Inorganica Chimica Acta, 41 (1980) 259–263
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Spectroscopic Investigations on the Molecular and Electronic Structure of $[Mo_3S_{13}]^{2-}$, a Discrete Binary Transition Metal Sulfur Cluster

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Received January 24, 1980

The only known discrete transition metal sulfur cluster $[Mo_3S_{13}]^{2-}$ *has been investigated spectroscopically (XPS, UV/VIS, IR and Raman) and by a cyclovoltammetric study. It turns out that the cluster consists of three Mo atoms with the oxidation state +IV and six* S_2^{2-} *ligands. A simplified MO treatment of the metal system in* $[Mo_3S_{13}]^{2-}$ *explains the diamagnetism of the compound, as well as the single bond character of the Mo–Mo bonds. The two absorption bands in the visible region are due to a transition within the* Mo_3 *metal system and the charge transfer transition* $\pi_v^*(S_2^{2-}) \rightarrow d(Mo)$.

Introduction

In the course of our studies on transition metal sulfur compounds we were able to isolate $[Mo_3^{IV}S_{13}]^{2-}$, the first discrete transition metal sulfur cluster [1, 2]. The trinuclear compound could be obtained by reaction of an aqueous solution of Mo^{IV} with S_2^{2-} [1] or simply by heating an aqueous solution of MoO_4^{2-} with polysulfide [2]. It was assumed that for Mo and W with d^n configuration cluster types are expected to be dumb-bell shaped (in the case of n = 1), triangular (n = 2), tetrahedral (n = 3) and octahedral (n = 4) (n indicating the number of metal–metal bonds) [1]. (Correspondingly $(NH_4)_2$-$[Mo_2S_{12}]$ could be obtained from a solution containing Mo^V [3]). The molecular and crystal structure of $(NH_4)_2[Mo_3S_{13}]$ has been determined by a single crystal X-ray diffraction study [4]. It was shown that the anion consists of a Mo_3 triangular cluster with bridging and terminal disulfur ligands. As practically nothing is known about the electronic structure of the metal–disulfur moiety and not much about the bonding in different types of triangular clusters of the early transition elements, we found it worthwhile to investigate $[Mo_3S_{13}]^{2-}$ spectroscopically. It is not yet properly emphasized in the chemical literature that for the heavier early transition elements the formation of isolated trinuclear clusters to which a variety of non-π-bonding ligands may be attached occurs very readily and under a variety of reaction conditions. The formation tendency for these trinuclear species, which are dominant for the early transition elements with intermediate oxidation states, is clearly very great [5].

Experimental

The X-ray photoelectron spectra were recorded using the ESCA 3 spectrometer of Vacuum Generators. The Al-K_α line (1486.6 eV) was used as the excitation source. The spectra were calibrated using the C $1s_{1/2}$ binding energy (at 285.0 eV) from pump oil and the N $1s_{1/2}$ binding energy (at 403.0 eV) of NH_4^+. The UV/VIS spectra were recorded using the Acta M IV spectrophotometer of Beckman Inc.. The values for the different bands of the spectra were calculated by performing a least squares fitting of the measured spectrum to the function

$$\epsilon = \sum_{i=1}^{4} \epsilon_i \cdot \exp\left[-\frac{(\tilde{\nu}_i - \tilde{\nu})^2}{\delta_i^2}\right] + A \cdot \exp(B\tilde{\nu})$$

(The exponential function was added in order to describe the high energy part of the spectrum). The number and positions of the Gaussian functions were also determined by the digital filter technique given by Marmet [6].

The infrared spectrum was recorded on a Perkin Elmer instrument (Model 180). The nujol mull technique with CsI or polyethylene plates was employed. The Raman spectrum of the solid compound was obtained with a Spex Ramalog 5M instrument equipped with a Coherent Laser CR 500 K using the 647.1 nm line. Cyclic voltammogramms were measured using the Polarecord E 506/E 505 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.) in EtOH electrode (E_N = +0.143 V) as reference electrode. The magnetism was measured on a Gouy balance of Bruker Physics.

