A couple of crystal modifications of complex of mixed-valent cluster \( \left( \text{VO}^{3+} \right) \text{2} \left( \text{VO}^{2+} \right) \text{3} \) and diethylenetriamine. By Z.H. Pan, M.C. Shao, S.M. Xu and Y.G. 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 CuKα radiation, we found the α-modification of title complex \( \text{VO}^{3+}\) (dien) \(_3\) prepared by dissolving \( \text{VO}^{3+} \) 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 \( \text{C}_{6} \) - P \( \text{6} \) \(_3\) with \( a=10.805(4) \text{ Å}, \ c=13.018(5) \text{ Å}, \ D_{\text{m}}=1.85 \text{ g cm}^{-3} \). The unit cell of \( \text{C}_{6} \) - P \( \text{6} \) \(_3\) is \( a=18.830(7) \text{ Å}, \ c=13.074(4) \text{ Å}, \ D_{\text{m}}=1.84 \text{ g cm}^{-3} \). The unit cell of \( \text{C}_{4} \) - P \( \text{6} \) \(_3\) is \( a=10.845(4) \text{ Å}, \ c=13.018(5) \text{ Å}, \ D_{\text{m}}=1.85 \text{ g cm}^{-3} \). The unit cell of \( \text{C}_{1} \) - P \( \text{6} \) \(_3\) is \( a=18.830(7) \text{ Å}, \ c=13.074(4) \text{ Å}, \ D_{\text{m}}=1.84 \text{ g cm}^{-3} \). The unit cell of \( \text{C}_{1} \) - P \( \text{6} \) \(_3\) is \( a=10.845(4) \text{ Å}, \ c=13.018(5) \text{ Å}, \ D_{\text{m}}=1.85 \text{ g cm}^{-3} \). The unit cell of \( \text{C}_{1} \) - P \( \text{6} \) \(_3\) is \( a=10.845(4) \text{ Å}, \ c=13.018(5) \text{ Å}, \ D_{\text{m}}=1.85 \text{ g cm}^{-3} \). The unit cell of \( \text{C}_{1} \) - P \( \text{6} \) \(_3\) is \( a=10.845(4) \text{ Å}, \ c=13.018(5) \text{ Å}, \ D_{\text{m}}=1.85 \text{ g cm}^{-3} \). The unit cell of \( \text{C}_{1} \) - P \( \text{6} \) \(_3\) is \( a=10.845(4) \text{ Å}, \ c=13.018(5) \text{ Å}, \ D_{\text{m}}=1.85 \text{ g cm}^{-3} \). The unit cell of \( \text{C}_{1} \) - P \( \text{6} \) \(_3\) is \( a=10.845(4) \text{ Å}, \ c=13.018(5) \text{ Å}, \ D_{\text{m}}=1.85 \text{ g cm}^{-3} \). The unit cell of \( \text{C}_{1} \) - P \( \text{6} \) \(_3\) is \( a=10.845(4) \text{ Å}, \ c=13.018(5) \text{ Å}, \ D_{\text{m}}=1.85 \text{ g cm}^{-3} \).

Very recently we have found a new form, namely, β-form coexisting with α-form in a preparation using aqueous solution of \( \text{VO}^{4+} \) and mixture of t-butyl hydroperoxide, diethylenetriamine, tolune and chloroform as starting materials. The β-form belongs to space group \( \text{C}_{6} \) - P \( \text{6} \) \(_3\) with \( a=16.830(7) \text{ Å}, \ c=13.074(4) \text{ Å}, \ D_{\text{m}}=1.84 \text{ g cm}^{-3} \). These two forms represent two different crystalline species, but consist of same molecules. Each complex molecule of β-form sits on a general position and has a backbone (\( \text{VO}^{3+} \)) with a non-crystalllogic symmetry of \( \text{C}_{6} \). The average lengths (Å) for different V-O and V-N bonds are given below:

- \( \text{V}=\text{O} \) 1.663(6);
- \( \text{V}=\text{Oe} \) 1.618(4);
- \( \text{Ve}=\text{Oe} \) 1.618(4);
- \( \text{V}=\text{Ob} \) 1.724(5);
- \( \text{Ve}=\text{Ob} \) 1.946(5);
- \( \text{Ve}=\text{Ne} \) 2.166(6);
- \( \text{Ve}=\text{Ne} \) 2.318(5).

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 \( \left( \text{VO}^{3+} \right) \text{2} \left( \text{VO}^{2+} \right) \text{3} \). The title compound is neither a simple vanadium oxide nor a polyvanadate. It contains a neutral cluster with mixed valence of \( \text{V}^{4+} \) and \( \text{V}^{3+} \). These two features justify our interest in this compound.

NEW REDUCED OXONIOTATES CONTAINING \( \text{Nb}^{5+} \) 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 \( \text{O}^{2-} \)-metals containing isolated or condensed clusters. Mo is characterized by a great number of corresponding oxides. The structures of \( \text{MoO}_{3} \) and \( \text{Mo}_{2} \text{O}_{5} \) 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 fluorescences as mineralizers. The crystal structure of \( \text{Mo}_{3} \text{O}_{11} \) \( (\text{II}) \) is in 1985, by XRD study with CuKα radiation, we found the α-modification of title complex \( \text{VO}^{3+}\) (dien) \(_3\) prepared by dissolving \( \text{VO}^{3+} \) in the mixture of diethylenetriamine, 30% aqueous solution of \( \text{H}_{2}\text{O}_2 \) and t-butyl hydroperoxide.