

09.5-16 A COUPLE OF CRYSTAL MODIFICATIONS OF COMPLEX OF MIXED-VALENT CLUSTER  $(VO_4^{3-})_2(VO^{2+})_3$  AND DIETHYLENTRIAMINE. By Z.H. Pan, M.C. Shao, S.M. Xu and Y.Q. Tang, Institute of Physical Chemistry, Peking University, Beijing, China.

To our knowledge the crystal structures of polynuclear complexes containing mixed-valent and mixed structural units of oxo-vanadium have been rarely reported in literature.

In 1985, by XRD study with  $CuK\alpha$  radiation, we first found the  $\alpha$ -modification of title complex  $V_5O_{11}(\text{dien})_3$  prepared by dissolving  $V_2O_5$  in the mixture of diethylenetriamine, 30% aqueous solution of  $H_2O_2$  and t-butyl hydroperoxide.

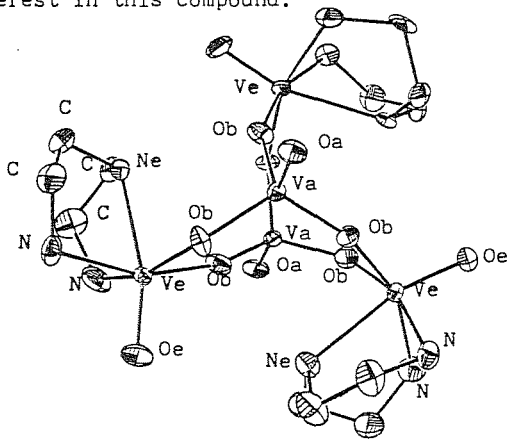
The compound crystallizes in space group  $C_{6h}^2 - P 6_3/m$  with  $a=10.845(4) \text{ \AA}$ ,  $c=13.018(5) \text{ \AA}$ ,  $D_m=D_x=1.85 \text{ g.cm}^{-3}$ . The unit cell of  $\alpha$ -form contains two discrete molecules both sitting on special positions possessing point symmetry of  $C_{3h}$ . We have described the main structural features of the molecule in Proceedings of International Symposium on Molecular Structure (1986, Beijing, page 282).

Very recently we have found a new form, namely,  $\beta$ -form coexisting with  $\alpha$ -form in a preparation using aqueous solution of  $VOSO_4$  and mixture of t-butyl hydroperoxide, diethylenetriamine, toluene and chloroform as starting materials.

The  $\beta$ -form belongs to space group  $C_6^2 - P 6_3$  with  $a=18.830(7) \text{ \AA}$ ,  $c=13.074(4) \text{ \AA}$ ,  $D_x=1.84 \text{ g.cm}^{-3}$ ,  $Z=6$ , and  $\mu=18.4 \text{ cm}^{-1}(\text{MoK}\alpha)$ . The least-squares refinement using 2471 reflections gave an agreement factor  $R=0.0343$ . These two forms represent two different crystalline species, but consist of same molecules. Each complex molecule of  $\beta$ -form sits on a general position and has a backbone  $(V_5O_{11})$  with a non-crystallographic symmetry of  $C_{3h}$ . The average lengths ( $\text{Å}$ ) for different V-O and V-N bonds are given below:

Va-Oa 1.663(6); Ve-Oe 1.618(4); Ve-N 2.166(6); Va-Ob 1.724(5); Ve-Ob 1.946(5); Ve-Ne 2.318(5).

According to the bonding character of vanadium, we were able to recognize that the cluster  $V_5O_{11}$  consists of two vanadate and three vanadyl groups as represented by  $(VO_4^{3-})_2(VO^{2+})_3$ . The title compound is neither a simple vanadium oxide nor a polyvanadate. It contains a neutral cluster with mixed valence of V(V) and V(IV). These two features justifies our interest in this compound.



09.5-17 NEW REDUCED OXONILOBATES CONTAINING  $Nb_6$ -CLUSTERS. By J. Köhler and A. Simon, Max-Planck-Institut für Festkörperforschung, D-7000 Stuttgart-80, FRG

There are many metal-rich halogenides and chalcogenides of the d-metals containing isolated or condensed clusters. Mo is characterized by a great number of corresponding oxides. The structures of  $NbO$  and  $Mg_3Nb_6O_{11}$  indicate that also the element Nb should form metal clusters in many oxoniobates.

