

08.2-23 THE CRYSTAL STRUCTURE OF THE TERNARY OXIDE $\text{Li}_2\text{Ca}_4\text{Si}_4\text{O}_{13}$. By L.E. Rendon-DiazMiron, M.E. Villa-fuerte-Castrejon, Instituto de Investigaciones en Materiales, Universidad Nacional Autonoma, Mexico 20 D.F., and C. Campana, Nicolet XRD Corp., Cupertino, CA 95014, U.S.A.

Four stable new ternary compounds had been reported in the system $\text{Li}_2\text{O}-\text{CaO}-\text{SiO}_2$ (A.R. West, J. Am. Ceram. Soc. (1978) **61**, No. 3-4) but no crystal chemistry was done on them. We grew crystals of the $\text{Li}_2\text{Ca}_4\text{Si}_4\text{O}_{13}$ phase of optimum size for crystal structure analysis. Single crystal diffraction diagrams show the material to be triclinic, $P\bar{1}$, $a = 10.4503 \pm 0.0027$, $b = 8.2312 \pm 0.0025$, $c = 7.1700 \pm 0.0021$, $\alpha = 77.713 \pm 0.024$, $\beta = 90.056 \pm 0.023$, $\gamma = 109.249 \pm 0.022$. The structure was solved using 2166 observed reflections. Full matrix least squares refinement with anisotropic temperature factors was terminated when $R = 0.038$ and $R_w = 0.041$. In this structure the silicon in tetrahedral coordination forms two types of anions: a $(\text{Si}_3\text{O}_{10})^{4-}$ unit like a zig-zag chain, and a $(\text{SiO}_4)^{4-}$ unit. The coordination polyhedra of the lithium is also a tetrahedron, but distorted, and joins together the two silicon anions, forming two-dimensional layers. The calcium has a distorted cube-like coordination polyhedron that links the silicon-lithium layers.

08.2-24 COMPOUND FORMATION AND CRYSTAL CHEMISTRY IN THE SYSTEM $\text{Li}_2\text{O} - \text{ZrO}_2 - \text{SiO}_2$. By Patricia Quintana, Universidad Nacional Autónoma de México, División de Estudios de Posgrado, Facultad de Química, Ciudad Universitaria, México 20, D.F., México and Anthony R. West, Chemistry Dept., Aberdeen University, Meston Walk, Old Aberdeen, Scotland, Great Britain.

The new ternary compound $\text{Li}_2\text{ZrSi}_5\text{O}_{15}$, found in the system $\text{Li}_2\text{O} - \text{ZrO}_2 - \text{SiO}_2$, has a monoclinic unit-cell of dimensions $a = 11.121(6)$, $b = 10.146(6)$, $c = 11.235(7)$ Å, $\beta = 100.26(6)^\circ$ and space group $P2_1/n$. Its crystal structure appears to be closely related to that of Zektzerite, $\text{LiNaZrSi}_5\text{O}_{15}$.

In the system $\text{Li}_2\text{O} - \text{ZrO}_2$ nine lithium zirconate phases have been prepared, five of which are new. One of the new phases is a high temperature polymorph of Li_4ZrO_4 and the others are metastable phases. The thermal behaviour and reaction pathways of formation of the new phases were studied and their X-ray powder patterns are reported.

08.2-25 CRYSTAL STRUCTURES OF SOME METAL SACCHARINATES. By G. Jovanovski and B. Kamenar, Faculty of Chemistry, University of Skopje and Faculty of Science, University of Zagreb, P.O. Box 153, 41001 Zagreb, Yugoslavia.

