

09.X-4 STRUCTURAL STUDIES OF CARBIDO-CARBONYL CLUSTERS IN THE COBALT SUBGROUP. By Dario Braga, Dipartimento di Chimica "G. Ciamician", Via F. Selmi, 2, Università di Bologna, Italy.

Carbido-carbonyl clusters of cobalt and rhodium (none is known for iridium) contain carbon atoms bonded only to metal framework atoms ("cage carbides"). The interstitial atoms act as true inner ligands holding from "inside" the metal cages. Moreover the carbide atoms, by providing electrons to the cluster orbitals, reduce the number of ligands required on the cluster surface thus conditioning both building up sequence and final stereo-geometries of the metal frameworks.

In this family, species of nuclearity ranging from 6 to 15 metal atoms and containing one or two interstitial atoms are known for both cobalt and rhodium. Despite the close similarities between the two structural chemistries the isostructural relationship is confined to the two dianions $[M_6C(CO)_6]^{2-}$ ($M=Co,Rh$) which possess a prismatic cage encapsulating the C-atom (S.Martinengo et al., J. Chem. Soc., Dalton Trans., 1985, 35). These dianions have been used as fruitful starting material to produce a large number of carbide derivatives, whose structural characterization has allowed rationalization of the factors controlling:

- the building sequence of high nuclearity species (V.G. Albano et al., J. Chem. Soc., Dalton Trans., 1985, 1309),
- the facile reversible interconversion of metallic frameworks observed for some hexanuclear species (V.G. Albano et al., J. Chem. Soc., Dalton Trans., 1986, 981),
- the relationship between ligand distribution and metal framework geometries and the occurrence of dynamic processes in solution,
- the steric and electronic requirements which drive formation of heterometallic species (B.T. Heaton et al., J. Chem. Soc., Dalton Trans., 1983, 2175 and references therein).

09.X-5 CLUSTER FRAMEWORK STRUCTURES FOR COMPOUNDS WITHIN THE $M_x(Zr_6X_{12}Z)_n$ FAMILY. By Robin P. Ziebarth and John D. Corbett, Department of Chemistry, Iowa State University, Ames, IA 50011 USA.

Bonding of terminal halide (X) atoms to all metal vertices in octahedral M_6X_{12} -type (edge-bridged) clusters is evidently necessary for stability. This feature allows for a considerable diversity of structure types within a $(M_6X_{12})_n$ compositional family, with 6 - n edge-bridging halides (from other clusters) and $0 \leq n \leq 6$ additional halide atoms occupying terminal positions on the cluster. However, structures for the traditional $(Nb,Ta)_6X_{12}$ clusters have been limited to $n = 2, 3$ by electronic requirements of these elements. The opportunity to exercise some control over the value of n and thence over the character of the network formed occurs with zirconium clusters because of both the need to bond an interstitial element (Z) within each cluster and the ability to insert M^I cations within an anionic cluster framework. This has led to the development of a considerable structural chemistry for a large family of compositions $M_x(Zr_6X_{12}Z)_n$, $0 \leq x \leq 4$, $0 \leq n \leq 4$, $Z = H, Be, B, C, N, Si, Fe, Co, K, \dots$. Some of the systematics and diversities of the new framework structure types found as well as of the low symmetry sites that may be occupied by xM^I cations will be outlined.

09.X-6 STRUCTURAL PATTERNS IN POLYMETALLIC COMPOUNDS WITH CHALCOGENIDES AND DERIVATIVES.

By Ian G. Dance, School of Chemistry, University of New South Wales, Kensington, NSW, Australia.

The fundamental anionic chalcogen-derived ligands RE^-, E_2^{2-}, E_x^{2-} , readily bridge metal atoms, and therefore form polymetallic compounds, both molecular and non-molecular in structure. Because direct bonding between metal atoms is of negligible or minor energetic significance in most of these compounds, it is the array of bonded metal and chalcogen atoms which is at the focus of structure analysis. However, the steric influences of the array of ligand substituents (R or E_x chains) and the geometry at the donor atom are factors which cannot be ignored: compounds with heteroligands in terminal positions are included in this analysis.

Molecular structures include monocycles $M_4, M_6, M_8, M_{12}, M_{14}$, some *arachno* polycyclic structures, and many *closo* polycyclic structures $M_4, M_5, M_6, M_8, M_9, M_{10}, M_{12}, M_{34}$. In the latter class the M_x and E_y arrays are generally polyhedra of higher symmetry than the M_xE_y polyhedron, while the ligand substituent array often has still lower symmetry. Structures are analysed and classified in terms of these polyhedra, and in terms of the fused M_2E_2, M_3E_3 and M_4E_4 cycles which compose them. Non-molecular structures have single- and double-stranded chains, two-dimensionally non-molecular lamellae, and three-dimensional networks.

Notions of structural analogy and congruence appear. There is structural analogy between one non-molecular metal thiolate and the aluminosilicate lattices; structural correspondence between other non-molecular metal thiolates and cristobalite; and structural congruence between polymetallic molecular complexes in this class and non-molecular binary metal chalcogenides. This latter congruence leads to hypotheses of larger super-molecular fragments of metal chalcogenides, and to considerations of their surface termination and charge.

09.1-1 CRYSTAL STRUCTURE AND HYDROGEN BONDING IN A PENTACHLOROTALLIUM (III) COMPOUND. M.A. James, Department of Chemistry, Mount Saint Vincent University, Halifax, Nova Scotia, Canada, B3M 2J6, B.D. James, Department of Inorganic and Analytical Chemistry, La Trobe University, Bundoora, Victoria, Australia 3083 and T.S. Cameron, Chemistry Department, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3.

The crystal structure of $(ClC_5H_4NH)_2 TlCl_5$ indicates a square pyramidal structure for the anion with three distinct sets of metal to chlorine distances; two Tl-Cl distances, longest at 2.545(5)Å, the Cl being involved in H-bonding to the pyridinium ring, two distances at 2.480(5)Å, and the apical Tl-Cl distance at 2.442(4)Å. The Tl atom is ≈ 0.5 Å above the basal plane. The two independent cations in the asymmetric unit are linked by H-bonds to the $TlCl_5$ anion giving discrete cation--anion--cation units. Each of the nitrogen hydrogens is involved in a fairly strong hydrogen bond to one Cl and a longer H-bond to a 2nd Cl resulting in asymmetrically bifurcated H-bonds. The strong H-bonding is expected because of the weakly basic nature of the 4-chloropyridine ($pK_a \approx 3.83$).

Crystal data: $C_{10}H_{10}Cl_7N_2Tl$

$P\bar{1}$, $a=7.605(3)$, $b=8.741(3)$, $c=14.531(4)$
 $\alpha=99.00(2)_3$, $\beta=84.33(3)$, $\gamma=109.16(3)$,
 $V=900.1(6)$ Å³, $Z=2$, $R=0.035$.