A series of oxoniobates with metal-metal bonds was prepared by varying the counter-cations taking fluorides as mineralizers. The crystal structure of  $Mg_3Nb_6O_{11}$  (I), known from powder diffraction data, was verified by single crystal measurements. The crystal structure of the isotopic  $Mn_3Nb_6O_{11}$  (II) was also determined. (I) and (II) contain discrete  $Nb_6$ -octahedra which are connected via the O-atoms according to  $[Nb_6O_6/2]^{1-10}O_6^{1-}$ .  $[Nb_6O_{12}]$ -clusters (differently connected) are also the essential building units in the new compounds  $Na(Si,Nb)Nb_3O_{19}$  (III),  $Na_3Al_2Nb_3O_{19}$  (IV) and a further oxide in the system  $Na-V-Nb-O$  (V) which is thus far only partially characterized; (III) and (IV) also contain  $NbO_6$ -octahedra with Nb in the oxidation states +4 and +5. The  $Nb^{4+}$  atoms form pairs ( $d_{Nb-Nb} < 270 \text{ pm}$ ) via an O-O edge. The counter-cations (Na, Al, Si, V) occupy holes in the anion part. The number of valence electrons in the  $Nb_6$ -clusters is 14 (I,II), 14.33 (III) and 15 (IV). The distances within the octahedra are short and are in the range 279 and 287 pm. The conditions for preparation, data concerning structure determination of single crystals, and chemical aspects of all five compounds are presented and discussed.

09.5-18 V-O BOND DISTANCES IN STRUCTURES OF HETEROPOLYVANADATES. By H. Ichida, T. Ozeki, K. Nagai, Y. Michiue & Y. Sasaki, Department of Chemistry, Faculty of Science, The University of Tokyo, Tokyo 113, Japan.

Structures of four heteropolyvanadates have been determined and compared in aspect of V-O bond distances.

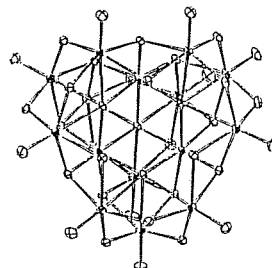
(I)  $(NH_4)_7[HSe_4V_{10}O_{37}] \cdot 9H_2O$ : Mr=1706.64, tetragonal,  $I4_2m$ ,  $a=20.829(3)$ ,  $c=21.580(3) \text{ \AA}$ ,  $U=9362 \text{ \AA}^3$ ,  $Z=8$ ,  $D_x=2.42$ ,  $D_m=2.46 \text{ Mg m}^{-3}$ ,  $\mu(\text{MoK}\alpha)=5.04 \text{ mm}^{-1}$ ,  $R=0.071$  for 2108 reflections.

(II)  $K_3[H_3Mn_3V_{12}O_{40}] \cdot 8H_2O$ : Mr=1758.7, triclinic,  $P1$ ,  $a=11.800(2)$ ,  $b=16.555(2)$ ,  $c=11.267(2) \text{ \AA}$ ,  $\alpha=102.91(1)$ ,  $\beta=109.48(1)$ ,  $\gamma=86.88(1)^\circ$ ,  $U=2022.9 \text{ \AA}^3$ ,  $Z=2$ ,  $D_x=2.90 \text{ Mg m}^{-3}$ ,  $\mu(\text{MoK}\alpha)=4.07 \text{ mm}^{-1}$ ,  $R=0.041$  for 7950 reflections.

(III)  $K_{10}[Mn_2V_{22}O_{64}] \cdot 20H_2O$ : Mr=3005.8, triclinic,  $P\bar{1}$ ,  $a=15.710(4)$ ,  $b=12.671(4)$ ,  $c=10.281(3) \text{ \AA}$ ,  $\alpha=113.62(2)$ ,  $\beta=92.56(3)$ ,  $\gamma=79.54(3)^\circ$ ,  $U=1843.1 \text{ \AA}^3$ ,  $Z=1$ ,  $D_x=2.67 \text{ Mg m}^{-3}$ ,  $\mu(\text{MoK}\alpha)=3.53 \text{ mm}^{-1}$ ,  $R=0.067$  for 8085 reflections.

(IV)  $Na_6[H_2I_2V_2O_{16}] \cdot 10H_2O$ : Mr=931.79, triclinic,  $P\bar{1}$ ,  $a=8.927(2)$ ,  $b=11.470(2)$ ,  $c=6.137(1) \text{ \AA}$ ,  $\alpha=95.83(1)$ ,  $\beta=98.00(2)$ ,  $\gamma=70.13(1)^\circ$ ,  $U=584.2 \text{ \AA}^3$ ,  $Z=1$ ,  $D_m=2.65$ ,  $D_x=2.65 \text{ Mg m}^{-3}$ ,  $\mu(\text{MoK}\alpha)=3.71 \text{ mm}^{-1}$ ,  $R=0.021$  for 3190 reflections.

Each structure is constructed by  $VO_6$  octahedra sharing edges or vertices with each other and heteroatom sites. (I) has an additional  $VO_5$  pyramidal geometry.  $SeO_3$ ,  $MnO_6$  and  $IO_6$  moieties are less distorted than  $VO_6$ . V-O bond distances are dependent on the coordination numbers of O atoms and are also influenced by the bond in the trans site.



$[H_3Mn_3V_{12}O_{40}]^{3-}$  anion