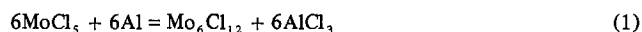


tungsten(II) bromide and its derivatives are exactly analogous to the preparation of tungsten(II) chloride and the separation techniques of molybdenum(II) bromide. Thus, 29.20 g of WBr_5 , 1.38 g of Al, 14.55 g of NaBr, and 26.68 g of $AlBr_3$ were loaded into a Vycor reaction tube and subjected to a reaction procedure as described for the tungsten chloride preparation. After reaction, the tube was opened in the drybox and a sample of the sublimed products was taken for an X-ray powder pattern. Subsequent treatment of the reaction mixture, which provided the acid hydrate $(H_3O)_2[(W_6Br_8)Br_6] \cdot 6H_2O$ in 45% yield, was exactly the same as that to obtain the corresponding molybdenum(II) bromide. The acid hydrate was decomposed to $(W_6Br_8)Br_4$ in vacuo at 350°, prior to analysis. *Anal.* Calcd for W_6Br_{12} : W, 53.49; Br, 46.51. Found: W, 53.74; Br, 46.49.

Discussion

In all of the reduction reactions given in this work the relative proportions of reactants were governed by eq 1 for



$MoCl_5$ and WBr_5 and by eq 2 for WCl_6 . Because the initial



reaction between Al and the higher halides may be quite vigorous and time must be permitted for formation of the fused salt $NaAlCl_4$ from NaCl and $AlCl_3$, it is very important that the temperature not be raised above 200° until after a few hours (ca. 6 hr at 200° generally was found to be adequate). In a few cases when the temperature was increased above 200° too rapidly, excessive pressures developed and the reaction tubes exploded. Also it is necessary to ensure that the ratio $AlCl_3:NaAlCl_4$ remains at less than 1.0 during the reaction; otherwise excessive pressure of $AlCl_3$ will result at the higher temperatures of 450–550°. Generally in the reactions given here, sufficient NaCl was added to the mixtures such that the molten $NaAlCl_4$ contained no more than 10–20 mole % $AlCl_3$ upon completion of the reaction. As noted below mixtures which contained excess NaCl were unsatisfactory because they resulted in reduced yields of the cluster compounds.

The results obtained here indicate that the molybdenum and tungsten cluster species $M_6Cl_8^{4+}$ or $M_6Br_8^{4+}$ are stable in the acidic fused salts $NaAlX_4-AlX_3$ ($X = Cl$ or Br). However the reaction conditions required to obtain optimum yields of the cluster compounds were initially unknown. In the course of establishing the optimum reaction conditions given above it was found that at temperatures less than 450° for reduction of the molybdenum halides, or 550° for reduction of the tungsten halides, relatively poor yields of the cluster compounds were obtained. Furthermore, reaction times less than those given above also resulted in reduced yields.

In all cases good yields of the cluster compounds were obtained only from melts containing excess aluminum halide. At least in the case of the tungsten chloride reductions, when a melt containing excess NaCl was used, the yield of $(W_6Cl_8)Cl_4$ was nil. Thus, attempted conversion directly to the salt $Na_2W_6Cl_{14}$ failed, and the inference is made that the cluster species $W_6Cl_8^{4+}$ is not stable in the basic, sodium chloride rich melts.

In the $AlCl_3$ -rich melts it is not obvious why the yields of $(W_6Cl_8)Cl_4$ and $(W_6Br_8)Br_4$ are low (ca. 50%) compared to those of the corresponding molybdenum compounds (>90%). That $(W_6Cl_8)Cl_4$ is stable in these acid melts is indicated by the following evidence. A sample of $(W_6Cl_8)Cl_4$ was dissolved in molten $NaAlCl_4-AlCl_3$ mixture and held for 48 hr at 450°. During this time no change in the yellow color of the melt was noticed, which indicated that no decomposition of the $W_6Cl_8^{4+}$ cluster had resulted. After further heating at 500° for 24 hr, the mixture was cooled and most of the

$(W_6Cl_8)Cl_4$ was recovered unchanged from the mixture.

