128. Collision-Induced Decomposition (CID) of Triangular $[Mo_3S_{7-x}Se_x]^{4+}$ Complexes ($x = 0, 3, 7$). A Liquid SIMS and FTMS/MS Study of $[Mo_3S_{7-x}Se_x(Et_2NCS_2)_3]^+$

by **Kaspar Hegetschweiler***
Laboratorium für Anorganische Chemie, ETH-Zentrum, CH-8092 Zürich

and **Pablo Caravatti**
Spectrospin AG, Industriestrasse 26, CH-8117 Fällanden

and **Vladimir P. Fedin**[1]) and **Maxim N. Sokolov**
Institute of Inorganic Chemistry, Russian Academy of Sciences,
Prospekt Lavrentyeva 3, 630090 Novosibirsk, Russia

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$[Mo_3S(S_2)_3(dtc)_3]I$, $[Mo_3S(SeS)_3(dtc)_3](dtc)$, and $[Mo_3Se(Se_2)_3(dtc)_3](dtc)$ (dtc = *N,N*-diethyldithiocarbamate) were investigated by liquid SIMS-FTMS. The fragmentation pathways were essentially the same for the three compounds and can be explained by two types of fragmentation processes: stepwise abstraction of S/Se atoms as exemplified by the series $[Mo_3X_z(dtc)_3]^+$ ($4 \leqslant z \leqslant 7$, X = S, Se), and ligand dissociation, as indicated by the generation of $[Mo_3X_z(dtc)_2]^+$ ($5 \leqslant z \leqslant 7$, X = S, Se). The exclusive elimination of the Se-atoms from $[Mo_3S(S_{ax}{-}Se_{eq})_3(dtc)_3]^+$ confirmed the inequivalent reactivity of the bridging atoms in axial and equatorial position as observed in previous studies. Collision-induced decomposition (CID) of $[Mo_3S_7(dtc)_3]^+$ (**1**), $[Mo_3S_6(dtc)_3]^+$ (**2**), $[Mo_3S(S_{ax}{-}Se_{eq})_3(dtc)_3]^+$ (**3**), and $[Mo_3Se_7(dtc)_3]^+$ (**4**) revealed distinctly different fragmentation reactions for the SIMS and CID mode. CID of **1**, **3**, and **4** resulted in a two-step reaction with the exclusive elimination of diatomic molecules XY (X,Y = S/Se). In the case of **3**, the selective elimination of Se_2 indicated the abstraction of two Se-atoms located in equatorial positions of two different bridging groups. This result is discussed in terms of mechanisms, based on labile $M{-}X_{eq}$ and inert $M{-}X_{ax}$ bonds with an intramolecular formation of a X_4 fragment prior to the elimination of X_2.

Introduction. – The recent advance in developing selective preparation methods for complexes containing the cluster cores $[Mo_3S(S_2)_3]^{4+}$ [1–5], $[Mo_3S(SSe)_3]^{4+}$ [3] [6], and $[Mo_3Se(Se_2)_3]^{4+}$ [7–10] resulted in the synthesis of a variety of novel compounds. The characterization of these complexes by X-ray analysis revealed an isostructural geometry for all three cluster cores (*Fig. 1*), containing a triangle of three Mo-atoms, capped by a single S- or Se-atom. Additional bridging is provided by three entities of S–S, Se–S, or Se–Se, respectively. The two atoms of these bridging groups are inequivalent and occupy an equatorial (in plane) and an axial (out of plane) position with respect to the Mo_3 triangle. Some characteristic reactivities of these cores have been established in solution: *i*) substitution of the peripheral ligands under complete preservation of the Mo_3X_7 core [1–5] [8] [9]; *ii*) elimination of the three atoms in equatorial position by suitable nucleophilic agents, resulting in complexes containing the $[Mo_3X_4]^{4+}$ core [1] [9] [11–14]; *iii*) anion binding by the three atoms in axial position [4] [5] [8–10]. However, no mechanistic details about these reactions are known so far.

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[1]) Present address: Fakultät für Chemie, Universität Bielefeld, Universitätstrasse 25, D-W-4800 Bielefeld.

