$(PPh_4)_2[Cl_2Fe(ReS_4)FeCl_2]_{0.7}[Cl_2Fe(MoS_4)FeCl_2]_{0.3}$: Containing Two Isostructural Complexes with Different Electronic Populations, Mössbauer Spectra and Electronic Structures

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Though the heterometallic linear 12 electron (formal number of metal valence electrons) species of the type $[Cl_2Fe(MS_4)FeCl_2]^{n-}$ ($n = 3$, M = V [1]; $n = 2$, M = Mo, W [2, 3]) could easily be obtained, it was not possible to isolate these with other electron populations, for instance, the reduced ones with 13 electrons. This is surprising because thiometallato complexes normally have strongly delocalized electronic states [4, 5]. The species have some relevance to the function of the heterometal cluster in nitrogenase. As we were now able to obtain the 13 electron species $[Cl_2Fe(ReS_4)FeCl_2]^{2-}$ (**1**), which occurs not only in the corresponding PPh_4^+ salt (**1a**) [6] but also more interestingly in the mixed crystal compound $(PPh_4)_2[Cl_2Fe(ReS_4)FeCl_2]_{0.7}[Cl_2Fe(MoS_4)FeCl_2]_{0.3}$ (**1b**) we found it worthwhile to study the electronic structure of the anion. **1** is also an example of the very few thioperrhenato complexes known (a very simple preparation method for the ReS_4^- species may be found in ref. 7). Other related rhenium sulfur species synthesized so far are: $[ReO(S_4)_2]^-$, $[ReS(S_4)_2]^-$ [7], $[Re_4S_4(S_3)_6]^{4-}$ [8] and $[(Cu_2Cl_3)_2(CuCl)(ReS_4)]^{3-}$ [9].

Black **1b** was isolated from a reaction mixture of $(NEt_4)[ReS_4]$, $(NEt_4)_2[MoS_4]$, $(PPh_4)Cl$ and $FeCl_2$ in CH_2Cl_2**. The structure of the anions in the mixed crystal compound **1b** is shown in Fig. 1 (for details of the crystal structure determination see legend to that Figure).

The Mössbauer spectra of **1a** and **1b** recorded at 4.2 K are also shown in Fig. 2. Corresponding spectra were measured at room temperature. Their least-squares fits using Lorentzians yield isomer shifts δ and quadrupole splittings ΔE_Q as given in Table I. A comparison of these values with the measured data of several thiomolybdato and -tungstato complexes of Fe, for instance $[Cl_2Fe(MoS_4)]^{2-}$ (**3**), $[Cl_2Fe(WS_4)]^{2-}$ (**4**) and $[Cl_2Fe(WS_4)FeCl_2]^{2-}$ (**5**), demonstrates that the above mentioned Mo and W complexes exhibit similar Mössbauer parameters, while the Re complex shows a significantly reduced ΔE_Q value. The parameters of the Re species are, however, in the order of magnitude of the species obtained from **2** by chemical reduction [2]. From the similarity in the parameters of bi- and trinuclear Mo and W complexes we conclude that the electron configuration of iron is practically the same for complexes **2** to **5**. The following estimate is therefore based on the MO scheme of the binuclear complex **3** [15], which has been extended to all trinuclear species in Fig. 3. The occupation of the MOs with predominant Fe3d character have therefore been chosen in analogy with the binuclear species, *i.e.* with a maximum number of unpaired electrons.