The crystal structure of sodium saccharinate 2/3 hydrate (1), magnesium disaccharinate heptahydrate (2), tetraaquadisaccharinatomanganese(II) dihydrate (3), and disaccharinatomercury(II) (4) have been examined by X-ray analysis based upon the intensity data collected on an automatic diffractometer. In structure (1) two Na^+ ions have C.N. six being surrounded by O atoms from water molecules, CO and SO_2 groups from saccharinates, the third Na^+ ion has also C.N. six but realized by five O atoms from the same groups and by one saccharinato N atom. The Na to O distances vary from 230.4 to 279.6 pm. In (2) Mg^{2+} ion is octahedrally surrounded by five O atoms from water molecules and one O atom from CO group. The Mg to O distances range from 203.0 to 211.3 pm. In (3) Mn atom is in the centre of symmetry and has octahedral coordination being bonded to four water-oxygen atoms and two saccharinato-nitrogen atoms. The Mn-O distances are 216.2 (2x) and 221.9 (2x), while Mn-N amounts to 228.1 pm (2x). In the unit cell of (4) there are two independent molecules, both with digonal characteristic coordination of Hg atoms. In one the Hg-N bond lengths are 203.8 and 205.0 pm, while in the other 202.9 and 205.8 pm, respectively. The N-Hg-N angles are 167.0° and 175.4° , respectively. In (1), (2) and (3) water molecules participate in hydrogen bonding with saccharinate ions. The saccharinate ions are planar with bond lengths and angles within expected values. The structures have been refined to R values of (1) 0.039, (2) 0.038, (3) 0.028 and (4) 0.062.

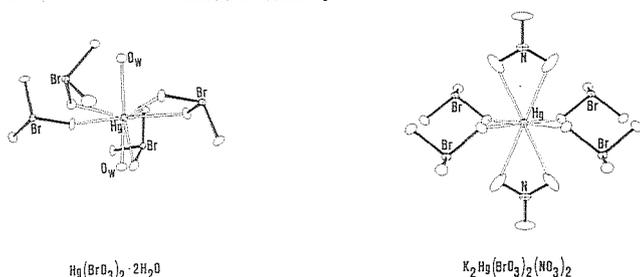
08.2-26 MERCURY(II) COMPOUNDS WITH HIGH COORDINATION NUMBERS. By K. Aurivillius and C. Stålhandske, Inorganic Chemistry, Chemical Center, University of Lund, P.O. Box 740, S-220 07 Lund 7, Sweden.

In mercury(II) compounds two-coordination is prevalent. In the coordination to O, Hg is in most cases linearly or almost linearly bonded at the short distances 2.0-2.2 Å. There are, however, often 3-5 more ligands at 2.4-2.9 Å, implying considerable weaker interactions. Four- and six-coordination for Hg(II) are rather unusual and coordination numbers higher than six have so far been reported only for $\text{K}_3[\text{Hg}(\text{NO}_2)_4]\text{NO}_3$ (Hall & Holland, Inorg. Chim. Acta (1969) **3**, 235; Power et al, Inorg. Nucl. Chem. Lett. (1972) **8**, 809), containing $[\text{Hg}(\text{NO}_2)_4]^{2-}$ ions. The eight oxygen atoms of the four nitrite groups form a highly distorted square antiprism around Hg with Hg-O bonds of 2.39-2.57 Å; the average value is 2.48 Å.

Eight-coordinated Hg has now also been found in the two Hg(II) bromates $\text{Hg}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$ and $\text{K}_2\text{Hg}(\text{BrO}_3)_2(\text{NO}_3)_2$. A preliminary X-ray study of $\text{Hg}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$ has shown that Hg is bonded to two water molecules [$\text{Hg}-\text{O}_w$ 2.33, 2.34 Å] and four bromate groups [$\text{Hg}-\text{O}$ 2.42-2.72 Å] (Fig. 1); the average Hg-O bond being 2.48 Å. A neutron diffraction study is planned and the result will be presented at the congress.

In $\text{K}_2\text{Hg}(\text{BrO}_3)_2(\text{NO}_3)_2$ the eight-coordination for Hg(II) is obtained by bonds to two nitrate [$\text{Hg}-\text{O}$ 4x2.589 Å] and four bromate groups [$\text{Hg}-\text{O}$ 4x2.434 Å] (Fig. 1) with an average Hg-O bond length of 2.50 Å.

