

orbitals are little perturbed along the series Fe, Ru, Os, the crystal field splitting ($10Dq$) is much greater for Os than the other two metal ions.²⁶ Thus, the energetic changes associated with precipitation are insufficient to effect the energy level reordering.

In summary, the reduction products of $[\text{Os}(\text{bpy})_3]^{2+}$ can be described by the spatially isolated orbital model discussed previously^{1,2,5,6} whereby the added electrons reside in orbitals localized on single ligand rings with minimal interligand interactions. The three-electron product appears more complicated, but the difference is likely attributable to increased metal character of the redox orbital rather than ligand interaction since no $S > 1/2$ behavior is evident. The unusual signal seen for the solids, $[\text{M}(\text{diimine})_3]^0$ ($\text{M} = \text{Fe}, \text{Ru}$), is concluded to be due to an essentially d^8 metal-localized configuration resulting from energy level reordering on precipitation. This behavior is consistent with the available data on the energy spacing between $L\pi^*$ and $d\sigma^*$ orbitals since $[\text{Os}(\text{bpy})_3]^0$ (solid) for which this spacing is largest gives only simple ligand-localized behavior. A similar metal-localized configuration might also be anticipated for the solid one-electron products of Fe and Ru (d^7 in this case) although it has not been possible to precipitate these species.

Experimental Section

$[\text{Os}(\text{bpy})_3]X_2$ ($X = \text{Cl}^-, \text{ClO}_4^-$) was provided by R. Donohoe of this department. The controlled-potential electrolysis to produce the reduction product for ESR was carried out at a potential at least 50 mV cathodic of the respective voltammetric peaks. The post-electrolysis cyclic voltammetry described previously²⁷ was used to verify the identity and stability of the reduced species. All three reduction products of $[\text{Os}(\text{bpy})_3]^{2+}$ are stable for periods of days. All other reagents, purification procedures, apparatus, and experimental conditions are the same as those described previously.^{2,6} The solid products were isolated by two-electron reductions of millimolar solutions of the parent ions in CH_3CN that resulted in nearly quantitative precipitation. The precipitate was allowed to settle, and the solvent/supporting electrolyte solution was decanted. The resulting moist solid was then pipetted into the ESR tubes and the remaining solvent was removed under vacuum. In all cases a small amount of supporting electrolyte remained mixed with the dry, powdered sample.

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Registry No. $[\text{Os}(\text{bpy})_3]^+$, 56977-22-1; $[\text{Os}(\text{bpy})_3]$, 56977-16-3; $[\text{Os}(\text{bpy})_3]^-$, 56977-25-4.

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Heteropolyatomic Anions of the Post Transition Metals. Synthesis and Structure of the Dileadantimonide(2-) Anion, $\text{Pb}_2\text{Sb}_2^{2-}$

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As has been recently described,² the general use of crypt to complex the alkali-metal counterions allows one to readily stabilize salts containing the polyatomic Zintl ions of the post transition elements relative to the corresponding intermetallic phases.

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Furthermore, the application of this method to heteroatomic systems allows the sampling of configurations and electronic structures that are evidently unknown or inaccessible in the homoatomic regime, for example, as the butterfly-shaped $\text{Tl}_2\text{Te}_2^{2-3}$ and the bicapped-antiprismatic TlSn_9^{3-4} . Thus, the expected tetrahedral species M_4^{4-} ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$) that are isoelectronic with P_4 etc. have not yet been isolated as this kind of salt, the stability of this configuration evidently being limited to the 1:1 intermetallic phases that these elements form with the alkali metals Na–Cs.^{5,6} On the other hand, the lower charge density achieved in the isoelectronic $(\text{M}^{\text{IV}}\text{M}^{\text{V}})_2^{2-}$ ions does appear to favor stability, as the $\text{Sn}_2\text{Bi}_2^{2-}$ example has been isolated and structurally characterized as the 2,2,2-crypt–potassium salt.⁷ In this case the nominal tetrahedra— D_{2d} in fact because of their heteroatomic nature—occur disordered over all possible orientations in the cation matrix so that only the tetrahedral average is found by X-ray diffraction. The present note reports the corresponding data for the antipode $\text{Pb}_2\text{Sb}_2^{2-}$ where the deviation from tetrahedral symmetry is probably greater and the disordering is found to be incomplete.

