

MS07.00.05 MINERALOMIMETIC CRYSTAL STRUCTURES OF CN-LINKED CADMIUM COMPLEXES. T. Iwamoto, Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Komaba, Meguro, Tokyo 153, Japan

Polymeric structures of cadmium cyanide and polycyanopolycadmates give a number of CN-linked mineralomimetic crystal structures like pyroxene, clays, H- and L-cristobalite, H-tridymite, zeolites, rutile, beryl, pyrite, etc., with or without guest molecules accommodated in inter- or intralayer space in 2D structures, or in cavities in 3D structures. The Cd atoms in the mineralomimetic structures take the positions corresponding not only to tetrahedral Si but also octahedral Fe, Mg, Ti, etc. The Cd-CN-Cd span longer than Si-O-Si or Si-O-M generates a more voluminous void space in the mineralomimetic latticework than in real minerals so that guest molecule or bulky secondary ligand is required to stabilise the latticework structure. In other words the guest or the ligand plays a role of template to stabilise the mineralomimetic structure. The zeolite-like 3D host of $[\text{Cd}_3(\text{CN})_7]^-$ gives isomorphous clathrates of C_6H_6 , PhMe, *o*- and *m*- $\text{C}_6\text{H}_4\text{Me}_2$, and PhEt of *Pnam* space group but the clathrates belong to *P63/mmc* and *Pa* for *p*- $\text{C}_6\text{H}_4\text{Me}_2$. Involvement of imidazole (imH) as a secondary ligand at octahedral or tetrahedral Cd in the host structures affords zeolite-like C_6H_6 and PhMe, beryl-like *m*- $\text{C}_6\text{H}_4\text{Me}_2$, rutile-like *p*- $\text{C}_6\text{H}_4\text{Me}_2$, and clay-like PhEt guest clathrates. Silica-like $\text{Cd}(\text{CN})_2$ host gives polymorphs similar to H- and L-cristobalite and H-tridymite depending upon the geometry of guest molecule. A pyrite(FeS_2)-like array of octahedral Cd^{2+} and $[\text{Cu}_2(\text{CN})_7]^{5-}$ isostructural to pyrosilicate-like $[\text{Cd}_2(\text{CN})_7]^{3-}$ is observed in $\text{H}_3[\text{Cd}\{\text{Cu}_2(\text{CN})_7\}]\cdot 14\text{H}_2\text{O}$ together with a rutile(TiO_2)-like array of hydrogen-bonded water molecules, $12\text{H}_2\text{O}$ ring like Ti^{4+} and $2\text{H}_2\text{O}$ like O^{2-} .

MS07.00.06 REVOLUTIONARY ADVANCES IN CRYSTALLOGRAPHIC ANALYSES OF HIGH-NUCLEARITY TRANSITION METAL CLUSTERS: FROM POINT-DETECTOR TO CCD AREA-DETECTOR SYSTEMS. Lawrence F. Dahl¹, Masaki Kawano¹, Jeffrey W. Bacon¹, John M. Bemis¹, Peter D. Mlynek¹, Nguyet T. Tran¹, Charles F. Campana², ¹Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706 ²Siemens Analytical X-Ray Instruments, 6300 Enterprise Lane, Madison, WI 53719

The availability of the SMART charge-coupled-device (CCD) area detector system approximately two years ago for collecting single-crystal X-ray diffraction data with $\text{MoK}\alpha$ radiation has proven to be crucial for our current research on giant-sized metallic and bimetallic clusters. This lecture will illustrate: (1) the much greater capability of the CCD system relative to a point-detector system in determining both the molecular architectures and stoichiometries of a number of geometrically unprecedented close-packed bimetallic Ni/Pd and Ni/Cu clusters, especially for weakly diffracting and/or small crystals; and (2) crystallographic problems that bedevil modern X-ray diffraction analysis of large metal clusters.

PS07.00.07 EFFECT OF ASCORBIC ACID AS REDUCING AGENT IN THE PREPARATION OF 1:1 CHLORO(L)Cu^I COMPLEXES(L:PYRIDINE, QUINOLINE, ACRIDINE). A. Alemi, S. Shirinevare, Dept. of inorganic. Chem., Tabriz Univ. Tabriz-Iran

Some $\text{Cu}^{\text{II}}\text{L}_2\text{Cl}_2$ (L:Acridine, pyridine and other Heterocyclic Amines) complexes were prepared by Dubsky et co-worker(1) and also PETER et al (2) were studied some characters and structure of these type complexes. Investigation of the Reaction between ascorbic acid and copper(II) chlorid in the presence of some heterocyclic amines (pyridine, quinoline, acridine) shows that, the product of reactions are in the form of $\text{Cu}^{\text{I}}\text{Cl L}$ complexes, and

also the reactions of $\text{Cu}^{\text{II}}\text{Cl}_2\text{L}_2$ complexes with ascorbic acid shows the same product, as we were found previously. In this study we were used elementary analysis, IR, FT-IR, NMR, XRD and also conductivity and magnetic susceptibility measurement of the products were examined. To summarize, the Role of ascorbic acid in two different reaction process is, no any ligand interaction with complexes. It should be noted that the action of ascorbic acid with $\text{Cu}(\text{II})$ complex with transformation of then to $\text{Cu}(\text{I})$ complex is a new method of Cu^{I} complex preparation from Cu^{II} complex without any ligand exchange.