Fig. 1 COORDINATION AROUND Hg IN



There also exist analogous Cd compounds with the compositions $\text{Cd}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$ (Murty & Murty, *Z. Kristallogr.* (1978) 148, 10) and $\text{K}_2\text{Cd}(\text{BrO}_3)_2(\text{NO}_3)_2$. We have found that $\text{Cd}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$ is isomorphous with $\text{Hg}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$ and that $\text{K}_2\text{Cd}(\text{BrO}_3)_2(\text{NO}_3)_2$ has most probably a structure very similar to that of the Hg-compound. The cell dimensions are close to those of $\text{K}_2\text{Hg}(\text{BrO}_3)_2(\text{NO}_3)_2$ but the space group has changed from Pnmm to $\text{P2}_1/\text{n}$.

08.2-27 TRIPOTASSIUM *cis*-DIBROMO (HYDROGENDISULFITE) PLATINATE(II) MONOHYDRATE $\text{K}_3[\text{Pt}(\text{SO}_3)_2\text{HBr}_2] \cdot \text{H}_2\text{O}$ (I) AND ITS STRUCTURAL RELATIONSHIP TO $\text{K}_3[\text{Pt}(\text{SO}_3)_2\text{HCl}_2]$ (II). D.K. Breitung, G. Petrikowski and G. Bauer, Institut für Anorganische Chemie, Universität Erlangen-Nürnberg, Egerlandstr. 1, D-8520 Erlangen, F.R.G.

(I) crystallizes in $\text{P2}_1/\text{c}$ with $a = 8.764(4)$, $b = 6.934(2)$, $c = 21.544(9)$ Å, $\beta = 99.32(4)^\circ$, $Z = 4$. The structure was solved by Patterson and Fourier methods using 1801 unique diffractometer data and refined to $R_w = 0.0288$. In the distorted square-planar anion Pt is surrounded by two S and two Br atoms in *cis* position. Short Pt-S and long Pt-Br bonds (averages 2.244 and 2.488 Å, respectively) suggest a strong trans influence of the sulfite ligand. An extremely short intramolecular hydrogen bond [O...H...O distance 2.380(8) Å] links the sulfite ligands to form a six-membered ring. The anions are arranged in layers, held together mainly by one kind of K^+ ions and H_2O molecules. Linkage of the layers is performed by two further sets of K^+ ions. In the anions of (II), $\text{Cmc}2_1$, $Z = 4$ (Kehr, W.G., Breitung, D.K. and Bauer, G. (1980). *Acta Cryst. B* 36, 2545-2550) and of (I) the Pt-S and hydrogen bonds are very similar. For comparison of the structural arrangements (I) is transformed by 1,0,0; 2,0,1; 0,-1,0 (setting $\text{P2}_1/\text{b}$) and (II) by 1/2, 1/2, 0; 0, 1, 0; 0, 0, 1. Then a' , c' and γ' are almost the same in both structures, with b' (I) about 2.4 times that of (II). Building blocks common to both structures are pairs of anions correlated by 2_1 axes ($\parallel c'$); in (II) these pairs are the translational unit, whereas in (I) pairs of such pairs correlated by inversion centres constitute the translational unit in the layers.

08.2-28 STRUCTURE DETERMINATION OF $\text{Li}_x\text{Pt}_3\text{O}_4$ AND $\text{Co}_x\text{Na}_y\text{Pt}_3\text{O}_4$ BY NEUTRON POWDER DIFFRACTION. By K.B. Schwartz, J.B. Parise, Department of Earth and Space Sciences, SUNY, Stony Brook, New York, USA and R.D. Shannon, Central Research and Development, E.I. du Pont de Nemours and Company, Wilmington, Delaware, USA.

