

08.2-21 CRYSTAL STRUCTURES OF RING SILICATES AND ALUMINOSILICATES WITH COMPLEX CATIONS. By Yu.I. Smolin, Yu.F. Shepelev, A.S. Ershov, Institute of Silicate Chemistry of the USSR Ac.Sc., Leningrad, USSR; and D. Hobbel, Inst. Inorg. Chem. of the DDR Ac.Sc., Berlin.

A discussion is made of crystal structures of tetramethylammonium  $8[\text{N}(\text{CH}_3)_4]\cdot\text{Si}_8\text{O}_{20}\cdot 64\text{H}_2\text{O}$  and tetraethylammonium  $6[\text{N}(\text{C}_2\text{H}_5)_4]\cdot\text{Si}_6\text{O}_{15}\cdot 36\text{H}_2\text{O}$  silicates as well as of tetramethylammonium aluminosilicate  $4[\text{N}(\text{CH}_3)_4]\cdot\text{Si}_4\text{Al}_4\text{O}_{12}(\text{OH})_8\cdot 24\text{H}_2\text{O}$  determined by X-ray diffraction at  $-100^\circ\text{C}$ . In the structure of TMA silicate the silicon-oxygen radical in the form of double four-membered ring  $\text{Si}_8\text{O}_{20}$  built up of silicon-oxygen tetrahedra is surrounded by six TMA groups which directly adjoin the anion. The nitrogen atoms of these complexes are located on the straight line passing through the anion centre and that of each tetragonal ring of the  $\text{Si}_8\text{O}_{20}$  group. In the TEA silicate structure the  $\text{Si}_6\text{O}_{15}$  silicon-oxygen radical is realized in the form of double three-membered ring  $\text{Si}_6\text{O}_{15}$ . Five of the six cationic groups also adjoin directly the anion. Two various conformations of TEA groups are shown to exist. The crystal structure of TMA aluminosilicate contains an isolated radical  $[\text{Si}_4\text{Al}_4\text{O}_{12}(\text{OH})_8]^{4-}$  in the form of double four-membered ring. The stability of anionic groups in aqueous solutions of the compositions studied can be explained by the peculiarities of their interaction with cations. In all the crystals the water molecules and terminal oxygens are bounded by hydrogen bonds in a three-dimensional network.

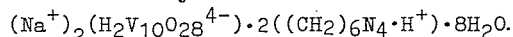
08.2-22 THE ACCOUNT OF THE STRUCTURAL DIFFERENCE BETWEEN  $\text{RbMnCl}_3$  AND  $\text{RbMnBr}_3$  by E.M.ALI Faculty of Science, King Saud University, Riyadh, Saudi Arabia.

The crystal structure of  $\text{RbMnCl}_3$  was determined by the author and others (Acta Cryst. (1977) B33, 256) to be hexagonal  $\text{P6}_3/\text{mmc}$ ,  $a=7.16(1)$ ,  $c=17.83(4)\text{Å}$ ,  $D_o=3.09$ ,  $D_x=3.11\text{gcm}^{-3}$ ,  $Z=6$ ; the unit cell accommodates six close-packed layers of composition  $\text{RbCl}_3$  with Mn ions situated between the layers, being octahedrally coordinated by Cl ions.

The crystal structure of  $\text{RbMnBr}_3$  was determined by the author and others (Acta Cryst. (1980) B36, 671) to be hexagonal  $\text{P6}_3/\text{mmc}$ ,  $a=7.56(2)\text{Å}$ ,  $c=6.35(2)\text{Å}$ ,  $D_o=3.97$ ,  $D_x=4.01\text{gcm}^{-3}$ ,  $Z=2$ . The unit cell consists of two hexagonally close-packed  $\text{RbBr}_3$  layers with Mn octahedrally coordinated by Br ions. The difference between these two structures is that we have six close-packed layers in  $\text{RbMnCl}_3$ , while there are two close-packed layers in  $\text{RbMnBr}_3$ . Moreover in the latter structure, the Mn-Br octahedra share opposite faces to form infinite chains of composition  $\text{MnBr}_3$  parallel to the c-axis, while in the  $\text{RbMnCl}_3$  structure that infinite chain does not exist.

The first reason to account for these differences is that the cation/anion ratio in  $\text{RbMnCl}_3$  is too large to permit the formation of infinite chains of Mn-Cl face shearing octahedra. The second reason is the polarization effect: the extra polarization of the bromine compared with the chlorine made  $\text{RbMnBr}_3$  isomorphous with  $\text{CsNiCl}_3$ , which has two close-packed layers, while  $\text{RbMnCl}_3$  does not.

