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On the Electronic Structure of Compounds with FeSMo Units. Properties of $[Cl_2FeS_2MoS_2]^{2-}$ (M = Mo, W)

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Recent EXAFS (Mo K edge) results for the FeMo protein of nitrogenase (from C. pasteurianum and A. vinelandii) and the low molecular weight iron-molybdenum cofactor (FeMo-co, isolated from the FeMo proteins with the Mo:Fe:S ratio ≈1:8:6 [1]) have shown that the Mo environment within the MoS_mFe_n cluster is very similar (3 or 4 bound S atoms with Mo–S distances of ≈2.36 Å and 2 or 3 Fe atoms with Mo–Fe distances of ≈2.72 Å [2]. Zumft [3] has shown that the treatment of the FeMo protein of C. pasteurianum leads to MoS_4^{2-} (The MoS_4^{2-} ion is most probably also responsible for the Cu deficiency disease in ruminants [4]). It may be possible that the above mentioned cluster type of FeMo-co will be synthesized in the near future from MoS_4^{2-}, which was first used by us as a ligand in transition metal coordination compounds [5]. (Fe–S–Mo linkages may be important in two different non-nitrogenase proteins of the genus Desulfovibrio, too [6]). It should be worthwhile to study the electronic structure of compounds with FeSMo moieties like $[Cl_2FeS_2MoS_2]^{2-}$, having similar Mo–Fe distances as FeMo-co [7]. $[Cl_2FeS_2WS_2]^{2-}$, the preparation of which is first described in this note, is also investigated.

Experimental

$[(C_6H_5)_4P][(C_6H_5CH_2)(CH_3)_3N][Cl_2FeS_2MoS_2]$ was prepared as previously described [7]. $[(C_6H_5)_4P][(C_6H_5CH_2)(CH_3)_3N][Cl_2FeS_2WS_2]$: a solution of 0.2 g $FeCl_2 \cdot 4H_2O$ and 0.4 g $[(C_6H_5CH_2)(CH_3)_3N]Cl$ in 50 ml CH_3CN is added to a solution of 1 g $[(C_6H_5)_4P]_2WS_4$ in 100 ml CH_3CN. After filtration and addition of 80 ml diethyl ether to the solution, red crystals of the compound precipitate. The W compound is isostructural with the Mo compound [7] (Crystallographic data of the W compound: triclinic; $P\bar{1}$; a = 13.263(3), b = 15.051(3), c = 10.087(2) Å, α = 82.07(2), β = 81,69(2), γ = 74.44(2)°; Z = 2).

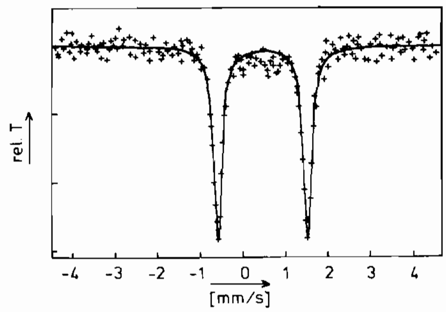
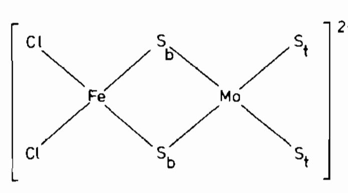


Fig. 1. Mössbauer spectrum of $[(C_6H_5)_4P][(C_6H_5CH_2)(CH_3)_3N][Cl_2FeS_2MoS_2]$.

The electronic absorption spectra were recorded with a Beckman Acta M IV spectrophotometer in CH_3CN solutions. Infrared spectra were obtained with a Perkin Elmer 180 spectrometer from CsI pellets. The resonance Raman spectrum of solid $[(C_6H_5)_4P][(C_6H_5CH_2)(CH_3)_3N][Cl_2FeS_2MoS_2]$ was measured with a Coderg instrument (T 800) using an Ar^+-laser source (λ_E = 4880 Å, 70 mW) and a rotating cell technique. The magnetic measurements were performed with the Faraday method at 295 K with a Bruker electromagnet (Mn - SU 10 type) and a Sartorius microbalance (type 4411). The cyclic voltammograms were measured using the Polarecord E505/506 of Metrohm Herisau (Pt electrodes as working and auxiliary electrodes, and an Ag/AgCl/LiCl (sat.) EtOH electrode (E_N = +0.143 V) as reference electrode; depolarisator concentrations: 10^{-3} M in 10^{-1} M solutions of $[(C_3H_7)_4N][PF_6]$ in CH_3CN). The Mössbauer measurements were performed with a standard apparatus in constant acceleration mode with a $^{57}Co/Rh$ (*ca.* 50 mCi) source at room temperature. The unit cell dimensions of the W compound were determined with a Syntex $P2_1$ four cycle diffractometer.

Results and Discussion

We will mainly refer to the complex



[7], as the results for the corresponding W compound are similar (see Table I).

TABLE I. Physical Properties of $[Cl_2FeS_2MoS_2]^{2-}$ and $[Cl_2FeS_2WS_2]^{2-}$.

