocarbonato complexes[28] *trans*-$[(CS_4)_2MoS]^{2-}$ and *cis*-$[(CS_4)_2Mo_2S_4]^{2-}$.

In this paper we report a general procedure for the synthesis of S_x^{2-} complexes, the structures of the $[Ni(S_4)_2]^{2-}$,[29] $[Zn(S_4)_2]^{2-}$, and $[(S_6)Mn(S_5)]^{2-}$ complexes, the reactivity of these complexes toward carbon disulfide, and the structure of the $(Ph_4P)_2[Ni(CS_4)_2]$ complex.

Experimental Section

Materials and Methods. Chemicals generally were used as purchased. Commercial grade dichloromethane (CH_2Cl_2) and acetonitrile (CH_3CN) were distilled from calcium hydride (CaH_2). Dimethylformamide (DMF) was dried over Linde 4A molecular sieves for 24 h and then distilled under reduced pressure at ~30 °C. Absolute ethanol was distilled after refluxing over magnesium ribbons. Benzene and diethyl ether were used without further purification. *n*-Pentane was distilled over CaH_2. All synthetic work was performed under anaerobic conditions in a Vacuum Atmospheres Dri-Lab glovebox, at ambient temperature (298 K) unless otherwise specified. The syntheses of dibenzyl trisulfide[30] (BzSSSBz) and of the $[M(SPh)_4]^{2-}$ complexes[31] have been described previously. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Physical Methods. Visible and ultraviolet spectra were obtained on Cary Models 118 and 219 spectrophotometers. A Debye-Scherrer camera with nickel-filtered copper radiation was utilized to obtain X-ray powder diffraction patterns.

Syntheses.[32] **$(Ph_4P)_2[(PhS)_2Zn(S_4)]$.** To a solution of $(Ph_4P)_2[Zn(SPh)_4]$[31] (1.2 g, 1.02 mmol) in 25 mL of CH_3CN was added solid BzSSSBz (0.6 g, 2.15 mmol) in small portions with stirring. The color of the solution changed from an initial yellow to orange-red. After the mixture was stirred for ca. 5 min, diethyl ether was added to incipient nucleation. After several hours yellow crystals formed and were isolated; yield 1.8 g (~48%). Anal. Calcd for $ZnS_6P_2C_{60}H_{50}$: C, 66.06; H, 4.63; P, 5.67; S, 17.63; Zn, 5.99. Found: C, 66.57; H, 4.46; P, 5.59; S, 17.20; Zn, 5.92.

$(Ph_4P)_2[(PhS)_2Zn(S_5)]$. This complex was prepared in a manner analogous to the one employed for the synthesis of the S_4^{2-} derivative except that a greater amount of BzSSSBz (1.5 g, 5.4 mmol) was allowed to react with the $(Ph_4P)_2[Zn(SPh)_4]$ complex (1.2 g, 1.02 mmol); yield 1.0 g (89%). Anal. Calcd for $ZnS_7P_2C_{60}H_{50}$: C, 64.18; H, 4.49; P, 5.52; S, 19.98; Zn, 5.82. Found: C, 63.71; H, 4.74; P, 5.70; S, 19.82; Zn, 6.01.

$(Ph_4P)_2[Zn(S_5)_2]$. This complex was obtained by a similar synthetic procedure using 1.2 g (1.02 mmol) of $(Ph_4P)_2[Zn(SPh)_4]$ and 3.0 g of BzSSSBz (10.80 mmol) in 25 mL of CH_3CN; yield 0.9 g of yellow-orange crystals (~85%). Anal. Calcd for $ZnS_{10}P_2C_{48}H_{40}$: C, 54.14; H, 3.79; P, 5.82; S, 30.11; Zn, 6.14. Found: C, 55.08; H, 3.69; P, 5.74; S, 29.36; Zn, 6.06.

$(Ph_4P)_2[Zn(S_6)_2]$. This complex was obtained by a synthetic procedure identical with the one followed in the synthesis of the corresponding S_5^{2-} complex and using 6.0 g of BzSSSBz (21.6 mmol) and 1.2 g (1.02 mmol) of $(Ph_4P)_2Zn(SPh)_4$ in 25 mL of CH_3CN. A total of 1.0 g of yellow crystals was isolated (~90% yield). Anal. Calcd for $ZnS_{12}P_2C_{48}H_{40}$: C, 51.06; H, 3.58; P, 5.48; S, 34.01; Zn, 5.79. Found: C, 50.42; H, 3.72; P, 5.48; S, 34.68; Zn, 5.68.

$(Et_4N)_2[Zn(S_4)_2]$. To a solution of $(Et_4N)_2[Zn(SPh)_4]$ (1.5 g, 2.0 mmol) in 50 mL of CH_3CN was added solid BzSSSBz (2.8 g, 10 mmol) in small portions with stirring. After it was stirred for 15 min, the solution was filtered, and dry diethyl ether was added to the filtrate until the first evidence of nucleation became apparent. After the mixture was allowed to stand for 24 h, crystals formed and were isolated, washed with two 10-mL portions each of ethanol and diethyl ether, and dried; yield 0.6 g (51%). Anal. Calcd for $ZnS_8N_2C_{16}H_{40}$: C, 32.99; H, 6.92; Zn, 11.22; S, 44.04. Found: C, 32.52; H, 7.29; Zn, 10.88; S, 41.36.

$(Ph_4P)_2[Zn(S_4)_2]$. To a solution of $(Ph_4P)_2Zn(S_5)_2$ (0.5 g, 0.47 mmol) in 40 mL of DMF was added with stirring triphenylphosphine (Ph_3P) (0.25 g, 0.94 mmol). After it was stirred for ca. 30 min, the solution was filtered, and diethyl ether was added to the filtrate until nucleation was noted. After the mixture was allowed to stand for 24 h, crystals formed and were isolated; yield 0.40 g (85%). The crystalline product had an X-ray powder pattern different from that of any of the other $(Ph_4P)_2Zn(S_x)_2$ complexes. Anal. Calcd for $ZnS_8P_2C_{48}H_{40}$: C, 57.61; H, 4.03; P, 6.19; Zn, 6.53; S, 25.63. Found: C, 57.06; H, 3.59; P, 6.22; Zn, 6.19; S, 22.53.

$(Ph_4P)_2[(PhS)_2Cd(S_5)]$. This yellow crystalline complex was isolated in ~80% yield from $(Ph_4P)_2Cd(SPh)_4$[31] and BzSSSBz with stoichiometries and reaction conditions *identical* with those employed for the synthesis of *either* the $(Ph_4P)_2[(PhS)_2Zn(S_4)]$ or $(Ph_4P)_2[(PhS)_2Zn(S_5)]$ complexes. Anal. Calcd for $CdS_7P_2C_{60}H_{50}$: C, 61.60; H, 4.32; P, 5.29; S, 19.18; Cd, 9.61. Found: C, 59.75; H, 4.42; P, 5.62; S, 19.98; Cd, 10.09. The X-ray powder pattern of this complex is identical with the one of the Zn analogue.

$(Ph_4P)_2[Cd(S_5)_2]$. The orange-yellow crystals of this complex were obtained in 78% yield from $(Ph_4P)_2Cd(SPh)_4$ and BzSSSBz with a stoichiometry and reaction conditions identical with those employed for the synthesis of the corresponding X-ray isomorphous Zn analogue complex. Anal. Calcd for $CdS_{10}P_2C_{48}H_{40}$: C, 51.85; H, 3.63; P, 5.57; S, 28.83; Cd, 10.11. Found: C, 52.21; H, 3.71; P, 5.50; S, 28.17; Cd, 8.97.

$(Ph_4P)_2[Ni(S_4)_2]$. To a solution of $(Ph_4P)_2[Ni(SPh)_4]$[31] (1.2 g, 1.02 mmol) in 25 mL of CH_3CN was added BzSSSBz (3.0 g, 10.8 mmol) with stirring. After it was stirred for 5 min, the dark brown-red solution was filtered and diluted with ether to incipient nucleation. The crystals that formed after several hours were collected, washed with diethyl ether, and dried; yield 0.5 g (52%). Anal. Calcd for $NiS_8P_2C_{48}H_{40}$: C, 57.99; H, 4.06; P, 6.23; S, 25.8; Ni, 5.91. Found: C, 57.41; H, 3.98; P, 6.11; S, 25.3; Ni, 5.98. The same material is obtained when the BzSSSBz to $(Ph_4P)_2[Ni(SPh)_4]$ molar ratio is 5:1.

$(Et_4N)_2[Ni(S_4)_2]$. This complex was obtained as octahedrally shaped single crystals in a reaction that employed $(Et_4N)_2Ni(SPh)_4$ and BzSSSBz in a 1:10 molar ratio in CH_3CN. Anal. Calcd for $NiS_8N_2C_{16}H_{38}$: C, 33.49; H, 6.68; N, 4.88; S, 44.70; Ni, 10.23. Found: C, 33.41; H, 6.71; N, 4.81; S, 44.06; Ni, 10.32.