Experimental Section

Materials and Synthesis. All manipulations were performed either in an inert atmosphere drybox or on a vacuum line. Antimony (99.9999%) was obtained from A. D. MacKay, Inc., lead (Certified Reagent) from Fischer Scientific Co., potassium ("purified") from J. T. Baker Chemical Co., and the 2-2-2-crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-[8.8.8]hexacosane) from Merck. Ethylenediamine (en) (Fisher Scientific Co.) was first dried by refluxing over CaH_2 and then stored over molecular sieve. The dark gray alloy composition KPbSb was prepared by fusion at 970 °C of stoichiometric amounts of the elements in a sealed tantalum tube enclosed in a fused silica jacket after which the sample was air quenched. Vessels used for crypt–alloy reactions have been previously described.^{8,9}

Important parameters in the reaction of this alloy with crypt in ethylenediamine not only include the length of time allowed for the reaction and for any necessary concentration of the solution prior to crystal growth but also include whether the solution is decanted from the alloy some time during the reaction or just before the crystallization step. The KPbSb composition readily formed a reddish brown solution that was decanted from the alloy after 1 week and crystals grown by slow solvent removal over 2 weeks, utilizing the small gradient achieved between the sample container at room temperature and water in an open Dewar flask. Black pseudo-hexagonal plates of $(\text{crypt-K})_2\text{Pb}_2\text{Sb}_2$ (I) separate first, followed by about twice as much of an unknown phase II. The metallic composition of the crystals was confirmed semiquantitatively by X-ray fluorescence. A shorter reaction time and a longer crystal growth period (and possibly inhomogeneities in the alloy) instead first yielded $(\text{crypt-K})_2\text{Sb}_4^{10}$ followed again by major amounts of phase II. If the solution was not decanted from unreacted alloy beforehand, the product crystals were free of lead, consisting of a small amount of the Sb_2^{2-} phase and a good yield of a second phase thought to contain Sb_3^{3-10} . Solution–alloy redistribution reactions that are time and concentration dependent are presumably responsible for some of these differences.

The prominent phase II forms as long thin blades that sometimes curl slightly when a hard vacuum is applied to remove all the solvent. Cutting the crystals for mounting tends to damage them. An adequate crystal for data collection was not found, but the cell volume would indicate a 3- anion without en ($a = 15.12 \text{ \AA}$, $b = 19.82 \text{ \AA}$, $c = 14.41 \text{ \AA}$, $\alpha = 94.3^\circ$, $\beta = 108.8^\circ$, $\gamma = 90.9^\circ$, $V = 4074 \text{ \AA}^3$ from diffractometer alignment after standard selection). A semiquantitative analysis of the products of the second reaction $[(\text{K}^+ - \text{crypt})_2\text{Sb}_4 + \text{II}]$ by X-ray fluorescence indicated the mixture was quite antimony rich; pseudo-square-planar PbSb_3^{3-} is one possibility based on known types of ions.

Crystal Data. Crystals of I were rinsed with dry heptane to remove unreacted crypt, and then suitable members were mounted into 0.3- or

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Table I. Lead and Antimony Percentages for $\text{Pb}_2\text{Sb}_2^{2-}$

atom	initial mult for $Z = 66.5$	final		
		% Pb	% Sb	av Z
PbSb1	1.023 (12)	65.7	34.3	71.4 (8)
PbSb2	0.907 (10)	40.2	59.8	63.5 (7)
PbSb3	0.849 (10)	27.0	73.0	59.4 (7)
PbSb4	1.027 (12)	67.1	32.9	71.8 (8)