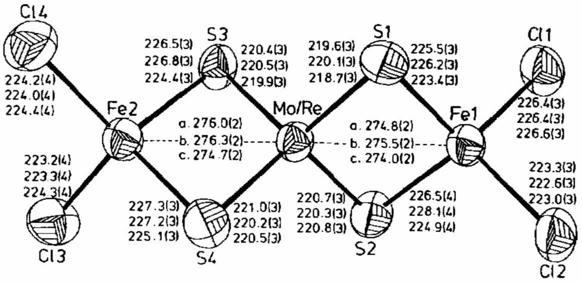

Fig. 1. Structure of the $[Cl_2Fe(ReS_4)FeCl_2]^{2-}/[Cl_2Fe(MoS_4)FeCl_2]^{2-}$ anions (the two anions occupy statistically the same positions) in crystals of $(PPh_4)_2[Cl_2Fe(ReS_4)FeCl_2]_{0.7}[Cl_2Fe(MoS_4)FeCl_2]_{0.3}$ (**1b**) with average bond lengths (pm). Below these bond lengths (a), the values for $(PPh_4)_2[Cl_2Fe(ReS_4)FeCl_2]_{0.5}[Cl_2Fe(MoS_4)FeCl_2]_{0.5}$ (b) and $(PPh_4)_2[Cl_2Fe(ReS_4)FeCl_2]$ (c) are given in addition. **1b** crystallizes in the triclinic space group $P\bar{1}$ ($a = 1018.6(3)$, $b = 1306.4(3)$, $c = 2018.7(6)$ pm, $\alpha = 100.58(2)$, $\beta = 100.69(2)$, $\gamma = 100.98(2)°$, $V = 2523.6 \times 10^6$ pm^3, $Z = 2$, $R = 0.062$ for 5087 independent reflections ($F_o > 3.92\sigma(F_o)$). The anions consist of three (two Cl_2FeS_2 and one Mo/ReS_4) edge sharing tetrahedra, which form a nearly linear metal atom array (Fe–Mo/Re–Fe = 179.3(1)°). The tetrahedra are only slightly distorted. The metal–sulfur and metal–chlorine distances all are between 219.6 and 227.3 pm and the bond angles (except the S–Fe–S angles: 101.8(1), 102.0(1)°) are in the region from 105.9 to 116.4°.

In a good approximation Mössbauer parameters can be calculated [15] from the Fe3d contribution to the 'Fe crystal-field' levels as obtained from the Extended Hückel calculations. For simplicity we 'duplicate' the Fe3d contributions to these MOs calculated for **3** to obtain pseudo-wavefunctions for the trinuclear species **1**, **2** and **5**. For example, the Fe3d participation of the two lowest energy MOs a_1

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The relative abundance of 1 and $[Cl_2Fe(MoS_4)FeCl_2]^{2-}$ (2**) depends on the ratio of MoS_4^{2-} and ReS_4^- in the reaction mixture.

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and b_2 of trimetallic species is constructed from the Fe3d participation of the lowest energy MO a_1 of the bimetallic species **3** according to

$$|\mathrm{Fe3d}(a_1, b_2)\,(\mathbf{1, 2, 5})\rangle = 2^{-1/2}\,[|\mathrm{Fe}^{(1)}3\mathrm{d}(a_1)\,(\mathbf{3})\rangle + |\mathrm{Fe}^{(2)}3\mathrm{d}(a_1)\,(\mathbf{3})\rangle]$$

(and so on for the further levels). The ΔE_Q value of **2** calculated using this procedure (both iron atoms are equivalent) is 1.99 mm s^{-1}. For a rough estimate of ΔE_Q for the Re complex, we simply add an extra electron into MO b_1 (located on the three metal atom sites and originating from a_2 in bimetallic systems; see Fig. 3); this yields a calculated ΔE_Q value for the two Fe sites of 1.35 mm s^{-1}, which agrees surprisingly well with the experimental value for **1b**. An increase of Fe3d-occupancy is expected to increase δ, however, through Fe → ReS_4 charge delocalization such an effect on δ is compensated (without further change in ΔE_Q); similar observations are due to other thiometallato ferrates upon reduction e.g. the couple $[Fe(WS_4)_2]^{2-/3-}$ has almost the same δ values [13].

