may take place, probably rigidifying the whole set of bonds in the adduct.[28] That the different steric constraints in the diastereomeric precursor complexes could have an ultimate influence on the specific rates of the electron-transfer step of the two reactions is reasonable in view of the fact that both nuclear and electronic factors of the rate constants of electron-transfer processes are highly sensitive to the separation and orientation of the redox centers.[29,30] This is indeed the case, as shown in Table II. Unfortunately, the complexity of the systems investigated makes it difficult at present to attempt any calculation of rate constants. A further complication arises from the fact that electron transfer between the substrate bound to the helical polypeptide in the surrounding of the catalytic centers and the iron(III) ion can proceed only by a remote-attack mechanism, probably making use of the π system of the peripheral quaterpyridine ligand of the active sites. This pathway is feasible on stereochemical grounds[20] and is consistent with the change in the reactivity patterns of the catalysis[31a] in going from low to high $[C]/[P]$ ratios (Table I and Figure 5). It is also reminiscent of the mechanism proposed for a number of redox reactions between ferriporphyrins or metalloproteins and different reductants.[4c,31,32] We may therefore conclude with some confidence that the stereoselective route to adrenochrome does not involve substitution on the iron center but that the reaction proceeds through an electron-transfer site far from the central metal ion, possibly the edge of quaterpyridyl group.

To summarize, depending upon the structural features of the catalysts, the oxidation of L-adrenaline can proceed by direct or remote attack, each pathway giving rise to quite different stereospecific effects because of the different stereochemical characteristics of the precursor complex. The kinetics of the catalysis are reminiscent of some enzymic peroxidatic reactions. The similarity is even greater if one considers that hemin bound to glutamyl residues is supposed to be the active site of catalases.[33] This similarity is, however, rather formal as the precursor complexes are different in the two cases, that of the oxidation reactions on peroxidases being probably a ternary adduct. Nevertheless, the specific effects of polypeptide matrices on the stereoselective pattern of the catalytic process may perhaps contribute to certain enzymic reactions.

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Registry No. II, 51-43-4; H_2O_2, 7722-84-1; peroxidase, 9003-99-0.

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Notes

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Stereochemistry of $[Cd_4(SC_6H_5)_{10}]^{2-}$, a Cage Complex Related to the Cadmium–Cysteinate Aggregates in Metallothioneins

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As observed earlier,[1] the adamantane-like cage $M_4(\mu\text{-}S)_6$ is the most frequently encountered structural unit of polynuclear metal thiolates. It has been established by X-ray analysis in $[M_4(SPh)_{10}]^{2-}$ (M = Mn(II),[2] Fe(II),[1,3] Co(II),[4] Zn(II)[5]), $[Fe_4(SPh)_6Cl_4]^{2-}$,[6] $[Zn_4(SPh)_8Cl_2]^{2-}$,[7] and $[Zn_4(SPh)_8(MeOH)]_n$.[8] In our ongoing development of metal–thiolate chemistry we have demonstrated the utility of the Fe(II)[9,10] and Co(II)[11] complexes as synthetic precursors of M–S–SR clusters. The adamantane-like structure of $[Fe_4(SEt)_{10}]^{2-}$ [12] demonstrates that the cage can be stabilized by a ligand other than benzenethiolate bridging two M(II) sites. The scope of cage formation with transition-element ions has also been examined. The preparation of a compound corresponding to the formulation $(Et_4N)_2[Cd_4(SPh)_{10}]$ and associated NMR studies[1] have provided evidence, although not definitive, for the existence of the cage structure containing a metal ion with a tetrahedral radius (0.92 Å[13]) some 0.12–0.20 Å larger than those of the preceding first-transition-series ions. The species $[Cd_4(SPh)_{10}]^{2-}$ has been mentioned on earlier occasions by Dance,[7,8] and the preparation of the Me_4N^+ salt has been described briefly by Choy et al.,[14] who depicted the anion as an adamantane-like cage. Structural data were not reported. A possible relationship between the structures of $[Cd_4(SPh)_{10}]^{2-}$ and the cadmium(II)–cysteinate aggregates in metallothionein proteins as deduced from ^{113}Cd NMR studies[15-19] has been raised by ourselves[1] and others.[8,20] To provide