0.5-mm capillaries in a drybox. They were suspected to be isostructural with (2,2,2-crypt-K) $_2\text{Sn}_2\text{Bi}_2\text{-en}$ (space group $P2_1$) based on oscillation and Weissenberg photographs that indicated a similarly sized monoclinic cell with the extinction condition $k \neq 2n$ for $0k0$. The cell volume determined more accurately on the diffractometer was also supportive of four crypt-K cations and therefore an anion of 2- charge ($Z = 2$), the value of 697 Å/cation also suggesting the presence of 2 solvent molecules per cell.³ Diffraction intensity data were collected on a plate-shaped crystal of dimensions $0.56 \times 0.45 \times 0.16$ mm with the aid of a Syntex P2 diffractometer at -80°C ($\lambda = 0.71007$ Å). An ω scan was used with minimum and maximum scan rates of 5.86 and 29.30°/min, respectively. A total of 5458 reflections with $2\theta < 50^\circ$ in the two octants HKL and $\bar{H}\bar{K}L$ were measured. Data were corrected for decay (18% overall based on three standard reflections measured every 60 reflections), absorption ($\mu = 71.0$ cm $^{-1}$, $0.35 \leq T \leq 1.00$), and Lorentz and polarization effects. A total of 3011 reflections were classified as observed [$I > 3\sigma(I)$], and averaging in the space group $P2_1$ gave a final data set of 2761 reflections. The monoclinic cell dimensions obtained from 2θ values tuned for 27 reflections with $25^\circ < 2\theta < 32^\circ$ are $a = 12.589$ (2) Å, $b = 20.735$ (2) Å, $c = 12.201$ (2) Å, $\beta = 118.97$ (1)° with $V = 2786.4$ (6) Å 3 , and $d(\text{calcd}) = 1.84$ g/cm 3 .

Structure Solution. The refinement was begun by assuming four 50:50 Pb:Sb positions ($Z = 66.5$) in an approximately tetrahedral $\text{Pb}_2\text{Sb}_2^{2-}$ anion analogous to that in (2,2,2-crypt-K $^+$) $_2\text{Sn}_2\text{Bi}_2\text{-en}$; this yielded $R = 0.22$. Subsequent electron density maps and least-squares refinements allowed the location of the potassium and crypt atoms of the two independent cations, which are indeed in similar positions to those in the $\text{Sn}_2\text{Bi}_2^{2-}$ salt. Since the space group $P2_1$ is acentric, the inverted image was refined, and R dropped significantly from 0.091 to 0.082. The atoms of the ethylenediamine solvent molecule could then be located on an

electron density map; these were somewhat better defined than in the $\text{Sn}_2\text{Bi}_2^{2-}$ structure and with more of a trans-type configuration.

Full-matrix least-squares refinement of all 62 atoms with anisotropic thermal parameters for the K and 50:50 Pb:Sb atoms yielded $R = 0.079$ and $R_w = 0.089$. Since the four heavy atoms are in independent positions, the Pb and Sb percentages at each are not fixed at 50:50 and so the multiplicities together with all other parameters were allowed to vary in several refinements to give the results shown in the second column in Table I. The four multipliers total 3.81, not 4.00 as they ought (the charge and therefore the ratio is fixed by the number of cations), but this was not considered significant since these values are dependent on other factors such as the size of the thermal parameters.⁷ Therefore, the multipliers were scaled to total 4.00 and converted to Pb and Sb percentages and new average scattering factor tables calculated for each atom. This process was repeated once more to give the final percentages and average atomic numbers listed in the table.

The final full-matrix refinement using these percentages with multiplicities fixed at unity converges at significantly lower residuals, $R = 0.071$ and $R_w = 0.078$. A final difference map was flat to ± 2 e/Å 3 near the heavy atoms and ± 1 e/Å 3 elsewhere. The 80 hydrogen atoms were not located, representing 10.7% of the total electron density. The programs utilized as well as the source of scattering factors were as referenced before.¹⁰

Results and Discussion

The final positional parameters for (2,2,2-crypt-K $^+$) $_2\text{Pb}_2\text{Sb}_2^{2-}\text{-en}$ are listed in Table II. Bond distances and angles for the $\text{Pb}_2\text{Sb}_2^{2-}$ anion are given in Table III. The distances in the crypt cations and en molecules, the observed and calculated structure factors, and heavy-atom thermal parameters appear in the supplementary material (Tables IV-VI).

