

## FA4-MS34-P01

**Crystallographic Study of N-O Schiff Bidentate Rhenium and Copper Complexes** Alice Brink,

Andreas Roodt, Hendrik G. Visser

*Department of Chemistry, University of the Free State, Bloemfontein 9300, South Africa*E-mail: [alice.brink@gmail.com](mailto:alice.brink@gmail.com)

Schiff bases are a versatile class of organic compounds which readily form stable complexes with a variety of transition metals. The broad field of interest is due to their potential in bio-inorganic chemistry, catalysis, magnetochemistry and as liquid crystals [1, 2]. These Schiff-base ligands also provide the possibility as linkers to target-based directing groups, such as antibodies and proteins. Due to the potential application of <sup>186/188</sup>Re radionuclides in radiotherapy [3, 4], there is considerable interest in the coordination chemistry of rhenium. The oxidation states of rhenium(I) and rhenium(V) are readily obtained and are stabilized by a variety of ligands [5]. Rhenium-Schiff base complexes attract interest due to the potential in radiotherapy and the ease by which the denticity, steric and electronic properties of the various ligand derivatives may be manipulated [6, 7]. Similarly, the use of <sup>64/67</sup>Cu radionuclides in radiotherapy is also very attractive, particularly with the longer half-lives which are available [8], and since the redox and coordination chemistry of copper I and II oxidation states is well understood.

This study is concerned with the coordinative and structural properties of neutral and mono-anionic bidentate Schiff base ligands (N, O and P) with rhenium(I) tricarbonyl and copper(II) complexes. A crystallographic and synthetic study will be presented and discussed, highlighting several interesting substitution observations which have been made.

[1] Hernández-Molina, R.; Mereros, A. *Comprehensive Coordination Chemistry II*, Elsevier Ltd., Vol. 1, 2003, 411. [2] Mayer, P.; Gerber, T.I.A.; Buyambo, B.; Abrahams, A. *Polyhedron*, 2009, 28, 1174. [3] Volkert, W.A.; Hoffman, T.J. *Chem. Rev.*, 1999, 99, 2269. [4] Botha, J.M.; Roodt, A. *Metal-Based Drugs*, 2008, 2008, Article ID 745989, doi:10.1155/2008/745989. [5] Rouschias, G. *Chem. Rev.*, 1974, 74, 531. [6] Middleton, A.R.; Masters, A.F.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.*, 1979, 542. [7] Sachse, A.; Mösch-Zanetti, N.C.; Lyashenko, G.; Wielandt, J.W.; Most, K.; Magull, J.; Dall'Antonia, F.; Pal, A.; Herbst-Immer, R. *Inorg. Chem.*, 2007, 46, 7129. [8] Anderson, C.J.; Welch, M.J. *Chem. Rev.*, 1999, 99, 2219.

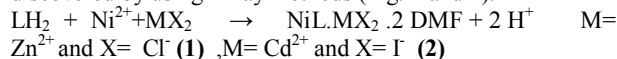
**Keywords: rhenium, copper, radiotherapy**

## FA4-MS34-P03

**Two Heteronuclear Coordination Compounds with Ni<sup>II</sup>M<sup>II</sup> Nuclear Structure.** Abdülkadir Akay<sup>a</sup>, Ümit Ergun<sup>a</sup>, Elif Gökçınar<sup>a</sup>, Ingrid Svoboda<sup>b</sup>, Orhan Atakol<sup>a</sup><sup>a</sup>Ankara University, Faculty of Science, Dept. of Chem., Ankara, Turkey, <sup>b</sup>Materials Science, Technical University Darmstadt, GermanyE-mail: [atakol@science.ankara.edu.tr](mailto:atakol@science.ankara.edu.tr)

Bis-N,N'(salicylidene)-1,3-propanediamine is an ONNO type ligand of (LH<sub>2</sub>) which is known to give polynuclear complexes [1-3]. For about the last 10 years a technique is used that employs the imine groups of Schiff bases of this class, after being reduced by NaBH<sub>4</sub>, to obtain a ligand of phenol-amine type which tends to give polynuclear complex similar as Bis-N,N'(salicylidene)-1,3-propanediamine.