1)Dubsky, J. V. et al colln. Czech. Chem. Commun, 1(1929)528
2)PETER, C. et al Aust. J. Chem 1989,42,115-36

PS07.00.08 RHENIUM(V)-OXO COMPLEXES WITH IMIDAZOLES: PRIME CANDIDATES FOR DISORDER, SUPERSTRUCTURE AND COUNTERION SUBSTITUTION. Suzanne Bélanger and André L. Beauchamp, Département de chimie, Université de Montréal, C.P. 6128, Succ. centre-ville, Montréal, Québec, H3C 3J7, Canada

Rhenium(V) dioxo complexes show interesting optical properties and a potential for applications as radiopharmaceuticals. To understand these properties, compounds with various imidazoles were prepared. These compounds proved to be a prolific source of challenging crystallographic problems.

A *trans* octahedral species containing an axial $\text{O}=\text{Re}=\text{O}$ unit and four equatorial imidazoles can possess a 4-fold axis, but symmetry is often lowered by the poorly scattering imidazoles adopting different orientations. In addition, instability generates ReO_4^- with liberation of protons. As a result, partial anion substitution by ReO_4^- and mixed $[\text{ReO}_2\text{L}_4]^+ / [\text{ReO}(\text{OH})\text{L}_4]^{2+}$ phases are not uncommon.

These features lead to space group ambiguity, disorder and extremely unstable refinement conditions. The correct structure is reached only after the unit cell, Laue symmetry and systematic absences have been carefully checked. Refinement in all possible space groups has to be considered and it must be ascertained that disorder is not an artefact due crystal twinning. The examples to be discussed include the oxobridged dimer $[\text{Re}_2\text{O}_3(\text{BimH}_2)_4]\text{Cl}_4$, a stoichiometric hemiprotonated phase $[\text{ReO}_2(\text{BimH})_4][\text{ReO}(\text{OH})(\text{BimH})_4](\text{ReO}_4)_3$ and two polymorphs of the oxo-methoxo compound $[\text{ReO}(\text{OCH}_3)(1-\text{MeIm})_4](\text{BPh}_4)_2$.

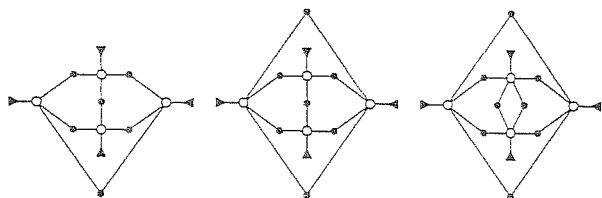
(BimH_2 = bi-imidazole, BimH = benzimidazole, $1-\text{MeIm}$ = 1-methylimidazole).

PS07.00.09 STRUCTURAL INVESTIGATIONS OF BIMETALLIC Sb_3^+ ETHOXIDES AND A COMPARISON TO RELATED STRUCTURES. U. Bemm and R. Norrestam, Department of Structural Chemistry, Stockholm University, S-106 91 Stockholm, Sweden.

By an systematic investigation of the Ni^{2+} and Mn^{2+} antimony ethoxide systems [1] several species are found. Seven of these compounds have been structurally investigated, e.g. $\text{Ni}_6\text{Sb}_4\text{O}_4(\text{OEt})_{16}(\text{HOEt})_4$ (**I**) [2], $\text{Mn}_7\text{Sb}_4\text{O}_4(\text{OEt})_{18}(\text{HOEt})_2$ (**II**) [4] and $\text{Mn}_8\text{Sb}_4\text{O}_4(\text{OEt})_{20}$ (**III**) [3], by single-crystal X-ray diffraction methods. Some of the species are structurally quite similar and have been investigated for further structural relationships, see e.g. figure below. The obtained metal and oxygen atom core fragments of the investigated structures have also been compared to other alkoxides and related compounds found with the Cambridge Structural Database System, CSDS. 90 structures were retrieved from the database and the investigation has resulted in a simple classification of the M_xO_y type, where the core fragment can be further described with the relation $[\mu_3, \mu_4, \mu_5][m_1, m_2, m_3, m_4, m_5, m_6]$. μ_a and μ_b are the coordinations around the oxygen atoms and the metal atoms, respectively. 90%

of the retrieved structures can be classified and divided into ten subgroups.

