

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,<sup>12</sup> and is consistent with theories requiring close approach between ground and excited states for efficient decay to ground state.<sup>12,13</sup> Thus we have additional evidence that cooperativity effects can give significant mechanistic information even in the presence of rather complex reaction mixtures.

**Acknowledgment.** Support by the National Science Foundation through Grant CHE-80-24644 is gratefully acknowledged.

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(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.

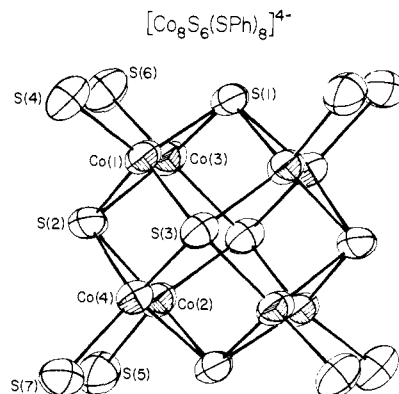
### Synthesis, Structure, and Properties of $[\text{Co}_8\text{S}_6(\text{SPh})_8]^{4-}$ Containing an Octanuclear $\text{Co}_8\text{S}_6$ Rhombic Dodecahedron Related to That of Cobalt Pentlandite

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The chemistry of the iron-sulfide-thiolate clusters  $[\text{Fe}_n\text{S}_n(\text{SR})_4]^{2-3-}$  ( $n = 2, 4$ ; R = alkyl, aryl) has been developed in considerable detail.<sup>2-8</sup> 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  $[\text{Fe}_6\text{S}_9(\text{S}-t\text{-Bu})_2]^{4-}$ ,<sup>9</sup>  $[\text{Fe}_6\text{S}_8(\text{PET}_3)_6]^{2+}$ ,<sup>10</sup> and  $[\text{Ni}_9\text{S}_9(\text{PET}_3)_6]^{2+}$ <sup>11</sup> and the presence of recog-



**Figure 1.** Structure of centrosymmetric  $[\text{Co}_8\text{S}_6(\text{SPh})_8]^{4-}$ , with inequivalent atoms labeled, 50% probability ellipsoids given, and phenyl rings omitted.

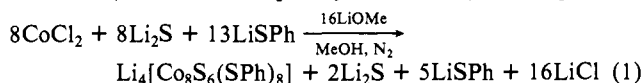
**Table I.** Structural Parameters of  $[\text{Co}_8\text{S}_6(\text{SPh})_8]^{4-}$  and Cobalt Pentlandite ( $\text{Co}_9\text{S}_8$ )

dist (Å)/ angle (deg)	$[\text{Co}_8\text{S}_6(\text{SPh})_8]^{4-}$			$\text{Co}_9\text{S}_8^a$
	anion 1	anion 2		
Co...Co	2.636 (2)–2.682 (2)	2.634 (2)–2.679 (2)		2.505 (1)
	2.662 (16) <sup>b</sup>	2.653 (19) <sup>b</sup>		
Co-S	2.214 (3)–2.244 (3)	2.214 (3)–2.236 (3)		2.227 (1)
	2.230 (10) <sup>c</sup>	2.225 (7) <sup>c</sup>		
Co-S(Ph)	2.228 (3)–2.250 (3)	2.239 (3)–2.246 (3)		
	2.241 (9) <sup>d</sup>	2.243 (3) <sup>d</sup>		
Co-S-Co <sup>e</sup>	72.3–74.1	72.6–74.0		68.44 (6)
	73.3 <sup>c</sup>	73.2 <sup>c</sup>		
S-Co-S	105.5–107.6	105.7–107.6		111.4 (5)
	106.5 <sup>c</sup>	106.6 <sup>c</sup>		

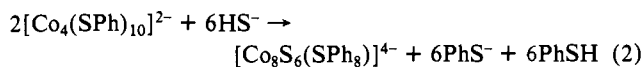
<sup>a</sup> Data from ref 21. <sup>b</sup> Mean of six values. <sup>c</sup> Mean of 12 values. <sup>d</sup> Mean of four values. <sup>e</sup> Co-Co-Co: anion 1, 89.2–91.1°; anion 2, 89.7–90.5°.