$\text{Li}_x\text{Pt}_3\text{O}_4$, a member of the $\text{Na}_x\text{Pt}_3\text{O}_4$ structural family (Bergner and Kohlhaas, *Z. Anorg. Allg. Chem.* (1973) 401, 15), has been synthesized by solid state reaction of LiF , LiNO_3 and PtO_2 . Refinement of neutron powder diffraction data by profile analysis (Rietveld, *J. Appl. Cryst.* (1969) 2, 65) has determined that $\text{Li}_{0.65}\text{Pt}_3\text{O}_4$ is not isostructural with $\text{Na}_x\text{Pt}_3\text{O}_4$ (space group $\text{Pm}\bar{3}\text{n}$), but belongs to the acentric subgroup P43n . $\text{Li}_{0.65}\text{Pt}_3\text{O}_4$, with unit cell dimension $a = 5.6242$ Å, contains Li in position 2a (0,0,0), Pt in position 6d (1/4, 0, 1/2) and O in position 8e (x,x,x) with $x = 0.2720(3)$. Equivalent isotropic temperature factors for Li, Pt and O are 2.8(4), 0.11(4) and 0.95(4), respectively. The structure is distinguished by distortion of the cubic coordination polyhedron about Li to two interpenetrating tetrahedra with Li-O distances of 2.22 Å and 2.65 Å. Pt coordination remains square-planar with a slight tetrahedral distortion and a Pt-O distance of 2.00 Å. Refinement of scattering power on the Li site yields a Li occupancy of 0.67(5) atoms per formula unit, in close agreement with chemical analysis (0.64(11) by atomic absorption). Final discrepancy factors for this refinement are $R_1 = 3.60$, $R_2 = 11.70$ and $R_3 = 15.94\%$. $\text{Co}_x\text{Na}_y\text{Pt}_3\text{O}_4$, with $x = 0.4$ and $y = 0.1$ as determined by atomic absorption, was synthesized by solid state reaction of CoF_2 , NaF , $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and PtO_2 . Neutron powder diffraction experiments have indicated the presence of reflections of the type $hhl: l \neq 2n$, in violation of both space groups $\text{Pm}\bar{3}\text{n}$ and P43n . This reduction in symmetry is a result of ordering of Co and Na on distinguishable eight-coordinated sites. $\text{Co}_x\text{Na}_y\text{Pt}_3\text{O}_4$ belongs to a subgroup of $\text{Pm}\bar{3}\text{n}$, either the centric $\text{Pm}\bar{3}$ or the acentric P23 . Both these space groups are characterized by positions at 0,0,0 and 1/2, 1/2, 1/2 unrelated by symmetry, which is compatible with ordering of Co and Na.

08.2-29 PREPARATION, X-RAY STRUCTURE OF THE LINEAR CHAIN MIXED-VALENCE TETRAKIS(DITHIOACETATO)DIPLATINUM IODIDE: $\text{Pt}_2(\text{CH}_3\text{CS}_2)_4\text{I}$. By C. Bellitto, A. Flamini, L. Gastaldi and L. Scaramuzza, C.N.R., Istituto Teoria, Struttura Elettronica Composti di Coordinazione, Area della Ricerca, P.B. 10, Monterotondo Staz. (Roma) Italy.

In the past decade there has been a considerable interest in the chemical and physical properties of highly conducting 1-D systems. (See for ex. "Synthesis and properties of low-dimensional materials", *Ann. N. York, Acad. Scie.* 313 (1978)). In an attempt to synthesize new partially oxidized compounds, we studied the reaction of tetrakis(dithiocarboxylato)diplatinum(II) complexes with halogens (C. Bellitto, A. Flamini, unpublished results). Here we report the reaction of the tetrakis(dithioacetato)diplatinum(II) with iodine, and the crystal and molecular structure of $\text{Pt}_2(\text{CH}_3\text{CS}_2)_4\text{I}$. Direct reaction of equimolecular tetrakis(dithioacetato)diplatinum(II) with iodine, in toluene, gives a dark violet powder of $\text{Pt}_2(\text{CH}_3\text{CS}_2)_4\text{I}$, while the same reaction carried out through a glass frit/polystyrol membrane, gives dark microcrystals of $\text{Pt}_2(\text{CH}_3\text{CS}_2)_4\text{I}$. The latter compound crystallizes in the monoclinic C2/c space group with cell dimension: $a = 16.838(4)$, $b = 8.633(2)$, $c = 13.634(4)$ Å, $\beta = 109.39(5)^\circ$, $Z = 8$. The structure was refined to $R = 0.06$ for 1206 significant reflections. The structure