	$[Cl_2FeS_2MoS_2]^{2-}$	$[Cl_2FeS_2WS_2]^{2-}$
^{57}Fe Mössbauer (295 K)		
IS[a]	0.480 ± 0.006	0.520 ± 0.012 mm s^{-1}
QS	2.100 ± 0.005	2.270 ± 0.010
Γ	0.250 ± 0.003	0.240 ± 0.008
μ_{eff} (293 K)[b]	5.0	5.1 BM
Electronic spectrum[c,d]	9.5	8.7 kK
	17.1	19.4
	~19.2	22.6
	21.2	24.1
	23.0	26.8
	31.9	
	~35.2	
IR spectrum		
$\nu(M-S_t)$	504/488	492/482 cm^{-1}
$\nu(M-S_b)$	448	443/438
ν(Fe–Cl)	332/322	331/321
Resonance Raman spectrum[e]		
$\delta_s(MoS_2)_b$[f]	158 cm^{-1}	
$\delta_s(MoS_2)_t$[f]	201	
$2\delta_s(MoS_2)_b$ (?)	325	
$\nu_s(Mo-S_b)$[f]	429	
$\nu_s(Mo-S_t)$[f]	493	
$2\nu_s(Mo-S_b)$	858	
$\nu_s(Mo-S_b) + \nu_s(Mo-S_t)$	918	
$2\nu_s(Mo-S_t)$	982	
Cyclic voltammogram	E_{red} = −1.2 (irreversible)	E_{red} = −1.3 V (irreversible)

[a]Relative to α-Fe at R.T. [b]Corrected for diamagnetic contributions. [c]The positions of the bands have been determined by a least-squares fitting. [d]For ε values see Fig. 3. [e]Tentative assignment (For the resonance Raman spectrum of MoS_4^{2-} see ref. [15]). [f]The four most intense lines are due to the four A_1 fundamentals of the coordinated MoS_4^{2-} ion with local C_{2v} symmetry. (The doubly bridging MoS_4^{2-} ligand in $[Cl_2FeS_2MoS_2FeCl_2]^{2-}$ with equivalent bonds gives rise only to intense lines due to two A_1 fundamentals [23]).

The magnetic measurements and ^{57}Fe Mössbauer data (Fig. 1) are in agreement with a tetrahedrally coordinated ferrous type high-spin complex [8], although the data differ considerably from those obtained for complexes with ligands such as Cl^-.

The value of the magnetic moment is significantly smaller than that of $[FeCl_4]^{2-}$ (~5.4 BM for complexes with different cations [9]). The small orbital reduction factor, according to the formula $\mu_{eff} = \mu_{eff}^{s.o.}(1 - 2k^2\lambda/\Delta)$ [9], indicates the strong electron delocalization Fe → ligand which increases from the W to the Mo compound as expected.

The low value of the isomer shift (0.480 mm s^{-1}) compared to those of other tetrahedrally coordinated ferrous high-spin complexes containing σ-donating ligands as for example $[FeCl_4]^{2-}$ (0.76 mm s^{-1} [10]) also indicates that the Fe 3d population is relatively low in the thiomolybdato complex (for theoretical background see [8]).

The electronic absorption spectra of both chloro complexes (Fig. 2) are similar to that of $[Fe(WS_4)_2]^{2-}$ [11], suggesting that the observed strong bands are due to transitions within the $Fe(MS_4)$-chromophore. The spectra of all three species show one band with low intensity in the NIR region, where normally transitions of predominant d → d character are expected. However, because bands due to $^5E \rightarrow {}^5T_2$ crystal field transitions are expected at much lower energy ($[FeCl_4]^{2-}$: ν_{max} = 4060 cm^{-1}, ε = 80 M^{-1} cm^{-1} [12]) strong Fe–MS_4^{2-} interactions have to be taken into account. Therefore it is not possible to distinguish between bands in the usual way (d → d, ligand → metal-CT, metal →

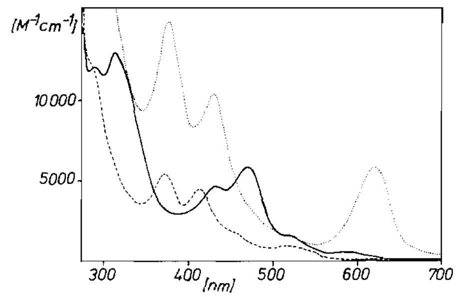


Fig. 2. Electronic absorption spectra of $[Cl_2FeS_2MoS_2]^{2-}$ (———), and $[Cl_2FeS_2WS_2]^{2-}$ (- - - - - - -). (For comparison the spectrum of $[(C_6H_5)_4P]_2[Fe(WS_4)_2]$ in CH_2Cl_2 (·······) is included.

ligand-CT, and ligand-internal transitions). The bands of medium intensity (17.1 and 19.2 kK for the Mo, 19.2 and 22.6 for the W complex) have to be assigned to transitions between MOs delocalized over the whole complex though a charge transfer character should be predominant. The higher energy bands rougly correspond to ligand internal transitions. The splitting is due to the lower symmetry in the complexes (MoS_4^{2-}: ν_1 = 21.4 kK, ν_2 = 31.5 kK; WS_4^{2-}: g_1 = 25.5 kK [14]). According to the stronger Fe–MoS_4^{2-} interaction the deviations from the free ion values are more pronounced in the Mo complex.