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

In one Co(II)/ $\text{S}^{2-}/\text{PhS}^-$  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  $n\text{-Pr}_4\text{N}^+$  salt. Subsequently a reaction system (eq 1) con-



taining excess methoxide<sup>9</sup> was found to afford the latter product in improved and reproducible yield (10%) after purification. Following separation of the usual black precipitate, addition of  $n\text{-Pr}_4\text{NBr}$  to the intense red-brown filtrate and recrystallization of the resultant solid (acetonitrile/ether) gave black air-sensitive crystals of composition  $(n\text{-Pr}_4\text{N})_4[\text{Co}_8\text{S}_6(\text{SPh})_8] \cdot \text{MeCN}$ .<sup>13</sup> Further experimentation led to reaction 2. Here treatment of



5 mmol of  $(n\text{-Pr}_4\text{N})_2[\text{Co}_4(\text{SPh})_{10}]^{14}$  in 200 mL of acetone with a small excess (20 mmol) of NaHS resulted in separation of microcrystalline  $(n\text{-Pr}_4\text{N})_4[\text{Co}_8\text{S}_6(\text{SPh})_8]$  in 50% yield after several hours.

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The structure of the compound was determined by X-ray diffraction. The unsolvated form<sup>15</sup> crystallizes in space group  $P2_1/c$  with  $a = 23.912(4)$  Å,  $b = 27.466(6)$  Å, and  $c = 17.173(6)$  Å,  $\beta = 90.86(2)^\circ$ , 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  $[\text{Co}_8(\mu_4\text{-S})_6]^{4+}$  core unit (idealized  $O_h$  symmetry) with nearly planar  $\text{Co}_2\text{S}_2$  faces.<sup>16</sup> 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  $\text{Co}_8$  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,  $[\text{Co}_8\text{S}_6(\text{SPh})_8]^{4-}$  is the inverse of  $[\text{Fe}_6(\mu_3\text{-S})_8(\text{PET}_3)_6]^{2+}$ ,<sup>10</sup> in which an  $\text{S}_8$  cube encompasses an  $\text{Fe}_6$  octahedron.

The following properties of  $[\text{Co}_8\text{S}_6(\text{SPh})_8]^{4-}$  have been observed in acetonitrile solution: (i) a red-purple color with intense S  $\rightarrow$  core charge-transfer bands at  $\lambda_{\text{max}}$  ( $\epsilon_M$ ) 343 (62900) and 518 (30800) nm obscuring tetrahedral Co(II)  $^4A_2 \rightarrow ^4T_1(\nu_2)$ ,  $^4T_1(P)$  ( $\nu_3$ ) ligand field bands (if present); (ii) EPR-silent (7 K); (iii)  $\mu_{\text{Co}} = 1.03\text{--}1.11 \mu_B$  (233–323 K); (iv) equivalent phenyl groups with  $^1\text{H}$  isotropic shifts of +2.79 (*o*-H), -1.21 (*m*-H), +4.48 (*p*-H) ppm (297 K); (v) chemically reversible ( $i_{p,c} \approx i_{p,a}$ , 100 mV/s) one-electron oxidation and reduction reactions at  $E_{1/2} = -0.54$  and  $-1.18$  V vs. SCE, respectively. Mononuclear  $[\text{Co}(\text{SPh})_4]^{2-}$ ,<sup>14,17</sup> and adamantane-like  $[\text{Co}_4(\text{SPh})_{10}]^{2-}$ <sup>14</sup> (mean Co...Co distance 3.87 (1) Å) display larger  $\mu_{\text{Co}}$  and isotropic shift values, all LMCT bands at  $\leq 440$  nm, and well-developed  $\nu_2$  and  $\nu_3$  features and do not sustain reversible oxidation and reduction reactions. The properties of  $[\text{Co}_8\text{S}_6(\text{SPh})_8]^{4-}$  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  $\text{Ni}_8(\mu_4\text{-PPH})_6(\text{CO})_8$ , which is described as containing a completely bonding metal cube.<sup>18</sup> A much closer precedent of the core unit of  $[\text{Co}_8\text{S}_6(\text{SPh})_8]^{4-}$  is found in the extended lattice of the natural<sup>19</sup> and synthetic<sup>20,21</sup> mineral pentlandite ( $\text{Co}_9\text{S}_8$ ). Here occur recognizable  $\text{Co}_8\text{S}_6$  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  $[\text{Co}_8\text{S}_6(\text{SPh})_8]^{4-}$  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., " $\text{Fe}_4\text{Ni}_4\text{S}_6$ " in one form of natural pentlandite,<sup>19</sup> "isolated"  $\text{Mo}_6\text{X}_8$  and  $\text{Mo}_9\text{X}_{11}$