$(Ph_4P)_2[(S_5)Mn(S_6)]$. To a solution of $(Ph_4P)_2[Mn(SPh)_4]$[31] (1.0 g, 0.95 mmol) in 30 mL of CH_3CN was added 2.6 g of BzSSSBz (9.3 mmol). A change in the color of the solution from yellow to red was detected immediately. After the solution was stirred for 10 min, ether was added until nucleation was apparent. The mixture was allowed to stand for 10 min, and then a yellow powder (which did not contain manganese) formed and separated out. At this stage, the solution was filtered and more ether was added. After the mixture was allowed to stand for 2–3 days, orange red crystals formed and were isolated; yield 0.8 g (72%). Anal. Calcd for $MnS_{11}P_2C_{48}H_{40}$: C, 53.26; H, 3.72; P, 5.70; S, 32.46; Mn, 5.06. Found: C, 53.63; H, 3.93; P, 5.76; S, 31.49; Mn, 5.19.

$(Ph_4P)_2[Ni(CS_4)_2]$. An amount of $(Ph_4P)_2[Ni(S_4)_2]$ (1.0 g) was dissolved in either CH_3CN or DMF (25 mL). To these solutions was added 2 mL of CS_2 with stirring. After 10 min of stirring, ether was added until nucleation was apparent, and the solutions were allowed to stand for 12 h. The black crystalline product that formed was isolated by filtration, washed several times with diethyl ether, and dried in vacuo; yield 0.95 g (93%). Anal. Calcd for $NiS_8P_2C_{50}H_{40}$: C, 58.98; H, 3.97; P, 6.08; S, 25.19; Ni, 5.77. Found: C, 58.09; H, 4.21; P, 6.17; S, 26.46; Ni, 5.57.

$(Ph_4P)_2Mn(CS_4)_2\cdot DMF$. To a solution of $(Ph_4P)_2[MnS_{11}]$ (1.0 g, 0.92 mmol) in 30 mL of DMF was added 20 mL of CS_2, and the solution was stirred for 5 min. To the bright red solution was added 10 mL of absolute ethanol and ether until the first signs of nucleation became apparent.

---

(25) Bolinger, C. M.; Rauchfuss, T. B. *Inorg. Chem.* **1982**, *21*, 3947.

(26) Bolinger, C. M.; Rauchfuss, T. B.; Rheingold, A. L. *Organometallics* **1982**, *1*, 1551.

(27) Halbert, T. R.; Hin Pan, W.; Stiefel, E. I. *J. Am. Chem. Soc.* **1983**, *105*, 5476.

(28) Coucouvanis, D.; Draganjac, M. *J. Am. Chem. Soc.* **1982**, *104*, 6820.

(29) While this manuscript was in preparation, a paper describing the synthesis and structural characterization of $(Et_4N)_2NiS_8$ appeared in the literature: Müller, A.; Krickemeyer, E.; Bögge, H.; Clegg, W.; Sheldrick, G. M. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*.

(30) Coucouvanis, D.; Kanatzidis, M.; Simhon, E.; Baenziger, N. C. *J. Am. Chem. Soc.* **1982**, *104*, 1874.

(31) Coucouvanis, D.; Murphy, C. N.; Simhon, E.; Stremple, P.; Draganjac, M. *Inorg. Synth.* **1982**, *21*, 23.

(32) Abbreviations used throughout this paper: Ph_4P = tetraphenylphosphonium cation, $[(C_6H_5)_4P]^+$; PhS = thiophenolate anion, $C_6H_5S^-$; Et_4N^+ = tetraethylammonium cation, $[(C_5H_5)_4N]^+$.

Table I. Summary of Crystal Data, Intensity Collection, and Structure Solution and Refinement

formula	$[(C_6H_5)_4P]_2Ni(CS_4)_2$	$[(C_2H_5)_4N]_2Zn(S_4)_2$	$[(C_2H_5)_4N]_2Ni(S_4)_2$	$[(C_6H_5)_4P]_2MnS_{11}$
mol wt	1016.7	581.4	574.7	1084.9
a, Å	9.231 (3)	12.410 (3)	10.475 (2)	23.266 (5)
b, Å	10.156 (3)	16.350 (1)	10.452 (2)	20.390 (3)
c, Å	13.694 (4)	13.906 (2)	12.738 (2)	23.894 (5)
α, deg	82.48 (1)	90.00	90.00	90.00
β, deg	72.12 (1)	95.73 (1)	90.00	118.03 (1)
γ, deg	85.51 (1)	90.00	90.00	90.00
Z; *V*, Å	1; 1211.3	4; 2821.6	2; 1394.2	8; 10,005
d_{calcd}, g/cm^3	1.40	1.37	1.37	1.40
d_{obsd},[a] g/cm^3	1.42 (2)	1.38 (2)	1.36 (2)	1.42 (2)
space group	$P\bar{1}$	$P2_1/c$	$Pnn2$	$P2_1/n$
cryst dimens, mm	0.50 × 0.47 × 0.18	0.61 × 0.77 × 0.81	0.40 × 0.38 × 0.44	0.56 × 0.18 × 0.17
radiation	Mo ($\lambda_{K\bar{\alpha}}$ = 0.710 69 Å)	Mo ($\lambda_{K\bar{\alpha}}$ = 0.710 69 Å)	Mo ($\lambda_{K\bar{\alpha}}$ = 0.710 69 Å)	Mo ($\lambda_{K\bar{\alpha}}$ = 0.710 69 Å)
abs coeff, cm^{-1}	8.7	3.67	12.8	7.7
no. of unique data	2184	3642	979	11 810
no. of data used ($F_o^2 > 3\sigma(F_o^2)$)	1971	2481	831	6495
data colled	$+h,\pm k,\pm l$ ($2\theta = 50$)	$+h,+k,\pm l$ ($2\theta = 50$)	$\pm h,\pm k,\pm l$ ($2\theta = 45$)	$h,\pm k,\pm l$ ($2\theta = 45$)
no. of variables	280	244	149	277
R,[b] %	2.99	6.23	4.08	12.07
R_w,[c] %	5.09	9.23	4.61	12.17

[a] Determined by flotation in a CCl_4^-/pentane mixture. [b] $R = \Sigma|\Delta F|/\Sigma|F_o|$. [c] $R_w = [\Sigma w(\Delta F)^2/\Sigma w|F_o|^2]^{1/2}$.

Upon standing overnight, the solution deposited orange-red clusters of crystals, yield 0.8 g. The compound is extremely oxygen sensitive in solution, and it turns blue-green instantaneously upon exposure to air. Anal. Calcd for $MnS_8P_2C_{53}H_{47}ON$: C, 58.56; H, 4.32; P, 5.70; S, 23.57; Mn, 5.06. Found: C, 59.34; H, 4.59; P, 5.68; S, 23.59; Mn, 5.0.

$(Ph_4P)_2[Mn(S_6)(CS_4)]$. To a solution of $(Ph_4P)_2[MnS_{11}]$ (1.0 g, 0.92 mmol) in 30 mL of CH_3CN was added 40 mL of CS_2, and the solution was stirred for ca. 5 min. To the solution was added 10 mL of absolute ethanol and ether until the first signs of nucleation became apparent. Upon standing, orange-red crystals formed and were isolated. Solutions of this compound are very air sensitive and show electronic spectra somewhat different from the spectra obtained for the $[Mn(CS_4)_2]^{2-}$ complex. Anal. Calcd for $MnS_{10}P_2C_{49}H_{40}$: C, 55.21; H, 3.76; S, 30.04; P, 5.82; Mn, 5.16. Found: C, 53.94; H, 3.93; S, 29.82; P, 5.70; Mn, 5.10.

X-ray Diffraction Measurements. Collection and Reduction of Data. Single crystals of $(Et_4N)_2[Zn(S_4)_2]$ (I), $(Et_4N)_2[Ni(S_4)_2]$ (II), $(Ph_4P)_2[(S_5)Mn(S_6)]$ (III), and $(Ph_4P)_2[Ni(CS_4)_2]$ (IV) were obtained by the slow diffusion of diethyl ether into CH_3CN solutions of the complexes. The crystals were sealed in quartz capillaries and used for data collection. Details concerning crystal characteristics and X-ray diffraction methodology are shown in Table I. For I, crystal intensity data were obtained on a Picker-Nuclear four-circle diffractometer according to a protocol already described.[33] Intensity data for II–IV were obtained on a Nicolet P3/F four-circle diffractometer. A detailed description of the instrument and the data acquisition procedures have been described previously.[24]

Determination of the Structure.[34] **$(Et_4N)[Zn(S_4)_2]$ (I).** The atomic positions of the zinc and the eight sulfur atoms of the $[Zn(S_4)_2]^{2-}$ dianion were determined by direct methods using the program MULTAN.[35] The correctness of these coordinates was verified in a three-dimensional Patterson synthesis map. The atoms of the cation were located in subsequent Fourier syntheses following least-squares refinements of the input atomic coordinates. The refinement of all the atoms with isotropic temperature factors in the centrosymmetric space group $P2_1/c$ gave a conventional *R* value of 0.1412. Further refinement of the structure with anisotropic temperature factors for all the non-hydrogen atoms gave a conventional *R* value of 0.0723. In the final refinement, the 40 hydrogen atoms were included in the structure factor calculation at their calculated positions (0.95 Å from the carbon atoms) but were not refined. The final *R* value[36] was 0.0623, and the weighted *R* value[36] was 0.0923. During the last cycle of refinement all parameter shifts were less than 10% of their esd's.

