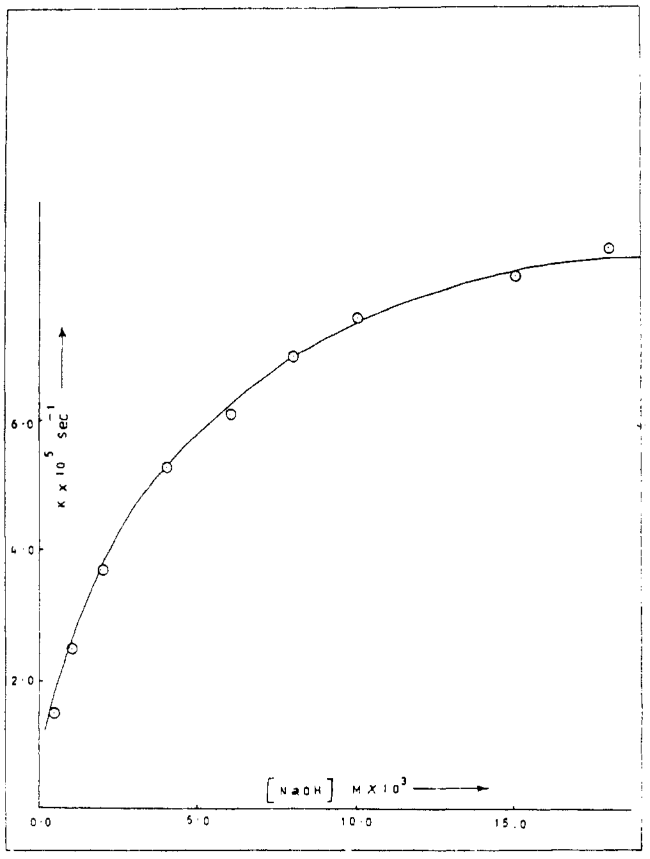

Figure 1. Plot of k_{obs} vs [NaOH] for base hydrolysis of $[Co(NH_3)_3(NO_2)_3]$. [complex] = 2.0×10^{-4} M at 50 °C.

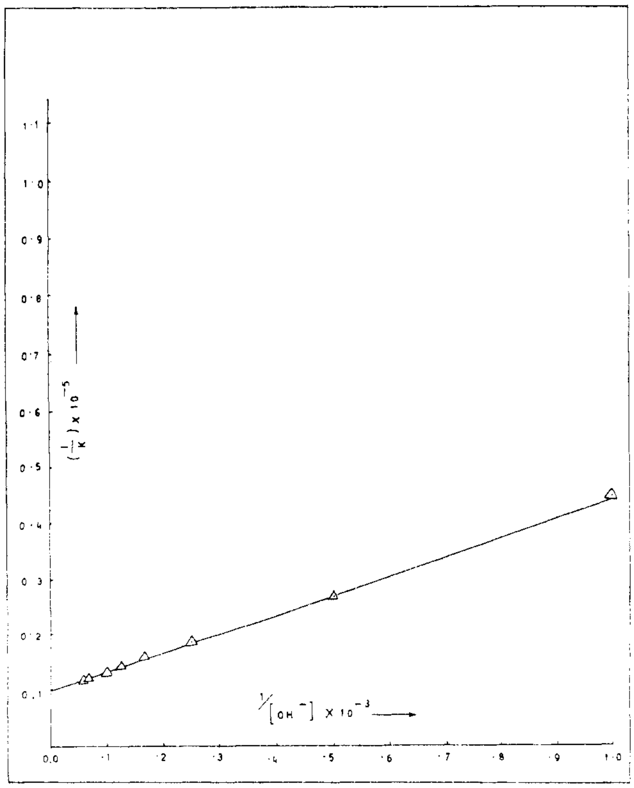

Figure 2. Base hydrolysis of $[Co(NH_3)_3(NO_2)_3]$ by NaOH presented as $1/k_{obs}$ vs $1/[OH^-]$. [complex] = 2.0×10^{-4} M at 50 °C.

