

Single Crystal Diffractometer

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The IPNS SCD has been in continuous operation for the past five years except for a few months during which the large area position-sensitive detector was rebuilt. The scintillation detector contains a 7 x 7 array of photomultiplier tubes (PMTs) and in 1996 it was determined that a noticeable degradation of the spatial resolution was due to noise from the PMTs after over 15 years of operation. To solve this problem, all 49 PMTs were replaced along with some of the internal electronics. More recently, work has progressed on the development of a new detector which would also be a prototype for detectors at the SNS. The current plan is to begin to replace the existing detector and electronics with two new detectors and a new data acquisition system by the middle of next year.

Although other types of experiments were performed, a major emphasis was on transition metal coordination complexes for a variety of scientific reasons. A series of osmium-dihydrogen-dihydride complexes from the laboratory of Greg Girolami (University of Illinois) is described in an accompanying Highlight. Brief descriptions of other selected experiments are given below:

Transition metal cluster complexes

Three transition metal molecular cluster complexes from the laboratory of F. A. Cotton (Texas A&M University) were characterized in the past five years. The first of these was the compound $(\text{Ph}_4\text{P})_3[\text{Zr}_6\text{Cl}_{18}\text{H}_5]$, **1**, which is a member of a class of octahedral hexazirconium compounds with Zr_6X_{12} ($\text{X} = \text{Cl}$ or Br) core units and with no atom at the center. The structure of **1** was characterized by a combined analysis of single-crystal X-ray and neutron diffraction data.¹ Difference Fourier maps based on the neutron data exhibited negative troughs on the triangular faces of the hexazirconium octahedron which were introduced into the structure as hydrogen atoms (Figure 1). Refinement of the atomic positional and occupancy parameters of the hydrogen atoms resulted in about 0.7 H atoms on each triangular face for a total of 5.47(15) hydrogen atoms. This is consistent with the ^1H NMR measurement and with the theoretical expectation of 5 hydrogen atoms in the cluster.

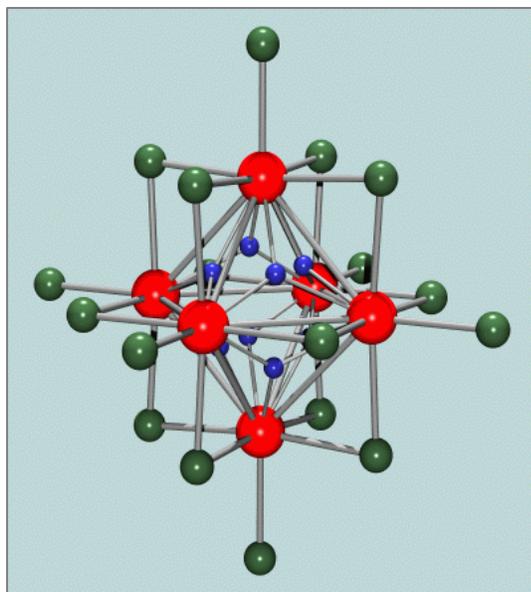


Figure 1. Structure of the tri-anion in the compound $[(C_6H_5)_4P]_3[Zr_6Cl_{15}H_5]$. Hydrogen atoms on each face of the hexazirconium octahedron have occupancies of about 0.7. Atom colors are: Zr, red; Cl, green; H, blue.

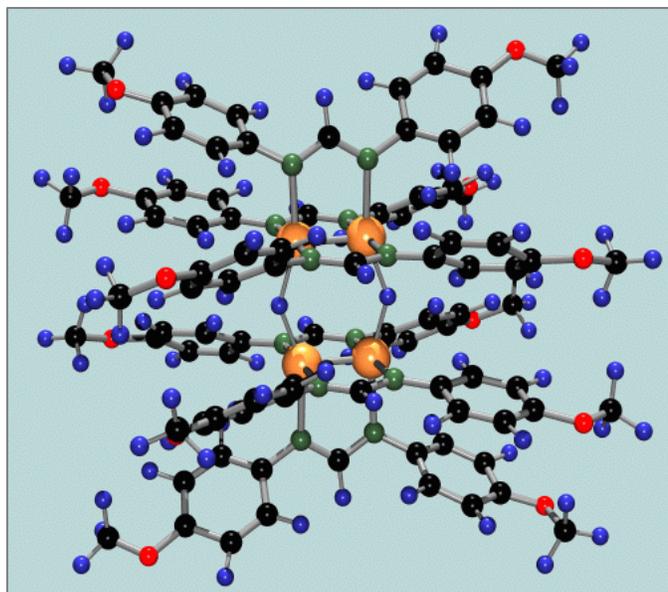


Figure 2. The structure of $[Mo_2(C_{13}H_{15}N_2O_2)_3]_2(\mu-H)_2$ at 20 K showing two pairs of quadruply bonded Mo_2^{4+} units linked by two bridging hydride atoms. Atom colors are: Mo, orange; H, blue; N, green; O, red; C, black.