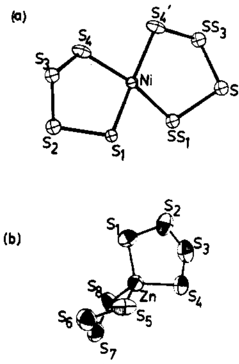

Figure 1. Structures of (a) the $[Ni(S_4)_2]^{2-}$ anion and (b) the $[Zn(S_4)_2]^{2-}$ anion showing the atom-labeling scheme. Thermal ellipsoids are drawn by ORTEP (Johnson, C. K. Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965) and represent 40% and 50% probability surfaces, respectively, for (a) and (b).

$(Et_4N)_2[Ni(S_4)_2]$ (II). The systematic absences observed for the reflections were consistent with either the centrosymmetric *Pnnm* or the noncentrosymmetric *Pnn*2 space groups. On the basis of *E* statistics, the noncentrosymmetric space group *Pnn*2 initially was chosen as the correct one, and the structure was successfully solved and refined in this space group. The two anions in the unit cell are required by symmetry to occupy special positions on the twofold axes at either 0, $^1/_2$, *z* or 0, 0, *z*. Placement of Ni atoms at 0, $^1/_2$, *z* and subsequent Fourier syntheses revealed the positions of the sulfur atoms and the atoms in the Et_4N^+ cations. Least-squares full-matrix refinement with this model led to R_w and *R* values of 0.19 and 0.17, respectively. At this stage a difference Fourier synthesis revealed three areas of electron density close to three of the four sulfur atoms in the S_4^{2-} ligand. This observation, and the rather high temperature factors for three of the input sulfur atoms, suggested that the new peaks in the map were "half-sulfur" atoms and that two S_4^{2-} ligands were in half-occupancy at two slightly different positions sharing one common sulfur atom. The new sulfur atoms were introduced at half-occupancy, and the occupancies of three of the original sulfur atoms were reduced by 50%. Refinement of this model (and of the occupancy factors) verified the assumed 50:50 positional disorder, and the calculations converged to R_w and *R* values[36] of 0.11 and 0.096. The refinement continued with anisotropic temperature factors assigned to all non-hydrogen atoms except for the 50% occupancy sulfur atoms. In addition, the hydrogen atoms were included in the structure factor calculations at their calculated positions but not refined. Convergence was reached after five cycles and gave R_w = 0.046 and *R* = 0.041. No significant residual electron density was found in the final Fourier difference map.

In a recent structure determination reported by Müller et al.[29] for the same compound, the structure was refined successfully in the tetragonal space group $P\bar{4}n2$ (*R* = 0.037) and no disorder of the S_4^{2-} ligand was

---

(33) Coucouvanis, D.; Simhon, E. D.; Stremple, P.; Ryan, M.; Swenson, D.; Baenziger, N. C.; Simopoulos, A.; Papaefthymiou, V.; Kostikas, A.; Petrouleas, V. *Inorg. Chem.* **1984**, *23*, 741.

(34) The crystallographic data reported in this paper were obtained at ambient temperature. Furthermore, due to the small values for μ, no absorption correction was applied to any of the data sets.

(35) Main, P.; Woolfson, M. M.; Germain, G. "MULTAN", A Computer Program for the Automatic Solution of Crystal Structures; University of York: York, England, 1971.

(36) $R_1 = \sum(F_o - |F_c|)/\sum F_o$; $R_w = (\sum w(F_o - |F_c|)^2/\sum wF_o^2)^{1/2}$.

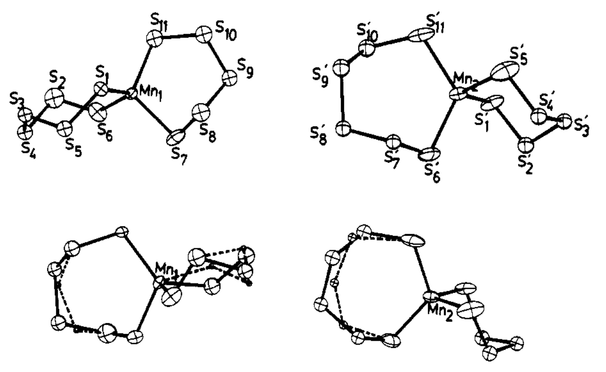

Figure 2. Two views each for the $[Mn(S_x)_2]^{2-}$ anions in $[MnS_{11}]^{2-}$ showing the atom-labeling scheme and the disorder in the structure. Thermal ellipsoids represent the 40% probability surfaces.

apparent. We attempted to solve the structure with our data in the space group $P\bar{4}n2$ (assuming that the experimentally determined unit cell dimensions of 10.475 (2) and 10.452 (2) Å were both equal to the mean value of 10.463 Å). The refinement did not converge and oscillated around an R value of 0.10. At this stage no ordered or disordered model seemed to be suitable for refinement. On the basis of these results we conclude that the conditions of crystallization are critical and that the $(Et_4N)_2Ni(S_4)_2$ "salt" can crystallize in both ordered and disordered fashion in two lattices of different space group symmetries but with very similar unit cells and apparently similar energies. The positional disorder evident in our structure results in an orthorhombic unit cell with dimensions slightly different from those of the tetragonal cell observed in the ordered structure.[29]

$(Ph_4P)_2[(MnS_{11})_{0.85}(MnS_{10})_{0.15}]$ (III). The positions of the Mn atoms in the two independent $[MnS_x]^{2-}$ anions in the asymmetric unit were located by direct methods using the program MULTAN.[35] The correctness of these positions was verified in a Patterson synthesis map. Subsequent Fourier electron density maps phased with the two Mn atoms revealed the positions of five sulfur and the four phosphorus atoms. At this stage the value of R was 0.44. The remaining sulfur atoms and the cation carbon atoms were located in subsequent difference Fourier maps. After five cycles of refinement of the two $[(S_6)Mn(S_5)]^{2-}$ anions and the four Ph_4P^+ cations, the R_w and R values were 0.22 and 0.17, respectively. A difference Fourier at this point revealed additional minor but real S_x^{2-} fragments around both of the Mn tetrahedral sites. The positions and relative weights of these fragments suggested that the site of one MnS_{11}^{2-} anion was occupied by MnS_{10}^{2-} as a minor component. The site of the other MnS_{11}^{2-} anion also was occupied by another minor MnS_{11}^{2-} component with a slightly different orientation of the S_5^{2-} and S_6^{2-} chelating rings (Figure 2). Refinement of the site occupation factors indicated that the minor to major component ratio for both sites was 30:70.

Due to the exceptionally large number of non-hydrogen atoms in the asymmetric unit, the phenyl rings of the Ph_4P^+ cation were refined as rigid groups with individual temperature factors assigned to all group atoms. Refinement by a block-matrix least-squares routine (available in the SHELX76 program package) reached convergence after 16 cycles. The final values for R_w and R were 0.12 and 0.12, respectively, and the hydrogen atoms were not included in the structure factor calculation. No significant residual electron density was found in the final Fourier difference map.

$[(Ph_4P)_2$-*trans*-$Ni(CS_4)_2]$ (IV). The Ni and two S atoms were obtained from the solution of a Patterson map. The remaining non-hydrogen atoms were revealed in subsequent Fourier synthesis maps. Full-matrix least-squares refinement of all the atoms in the asymmetric unit with isotropic temperature factors converged to values for R_w and R of 0.088 and 0.075, respectively. Anisotropic temperature factors were introduced to all non-hydrogen atoms, and refinement continued. After five cycles of refinement convergence was reached and R_w and R were 0.060 and 0.041. In the last cycles of refinement the 20 hydrogen atoms were introduced in the structure factor calculation at their calculated positions (0.95 Å from the C atoms) but were not refined. The final R values were 0.051 and 0.029.