π-bonding ligand in the complex would tend to stabilize the transition state $Co-NH_2 \cdots H \cdots OH^-$ by enhancing the delocalization of the p electrons on the amido nitrogen.[12]

This clearly demonstrates the D_{cb} nature of the mechanism. Whether it is D(ish)cb or D_{cb} (or even Id(ish)cb) mechanism (in the purist's sense)[13] will be subject of detailed report on the base hydrolyses of other nonelectrolyte complexes of types $[Co(SCN)_3(NH_3)_3]$, $[Co(N_3)_3(NH_3)_3]$, and I.

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Stability Range of Heterometal Cubane-Type Clusters MFe_3S_4: Assembly of Double-Cubane Clusters with the $ReFe_3S_4$ Core

It is now apparent that the heterometal cubane-type clusters $[MFe_3S_4L_n]^z$ with anionic terminal ligands L (n = 3–5) and overall negative charge z = 1– to 4– exhibit a stability plateau at the 50–52e cores $[MFe_3S_4]^q$ (q = 1+ to 4+). Under the conditions of cluster assembly systems, which contain an Fe(II) or Fe(III) salt, $[VS_4]^{3-}$ or $[MS_4]^{2-}$ (M = Mo, W), and L = RS^- or halide, the heterometal is reduced, a portion of the iron reactant is reduced or oxidized, and the *isoelectronic* (51e) core oxidation levels $[VFe_3S_4]^{2+}$[1,2] and $[MFe_3S_4]^{3+}$[2-5] are formed without exception.[6] Oxidation levels differing by one electron are recoverable from these by redox reactions. Since the initial syntheses of $MoFe_3S_4$ and WFe_3S_4 clusters in 1978–80,[3,4] the stability range of MFe_3S_4 clusters has been tested only by the synthesis of those with M = V.[1,2] We report here a significant extension of this range, with implications for the stabilities of as yet unrealized clusters.

The findings that $[ReS_4]^-$[9-11] in acetonitrile undergoes a chemically reversible one-electron reduction[12] at $E_{1/2} = -1.12$ V

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(6) When L = $R_2NCS_2^-$, a more highly oxidized core ($[MoFe_3S_4]^{5+}$) has been obtained;[7] this result is another manifestation of the stabilization of high oxidation states by dithiocarbamates. The compound $[(OC)_3MoFe_3S_4(SEt)_3]^{3-}$[8] contains a more reduced core ($[MoFe_3S_4]^0$) but was not made by an assembly reaction of the above type. On a structural basis, this cluster is a weak complex between $[Fe_3S_4(SEt)_4]^{3-}$ and the $Mo(CO)_3$ fragment, whereas in other $MoFe_3S_4$ cubanes the Mo atom is tightly integrated into the core.[2-5]

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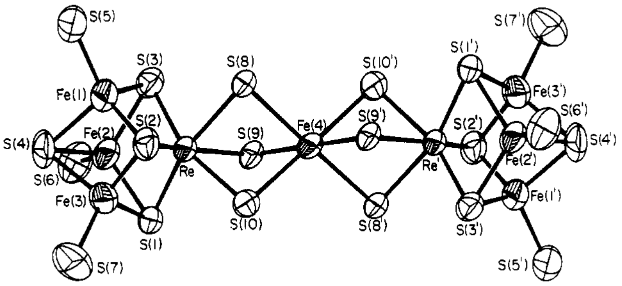

