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Delocalized Molecular Orbitals in the Trimetallic Thioheteroanion $[S_2WS_2CoS_2SW_2]^{2-}$: Spectroscopic and Cyclic Voltammetric Results

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Introduction

Transition metal sulfur aggregates are of interest because of their relevance to biological electron transfer processes, as they play a key role in electron transfer enzymes. In this context polynuclear metal–metal sulfur compounds having delocalized molecular orbitals and showing a reversible electrochemical reduction are especially important. In this note it will be shown that the trimetallic thioheteroanion $[Co(WS_4)_2]^{2-}$ [1], the structure of which is known from an X-ray study [2] (Fig. 1), has unusual electronic properties with delocalized orbitals and can reversibly be reduced. Thiometallates are interesting ligands, because they possess low-lying unoccupied orbitals [1].

Experimental

$[(C_6H_5)_4P]_2[Co(WS_4)_2]$ and $[(C_2H_5)_4N]_2[Co(WS_4)_2]$ were prepared as previously described [1]. The esr spectrum of a polycrystalline sample of $[(C_6H_5)_4P]_2[Co(WS_4)_2]$ (diluted with the diamagnetic isostructural host $[(C_6H_5)_4P]_2[Zn(WS_4)_2]$ [3]) was recorded at 5.3 K with a Varian spectrometer (Dr. J. Ammeter, Zurich). The cyclic voltammogram was measured using thw Polarecord E 505/E 506 of Metrohm Herisau in connection with a Philips function generator (PM 5127) and a Linseis x–y recorder. A three electrode geometry was used with Pt electrodes as working and auxiliary electrodes and an Ag/AgCl/LiCl (sat.) EtOH electrode (E_N = +0.143 V) as reference electrode. The depolarisator concentration was 10^{-3} *M* in a 10^{-1} *M* solution of $[(C_2H_5)_4N][PF_6]$ (as supporting electrolyte) in DMF. For experimental details concerning the electronic spectrum and the magnetic measurements see Table I.

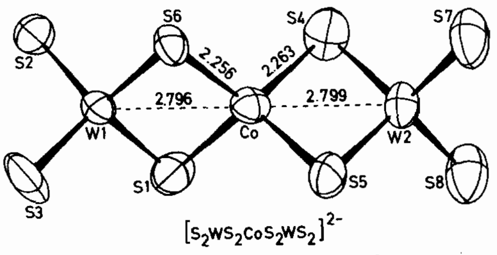

Fig. 1. ORTEP drawing of $[Co(WS_4)_2]^{2-}$ [2].

TABLE I. Physical Properties and Selected Structural Parameters of $[Co(WS_4)_2]^{2-}$.

μ_{eff}	4.00 BM[a]
ESR	$g_1 = 2.054$ $g_2 = 2.035$ $g_3 = 2.002$
Electronic Spectrum[b]	8.6 kK (25)
	12.2 kK (5300)
	17.9 kK (250)
	25.8 kK (strong)
Cyclic Voltammogram	$E^1_{1/2} = -0.52$ V
	$E^2_{1/2} = -2.04$ V
Co–S Distance (average)	2.26 A
Co–W Distance (average)	2.80 A

[a] Measured at 293 K, corrected for diamagnetic and TIP contributions. [b] In dichloromethane solution at 293 K (in brackets are ε values in M^{-1} cm^{-1}).

Results and Discussion

The unusual electronic structure of $[Co(WS_4)_2]^{2-}$, *a compound with metal centers of very different oxidation states within a four-membered ring system* (see Fig. 1), is nicely demonstrated by the electronic absorption and esr spectra, as well as by magnetic measurements, a cv study, and a qualitative MO calculation.

The esr spectrum (Fig. 2) shows an almost isotropic g tensor, which is consistent with the structure of the CoS_4 central unit (only small deviations from

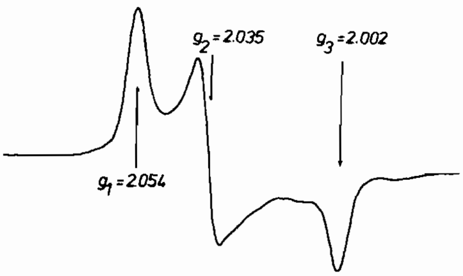

Fig. 2. ESR spectrum of $[(C_6H_5)_4P]_2[Co(ES_4)_2]$ in $[(C_6H_5)_4P]_2[Zn(WS_4)_2]$.