Table II. Positional Parameters and Their Standard Deviations for $(Et_4N)_2Zn(S_4)_2$

atom	x	y	z
Zn(1)	0.26852 (8)	0.95827 (6)	0.74643 (7)
S(1)	0.2384 (2)	1.0914 (2)	0.8068 (2)
S(2)	0.0742 (3)	1.0853 (2)	0.8104 (2)
S(3)	0.0494 (3)	0.9719 (2)	0.8658 (2)
S(4)	0.1046 (2)	0.8936 (2)	0.7653 (2)
S(5)	0.4321 (2)	0.9179 (2)	0.8321 (2)
S(6)	0.5052 (2)	0.8640 (2)	0.7238 (2)
S(7)	0.4675 (3)	0.9357 (2)	0.6058 (2)
S(8)	0.3012 (3)	0.9328 (2)	0.5853 (2)
N(1-A)	0.3122 (5)	0.8718 (3)	0.1626 (4)
C(1-A)	0.2533 (9)	0.8021 (8)	0.2155 (9)
C(2-A)	0.373 (1)	0.8344 (8)	0.0909 (9)
C(3-A)	0.390 (1)	0.9109 (7)	0.2375 (9)
C(4-A)	0.233 (1)	0.9354 (7)	0.1231 (9)
C(5-A)	0.199 (1)	0.8297 (9)	0.3035 (9)
C(6-A)	0.293 (1)	0.7940 (8)	0.0063 (8)
C(7-A)	0.470 (1)	0.8577 (8)	0.295 (1)
C(8-A)	0.279 (1)	1.0026 (7)	0.0688 (7)
N(2-B)	0.8251 (5)	0.8165 (4)	0.5025 (4)
C(1-B)	0.8403 (7)	0.8273 (6)	0.6129 (5)
C(2-B)	0.7055 (6)	0.8251 (6)	0.4645 (6)
C(3-B)	0.8836 (7)	0.8827 (6)	0.4521 (6)
C(4-B)	0.8673 (6)	0.7333 (6)	0.4820 (7)
C(5-B)	0.8039 (9)	0.9084 (7)	0.6474 (7)
C(6-B)	0.6338 (9)	0.7610 (7)	0.5018 (8)
C(7-B)	1.0026 (9)	0.8847 (8)	0.4789 (8)
C(8-B)	0.859 (1)	0.7104 (8)	0.3763 (9)

Table III. Positional Parameters and Their Standard Deviations for $(Et_4N)_2NiS_8$[a]

atom	x	y	z
Ni	0.5000	1.0000	1.0000
S(4)	0.3845 (04)	0.0767 (04)	−0.1277 (03)
S(1)	0.4319 (08)	0.0924 (08)	0.1397 (06)
S(2)	0.2592 (08)	0.1855 (07)	0.0944 (07)
S(3)	0.3093 (08)	0.2566 (08)	−0.0501 (08)
SS(1)	0.4163 (06)	0.1330 (07)	0.1192 (05)
SS(2)	0.2449 (08)	0.1882 (07)	0.0479 (08)
SS(3)	0.3119 (08)	0.2397 (08)	−0.0955 (08)
N	0.7938 (07)	0.2956 (07)	0.0010 (09)
C(1)	0.7858 (12)	0.1793 (12)	0.0694 (09)
C(2)	0.8979 (14)	0.1574 (17)	0.1440 (11)
C(3)	0.6767 (11)	0.2867 (13)	−0.0710 (10)
C(4)	0.6588 (14)	0.3977 (15)	−0.1457 (11)
C(5)	0.7916 (12)	0.4208 (13)	0.0619 (10)
C(6)	0.6771 (17)	0.4408 (17)	0.1264 (12)
C(7)	0.9191 (11)	0.2947 (14)	−0.0612 (09)
C(8)	0.9382 (16)	0.1778 (18)	−0.1283 (12)

[a] SS(1), SS(2), and SS(3) represent the sulfurs of the second component occupying the site.

Crystallographic Results. The final atomic positional and thermal parameters for $(Et_4N)_2Zn(S_4)_2$ (I), $(Et_4N)_2Ni(S_4)_2$ (II), and $(Ph_4P)_2Ni(CS_4)_2$ (IV), are compiled in Tables II, III and IV, respectively. The corresponding tables for $(Ph_4P)_2MnS_{11}$ (III) have been deposited as supplementary material. Intramolecular distances and angles for I and II are given in Table V, for III in Table VI, and for IV in Table VII. A table with interatomic distances and angles for the minor component in III has been deposited.

The atom-labeling scheme is shown in Figure 1 for I and II, in Figure 2 for III, and in Figure 3 for IV. Tables of the observed values of F, their esd's, and the $|F_o| - |F_c|$ values have been deposited as supplementary material.

Results and Discussion

(1) Synthesis. In polar media the RS^--catalyzed dissociation of aliphatic trisulfides results in the generation of S_x^0 fragments (x = 2–6) that in the presence of suitable reducing agents form the anionic S_x^{2-} polysulfide ligands. The PhS^- ligands in the $[M(SPh)_4]^{2-}$ complex anions[31,37] are oxidized readily by the S_x^0 fragments according to the reaction (1). The effectiveness of

$$[M(SPh)_4]^{2-} + 2S_x^0 \rightarrow [M(S_x)_2]^{2-} + 2PhSSPh \qquad (1)$$

---

[37] Coucouvanis, D.; Swenson, D.; Baenziger, N. C.; Murphy, C.; Holah, D. G.; Sfarnas, N.; Simopoulos, A.; Kostikas, A. *J. Am. Chem. Soc.* **1981**, *103*, 3350.

Table IV. Positional Parameters and Standard Deviations in the Anion of $(Ph_4P)_2Ni(CS_4)_2$

atom	*x*	*y*	*z*
Ni	0	0	0
S(1)	−0.0418 (1)	−0.0458 (1)	−0.13903 (8)
S(2)	−0.2915 (1)	0.0069 (1)	0.22555 (8)
S(3)	0.2433 (1)	0.0273 (1)	−0.07355 (9)
S(4)	0.1187 (2)	0.9395 (1)	0.63918 (8)
C	0.1202 (5)	0.9622 (3)	0.7580 (3)
P	0.6040 (1)	0.50391 (8)	0.23997 (6)
C(1)	0.7444 (4)	0.5243 (3)	0.3027 (2)
C(2)	0.7818 (5)	0.6496 (4)	0.3157 (3)
C(3)	0.9017 (5)	0.6663 (4)	0.3527 (3)
C(4)	0.9829 (5)	0.5584 (5)	0.3779 (3)
C(5)	0.9471 (5)	0.4349 (4)	0.3652 (3)
C(6)	0.8292 (5)	0.4161 (3)	0.3265 (3)
C(7)	0.7028 (4)	0.4864 (3)	0.1075 (2)
C(8)	0.7715 (4)	0.5955 (4)	0.0404 (3)
C(9)	0.8572 (5)	0.5795 (4)	−0.0600 (3)
C(10)	0.8754 (5)	0.4561 (5)	−0.0925 (3)
C(11)	0.8129 (5)	0.3468 (4)	−0.0244 (3)
C(12)	0.7244 (4)	0.3613 (3)	0.0753 (3)
C(13)	0.4782 (4)	0.6450 (3)	0.2534 (3)
C(14)	0.4077 (5)	0.6758 (4)	0.3528 (3)
C(15)	0.3065 (5)	0.7777 (4)	0.3699 (3)
C(16)	0.2736 (5)	0.8512 (4)	0.2872 (4)
C(17)	0.3418 (5)	0.8227 (4)	0.1899 (3)
C(18)	0.4448 (5)	0.7185 (4)	0.1712 (3)
C(19)	0.4881 (4)	0.3608 (3)	0.2998 (2)
C(20)	0.4864 (5)	0.2937 (4)	0.3936 (3)
C(21)	0.3841 (6)	0.1909 (4)	0.4382 (3)
C(22)	0.2864 (5)	0.1559 (4)	0.3899 (3)
C(23)	0.2877 (5)	0.2207 (4)	0.2968 (4)
C(24)	0.3872 (5)	0.3244 (4)	0.2501 (3)

this reaction, which has been used for the synthesis of the complexes reported herein, has been demonstrated previously in the synthesis of the $[(S_5)FeS_2Fe(S_5)]^{2-}$,[6] $[Fe_4S_4Cl_4]^{2-}$,[38] and $[(S_5)FeS_2MS_2]^{2-}$[7] (M = Mo, W) complexes from the $[(PhS)_2FeS_2Fe(SPh)_2]^{2-}$,[39] $[Fe_4(SPh)_6Cl_4]^{2-}$,[38] and $[(PhS)_2FeS_2MS_2]^{2-}$[7] complexes, respectively.

The mechanism for the generation of S_x^0 fragments, in solutions containing thiophenolate complexes and dibenzyl trisulfide, could be similar to the one proposed[40] for the RS^--catalyzed dissociation of thiocystine (Scheme I). Higher order polysulfides are likely to form readily according to the deceivingly simple general equilibrium reaction[41]

$$xS_y^0 \rightleftarrows yS_x^0$$

and in turn are expected to give rise to dialkyl polysulfides

$$S_x^0 + RS^- \rightleftarrows RSS_x^-$$

$$RS'SR + RSS_x^- \rightleftarrows RSS_xSR + R'S^-$$

Scheme I

$$RSSSR + R'S^- \rightleftarrows RSS^- + R'SSR$$

$$RSS^- \rightleftarrows RS^- + S^0$$

$$RS^- + R'SSR \rightleftarrows RSSR + R'S^-$$

$$\text{or} \quad RSSSR + R'S^- \rightleftarrows RSSR + R'S^- + S^0$$

Table V. Intramolecular Bond Distances (Å) and Angles (deg) in the MS_x Complexes[a] (M = Zn, Ni)

