$[ReS_4]^{\ominus}$ as an Unusually Strong σ-Acceptor Ligand: $[Cl_2Fe(ReS_4)FeCl_2]^{2\ominus}$, a Linear Heterometallic Cluster With an Odd Number of Electrons**

Achim Müller*, Erich Krickemeyer, Friedrich-Wilhelm Baumann, Rainer Jostes, and Hartmut Bögge

Abstract: $[ReS_4]^{\ominus}$ ($Et_4N^{\oplus}$ salt) reacts with $FeCl_2$ in the presence of $(Ph_4P)Cl$ in dichloromethane to give the first solid thiorhenato complex $[Cl_2Fe(ReS_4)FeCl_2]^{2\ominus}$ as $Ph_4P^{\oplus}$ salt, which contains a linear metal atom array with an odd number of electrons.

Thiometalates like $[MoS_4]^{2\ominus}$ and $[WS_4]^{2\ominus}$ (with d^0 electronic configuration) are unique species regarding their relevance to problems of bioinorganic chemistry and heterogeneous catalysis (hydrodesulfurization) but also with respect to their reactivity, versatility in their coordination behaviour (for the first published discrete complex see[1]), and their electron withdrawing power[2,3]. The first pure salt with an $[ReS_4]^{\ominus}$ ion was isolated only rather late[4] (the earlier reported «$TlReS_4$» was a mixture of Tl_2S and Re_2S_7[4]). Crystalline thiorhenato complexes were unknown.

By reaction of a solution of $(NEt_4)ReS_4$[5] in CH_2Cl_2 with $FeCl_2$ in the presence of $(PPh_4)Cl$ we now obtained dark brown needles of

$$(Ph_4P)_2\,[Cl_2Fe(ReS_4)FeCl_2]\quad \mathbf{1}$$

The structure of **1** has been determined from a single crystal structure analysis[6].

The molecular structure of the discrete linear anion $[Cl_2Fe(ReS_4)FeCl_2]^{2\ominus}$ **1a** in crystalline **1** is shown in Fig. 1 (including bond lenghts and angles). The structure can be described as an array of three edge-connected tetrahedra, with the central tetrahedral $\{S_2ReS_2\}$ unit bridging the two terminal $FeCl_2$ groups. The Fe ··· Re ··· Fe moiety is almost linear with Fe ··· Re distances of 2.740 (2) and 2.747 (2) Å. As expected, the average Re–S bond length (2.200 Å) is greater than that reported for $(Et_4N)\,[ReS_4]$ (2.125 Å)[5] – mainly due to an increase of electron density within the $\{ReS_4\}$ unit.

The short Fe ··· Re distances, results of magnetic measurements ($\mu_{eff} = 7.62\ \mu_B$ at 290 K), Mößbauer data ($\delta = 0.46$ (α-Fe) and $\Delta E_Q = 1.35$ mm/s at 293 K), the UV/VIS spectrum (band maxima in CH_2Cl_2: 550, 495, 415 (ε values about 5×10^3 L/mol cm), 300 nm (sh)), EH-SCCC-MO calculations, as well as the resonance-Raman spectrum (solid **1**/λ_e = 488.0 nm: $\nu_s(ReS) = 450\ cm^{-1}$; IR of solid **1**/nujol: $\nu_{as}(ReS) = 446\ cm^{-1}$) indicate strong metal–metal- and metal (Fe)–σ-acceptor-ligand (ReS_4) interactions [as inferred from: rather small isomeric shifts δ, no clear overtone progression of $\nu_s(ReS)$ in the resonance-Raman spectrum (see [7]), the band maxima and especially their extinction coefficients in the electronic spectrum, which do not simply correspond to those which would be expected for separated $\{ReS_4\}$ and $\{FeCl_2S_2\}$ chromophores].

It is remarkable, that the trimetallic linear species **1a** is obtained with 13 electrons and not $[Cl_2Fe(ReS_4)FeCl_2]^{\ominus}$,

*Correspondence: Prof. Dr. A. Müller
Anorganische Chemie I
Fakultät für Chemie der Universität
Postfach 8640, D-4800 Bielefeld 1
(Bundesrepublik Deutschland)

**Acknowledgement: This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Minister für Wissenschaft und Forschung des Landes Nordrhein-Westfalen. Specially we thank Prof. Dr. *A. Trautwein* und Dr. *E. Bill* for measuring the Mößbauer spectra.