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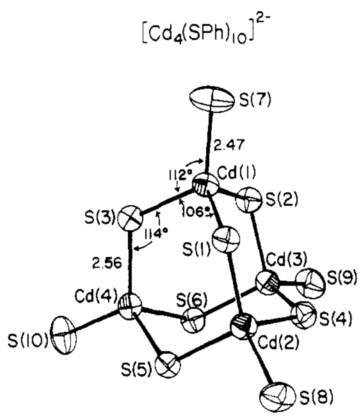

Figure 1. Structure of $[Cd_4(SPh)_{10}]^{2-}$ (phenyl groups omitted), showing 50% probability ellipsoids, the atom-numbering scheme, and mean values of independent bond angles and distances (Å) under idealized T_d symmetry.

structural definition of $[Cd_4(SPh)_{10}]^{2-}$ and examine this relationship, we report here the results of an X-ray structural determination of the complex.

Experimental Section

A crystal of dimensions 0.22 × 0.30 × 0.48 mm was obtained by vapor diffusion of ether into an acetonitrile solution of the compound formulated as $(Et_4N)_2[Cd_4(SPh)_{10}]$ on the basis of elemental analysis.[1] By use of a Nicolet R3m diffractometer and graphite-monochromatized Mo Kα radiation the following crystal data were obtained by least-squares treatment of 25 indexed, machine-centered reflections ($25° < 2\theta < 30°$): $a = 13.846$ (5) Å, $b = 34.782$ (6) Å, $c = 21.528$ (8) Å, $\beta = 130.84$ (2)°. Data were collected at ambient temperature by the $\theta/2\theta$ scan technique at variable scan speed (3–30°/min) and background intensities for one-fourth of the scan times at the limits of the 1.6° scan range. Check reflections exhibited no decay. The systematic absences $h0l$ ($h = 2n + 1$) and $0k0$ ($k = 2n + 1$) uniquely define the monoclinic space group $P2_1/c$. The data were transformed to the equivalent nonstandard space group $P2_1/n$: $a = 13.846$ (5) Å, $b = 34.782$ (6) Å, $c = 16.291$ (4) Å, $\beta = 90.82$ (2)°, $V = 7844$ (3) Å^3, $Z = 4$ for $C_{74}H_{86}Cd_4N_2S_{10}$ ($M_r = 1773.3$), $d_{calcd} = 1.502$ g/cm^3, $d_{obsd} = 1.50$ g/cm^3. An empirical absorption correction was applied ($\mu = 13.5$ cm^{-1}). The SHELXTL program package (Nicolet XRD Corp., Fremont, CA) was used for data processing and structure solution and refinement. Cadmium atom positions were found by direct methods and those of other non-hydrogen atoms from Fourier maps on the partially refined structure with the Cd atoms refined anisotropically. Benzene rings were treated as rigid groups (C–C = 1.395 Å). One of the cations, identified as Et_3NH^+, exhibited a disorder of methylene carbon atoms, each having equal occupancy. The other cation (Et_4N^+) as well-behaved. Final refinement included all atoms except one carbon atom of the disordered cation treated anisotropically and fixed contributions from hydrogen atoms (C–H = 0.96 Å) with temperature factors set at 1.2 times that of the bonded carbon atom. With use of 5082 data ($I > 3\sigma(I)$) the refinement yielded the conventional discrepancy factors R (R_w) = 3.9% (4.2%) and a goodness of fit of 1.35. The X-ray analysis was performed on the compound $(Et_4N)(Et_3NH)[Cd_4(SPh)_{10}]$ rather than on the $(Et_4N^+)_2$ salt, for which $d_{calcd} = 1.524$ g/cm^3. The two compounds are indistinguishable from the analytical data reported.[1] Anion positional parameters are listed in Table I.[21]

Results and Discussion

The crystal structure of $(Et_4N)(Et_3NH)[Cd_4(SPh)_{10}]$ consists of discrete cations and anions. Cation structures are unexceptional.[21] The structure of the Cd_4S_{10} portion of the anion is given in Figure 1, and a stereoview of the entire anion is presented in Figure S-1 (supplementary material). Selected interatomic distances and angles are compiled in Table II.