	$[(C_2H_5)_4N]_2$-$[(S_4)_2Zn]$[b]	$[(C_2H_5)_4N]_2$-$[(S_4)_2Ni]$[c]	
	Distances		
M-S(1)	2.376 (3)	2.146 (7)[d]	2.195 (2)[e]
M-S(4)	2.331 (3)	2.179 (3)[f]	
M-S(5)	2.343 (2)	2.238 (7)	
M-S(8), {S(4)′}[g]	2.354 (3)		
mean	2.351 (19)	2.188 (47)	2.185[h]
S(1)-S(2)	2.045 (4)	2.134 (12)	2.073 (2)
S(2)-S(3)	2.044 (5)	2.053 (11)	2.037 (4)
S(3)-S(4)	2.062 (5)	2.266 (10)	2.073 (2)
S(5)-S(6)	2.034 (5)	2.093 (12)	
S(6)-S(7)	2.032 (5)	2.029 (12)	
S(7)-S(8), {S(4)′}[g]	2.056 (5)	1.914 (9)	
mean	2.046 (12)	2.08 (12)	2.061 (21)
S(1)-S(5)	3.712 (14)	2.849 (9)	
S(4)-S(8)	3.721 (5)		
S(1)-S(4)	3.655 (5)	3.445 (12)	
S(5)-S(8), {S(4)′}	3.655 (5)	3.216 (9)	
S(4)-S(5)	4.097 (5)		
S(1)-S(8), {S(4)′}	4.159 (5)	2.903 (9)	
	Angles		
S(1)-M-S(4)	101.90 (13)	105.5 (2)[d]	99.1 (1)[e]
S(1)-M-S(5)	103.73 (13)	81.02 (2)	83.0 (1)
S(1)-M-S(8)	123.13 (17)		
S(4)-M-S(5)	122.42 (14)		
S(4)-M-S(8), {S(4)′}[g]	105.22 (14)	83.5 (2)	
S(5)-M-S(8), {S(4)′}[g]	102.19 (13)	93.4 (2)	
M-S(1)-S(2)	99.00 (11)	105.3 (4)	105.1 (1)
M-S(4)-S(3)	98.47 (12)	100.0 (3)	
M-S(5)-S(6)	100.00 (12)	102.3 (3)	
M-S(8)-S(7)	97.46 (11)	112.9 (3)	
S(1)-S(2)-S(3)	104.0 (2)	101.0 (4)	99.4 (1)
S(2)-S(3)-S(4)	103.6 (2)	100.3 (4)	
S(5)-S(6)-S(7)	105.3 (2)	99.6 (5)	
S(6)-S(7)-S(8)	104.2 (2)	95.4 (4)	

[a] The numbering scheme is in analogous reference to Figure 1. [b] The structural parameters for the counterions in this complex are unexceptional. Thus, for $(C_2H_5)_4N^+$, the mean value of the C-N bonds is 1.522 (24) Å (range 1.492 (14)-1.549 (14) Å) and the mean value for the C-C bonds is 1.502 (26) Å (range 1.463 (19)-1.517 (18) Å). [c] In this complex the mean value of the C-N bonds in the $(C_2H_5)_4N^+$ cations is 1.510 (39) Å (range 1.443-1.575 Å). The mean value for the C-C bonds is 1.520 (16) Å (range 1.443 (4)-1.599 (14) Å). [d] This work. [e] From ref 29. [f] S(4) is the only sulfur atom not subject to disorder. [g] In the $[(S_4)_2Ni]^{2-}$ anion S(4) and S(4)′ are in the same molecule and are the only two sulfur atoms related by the twofold axis of symmetry. [h] The anion in this structure is required to possess D_2 point symmetry.

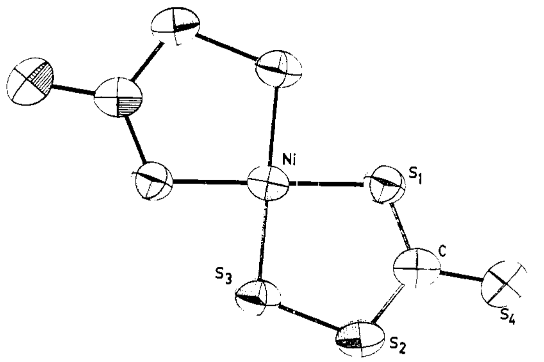

Figure 3. Structure and labeling scheme for the $[Ni(CS_4)_2]^{2-}$ anion. Thermal ellipsoids represent the 50% probability surfaces.

The catalytic effect of RS^- in the generation of higher order polysulfides from dibenzyl trisulfide is apparent in NMR studies.

---

(38) Initially crystals of the $(Ph_4P)^+$ salt of this anion were examined. A more severe disorder was observed in the crystal structure of $(Ph_4P)_2Ni(S_4)_2$. The latter crystallizes in the triclinic space group $P\bar{1}$ with a = 10.451 (3) Å, b = 10.847 (3) Å, c = 11.166 (3) Å, α = 75.33 (2)°, β = 84.55 (2)°, and γ = 73.28 (2)°, Z = 1, V = 1172 (1) Å^3. The structure was refined to R = 9.9%. The Ni atom is positioned at the center of symmetry and is coordinated by S_4^{2-} ligands that adopt *three* different conformations at the same crystallographic site. No meaningful parameters for the $(Ni(S_4)_2)^{2-}$ anion could be obtained from this study.

(39) Mayerle, J. J.; Denmark, S. E.; DePamphilis, V. B.; Ibers, J. A. Holm, R. H. *J. Am. Chem. Soc.* **1975**, *97*, 1032.

(40) Abdolrasulnia, R.; Wood, J. L. *Bioorg. Chem.* **1980**, *9*, 253.

(41) Tebbe, F. N.; Wasserman, E.; Peet, W. G.; Vatvars, A.; Hayman, A. C. *J. Am. Chem. Soc.* **1982**, *104*, 4971.

Table VI. Intramolecular Bond Distances (Å) and Angles (deg) in the $[(S_5)Mn(S_6)]^{2-}$ Complex[a]

Distances

Mn(1)–S(1)	2.451 (7)	Mn(2)–S(1)′	2.446 (6)
Mn(1)–S(6)	2.416 (7)	Mn(2)–S(5)′	2.432 (10)
Mn(1)–S(7)	2.419 (7)	Mn(2)–S(6)′	2.401 (9)
Mn(1)–S(11)	2.439 (7)	Mn(2)–S(11)′	2.393 (6)
mean	2.431 (16)	mean	2.418 (25)
S(1)–S(2)	2.07 (1)	S(1)′–S(2)′	2.02 (1)
S(2)–S(3)	1.88 (1)	S(2)′–S(3)′	2.00 (1)
S(3)–S(4)	2.08 (1)	S(3)′–S(4)′	2.03 (1)
S(4)–S(5)	2.01 (2)	S(4)′–S(5)′	1.99 (1)
S(5)–S(6)	1.78 (2)	S(6)′–S(7)′	1.85 (2)
S(7)–S(8)	1.82 (1)	S(7)′–S(8)′	2.05 (2)
S(8)–S(9)	2.06 (2)	S(8)′–S(9)′	2.05 (2)
S(9)–S(10)	1.93 (2)	S(9)′–S(10)′	2.05 (2)
S(10)–S(11)	2.18 (2)	S(10)′–S(11)′	1.96 (1)
mean	1.98 (13)	mean	2.00 (6)
S(1)–S(6)	4.12 (2)	S(1)′–S(5)′	3.95 (2)
S(7)–S(11)	3.94 (2)	S(6)′–S(11)′	4.17 (2)

Angles

S(1)–Mn(1)–S(7)	115.8 (3)	S(1)′–Mn(2)–S(5)′	108.1 (3)
S(1)–Mn(1)–S(11)	118.1 (3)	S(1)′–Mn(2)–S(6)′	107.7 (3)
S(1)–Mn(1)–S(6)	115.8 (3)	S(5)′–Mn(2)–S(6)′	98.9 (3)
S(6)–Mn(1)–S(7)	98.5 (3)	S(5)′–Mn(2)–S(11)′	116.7 (3)
S(6)–Mn(1)–S(11)	97.2 (3)	S(1)′–Mn(2)–S(11)′	103.9 (3)
S(7)–Mn(1)–S(11)	108.3 (4)	S(6)′–Mn(2)–S(11)′	120.9 (3)
mean	109.0 (9.2)	mean	109.4 (8.1)
Mn(1)–S(1)–S(2)	105.9 (3)	Mn(2)–S(1)′–S(2)′	94.4 (3)
Mn(1)–S(6)–S(5)	112.8 (5)	Mn(2)–S(5)′–S(4)′	98.4 (4)
Mn(1)–S(7)–S(8)	88.8 (5)	Mn(2)–S(6)′–S(7)′	110.5 (5)
Mn(1)–S(11)–S(10)	100.5 (6)	Mn(2)–S(11)′–S(10)′	101.4 (4)
S(1)–S(2)–S(3)	110.3 (5)	S(1)′–S(2)′–S(3)′	108.0 (4)
S(2)–S(3)–S(4)	112.6 (7)	S(2)′–S(3)′–S(4)′	106.4 (4)
S(3)–S(4)–S(5)	105.0 (7)	S(3)′–S(4)′–S(5)′	111.1 (5)
S(4)–S(5)–S(6)	111.2 (7)	S(6)′–S(7)′–S(8)′	110.6 (9)
S(7)–S(8)–S(9)	104.7 (6)	S(7)′–S(8)′–S(9)′	107.9 (8)
S(8)–S(9)–S(10)	103.0 (10)	S(8)′–S(9)′–S(10)′	105.9 (7)
S(9)–S(10)–S(11)	111.5 (8)	S(9)′–S(10)′–S(11)′	106.4 (6)

[a] The numbering scheme is given in Figure 2. The data refer to the 70% major components for the two anions in the asymmetric unit.

