effect for the loss of coordinated CO. Certainly H^- has a strong activating trans effect in many complexes. However its trans effect is hardly greater than that of CO or of CH_3^-, as judged both by kinetic and structural data.[21] Furthermore Brown has shown that in octahedral metal carbonyls, the activation occurs specifically in the cis positions to the activating ligand.[22] This is in agreement with the products observed in A and B, where the entering ligands are cis to both hydrides.

However it also has been shown[22] that the donor atoms which give cis activation are N, O, and halogen[23] or carbon in groups such as CH_3CO, COOH, and $COOCH_3$.[22] These are relatively hard donor atoms and hydride would be anomalous in this list. Indeed it would be expected that an electron-donating substituent such as H^- would increase the electron density on the metal and make CO loss more difficult. A formyl group would be labilizing, as needed in the final stages of Scheme I. Finally it seems unlikely that CO is being lost as rapidly from $H_2Fe(CO)_4$ as needed for its ligand substitution reactions. This should constitute a path for thermal decomposition as seen for other hydrides.[9,19] However, the kinetics of decomposition of $H_2Fe(CO)_4$ show clearly that this is not the case.[24]

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Registry No. $H_2Fe(CO)_4$, 12002-28-7; $H_2Ru(CO)_4$, 42781-58-8; $HRu(CO)_4^-$, 77482-04-3; $H_2Fe(CO)_3PPh_3$, 77482-05-4; $H_2Fe(CO)_3P(OMe)_3$, 77482-06-5; $H_2Fe(CO)_2[P(OMe)_3]_2$, 77482-07-6; *trans*-$Fe(CO)_3(PPh_3)_2$, 21255-52-7; $H_2Ru(CO)_3P(OMe)_3$, 77482-08-7; $H_2Ru(CO)_2[P(OMe)_3]_2$, 77482-09-8; $HRu_3(CO)_{11}^-$, 77482-10-1.

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(24) The rate of decomposition is first order in $H_2Fe(CO)_4$ and independent of $HFe(CO)_4^-$ or added CO, at low CO concentrations.

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Generation of Transition-Metal Polysulfide Ions in the Gas Phase by Sequential Reactions of Metal Ions with Ethylene Sulfide

Sir:

The ability of sulfur atoms to form long chains is well-known.[1] Elemental sulfur, itself, is an eight-membered ring with a "crown" structure in its most common allotrope. The structure of the S_8 molecule in the gas phase has been determined by electron diffraction as having the same puckered ring structure as in the solid state.[2] An eight-membered ring of seven sulfurs and an imide group, S_7NH, has also been characterized.[3]

In addition alkali polysulfides,[4] hydrogen polysulfides,[5] and organic salts of hydrogen polysulfides[6] have been isolated. Characterization of these species by X-ray and Raman spectroscopy indicate that generally these chains all have unbranched and nonplanar structures.[1,7]

Several organometallic complexes with polysulfide ligands are known as well, beginning with $(NH_4)_2Pt[S_5]_3$ first prepared in 1903 and finally characterized by X-ray in 1967.[8] The structure consists of three five-membered sulfur chains coordinated to a central platinum atom forming with Pt three six-membered rings in chair configuration with overall octahedral coordination. Egen and Krause were able to prepare a tetrasulfide-containing complex using a nickel(II) mercaptide as a template.[9] Kopf's research group has prepared Cp_2MS_5 (M = V or Ti)[10] and Cp_2MS_4 (M = Mo or W)[11] which have crystallographically been confirmed as five-[12] and four-membered[13] nonplanar sulfur rings, respectively. In this correspondence we report the formation of metal polysulfide ions in the gas phase by sequential reactions of metal ions with ethylene sulfide.

Ion cyclotron resonance[14,15] (ICR) has often been successfully applied to inorganic systems.[16] Recently our laboratory developed the technique of laser ionization ICR[17-19] wherein virtually any atomic metal ion may be generated from a pure metal sample and reacted with various background gases for times approaching a second with subsequent mass analysis of charged products. Metal ions may also be generated by electron impact on volatile inorganic complexes, but they may comprise only a few percent of the total ion current in a large background of parent and other fragment ions. Our primary interest has been the development of metal ions as selective chemical ionization reagents,[19] while at the same time developing a mechanistic approach to prediciting reactivity. Sulfur compounds are of particular interest as analogues of oxygenated species, allowing us to investigate "hard–soft" effects on metal reactivity. Also, sulfur is a real problem in the petroleum industry, and several works have indicated that metal complexes may be effective desulfurization agents.[20]

During our studies of metal ion reactions with sulfur compounds, we observed unexpected behavior with ethylene sulfide. Upon reaction with Fe^+, Co^+, V^+, and Ti^+ successive attachments of sulfur was the dominant process in each case.