08.2-23 THE CRYSTAL STRUCTURE OF ADDITION COMPOUND OF SODIUM TETRAHYDROGEN DECAVANADATE AND HEXAMETHYLENETETRAMINE. By Mei-Cheng Shao, Ze-Ying Zhang, Chun-An Bai, Lin Zhang and You-Qi Tang, Institute of Physical Chemistry, Peking University, Beijing, The People's Republic of China. By using  $\text{NH}_4\text{VO}_3$ , NaOH and HMT (hexamethylene-tetramine) in aqueous solution with  $\text{pH}\sim 6$ , we have got the title adduct which crystallizes in  $\text{P}\bar{1}$  with cell constants  $a=9.589(2)\text{Å}$ ,  $b=10.486(2)\text{Å}$ ,  $c=11.139(3)\text{Å}$ ,  $\alpha=103.27(2)^\circ$ ,  $\beta=98.20(2)^\circ$ ,  $\gamma=103.16(2)^\circ$  and  $D=2.29\text{gcm}^{-3}$ . Intensities of 2831 independent reflections were collected with  $\text{MoK}\alpha$  radiation. The coordinates of all V atoms were found from successive Fourier and difference syntheses. The block-diagonal least-square refinement for all atomic parameters gave a final discrepancy factor  $R=0.0279$ . The compound has been identified definitely as



Two of the six protons of decavanadic acid are captured by two HMT molecules, forming the protonated cation  $(\text{HMT}\cdot\text{H}^+)$ , two are replaced by  $\text{Na}^+$  ions and the remaining two are kept by acid group itself to form the protonated species  $(\text{H}_2\text{V}_{10}\text{O}_{28}^{4-})$ . Both the interesting protonated cation and anion have been confirmed by several evidences, such as the significant lengthening effect of the N-C bonds during the attachment of proton to N atom of HMT. Due to the good qualities of the crystals, it is thought to be possible to utilize this kind of adduct to separate vanadium from other elements.

08.2-24 BLEIHALOGENIDE UNGEWÖHNLICHER ZUSAMMENSETZUNG UND STRUKTUR. Von U. Georgy und K.-F. Tebbe. Institut für Anorganische Chemie der Universität zu Köln, Greinstraße 6, D-5000 Köln 41. Bundesrepublik Deutschland.

In der älteren Literatur beschriebene Halogenüberschuß-Verbindungen des Bleis werden röntgenkristallographisch und strukturell untersucht. Das variationsfähige Iodid von Wells {Z. anorg. Chem. 4. 346 (1893)}  $[\text{K}_3\text{Pb}_2\text{I}_8\cdot 4\text{H}_2\text{O}]$  ( $\text{P4}/\text{mmm}$ ,  $a=13.183$ ,  $c=4.539\text{Å}$ ,  $Z=1$ ) enthält parallel den Oktaederketten  $[\text{PbI}_{4/2}\text{I}_2]^{2-}$  längs  $[001]$  durch Kaliumionen. Wassermoleküle und Triiodidionen teilweise fehlgeordnet gefüllte Kanäle. Die Schweratom-Teilstruktur des Iodids von Johnson {J. chem. Soc. 33. 183 (1878)}  $[\text{5Pb}(\text{ac})_2\cdot 3\text{KI}_3]$  ( $\text{Cmcm}$ ,  $a=26.455$ ,  $b=23.565$ ,  $c=19.298\text{Å}$ ,  $Z=8$ ) läßt einen schichtartigen Aufbau aus Bleiatomen erkennen, der durch Triiodidionen und Iodid-Iod-Ketten  $[\text{I}\cdots\text{I}\cdots\text{I}_2]$  gestützt wird. Das Salz von Gröger {Mh. Chem. 3. 510 (1892)}  $[\text{Pb}_2\text{I}_5(\text{OH})_2]$  ( $\text{P2}_1/\text{n}$ ,  $a=9.599$ ,  $b=12.293$ ,  $c=10.689\text{Å}$ ,  $\beta=106.31^\circ$ ,  $Z=4$ ) enthält neben Polyiodid-Gruppen und -Verbänden vermutlich Polyhydroxobleikationen. Mit der abschließenden Strukturanalyse dieser und der Darstellung, Untersuchung und strukturellen Charakterisierung weiterer Substanzen sind wir beschäftigt. In diesen Verbindungen gibt es bisher keine Hinweise auf eine Valenzmischung in der Blei-Teilstruktur. Der Halogenüberschuß wird stets in Polyhalogenid-Ionen gebunden.

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