A second study involved one of the products obtained from investigations into ways of joining dinuclear, multiply bonded transition metal units (doublets) to form tetranuclear molecules (quartets). The structural analysis of a molecule consisting of two pairs of quadruply bonded Mo_2^{4+} units linked by two bridging hydride ligands, $[Mo_2(C_{13}H_{15}N_2O_2)_3]_2(\mu-H)_2$, **2**, is

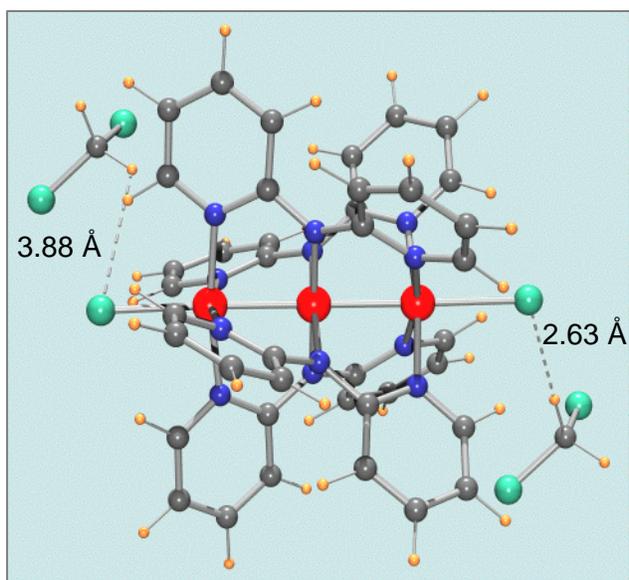


Figure 3. Structure of $Co_3(dpa)_4 \cdot CH_2Cl_2, 3 \cdot CH_2Cl_2$ (dpa = di(2-pyridyl)amide) at 20 K. The dashed lines and labels indicate the shortest chloride ligand to methylene chloride hydrogen distance at each end of the molecule.

shown in Figure 2.² The average Mo–Mo quadruple bond distance in **2** is 2.075(3) Å and the average Mo–H distance is 1.84(2) Å. The triclinic crystals contains two independent molecules, each on a center of inversion, such that there are 220 independent atoms.

A third investigation was of a polynuclear complex that did not contain any hydride ligands, but exhibited an order-disorder transition involving a hydrogen bond to a metal-bound ligand.³ The molecule, shown in Figure 3, is a linear tricobalt complex $Co_3(dpa)_4Cl_2$ (**3**; dpa = di(2-pyridyl)amide) which crystal-

lizes from methylene chloride as either an orthorhombic form, $3 \cdot \text{CH}_2\text{Cl}_2$, or a tetragonal form, $3 \cdot 2\text{CH}_2\text{Cl}_2$. Magnetic susceptibility measurements of both forms show a magnetic moment of $\sim 1.8 \mu_{\text{B}}$ at low temperatures with a gradual increase to $\sim 2.6 \mu_{\text{B}}$ at temperatures above 150-200 K, which can be explained in terms of spin crossover at higher temperatures of an isolated Co^{II} atom. This model is consistent with the structure of $3 \cdot 2\text{CH}_2\text{Cl}_2$ which is unsymmetrical with a short and a long Co–Co distance. However, the room temperature structure of $3 \cdot \text{CH}_2\text{Cl}_2$ is completely symmetric with two equivalent Co–Co distances. On the SCD, a crystal of $3 \cdot \text{CH}_2\text{Cl}_2$ which was cooled to 20 K, exhibited violations of the $Pnn2$ space group consistent with the monoclinic subgroup Pn . Because the β -angle is nearly 90° the low temperature phase is twinned about the a axis. Analysis of the twinned data showed that the methylene chloride molecule, which is disordered about two orientations at room temperature, is ordered with one orientation at low temperature, permitting a weak hydrogen bond to one of the cobalt-bonded chlorine ligands, but not to the other. Thus, although the two independent Co–Co distances remain essentially equivalent, the Co–Cl distances differ by 0.06 \AA due to the different hydrogen bonding environments at each end of the tricobalt molecule.