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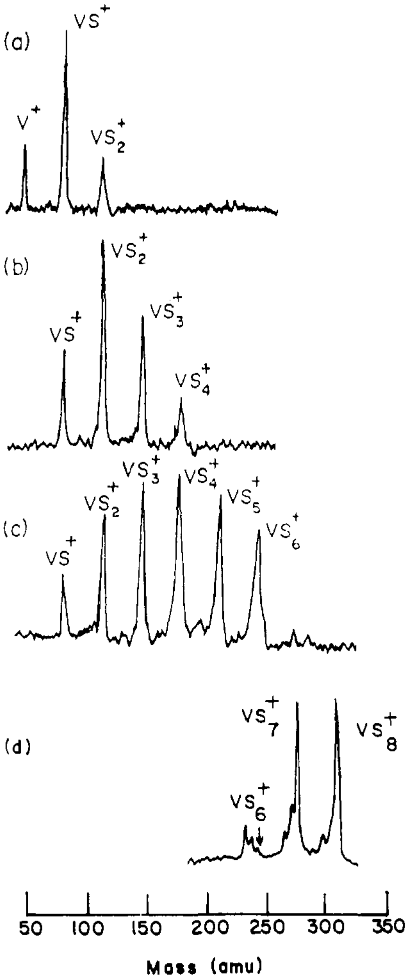


Figure 1. V^+ chemical ionization mass spectra of ethylene sulfide at neutral-gas pressures of approximately (a) 1×10^{-7} torr, (b) 2×10^{-7} torr, (c) 5×10^{-7} torr, and (d) 5×10^{-6} torr. Other conditions were a trapping time of 250 ms and an observing frequency of 65.2 kHz.

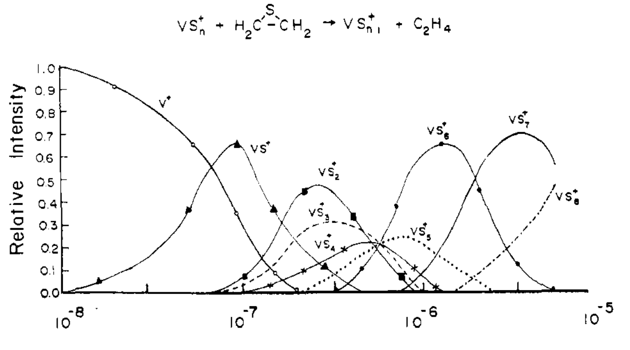
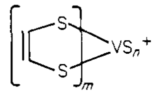


Figure 2. Variation with ethylene sulfide pressure of the relative ion abundances for the polysulfide products in the reaction of V^+ with ethylene sulfide.

Table I. Fit of Masses Observed at Maximum Resolution to the General Formula



mass	*m*	*n*	obsd[a]
51	0	0	yes
83	0	1	yes
115	0	2	yes
141	1	0	no
147	0	3	yes
173	1	1	yes
179	0	4	yes
205	1	2	yes
211	0	5	yes
231	2	0	yes
237	1	3	yes
243	0	6	yes
263	2	1	yes
269	1	4	yes
275	0	7	yes
295	2	2	yes
301	1	5	unresolved
307	0	8	yes
321	3	0	beyond mass range
333	1	6	beyond mass range

[a] Within the uncertainty of ±2 amu.

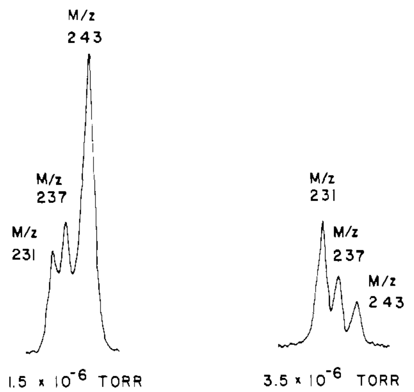
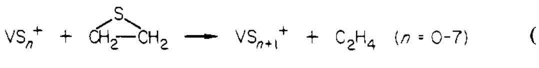


Figure 3. Resolved spectra of the VS_6^+ mass region. Peaks at m/z 231 ± 2 and m/z 237 ± 2 which increase relative to m/z 243 ± 2 (VS_6^+) at higher pressures are postulated to be dithiolenes (see Table I).