clusters in certain  $\text{Mo-X}^{22}$  and  $\text{M-Mo-X}^{23}$  phases). A second is the occurrence of a  $\text{M}_8\text{S}_6$  framework in the Fe-Mo-S cluster that is the  $\text{FeMo}$  cofactor of nitrogenase. The species  $[\text{L}_3\text{MoFe}_7\text{S}_6(\text{SR})_7]^{2-}$ ,<sup>24</sup> containing the  $\text{MoFe}_7\text{S}_6$  core, offers reasonable consistency with current analytical and spectroscopic data of the cofactor. Such complexes and  $[\text{Co}_8\text{S}_6(\text{SPh})_8]^{3-}$ ,<sup>5</sup> are current objects of synthesis in this laboratory.

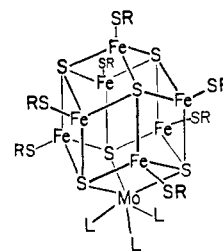
**Acknowledgment.** This research was supported by NSF Grant CHE 81-06017. X-ray and NMR equipment used in this research were funded by NSF Grants CHE 80-00670 and CHE 80-08891.

**Registry No.**  $(n\text{-Pr}_4\text{N})_4[\text{Co}_8\text{S}_6(\text{SPh})_8]$ , 80753-71-5;  $(n\text{-Pr}_4\text{N})_2[\text{Co}_4(\text{SPh})_{10}]$ , 80720-97-4.

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(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.<sup>25</sup> The  $\text{MoFe}_3\text{S}_3$  core fragment is geometrically similar to one Mo site configuration deduced from EXAFS analysis of enzyme and cofactor.<sup>26</sup>



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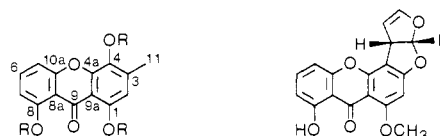
## Fungal Xanthone Biosynthesis. Distribution of Acetate-Derived Oxygens in Ravenelin

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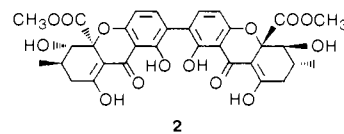
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Ravenelin (**1**) is a xanthone pigment isolated from the mycelium



1 R = H

7 R = Ac



2

of the phytopathogenic fungi *Helminthosporium ravenelii* and *H. turcicum*.<sup>1,2</sup> 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 K $\alpha$  radiation)  $\leq 43^\circ$  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 non-hydrogen 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  $[\text{Co}_8\text{S}_6(\text{SPh})_8]^{4-}$ , whose metrical features are in satisfactory agreement with those in the table.

(16) Displacements from unweighted least-squares planes: Co,  $-(0.04\text{--}0.05)$  Å; S,  $0.04\text{--}0.05$  Å.

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