The present compound is isostructural with the $\text{Sn}_2\text{Bi}_2^{2-}$ salt although the pair of crystals investigated were enantiomeric. The lower temperature utilized for the data collection for $\text{Pb}_2\text{Sb}_2^{2-}$ is probably important in both the 20–25% reduction in the residuals and the distinctly smaller thermal parameters obtained. The latter appear to be characteristic of the structure, however, as their distributions in the two anions are much the same in the two structures. The structure is pseudohexagonal, and the solvent

Table II. Positional Parameters for (2,2,2-crypt-K) $_2\text{Pb}_2\text{Sb}_2\text{-en}$

atom	x	y	z	atom	x	y	z		
PbSb1 ^a	0.9664 (2)	1.0000	0.1276 (2)	PbSb4	0.8588 (2)	0.8790 (2)	0.9791 (2)		
PbSb2	0.8892 (2)	0.9972 (2)	0.8592 (2)	K1	0.1676 (6)	0.7931 (4)	0.6294 (6)		
PbSb3	0.7082 (2)	0.9951 (2)	0.9434 (2)	K2	0.4973 (6)	0.8157 (4)	0.3025 (6)		
atom	x	y	z	$B, \text{Å}^2$	atom	x	y	z	$B, \text{Å}^2$
N10 ^b	0.201 (2)	0.937 (2)	0.630 (3)	4.5 (7)	C31	0.171 (4)	0.961 (2)	0.506 (4)	6.8 (11)
O13	0.006 (2)	0.875 (1)	0.656 (2)	3.9 (4)	C32	0.209 (3)	0.910 (2)	0.437 (4)	5.0 (8)
O16	0.955 (2)	0.741 (1)	0.627 (2)	3.6 (4)	C34	0.173 (3)	0.812 (2)	0.334 (3)	3.5 (7)
N19	0.137 (2)	0.650 (1)	0.631 (2)	3.5 (5)	C35	0.109 (3)	0.751 (2)	0.315 (3)	3.9 (7)
O23	0.385 (2)	0.847 (1)	0.806 (2)	3.7 (5)	C37	0.108 (3)	0.654 (2)	0.411 (3)	4.9 (8)
O26	0.348 (2)	0.717 (1)	0.834 (2)	2.5 (4)	C38	0.163 (3)	0.617 (2)	0.540 (3)	3.6 (7)
O33	0.157 (2)	0.852 (1)	0.418 (2)	4.7 (5)	C41	0.639 (3)	0.973 (2)	0.316 (3)	4.4 (8)
O36	0.160 (2)	0.715 (1)	0.429 (2)	3.5 (4)	C42	0.687 (3)	0.931 (2)	0.252 (3)	4.1 (7)
N40	0.513 (3)	0.957 (1)	0.284 (3)	4.5 (7)	C44	0.759 (3)	0.822 (2)	0.242 (3)	4.3 (8)
O43	0.700 (2)	0.865 (1)	0.292 (2)	3.5 (4)	C45	0.776 (3)	0.756 (2)	0.289 (3)	5.0 (8)
O46	0.651 (2)	0.732 (1)	0.253 (2)	3.8 (5)	C47	0.660 (3)	0.670 (2)	0.288 (4)	5.1 (9)
N49	0.485 (3)	0.675 (2)	0.323 (3)	5.2 (7)	C48	0.538 (4)	0.640 (2)	0.269 (4)	6.7 (11)
O53	0.313 (2)	0.879 (1)	0.087 (2)	3.3 (4)	C51	0.432 (3)	0.980 (2)	0.156 (3)	4.9 (8)
O56	0.278 (2)	0.754 (1)	0.142 (2)	3.6 (4)	C52	0.304 (3)	0.946 (2)	0.102 (3)	5.0 (8)
O63	0.516 (2)	0.896 (1)	0.502 (2)	3.8 (5)	C54	0.197 (3)	0.850 (2)	0.031 (3)	3.8 (7)
O66	0.551 (2)	0.764 (1)	0.541 (2)	4.3 (5)	C55	0.208 (3)	0.781 (2)	0.017 (3)	4.4 (8)
C11	0.127 (3)	0.968 (2)	0.672 (3)	5.3 (9)	C57	0.280 (3)	0.683 (2)	0.135 (3)	4.1 (7)
C12	0.996 (3)	0.940 (2)	0.618 (4)	5.5 (9)	C58	0.355 (3)	0.657 (2)	0.274 (3)	5.4 (9)
C14	0.885 (3)	0.849 (2)	0.627 (3)	3.8 (7)	C61	0.480 (3)	0.989 (2)	0.365 (3)	4.9 (7)
C15	0.908 (3)	0.786 (2)	0.687 (3)	3.9 (7)	C62	0.545 (3)	0.964 (2)	0.505 (3)	4.9 (9)
C17	0.958 (3)	0.675 (2)	0.662 (3)	4.8 (8)	C64	0.580 (3)	0.867 (2)	0.632 (3)	4.6 (8)
C18	0.007 (3)	0.634 (2)	0.594 (3)	3.3 (6)	C65	0.531 (3)	0.802 (2)	0.623 (4)	5.1 (9)
C21	0.327 (4)	0.955 (2)	0.712 (4)	6.6 (11)	C67	0.513 (4)	0.697 (2)	0.540 (4)	6.5 (11)
C22	0.386 (4)	0.909 (2)	0.834 (4)	5.4 (9)	C68	0.544 (3)	0.656 (2)	0.466 (3)	4.9 (8)
C24	0.463 (3)	0.810 (2)	0.916 (3)	4.1 (7)	NEN1	0.216 (7)	0.119 (4)	0.160 (7)	18 (3)
C25	0.469 (3)	0.743 (2)	0.889 (3)	3.7 (7)	CEN2	0.169 (9)	0.179 (6)	0.090 (10)	20 (4)
C27	0.348 (3)	0.652 (2)	0.818 (3)	3.1 (6)	CEN3	0.201 (9)	0.170 (6)	-0.010 (10)	19 (3)
C28	0.217 (2)	0.624 (2)	0.758 (3)	3.0 (6)	NEN4	0.160 (4)	0.118 (3)	0.906 (4)	11 (1)