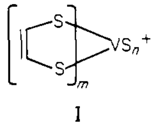
Al^+ and Cu^+ were found only to attach directly at high pressures. As a specific example, V^+ was found to attach at least eight sulfur atoms by reaction 1 (VS_9^+ is beyond our mass range).



$$\mathrm{VS}_n^+ + \overset{S}{\mathrm{CH_2{-}CH_2}} \longrightarrow \mathrm{VS}_{n+1}^+ + \mathrm{C_2H_4}\quad (n = 0\text{-}7) \qquad (1)$$

Figure 1 shows typical mass spectra of the V^+, ethylene sulfide system at several neutral-gas pressures. These and similar data were used to plot the variation of ion abundance with pressure shown in Figure 2. Additionally we have observed at least five sulfur attachments to Co^+ and Ti^+ and at least six attachments to Fe^+. Only Ti^+ shows a small abundance of ethylene and parent attachment [i.e., $Ti(C_2H_4)^+$ and $Ti(C_2H_4S)^+$] at lower pressures. Interestingly, although Ti^+ reacts with ethylene oxide to form TiO^+, subsequent reactions to produce TiO_2^+ and TiO_3^+ do not occur.[16c] In addition the reaction chemistry with ethylene sulfide contrasts the observation that various metal ions react with ethylene oxide to form MCH_2^+.[16e]

Although low resolution is a problem (±2 amu), all the resolved product ions for the V^+, ethylene sulfide system are listed in Table I. It appears that, after two sulfur attachments, H_2 loss begins to compete with C_2H_4 loss in subsequent dissociative attachments. This results in what we postulate to be the formation of stable dithiolenes (species I) appearing at 6 and 12 amu below the VS_n^+ species (Figure 3).



I
$m = 1,2$
$n = 1\text{-}6$

Metal dithiolenes[21] are well-known and very stable species in condensed phases. With this type of compound, all the nonpolysulfide masses in the V^+, ethylene sulfide system can be rationalized. (see Table I). The "dithiolenes" appear at high pressure relative to the polysulfide species and appear to be far less reactive.

The "dithiolene" type structures are indicated only because of their solution analogues and their apparent fit to the observed masses. Additional sulfurs may occupy vacant coordination sites or even insert into the ring system as has been seen in solution for dithiolate complexes,[22] but there is no experimental basis for any of these structures. Indeed, we make no claims as to the structure of the metal polysulfides although we assume that rings are involved on the basis of the work cited earlier and the fact that at least eight attachments have been seen. ICR photodissociation[23,24] techniques allow indirect observation of the optical absorption spectra of gas-phase ions, which should allow better estimates of the structures to be made. We are curently modifying our instrument to allow simultaneous laser ionization, photodissociation experiments.

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Registry No. Ethylene sulfide, 420-12-2; Fe, 7439-89-6; Co, 7440-48-4; V, 7440-62-2; Ti, 7440-32-6; Al, 7429-90-5.

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Absolute Configuration and Circular Dichroism of the Lanthanide Complex Trisodium Tris(oxydiacetato)europate(III) Bis(sodium tetrafluoroborate) Hexahydrate

Sir:

We report the first correlation of circular dichroism (CD) and absolute configuration in a lanthanide complex. Single crystals of the title compound, $Na_3Eu(C_4H_4O_5)_3\cdot 2NaBF_4\cdot 6H_2O$, were prepared as follows. A stoichiometric amount of Eu_2O_3 was dissolved in $C_4H_4O_5H_2$ (oxydiacetic acid). This is a fairly strong acid, and the Eu_2O_3 dissolves easily at room temperature. The resultant solution was brought to neutral pH by addition of NaOH solution. A 2 molar ratio of $NaBF_4$ was added to this solution. Crystals were grown by slow evaporation at ambient temperature in Teflon beakers. This procedure is similar to that used previously to prepare the ClO_4^- double salts[1-3] $Na_3Ln(C_4H_4O_5)_3\cdot 2NaClO_4\cdot 6H_2O$. The morphologies of the tetrafluoroborate and perchlorate salts are identical.

Table I. Spectroscopic Parameters for $Na_3Eu(C_4H_4O_5)_3\cdot 2NaBF_4\cdot 6H_2O$ at Room Temperature

transition	energy	rotational strength[a]	dipole strength[b]	g[c]
$^7F_0(A_1) \rightarrow {}^5D_1(E)$	18 981	-0.13×10^{-42} (-400)[e]	1.3×10^{-42} (0.7)[e]	-0.42
$^7F_0(A_1) \rightarrow {}^5D_2(2E)$[d]	21 490	-0.10×10^{-42} (-200)	3.2×10^{-42} (1.4)	-0.13

[a] In units of $esu^2\ cm^2$. The numbers in parentheses are the peak $[\theta]$ values (deg dL $dm^{-1}\ mol^{-1}$). All values have an error of ±20%. [b] In units of $esu^2\ cm^2$. The numbers in parentheses are the peak ϵ values ($cm^2\ mol^{-1}$). [c] $g = 4R/D$. [d] This is the higher energy E level. [e] The two bands have different bandwidths so the ratios of ϵ's and $[\theta]$'s are not directly proportional to the ratios of dipole strengths and rotational strengths.