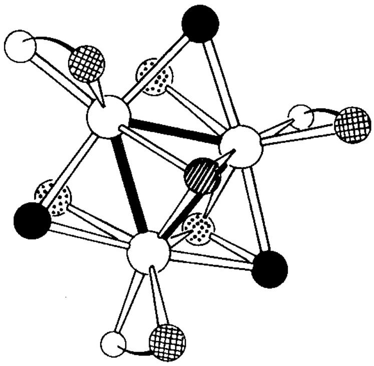

Fig. 1. *Structure of* $[Mo_3X(XY)_3(dtc)_3]^+$ (X,Y = S,Se) *with three different types of chalcogene atoms in the cluster core: the trigonal* μ_3*-X* (hatched circle), *equatorial* (closed circles), *and axial* (dotted circles) *positions in the* μ*-YX groups.* The coordinated S-atoms of dtc are shown as cross-hatched circles (*cis*-position) and small open circles (*trans*-position with respect to μ_3-X). The three large open circles represents the Mo_3 triangle.

In the mass spectra of a variety of $[Mo_3S_7L_3]$ complexes[2]), a well defined fragmentation pattern has been elucidated with the stepwise degradation of $[Mo_3S_7L_3]$ to $[Mo_3S_4L_3]$ and the loss of one ligand as main reactions [15]. In this study, ion generation was obtained by dissolving the sample in a matrix of 2-nitrobenzyl alcohol, followed by the exposure to the bombardment with a beam of Cs^+ ions (L-SIMS). The precise mechanism of ionization for FAB or L-SIMS is still discussed controversially in literature [16]. Three different processes have been discussed: in the model of *preformed ions* the basic ionization processes have been assumed to occur in the matrix. The model of the *selvege region* postulates an ionization in a transition zone of the liquid and gaseous phase. Also *ionization in the gaseous phase* has been taken into account.

In this contribution, we report the results of an extended liquid SIMS FTMS study, including the subsequent collision-induced decomposition (CID) of the *N,N*-diethyldithiocarbamato (dtc) complexes $[Mo_3S(S_2)_3(dtc)_3]^+$, $[Mo_3S(SSe)_3(dtc)_3]^+$, and $[Mo_3Se(Se_2)_3(dtc)_3]^+$. The results are discussed with regard to the molecular dynamics and reactivity of such complexes in solution and gaseous phase. For a current review of the FTMS technique, see [17].

Results and Discussion. – The fragmentation of $[Mo_3S(S_2)_3(dtc)_3]^+$ (*Fig. 2a*) has been discussed in [15]. The analogous $[Mo_3Se(Se_2)_3(dtc)_3]^+$ showed essentially the same reactivity as described by the two sequences:

a) $[Mo_3Se_7(dtc)_3]^+ \rightarrow [Mo_3Se_6(dtc)_3]^+ \rightarrow [Mo_3Se_5(dtc)_3]^+ \rightarrow [Mo_3Se_4(dtc)_3]^+$

b) $[Mo_3Se_7(dtc)_3]^+ \rightarrow [Mo_3Se_7(dtc)_2]^+ \rightarrow [Mo_3Se_6(dtc)_2] \rightarrow [Mo_3Se_5(dtc)_2]^+$.

In contrast to the previous investigation [15], a peak assignable to $[Mo_3X_4(dtc)_2]^+$ has also been detected for all three compounds. For $[Mo_3S(SSe)_3(dtc)_3]^+$, the exclusive elimination of the Se-atoms has been observed as expressed by the series $[Mo_3S_4Se_3(dtc)_3]^+$,

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[2]) L represents a bidentate ligand as shown in *Fig. 1*.