The structure of a ditantalum complex, **4**, prepared in the laboratory of Ziling (Ben) Xue (University of Tennessee, Knoxville) is shown in Figure 4.⁴ This molecule is the product of the

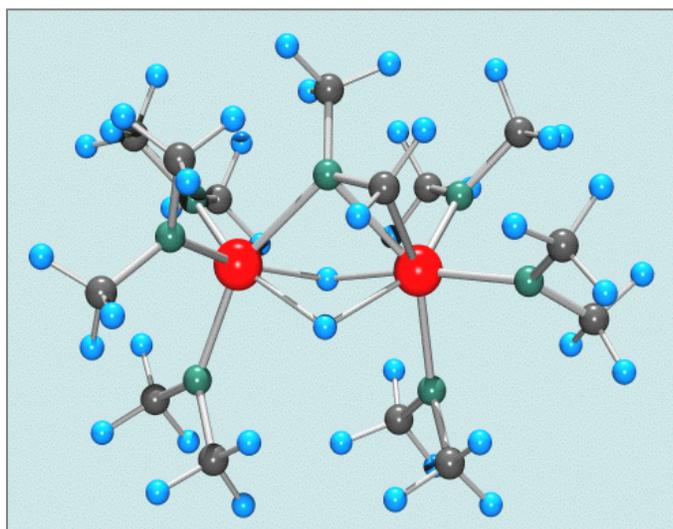


Figure 4. Single crystal neutron structure of $(\text{Me}_2\text{N})_3\text{Ta}(\mu\text{-H})_2(\mu\text{-}N\text{-}\eta^2\text{-}N, C\text{-CH}_2\text{NMe})\text{Ta}(\text{NMe}_2)_3$, **4**. Atom colors: Ta, red; N, green; C, dark gray; H, blue.

reaction of $\text{Ta}(\text{NMe}_2)_5$ with silanes H_2SiRPh ($\text{R} = \text{Me}, \text{Ph}$) and involves the β -H elimination from one of the amide ligand methyl groups to form a direct Ta–C bond. This is not a typical C–H bond oxidative-addition reaction since deuterium labeling experiments show the hydride atoms originate from the silane, not the amide ligand, and the C–H proton is transferred to an amide nitrogen atom to form free HNMe_2 . This reaction has potential significance with regard to

understanding of the formation of M–C bonds in chemical vapor deposition (CVD) processes involving transition metal amides ($M(NR_2)_n$ precursors).

Molecular Distortions Via Hydrogen Bonding Networks

A topic of continued interest has been our investigations of the isotope and pressure switchable Jahn-Teller distortion in the ammonium copper Tutton salt, $(NH_4)_2[Cu(H_2O)_6](SO_4)_2$, **5**, in collaboration with Michael Hitchman (University of Tasmania, Australia) and others. In this compound, the direction of the Jahn-Teller elongation has been shown to switch between two orthogonal directions by the application of pressure or by deuteration (see Figure 5). The switch is a concerted cooperative process transmitted by the hydrogen bonding network and involving a rotation of the ammonium cation. In this latest study, a crystal that was 58%/42% H/D was examined and shown to be nearly identical to the pure hydrogenated salt without any evidence of disorder.⁵ This was the case even though EPR measurements indicate that the