Figure 1. Structure of $[Re_2Fe_7S_8(SEt)_{12}]^{2-}$, showing 50% probability ellipsoids and the atom-labeling scheme. Primed and unprimed atoms are related by an inversion center at Fe(4). Ranges of selected distances (Å) and angles (deg) are listed as follows. Bridge unit: Re⋯Re' = 6.850 (2), Re⋯Fe = 3.425 (1), Re–S = 2.490 (7)–2.493 (8), Fe–S = 2.495 (7)–2.524 (8), S–Re–S = 78.1 (3)–79.0 (2), Re–S–Fe = 86.1 (3)–86.8 (2), S–Fe–S = 77.1 (3)–78.5 (2), S–Fe–S' = 101.5 (2)–102.9 (3). Subclusters: Re–S(1–3) = 2.325 (8)–2.340 (7), Re–Fe = 2.680 (4)–2.713 (5), Fe–Fe = 2.693 (7)–2.717 (6), Fe–S(1–3) = 2.243 (9)–2.259 (9), Fe–S (4) = 2.267 (11)–2.307 (10), Fe–S (5–7) = 2.198 (12)–2.211 (11), S–Re–S(8–10) = 86.2 (3)–89.0 (3), S–Re–S = 102.7 (3)–104.0 (3), Re–S–Fe = 71.6 (3)–72.5 (3), S–Fe–S = 102.8 (4)–109.3 (3), Fe–S–Fe = 72.1 (3)–74.1 (3). The data involve atoms S(5–7) only in terminal Fe–S distances. The angles Fe–Re–Fe, Re–Fe–Fe, and Fe–Fe–Fe are within ±1° at 60°.

and a second reduction at $E_{1/2}$ = −1.99 V and that linear $[Cl_2FeReS_4FeCl_2]^{2-}$ can be prepared[13] imply feasibility of this tetrathiometalate in cluster synthesis. A reaction system initially containing $(Et_4N)[ReS_4]$[11]/6 $FeCl_2$/13 NaSEt/Et_4NCl in 250 mL of methanol[12] afforded after 24 h a suspension of a dark brown solid in a green-brown solution. The solid was collected, washed with methanol, and suspended in acetonitrile. The mixture was stirred for 2 h, its filtrate was evaporated to dryness, and the residue was recrystallized from acetonitrile/ether to give 0.27 g of black crystalline product **1**. The green-brown solution was evaporated to dryness, the residue was suspended in acetonitrile, and the mixture was stirred for 2 h. Removal of solvent from the filtrate of the suspension followed by recrystallization as above gave 1.80 g of very dark green microcrystalline product **2**.

Product **1** crystallizes in orthorhombic space group *Pcab* (No. 61) with a = 12.316 (6) Å, b = 15.951 (5) Å, c = 38.44 (1) Å, and Z = 4 and was identified by a structural determination[12] as $(Et_4N)_2[Re_2Fe_7S_8(SEt)_{12}]$. The structure of the anion, shown in Figure 1, consists of two $ReFe_3S_4(SEt)_3$ cubane-type subclusters bridged by a trigonally distorted octahedral $Fe(SEt)_6$ unit with the Fe atom at a crystallographically imposed inversion center. This unusual structural type has been encountered previously with clusters $[M_2Fe_7S_8(SR)_{12}]^{3-,4-}$ (M = Mo, W).[14,15] The mean bridge Fe–S distance of 2.511 (15) Å is consistent only with Fe(II). Further, the less intense of the two doublets observed in the Mössbauer spectrum[12,16] with δ = 0.72 mm/s and ΔE_Q = 2.04 mm/s at 80 K requires high-spin Fe(II).[15,17] Were the bridge atom Fe(III), Fe–S distances near 2.31 Å and a smaller quadrupole splitting and an isomer shift of ca. 0.30 mm/s, as found for $[M_2Fe_7S_8(SR)_{12}]^{3-}$,[14,15] would be expected. Consequently, the core oxidation level of the subclusters is $[ReFe_3S_4]^{4+}$; i.e., it is isoelectronic with the 51e cores containing V, Mo, and W. For the more intense doublet, δ = 0.25 mm/s at 80 K. On the basis of the empirical relationship between isomer shift and mean oxidation state s of a Fe atom in a tetrahedral FeS_4 site[18] (δ = 1.44 − 0.43s), s is intermediate between 2.67+ and 3+, leading to a Re oxidation state of 3+ or 4+. Delocalized electronic structures are a consistent and distinctive feature of all heterometal cubanes.[2]