Table I. Positional Parameters of $[Cd_4(SPh)_{10}]^{2-}$ [a]

atom	*x*	*y*	*z*
Cd(1)	−0.1387 (1)	0.1320 (1)	0.4045 (1)
Cd(2)	0.0626 (1)	0.0795 (1)	0.2551 (1)
Cd(3)	−0.1316 (1)	0.1577 (1)	0.1377 (1)
Cd(4)	−0.2320 (1)	0.0470 (1)	0.2270 (1)
S(1)	0.0244 (2)	0.0974 (1)	0.4020 (2)
S(2)	−0.1838 (2)	0.1774 (1)	0.2828 (2)
S(3)	−0.2627 (2)	0.0815 (1)	0.3626 (1)
S(4)	0.0458 (2)	0.1402 (1)	0.1671 (2)
S(5)	−0.0553 (2)	0.0271 (1)	0.2050 (2)
S(6)	−0.2244 (2)	0.0963 (1)	0.1085 (2)
S(7)	−0.1446 (3)	0.1636 (1)	0.5397 (2)
S(8)	0.2233 (2)	0.0526 (1)	0.2222 (2)
S(9)	−0.1637 (3)	0.2080 (1)	0.0347 (2)
S(10)	−0.3586 (2)	0.0027 (1)	0.1775 (2)
C(11)	0.1035 (6)	0.1363 (2)	0.4260 (4)
C(21)	0.1710 (6)	0.1309 (2)	0.4888 (4)
C(31)	0.2344 (6)	0.1603 (2)	0.5099 (4)
C(41)	0.2303 (6)	0.1950 (2)	0.4683 (4)
C(51)	0.1628 (6)	0.2004 (2)	0.4056 (4)
C(61)	0.0994 (6)	0.1710 (2)	0.3844 (4)
C(12)	−0.1287 (7)	0.2223 (3)	0.3069 (5)
C(22)	−0.1515 (7)	0.2409 (3)	0.3795 (5)
C(32)	−0.1091 (7)	0.2759 (3)	0.3987 (5)
C(42)	−0.0439 (7)	0.2925 (3)	0.3452 (5)
C(52)	−0.0211 (7)	0.2739 (3)	0.2725 (5)
C(62)	−0.0635 (7)	0.2389 (3)	0.2534 (5)
C(13)	−0.2478 (4)	0.0430 (2)	0.4356 (5)
C(23)	−0.3225 (4)	0.0347 (2)	0.4887 (5)
C(33)	−0.3145 (4)	0.0039 (2)	0.5424 (5)
C(43)	−0.2318 (4)	0.0187 (2)	0.5429 (5)
C(53)	−0.1570 (4)	0.0103 (2)	0.4898 (5)
C(63)	−0.1650 (4)	0.0205 (2)	0.4362 (5)
C(14)	0.0973 (6)	0.1272 (2)	0.0705 (6)
C(24)	0.1575 (6)	0.1536 (2)	0.0329 (6)
C(34)	0.1982 (6)	0.1450 (2)	0.0423 (6)
C(44)	0.1786 (6)	0.1100 (2)	0.0798 (6)
C(54)	0.1184 (6)	0.0836 (2)	0.0421 (6)
C(64)	0.0778 (6)	0.0922 (2)	0.0330 (6)
C(15)	−0.0362 (4)	−0.0162 (2)	0.2632 (4)
C(25)	−0.1072 (4)	0.0444 (2)	0.2592 (4)
C(35)	−0.0945 (4)	−0.0787 (2)	0.3014 (4)
C(45)	−0.0109 (4)	−0.0849 (2)	0.3475 (4)
C(55)	0.0601 (4)	−0.0567 (2)	0.3515 (4)
C(65)	0.0474 (4)	−0.0224 (2)	0.3094 (4)
C(16)	−0.3451 (6)	0.1123 (2)	0.0901 (4)
C(26)	−0.4146 (6)	0.1119 (2)	0.1507 (4)
C(36)	−0.5095 (6)	0.1216 (2)	0.1315 (4)
C(46)	−0.5349 (6)	0.1318 (2)	0.0517 (4)
C(56)	−0.4654 (6)	0.1322 (2)	−0.0089 (4)
C(66)	−0.3705 (6)	0.1225 (2)	0.0103 (4)
C(17)	−0.2672 (8)	0.1780 (3)	0.5499 (5)
C(27)	−0.2896 (8)	0.2154 (3)	0.5719 (5)
C(37)	−0.3854 (8)	0.2261 (3)	0.5818 (5)
C(47)	−0.4587 (8)	0.1994 (3)	0.5697 (5)
C(57)	−0.4362 (8)	0.1620 (3)	0.5476 (5)
C(67)	−0.3404 (8)	0.1513 (3)	0.5378 (5)
C(18)	0.3156 (6)	0.0746 (2)	0.2759 (5)
C(28)	0.4007 (6)	0.0541 (2)	0.2872 (5)
C(38)	0.4775 (6)	0.0703 (2)	0.3306 (5)
C(48)	0.4690 (6)	0.1071 (2)	0.3627 (5)
C(58)	0.3839 (6)	0.1276 (2)	0.3514 (5)
C(68)	0.3072 (6)	0.1114 (2)	0.3080 (5)
C(19)	−0.1679 (5)	0.1827 (2)	−0.0611 (5)
C(29)	−0.0973 (5)	0.1564 (2)	−0.0824 (5)
C(39)	−0.1003 (5)	0.1390 (2)	−0.1591 (5)
C(49)	−0.1739 (5)	0.1481 (2)	−0.2146 (5)
C(59)	−0.2445 (5)	0.1744 (2)	−0.1933 (5)
C(69)	−0.2415 (5)	0.1917 (2)	−0.1166 (5)
C(110)	0.3718 (7)	−0.0377 (3)	0.2395 (5)
C(210)	0.3866 (7)	−0.0730 (3)	0.2017 (5)
C(310)	0.3997 (7)	−0.1057 (3)	0.2488 (5)
C(410)	0.3981 (7)	−0.1032 (3)	0.3339 (5)
C(510)	0.3833 (7)	−0.0679 (3)	0.3717 (5)
C(610)	0.3702 (7)	−0.0352 (3)	0.3245 (5)