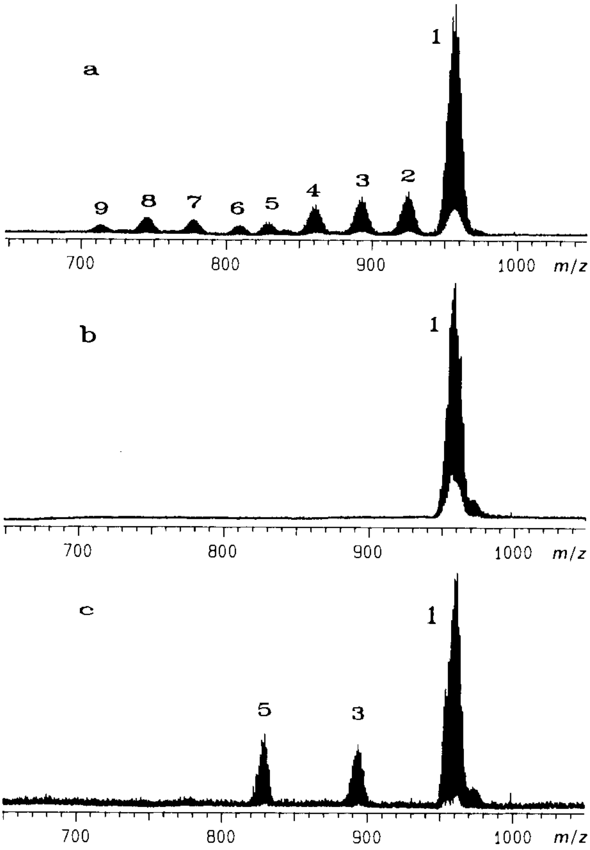

Fig. 2. *CID of* $[Mo_3S_7(dtc)_3]^+$. *a*) L-SIMS spectrum with the peak assignments: *1–4*: $[Mo_3S_x(dtc)_3]^+$ $(4 \leq x \leq 7)$, *5*: $[Mo_3S_3(dtc)_3]^+$, *6–9*: $[Mo_3S_x(dtc)_2]^+$ $(4 \leq x \leq 7)$; *b*) Verification of the selection step: isolation of $[Mo_3S_7(dtc)_3]^+$; *c*) CID products of the selected $[Mo_3S_7(dtc)_3]^+$ isotopes.

$[Mo_3S_4Se_2(dtc)_3]^+$, $[Mo_3S_4Se(dtc)_3]^+$, $[Mo_3S_4(dtc)_3]^+$, but no S abstraction has been detected. This is obviously a consequence of the particular structure of the $[Mo_3S(SSe)_3]$ core with the three Se-atoms in equatorial position as recently elucidated by X-ray analysis [3] [6]. It has been demonstrated that the atoms in equatorial positions, but not in axial positions, easily undergo exchange reactions [1] [3] [6] [18]. Thus, the major fragmentation reactions of all three complexes are basically expressed by the two processes *a*) stepwise elimination of three S- or Se-atoms, located in the equatorial position of the bridging groups and *b*) elimination of one ligand molecule. It is interesting to note that the observed fragmentation is in close accordance with the basic solution chemistry of these complexes [19].

Collision-induced decomposition (CID) is a powerful method to elucidate the possible fragmentation channels of a given ion [16]. In this study, CID was performed inside the trapped-ion cell of a FTMS spectrometer. After an unselective trapping of all ions resulting from the L-SIMS ionization, the undesired ions were removed selectively from the cell. The remaining, selected ions[3]) were then accelerated, and a small amount of room-temperature Ar gas was then introduced into the cell. The collisions of the accelerated ions with the Ar-atoms resulted in an excitation and fragmentation of the ions. Considering the kinetic energy of the Mo-containing ions ($\sim$ 110 eV), and the mean free path (47 m) and the thermal energy ($\leqslant$ 0.1 eV) of the Ar-atoms, a number of $\sim$ 100 collisions[4]) prior to the detection and an excitation energy of $\leqslant$ 4.4 eV[5]) can be estimated. It is interesting to note that this excitation energy lies in the range of usual bond energies. The CID spectra of $[Mo_3S(S_2)_3(dtc)_3]^+$, $[Mo_3S_2(S_2)_2(dtc)_3]^+$, $[Mo_3S(SSe)_3(dtc)_3]^+$, and $[Mo_3Se(Se_2)_3(dtc)_3]^+$ exhibited a striking difference to the fragmentation observed under pure L-SIMS conditions. As an example, the result for $[Mo_3S(S_2)_3(dtc)_3]^+$ is presented in *Fig. 2*.

A concluding summary of the CID reactions observed in this investigation is given in the following scheme:

$$[Mo_3S_7(dtc)_3]^+ \xrightarrow{-S_2} [Mo_3S_5(dtc)_3]^+ \xrightarrow{-S_2} [Mo_3S_3(dtc)_3]^+$$

$$[Mo_3S_6(dtc)_3]^+ \xrightarrow{-S_2} [Mo_3S_4(dtc)_3]^+$$

$$[Mo_3S_4Se_3(dtc)_3]^+ \xrightarrow{-Se_2} [Mo_3S_4Se(dtc)_3]^+ \xrightarrow{-SSe} [Mo_3S_3(dtc)_3]^+$$

$$[Mo_3Se_7(dtc)_3]^+ \xrightarrow{-Se_2} [Mo_3Se_5(dtc)_3]^+ \xrightarrow{-Se_2} [Mo_3Se_3(dtc)_3]^+$$