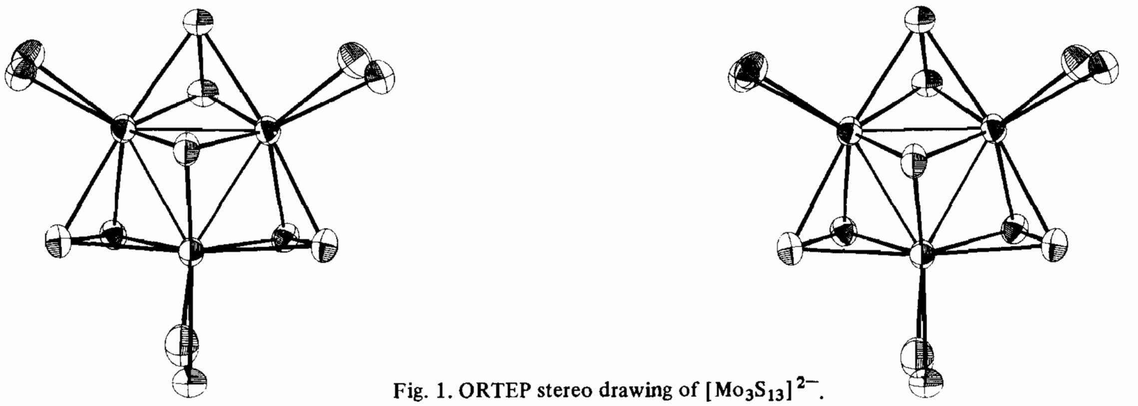

Fig. 1. ORTEP stereo drawing of $[Mo_3S_{13}]^{2-}$.

TABLE I. Binding Energies of $[MoS_4]^{2-}$, $[Mo_2S_{12}]^{2-}$, $[Mo_3S_{13}]^{2-}$ and some Mo-Compounds.

	S_{2p}	Mo $3d_{5/2}$	Mo $3d_{3/2}$	Mo $3p_{3/2}$	Mo $3p_{1/2}$	Ref.
$(NH_4)_2[MoS_4]$	163.8	231.4	234.7	397.9	415.2	This work[a]
$(NH_4)_2[MoO_4]$	–	232.1	235.2	–	–	[b]
$(NH_4)_2[Mo_2S_{12}]$	163.9	230.3	233.4	397.1	414.5	This work[a]
$MoCl_5$	–	231.0	234.5	–	–	[b]
$(NH_4)_2[Mo_3S_{13}]$[d]	163.5	230.1	233.0	395.3	413.0	This work[c]
MoO_2	–	230.9	233.9	–	–	[b]

[a] Calibrated to N 1s of $(NH_4)^+$ at 403.0 eV. [b] W. E. Swartz Jr., D. E. Hercules, *Mol. Chem.*, *43*, 1774 (1971). [c] Calibrated to C $1s_{1/2}$ at 285.0 eV (the signal of N 1s was not resolved). [d] Peaks due to the different type of S atoms could not be resolved.

$(NH_4)_2[Mo_3S_{13}]$ was prepared with the method given in reference [2]. The compounds with Mo isotopes were prepared on a milligram scale. ^{92}Mo (98.3%) and ^{100}Mo (97.4%) were purchased from Oakridge National Laboratory.

Results and Discussion

Structural Details

$(NH_4)_2[Mo_3S_{13}]$ crystallizes in the monoclinic space group *Cm*. (The compound contains variable and non-stochiometric amounts of water, which is disordered in the crystal. A refinement of the single crystal data of ref. [1] gives for occupation factor g = 0.5 a B_{iso} value for the water molecule of 7.0(1) Å^2 (at the position 0.399(4) (x), 0.139(2) (y), 0.944(7) (z)), leaving all other parameters constant). The structure consists of isolated $[Mo_3S_{13}]^{2-}$ units, with three Mo atoms at the vertices of a triangle and a unique S atom above its center, the average Mo–Mo distance being 2.722 Å. There are bridging as well as terminal disulfur units as ligands lying above and below the Mo_3-plane [4]. Each molybdenum is pseudo-tetrahedrally coordinated to one terminal, two bridging disulfur units (the average S–S distances being 2.06 Å and 2.02 Å respectively [4]) and the unique sulfur atom above the plane (see Fig. 1).

The site symmetry of the anion is C_s though the ideal symmetry is C_{3v}. This corresponds to the asymmetric coordination of the disulfur moieties.

The existence of Mo–Mo bonds is suggested by the short Mo–Mo distance, the diamagnetism of the compound, as well as the vibrational spectrum, and can be explained on the basis of a simplified MO treatment.

X-ray Photoelectron Spectra

In Table I binding energies of $(NH_4)_2[MoS_4]$, $(NH_4)_2[Mo_2S_{12}]$, $(NH_4)_2[Mo_3S_{13}]$ and some representative Mo compounds in different oxidation states are given. Figure 2 shows the photoelectron spectra in the region of S $2s_{1/2}$ and Mo 3d binding energies. The S $2s_{1/2}$ and S 2p ($p_{1/2}$ and $p_{3/2}$ are not resolved) peaks show no significant shift indicating the electron density of the sulfur atoms, being almost the same in the three compounds, though ligands of the formal type S^{2-} and S_2^{2-} have to be considered. The S 2p binding energies are of the same magnitude as those of other complexes with sulfur containing ligands (with "reduced" sulfur like S^{2-}, $-C-S^-$, $-C-S-C-$, $C=S$) [7].