In this study, Bis-N,N'(2-hydroxybenzyl)-1,3-propanediamine was obtained by reducing Bis-N,N'(salicylidene)-1,3-propanediamine with NaBH<sub>4</sub> and by using this compound, complexes of Ni(II)-Cd(II)<sub>2</sub> and Ni(II)-ZnCl<sub>2</sub> nuclear structures were synthesized. These complexes were then characterised by Thermogravimetry, IR spectroscopy, elemental analysis and their molecular structures were discovered by using X-ray methods (Fig. 1 and 2).



In the complexes, Ni(II) ion is in octahedral conformation located between the iminic nitrogens and phenolic oxygens of the organic ligand and two DMF molecules. The phenolic oxygens also coordinate the Cd(II) ions, forming a  $\mu$  bridge. The octahedron has a distorted shape and the axial axis of it could not be clearly uncovered by the bond angles. Presumably, the oxygens of the DMF molecules are in axial position. On the other hand, Zn(II) and Cd(II) are located in an extremely distorted tetrahedral coordination sphere between the two phenolic oxygens and the two halogens. The tetrahedron shapes are almost the same because of the distance between the halogen ions. Given below is the crystallographic data of the complexes, structures of which were determined in this study.

For **1**, [C<sub>23</sub>H<sub>34</sub>Cl<sub>2</sub>N<sub>4</sub>NiO<sub>4</sub>Zn], P<sub>bca</sub>, a= 13.5709(8), b= 19.539(2) c= 20.887(2) Å,  $\alpha = \beta = \gamma = 90^\circ$ , Z= 8, D= 1.500 Mg/m<sup>3</sup>, (Data/parameters)= 5655/326, I>2 $\sigma$ , R, R<sub>w</sub>→0.0345, 0.0627, GOF=0.996,  $\Delta\rho_{\text{max}}$ ,  $\Delta\rho_{\text{min}}$ →0.303, -0.283 e.Å<sup>-3</sup>,  $\lambda = 0.71073$  Å.

For **2**, [C<sub>23</sub>H<sub>34</sub>Cd I<sub>2</sub>N<sub>4</sub>NiO<sub>4</sub>], P<sub>bca</sub>, a= 20.230(5), b= 14.607(1) c= 20.648(4) Å,  $\alpha = \beta = \gamma = 90^\circ$ , Z= 8, D= 1.863 Mg/m<sup>3</sup>, (Data/parameters)=6195/320, I>2 $\sigma$ , R, R<sub>w</sub>→0.0667, 0.2213 GOF=0.992,  $\Delta\rho_{\text{max}}$ ,  $\Delta\rho_{\text{min}}$ →2.147, -2.140 e.Å<sup>-3</sup>,  $\lambda = 0.71073$  Å.

The dihedral angles between the planes N1N1Ni2/N1C8C10N2 and C8C9C10/N1C8C10N2 show that in both complexes, the chelat rings formed between the iminic nitrogens and Ni(II) ions have a chair conformation close to ideal.

[1] Fukuhara C., Tsuneyoshi K., Matsumoto N., Kida S., Mikuriya M., Mori M., *JCS Dalton Trans.* 1990, 3473. [2] reglinski J., Taylor M.K., Kennedy A.R., *Inorg. Chem. Comm.* 2006, 9, 736. [3] Shi DH., You ZL., Xu C., Zhang Q., Zhu HL., *Inorg. Chem. Comm.* 2007, 10, 404.

**Keywords: heterodinuclear complexes, reduced Schiff base, ONNO type ligand**

## FA4-MS34-P04

**Synthesis, crystal structure and magnetic properties of a cyano-bridged two-dimensional assembly** [Fe(L)]<sub>2</sub>[Fe(CN)<sub>6</sub>]. Fatma Cagnur Alakus, Hulya Kara*Department of Physics, Balikesir University, Balikesir, Turkey*E-mail: [cagnuralakus@hotmail.com](mailto:cagnuralakus@hotmail.com)

