

S₁₆

DISTRIBUTION AND STEREOCHEMISTRY OF FLUORO- AND OXO-LIGANDS IN
MONOMERIC, DIMERIC AND TETRAMERIC FLUOROVANADATES AND -MOLYBDATES

Norbert Buchholz, Manfred Leimkühler and Rainer Mattes*

Anorganisch-Chemisches Institut der Universität Münster, Corrensstrasse 36, 4400 Münster (F.R.G.)

The crystal structures of the following compounds with vanadium in the +V, +IV and +III, and molybdenum in the +VI oxidation states have been studied:

$(\text{NH}_4)_3\text{VO}_2\text{F}_4$	<u>A</u>
$(\text{NMe}_4)_3\text{V}_2\text{O}_4\text{F}_5$	<u>B</u>
$(\text{NMe}_4)_3\text{V}_2\text{O}_2\text{F}_7$	<u>C</u>
$(\text{NMe}_4)_2\text{KV}_2\text{O}_4\text{F}_5 \cdot \text{H}_2\text{O}$	<u>D</u>
$(\text{NMe}_4)_3\text{V}_2\text{F}_9$	<u>E</u>
$(\text{NMe}_4)_3\text{Mo}_4\text{O}_{12}\text{F}_3$	<u>F</u>

Structure determination has been severely complicated in most compounds by disorder. A, known since 1889 (E. Petersen, J. Prakt. Chemie, 40, 271 (1889)), contains two non-equivalent $\text{VO}_2\text{F}_4^{3-}$ groups. One is disordered, but in the other the oxo-ligands clearly occupy cis-positions, in contrast to recent suggestions (U.R.K.Rao, K.S.Venkateswarlu, B.R.Wani, Mol.Phys. 47, 637(1982) and R.J.Gillespie, U.R.K.Rao, J.Chem.Soc., Chem.Comm. 422 (1983)). The anions of B, C, D and E consist of face-sharing bioctahedral $\text{V}_2(\text{O},\text{F})_9$ units. The common face is occupied by fluoro-ligands only. In B and C, with the dimeric units on crystallographically threefold axes, the terminally bonded oxo- and fluoro-ligands are disordered. In the closely related structure of D the threefold degeneracy is lifted, but the bond distances indicate clearly that two of the three terminal sites are still affected by disorder of oxygen and fluorine atoms. Despite rather small vanadium-vanadium distances, the bioctahedral anions are remarkably stable even in the soft cationic matrix. It was suggested earlier, that these anions could be stabilized only in their Tl, Rb or Cs salts with a $\text{Cs}_3\text{Fe}_2\text{F}_9$ type structure (R. Mattes and H. Förster, J. Less Common Metals 87, 237 (1982)). The vibrational spectra of compounds B, C, D and E agree completely with the crystallographic results. F contains a new type of oxofluoroanion or polymolybdate. Two face-sharing bioctahedral units are connected by bridging fluoro- and oxo-ligands to a tetrameric anion with a four-coordinated fluorine atom close to the center of a rectangle of molybdenum atoms.