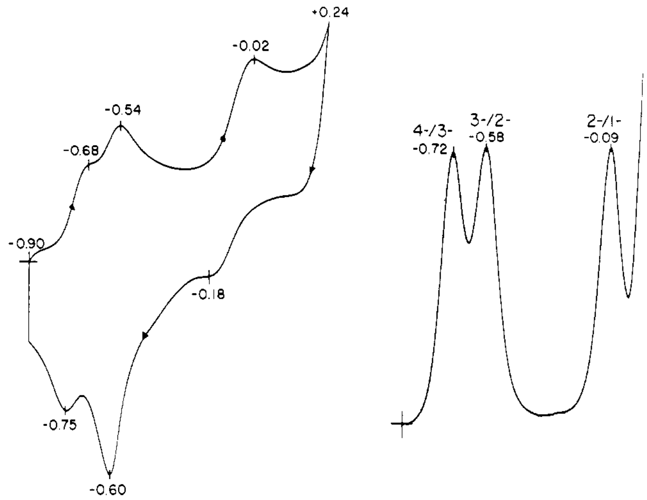

Figure 2. Redox reactions of $[Re_2Fe_7S_8(SEt)_{12}]^{4-}$ in acetonitrile solution:[12] left, cyclic voltammogram; right, differential-pulse voltammogram. Peak potentials and redox processes are indicated.

Excluding orientations of the ethyl groups of bridging (b) and terminal (t) thiolate ligands, $[Re_2Fe_7S_8(SEt)_{12}]^{2-}$ is nearly congruent structurally with the Fe(II)-bridged Mo and W double cubanes $[M_2Fe_7S_8(SR)_{12}]^{4-}$.[14] The bridge is slightly contracted in the Re cluster, mainly as a consequence of the shorter mean $Re–S_b$ bond distance of 2.491 (2) Å (2.56–2.57 Å in the other clusters). This leads to $Re⋯Fe_b$ and Re⋯Re separations of 3.425 (1) and 6.850 (2) Å, respectively, compared with 3.46–3.47 and 6.92–6.94 Å in the Mo and W cases. Demonstration of product **1** as $(Et_4N)_2[Re_2Fe_7S_8(SEt)_{12}]$ allows evaluation of the purified yield as 12%, quantitation of the UV/visible spectrum, and assignment of the isotropically shifted ^1H NMR spectrum.[16] Indeed, the latter spectrum is sufficiently similar to that of $[W_2Fe_7S_8(SEt)_{12}]^{4-}$ [15] to have permitted recognition of structure prior to the X-ray determination.

Product **2** has been identified primarily by its electrochemical behavior. Diffraction-quality crystals have not yet been obtained. Cyclic and differential-pulse voltammograms[12] are shown in Figure 2. The compound shows three chemically reversible oxidations, at E_p = −0.72, −0.58, and −0.09 V. When $[Re_2Fe_7S_8(SEt)_{12}]^{2-}$ was similarly examined, the cluster also displayed three one-electron reactions, an oxidation at −0.10 V and successive reductions at −0.60 and −0.73 V. Hence, both clusters support the four-membered electron-transfer series below, which serves to identify product **2** as the two-electron reduction product of **1**, viz., $(Et_4N)_4[Re_2Fe_7S_8(SEt)_{12}]$. The compound was obtained in 71%