A cyano-bridged Fe(III)-Fe(III) complex, [Fe(L)(MeOH)]<sub>2</sub>[Fe(CN)<sub>6</sub>](NEt<sub>4</sub>)(1) (L = N,N-bis(5-chlorosalicylidene)-1,2-diaminopropane) have been prepared and structurally and magnetically characterized. The compound 1 crystallizes in monoclinic space group P2(1)/n with a= 12.470, b= 15.441, c= 15.295 Å,  $\beta = 113.31^\circ$ . Single crystal X-ray analysis reveals that the complex assumes a cyano-bridged Fe<sub>2</sub>Fe unit. The two CN in the equatorial plane

of the  $[\text{Fe}(\text{CN})_6]^{3-}$  moiety bridge two Fe ions, each in the trans position, which results in a 2D hydrogen bonded structure giving a  $[\text{Fe}-\text{NC}-\text{Fe}-\text{CN}-\text{Fe}]$  linkage. The Fe ion assumes an octahedral geometry, in which the equatorial sites are occupied by  $\text{N}_2\text{O}_2$  donor atoms of the Schiff base ligand, and the two axial positions are filled by two cyanide ion of  $[\text{Fe}(\text{CN})_6]^{3-}$ . The magnetic measurement showed this complex to exhibit antiferromagnetic behavior.

**Keywords:** cyanide complexes, molecular magnets, crystal engineering

#### FA4-MS34-P05

**Novel Chiral MOFs Constructed by both Mixed Metals and Dicarboxylate Ligands.** Zakariae Amghouz<sup>a,b</sup>, Laura Rocés<sup>a</sup>, José R. García<sup>a</sup>, Santiago García-Granda<sup>a</sup>, Badredine Souhail<sup>b</sup>, Luís Mafra<sup>c</sup>, Fanian Shi<sup>c</sup>, João Rocha<sup>c</sup>, <sup>a</sup>*Departamentos de Química Física y Analítica y Química Orgánica e Inorgánica, Universidad de Oviedo, Spain.* <sup>b</sup>*Département de Chimie, Faculté des Sciences, Université Abdelmalek Essaâdi, Tétouan, Morocco.* <sup>c</sup>*Department of Chemistry, CICECO, University of Aveiro, Portugal.*  
E-mail: [amghouz.uo@uniovi.es](mailto:amghouz.uo@uniovi.es)

Metal–Organic Frameworks (MOFs), also known as coordination polymers, materials composed of metal ions or metal clusters as nodes and multifunctional organic linkers, are currently one of the most active and attractive research fields in the materials science, owing to their wide variety of fascinating architectures and topologies, and their wide range of potential applications in gas storage and separation, catalysis, magnetism, luminescence, and so on. Those properties provide many possibilities to construct attractive multifunctional materials. The design of chiral MOFs attracts much attention recently because of their potential applications in asymmetric catalysis and chiral separation [1,2]. Nevertheless, the attempts for construction of chiral lanthanides-based MOFs are still rare [3,4] and even more challenging than those based on transition metals. Herein, we will confine ourselves to report two novel chiral Yttrium-based MOFs with fascinating architectures, as first example up to now, of chiral structure containing both mixed Y(III)-Na(I) metals and chiral flexible-achiral rigid dicarboxylate ligands, obtained as single phase under hydrothermal conditions. Their structures were solved by single crystal XRD, and characterized by <sup>13</sup>C CPMAS NMR, thermal analyses (TG-MS and DSC) and X-ray thermodiffraction. The crystal structure reveals that both compounds are extended in the 2D space, the 3D stability of the frameworks is provided through strong hydrogen bond interactions, and the both compounds exhibit reversible dehydration process with different rehydration kinetic.

[1] Kesanli, B.; Lin, W. B. *Coord. Chem. Rev.* 2003, 246, 305. [2] Ma, L.; Abney, C.; Lin, W. *Chem. Soc. Rev.* 2009, 38, 1248. [3] Thushari, S.; Cha, J. A. K.; Sung, H. H. Y.; Chui, S. S. Y.; Leung, A. L. F.; Yen, Y. F.; Williams, I. D. *Chem. Commun.* 2005, 5515. [4] Tang, Y.; Tang, K. Z.; Liu, W. S.; Tan, M. Y. *Sci. China Ser. B-Chem.* 2008, 51, 614.

**Acknowledgements:** Financial support given by Spanish MICINN (MAT2006–01997, Factoría de Cristalización Consolider Ingenio 2010 and FPI grant BES-2007-14340), and FEDER founding, is acknowledged.