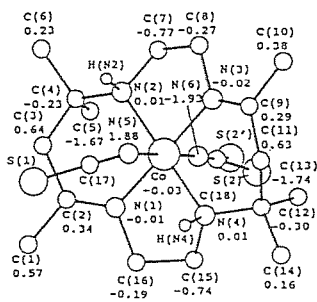
Figure Comparison of the metal and oxo-oxygen atom core fragment of the three structures I, II and III, respectively.



- [1] Westin, G.; Nygren, M. (1994). *J. Mater. Chem.* 4(8), 1275
 [2] Bemm, U.; Norrestam, R.; Nygren, M.; Westin, G. (1993). *Inorg. Chem.* 32, 1597
 [3] Bemm, U.; Norrestam, R.; Nygren, M.; Westin, G. (1995). *Inorg. Chem.* 34, 2367
 [4] Bemm, U.; Norrestam, R.; Nygren, M.; Westin, G. (1996) *J. Solid State Chem.*, subm.

PS07.00.10 CRYSTAL STRUCTURE OF TRANS-DIISOTHIOCYANATO(5,7,7,12,14,14-HEXAMETHYL-1,4,8,11-TETRAAZACYCLOTETRADECA-4,11-DIENE) COBALT(III) THIOCYANATE. B. H. Chen¹, T. H. Lu², W. T. Huang¹, H. H. Yao¹, J. M. Lo¹, and C. S. Chung³ ¹Department of Nuclear Science, ²Department of Physics, and ³Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 300, ROC

Transition-metal complexes of macrocyclic ligand containing asymmetric centers have been studied extensively, because of their particular stereochemistry. The crystal structure of trans-dichloro(c-meso-3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclopentadeca-4,11-diene) cobalt(III) perchlorate have been reported previously (Lu et al., *J. Chin. Chem. Soc.*, 1992, 39, 343-345). Here we report crystal structure of the title complex. Orthorhombic, $P2_12_12_1$, $a=12.169(2)$, $b=13.576(1)$, $c=14.929(1)\text{\AA}$, $R=0.051$, $wR=0.055$ for 2804 observed reflections. The Co(III) ion is six coordinated in a distorted octahedral geometry with the four N atoms of the two isothiocyanato group axial. The quadridentate macrocyclic ligand is in planar conformation with the two five-membered rings in gauche form and the two six-membered ring in twist form. The complex has the RR or SS configuration for the two chiral amine N centers. The intermolecular hydrogen bonds among the two NH groups and the unbonded thiocyanate ion help to stabilize the crystal structure.



PS07.00.11 TO BEND OR NOT TO BEND—STRUCTURAL STUDIES OF OXO-BRIDGED BINUCLEAR TITANIUM COMPLEXES. Michael Y. Chiang, Bella M. Chen, Hui-Wen Feng, Department of Chemistry, National Sun Yat-Sen University, Kaohsiung, Taiwan, Republic of China

Oxo-bridged binuclear transition metal complexes often display a wide MOM angle much larger than the HOH angle of 104.5° found in water. In extreme case it reaches the 180° limit becoming linear. Although most people agree the geometry may be governed by steric reasons, no one can be sure of that. We have examined three crystal structures of the same complex, μ -oxo-bis[chlorobis(2,4-pentanedionato)titanium(IV)], and found both linear and bent Ti-O-Ti moieties. The bent geometry was found in the crystal structure done by Watenpaugh et al. involving the aforementioned Ti complex with cocrystallized chloroform (1). However we have found two structures of the same complex, with and without cocrystallized acetonitrile, both displaying linear Ti-O-Ti framework. Detailed structural comparison among the three crystal structures as well as other related group IVB complexes will be presented.

- (1) K. Watenpaugh and C. N. Caughlan, *Inorganic Chemistry* 6, 963-967 (1967)

PS07.00.12 STRUCTURAL SYSTEMATICS OF TRANSITION METAL TRIPHOSPHORUS MACROCYCLES. Simon J. Coles and Michael B. Hursthouse Department of Chemistry University of Wales, Cardiff, P.O. Box 912, Cardiff, Cf1 3Tb, U.K.

A number of transition metal triphosphacyclododecane complexes have been structurally characterised by X-ray crystallography, enabling a systematic structural study, the results of which have been incorporated into the development of extended force field parameter sets for transition metal complexes.

Data for the air-sensitive crystals of these complexes were collected on the FAST TV Area detector, equipped with an Oxford Cryosystems low temperature device, using the oil drop mounting method. Structures were solved using the SHELX suite of programs to give experimental parameters.

A force field parameter set for the complex $[\text{Cr}(\text{CO})_3\{\text{cyclo}(\text{HPC}_3\text{H}_6)_3\}]$ was derived, using the classical approach, giving force constants for stretch and bend parameters and energy barriers for torsional and nonbonded interaction parameters. This extended force field parameter set is applied to the molecular modelling of structures determined by X-ray diffraction, in order to determine the accuracy of the derived parameters, and then used to model uncharacterised structures. Molecular mechanics calculations were performed using the software packages HyperChem and Cerius², which have also been used to perform semi-empirical calculations upon these systems.