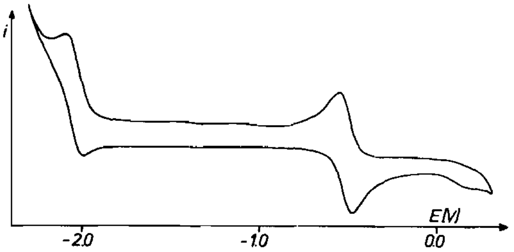

Fig. 3. Cyclic voltammogram of $[(C_2H_5)N]_2[Co(WS_4)_2]$ in DMF solution.

ideal tetrahedral geometry [2]). The observed transition occurs between the two components of the lowest Kramer doublet of the $^4A_2$ state (assuming T_d symmetry for CoS_4). The g_{av} value (2.030) is very similar to the free electron value, indicating a strong Co → ligand electron delocalization (according to the formula [4] $g_{av} = g_e (1 - 4k^2\lambda_o/\Delta)$). With the free electron value of λ_o for Co^{2+} -178 cm^{-1}) and typical values of Δ (4000 cm^{-1} in compounds with tetrahedral CoS_4 chromophores [4]) a very small orbital reduction factor k is obtained ($k^2 \sim 0.1$). The result is consistent with a very low value of the magnetic moment for a tetrahedrally coordinated Co^{2+} [4] (see Table I), as according to the formula [4] $\mu_{eff} = \mu_{eff}^{s.o.} (1 - 4k^2\lambda_o/\Delta)$ a corresponding very small k^2 value is obtained, too.

The electronic spectrum (see Table I) shows an interesting feature due to the unusual electronic structure: there is a very intense band at low energy in the ir region at 12.2 kK (the corresponding band shows a strong blue shift in the series $[Co(WS_4)_2]^{2-}$, $[Co(WOS_3)_2]^{2-}$, $[Co(WO_2S_2)_2]^{2-}$ [5]). As the spectrum of $[Co(WS_4)_2]^{2-}$ is dominated by the intense band of the ligand internal transition at 25.8 kK and the above mentioned one, it is difficult to assign weaker bands having predominant d → d character.

The electronic properties suggested that $[Co(WS_4)_2]^{2-}$ would show reversible reduction processes like the analogous species $[Ni(WS_4)_2]^{2-}$, $[Ni(WOS_3)_2]^{2-}$ and $[Ni(WO_2S_2)_2]^{2-}$ [6]. As inferred by the cyclic voltammogram, the complex can be electrochemically reduced in two one-electron processes

$$[Co(WS_4)_2]^{2-} \overset{1e}{\rightleftharpoons} [Co(WS_4)_2]^{3-} \overset{1e}{\rightleftharpoons} [Co(WS_4)_2]^{4-}$$

at least the first reduction of which is a reversible one (see Fig. 3 and Table I). The stabilization of the *formal* oxidation state 0 for Co can also be explained by the electron delocalization Co → WS_4^{2-}. The additional electrons are filled into orbitals having predominant Co 3d character (see below).

The electronic structure of the complex can only be understood on the basis of a detailed molecular orbital study, which takes into account the strong interactions between the central atom and the WS_4^{2-} ligands. The electronic structure of the free ligand is well known [7]. The HOMO's of WS_4^{2-} ($3t_2$ and t_1) are predominant π(S) orbitals. Both the direction of these orbitals and their energy ($3t_2$: -100 kK, t_1: -85 kK, calculated in a SCCC MO study [8]) favour the coordination of the Co^{2+} (3d VOIP: -89.3 kK, calculated in a SCCC MO study of CoS_4^{6-} [9]). The free ligand possesses low-lying unoccupied orbitals, which have predominantly W 5d character (2e: -56 kK, $4t_2$: -48 kK). The overlap between the Co 3d and W 5d functions at the distance of 2.80 Å shows that a direct metal–metal interaction cannot be neglected.

The first results of an EH molecular orbital study (taking into account the D_{2d} symmetry) indicate the following details of the electronic structure. There are two lower energy (a_1 and b_2, filled) and three higher energy (e and b_1, half filled) MOs having predominant Co 3d character in the complex (they correspond to the crystal field levels of Co^{2+} (T_d)). The higher energy MOs of these show a strong contribution of the t_1 and a minor contribution of the 2e and $4t_2$ ligand orbitals. The energy difference between mainly non-bonding π(S) orbitals and the half filled orbitals with mainly Co 3d character is roughly 10 kK. This suggests that the strong absorption band at 12.2 kK has to be assigned to a π(L) → d (Co) charge transfer transition.

The unusual electronic structure of $[Co(WS_4)_2]^{2-}$, having delocalized MOs, is nicely proved by the reported spectra, magnetic measurements, and the molecular orbital study, and explains the interesting electrochemical properties. The strong metal–ligand interactions are in agreement with the structural data: the average Co–S bond length (2.26 Å) is shorter than the reported for $[Co(SC_6H_5)_4]^{2-}$ (2.33 Å) [10]. Thioheteroanions like $[Co(WS_4)_2]^{2-}$ are interesting complexes with ligands having low-lying unoccupied orbitals and metal centers of very different oxidation states in four-membered ring systems.

Acknowledgements

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