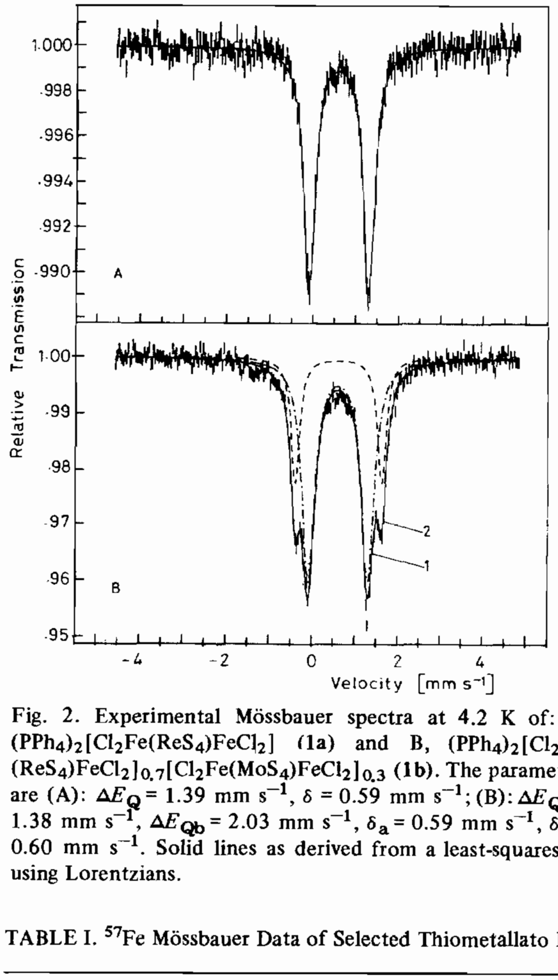

Fig. 2. Experimental Mössbauer spectra at 4.2 K of: A, $(PPh_4)_2[Cl_2Fe(ReS_4)FeCl_2]$ (**1a**) and B, $(PPh_4)_2[Cl_2Fe(ReS_4)FeCl_2]_{0.7}[Cl_2Fe(MoS_4)FeCl_2]_{0.3}$ (**1b**). The parameters are (A): ΔE_Q = 1.39 mm s^{-1}, δ = 0.59 mm s^{-1}; (B): ΔE_{Qa} = 1.38 mm s^{-1}, ΔE_{Qb} = 2.03 mm s^{-1}, δ_a = 0.59 mm s^{-1}, δ_b = 0.60 mm s^{-1}. Solid lines as derived from a least-squares fit using Lorentzians.

For the understanding of the electronic properties of thiometallato complexes of metal atoms M′ with open-shell d^n configuration it is important to inspect the MOs with predominant M′ md character (e.g. Fe3d), which correspond to crystal-field levels in a very crude approximation. Typical for all $[L_2Fe(MS_4)]^{n-}$ systems (L = Cl^-, SPh^-, $\frac{1}{2}MS_4{}^{n-}$ etc.) is the strong stabilization of the 'axial Fe3d level' a_1 (originating from e) and the pronounced splitting between the two levels originating from the 'crystal-field' e level (a_1 and a_2 for C_{2v} symmetry, a_1 and b_1 in D_{2d} systems like $[Fe(MS_4)_2]^{n-}$), *cf.* the MO scheme of Fig. 3. The upper of these two 'Fe3d' levels is directly involved in all redox processes of thiometallato ferrates (with formal $Fe^{II} \leftrightarrow Fe^{I}$ transitions) and, from MO calculations, turns out to be an almost pure metal atom centered MO with a very high M nd participation (M nd = V3d, Mo4d, W5d, Re5d). The build-up of such an orbital can be described as a δ-combination of the involved AOs, but with very low overlap (S_δ(Fe3d, M nd) ≈ 0.01 at internuclear distances of *ca.* 2.8 Å). These considerations hold for all known types of Fe–$MS_4{}^{n-}$ complexes (*i.e.* for $[L_2Fe(MS_4)]^{n-}$, $[Fe(MS_4)_2]^{n-}$ and $[Cl_2Fe(MS_4)FeCl_2]^{n-}$). Hence, the (interesting) electronic properties of **1** can be visualized using the qualitative MO scheme of Fig. 3 (the 'additional' electron and the corresponding MO are indicated by bold type.)