Reveived: June 16, 1986 [FC 72]

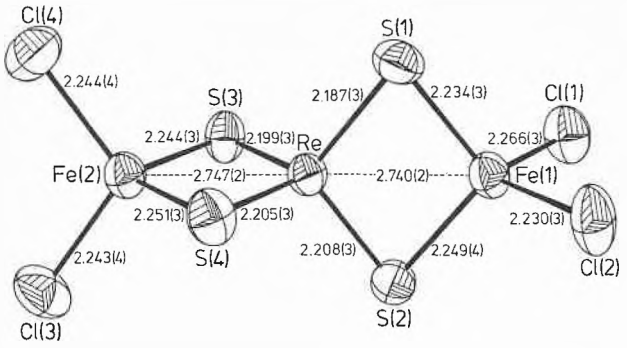

Fig. 1. Structure of the anionic complex $[Cl_2Fe(ReS_4)FeCl_2]^{2\ominus}$. Distances shown are given in Å. Bond angles (in °; all e.s.d.s. are (1)): Fe(1)–Re–Fe(2) 179.5, S(1)–Re–S(2) 105.2, S(1)–Re–S(3) 111.9, S(1)–Re–S(4) 111.1, S(2)–Re–S(3) 111.3, S(2)–Re–S(4) 112.2, S(3)–Re–S(4) 105.3, S(1)–Fe(1)–S(2) 102.3, S(1)–Fe(1)–Cl(1) 112.2, S(1)–Fe(1)–Cl(2) 109.6, S(2)–Fe(1)–Cl(1) 114.1, S(2)–Fe(1)–Cl(2) 111.6, Cl(1)–Fe(1)–Cl(2) 107.1, S(3)–Fe(2)–S(4) 102.3, S(3)–Fe(2)–Cl(3) 116.6, S(3)–Fe(2)–Cl(4) 107.5, S(4)–Fe(2)–Cl(3) 107.7, S(4)–Fe(2)–Cl(4) 113.6, Cl(3)–Fe(2)–Cl(4) 109.2, Re–S(1)–Fe(1) 76.6, Re–S(2)–Fe(1) 75.9, Re–S(3)–Fe(2) 76.4, Re–S(4)–Fe(2) 76.1.

the corresponding species to $[Cl_2Fe(MS_4)FeCl_2]^{n\ominus}$ (n = 2: M = Mo, W[9,10]; n = 3: M = V[8]) only with 12 electrons. (These complexes cannot be reduced to the trianions and tetraanions, respectively, with 13 electrons[10]). This is due to the fact, that $[ReS_4]^{\ominus}$ is an even stronger electron withdrawing (σ-acceptor) ligand than $[MoS_4]^{2\ominus}$ or $[WS_4]^{2\ominus}$ leading to an extreme electron delocalization over the whole system (with stabilization of MO's involved in the reduction process). Therefore it is useless to assign formal oxidation numbers to the metal atoms. Thus the coordination chemistry of the thiorhenate ions should be expected to differ significantly from that of $[MS_4]^{n\ominus}$ species (M = V, Mo, W; n = 2, 3).

[1] A. Müller, E. Diemann, *Chem. Commun.* (1971) 65.
[2] E. Diemann, A. Müller, *Coord. Chem. Rev. 10* (1973) 79.
[3] A. Müller, E. Diemann, R. Jostes, H. Bögge, *Angew. Chem. 93* (1981) 957; *Angew. Chem. Int. Ed. Engl. 20* (1981) 934; A. Müller, *Polyhedron 5* (1986) 323.
[4] A. Müller, E. Diemann, V.V.K. Rao, *Chem. Ber. 103* (1970) 2961; A. Müller, B. Krebs, *Naturwissenschaften 53* (1966) 178.
[5] A. Müller, E. Krickemeyer, H. Bögge, M. Penk, D. Rehder, *Chimia 40* (1986) 50.
[6] Crystal data: $C_{48}H_{40}Cl_4Fe_2P_2ReS_4$, M_r = 1246.8; triclinic, space group $P\bar{1}$; a = 10.173 (2), b = 13.064 (2), c = 20.181 (4) Å, α = 100.60 (1), β = 100.70 (2), γ = 100.87 (1)°, V = 2520.7 Å^3, ρ_{calc} = 1.64 g cm^{-3}; Z = 2; F(000) = 1234, $\mu(Mo_{K\alpha})$ = 34.65 cm^{-1}. Diffraction data were collected using a Syntex $P2_1$-diffractometer (ω-scan, at 21°C). The structure was solved by conventional heavy-atom methods. Least squares refinements (with the phenyl rings refined as regular hexagons; C–C = 1.395 Å, C–H = 0.96 Å, C–C–C = C–C–H = 120°, $U(H_n) = 1.2\ U(C_n)$) converged at an R value of 0.060 for 6729 independent reflections [$F_0 > 3.92\ \sigma(F_0)$; $4° < 2\theta < 50°$].
[7] A. Müller, W. Hellmann, *Spectrochim. Acta A41* (1985) 359.
[8] Y. Do, E.D. Simhon, R.H. Holm, *Inorg. Chem. 24* (1985) 4635.
[9] A. Müller, S. Sarkar, A.-M. Dommröse, R. Filgueira, *Z. Naturforsch. B35* (1980) 1592.
[10] D. Coucouvanis, E.D. Simhon, P. Stremple, M. Ryan, D. Swenson, N.C. Baenziger, A. Simopoulos, V. Papaefthymiou, A. Kostikas, V. Petrouleas, *Inorg. Chem. 23* (1984) 741.