^a Pb and Sb percentages are listed in Table I. ^b The first digit identifies the chain (1, 2, and 3, crypt 1; 4, 5, and 6, crypt 2), and the second, the position along the chain.

Table III. Distances and Angles in $\text{Pb}_2\text{Sb}_2^{2-}$

atoms	dist, Å	atoms	angles, deg	atoms	angles, deg
1-2	2.931 (3)	2-1-3	59.79 (6)	1-3-2	60.23 (6)
1-3	2.924 (2)	2-1-4	60.10 (10)	1-3-4	61.41 (7)
1-4	3.006 (4)	3-1-4	59.95 (10)	2-3-4	60.74 (11)
2-3	2.918 (3)	1-2-3	59.98 (6)	1-4-2	58.70 (9)
2-4	2.974 (5)	1-2-4	61.20 (7)	1-4-3	58.65 (9)
3-4	2.963 (5)	3-2-4	60.39 (11)	2-4-3	58.88 (10)

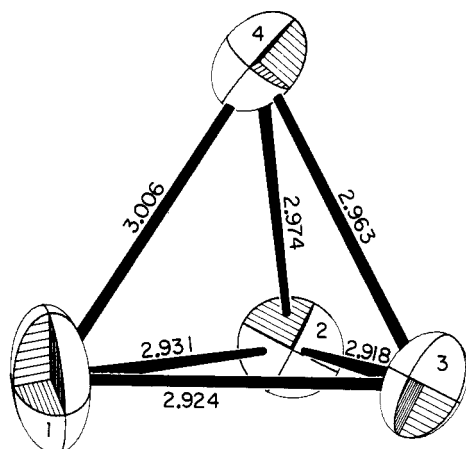


Figure 1. Partially disordered $\text{Pb}_2\text{Sb}_2^{2-}$ anion, with the b axis approximately vertical (50% thermal ellipsoids).

molecule appears to simply fill a cavity with no significant interaction with the anions. The shortest distance PbSb1-Nen1 at 3.87 (8) Å is not significantly less than distances to crypt carbons such as PbSb2-C12 at 3.96 (4) Å where hydrogen may also be important.

A view of the $\text{Pb}_2\text{Sb}_2^{2-}$ anion is shown in Figure 1. For complete disorder the observed cluster geometry would represent a mean tetrahedral configuration, each edge being an average of one Pb-Pb, one Sb-Sb, and four Pb-Sb distances. Although this was substantially the case in $\text{Sn}_2\text{Bi}_2^{2-}$, the present $\text{Pb}_2\text{Sb}_2^{2-}$ is only partially disordered. The refined occupancies (Table I) range from 27% lead at atom 3 to 66 and 67% lead at atoms 1 and 4. Correspondingly, the bond PbSb1-PbSb4 has the most Pb-Pb character and is significantly longer (3.006 Å) than the others while the bond with the most Sb-Sb character (PbSb2-PbSb3) is the shortest (2.918 Å) but not significantly so. The observed $\text{Pb}_2\text{Sb}_2^{2-}$ anion still exhibits a remarkable resemblance to $\text{Sn}_2\text{Bi}_2^{2-}$; both anions have longer distances to atom 4 and a very similar elongation of the thermal ellipsoid of atom 1. It is probable that these effects arise from the crystal packing with the crypt cations.

