

## SHORT COMMUNICATIONS

### SYNTHESIS AND INFRARED STUDY OF SOME NEW SELENATO AND MOLYBDATO DERIVATIVES

Abdou S. Sall, Oumar Sarr and Libasse Diop,  
Laboratoire de Chimie Minerale, Department de Chimie, Faculte des  
Sciences et Techniques, Universite C.A. Diop de Dakar, Senegal

(Received 3 January 1992)

**ABSTRACT.** The title compounds have been synthesized and tentative polymeric or discrete structures suggested on the basis of their IR data. In all of these derivatives, the anion behaves as polydentate.

#### INTRODUCTION

Several selenium containing complexes were reported where the selenato ligand behaves as monodentate [1,2] or polydentate [3-5]. In our previous investigation [6-9] adducts and derivatives containing coordinating oxoanions have been studied. Here we report on the synthesis and characterization of some selenato and molybdato derivatives and also suggest structures based on their IR spectra.

#### EXPERIMENTAL

The ligand,  $(Me_4N)_2 SeO_4$ , was prepared according to literature method [7]. All of the title compounds were obtained as precipitates by mixing ethanolic solutions of the metal halides, namely  $HgCl_2$ ,  $ZnCl_2$ ,  $FeCl_3$  and  $SbCl_5$ , with the ligand in appropriate stoichiometric ratios. The precipitates were filtered and washed with hot ethanol and acetone and dried over  $P_2O_5$ . All reagents and solvents were obtained from Merck. The IR were recorded on a PE 580 spectrophotometer as nujol mulls using CsI plates. Elemental analyses were performed by the microanalytical laboratory of the department of inorganic chemistry of Padua University (Italy). Satisfactory agreement was observed between the calculated and experimental analytical data.

#### RESULTS AND DISCUSSION

The IR spectral data of the compounds synthesized are summarized in Table 1.  $(Me_4N)_2 M_2''(XO_4)_2$  ( $M=Hg,Zn; X=Se,Mo$ ). The formulas for these compound have

similarity to those of  $(Me_4N)_2(SnMe_2)_2(SeO_4)_3$ . The structures of the latter compounds have been reported [6]. Considering octahedral or tetrahedral environment for the metal, two possible structures can be formulated. If the metal environment is octahedral, a three-dimensional structure with tetra-unidentate non spectroscopically equivalent oxoanions can be suggested.

Table 1: Infrared spectra of the selenato and molibdato derivatives

Derivatives	Frequencies ( $cm^{-1}$ ) and assignments
$Hg_2(SeO_4)_3(Me_4N)_2^+$	$\nu_3=840$ (vs); $\nu_1=770$ (trace); $\nu_3^*=960$ (s), 905 (s), 855 (vs); $\nu_1^*=790$ (s); $\nu_4=385$ (m); $\nu_2^*=320$ (m); $\nu_{HgO}=245$ (m)
$Zn_2(MoO_4)_3(Me_4N)_2^+$ 2/3 EtOH	$\nu_3=820$ (vs); $\nu_3^*=935$ (s), 885 (s), 850 (s); $\nu_1^*=795$ (s); $\nu_4^*=400$ (m), 385 (m), 360 (m); $\nu_4=325$ (m); $\nu_2^*=305$ (m); $\nu_{ZnO}=255$ (w), 235 (w), 205 (w)
$Sb(SeO_4)_2Me_4N$	$\nu_3=880$ (vs), 850 (sh); $\nu_4=440$ (s), 415 (sh), 395 (sh); $\nu_{SbO}=245$ (m)
$Fe(SeO_4)_2Me_4N$	$\nu_3=840$ (vs); $\nu_3^*=925$ (vs), 895 (s), 870 (s); $\nu_1^*=824$ (s) $\nu_4=500$ (s), 465 (s), 420 (s); $\nu_4=390$ (vs); $\nu_2^*=340$ (m); $\nu_{FeO}=290$ (m), 265 (m)

$\nu_1$  and  $\nu_1^*$  are relative to a  $Td$  and a  $C_{2v}$  anion, respectively; vs=very strong; s=strong; m=medium; w=weak; sh=shoulder.

Similarly if the environment around the metal ion is tetrahedral, a discrete structure with one bichelating and two chelating oxoanions is a possibility as in  $(Me_4N)_2(SnMe_2)_2(SeO_4)_3$ . The IR data of the selenato and molybdato derivatives suggest a structure which consists of a central bichelating  $Td$  anions and two external anions belonging to  $C_{2v}$  point group. By comparison with the IR data of  $SnBu_2SeO_4$  [6], we can assign the bands at 840 and 385  $cm^{-1}$  to  $\nu_3$  and  $\nu_4$  relative to the central selenato while the other bands are assigned to external  $C_{2v}$  selenates. The tentative structure is depicted in Fig. 1.

