

**PS07.01.04 X-RAY DIFFRACTION ANALYSIS OF GEOMETRY CHANGES ON EXCITATION: THE GROUND STATE AND EXCITED STATE STRUCTURES OF  $K_2[Ru(NO_2)_4(NO)(OH)]$ .** Dmitry V. Fomitchev and Philip Coppens, Department of Chemistry, State University of New York at Buffalo, Buffalo, NY 14260-3000, USA

In the potassium nitroso-hydroxytetranitro ruthenate,  $K_2[Ru(NO_2)_4(NO)(OH)]$ , two light-induced long-lived metastable excited states can be populated by irradiation at low temperature with 458 nm radiation from an Ar<sup>+</sup> laser [1]. In continuation of our diffraction studies of excited state complexes [2], we have collected data sets at 50K before and after exposure to the exciting radiation. In the excited state experiment, the second metastable state was eliminated by maintaining the crystal at 160K for 5 min. The imaging plate data collection technique and seed-skewness integration method were used [3]. 1571 and 2057 reflections were obtained for the least squares refinement of the ground and excited state structures respectively. Final agreement factors are R=0.024, Rw=0.029 and R=0.025, Rw=0.030, for the two data sets. The population of the metastable excited state was estimated as 16%, based on a differential scanning calorimetry experiment.

The statistically significant geometrical distortions of the metastable state are an elongation of the Ru-N(nitrosyl) bond by 0.079(15) Å from 1.769(3) Å to 1.848(15) Å and a decrease in the angle Ru-N-O by 4.0(1.0)° from 174.0(2)° to 170.1(1)°. This is similar to our previous results on the first metastable electronic state of  $[Fe(CN)_5(NO)]^{2-}$  [2], though the angular change is larger in the Ru-compound. The elongation of N-O bond, expected from the shift of the stretching frequency of (NO) from 1886 cm<sup>-1</sup> to 1722 cm<sup>-1</sup> [1], was not observed in either study:

(1) Th. Woike and S. Haussühl, *Solid State Comm.* 86, 333 (1993).

(2) M. R. Pressprich, M. A. White, Y. Vekhter, P. Coppens, *J. Am. Chem. Soc.* 116, 5233 (1994).

(3) R. Bolotovskiy, M. A. White, A. Darovsky, P. Coppens, *J. Appl. Cryst.* 28, 86 (1995).

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**PS07.01.05 STRUCTURAL PECULIARITIES OF MIXED-LIGAND Zn(II) DIALKYL DITHIOCARBAMATE COMPLEXES WITH NITROGEN-CONTAINING HETEROCYCLES.** L.A. Glinskaya, R.F. Klevtsova, S.M. Zemskova, S.V. Larionov, Institute of Inorganic Chemistry, Novosibirsk 90, Russia

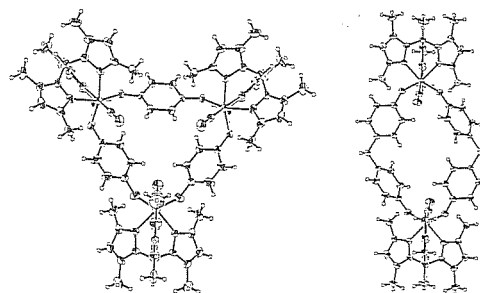
An aimed synthesis and a structural study of a large group of chemical compounds with variable properties of ligands or metals make possible to establish a composition-structure-property correlation. We have synthesized some volatile mixed-ligand complexes (MLC) of zinc(II) dialkyl dithiocarbamates with (i) alkyl substituents of a different length and with different steric structures; (ii) various N heterocycles i.e., Phen(L1), 2,2'-Bipy(L2), 4,4'-Bipy(L3). Single crystals were prepared and studied by X-ray structure analysis. Structural features of five MLC were discussed.

N	Complexes		Zn-S	Zn-N	CN
1	Zn(Et <sub>2</sub> Dtc) <sub>2</sub> L1	P1(-)	2.44-2.64	2.18; 2.25	6
2	Zn(Et <sub>2</sub> Dtc) <sub>2</sub> L2	Pnaa	2.49-2.57	2.18; 2.18	6
3	Zn(Me <sub>2</sub> Dtc) <sub>2</sub> L1	C2/c	2.45-2.57	2.18; 2.21	6
4	Zn <sub>2</sub> (Et <sub>2</sub> Dtc) <sub>4</sub> L3	Pnca	2.33-2.63	2.10	5
5	Zn <sub>2</sub> (i-Bu <sub>2</sub> Dtc) <sub>4</sub> L3	P1(-)	2.33-2.64	2.07	5

The crystal structures consist of monomeric (1-3) or binuclear (4,5) molecules linked through van der Waals contacts. Coordination polyhedra of the central Zn atom are a distorted tetragonal pyramid and a trigonal bipyramid for CN=5, and a distorted octahedron for CN=6. We have considered a molecule packing mode and revealed a correlation between Zn-S and Zn-N distances and a polyhedron shape. The thermal properties of MLC in vacuum and in air were studied. This research allowed us to introduce some MLC as molecular precursors for preparing ZnS films by the CVD method.

**PS07.01.06 STRUCTURAL FEATURES OF METALLO-CYCLOPHANES CONTAINING TWO, THREE AND FOUR OCTAHEDRAL METAL CENTRES.** Thomas A. Hamor, Hongli Chen, Ferida S McQuillan, Timothy E. Berridge, Helen A. Hinton, and Christopher J. Jones, School of Chemistry, University of Birmingham, Birmingham B15 2TT, UK.

In the context of host-guest chemistry, the incorporation of transition metal atoms into cyclophanes provides a means of introducing new properties such as Lewis acidity or redox activity into the macrocyclic structures. These structures are based on -[M(Tp\*)(Z)]- {Tp\*=tris(3,5-dimethylpyrazolyl)hydroborate, M=Mo or W, Z=NO} units, linked by bifunctional agents, such as 1,4-dihydroxybenzene or 2,7-dihydroxynaphthalene. Steric isomerism at the metal centres has been characterised; the accessibility of the central cavity to guest molecules is affected specifically by the orientation of the nitrosyl groups. Views of two- and three-metal centre macrocycles, based on area-detector X-ray data are shown below. Examples of fourmetal centre structures, and other two and three-centre structures will be presented.



**PS07.01.07 THE STRUCTURE OF COORDINATION COMPOUND OF Cu(II) WITH AMINOGUANYDINE SULFATE.** Khudayarov A.B., Mirjalolov F.F., Sharipov Kh.T, Institute of Chemistry, RO"Spetsplav", Uzbekistan.

Coordination compound of Cu(II) with aminoguanidine sulfate was obtained and its structure determined by X-ray diffraction method. Found that  $2[Cu(C_2N_3H_6)_2SO_4] \cdot H_2O$  crystallizes in monoclinic space group P2<sub>1</sub>/c, a=14.188(4), b=5.637(1), c=14.079(4), β=97.5°, d=1.68g/cm<sup>3</sup>, Z=4, R=0.085. The special positions for two Cu<sup>2+</sup> ions having planar-square coordination are discovered. Planar aminoguanidine molecules bonded to metal through nitrogen atoms and hydrogen-bonded to both sulfate ion and H<sub>2</sub>O. The positive charges of protonized aminoguanidine infive-membered rings are delocalized.