[a] Numbering scheme: C(*xy*) is C(*x*) of ring S(*y*).

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(21) See paragraph at end of paper regarding additional structural data in the supplementary material.

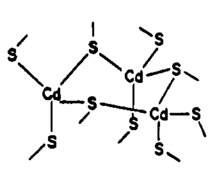
Table II. Selected Interatomic Distances (Å) and Angles (deg) for $[Cd_4(SPh)_{10}]^{2-}$

	$Cd\text{-}S_t$[a]		
Cd(1)-S(7)	2.465 (4)	Cd(4)-S(10)	2.463 (4)
Cd(2)-S(8)	2.480 (3)	mean	2.467 (9)[b]
Cd(3)-S(9)	2.460 (4)		
	$Cd\text{-}S_b$[a]		
Cd(1)-S(1)	2.559 (3)	Cd(3)-S(2)	2.574 (3)
Cd(1)-S(2)	2.603 (3)	Cd(3)-S(4)	2.569 (3)
Cd(1)-S(3)	2.544 (3)	Cd(3)-S(6)	2.533 (3)
Cd(2)-S(1)	2.535 (3)	Cd(4)-S(3)	2.553 (3)
Cd(2)-S(4)	2.561 (3)	Cd(4)-S(5)	2.573 (3)
Cd(2)-S(5)	2.572 (3)	Cd(4)-S(6)	2.587 (3)
		mean	2.56 (2)
	Cd···Cd		
Cd(1)–Cd(2)	4.149 (3)	Cd(2)–Cd(3)	4.259 (3)
Cd(1)–Cd(3)	4.439 (3)	Cd(2)–Cd(4)	4.250 (3)
Cd(1)–Cd(4)	4.320 (3)	Cd(3)–Cd(4)	4.351 (3)
		mean	4.30 (10)
	$S_b\cdots S_b$		
S(1)-S(2)	4.434 (4)	S(3)-S(5)	4.316 (4)
S(1)-S(3)	4.055 (4)	S(3)-S(6)	4.213 (5)
S(1)-S(4)	4.120 (4)	S(4)-S(5)	4.224 (5)
S(1)-S(5)	4.171 (4)	S(4)-S(6)	4.139 (5)
S(2)-S(3)	3.750 (5)	S(5)-S(6)	3.695 (4)
S(2)-S(4)	3.938 (5)	mean	4.09 (22)
S(2)-S(6)	4.036 (5)		
	S–C		
range	1.719 (8)–1.800 (8)	mean	1.78 (3)
	$S_b\text{–}Cd\text{–}S_t$		
S(1)–Cd(1)–S(7)	105.3 (1)	S(2)–Cd(3)–S(9)	112.8 (1)
S(2)–Cd(1)–S(7)	113.5 (1)	S(4)–Cd(3)–S(9)	117.3 (1)
S(3)–Cd(1)–S(7)	121.1 (1)	S(6)–Cd(3)–S(9)	112.6 (1)
S(1)–Cd(2)–S(8)	119.8 (1)	S(3)–Cd(4)–S(10)	116.8 (1)
S(4)–Cd(2)–S(8)	105.4 (1)	S(5)–Cd(4)–S(10)	117.4 (1)
S(5)–Cd(2)–S(8)	103.3 (1)	S(6)–Cd(4)–S(10)	102.0 (1)
		mean	112.3
	$S_b\text{–}Cd\text{–}S_b$		
S(1)–Cd(1)–S(2)	118.4 (1)	S(2)–Cd(3)–S(4)	99.9 (1)
S(1)–Cd(1)–S(3)	105.2 (1)	S(2)–Cd(3)–S(6)	104.4 (1)
S(2)–Cd(1)–S(3)	93.5 (1)	S(4)–Cd(3)–S(6)	108.4 (1)
S(1)–Cd(2)–S(4)	107.9 (1)	S(3)–Cd(4)–S(5)	114.7 (1)
S(1)–Cd(2)–S(5)	109.5 (1)	S(3)–Cd(4)–S(6)	110.1 (1)
S(4)–Cd(2)–S(5)	110.8 (1)	S(5)–Cd(4)–S(6)	91.5 (1)
		mean	106.2
	$Cd\text{–}S_b\text{–}Cd$		
Cd(1)–S(1)–Cd(2)	109.1 (1)	Cd(2)–S(4)–Cd(3)	112.2 (1)
Cd(1)–S(2)–Cd(3)	118.0 (1)	Cd(2)–S(5)–Cd(4)	111.4 (1)
Cd(1)–S(3)–Cd(4)	115.9 (1)	Cd(3)–S(6)–Cd(4)	116.4 (1)
