formation k_a and decay of the exciplex k_{ed}. We note that a concerted 2 + 2 mechanism requires a C_2 axis during the course of the cycloaddition, and therefore, the effect on the transition-state energy between the two deactivation pathways will be additive and the effect on the asymmetric induction will be multiplicative. The fact that the additional chiral group leads to no increase in optical yield indicates that only one of the prosthetic groups is involved in the rate-determining step.

Still unanswered is the question of how the partition between decay and product formation is affected by chiral substitution. The most plausible nonconcerted mechanism involves the intervention of a 1,4-biradical either as an exciplex or after its decay to the ground-state energy surface (see Figure 4). We would expect bonding for the methyl bornyl fumarate to occur at the least crowded site of the fumarate moiety, i.e., at the methyl end. This should also lead to the least asymmetric induction, since the chiral group is farther away from the reaction center and decay would be relatively unaffected. In fact the opposite is the case. All the asymmetric induction occurs with the first chiral group. This apparent contradiction is resolved if we equate k_a with the formation of the second bond. Thus asymmetric induction is controlled by the rate at which the 1,4-biradical intermediate progresses to product. As far as we know, this is the first evidence that a biradical or unsymmetrical intermediate can give rise to stereospecific products, a possibility first suggested by Michl several years ago,[12] and is consistent with theories requiring close approach between ground and excited states for efficient decay to ground state.[12,13] Thus we have additional evidence that cooperativity effects can give significant mechanistic information even in the presence of rather complex reaction mixtures.

(12) Michl, J. *Pure Appl. Chem.* **1975**, *41*, 507.

(13) More precisely, k_a competes not with k_{ed} but with that fraction of k_{ed} that involves return to ground state. The results on asymmetric induction, therefore, provide indirect evidence that formation of the 1,4-biradical is in fact the method of deactivation of the exciplex.
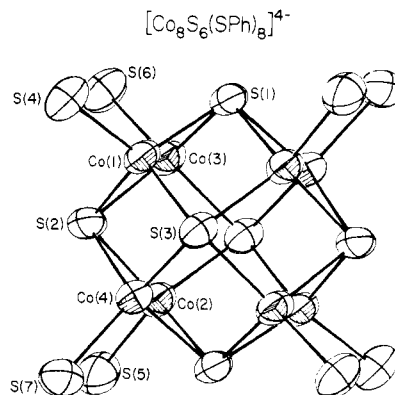
Synthesis, Structure, and Properties of $[Co_8S_6(SC_6H_5)_8]^{4-}$ Containing an Octanuclear Co_8S_6 Rhombic Dodecahedron Related to That of Cobalt Pentlandite

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The chemistry of the iron–sulfide–thiolate clusters $[Fe_nS_n-(SR)_4]^{2-,3-}$ (n = 2, 4; R = alkyl, aryl) has been developed in considerable detail.[2–8] As yet a comparably extensive chemistry of other discrete homonuclear metal–sulfide–thiolate clusters has not emerged. In particular, attempts to prepare analogous cluster species with other first-transition-series ions, employing corresponding synthetic procedures, have repeatedly failed in our hands. However, the recent syntheses of $[Fe_6S_9(S-t-Bu)_2]^{4-}$,[9] $[Fe_6S_8-(PEt_3)_6]^{2+}$,[10] and $[Ni_9S_9(PEt_3)_6]^{2+}$[11] and the presence of recog-

(1) U. K. SERC/NATO Postdoctoral Fellow, 1980–1981.
(2) Holm, R. H. *Acc. Chem. Res.* **1977**, *10*, 427.
(3) Ibers, J. A.; Holm, R. H. *Science (Washington, D.C.)* **1980**, *209*, 223.
(4) Laskowski, E. J.; Frankel, R. B.; Gillum, W. O.; Papaefthymiou, G. C.; Renaud, J.; Ibers, J. A.; Holm, R. H. *J. Am. Chem. Soc.* **1978**, *100*, 5322.
(5) Laskowski, E. J.; Reynolds, J. G.; Frankel, R. B.; Foner, S.; Papaefthymiou, G. C.; Holm, R. H. *J. Am. Chem. Soc.* **1979**, *101*, 6562.
(6) Reynolds, J. G.; Holm, R. H. *Inorg. Chem.* **1981**, *20*, 1873.
(7) Hagen, K. S.; Reynolds, J. G.; Holm, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 4054.
(8) Mascharak, P. K.; Papaefthymiou, G. C.; Frankel, R. B.; Holm, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 6110.
(9) Christou, G.; Holm, R. H.; Sabat, M.; Ibers, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 6269.