Table VII. Intramolecular Bond Distances (Å) and Angles (deg) in the $[(C_6H_5)_4P]_2Ni(CS_4)_2$ Complex[a]

Distances

Ni–S(1)	2.165 (2)	S(4)–C	1.678 (4)
Ni–S(3)	2.174 (2)	S(2)–S(3)	2.064 (2)
S(1)–C	1.707 (4)	S(1)–S(3)	3.174 (2)
S(2)–C	1.711 (5)	S(1)–S(3)[b]	2.959 (2)

Angles

S(1)–Ni–S(3) exo	85.99 (7)	S(1)–C–S(4)	122.1 (2)
S(1)–Ni–S(3) endo	94.01 (7)	S(1)–C–S(2)	120.0 (2)
Ni–S(1)–C	112.2 (1)	S(2)–C–S(4)	117.8 (2)
Ni–S(3)–S(2)	107.76 (6)	C–S(2)–S(3)	105.9 (2)

[a] The numbering scheme is given in Figure 3. [b] Interligand distance.

Solutions of BzSSSBz in benzene (0.1 M) are stable over long periods of time, and only a single $-CH_2$ resonance is observed in the NMR spectrum at 3.73 ppm. Upon addition of thiophenol and tributylamine to these solutions (to a final concentration of $Bu_3NH^+RS^-$ of 0.01 M), new $-CH_2$ resonances appear at 3.80, 4.25, and 4.33 ppm and increase in intensity with time. By comparison to "authentic" compounds, the resonances at 3.80 and 4.25 ppm are assigned to BzSSBz and $BzS(S)_2SBz$, respectively. The resonance at 4.33 ppm most likely is due to a mixture of higher order polysulfides. The same effects are observed in the NMR spectra of BzSSSBz in DMF solution when catalytic amounts of $(Ph_4P)_2Zn(SPh)_4$ are added.

A variety of products are obtained from the RSSSR oxidation of $[Zn(SPh)_4]^{2-}$ (eq 1). The formation of these compounds (Table VIII) depends on the trisulfide to $[Zn(SPh)_4]^{2-}$ concentration ratio. The larger metallocycles, ZnS_6 and ZnS_5, form when this ratio is 20 and 10, respectively, with a $[Zn(SPh)_4]^{2-}$ concentration of 4×10^{-2} M. The mixed-ligand complexes $[(PhS)_2ZnS_x]^{2-}$ (x = 4, 5) are obtained when the RSSSR to $[Zn(SPh)_4]^{2-}$ ratios are ≤5. The $[Zn(S_4)_2]^{2-}$ complex could be obtained only with Et_4N^+ as a counterion, and its selective precipitation very likely is due to favorable lattice energy by comparison to Et_4N^+ salts of the $[(PhS)_2ZnS_4]^{2-}$, $[(PhS)_2ZnS_5]^{2-}$, and $[Zn(S_5)_2]^{2-}$ anions that very likely are present in solution as well. The Ph_4P^+ salt of the $[Zn(S_4)_2]^{2-}$ anion could be obtained by sulfur abstraction from $(Ph_4P)_2[Zn(S_5)_2]$. The reaction of Ph_3P with $(Ph_4P)_2[Zn(S_5)_2]$ in DMF in a 2:1 molar ratio proceeds readily, and $(Ph_4P)_2[Zn(S_4)_2]$ is obtained in high yield. The successful selective precipitation of the individual types of $[Zn(S_x)_2]^{2-}$ complexes is verified not only by elemental analyses but also by the characteristic, unique X-ray powder patterns for each of the complexes in Table VII. Attempts to recrystallize salts of the $[Zn(S_x)_2]^{2-}$ complexes from CH_2Cl_2 solutions resulted in decomposition of the complexes and formation of $ZnCl_4^{2-}$. The reactivity of CH_2Br_2 toward coordinated S_x^{2-} anions has been noted recently.[42]

The reactions of $[Cd(SPh)_4]^{2-}$ with RSSSR do not parallel those of the $[Zn(SPh)_4]^{2-}$ complex. Only the $[(PhS)_2CdS_5]^{2-}$ complex is obtained when the RSSSR to $[M(SPh)_4]^{2-}$ concentration ratios are either 2 or 4, and only the $[(S_5)_2Cd]^{2-}$ complex is obtained when the reactant concentration ratios are either 10 or 20.

A preference for S_x^{2-} size also is apparent in the Ni system where, under identical concentration conditions to those employed for the synthesis of the $[M(S_5)_2]^{2-}$ complexes (M = Zn, Cd), only the $[Ni(S_4)_2]^{2-}$ complex could be obtained. In the Mn(II) system either S_5^{2-} or S_6^{2-} ligands can accommodate the tetrahedrally coordinated high-spin ($\mu_{\text{eff}}^{\text{cor}} = 5.65\ \mu_B$ Mn(II) ion. Unlike the Zn system where the $[Zn(S_5)_2]^{2-}$ and $[Zn(S_6)_2]^{2-}$ complexes crystallize in different lattices, the corresponding Mn(II) complexes are isomorphous and cocrystallize readily.

The polysulfide complexes reported herein can be obtained also from the $[M(SPh)_4]^{2-}$ anions with elemental sulfur as the oxidizing agent.

The synthesis of several other polysulfido complexes such as $[Cu_3(S_6)_3]^{3-}$,[16] $[Cu_6S_{17}]^{2-}$,[21] $[Hg(S_6)_2]^{2-}$,[20] and $[AuS_9]^-$[22] can be accomplished by metathesis reactions using S_x^{2-} solutions. At present it is not entirely clear how the sulfur content of polysulfide solutions influences the distribution of S_x^{2-} fragments at equilibrium and how this distribution affects the formation of the $[M(S_x)_n]^{2-}$ complexes. In view of the plethora of possible monomeric and cluster complexes that can form, however, it is essential that, for a particular counterion, such variables as sulfur content, concentration of reagents, temperature, and reaction times are carefully monitored.

The recently reported synthesis of $[AuS_9]^-$ anion[22] that contains the S_9^{2-} bidentate chelate is most interesting and demonstrates that the isolation of the rare S_9^{2-} fragment can be achieved preferentially by a metal ion from an equilibrium mixture by virtue of the thermodynamic stability of the MS_x product. In the $[AuS_9]^-$ anion the nearly linear S–Au–S coordination (176°) can be achieved with minimum strain only with the flexible S_9^{2-} bidentate chelate.

The reactions of the $[(S_x)_2M]^{2-}$ complexes with electrophiles such as CS_2 and RC≡CR (R = $COOCH_3$) seem to parallel similar reactions that are known to occur with the $[(S_4)_2MoS]^{2-}$,[23] $[(S_4)Mo_2S_4(S_2)]^{2-}$,[43] $[Fe_2S_{12}]^{2-}$,[24] $(MeCp)_2V_2S_5$,[26] and $(Cp)_2TiS_5$[25] complexes. In these reactions the products contain the $(CH_3COO)_2C_2S_2^{2-}$ and CS_4^{2-} ligands, which are obtained by what appear to be cycloaddition reactions of either RC≡CR or CS_2 to the coordinated S_2^{2-} ligands.

The reaction of CS_2 with the $[(S_4)_2Ni]^{2-}$ and $[(S_5)Mn(S_6)]^{2-}$ complexes is rapid, and the $[(CS_4)_2Ni]^{2-}$, $[(CS_4)_2Mn]^{2-}$,[44] and

---

(42) Giolando, D. M.; Rauchfuss, T. B. *Organometallics* **1984**, *3*, 487.
(43) Coucouvanis, D.; Draganjac, M. *J. Am. Chem. Soc.* **1982**, *104*, 6820.

Table VIII. Synthesis of the MS_x Complexes in CH_3CN

$[RSSSR]/[M(SPh)_4{}^{2-}]$	M; $10^2[M]$, mol L^{-1}			
	Mn; 3.2	Ni; 4.0	Cd; 4.0	Zn; 4.0
2^a			$[(PhS)_2CdS_5]^{2-}$	$[(PhS)_2ZnS_4]^{2-}$
5^a		$[(S_4)_2Ni]^{2-}$	$[(PhS)_2CdS_5]^{2-}$	$[(PhS)_2ZnS_5]^{2-}$
10^a	$[(S_5)Mn(S_6)]^{2-}$	$[(S_4)_2Ni]^{2-}$	$[(S_5)_2Cd]^{2-}$	$[(S_5)_2Zn]^{2-}$
20^a			$[(S_5)_2Cd]^{2-}$	$[(S_6)_2Zn]^{2-}$
5^b				$[(S_4)_2Zn]^{2-}$

^{a} Ph_4P^+ counterion. ^{b} Et_4N^+ counterion.