It is likely that there is a larger kinetic barrier to formation of the tungsten cluster species than for the corresponding molybdenum clusters. This is evidenced by the higher reaction temperature (550°) required to obtain substantial yields of the tungsten compounds as opposed to the molybdenum compounds (450°). In the case of both molybdenum and tungsten no evidence for unreacted aluminum metal was found in the mixtures resulting from reactions at lower temperatures. This suggests that reduction to molybdenum(II) or tungsten(II) species is complete but that conversion of these species to the $M_6X_8^{4+}$ cluster compounds is a much slower process. Evidently the kinetic barrier in the formation of the cluster compounds stems from the hindered conversion of the precursor, reduced species to the $M_6X_8^{4+}$ cluster units. If this is the case other interesting compounds possibly could be isolated from the fused-salt solutions, and further work on the nature of the precursor species in the solutions is indicated.

Registry No. $(Mo_6Cl_8)Cl_4$, 21057-59-0; $(Mo_6Br_8)Br_4$, 43140-50-7; $(W_6Cl_8)Cl_4$, 43140-51-8; $(W_6Br_8)Br_4$, 43140-52-9; $MoCl_5$, 10241-05-1; WCl_6 , 13283-01-7; Al, 7429-90-5.

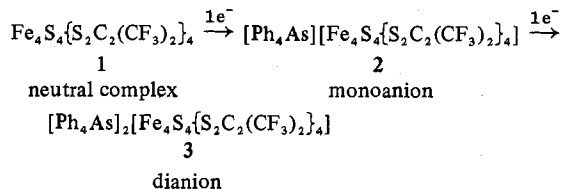
Contribution from the Francis Bitter National Magnet Laboratory,¹ Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, and from the Departments of Chemistry, Northeastern University, Boston, Massachusetts 02115, Brookhaven National Laboratory, Upton, New York 11973, and Louisiana State University in New Orleans, New Orleans, Louisiana 70122

Electronic Structure of Some Cubane-Like Fe_4S_4 Clusters. Magnetic Field Mossbauer Results

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A series of polynuclear iron-sulfur cluster compounds was first prepared by Balch.² By successive one-electron reductions the neutral dithiolene complex was converted to the mono- and dianions of the following composition



Balch deduced the quadrameric nature of the clusters from a variety of physicochemical results. The actual structure of the dianion has recently been determined by an X-ray study which shows the quadramer to consist of a distorted Fe_4S_4 cube formed by interpenetration of S_4 and Fe_4 tetrahedra.³ In addition, unperturbed Mossbauer spectral studies^{2,3} show all of the iron atoms of these cluster systems to be equivalent and indicate that the three compounds are very similar in

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electronic structure. In particular, the isomer shift changes by relatively small amounts with the one-electron reductions corresponding to the transformation $1 \rightarrow 2 \rightarrow 3$, and the variation of quadrupole splittings among the compounds is ~ 0.07 mm/sec, *i.e.*, nearly within experimental error. However, magnetic susceptibility measurements show that **2** is paramagnetic, while **1** and **3** are diamagnetic. In order to better understand the electronic environment of these systems, a Mossbauer study of these clusters in external magnetic fields was undertaken in the present investigation.

In light of the existing physical data for Fe_4S_4 systems, one can envision two extreme approaches to the changes of electronic structure for system **1** on reduction to **2** and **3**. The additional electron(s) may be viewed as entering a molecular orbital of primarily metal character where the four metal ions of the Fe_4S_4 units contribute equally to the MO. The MO is probably antibonding in view of recent theoretical and crystallographic studies of similar cluster systems.⁴ However, because **2** is paramagnetic, one would expect a magnetic hyperfine field at each iron site in the low-temperature, high external field Mossbauer spectra; *i.e.*, the field at the nucleus H_n would not be equal to the external field H_o . Only one spectrum would be obtained if all the sites are equivalent; if there is iron atom inequivalency in the applied field, then a superposition of two or more spectra would be obtained. Such inequivalency (on a pairwise basis) has been suggested from the apparent observation of two Zeeman patterns in the magnetic field Mossbauer spectrum of high potential iron protein from Chromatium.⁵

The diamagnetic species will of course exhibit the typical triplet-doublet magnetic field Mossbauer spectrum⁶ characteristic of a rapidly relaxing paramagnet or a diamagnet with $\Delta E \gg \mu_N H_o$. This will be the case⁷ whether **1** and **3** are diamagnetic by virtue of spin pairing for the individual metal atoms or diamagnetic *via* strong antiferromagnetic exchange among the metal atoms resulting in a diamagnetic (singlet) ground state for the entire cluster. The field at the nucleus H_n will now be equal to the applied field H_o (as long as the interaction of H_o with the individual ion moments is small with respect to the antiferromagnetic exchange energy).