In thiometallato ferrates, we (generally) observe increasing Fe → $MS_4{}^{n-}$ delocalization in the series

TABLE I. ^{57}Fe Mössbauer Data of Selected Thiometallato Ferrates at Room Temperature[a]

		δ	ΔE_Q	Reference
$[Cl_2Fe(ReS_4)FeCl_2]^{2-}$	(1)	0.46	1.38	this work
$[Cl_2Fe(MoS_4)FeCl_2]^{2-}$	(2)	0.48	1.96	this work (see also 10, 11)
$[Cl_2Fe(MoS_4)]^{2-}$	(3)	0.48	2.10	12
$[Cl_2Fe(WS_4)]^{2-}$	(4)	0.52	2.27	12
$[Cl_2Fe(WS_4)FeCl_2]^{2-}$	(5)	0.52	2.10	11
$\{[Cl_2Fe(MoS_4)FeCl_2]^{2-}\}_x$		0.50	1.12	2
$[Fe(MoS_4)_2]^{3-}$		0.37	0.97	11
$[Fe(WS_4)_2]^{2-}$		0.44	2.65	13
$[Fe(WS_4)_2]^{3-}$		0.45	1.03	13
$(PPh_4)Fe(MoS_4)$		0.41	0.79	14

[a] [mm s^{-1}] δ relative to α-Fe at RT.