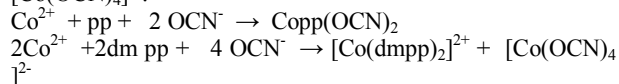
**Keywords:** Chiral MOFs, Hydrothermal Synthesis, Structural Determination

#### FA4-MS34-P06

**Two New Co(II) Complexes with NNN Type Pyrazol Ligands** Orhan Atakol<sup>a</sup>, Sevi Öz<sup>a</sup>, Ingrid Svoboda<sup>b</sup>, Sefa Durmuş<sup>c</sup>, Raif Kurtaran<sup>d</sup>, Cengiz Arıcı<sup>e</sup>  
<sup>a</sup>*Ankara University, Faculty of Science, Ankara, Turkey*  
<sup>b</sup>*Materials Science, Technical University Darmstadt, Germany*  
<sup>c</sup>*Duzce University, Faculty of Science and Art, Duzce, Turkey*  
<sup>d</sup>*Balikesir University, Faculty of Science and Art, Balikesir, Turkey*  
<sup>e</sup>*Hacettepe University, Faculty of Eng. Ankara, Turkey*  
E-mail: [atakol@science.ankara.edu.tr](mailto:atakol@science.ankara.edu.tr)

Bis-2,6(Pyrazol-1-yl)pyridine and its derivatives involving alkyl groups are terpyridyl like ligands which have been known since 1990 [1]. For about last 20 years, many transition metal complexes have been prepared with this ligand [2]. It is also known for a long time that ions of azide, cyanate and thiocyanate pseudohalogenides have a tendency to form  $\mu$  bridges [3]. In this study, it had been planned to prepare polynuclear Co(II) complexes next of bis-2,6(Pyrazol-1-yl)pyridine and cyanate ions. However, the result was not as expected, mononuclear Co(II) complexes were obtained instead.

In this study, Bis-2,6(Pyrazol-1-yl)pyridine (pp) and bis-2,6(3,5-dimethylpyrazol-1-yl)pyridine (dmpp) have been used to obtain, two completely different complexes. The complex synthesized with Bis-2,6(Pyrazol-1-yl)pyridine (pp) is a neutral one in which Co(II) ion is coordinated by the three nitrogens of the organic ligand and the oxygens of cyanate group. The complex synthesized with bis-2,6(3,5-dimethylpyrazol-1-yl)pyridine (dmpp) on the other hand, is an ionic complex in which the organic ligand and one Co(II) ion forms the cationic sphere and the anionic sphere is found to be  $[\text{Co}(\text{OCN})_4]^{2-}$ .



The crystallographic data of the complexes is given below:

$[\text{C}_{11}\text{H}_9\text{CoN}_7\text{O}_2]$ , monoclinic  $C_{2/c}$ ,  $a = 14.469(2)$ ,  $b = 9.161(1)$ ,  $c = 12.658(1)$  Å  $\beta = 122.10(1)^\circ$ ,  $Z = 4$ ,  $D = 1.655 \text{ Mg/m}^3$ , (Data/parameters) = 1459/106,  $I > 2\sigma$ ,  $R, R_w \rightarrow 0.0371, 0.1229$ ,  $\text{GOF} = 1.142$ ,  $\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}} \rightarrow 0.680, -0.408 \text{ e.}\text{\AA}^{-3}$ ,  $\lambda = 0.71073$  Å.

$[\text{C}_{34}\text{H}_{34}\text{Co}_2\text{N}_{14}\text{O}_4]$ ,  $P_{bca}$ ,  $a = 16.5704(12)$ ,  $b = 18.6340(13)$ ,  $c = 23.5881(14)$  Å  $\alpha = \beta = \gamma = 90^\circ$ ,  $Z = 8$ ,  $D = 1.497 \text{ Mg/m}^3$ , (Data/parameters) = 6234/489,  $I > 2\sigma$ ,  $R, R_w \rightarrow 0.0509, 0.1587$ ,  $\text{GOF} = 1.000$ ,  $\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}} \rightarrow 0.380, -0.375 \text{ e.}\text{\AA}^{-3}$ ,  $\lambda = 0.71073$  Å.

[1] Jameson D.L., Goldsby K.A., *J. Org. Chem.* 1990, 55, 4992. [2] Atalano V.J., Kurtaran R., Heck R.A., Öhman A., Hill M.G., *Inorg. Chim. Acta* 1999, 286, 181 [3] Ribas J., Escuer A., Monfort M., Vicente R., Cortes R., Lezama L., Rojo T., *Coord. Chem. Rev.* 1999, 193-195, 1068.

**Keywords:** NNN type ligand, pyrazolyl complexes, Co(II)