$Me_4NM^III(SeO_4)_2$  ( $M^III=Sb, Fe$ ). The IR data for the antimony derivatives suggest a  $Td$  symmetry for the selenato anion. The presence of  $\nu_{SbO}$  at 240  $cm^{-1}$  indicates coordination between  $SeO_4^{2-}$  and Sb. Two tridimensional structures can be considered: one containing a tetra-unidentate selenate, the antimony being surrounded by eight selenates, and a second one containing four bichelating selenates around antimony. A similar structure has been forwarded for Sn in  $Sn(NO_3)_4$  [10] and in  $Sn(CH_3COOH)_4$  [11]. The lack of complexity in the spectrum led us to propose the latter structure as in Fig. 2. The IR spectrum of the ferric derivatives indicates two types of selenates. The bands at 840  $cm^{-1}$  and 390  $cm^{-1}$  indicate a bichelating selenate. The other stretching bands are characteristic of  $C_{2v}$  point group selenates. These features suggest an infinite layer structure where infinite chains of  $Fe^III$  linked by bichelating selenates as depicted in Fig.

3. The different values for the  $v_{FeO}$  indicate different sites for the selenates.

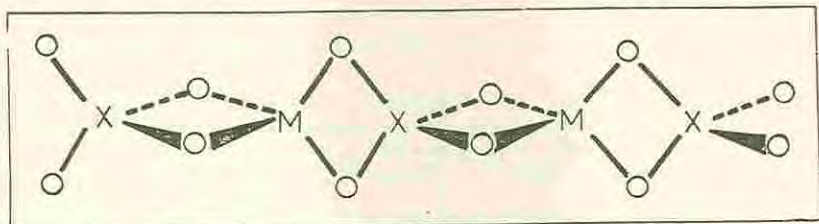


Fig. 1 Tentative structures for  $(Me_4N)_2(SnMe_2)_2(SeO_4)_3$

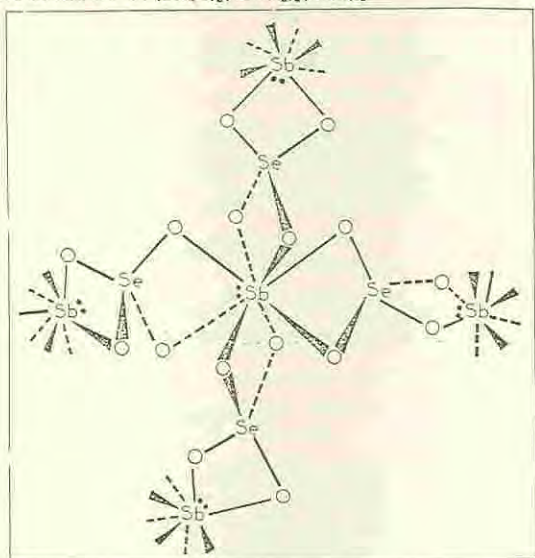


Fig. 2 Proposed structure for  $Me_4NM^{III}(SeO_4)_2$

## CONCLUSION

The title derivatives have polymeric or discrete structures. In all these derivatives, the oxoanions act as monochelates, bridged bi-unidentate or bridged bichelates, but never as monodentate. The structural differences between  $Sb^{III}$  and  $Fe^{III}$

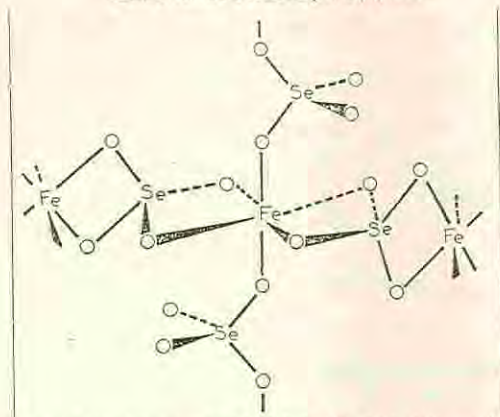


Fig. 3 Infinite layer structure of  $\text{Fe}^{\text{III}}$  linked by bichelating selenates.

derivatives can be linked to size of the central metal. The small size of  $\text{Fe}^{\text{III}}$  compared to  $\text{Sb}^{\text{III}}$  does not allow the presence of two bichelating and two bridged bidentate selenates (octahedral environment).

### ACKNOWLEDGEMENTS

Equipment support from Professors M. Vidali and Pecile (University of Padua)-Italy and financial support from TWAS (Italy) to O. S and A.S.C are acknowledged.

### REFERENCES

1. R.G. Brown and S.D. Ross, *Spectrochim. Acta*, **26A**, 955 (1970).
2. S.D. Ross and A.Thomas, *Spectrochim. Acta*, **26A**, 971 (1970).
3. B.F.E. Ford, J.R. Sams, R.G. Goel, and D.R. Ridely, *J. Inorg. Chem.*, **33**, 23 (1971).
4. C. Benelli, M. Divaira, G. Noccioli and L.Sacconi, *Inorg. Chem.*, **16**, 182 (1977).
5. B.J. Hathaway, "Comprehensive Coordination Chemistry", Vol.2, Pergamon press, (1987) p 413 .
6. O. Sarr and L. Diop, *Spectrochim. Acta*, **46A**, 1239 (1990).
7. O. Sarr and L. Diop, *Bull. Chem. Soc. Ethiop.*, **4**, 137 (1990).
8. A.S. Sall and L. Diop, *Inorg. Chim. Acta*, **171**, 53 (1990).
9. M. Lahlou and L. Diop, *Spectrochim. Acta*, **47A**, 12, 1775 (1991).
10. C.D. Gardner, P. Sutton and S.C. Wallwork, *J. Chem. Soc.(A)* 1949 (1967).
11. N.W. Alcock and V.L. Tracy, *Acta Crystallogr. Sect.B*, **80** (1979).