$[Co_8S_6(SPh)_8]^{4-}$

Figure 1. Structure of centrosymmetric $[Co_8S_6(SPh)_8]^{4-}$, with inequivalent atoms labeled, 50% probability ellipsoids given, and phenyl rings omitted.
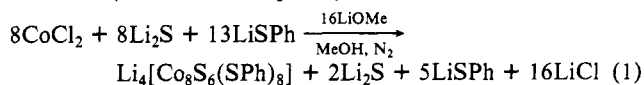
Table I. Structural Parameters of $[Co_8S_6(SPh)_8]^{4-}$ and Cobalt Pentlandite (Co_9S_8)

| dist (Å)/ angle (deg)	$[Co_8S_6(SPh)_8]^{4-}$		Co_9S_8[a]
	anion 1	anion 2	
Co⋯Co	2.636 (2)–2.682 (2) 2.662 (16)[b]	2.634 (2)–2.679 (2) 2.653 (19)[b]	2.505 (1)
Co–S	2.214 (3)–2.244 (3) 2.230 (10)[c]	2.214 (3)–2.236 (3) 2.225 (7)[c]	2.227 (1)
Co–S(Ph)	2.228 (3)–2.250 (3) 2.241 (9)[d]	2.239 (3)–2.246 (3) 2.243 (3)[d]	
Co–S–Co[e]	72.3–74.1 73.3[c]	72.6–74.0 73.2[c]	68.44 (6)
S–Co–S	105.5–107.6 106.5[c]	105.7–107.6 106.6[c]	111.4 (5)

[a] Data from ref 21. [b] Mean of six values. [c] Mean of 12 values. [d] Mean of four values. [e] Co–Co–Co: anion 1, 89.2–91.1°; anion 2, 89.7–90.5°.

nizable (but nondiscrete) clusters in sulfide minerals[12] are considered to presage a rich chemistry of metal–sulfide clusters having core structural features different from those of $[Fe_nS_n(SR)_4]^{2-,3-}$. For this reason Co(II)/S^{2-}/RS$^-$ reaction systems, among others, are being further explored.

In one Co(II)/S^{2-}/PhS$^-$ system, containing ∼1:1:6 mol ratio of reactants in methanol, a copious intractable black solid was formed together with a soluble product, isolable in slight yield as its n-Pr$_4$N$^+$ salt. Subsequently a reaction system (eq 1) containing excess methoxide[9] was found to afford the latter product

$$8CoCl_2 + 8Li_2S + 13LiSPh \xrightarrow[\text{MeOH, N}_2]{\text{16LiOMe}}$$
$$Li_4[Co_8S_6(SPh)_8] + 2Li_2S + 5LiSPh + 16LiCl \quad (1)$$

in improved and reproducible yield (10%) after purification. Following separation of the usual black precipitate, addition of n-Pr$_4$NBr to the intense red-brown filtrate and recrystallization of the resultant solid (acetonitrile/ether) gave black air-sensitive crystals of composition $(n$-Pr$_4$N$)_4[Co_8S_6(SPh)_8]\cdot$MeCN.[13] Further experimentation led to reaction 2. Here treatment of

$$2[Co_4(SPh)_{10}]^{2-} + 6HS^- \rightarrow$$
$$[Co_8S_6(SPh)_8]^{4-} + 6PhS^- + 6PhSH \quad (2)$$
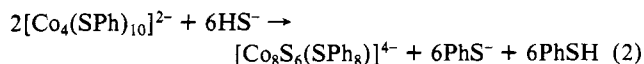
5 mmol of $(n$-Pr$_4$N$)_2[Co_4(SPh)_{10}]$[14] in 200 mL of acetone with a small excess (20 mmol) of NaHS resulted in separation of microcrystalline $(n$-Pr$_4$N$)_4[Co_8S_6(SPh)_8]$ in 50% yield after several hours.

(10) Cecconi, F.; Ghilardi, C. A.; Midollini, S. *J. Chem. Soc., Chem. Commun.* **1981**, 640.
(11) Ghilardi, C. A.; Midollini, S.; Sacconi, L. *J. Chem. Soc., Chem. Commun.* **1981**, 47.
(12) Vaughan, D. J.; Craig, J. R. "Mineral Chemistry of Metal Sulfides"; Cambridge University Press: New York, 1978.
(13) Anal. Calcd for $C_{98}H_{155}Co_8N_5S_{14}$: C, 50.66; H, 6.72; Co, 20.30; N, 3.01; S, 19.32. Found: C, 50.74; H, 6.85; Co, 20.52; N, 3.21; S, 18.66.
(14) Dance, I. G. *J. Am. Chem. Soc.* **1979**, *101*, 6264.