Conclusions. – The three clusters $[Mo_3S_7(dtc)_3]^+$, $[Mo_3S_4Se_3(dtc)_3]^+$, and $[Mo_3Se_7(dtc)_3]^+$ showed a very similar reactivity not only in the L-SIMS spectrum but also in the CID spectrum. However, the spectra revealed distinctly different fragmentation reactions for L-SIMS and CID. The basic fragmentation observed in the L-SIMS spectrum is closely related to established reactions in solution. However, species of the composition $[Mo_3X_3(dtc)_3]^+$, the dominant fragmentation products upon CID, which have never been observed in solution, appeared also in small amounts in the L-SIMS spectrum (*Fig. 2, Peak 5*). This observation clearly supports the suggestion that the observed ions in the L-SIMS spectrum are the result of, at least, two independent processes: S/Se-atom abstraction and ligand dissociation of solvated molecules in the matrix on the one hand and collision-induced X_2 elimination in the gaseous phase on the other hand. Nevertheless, the L-SIMS spectrum is strongly dominated by processes assigned to solution chemistry, indicating that ion generation and fragmentation preferably occur in the matrix. The hypothesis of different fragmentation processes is also supported by the detection of the ion $[Mo_3X_4(dtc)_2]^+$. No significant amount of these species has been reported recently in the FAB spectrum of $[Mo_3S_7(dtc)_3]I$ [15]. The re-investigation of these

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[3]) In the present investigation, all isotope combinations of $[Mo_3X_7(dtc)_3]^+$ (X = S, Se) were selected for the subsequent CID experiment. The slight modification of the isotope pattern after the selection step (*Fig. 2*) is a consequence of a not completely uniform interference of the selection pulse with the different isotopes.

[4]) It must be considered that the cross section of the Mo-containing ions is unknown but substantially larger than that of an Ar-atom.

[5]) It is not possible to determine the amount of energy which is available for excitation of one ion. The above mentioned value is calculated assuming a completely inelastic collision, and must be regarded as an upper limit.

experiments confirmed the absence of this species under the previously described conditions. Thus, the amount of species formed by different ionization processes strongly depends on particular experimental conditions.

In contrast to the fragmentation under L-SIMS conditions, no abstraction of single Se- or S-atoms has been observed for CID, but diatomic molecules S_2 and Se_2 were eliminated exclusively. $[Mo_3X_3(dtc)_3]^+$ was the final species of this process, and no further fragmentation has been observed. Thus, it seems that this ion is quite stable in gaseous phase. Nothing is known about the structure of $[Mo_3X_3(dtc)_3]^+$. If we suppose the conventional oxidation numbers –II for S and Se, and the charge –1 for dtc, this complex must be regarded as a reduced species with the core $[Mo(IV)Mo(III)_2X_3]^{4+}$. The elimination of Se_2 from $[Mo_3S_4Se_3(dtc)_3]^+$ indicates clearly that two atoms located in the equatorial position of two *different* bridging units were abstracted. This phenomenon is explained by the mechanism shown in *Fig. 3*. In this context, it is interesting to note that both the reactivity in solution and in the gaseous phase are based on labile bonds $Mo-X_{eq}$ (X = S, Se).

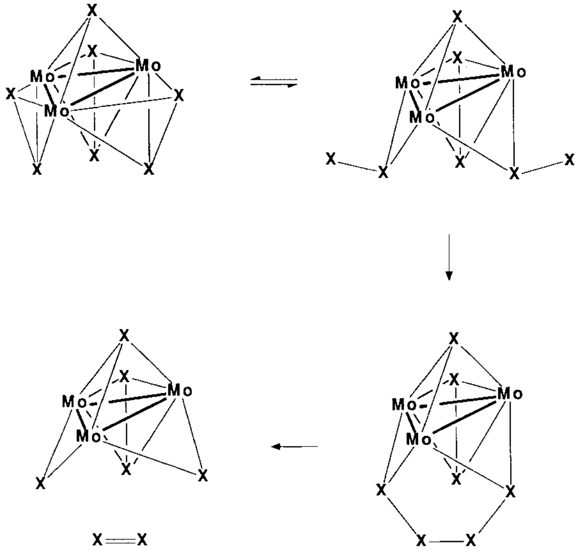

Fig. 3. *Postulated mechanism for collision-induced X_2 elimination* (X = S, Se) *from $[Mo_3X_7(dtc)_3]^+$ in gaseous phase. i)* Rupture of the labile $Mo-X_{eq}$ bonds, *ii)* intramolecular formation of a coordinated X_4 fragment, *iii)* elimination of X_2. The dtc ligands are omitted for clarity.