The Mo binding energies of $[Mo_2S_{12}]^{2-}$ and $[Mo_3S_{13}]^{2-}$, compared to that of hexavalent Mo in $[MoS_4]^{2-}$, can be understood, if the ligands are considered as S_2^{2-} and not as S_2 (see [8]). This results in formal oxidation states +V for Mo in $[Mo_2S_{12}]^{2-}$ and

+IV in $[Mo_3S_{13}]^{2-}$. Under this assumption the data follow the binding energy order

$$Mo(VI) > Mo(V) > Mo(IV)$$

as expected. This is illustrated in Fig. 2.

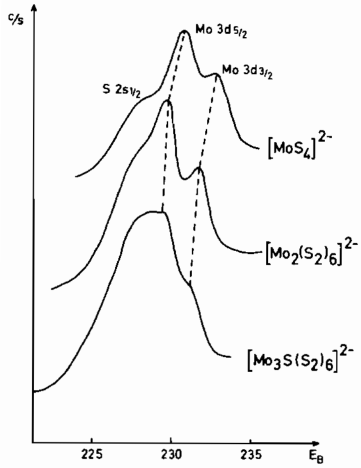

Fig. 2. XPS spectrum of $[MoS_4]^{2-}$, $[Mo_2S_{12}]^{2-}$ and $[Mo_3S_{13}]^{2-}$ in the region of the Mo 3d binding energies.

Cyclic Voltammogram of $[Mo_3S_{13}]^{2-}$

The cyclic voltammogram shows two irreversible reduction waves at −1.03 V and −1.28 V, respectively (against Ag/AgCl/LiCl(sat.) in EtOH, $E_N = +0.143$ V). The irreversibility of the reductions suggests that the LUMO has antibonding character in contrast to other trinuclear cluster compounds with structure types having a nonbonding orbital (see below).

MO Calculation and Electronic Structure of the Mo_3 *System*

The electronic structure of the cluster can be explained in terms of a *very simplified MO treatment.* In the $\{Mo(S_2)_3S\}$ unit (at each corner of the triangle) the Mo atom can be regarded as being pseudo-tetrahedrally coordinated by one S^{2-} and three S_2^{2-} ligands (see Fig. 1). Taking into account that the metal–ligand bonding orbitals can be constructed from three 4d (d_{xy}, d_{xz}, d_{yz}), the 5s and 5p metal AO s, the two 4d metal orbitals (d_{z^2} and $d_{x^2-y^2}$) remain for the bonding to the other metal atoms of the cluster. The coordinate system is that one usually used for tetrahedral complexes [9] (see Fig. 3).

Hückel-type calculations were carried out using the procedure described by Cotton and Haas [10] (for details see Appendix). The results of these calculations are reported in Fig. 4 in form of an energy diagram. There are the bonding orbitals $1a_1$ and 1e in the Mo_3 cluster system giving the electron configuration $(1a_1)^2(1e)^4$. The unoccupied MO s $1a_2$ and 2e are antibonding ones. This corresponds to single bonds between the metal atoms. Therefore the stability of the cluster and the diamagnetism can be understood.

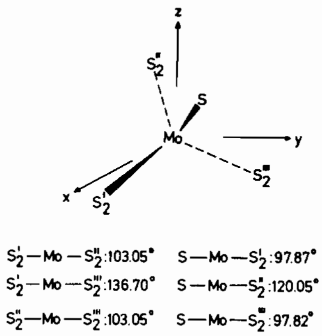

Fig. 3. Local coordinate system for the individual molybdenum sites. X and Y lie in the Mo_3 plane and Z is perpendicular to the plane.

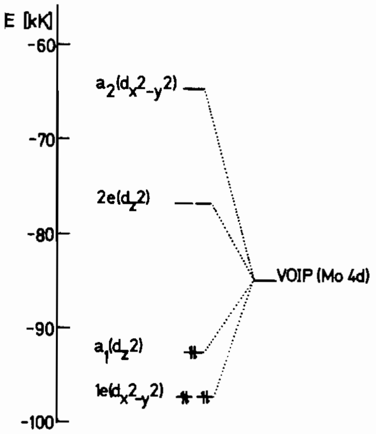

Fig. 4. Molecular orbital scheme for the Mo_3 system with orbital energies [in kK].