		mean	113.8

[a] t = terminal and b = bridging ligand. [b] The standard deviation of the mean was estimated from $\sigma \approx s = [(\Sigma x_i^2 - n\bar{x}^2)/(n-1)]^{1/2}$.

The principal structural features of $[Cd_4(SPh)_{10}]^{2-}$ are summarized as follows. (i) The complex contains an adamantane-like $Cd_4(\mu\text{-}S)_6$ cage, composed of a distorted Cd_4 tetrahedron (Cd–Cd–Cd = 56.9 (1)–63.7 (1)°, mean 60.0 (1.9)°) and a highly and irregularly distorted S_6 octahedron. The cage does not closely approach the T_d symmetry of adamantane. (ii) Departure of the cage from T_d symmetry is especially emphasized by the large ranges of $S_b\cdots S_b$ nonbonded distances (3.695 (4)–4.434 (4) Å) and $S_b\text{–}Cd\text{–}S_b$ angles (91.5 (1)–118.4 (1)°). (iii) Each Cd(II) atom has one terminal thiolate ligand bound in a distorted tetrahedral CdS_4 unit. Substantial deviations from local C_{3v} symmetry are apparent from large variations in $S_b\text{–}Cd\text{–}S_t$ and $S_b\text{–}Cd\text{–}S_b$ angles of each unit. (iv) The mean of the $Cd\text{–}S_t$ bond lengths is 0.09 Å smaller than that of $Cd\text{–}S_b$ bonds. These values span the mean Cd–S distance (2.54 (1) Å) in tetrahedral $[Cd(SPh)_4]^{2-}$.[22] The mean $Cd\text{–}S_b$ distance is at the high end of the range of such distances (2.50–2.58 Å) in tetrahedral CdS_4 units of thiolate complexes.[23-26] (v) The six axial phenyl groups in the four chairlike $Cd_3(\mu\text{-}S)_3$ rings of the cage occur in the 2-2-1-1 pattern,[21] specified by the number of axial substituents in each ring. (vi) The volumes of the Cd_4 (9.46 Å^3) and S_6 (32.23 Å) portions of the cage (calculated from atomic coordinates) are 39% and 31% larger, respectively, than those in $[Co_4(SPh)_{10}]^{2-}$, the smallest M(II) cage complex. As shown for $M_4(\mu\text{-}S)_6$ cages[1,2] component volumes scaled to $[Co_4(SPh)_{10}]^{2-}$ as a base change in close proportion to changes in the Shannon[13] M(II) tetrahedral radii. Features i–iv, with different quantitative measures, apply to all M(II) cage complex structures,[1-8] which are compared elsewhere.[2]

