C-198  09. STRUCTURES OF ORGANIC AND COORDINATION COMPOUNDS

09.5-16  A COUPLE OF CRYSTAL MODIFICATIONS OF COMPLEX OF MIXED-VALENT CLUSTER \((\text{VO}_3^3-)_{2}^{2} (\text{VO}_2^2-)_{3}\) AND DIETHYLENETRIAMINE. 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 \(\text{VO}_3\)(dien)\(_3\) prepared by dissolving \(\text{VO}_2\) in the mixture of diethylenetriamine, 30\% aqueous solution of \(\text{H}_2\text{O}_2\) and t-butyl hydroperoxide. The compound crystallizes in space group \(P\overline{6}m\) with \(a=10.805(4)\,\AA\), \(c=13.016(5)\,\AA\), \(D_m=\text{Dx}=1.85\, \text{g}\cdot\text{cm}^{-3}\). The unit cell of \(\alpha\)-form contains two discrete molecules both sitting on special positions possessing point symmetry \(C_{3h}\). We have described the main structural features of the molecule in Proceedings of International Symposium on Molecular Structure (1985, 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 \(\text{VOSO}_4\) and mixture of t-butyl hydroperoxide, diethylenetriamine, toluene and chloroform as starting materials.

The \(\beta\)-form belongs to space group \(C\overline{6} 2-P\overline{6} m\) with \(a=16.830(7)\,\AA\), \(c=13.074(4)\,\AA\), \(D_m=\text{Dx}=1.84\, \text{g}\cdot\text{cm}^{-3}\), \(Z=6\), and \(\mu=18.4\, \text{cm}^{-1}\) (MoK\(\alpha\)). The least-squares refinement using 2471 reflections gave an agreement factor \(R\overline{2}=0.0343\). 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 \((\text{VO}_2\)\(_2^2\)) with a non-crystallographic symmetry of \(C_{3h}\). The average lengths(A) for different V-O and V-N bonds are given below:

\begin{align*}
\text{Va-0a} & =1.663(6) \quad \text{Ve-0e} =1.618(4) \quad \text{Ve-Ne} =2.318(5) \\
\text{Va-Ob} & =1.724(5) \quad \text{Ve-Nc} =2.166(6) \quad \text{Ve-Nd} =2.158(5)
\end{align*}

According to the bonding character of vanadium, we were able to recognize that the cluster \(\text{V}_5\text{O}_{11}\) consists of two vanadate and three vanadyl groups as represented by \((\text{VO}_2\)\(_2^2\)-(\text{VO}_3^3-)\)\(_3\). The title compound is neither a simple vanadium oxide nor a polyvanadate. It contains a neutral cluster with mixed valence of \(V(\text{IV})\) and \(V(\text{V})\). These two features justifies our interest in this compound.

09.5-17  NEW REDUCED OXONIOBATES 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 chloro- and bromo-oxoniobates which are connected via the O-Atoms according to \(\text{Nb}_6\text{O}_{12}\)\(_2^-\). \(\text{Nb}_6\text{O}_{12}\)-clusters (different shapes) are also the essential building units in the new compounds \(\text{Na}(\text{Si},\text{Nb})\text{O}_{12}\text{O}_9\) (III), \(\text{Na}_2\text{Al}_2\text{Nb}_6\text{O}_{12}\) (IV) and a further oxide in the system \(\text{Na}_{3-x}\text{O}-\text{O}-\text{O}_x\) (V) which is thus far only partially characterized; (III) and (IV) also contain \(\text{Nb}_6\text{O}_{12}\)-octahedra with Nb in the oxidation states +4 and +5. The Nb\(_n\)\(_x\)-atoms form pairs \((\text{O}_n\text{Nb}-\text{O}_m\text{Nb})\) pm via an O-O edge. The cluster-cations \(\text{Na},\text{Al},\text{Si},\text{V}\) occupy holes in the anion part.

The number of valence electrons in the \(\text{Nb}_6\text{O}_{12}\)-clusters is 14 (I.II), 14.33 (III) and 15 (IV). The distances within the octahedra are short and are in the range 279 pm. The conditions for preparation, data concerning structure determination of single crystals, and chemical aspects of all five compounds are presented and discussed.