The vibrational infrared spectrum shows the typical splitting pattern of the bidentate coordinated MoS_4^{2-} ligand $\nu(Mo{-}S_t)$ at higher wave numbers and $\nu(Mo{-}S_b)$ at lower wave numbers) [15]. These vibrations are rather pure according to a normal coordinate analysis and the measurements of metal isotope shifts (Ni, Zn, Mo) in the corresponding compounds $[Ni(MoS_4)_2]^{2-}$ [16] and $[Zn(MoS_4)_2]^{2-}$ [17].

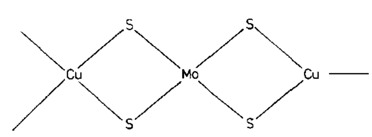
An interesting resonance Raman effect (preliminary results) has been observed using a 4880 Å line, which lies within the absorption band of the 21.2 kK transition (see Fig. 2). The spectrum shows the strongly enhanced lines due to the fundamentals $\nu(Mo{-}S_t)$, $\nu(Mo{-}S_b)$, and other lines listed in Table I. As only vibrations of the MoS_4^{2-} chromophore are practically affected, the 21.2 kK transition is predominantly a ligand internal one. In contrast to species of the type $[M'(MO_nS_{4-n})_2]^{2-}$ (M' = Ni, Co; M = Mo, W; n = 0, 1, 2) [11, 13, 18] the $[Cl_2FeS_2MS_2]^{2-}$ ions do not show reversible reduction processes. The d electron delocalization, which is limited to a smaller fragment in the chloro complexes, accounts for the ability of the trimetallic systems like

$$[Co(WS_4)_2]^{2-} \rightleftharpoons [Co(WS_4)_2]^{3-} \rightleftharpoons [Co(WS_4)_2]^{4-}$$

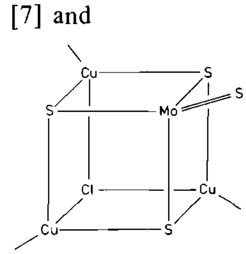
to exist with a range of electron population.

The electronic structure of $[Cl_2FeS_2MoS_2]^{2-}$ was studied by SCCC EH calculations, from which we obtained the following results. Since the Fe 3d AOS have essentially the same energy (~–90 kK) as the HOMO of the free MoS_4^{2-}, which is located on the sulfur atoms [14] (t_1: –85 kK), the latter acts as a strong σ-donor ligand, but also as a strong π-acceptor because of its low-lying unoccupied orbitals (2e: –61 kK [19]). Due to the complex formation the electron density at the Fe centre is decreased and it is increased at Mo compared to the free MoS_4^{2-}. The electron density at the terminal S atoms is only slightly reduced. (The overlap populations and thus the bond orders are increased in the $Mo{-}S_t$ bonds and decreased in the $Mo{-}S_b$ bonds). The calculation therefore suggest that further complex formation should be possible at the terminal S atoms of a Fe-(MoS_4) moiety [7]. (The Fe → M electron delocalization is stronger in the Mo complex than in the W complex). According to the Fe–Mo distance (2.775 Å [7]) metal–metal bonding has to be taken into consideration. This is in agreement with the calculated values of the overlap integrals between Fe 3d and Mo 4d AOs at the above mentioned distance.

The replacement of two coordination sites of $[FeCl_4]^{2-}$ by the bidentate π-acceptor MoS_4^{2-} ligand leads to a drastic electron density reduction at the central Fe atom. The electron delocalization is even stronger in $[Cl_2FeS_2MoS_2]^{2-}$ than in $[Fe(SPh)_4]^{2-}$ [20] and $[Fe(S_2\text{-}o\text{-}xyl)_2]^{2-}$ [21] (replacement of all σ-donor ligands) according to the Mössbauer and susceptibility data of the latter compounds. The ability of MoS_mFe_n groups present in the FeMo proteins to delocalize and transfer electron density could be supported by similar studies of other compounds with FeSMo moieties (see also [22]). The MO calculations have shown that the MoS_4^{2-} anion can act as a multibridging ligand. A doubly bridging MoS_4^{2-} ligand, which can be identified by the resonance Raman effect [23], exists in the complex $[Cl_2FeS_2MoS_2FeCl_2]^{2-}$ [23, 24]. The compound can easily be prepared directly from the components [23]. (More Fe atoms can probably be coordinated to the MoS_4 unit in the reduced complex). Cu complexes with doubly and triply bridging MoS_4^{2-} ligands having the following core units.



[7] and



[25] are also known.

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