The lowest wavelength transition within the chromophor Mo_3 should take place between one of the bonding MO s and the 2e level. The calculation suggests that this transition is in the visible region. It is symmetry allowed and is expected to be of a higher intensity than the d–d transitions in monomeric species. The number of MO s and their energy separation in clusters are dependent on the coordination number of the metal atoms. This has important consequences for the electrochemistry and optical properties of the compounds. Up to now three different structural types of trinuclear molybdenum clusters are known: with a formal seven coordination of each metal atom and one μ_3 ligand (*e.g.* $[Mo_3S_{13}]^{2-}$), with a seven coordination and two μ_3 ligands (*e.g.* $[Mo_3(OAc)_6(CH_3CH_2O)_2(H_2O)_3]^{2+}$ [11]) and with an octahedral coordination (*e.g.* $[Mo_3O_4(C_2O_4)_3(H_2O)_3]^{2-}$ [12]). The last type of compounds exist with 6, 7, and 8 electrons in the

TABLE II. MO s for the Mo_3-System.

$\|a_1>$:	$\frac{1}{\sqrt{3}}(d_{z^2}{}^{(1)} + d_{z^2}{}^{(2)} + d_{z^2}{}^{(3)})$
$\|2e>$:	$\frac{1}{\sqrt{2}}(d_{z^2}{}^{(2)} - d_{z^2}{}^{(3)})$
	$\frac{1}{\sqrt{6}}(2d_{z^2}{}^{(1)} - d_{z^2}{}^{(2)} - d_{z^2}{}^{(3)})$
$\|a_2>$:	$\frac{1}{\sqrt{3}}(d_{x^2-y^2}{}^{(1)} + d_{x^2-y^2}{}^{(2)} + d_{x^2-y^2}{}^{(3)})$
$\|1e>$:	$\frac{1}{\sqrt{2}}(d_{x^2-y^2}{}^{(2)} - d_{x^2-y^2}{}^{(3)})$
	$\frac{1}{\sqrt{6}}(2d_{x^2-y^2}{}^{(1)} - d_{x^2-y^2}{}^{(2)} - d_{x^2-y^2}{}^{(3)})$

metal system [13] (in contrast to $[Mo_3S_{13}]^{2-}$ there exists a weakly bonding or nonbonding orbital) and has been discussed by Cotton [14]. A review about the chemistry, electronic and molecular structure of trinuclear clusters of the early transition elements will be published by Jostes, Müller and Cotton [5].

Electronic Absorption Spectrum of $[Mo_3S_{13}]^{2-}$

The spectrum shows two main peaks at 18.5 (ν_1) and 21.5 (ν_2) and two other not well defined ones at 27 (ν_3) and 30 kK (ν_4), the intensities of which were calculated by a least squares fitting (see Table III and Fig. 5).

TABLE III. UV/VIS Spectrum of $[Mo_3S_{13}]^{2-}$ in Dimethylacetamide.

	ν_i[kK]	δ_i[kK]	$\epsilon_i[10^3\,M^{-1}\,cm^{-1}]$
ν_1	18.5	1.6	1.1
ν_2	21.5	2.2	3.6
ν_3	(~27 ?)		
ν_4	(~30 ?)		

According to the results of the MO calculations ν_1 should be due to a transition within the molybdenum cluster system. This assignment is supported by the fact that the tri-nuclear cluster $[Mo_3^{IV}O_4(C_2O_4)_3(H_2O)_3]^{2-}$ shows an absorption band with almost the same intensity [12], which has to be assigned to a transition within the Mo_3 chromophor [5]. The second band ν_2 can be assigned to a $\pi_v^*(S_2^{2-}) \rightarrow \sigma^*(d(Mo))$ LMCT transition of the $Mo(S_2)$ moiety [8]. (Due to the side-on configuration of S_2^{2-} the π_g^* level splits into an in-plane orbital π_h^* forming a σ-bond to the metal and an out-of-plane orbital with nonbonding character and higher energy giving the ground state electron configuration $\ldots(\pi_h)^2(\pi_v)^2(\pi_h^*)^2(\pi_v^*)^2$). The discussed type of transfer bands are observed at nearly 21 kK in all S_2^{2-} complexes having central atoms with a rather high optical electronegativity [8].