Table II. Coordinates of $Na_3Eu(C_4H_4O_5)_3\cdot 2NaBF_4\cdot 6H_2O$ with Respect to Rhombohedral Axes

atom[a]	x	y	z
Eu	0	0	0
Na(1)	0.2145 (4)	0.7855	0.5
Na(2)	0.8007 (1)	0.8007	0.8007
B	0.5707 (4)	0.5707	0.5707
F(1)	0.4684 (2)	0.4835 (2)	0.7068 (2)
F(2)	0.6187 (3)	0.6187	0.6187
O(1)	0.2573 (4)	−0.2573	0
O(2)	−0.0294 (1)	−0.2509 (1)	0.1041 (1)
O(3)	0.0624 (2)	−0.5161 (1)	0.1541 (2)
O(W)	0.0781 (2)	0.7115 (2)	0.7824 (1)
C(1)	0.2564 (2)	−0.4148 (2)	0.0624 (2)
C(2)	0.0828 (1)	−0.3941 (1)	0.1134 (1)
H(1)	0.281 (3)	−0.480 (4)	0.165 (4)
H(2)	0.334 (3)	−0.466 (3)	−0.008 (3)
H(W1)	0.091 (4)	0.827 (4)	0.744 (4)

[a] The numbering system is shown in Figure 1 and is consistent with ref 1–3.

Table III. Bond Distances (Å) in $Na_3Eu(C_4H_4O_5)_3\cdot 2NaBF_4\cdot 6H_2O$

Na(1)–O(3)	2.583 (3)	Eu–O(1)	2.495 (2)
Na(1)–F(1)	2.337 (5)	Eu–O(2)	2.395 (2)
Na(1)–O(W)	2.292 (4)	O(1)–C(1)	1.418 (3)
Na(2)–O(3)	2.347 (4)	C(1)–C(2)	1.518 (4)
Na(2)–O(W)	2.474 (5)	C(2)–O(2)	1.263 (2)
B–F(1)	1.382 (4)	C(2)–O(3)	1.240 (2)
B–F(2)	1.365 (4)		

Table IV. Selected Bond Angles (Deg) in $Na_3Eu(C_4H_4O_5)_3\cdot 2NaBF_4\cdot 6H_2O$

O(1)–Eu–O(2)	63.4 (1)	O(3)–Na(1)–O(3)	101.4 (2)
O(1)–Eu–O(2)	74.3 (1)	O(3)–Na(1)–F(1)	85.1 (2)
O(1)–Eu–O(2)	135.9 (1)	O(3)–Na(1)–F(1)	172.6 (2)
O(2)–Eu–O(2)	77.9 (1)	O(3)–Na(1)–O(6)	82.8 (2)
O(2)–Eu–O(2)	88.1 (1)	O(3)–Na(1)–O(6)	87.6 (2)
O(2)–Eu–O(2)	126.7 (1)	F(1)–Na(1)–F(1)	88.6 (3)
O(2)–Eu–O(2)	148.6 (1)	F(1)–Na(1)–O(6)	89.7 (2)
C(1)–O(1)–C(1)	115.2 (2)	F(1)–Na(1)–O(6)	101.2 (2)
O(1)–C(1)–C(2)	109.1 (2)	O(6)–Na(1)–O(6)	164.8 (2)
C(1)–C(2)–O(2)	117.7 (3)	O(3)–Na(2)–O(3)	104.9 (2)
C(1)–C(2)–O(3)	118.1 (2)	O(3)–Na(2)–O(6)	84.1 (2)
O(2)–C(2)–O(3)	124.7 (3)	O(3)–Na(2)–O(6)	85.9 (2)
F(1)–B–F(1)	108.7 (3)	O(3)–Na(2)–O(6)	163.5 (2)
F(1)–B–F(2)	110.1 (3)	O(6)–Na(2)–O(6)	82.6 (2)

X-ray and CD/absorption data were recorded from fragments of the same large crystal. The CD/absorption data were collected at ambient temperature with use of Jasco J-20 spectropolarimeter, which has had an absorption mode added to it, interfaced with a Spex 0.85-m double monochromator. All spectra are sample limited in resolution. Table I gives some of the CD/absorption data. Within experimental error, these data are identical with those for the ClO_4^- salt,[4-5] where all other observed transitions, $^7F_1 \rightarrow {}^5D_{0-2}$, also have a negative

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