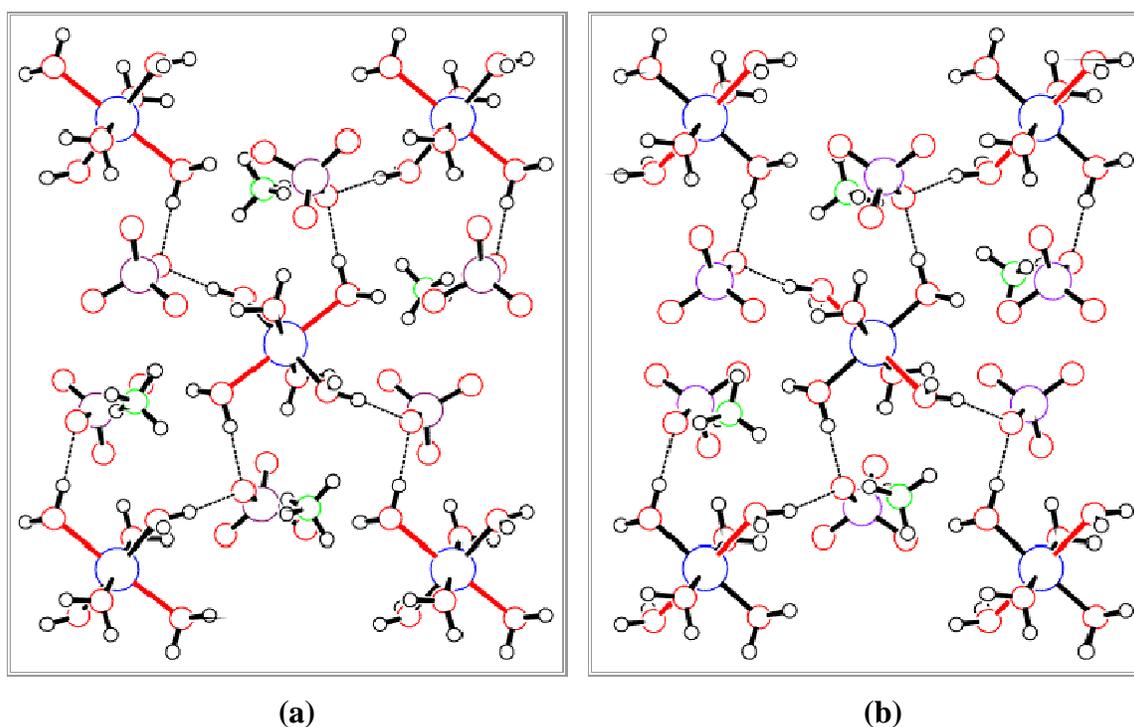


Figure 5. The two types of packing in the *ab* plane of the ammonium copper Tutton salt, $(NH_4)_2[Cu(H_2O)_6](SO_4)_2$. The long Cu-O bonds (~ 2.3 Å) are shown in red and the short bonds (~ 2.0 Å) are shown in black. Selected H-bonds are shown as dashed lines. (a) The structure of the fully deuterated salt, $(ND_4)_2[Cu(D_2O)_6](SO_4)_2$. (b) The structure of the fully hydrogenated salt, of the 42% deuterated salt, and of the fully deuterated salt under an applied pressure of ~ 300 bar. Note the 90 degree switch in the Jahn-Teller distortion between panel (a) and (b).

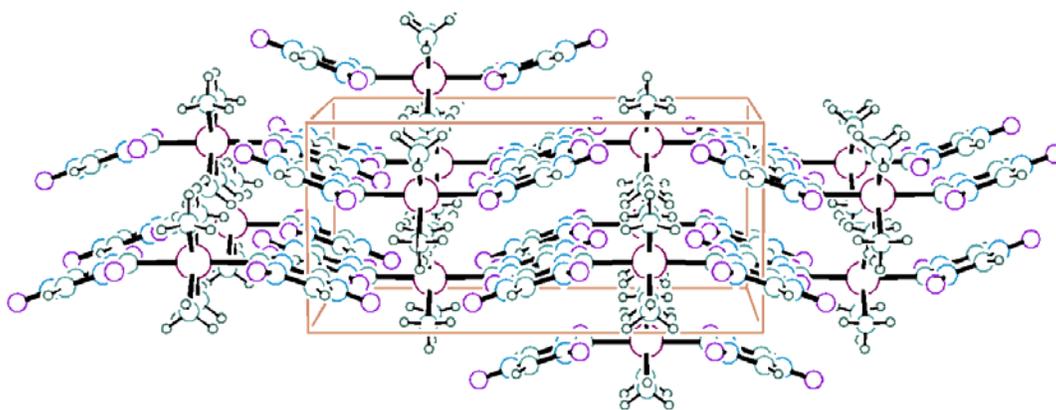


Figure 6. Packing of *trans*-[Ni(cyan- κ N)₂(NH₃)₄] at $T = 13$ K, $P = 0$. The dihedral angle between the coordinated cyanurate ligands is $35.16(1)^\circ$, whereas at room temperature the ligands are coplanar with the nickel atom.

structure changes quite abruptly at $\sim 50\%$ deuteration. The possible influence of deuteration upon the hydrogen-bonding distances and the Jahn-Teller radius are possible reasons for the switch.

In a series of experiments with Larry Falvello (University of Zaragoza, Spain) and coworkers, the continuous smooth distortion of a nickel complex characteristic of a second order phase transition was examined by X-ray and neutron diffraction at temperatures ranging from 11 to 298 K,⁶ and under applied pressure.⁷ The six coordinate nickel cyanurate complex, *trans*-[Ni(cyan- κ N)₂(NH₃)₄], participates in an extended chain formed by hydrogen bonding between ligands of adjacent molecules. At room temperature, the nickel atom and the two cyanurate ligands are coplanar. Upon cooling or with the application of pressure, the molecule distorts such that the cyanurate ligands are bent out of the coordination plane due to the coupling of the molecule to its hydrogen-bonded network in the solid (Figure 6). This system provides an opportunity to study a transition-metal center spectroscopically in a continuously changing ligand field.

Summary

The above experiments indicate a great deal of scientific activity by SCD users in the area of transition metal coordination and cluster compounds in which hydride ligands, dihydrogen ligands, and hydrogen bonding play important roles. Some other topics of investigations included crystalline materials with possible low barrier hydrogen bonds, phase transitions in minerals,⁸⁻¹⁰ anharmonicity due to antiferromagnetic ordering,¹¹ and high- T_c ¹² and CMR materi-

als,¹³ in addition to others. Thus, the SCD continues to provide useful data for a variety of single crystal studies. With the planned upgrade consisting of two or more new detectors and a new data acquisition system, in the future we expect to be able to perform experiments in shorter times and to attempt more difficult and challenging experiments than is currently feasible.

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