The structure of the compound was determined by X-ray diffraction. The unsolvated form[15] crystallizes in space group $P2_1/c$ with $a = 23.912$ (4) Å, $b = 27.466$ (6) Å, and $c = 17.173$ (6) Å, $\beta = 90.86$ (2)°, and $Z = 4$. There are two independent anions, both lying on inversion centers, and four independent cations in the asymmetric unit. The configuration of the anion, shown in Figure 1, consists of a cube of cobalt atoms within bonding distance (mean Co⋯Co distance in the two anions, 2.66 Å) circumscribed by a concentric octahedron of nonbonding sulfur atoms. This arrangement generates a rhombic dodecahedral $[Co_8(\mu_4\text{-}S)_6]^{4+}$ core unit (idealized O_h symmetry) with nearly planar Co_2S_2 faces.[16] Each cobalt atom occupies a site of local idealized C_{3v} symmetry with coordination completed by a terminal benzenethiolate ligand whose Co–S bond is an extension of the body diagonal of the Co_8 cube. Ranges and mean values of structural parameters of the two anions are collected in Table I. In terms of metal and core sulfur atom positions, $[Co_8S_6(SPh)_8]^{4-}$ is the inverse of $[Fe_6(\mu_3\text{-}S)_8(PEt_3)_6]^{2+}$,[10] in which an S_8 cube encompasses an Fe_6 octahedron.

The following properties of $[Co_8S_6(SPh)_8]^{4-}$ have been observed in acetonitrile solution: (i) a red-purple color with intense S → core charge-transfer bands at λ_{max} (ϵ_M) 343 (62 900) and 518 (30 800) nm obscuring tetrahedral Co(II) $^4A_2 \rightarrow {}^4T_1$ (ν_2), $^4T_1$(P) (ν_3) ligand field bands (if present); (ii) EPR-silent (7 K); (iii) μ_{Co} = 1.03–1.11 μ_B (233–323 K); (iv) equivalent phenyl groups with ^{1}H isotropic shifts of +2.79 (*o*-H), −1.21 (*m*-H), +4.48 (*p*-H) ppm (297 K); (v) chemically reversible ($i_{p,c} \simeq i_{p,a}$, 100 mV/s) one-electron oxidation and reduction reactions at $E_{1/2} = -0.54$ and −1.18 V vs. SCE, respectively. Mononuclear $[Co(SPh)_4]^{2-}$[14,17] and adamantane-like $[Co_4(SPh)_{10}]^{2-}$[14] (mean Co⋯Co distance 3.87 (1) Å) display larger μ_{Co} and isotropic shift values, all LMCT bands at ≤440 nm, and well-developed ν_2 and ν_3 features and do not sustain reversible oxidation and reduction reactions. The properties of $[Co_8S_6(SPh)_8]^{4-}$ and their differences with those of the foregoing species afford the view of an intact cluster in solution containing essentially equivalent and electronically coupled Co(II) sites.

Discrete species containing a cubic arrangement of directly interacting metal atoms are most uncommon. Indeed, the only previous example is $Ni_8(\mu_4\text{-}PPh)_6(CO)_8$, which is described as containing a completely bonding metal cube.[18] A much closer precedent of the core unit of $[Co_8S_6(SPh)_8]^{4-}$ is found in the extended lattice of the natural[19] and synthetic[20,21] mineral pentlandite (Co_9S_8). Here occur recognizable Co_8S_6 clusters that are linked by coordination to octahedral cobalt and tetrahedral sulfide sites. The comparison in the table demonstrates the structural similarity; metrical deviations between the soluble and mineral clusters may be due partly to the lower mean oxidation state of cobalt in the latter.

The synthesis and characterization of $[Co_8S_6(SPh)_8]^{4-}$ provides a new structural type for clusters constructed of weak field ligands and raises several attractive possibilities. One is the synthesis of other chalcogenide (X) clusters, perhaps solubilized as thiolate derivatives, that are known only in the solid state (e.g., "$Fe_4Ni_4S_6$" in one form of natural pentlandite,[19] "isolated" Mo_6X_8 and Mo_9X_{11}

clusters in certain Mo–X[22] and M–Mo–X[23] phases). A second is the occurrence of a M_8S_6 framework in the Fe–Mo–S cluster that is the FeMo cofactor of nitrogenase. The species $[L_3MoFe_7S_6(SR)_7]^{z-}$,[24] containing the MoFe7S6 core, offers reasonable consistency with current analytical and spectroscopic data of the cofactor. Such complexes and $[Co_8S_6(SPh)_8]^{3-,5-}$ are current objects of synthesis in this laboratory.