$[(S_6)(CS_4)Mn]^{2-}$[44] complexes form and can be isolated as crystalline Ph_4P^+ salts. The former of these complex anions show the C=S stretching vibration at 905 cm^{-1} and has been synthesized earlier by the addition of elemental sulfur[45] to the $[(CS_3)_2Ni]^{2-}$ complex.[46] The electronic properties of the $[(CS_4)_2Ni]^{2-}$ complex reported herein are identical with those reported[46] earlier, and as reported at that time,[46] this anion reacts readily with Ph_3P to form the $[(CS_3)_2Ni]^{2-}$ complex.

The electronic spectra of the $[M(S_x)_2]^{2-}$ complexes are unexceptional. A feature that is characteristic for the MS_x complexes for $x \geq 5$ is a low-energy electronic transition at 610 nm observed in the spectra of the $[Zn(S_5)_2]^{2-}$, $[Cd(S_5)_2]^{2-}$, $[Zn(S_6)_2]^{2-}$, and $[(S_5)Mn(S_6)]^{2-}$ anions in DMF solution. This transition very likely is due to the $S_3^{-}\cdot$ radical anion[47] that is obtained by ligand dissociation in DMF. In CH_3CN solution this low-energy transition has not been detected for these complexes, which display only the intraligand and L → M transitions as predominant features between 410 and 390 nm. The square-planar $[Ni(S_4)_2]^{2-}$ and $[Ni(CS_4)_2]^{2-}$ complexes have very similar electronic spectra and contain low-energy absorptions at 470 and 455 nm, respectively.

(2) Structures. (a) $(Et_4N)_2Zn(S_4)_2$. The unit cell of the monoclinic ($P2_1/c$) lattice contains eight Et_4N^+ cations and four $[Zn(S_4)_2]^{2-}$ anions located on general positions. There exist no unusual interionic interactions, and the ions are well separated in the lattice. In the cations, the $\overline{\text{C–N}}$ bond length is 1.510 (11) Å (range 1.443 (13)–1.575 (13) Å) and the $\overline{\text{C–C}}$ bond length is 1.510 (15) Å (range 1.479 (16)–1.599 (18) Å). The interatomic distances and angles in the anion are given in Table IV. The Zn(II) ion is coordinated tetrahedrally by two bidentate $S_4{}^{2-}$ ligands. Each of the two $Zn(S_4)$ rings in the anion adopt the "half-chair" conformation, and as found for the $Ni(S_4)$ rings, the "distant" sulfur atoms, S_2, S_3 and S_6, S_7 (Figure 1b) are located at either side of the ZnS(1)S(4) and ZnS(5)S(8) planes, respectively. The distances to these planes are comparable to the corresponding ones in the NiS_4 rings.

The $\overline{\text{Zn–S}}$ bond in the $[Zn(S_4)_2]^{2-}$ complex, at 2.351 (19) Å, is very similar to the $\overline{\text{Zn–S}}$ bond in the $[Zn(SPh)_4]^{2-}$ complex[37] at 2.353 (14) Å, although an unusually wide range in Zn–S bond lengths (2.376 (3)–2.331 (3) Å) is found in the former. The mean value of the S–S bonds at 2.046 (12) Å compares favorably with the $\overline{\text{S–S}}$ bond in $S_7{}^{2-}$ (2.030 (31) Å[47] and orthorhombic sulfur (2.037 (5) Å)[48] and is slightly shorter than the $\overline{\text{S–S}}$ bond of the $S_4{}^{2-}$ anion in $BaS_4{\cdot}H_2O$ (2.069 (2) Å).[49]

(b) $(Et_4N)_2Ni(S_4)_2$.[38] The nickel atom is situated on a twofold axis. Two half-occupancy $S_4{}^{2-}$ ligands coordinated to the nickel atom are located in such a manner so as to share one of the metal-bound sulfur atoms (S(4)). The ligands related by the twofold axis of symmetry do not belong to the same $[Ni(S_4)_2]^{2-}$ complex. Instead, the two half-occupancy $[Ni(S_4)_2]^{2-}$ complexes contain two nonsymmetry-related $S_4{}^{2-}$ ligands and *do not have* crystallographically imposed twofold symmetry (Figure 1a). The crystallographically related S(1)–S(2)–S(3)–S(4) and S(1)′-S(2)′-S(3)′-S(4)′ ligands show a very close interligand contact (S(1)–S(1)′ = 2.4 Å) and result in a rather distorted $[Ni(S_4)_2]^{2-}$ complex anion. The same behavior is observed for the crystallographically related SS(1)–SS(2)–SS(3)–S(4) and SS(1)′-SS(2)′-SS(3)′-S(4)′ pair of ligands. Chemically acceptable anions are obtained in the "crossed" [S(1)–S(2)–S(3)–S(4)]Ni[SS(1)-SS(2)-SS(3)-S(4)′] combination (Figure 1a). The SS(1)–S(4)′-Ni-S(1)–S(4) unit is not planar and can best be described in terms of two NiS_2 units (Ni–SS(1)–S(4)′; Ni–S(1)–S(4)) twisted relative to each other by 19.7° and giving rise to a NiS_4 core with D_2 symmetry. Crystallographically imposed D_2 symmetry also has been reported for $[Ni(S_4)_2]^{2-}$ in the previous structure determination[29] (see Experimental Section).

As pointed out previously[17] two conformations of the MS_4 metallocycles have been observed. The half-chair conformation, which is found in the structures of $(C_5H_5)_2MoS_4$[14] and $(C_5H_5)_2WS_4$,[15] is characterized by equidistant central atoms from and on opposite sites of the plane that contains the metal and the two coordinated S atoms. In the "puckered" (envelope) conformation, which is found in the structures of the $[(S_4)_2MoS]^{2-}$, $[(S_4)_2MoO]^{2-}$, and $[Mo_2S_{10}]^{2-}$ complexes,[17] the central S atoms lie both above and on one side of the plane defined by the metal and the two coordinated S atoms. The distances from the plane are nonequivalent, with one being short (0.3 Å) and the other long (1.3 Å).

In the structure of II the half-chair conformation is observed and the central sulfur atoms S(2), S(3) and SS(2)′, SS(3)′ are found 0.41 and −0.73 Å and 0.71 and −0.51 Å from the NiS(4)S(1) and NiS(4)′SS(1) planes respectively.

The Ni–S(4) distance in the structure of II is not affected by the disorder and at 2.179 (3) Å is very similar to the one reported in the previous structure determination[29] (2.185 (2) Å). The alternation in the S–S bond lengths within the coordinated $S_4{}^{2-}$ ligands in II is not as clear as previously reported.[29] A comparison of the structural parameters for II in the ordered tetragonal and disordered orthorhombic lattices is shown in Table V. The large standard deviations (and low accuracy) for most values in the latter are due to the crystallographic disorder.

(c) $(Ph_4P)_2[MnS_{11}]$. With two independent anions and four $(C_6H_5)_4P^+$ cations in the asymmetric unit, the structure has an unusually large number of parameters and the problem is further exacerbated by the multiple occupancy of the anion sites. As a consequence of this crystallographic disorder the structures of the $[MnS_{10}]^{2-}$ and $[MnS_{11}]^{2-}$ anions are not of high accuracy, particulary regarding the intraligand distances and angles. The disorder that affects the $S_6{}^{2-}$ and $S_5{}^{2-}$ ligands in the anions (Figure 2) does not allow for a meaningful detailed analysis of either the conformation or the S–S bonding in the MnS_5 and MnS_6 metallocycles. Problems associated with disorder in a MS_6 ring have been reported[16] for the CuS_6 rings in the $[Cu_3S_{18}]^{3-}$ cluster. In the $[Hg(S_6)_2]^{2-}$ complex[20] the HgS_6 rings are somewhat better defined and display the crown conformation apparent in the MnS_6 unit (Figure 2). The MnS_5 unit displays the chair conformation previously found with the FeS_5 units in the $[Fe_2S_{12}]^{2-}$ complex.[6]

---

[44] A detailed study of the reactivity and structure of this complex is currently in progress.

[45] Coucouvanis, D.; Fackler, J. P. *J. Am. Chem. Soc.* **1967**, *89*, 1346.

[46] Fackler, J. P.; Coucouvanis, D. *J. Am. Chem. Soc.* **1966**, *88*, 3913.

[47] Kanatzidis, M. G.; Baenziger, N. C.; Coucouvanis, D. *Inorg. Chem.* **1983**, *22*, 290.

[48] Abrahams, S. C. *Acta Crystallogr.* **1955**, *8*, 661.

[49] Abrahams, S. C.; Bernstein, J. L. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1969**, *B25*, 2365.