An alternate model for reduction of compound **1** involves the additional electron(s) entering a MO composed equally and primarily of the dithiolene sulfur ligands, in which case again the three complexes would remain relatively similar. However, in the case of the paramagnetic monoanion, the delocalization of the unpaired electron would result in the observation of no magnetic hyperfine field except for the possibility of rather small internal fields (< 1 kG) arising from transferred hyperfine interaction from ligand to metal.

The experimental results are shown in Figure 1 for the dianionic complex **3**. The spectra are characteristic of a diamagnet and complexes **1** and **2** exhibit essentially identical spectra. All of the systems have positive principal components of the electric field gradient tensor V_{zz} , (the triplet at lower velocity than the doublet) and near axial symmetry ($\eta \approx 0$).

The effective magnetic field at the iron nucleus is given by

$$H_n = H_o + H_{hf}$$

where H_{hf} is the field due to the magnetic hyperfine interac-

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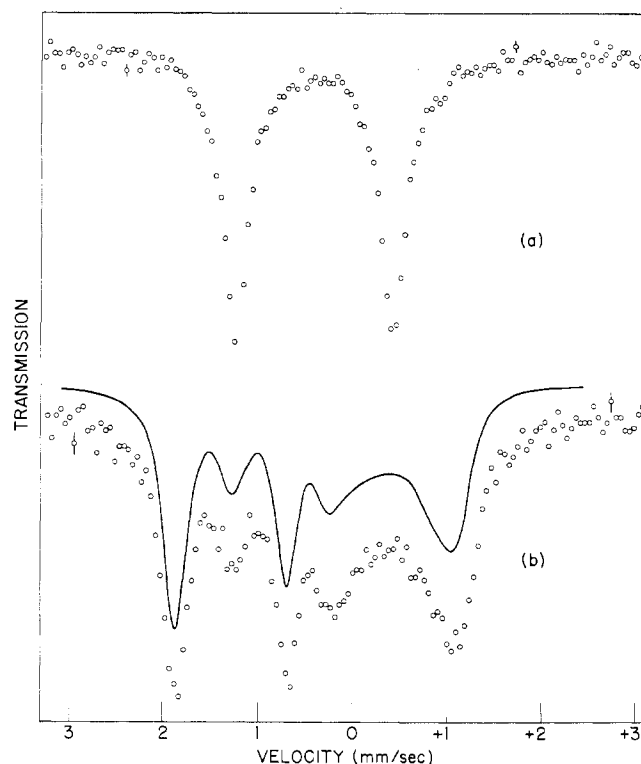


Figure 1. Mossbauer spectra of compound **3** using a ^{57}Co in Cu source: (a) at 4.2 K, $H_o = 0$; (b) at 4.2 K, $H_o = 50$ kOe, with H_o parallel to the γ -ray transmission direction. The experimental parameters from (a) are $\Delta E_Q = 1.64$ mm/sec and isomer shift $\delta = +0.08$ mm/sec relative to iron metal (source and absorber at 4.2 K). The solid line in (b) is a theoretical powder spectrum calculated with $H_o = 50$ kOe, $\Delta E_Q = +1.64$ mm/sec, and $\eta = 0$. Simulated spectra with η as large as 0.3 were also compatible with the experimental spectra.

tion. We have computer simulated the spectra of compounds **1-3** and in every case $H_{eff} = H_o$ within experimental error (± 1 kG). This, in addition to the field dependence (fields varying from 40 to 65 kG) of the spectra, establishes $H_n = 0$. Thus our results, especially in the case of complex **2**, strongly support the second model outlined above, namely, that the additional electron(s) are highly delocalized to the sulfur ligands. While this is not entirely unexpected for dithiolene type ligands, we do not feel that this has been previously demonstrated as clearly as in the present study. Whether or not this behavior extends to neutral^{4a} and cationic^{4b} complexes of the types $\text{Cp}_4\text{Fe}_4(\text{CO})_4$ and $\text{Cp}_4\text{Fe}_4\text{S}_4$ (Cp = cyclopentadienide) is currently under investigation.

To conclude, it is worthwhile to point out that the sign (positive) of V_{zz} in these systems is consistent with the coordination environment found³ for the dianion, namely, distorted trigonal bipyramidal where the bonding electrons are probably the primary origin of the electric field gradient and V_{zz} positive is expected for the stronger in-plane bonding.

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Registry No. **3**, 12572-52-0.