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(12) Experimental details are as follows. All operations were performed under a pure dinitrogen atmosphere. The cluster assembly reaction was conducted at ambient temperature; in this system, 1 equiv = 2.25 mmol. Redox potentials were determined by cyclic voltammetry (50 mV/s, 0.2 M $(n-Bu_4N)(PF_6)$ and are referenced to SCE. X-ray diffraction data of **1** were collected at 25 °C with use of graphite-monochromatized Mo Kα radiation; d_{calc} (d_{obs}) = 1.77 (1.79) g/cm³ (CH_2Br_2/CCl_4). An empirical absorption correction (PSICOR) was applied. From 7448 total reflections, the structure was solved with 2623 unique data ($I > 3\sigma(I)$). All Re, Fe, and S atoms were located by direct methods (MULTAN), and other non-hydrogen atoms, by Fourier techniques (CRYSTALS). The Re, Fe, S, and N atoms were described anisotropically. Carbon atoms, some of which appeared disordered, were isotropically refined by using block cascade least-squares refinement. Anisotropic refinement converged at R (R_w) = 7.4% (10.8%). Mössbauer spectra were recorded with a constant-acceleration spectrometer equipped with a ^{57}Co source in Rh matrix. Isomer shifts (δ) are referenced to Fe metal at 4.2 K.

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(16) Properties of compound **1** are as follows. Mössbauer spectra at 80 (180) K: δ = 0.72 (0.68) mm/s, ΔE_Q = 2.04 (1.91) mm/s (bridge Fe); δ = 0.25 (0.22) mm/s, ΔE_Q = 0.86 (0.77) mm/s (subcluster Fe). λ_{max} (ϵ_M) (DMF): 290 (91 000), 392 nm (57 000). ^1H NMR (MeCN, 297 K): δ 77.6 (t-CH_2), 10.8 (t-CH_3), −25.1 (b-CH_3). In this spectrum and that of compound **2**, the broad b-CH_2 signal is not observable at 297 K but has been located at higher temperatures (δ 84, 332 K).

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purified yield. Its ^{1}H NMR spectrum[19] is analogous to that of **1** and supports the structural assignment.

$$[Re_2Fe_7S_8(SEt)_{12}]^{4-} \xrightleftharpoons[-0.72\ V]{E_3} [Re_2Fe_7S_8(SEt)_{12}]^{3-} \xrightleftharpoons[-0.58\ V]{E_2}$$
$$[Re_2Fe_7S_8(SEt)_{12}]^{2-} \xrightleftharpoons[-0.09\ V]{E_1} [Re_2Fe_7S_8(SEt)_{12}]^{-}$$

If we start from the dianion, step E_1 most probably corresponds to the oxidation of bridge Fe(II) to Fe(III),[20] and steps E_2 and E_3 are due to reductions of the subclusters. Further demonstration of subcluster reduction follows from the Mössbauer spectrum at 80 K.[19] Reduction influences the isomer shifts of both bridge Fe(II) and subcluster Fe, indicating some delocalization of the added electron density onto the bridge. The difference in isomer shift of subcluster Fe between $[Re_2Fe_7S_8(SEt)_{12}]^{4-}$ and $[Re_2Fe_7S_8(SEt)_{12}]^{2-}$ is 0.09 mm/s. From the empirical relationship, this corresponds to ca. 65% of that required for reduction of a subcluster Fe_3 set by one electron. While the argument is rather approximate,[21] we consider the data sufficient to demonstrate subcluster reduction to the $[ReFe_3S_4]^{3+}$ level, isoelectronic with $[MoFe_3S_4]^{2+}$ as found in several isolated reduced clusters. The range of $[MoFe_3S_4]^{2+,3+}$ isomer shift differences[18,22] (0.11–0.16 mm/s) borders on the high side of the $[ReFe_3S_4]^{3+,4+}$ value of 0.09 mm/s. Thus, in both the Mo and Re clusters, reduction occurs largely on the Fe atoms, a behavior now understandable in terms of the electronic structure of a $[MoFe_3S_4]^{3+}$ cluster.[23]

