C - 22208. INORGANIC AND MINERALOGICAL CRYSTALLOGRAPHY

CRYSTAL STRUCTURES OF RING SILICA-08.2–21 TES 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 $8[N(CH_3)] \cdot Si8_{020} \cdot 64H_{20}$ and tetraethylammonium $6[N(C_2H_5)_4]$, Si_6O_{15} , $36H_2O$ sitetraethylammonium $6[N(C_2H_5)_4] \cdot Si_6O_{15} \cdot 36H_2O$ si-licates as well as of tetramethylammonium alu-minosilicate $4[N(CH_3)_4] \cdot Si_4Al_4O_{12}(OH)_8 \cdot 24H_2O$ determined by X-ray diffraction at -100°C. In the structure of TMA silicate the silicon-oxy-gen radical in the form of double four-membe-red ring Si_8O_2 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 Si_8O_2 group. In the TEA silicate structure the form of double three-membered ring Si_6O_{15} . the form of double three-membered ring Si₆0₁₅. Five of the six cationic groups also adjoin¹⁵ directly the anion. Two various conformations of TEA groups are shown to exist. The crystal structure of TMA aluminosilicate contains an isolated radical $[Si_4Al_4O_{12}(OH)_8]^{4-}$ in the form of double four-membered ring. The stability of order of a stability of a stabilit ty 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 molecu-les and terminal oxygens are bounded by hydrogen bonds in a three-dimensional network.

08.2-22 THE ACCOUNT OF THE STRUCTURAL DIFFERENCE BETWEEN RbMnCl₃ AND RbMnBr₃

DIFFERENCE BETWEEN RbMnCl₃ AND RbMnBr₃ by <u>E.M.ALI</u> Faculty of Science, King Saud University, Riyadh, Saudi Arabia. The crystal structure of RbMnCl₃ was deter-mined by the author and others (Acta Cryst.(1977) <u>B33</u>, 256) to be hexagonal P6₃/mmc, a=7.16(1), c =17.83(4)A, D₀=3.09, D_x=3.11gcm⁻³, Z=6; the unit cell accommodates six close-packed layers of composition RbCl₃ with Mn ions situated between the layers, being octabedrally situated between the layers, being octahedrally

situated between the layers, being occanedrally coordinated by Cl ions. The crystal structure of RbMnBr₃ was deter-mined by the author and others (Acta Cryst.(1980) <u>B36</u>, 671) to be hexagonal P6₃/mmc, a=7.56(2)A, c=6.35(2)A, D₀=3.97, D_x=4.01gcm⁻³, Z=2. The unit cell consists of two hexagonally close-packed RbBr₃ layers with Mn octahedrally coordinated by Br ions. The difference between these two structures is that we have six closecnese two structures is that we have six close-packed layers in RbMnCl₃, while there are two close-packed layers in RbMnBr₃. Moreover in the latter structure, the Mn-Br octahedra share opposite faces to form infinite chains of composition MnBr₃ parallel to the c-axis, while in the RbMnCl₃ structure that infinite chain does not exist.

does not exist. The first reason to account for these dif-ferences is that the cation/anion ratio in $RbMnCl_3$ is too large to permit the formation of infinite chains of Mn-Cl face shearing octa-The second reason is the polarization hedra. effect: the extra polarization of the bromine compared with the chlorine made RbMnBr₃ iso-morphous with CsNiCl₃, which has two close-packed layers, while RbMnCl₃ does not.

THE CRYSTAL STRUCTURE OF ADDITION 08.2-23 COMPOUND OF SODIUM TETRAHYDROGEN DECAVANADATE COMPOUND OF SOLIDAR TETRAHIDROGEN DECAVARADATE AND HEXAMETHYLENETETRAMINE. By <u>Mei-Cheng Shao</u>, Ze-Ying Zhang, Chun-An Bai, Lin Zhang and You-Qi Tang, Institute of Physical Chemistry, Peking University, Beijing, The People's Re-public of China. By using NH4VO3, NaOH and HMT (hexamethylene-tetramine) in aqueous solution with pH~6, we

tetramine) in aqueous solution with pH~6, we have got the title adduct which crystallizes in P-1 with cell constants a=9.589(2) Å, b=10.486(2) Å, c=11.139(3) Å, α =103.27(2), β =98.20(2)°, γ =103.16(2)° and D=2.29 g.cm⁻³. Intensities of 2831 independent reflections were collected with MoK_x radiation. The coordinates of all V atoms were found from successive Fourier and difference syntheses. The block-digonal least-square refinement for The block-digonal least-square refinement for all atomic parameters gave a final discrepancy factor R=0.0279. The compound has been iden-tified definitely as

 $(\text{Na}^+)_2(\text{H}_2\text{V}_{10}\text{O}_{28}^{4-})\cdot 2((\text{CH}_2)_6\text{N}_4\cdot\text{H}^+)\cdot 8\text{H}_20.$

Two of the six protons of decavanadic acid are captured by two HMT molecules, forming the protonated cation (HMT·H⁺), two are replaced by Na⁺ ions and the remaining two are kept by acid group itself to form the pro-tonated species ($H_2V_{10}O_28^{4-}$). Both the inter-esting 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 ul-tilize this kind of adduct to separate vana-dium from other elements.

BLEIHALOGENIDE UNGEWÖHNLICHER ZUSAM-08.2-24 MENSETZUNG 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 Halogen-Überschuß - Verbindungen des Bleis werden rönt= genkristallographisch und strukturell unter= sucht. Das variationsfähige Iodid von Wells {Z. anorg. Chem. <u>4</u>. 346 (1893)} 'K₃Pb₂I₈·^{4H}₂O' (P4/mmm. a = 13.183. c = 4.539 Å. Z = 1) enthält parallel den Oktaederketten $\frac{1}{2} \left[PbI_{4/2}I_2 \right]^{2-1}$ längs [001] durch Kaliumionen. Wassermoleküle und Triiodidionen teilweise fehlgeordnet gefüllte Kanäle. Die Schweratom - Teilstruktur des Iodids von Johnson {J. chem. Soc. <u>33</u>. 183 (1878)} '5Pb(ac)₂·3KI₃' (Cmcm, a = 26,455, b = 23,565c = 19,298 Å, Z = 8) läßt einen schichtartigen Aufbau aus Bleiatomen erkennen, der durch Tri-iodidionen und Iodid-Iod - Ketten $\frac{1}{m}(\cdot \cdot I \cdot \cdot \cdot I_2 \cdot)$ gestützt wird. Das Salz von Gröger {Mh. Chem. <u>3</u>. 510 (1892)} 'Pb₂I₅(OH)₂' (P2₁/n. a = 9.599. b = 12,293, c = 10.689 Å, ß = 106.31°, Z = 4) ent= hält 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. Diese Arbeit wurde von der Deutschen Forschungs gemeinschaft durch Sachmittel unterstützt.