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 isoelectronic 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(sp^2) bonds, are often shorter than M-C(sp^3) 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-defficient 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

$[(CH_3)_3Si]_6\ Si_6O_{15}$ with space group $P2_1/c$, a=21.386(3), b=23.510(3), c=10.959(2) Å, β=119.75(5)°;

$[(CH_3)_3Si]_8\ Si_8O_{20}$ with space group P1, a=10.819(5), b=13.501(5), c=10.816(5) Å, α=103.27(6), β=83.27(6)°, γ=99.22(6)°;

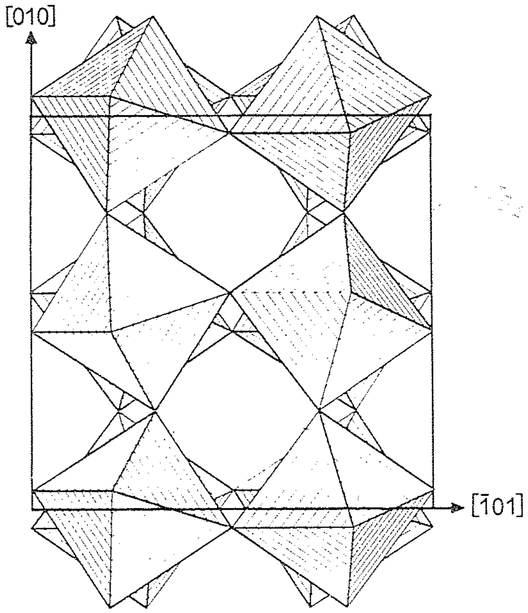
$[(CH_3)_3Si]_{10}\ Si_{10}O_{25}$ with space group $P2_1/c$. a=15.43(1), b=44.36(2), c=12.62(1)Å, β=111.9(1)°.

have been determined on single crystals obtained by trimethylsilylation of tetraethyl-, tetramethyl- and tetrabuthyl-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 $[(CH_3)_3Si]_{10}\ Si_{10}O_{25}$ molecule is a double five-membered ring composed of silicon-oxygen tetrahedra with joined tri-methylsilyl groups. Although the structure of TBA silicate $N(n\text{-}C_4H_9)_4OH{\cdot}1SiO_2{\cdot}26.5H_2O$ 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 $[Si_{10}O_{25}]^{10-}$ radical is quite close to that of the central part of the $[(CH_3)_3Si]_{10}\ Si_{10}O_{25}$ 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. Schmalle 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 $Pm\bar{3}m$ (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

is presented by a STRUPLO-plot [R.X. Fischer, J. Appl. Cryst. 1985, 18, 258 - 262].



Arrangement of the corner-linked RuO_6-octahedra in $CaRuO_3$; projection along [101]

04.2-1 4-PHENYL PYRIDINE: A NEW LIGAND IN WERNER CLATHRATES.

L.R. Nassimbeni and M.W. Taylor.
Physical Chemistry, University of Cape Town, Rondebosch 7700, South Africa.

We have elucidated the structures of a series of compounds of the type:

$Ni(NCS)_2(4\text{-}PhPy)_4.nG$

Cmpd.	n	G	Space Group
I	-	-	Pbca
II	2	o-xylene	Fdd2
III	2	m-xylene	C2/c
IV	1	p-xylene + DMSO	P$\bar{1}$
V	1	4-PhPy+methyl cellosolve	$P2_1/n$

Rotational freedom of the substituted pyridine has been advanced as a possible reason for the host molecules, in Werner Clathrates, to adopt a suitable conformation to allow accomodation of a guest molecule. This host complex offers eight moeities each of which can independently rotate, thus offering many possible conformations.

We have undertaken a series of comparisons between the eight torsion angles in each compound to try and relate them to their structure and to the size and shape of the channel in which the guest molecules are accommodated.

04.2-2 SOLID STATE N-BROMOSUCCINIMIDE-BROMIDE COMPLEXES. By J. Albertsson and C. Svensson, Inorganic Chemistry 2, Chemical Center, University of Lund, P.O.Box 124, S-221 00 Lund, Sweden

N-Bromosuccinimide (SBr: 1-bromo-2,5-pyrrolidinedione) serves as a brominating agent in the presence of tetra-alkylammonium bromides. There is strong evidence that 1:1 SBr/Br^- complexes play a vital role in the mechanism by which addition products are formed by SBr and olefins. The SBr/Br complex should slowly decompose into succinimide, polymaleimide and tribromide ions so the latter species could be responsible for the addition reaction. Bromide ion acts as a catalyst for the electron transfer oxidation of ferrocene to ferricinium ion by SBr, in all probability by forming the SBr/Br^- complex which should be a strong oxidant.

In order to study the possible formation of distinct SBr•••Br bonds and their influence on the N-Br bond in SBr we are investigating the crystal structures of $SBr{\cdot}(C_2H_5)_4NBr$ and SBr•1/3CsBr. The tetraethylammonium compound crystallizes in $P2_1/n$, a=18.091(3), b=8.925(2), c=10.587(4) Å, β=103.10(2)°, V=1665(1) Å^3, Z=4, D_x=1.549(1) g cm^{-3}, μ=12.30 cm^{-1} (MoKα). The caesium compound crystallizes in R$\bar{3}$, a=14.013(2), c=17.921(9) Å, V=3047(1) Å^3, Z=18, D_x=2.441(1) g cm^{-3}, μ=96.6 cm^{-1} (MoKα). While the former compound most probably contains a 1:1 complex the caesium ion, which is smaller than the tetraethylammonium ion, induces the formation of $[Br(SBr)_3]^-$ complex in the solid state (Svensson et al, Acta Cryst. 1986, C42, 1502-1505).

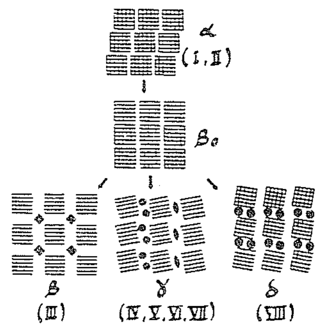
The bonding situation around the N-Br bond in the SBr/Br^- complexes should be comparable to that in recently prepared "hypervalent" halogen species (Farnham & Calabrese, J. Am. Chem. Soc. 1986, 108, 2449-2451). We are now working with salts of the complex $[S'Br{\cdots}S']^-$ where S' is tetramethyl substituted succinimide.

04.2-3 HOST-GUEST INTERACTIONS IN WERNER CLATHRATES.

L.R. Nassimbeni, M.H. Moore and M.L. Niven, Department of Physical Chemistry, University of Cape Town, Rondebosch 7700 South Africa.

We have synthesised and characterised the structures of a series of compounds of general formula

$Ni(NCS)_2(4Et\text{-}Py)_4{\cdot}nG$



Cmpd	nG
I,II	-
III	½ CCl_4
IV	1 p-xylene
V	1 m-xylene
VI	1 o-xylene
VII	2 CS_2
VIII	2 CCl_4

The structures can be grouped into distinct phases α, β, γ, δ and their structural relations are discussed. The geometry of the channels was mapped in detail with the program OPEC (Gavezzotti 1984). Differential Thermal Analysis and Thermal Gravimetric Analysis of these compounds have allowed us to understand their thermal decomposition patterns and to estimate the enthalpy of the host-guest interactions.