

04.1-6 TRANSITION METAL - CARBON BOND DISTANCES AND A REVISION OF COVALENT RADII. By A.S.Batsanov and Yu.T.Struchkov, A.N.Nesmeyanov Institute of Organoelement Compounds, Moscow, U.S.S.R.

Metal-carbon bond distances in various types of transition metal complexes (with σ -ligands, multiple-bonded carbene, carbyne and carbonyl ligands, π -cyclopentadienyl and π -arene ligands) are reviewed. These distances systematically increase with the number of valence electrons in the metal atom outer shell and are maximum for 18-electron complexes. In iso-electronic complexes the M-C distances depend strongly on the nature of other ligands at the metal atom, especially for metals of the 2-nd and 3-rd transition series. E.g., M-C σ -bonds in the complexes containing carbonyl ligands are usually longer than in π -cyclopentadienyl complexes. It is well known that formally single M-C bonds formed by σ -vinyl, aryl and acyl ligands, i.e. M-C(sp²) bonds, are often shorter than M-C(sp³) bonds in similar complexes. We have examined this effect on large amount of data. The shortening proves to be maximum (0.10-0.15 Å) for electron-rich complexes of middle-transition metals (but negligible for electron-deficient complexes of the same metals!) and decreases both for early- and post-transition metals. Systems of covalent radii previously proposed for transition metals in their π -complexes are revised. The relation between "inorganic" and "organometallic" metal radii and the problem of the "boundary" between the areas of their applicability are discussed.

04.1-7 CRYSTALLINE POLYSILICIC ACIDS ESTERS WITH CAGE LIKE STRUCTURES. By Yu.I.Smolin, Yu. F. Shepelev, Institute of Silicate Chemistry of the USSR Acad. Sci., Leningrad, USSR and D. Hoebbel, Institute of Inorganic Chemistry of the DDR Acad. Sci., Berlin, DDR.

The results of X-ray structural analysis of a new class of compounds - crystalline polysilicic acids esters are discussed. The crystal structures of compounds

$[(\text{CH}_3)_3\text{Si}]_6 \text{Si}_6\text{O}_{15}$ with space group P2₁/c, $a=21.386(3)$, $b=23.510(3)$, $c=10.959(2)$ Å, $\beta=119.75(5)^\circ$;

$[(\text{CH}_3)_3\text{Si}]_8 \text{Si}_8\text{O}_{20}$ with space group P1, $a=10.819(5)$, $b=13.501(5)$, $c=10.816(5)$ Å, $\alpha=103.27(6)$, $\beta=83.27(6)^\circ$, $\gamma=99.22(6)^\circ$;

$[(\text{CH}_3)_3\text{Si}]_{10} \text{Si}_{10}\text{O}_{25}$ with space group P2₁/c. $a=15.43(1)$, $b=44.36(2)$, $c=12.62(1)$ Å, $\beta=111.9(1)^\circ$.

have been determined on single crystals obtained by trimethylsilylation of tetraethyl-, tetramethyl- and tetrabutyl-ammonium silicates, respectively. It is established that the molecules obtained from tetraethyl- and tetramethylammonium silicates are double trigonal and double tetragonal rings composed of silicon-oxygen tetrahedra with tetramethyl-silyl groups joined to the terminal oxygen atoms. The central part of these molecules is shown to be close in structure to anionic groups of the corresponding silicates whose structures have been described earlier (Yu.I.Smolin, Yu.F.Shepelev, P.Pomes, D.Hoebbel and W. Wieker, Kristallografiya, 1979, 24, 38-44; Yu.I.Smolin, Yu.F. Shepelev, A.S. Ershov, D.Hoebbel and W. Wieker, Ibid., 1984, 29, 712-721). The $[(\text{CH}_3)_3\text{Si}]_{10} \text{Si}_{10}\text{O}_{25}$ molecule is a double five-membered ring composed of silicon-oxygen tetrahedra with joined tri-methylsilyl groups. Although the

structure of TBA silicate $\text{N}(\text{n-C}_4\text{H}_9)_4\text{OH}\cdot\text{SiO}_2\cdot 26.5\text{H}_2\text{O}$ has not been determined, D. Hoebbel, W. Wieker, P. Franke and A. Otto (Z.anorg.allgem.Chem., 1975, 418, 35-44) showed that it should contain anionic radicals in the form of double five-membered rings. It can be assumed to a high degree of probability that the configuration of the $[\text{Si}_{10}\text{O}_{25}]^{10-}$ radical is quite close to that of the central part of the $[(\text{CH}_3)_3\text{Si}]_{10} \text{Si}_{10}\text{O}_{25}$ molecule described. Silicate radicals in the form of double trigonal, tetragonal and five-membered rings also exist in solutions of silicates with tetraalkylammonium groups and can be considered as primary units in formation of zeolite structures.

04.1-8 COMPARATIVE STUDIES ON THE CRYSTAL STRUCTURES OF THE PEROVSKITES CaRuO_3 AND SrRuO_3 By A. Reller, H. Schmalte and W. Bensch, Institute for Inorganic Chemistry, University of Zürich, Winterthurerstr. 190, 8057 Zürich, Switzerland.

Ternary metal oxides adopting the perovskite structure exhibit a vast range of possible metal combinations and, as a consequence, remarkable differences of their physico-chemical properties. The structures of these compounds vary between perfectly cubic and - owing to distortions - lower symmetries. There exist only few structure determinations, however, which provide a detailed characterization of the kind of distortions actually present.

We set out to analyze the crystal structures of CaRuO_3 and SrRuO_3 [P.R. Van Loan, Ceramic Bull. 1972, 51, 231-242], two phases with interesting reactivity as catalysts or electrode materials [A. Reller, Ber. Bunsenges. Phys. Chem. 1986, 90, 742-745]. Single crystals of both phases with geometrical dimensions within the range of few tenths of a millimeter have been grown from a CaCl_2 or SrCl_2 flux respectively at 1200 K.

SrRuO_3 adopts the perfect cubic structure of perovskite, space group Pm3m (Int. Tab. no. 221), with $a = 0.3910(1)$ nm and $Z = 1$. The structure has been refined to an R-value of 3.2%.

CaRuO_3 adopts an orthorhombic structure, space group Pnma (Int. Tab. no. 62) with $a = 0.5524(1)$ nm, $b = 0.7649(2)$ nm, $c = 0.5354(1)$ nm and $Z = 4$.

This structure has been refined to an R-value of 3.1%. The lowering of the symmetry from cubic to orthorhombic is caused by a distorted arrangement of the corner-linked RuO_6 -octahedra, as it