While similarities between $[Re_2Fe_7S_8(SEt)_{12}]^{2-,4-}$ and structurally analogous Mo and W clusters have been noted, there are significant differences. The $[ReS_4]^-$:Fe(II):RS$^-$ mole ratio of 1:6:13 in the foregoing assembly system subsumes the stoichiometric ratios required for the formation of $[Re_2Fe_7S_8(SEt)_{12}]^{2-,4-}$ (1:3.5:7,8) as well as that for the thiolate-bridged double cubanes $[M_2Fe_6S_8(\mu_2\text{-}SEt)_3(SEt)_6]^{-,3-}$ (1:3:5.5,6.5). The latter are readily prepared by assembly reactions.[24] In systems closely approaching these mole ratios, we have observed formation of black insoluble material, one or both of the clusters $[Re_2Fe_7S_8(SEt)_{12}]^{2-,4-}$, and two other paramagnetic species with t-CH$_2$ shifts of δ 60–70. Current work is directed toward the isolation and identification of these species. The formation of a mixture of clusters containing bridge Fe(II) in the original assembly system is a consequence of the E_1, E_2, and E_3 potentials. These are shifted by at least 0.7–0.8 V to less negative values vs those for $[M_2Fe_7S_8(SEt)_{12}]^{3-,4-,5-,6-}$ because of the smaller negative charge of isoelectronic clusters. Subclusters with M = Mo and W are not reduced chemically under preparative conditions owing to the very negative potentials required (−1.5 to −1.7 V[15]). Further, the E_2 and E_3 steps of these clusters are not resolved,[15] whereas $E_2 - E_3 = 0.14$ V for the resolved steps of the Re clusters. This difference cannot result from the slightly smaller subcluster separation but rather arises from the larger incremental increase in cluster negative charge upon reduction.

With the preparation and structural proof of four 51e clusters MFe_3S_4 with M = V, Mo, W, and Re, it is now highly probable that some or all of the unknown clusters containing the five remaining heterometals from groups 5–7 will be stable. Certainly, the present work strongly implies stability of $TcFe_3S_4$ clusters. However, $[TcS_4]^-$ is unknown. All MFe_3S_4 clusters have been prepared from the corresponding tetrathiometalates in assembly systems or from precursors requiring these anions. Inasmuch as $[MS_4]^{3-}$ (M = Nb, Ta) are unknown in discrete, soluble forms,[25] and $[CrS_4]^{2-}$ and $[MnS_4]^-$ cannot be prepared, the challenge that remains is the synthesis of these MFe_3S_4 clusters by methods that do not require tetrathiometalates. The electronic, structural, and reactivity properties of $ReFe_3S_4$ clusters will be the subjects of future reports.

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Supplementary Material Available: Tables of atom positional and thermal parameters and bond distances and angles of compound **1** (4 pages). Ordering information is given on any current masthead page.

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(19) Properties of compound **2** are as follows. Mössbauer spectra at 80 (200) K: $\delta = 0.92$ (0.81) mm/s, $\Delta E_Q = 1.80$ (1.69) mm/s (bridge Fe); $\delta = 0.34$ (0.27) mm/s, $\Delta E_Q = 0.93$ (0.85) mm/s (subcluster Fe). λ_{max} (ϵ_M) (DMF): 276 (88 000), 384 nm (54 000). ^{1}H NMR (MeCN, 297 K): δ 72.8 (t-CH$_2$), 13.1 (t-CH$_3$), −25.1 (b-CH$_3$), 81 (b-CH$_2$, 318 K).

(20) This assignment is made of the basis of the behavior of $[M_2Fe_7S_8(SR)_{12}]^{3-,4-}$ clusters,[15] which show bridge reduction before cluster reduction; i.e., $E_1 > E_2, E_3$. This redox sequence could be proven because both Fe(II) and Fe(III) clusters were isolated. Isolation of a similar Fe(III)-bridged cluster here is problematical because of the partial overlap of E_1 with multielectron oxidation at a slightly more positive potential (Figure 2).

(21) The empirical δ/s relationship, which affords a rough indication of charge distribution in a cluster, was derived from data at 4.2 K.[18] Because of only small changes in isomer shifts between the two temperatures, it can be applied, but somewhat less accurately, at 80 K. The spectra of the two clusters are complicated at very low temperatures by relaxation effects and distribution of the cluster Fe atoms over two subsites.

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