Studies of metallothioneins from different sources by Armitage and co-workers[15-19] using ^{113}Cd NMR have provided the most incisive information concerning the structures of metal coordination sites. For mammalian proteins sequestration of the seven Cd(II) ions into the aggregates $Cd_3(Cys\text{-}S)_9$ (**1**) and $Cd_4(Cys\text{-}S)_{11}$ (**2**) has been deduced. The indicated structures utilize all 20 cysteinyl residues, known from chemical evidence to lack free thiol groups, and involve distorted tetrahedral coordination sites. The consistencies of signal multiplicities and chemical shifts[18] of proteins from different sources argue for structural constancy of the aggregates, one of which (**2**) has been identified in a polypeptide cleaved from the native rat liver protein and having 11 cysteinyl residues and >3 Cd atoms.[19] Crab metallothionein has two aggregates **1**.[17] The proposed structures **1** and **2** contain distorted tetrahedral CdS_4 units and $Cd_3(\mu\text{-}S)_3$ rings. The former find substantial precedent in the structures of cadmium(II)–thiolate complexes[14,22-24,26] including $[Cd_4(SPh)_{10}]^{2-}$ and are consistent with spectral and magnetic data for M(II)-substituted proteins,[20,27] strongly deshielded ^{113}Cd chemical shifts found in synthetic Cd–SR complexes,[28,29] and the presence of nuclear quadrupole interactions in the ^{111}Cd γ-ray spectrum of a liver protein.[30] The feasibility of $Cd_3(\mu\text{-}S)_3$ rings in the proteins is well supported by the occurrence of such rings in $[Cd_4(SPh)_{10}]^{2-}$. This is the only characterized tetranuclear Cd(II)–SR complex; trinuclear Cd(II)–SR species have not been reported. Nearly all other cadmium(II) thiolates of known structure are of higher nuclearity,[14,23,24,26,31] and none contains a $Cd_3(\mu\text{-}SR)_3$ ring. However, $[Cd_{10}(\mu_3\text{-}S)_4(\mu\text{-}SPh)_{12}(SPh)_4]^{4-}$, prepared by reaction of $[Cd_4(SPh)_{10}]^{2-}$ and elemental sulfur, contains four fused adamantane-like cages.[14] Comparable Cd(II)–SR bond distances are within ~0.01 Å of those of $[Cd_4(SPh)_{10}]^{2-}$.



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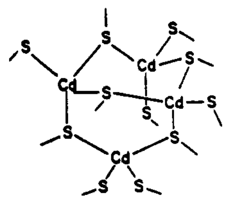

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Supplementary Material Available: Listings of positional and thermal parameters of cations, thermal parameters of the anion, calculated H atom coordinates and temperature factors, and calculated and observed structure factors and a stereoview of the anion (36 pages). Ordering information is given on any current masthead page.

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Characterization of a Dimeric Iron(III) Complex of *N*,*N'*-Ethylenebis(salicylamine)

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In the literature there are a number of reports of iron(III) complexes of the ligand *N*,*N'*-ethylenebis(salicyclideneamine), salen, which include both five- and six-coordinate iron atoms as well as monomeric and dimeric species.[1-6] Some of the dimeric complexes contain oxo bridges while others contain an alkoxy bridge. The variations depend upon the method of preparation and the crystallization procedures used. Recently we have reported the preparation of a dihydroxy-bridged Fe(III) complex of the hydrogenated form of salen, namely, *N*,*N'*-ethylenebis(salicylamine), salen–H.[7] Here we report the preparation and characterization of a dialkoxy-bridged complex of this ligand. The ligand differs from salen in that it contains saturated nitrogen atoms; therefore, greater flexibility of the ligand is expected and the planarity of the ligand in bonding may be disturbed.