(22) Chevrel, R.; Sergent, M.; Prigent, J. *Mat. Res. Bull.* **1974**, *9*, 1487.
(23) Guillevic, J.; Bars, O.; Grandjean, D. *Acta Crystallogr. Sect. B*, **1976**, *B32*, 1338. Grüttner, A.; Yvon, K.; Chevrel, R.; Potel, M.; Sergent, M.; Seeber, B. *Ibid.* **1979**, *B35*, 285. Potel, M.; Chevrel, R.; Sergent, M. *Ibid.* **1981**, *B37*, 1007.
(24) The proposed structure, obtained by replacing cobalt atoms with seven iron atoms and a molybdenum atom in a trigonal octahedral site, is given below. Thiolate ligands, shown for the sake of definiteness, are absent in the cofactor but not necessarily in the native enzyme. The core composition falls within the range of analytical atom ratios of the cofactor: (7–8)Fe/(4–6)-S/Mo.[25] The MoFe₃S₃ core fragment is geometrically similar to one Mo site configuration deduced from EXAFS analysis of enzyme and cofactor.[26]
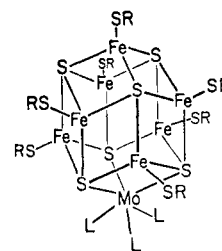
(25) Shah, V. K.; Brill, W. J. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 3249. Burgess, B. K.; Jacobs, D. B.; Stiefel, E. I. *Biochim. Biophys. Acta* **1980**, *614*, 196. Smith, B. E. In "Molybdenum Chemistry of Biological Significance"; Newton, W. E., Otsuka, S., Ed., Plenum Press: New York, 1980; pp 179–190.
(26) Cramer, S. P.; Hodgson, K. O.; Gillum, W. O.; Mortenson, L. E. *J. Am. Chem. Soc.* **1978**, *100*, 3398. Cramer, S. P.; Gillum, W. O.; Hodgson, K. O.; Mortenson, L. E.; Stiefel, E. I.; Chisnell, J. R.; Brill, W. J.; Shah, V. K. *Ibid.* **1978**, *100*, 3814.
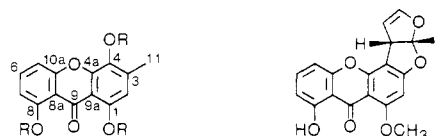
Fungal Xanthone Biosynthesis. Distribution of Acetate-Derived Oxygens in Ravenelin

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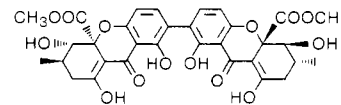Edmonton, Alberta, Canada T6G 2G2*

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Ravenelin (**1**) is a xanthone pigment isolated from the mycelium

1 R = H
7 R = Ac

3

2

of the phytopathogenic fungi *Helminthosporium ravenelii* and *H. turcicum*.[1,2] Although its biological function is undetermined,

(15) The compound has been obtained in solvated and unsolvated forms in different recrystallizations from acetonitrile/ether; the latter afforded superior crystals. From 7830 unique data ($I > 2.5\sigma(I)$) collected in the range $3.5 \leq 2\theta$ (Mo Kα radiation) ≤ 43° with a Nicolet R3M four-circle automated diffractometer, the structure was solved by use of direct methods (MULTAN) and subsequent difference Fourier maps. Anisotropic refinement of all nonhydrogen atoms with phenyl groups as rigid bodies gave $R = 5.9\%$ and the anion parameters in the table; hydrogen atoms have not been included in the refinement. A solvated form crystallizes in space group $P2_1/n$. Current refinement to $R = 9.9\%$ confirms the presence of $[Co_8S_6(SPh)_8]^{4-}$, whose metrical features are in satisfactory agreement with those in the table.
(16) Displacements from unweighted least-squares planes: Co, −(0.04–0.05) Å; S, 0.04–0.05 Å.
(17) Holah, D. G.; Coucouvanis, D. *J. Am. Chem. Soc.* **1975**, *97*, 6917. Swenson, D.; Baenziger, N. C.; Coucouvanis, D. *Ibid.* **1978**, *100*, 1932.
(18) Lower, L. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1976**, *98*, 5046.
(19) Rajamani, V.; Prewitt, C. T. *Can. Mineral.* **1973**, *12*, 178.
(20) Geller, S. *Acta Crystallogr.* **1962**, *15*, 1195.
(21) Rajamani, V.; Prewitt, C. T. *Can. Mineral.* **1975**, *13*, 75.