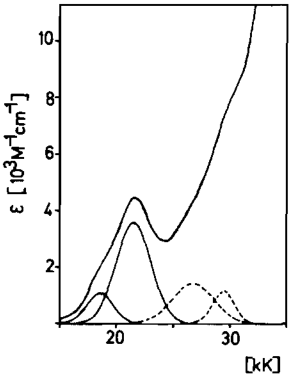

Fig. 5. UV/VIS absorption spectrum of $[Mo_3S_{13}]^{2-}$ in dimethylacetamide.

Infrared and Raman Spectra

It is difficult to assign all 42 vibrational fundamentals, which, assuming C_{3v} symmetry, can be classified according to $\Gamma(C_{3v}) = 10A_1 + 4A_2 + 14E$. Therefore we intend to discuss bands due to the ν(SS) and ν(MoMo) vibrations, only.

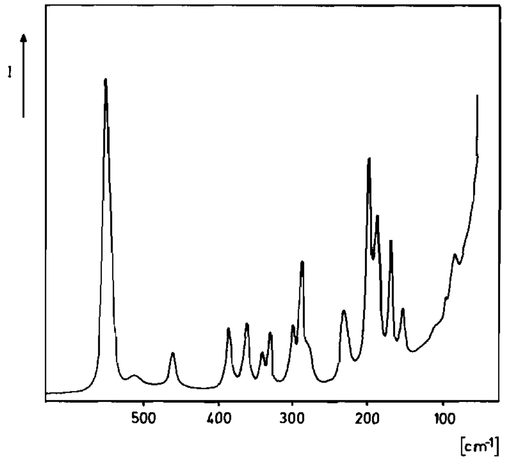

Fig. 6. Raman spectrum of solid $(NH_4)_2[Mo_3S_{13}]$.

The Raman spectrum is presented in Fig. 6. Its dominating bands with highest intensity are those due to symmetric vibrations of the homonuclear moieties S–S and Mo–Mo. This could be confirmed by measuring the ^{92}Mo–^{100}Mo isotope shifts. The intense Raman line at 197 cm⁻¹ (ν_S(Mo–Mo)-A_1) shows an isotope shift of 2.3 cm⁻¹, ν_{as}(Mo–Mo) vibration at

151 cm^{-1}, an isotope shift of 2.2 cm^{-1}. This frequency region is characteristic for vibrations of Mo–Mo bonds with single bond character. (But it should be noted that the metal stretching vibrations are strongly coupled with ν(Mo–S) vibrations, which reduce the magnitude of the isotope shift). Though the ν(SS) vibrations are coupled (they show a ^{92}Mo–^{100}Mo isotope shift of roughly 1 cm^{-1}), it can be concluded that their frequency is of an order of magnitude, which is expected for S_2^{2-} complexes. According to the different bond lengths of the bridging and terminal S_2^{2-} groups there are bands at higher (550 cm^{-1}, stretching vibration of bridging S_2^{2-}) and lower wavenumbers (500 cm^{-1}, terminal S_2^{2-}). It is interesting that the line due to the $\nu(S\text{–}S)_{bridge}$ vibration has a much higher Raman intensity than that one due to $\nu(S\text{–}S)_{term.}$. The bands of both types of vibration in the infrared spectrum are of comparable intensity.

Though it is difficult to assign all different ν(MoS) vibrations, it is clear that the 460 cm^{-1} band (ir or Raman), showing an isotope shift of 5.8 cm^{-1}, is due to a vibration of the μ_3-S atom against the Mo_3 plane as the corresponding Mo–S distance (2.353 Å) is significantly shorter than the other Mo–S distances.

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and the Minister für Wissenschaft und Forschung (NRW) for financial support.

Appendix

On the basis of the overall C_{3v} symmetry the metal orbitals d_{z^2} and $d_{x^2-y^2}$ are combined into symmetry adapted MO's (Table II).

Using the procedure of Cotton and Haas [10] the orbital energies are obtained as functions of the appropriate overlap integrals and the valence orbital-ionization potential (VOIP) of the metal. The overlap integrals were computed as linear combinations of the basic integrals S_σ, S_π and S_δ. The numerical values of the overlap integrals were computed using a modified version of the computer program given by Cook [15]. The metal wave function used was that of neutral Mo obtained by Roothaan and Synek [16] and the numerical value of the VOIP used was that one used for 4d of $Mo^{IV}S_2$ [17]. The off-diagonal matrix elements H_{ij} were approximated by the expression

$$H_{ij} = 2H_{ii}S_{ij}.$$

Note added in proof. The thermal decomposition of $(NH_4)_2[Mo_3S_{13}]\cdot nH_2O$ (n = 0–2) together with the problem of crystal water content will be reported in a later paper.

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