Table IX. Influence of M-S Bonding in the Structural Parameters (Å) of the Coordinated CS_4^{2-} Ligands

compd	M-S(1)	M-S(3)	S(2)-S(3)	S(1)-C	S(2)-C	S(4)-C	ref
$(Ph_4P)_2Ni(CS_4)_2$	2.174 (2)	2.165 (2)	2.064 (2)	1.707 (4)	1.711 (5)	1.678 (4)	*a*
trans-$(Ph_4P)_2Mo(S)(CS_4)_2$[b]	2.386 (3)	2.320 (3)	2.102 (5)	1.735 (12)	1.719 (12)	1.640 (11)	28
	2.380 (3)	2.333 (3)	2.100 (5)	1.739 (12)	1.709 (23)	1.662 (11)	
cis-$(Et_4N)(Ph_4P)Mo(S)(CS_4)_2$	2.376 (3)	2.320 (3)	2.105 (4)	1.756 (10)	1.726 (11)	1.615 (9)	51

[a] This work. [b] Contains two symmetry-independent CS_4^{2-} ligands:

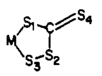

Table X. Influence of M-S Bonding in the S-S Bonding (Å) of the Coordinated S_4^{2-} Ligands

compd	S(1)-S(2)	S(2)-S(3)	S(3)-S(4)	M-S(1)	M-S(4)	ref
$(Et_4N)_2Zn(S_4)_2$[a]	2.045 (4)	2.044 (5)	2.062 (5)	2.376 (3)	2.331 (3)	*b*
	2.034 (5)	2.032 (5)	2.056 (5)	2.343 (2)	2.354 (3)	
$(Et_4N)_2Ni(S_4)_2$[c]	2.073 (2)	2.037 (4)	2.073 (2)	2.185 (2)	2.185 (2)	*d*
$(Ph_3P)_2PtS_4$	2.024 (8)	2.022 (10)	2.081 (10)	2.360 (6)	2.366 (5)	*e*
$(Ph_4P)_2Mo_2S_{10}$[f]	2.093 (4)	2.018 (4)	2.053 (3)	2.399 (2)	2.427 (2)	*g*
$(Ph_4As)_2Mo_2S_{10}$[h]	2.019 (5)	1.970 (6)	2.115 (5)	2.409 (2)	2.403 (3)	*i*
$(Et_4N)_2MoS_9$	2.107 (1)	2.012 (1)	2.166 (1)	2.387	2.331 (1)	*g*
$(Et_4N)_2MoS_8O$	2.120 (3)	2.008 (3)	2.159 (3)	2.395 (2)	2.363 (2)	*g*
$(\eta^5\text{-}C_5H_5)_2Mo(S_4)$	2.081 (8)	2.018 (9)	2.085 (7)			*j*
$(\eta^5\text{-}C_5H_5)_2W(S_4)$	2.105 (7)	2.016 (8)	2.116 (9)			*k*
$[Cu_6S_{17}]^{2-}$	2.107 (4)	2.001 (6)	2.107 (4)			*l*
	2.088 (3)	2.033 (4)	2.089 (4)			
$BaS_4 \cdot H_2O$	2.069 (4)	2.063 (4)	2.069 (4)			*m*
	2.079 (3)	2.062 (4)	2.079 (3)			
$[C_6H_2(OEt)_2S_4]_2$	2.028 (5)	2.068 (5)	2.027 (5)			*n*
	2.034 (5)	2.067 (5)	2.024 (5)			

[a] The $[Zn(S_4)_2]^{2-}$ anion contains two crystallographically independent S_4^{2-} ligands. [b] This work. [c] The $[Ni(S_4)_2]^{2-}$ anion possesses D_2 symmetry. [d] Reference 29. [e] Reference 13. [f] For the S_4^{2-} ligand not subject to disorder. [g] Reference 17. [h] From the major component in a disordered structure. [i] Reference 18. [j] Reference 14. [k] Reference 15. [l] Reference 21. [m] Reference 49. [n] Reference 53.

The Mn-S bond length, derived from the eight Mn-S bonds in the two crystallographically independent MnS_4 cores (Table V) at 2.425 (21) Å, is similar to the Mn-S bond in the $[(PhS)_4Mn]^{2-}$ complex[37,50] (2.442 (13) Å).

(d) $(Ph_4P)_2Ni(CS_4)_2$. In the present crystallographic study the structure proposed earlier for the $[Ni(CS_4)_2]^{2-}$ complex anion (Figure 3) is verified. The location of the Ni atom on a crystallographic center of symmetry results in a rigorously planar NiS_4 unit. The remaining ligand atoms also lie on the same plane and the largest deviation from the best plane, containing all the atoms in the anion, is not greater than 0.1 Å. The CS_4^{2-} ligands (Table IX) in the $[Ni(CS_4)_2]^{2-}$ complex, by comparison to the ligands in the $[(CS_4)_2MoS]^{2-}$ and $[(CS_4)Mo_2S_4)]^{2-}$ complexes,[28] show a longer S-S bond. This difference may be associated with more effective S $\rightarrow$ M π bonding in the Mo complexes (vide infra).

(e) The S_4^{2-} and CS_4^{2-} Ligands. With the exception of the S_4^{2-} anions in the $(Et_4N)_2Zn(S_4)_2$ and $BaS_4 \cdot H_2O$[49] compounds, the S_4^{2-} ligand, in complexes containing the MS_4 metallocycles, shows an interesting alternation in the S-S bonds (Table X). This structural feature, which is particularly pronounced in MS_4 units that contain metal ions with partially filled d shells (M = Mo, W, Ni), also is observed for the Se-Se bonds in the $IrSe_4$ metallocycle.[52] The origin of the S-S bond alternation in the MoS_4[14,17] and WS_4[15] metallocycles originally was attributed[14,17] to significant p_π-d_π S-M bonding. More recently, SCF-Xα-SW calculations on the hypothetical $[Ir(Se_4)(PH_3)_4]^+$ model completely support this contention and show that the Se atoms are linked mainly by p_σ bonds with some p_π bonding.[52] Charge density maps indicate that the central Se-Se bond in the Se_4^{2-} ligand (for which a bond order of 1.15 is calculated) is stronger than the outer Se-Se bonds.

In the MS_4 complexes that show a significant alternation in the S-S bond lengths (M = Mo(IV), Mo(V)[17]) the S-S bonds proximal to the metal have lengths that qualitatively show an inverse relationship to the respective M-S bond lengths (Table X). The ability of the S-S group to enhance S-M, p_π-d_π bonding also is apparent in the structures of the MCS_4 complexes (Table IX). In trans-[28] and cis-[51] $[MoS(CS_4)_2]^{2-}$ the Mo-S bonds adjacent to the S-S part of the ligand always are significantly shorter than the Mo-S bonds adjacent to the C-S part of the ligand (Tables VII and IX).

The lengthening of the S-S bonds may account for the exceptional reactivity of the MS_4 and MCS_4 complexes. The former readily form dithiolene complexes by what appears to be electrophilic attack on the coordinated S_4^{2-} ligand and loss of S_2.[23] The latter (for M = Mo) readily lose CS_2 in solution under reduced pressure to form MS_2 complexes.[28]

Acknowledgment. This work has been supported generously by a grant from the National Science Foundation (No. CHE-79-0389).

Registry No. I, 93714-63-7; II, 87861-75-4; III, 93714-70-6; IV, 93780-89-3; $(Ph_4P)_2[(PhS)_2Zn(S_4)]$, 93714-55-7; $(Ph_4P)_2[(PhS)_2Zn(S_5)]$, 93714-57-9; $(Ph_4P)_2[Zn(S_5)_2]$, 93714-59-1; $(Ph_4P)_2[Zn(S_6)_2]$, 93714-61-5; $(Ph_4P)_2[Zn(S_4)_2]$, 93714-64-8; $(Ph_4P)_2[(PhS)_2Cd(S_5)]$, 93714-66-0; $(Ph_4P)_2[Cd(S_5)_2]$, 93714-68-2; $(Ph_4P)_2[Ni(S_4)_2]$, 93780-88-2; $(Ph_4P)_2[Mn(CS_4)_2]$, 93714-72-8; $(Ph_4P)_2[Mn(Sc)(CS_4)]$, 93714-74-0; $(Ph_4P)_2[Zn(SPh)_4]$, 57763-43-6; BzSSSBz, 6493-73-8; $(Et_4N)_2[Zn(SPh)_4]$, 93714-75-1; $(Ph_4P)_2[Cd(SPh)_4]$, 66281-86-5; $(Ph_4P)_2[Ni(SPh)_4]$, 57927-74-9; $(Et_4N)_2[Ni(SPh)_4]$, 93841-89-5; $(Ph_4P)_2[Mn(SPh)_4]$, 57763-32-3; CS_2, 75-15-0; S_4^{2-}, 12597-07-8; S_5^{2-}, 12597-12-5; S_6^{2-}, 12597-13-6.

Supplementary Material Available: Listings of structure factors for $(Et_4N)_2[Zn(S_4)_2]$, $(Et_4N)_2Ni(S_4)_2$, $(Ph_4P)_2MnS_{11}$, and $(Ph_4P)_2Ni(CS_4)_2$, thermal parameters for all complexes, positional parameters for $(Ph_4P)_2MnS_{11}$, and interatomic distances and angles for the minor component in the structure of $(Ph_4P)_2MnS_{11}$ (70 pages). Ordering information is given on any current masthead page.

---

(50) Swenson, D.; Baenziger, N. C.; Coucouvanis, D. *J. Am. Chem. Soc.* **1978**, *100*, 1932.
(51) Draganjac, M. Ph.D. Thesis, University of Iowa, 1983.
(52) Ginsberg, A. P.; Osborne, J. H.; Sprinkle, C. R. *Inorg. Chem.* **1983**, *22*, 1781.
(53) Rucci, J. S., Jr.; Bernal, I. *J. Chem. Soc., Chem. Commun.* **1979**, 1453.