Appropriate bond lengths for Pb-Pb and Sb-Sb can be estimated from those in Sb_7^{3-} ¹⁰ and Pb_5^{2-} .¹¹ The averages of all distances in these are 3.081 and 2.782 Å, respectively, while use of only the axial-equatorial lengths in Pb_3^{2-} and the basal distances in Sb_7^{3-} gives 3.002 and 2.858 Å, respectively. The latter procedure provides somewhat better values with $\text{Sn}_2\text{Bi}_2^{2-}$,⁷ probably because these distances involve similarly constrained and triply bonded atoms. Either way, the average Pb-Sb bond is 2.93 Å, which compares well with the observed average of 2.953 Å.

The difference estimated for Pb-Pb vs. Sb-Sb and Sn-Sn vs. Bi-Bi distances in these mixed species is not large, 0.14 and 0.11 Å (4-5%), respectively. This means the actual D_{2d} species has only a relatively small deviation from T_d symmetry, and this allows more or less complete disorder in the cavity between the crypt- K^+ cations. The partial order achieved with $\text{Pb}_2\text{Sb}_2^{2-}$ is consistent with the somewhat larger asymmetry estimated.

A pair of elements from different periods has been used throughout these studies of mixed anions so that these could be distinguished in the products by X-rays. In fact this proves to be of little value in these tetraatomic structures. We have not

attempted the synthesis of $\text{Sn}_2\text{Sb}_2^{2-}$ or $\text{Pb}_2\text{Bi}_2^{2-}$ but are certain they are stable and well disordered in this structure. Stabilities of the mixed neutral species $\text{Sb}_x\text{Bi}_{4-x}$ are linear with composition,¹² and those of the mixed anions from different groups presumably behave quite similarly. However, the stabilities of alternate species (e.g., Sb_4^{2-} , PbSb_3^{3-} , Pb) are likely to be more important as far as the products found than just that of the ion of interest.

The homoatomic tetrahedra clusters of the elements from silicon through lead are known in the 1:1 intermetallic phases with sodium through cesium.^{5,13} Doubtless, these do not contain ions with the full 4- charge, rather some electron density is instead delocalized onto the cations. No polyatomic ions with this high a charge density have been isolated from molecular solvents with cryptated cations. The related $(\text{M}^{\text{IV}}_3\text{M}^{\text{V}})^{3-}$ or $(\text{M}^{\text{IV}}\text{M}^{\text{V}}_3)^{1-}$ ions have not been identified either, the latter perhaps because inadequate anion separation that would be provided by a single cation (no 1- ions are known). However, many more of these cations probably exist in solution, and it may be only that the correct cation, solvent, alloy phase, reaction parameters, and isolation techniques have not yet been found.

Acknowledgment. We are indebted to Professor R. A. Jacobson for continued use of the diffraction facilities and programs.

Supplementary Material Available: Listings of additional bond distances, observed and calculated structure factors, and anisotropic thermal parameters in the crypt cations (Tables IV-VI) (10 pages). Ordering information is given on any current masthead page.

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Convenient, High-Yield Synthesis of $(\text{Et}_4\text{N})_2[\text{Fe}_2\text{OCl}_6]$

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Much attention has been focused recently upon oxo-bridged diiron(III) complexes. In addition to being a common hydrolysis product of ferric salts and an oxidation product of ferrous compounds, $\{\text{Fe}_2\text{O}\}^{4+}$ units are known or believed to comprise the active centers of various metalloproteins. Included here are the dioxygen binding site in hemerythrins¹ and the functional cores of *Escherichia Coli* ribonucleotide reductase,² beef spleen purple acid phosphatase, and porcine uteroferrin.³ Recently we reported⁴ the synthesis and properties of several oxo- and hydroxo-bridged diiron(III) compounds as models for the diiron sites in these proteins. During the course of this work, $(\text{Et}_4\text{N})_2[\text{Fe}_2\text{OCl}_6]$ was found to be a useful starting material, particularly for the synthesis

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