However, in solution, the diatomic chalcogenide bridges were degraded in a bimolecular reaction by the attack of a nucleophile, whereas in gaseous phase a unimolecular reaction occurred. The labile $Mo-X_{eq}$ bonds correspond well with the structural properties of the $[Mo_3X_7]$ core. A comparison of a variety of $[Mo_3X_7]$ complexes established a significantly longer $Mo-X_{eq}$ bond compared to the corresponding $Mo-X_{ax}$ bond [4] [8].

In agreement with this mechanism, we observed the elimination of S_2 from $[Mo_3S_6(dtc)_3]^+$, leading to $[Mo_3S_4(dtc)_3]^+$ without any further fragmentation for this particular molecule in the CID spectrum. Obviously, $[Mo_3S_4(dtc)_3]^+$ is not a precursor of

$[Mo_3S_3(dtc)_3]^+$, and $[Mo_3X_3(dtc)_3]^+$ is exclusively generated by X_2 elimination from $[Mo_3X_5(dtc)_3]^+$ in the gaseous phase. Again, this reaction must be initiated by the rupture of the labile $Mo{-}X_{eq}$ bonds as indicated by the elimination of SeS from $[Mo_3S_4Se(dtc)_3]^+$.

No ligand dissociation at all has been observed in the CID spectrum. The generation of $[Mo_3S_7(dtc)_2]^+$, $[Mo_3S_6(dtc)_2]^+$, and $[Mo_3S_5(dtc)_2]$ in the FAB spectrum has been explained by the postulation of an oxidative addition of a S–S group to Mo [15]. However, the absence of ligand dissociation for CID strongly supports a more complicated process where solvent molecules also participate in the reaction.

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Experimental Part

Materials. $[Mo_3S_7(dtc)_3]I$ [4], $[Mo_3Se_7(dtc)_3](dtc)$ [9], and $[Mo_3S_4Se_3(dtc)_3](dtc)$[6] [20] were prepared according to previously published methods. All other reagents were commercially available products of reagent-grade quality.

Mass Spectrometry. Mass spectra were recorded on an *APEX 47e Fourier*-Transform Ion-Cyclotron-Resonance Mass Spectrometer[7]) from *Bruker Spectrospin* (4.7 Tesla), equipped with the standard ion source, which was placed outside the r.t. bore of the superconducting magnet. The differentially pumped vacuum system allowed a base pressure of 10^{-9} mbar in the analyzer cell system, 1 µl of a 1 % sample solution (CH_2Cl_2) was mixed with 1 µl of 3-nitrobenzyl alcohol on a stainless steel target. The target was then introduced into the ion source. L-SIMS spectra were obtained by bombarding the sample with a pulsed Cs^+ beam (12 keV, pulse length 100 ms) provided by a Cs^+-ion gun from *Phrasor Scientific Inc.* For the CID spectra, ion generation was performed in the same way. Undesired ions were then selectively removed from the trapped-ion cell by applying suitable electric radiofrequency pulses. The remaining ions were accelerated simultaneously to a kinetic energy of *ca.* 110 eV (radius of the cyclotron orbit, 1 cm). A 20-ms r.t. Ar-gas pulse was then applied to raise the pressure briefly to a value of *ca.* 10^{-5} mbar. During a delay of 1 s, the activated ions were allowed to interact with the neutral Ar gas. The spectrum of the CID products was recorded using the standard procedure of FT-ICR spectrometry [17]. Assignments of the peaks in the SIMS spectra are based on the analysis of the isotope pattern including all isotopes of C, N, S, Se, and Mo with natural abundance $\geq 0.01\,\%$.

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[6]) The sample contained some traces of $[Mo_3S_5Se_2(dtc)_3](dtc)_3$.

[7]) Succeeding model of the *CMS 47X* FT-ICR spectrometer [21] with improved data-processing capabilities.

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