Experimental Section

(1) Preparation of $[Fe(salen–H)Cl]_2 \cdot 2H_2O$. The procedures followed were those of Gerloch et al.[4] The ligand (1.4 g) was dissolved in 30 mL of ethanol (or methanol). Anhydrous $FeCl_3$ (1.0 g) was dissolved in 10 mL of ethanol. The iron solution was added to the ligand solution, and immediately a dark purple solution formed. This solution was stirred for 30 min and then filtered. A purple-black precipitate was collected and washed with water and then with ethanol; mp 250 °C dec. Anal. Calcd for $[Fe(C_{16}H_{18}N_2O_2)Cl]_2 \cdot 2H_2O$: C, 50.82; H, 5.31; N, 7.38; Fe, 14.71; Cl, 9.34. Found: C, 50.76; H, 5.06; N, 7.22; Fe, 15.49; Cl, 9.52. No molecular weight was obtained for this complex due to the low solubility in common organic solvents. All attempted procedures for crystallization failed. Similar procedures using $FeBr_3$ instead of the chloride gave no precipitate but only a deep purple solution; therefore characterization of a corresponding complex could not be done.

(2) Instrumentation. Thermal analysis was done on a Du Pont 751 thermogravimetric analyzer and a 990 thermal analyzer in an argon atmosphere with a flow rate of 50 cm^3/min and a heating rate of 100 °C/10 min.

Elemental analyses were done by Galbraith Laboratories, Knoxville, TN.

The mass spectrum was obtained on a Hewlett-Packard 5985B GC/MS system by direct probe. The temperature was varied from 30 to 300 °C over approximately a 15-min period of time.

The electric conductivity of methanol and acetone solutions was measured by mean of a Lazar Cond-156 conductivity probe.

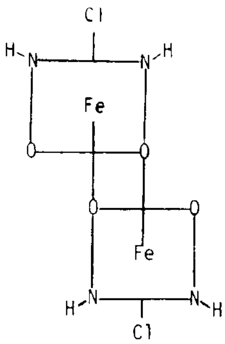

Figure 1. Proposed structure for $[Fe(salen–H)Cl]_2 \cdot 2H_2O$.

The UV–visible spectra were obtained on a Cary 14 spectrophotometer. Samples were run on 10^{-4} M solutions in methanol, water, and pyridine. The infrared spectra were obtained on a Perkin-Elmer 621 spectrophotometer. The samples were run as KBr pellets from 4000 to 200 cm^{-1} and on a polyethylene disk from 400 to 200 cm^{-1}.

The EPR spectra were taken on a Varian E-4 EPR spectrometer. A powder spectrum was obtained at room temperature, and a pyridine solution spectrum was obtained both at room temperature and at −180 °C in a quartz low-temperature cell. Variable-temperature magnetic susceptibility data were obtained on ~10-mg samples by using the Faraday method. Liquid nitrogen was used as the cryogenic material to obtain the low-temperature readings. The standard used was $Hg[Co(SCN)_4]$. Details of the Mössbauer spectrometer have been reported previously.[8]

Results and Discussion

The structure of $[Fe(salen–H)Cl]_2 \cdot 2H_2O$ is assumed to be that similar to the salen complex having the same formulation as shown in Figure 1. The only difference is that the compound presented here has waters of crystallization attached. The evidence in support of this structure is given in the following paragraphs as the experimental data are presented and discussed.

The thermogravimetric analysis (TGA) curve shows a decrease in weight of approximately 4% at 250 °C. This corresponds to the loss of two waters of crystallization (4.6% calcd) and is similar to other reports of the loss of water from iron complexes.[9,10] Loss of HCl corresponding to a hydrochloride salt would require the loss of 9.5% by weight. Gradual decomposition of the complex occurs in the range 280–650 °C, and then the TGA curve levels off. No organic material was found in the final residue and is therefore assumed to be Fe_2O_3.[10]

Since no molecular weight could be obtained in solution, the mass spectrum of the solid was taken to see if any information could be obtained. The spectrum did not reveal a parent peak expected at *m/e* 759 for the proposed dimer, at *m/e* 722 with the loss of the two waters of crystallization, or at *m/e* 686 for $[Fe(salen–H)OH]_2$ with the loss of HCl from a hydrochloride salt. Instead, peaks were observed at *m/e* 361 and 359. The peak at *m/e* 361 can easily be explained by the

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