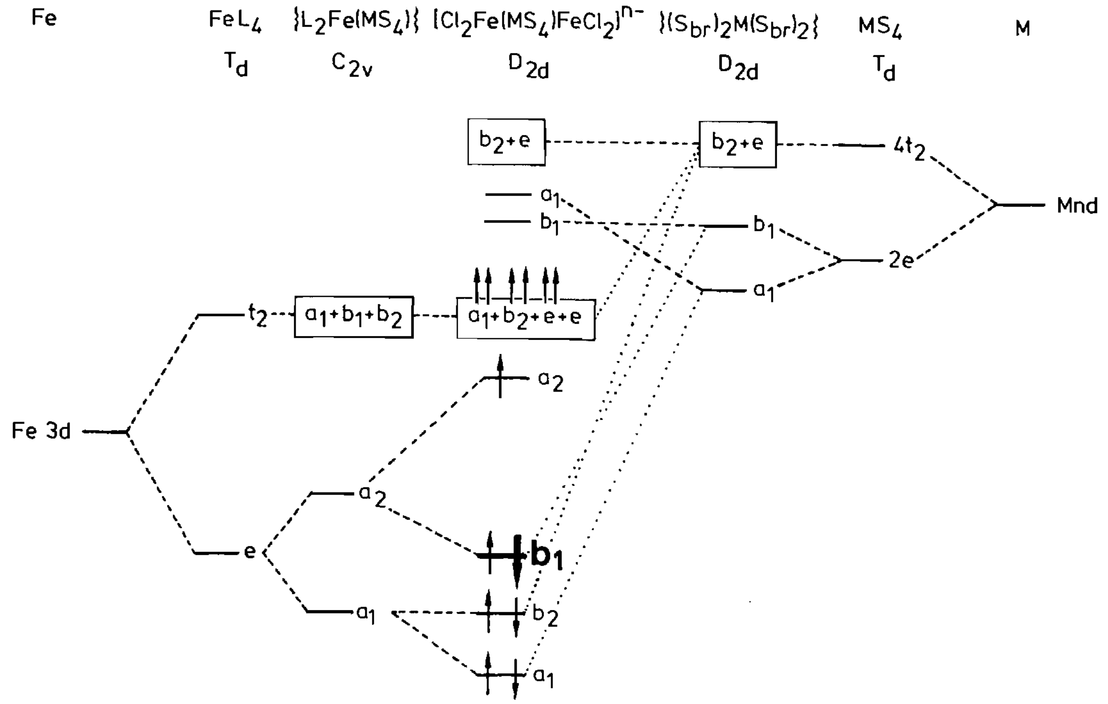

Fig. 3. MO scheme for complexes **1**, **2** and **5** as well as correlations to complexes **3** and **4** and MS_4^{n-}; the b_2 level indicated by bold type is doubly occupied for **1**, singly occupied for **2** and **5**; in the $[Cl_2Fe(MS_4)FeCl_2]^{n-}$ type complexes, the boxed 'Fe3d' levels ($a_1 + a_2 + e + e$) are singly occupied. Correlation lines indicated by – – – mark major contributions, those indicated by · · · minor contributions. Only orbitals with predominant Fe3d and M nd character are shown. Note that the correlation $\{L_2Fe(MS_4)\}$ to $[Cl_2Fe(MS_4)FeCl_2]^{n-}$ includes a formal doubling of the Fe3d orbitals.

TABLE II. Selected Data of SCCC–Extended Hückel calculations of $[Cl_2Fe(MS_4)FeCl_2]^{n-}$ [a]

	M/*n*				
	V/3	W/2	Mo/2	Re/1	Re/2
Charge on					
Cl	−0.5872	−0.5687	−0.5600	−0.5141	−0.5759
S	−0.2947	−0.0408	−0.0548	+0.1550	−0.0162
Fe	+0.1615	+0.1613	+0.1596	+0.1728	+0.1493
M	+0.2232	+0.1322	+0.1572	+0.1080	+0.0870
$E(a_2) - E(b_1)$ (10^3 cm^{-1})	4.24	5.05	5.35	6.58	5.20
Population analysis of b_1 (%)					
Fe3d	86.7	84.7	82.6	79.8	66.5
M nd	5.9	7.5	9.4	10.4	11.7

[a] For further details see ref. 16.

M = V < W < Mo < Re (*cf.* also the differences of the ^{57}Fe isomer shift of **1** compared to the reduced form of **2**). This is illustrated in Table II which contains selected results of our Extended Hückel calculations on complexes of the type $[Cl_2Fe(MS_4)FeCl_2]^{n-}$. The degree of delocalization is caused by a corresponding decrease of the M nd energies (≙ −VOIP), and thus of the LUMO 2e of the free MS_4^{n-} ions. In the same series, the 'redox MO' b_1 of $[Cl_2Fe(MS_4)FeCl_2]^{n-}$ is stabilized (increasing energy difference for $E(a_2) - E(b_1)$) by increasing M nd participation relative to the 'non-interacting' a_2 level, which by symmetry restrictions, has no such M nd contributions. For M = Re, this stabilization is so strong that the 'reduced' form **1** (for instance in **1a**) is formed and not a species with an electron population corresponding to **2** or **5**. A comparison of calculated net charges for $[Cl_2Fe(ReS_4)FeCl_2]^{n-}$ ($n = 1, 2$) shows that the 'additional' charge in **1** is mainly located on the S atoms. This result is in agreement with those of other metal sulfur systems where it was found that electrons added to the system go mainly to the sulfur ligands, although in the original system the MOs which receive these electrons are composed strongly from M nd orbitals (see also refs. 13, 17, 18).

Generalizing our results, we can formally distinguish between the 'direct' M' → M electron delocalization of Fe–MS_4^{n-} systems (where additional charge primarily 'goes' into non-bonding metal localized MOs and is consecutively rearranged) and the 'indirect' M' → M electron delocalization of, for example, Co– and Ni–MS_4^{n-} systems (where additional charge 'goes' mainly into sulfur localized MOs [18, 19]).

Complexes **2** and **5** have been shown to contain anti-ferromagnetically coupled Fe^{II} (d^6, $S' = 2$) centers (with rather small values of coupling constants [10]). In accordance with this, the observed room temperature magnetic moment of **1** [6] is somewhat reduced compared to a hypothetical value for a complex with non-interacting formal Fe^{II} ($S' = 2$) and Fe^{I} ($S' = 3/2$) centers.

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