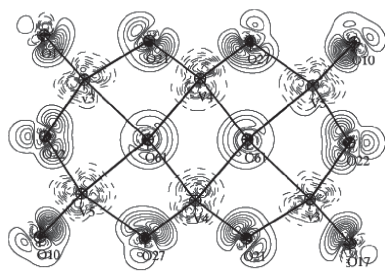


**s2.m10.o4 Investigation of the Cytosine-Decavanadate Interaction from an Experimental Charge Density: a Supramolecular Arrangement of  $\text{Na}_3\text{V}_{10}\text{O}_{28}(\text{C}_4\text{N}_3\text{OH}_5)_3(\text{C}_4\text{N}_3\text{OH}_6)_3 \cdot 10\text{H}_2\text{O}$  in the Solid State.** N. Bosnjakovic-Pavlovic<sup>a,b</sup>, N. Bouhmaida<sup>a,c</sup>, A. Spasojevic-de Biré<sup>a</sup>, I. Correia<sup>d</sup>, I. Tomaz<sup>d</sup>, F. Avecilla<sup>e</sup>, J. Pessoa<sup>d</sup>, U.B. Mioc<sup>b</sup>, and N.E. Ghermani<sup>a,f</sup>, <sup>a</sup>Ecole Centrale Paris, SPMS UMR CNRS 8580 1 Grande Voie des Vignes 92295 Châtenay-Malabry, France; <sup>b</sup>Faculty of Physical Chemistry P.O. Box 137, 11001 Belgrade, Serbia-Montenegro; <sup>c</sup>LSM, Faculté des Sciences Semlalia, P.O. Box 2390, 40000 Marrakech, Morocco; <sup>d</sup>Centro de Química Estrutural, Instituto Superior Tecnico, Av. Rovisco Pais, P-1049-001 Lisboa, Portugal; <sup>e</sup>Departamento de Química Fundamental, Facultad de Ciencias, Campus da Zapateira s/n, 15071 A Coruna, Spain; <sup>f</sup>PPB UMR CNRS 8612, Faculté de Pharmacie 5 Rue Jean-Baptiste Clément, 92296 Châtenay-Malabry, France. E-mail: nada@spms.ecp.fr, nadab@ffh.bg.ac.yu

**Keywords: Decavanadate; Cytosine; Vanadium; Electron Density; Electrostatic Potential**

X-ray diffraction measurements were carried out on a Siemens SMART CCD diffractometer from room to 100 K using  $\text{MoK}_\alpha$  radiation. The title complex crystallizes in the P space group at room temperature. Below 200 K, we have observed substructure diffraction peaks which double the unit cell vanishing the centre of inversion. High resolution data collection was performed at 210 K to a resolution of 0.44 Å for an electron density study. The crystal packing shows a supramolecular network where the decavanadate anions are bridged by the sodium cations on the one hand and cytosine molecules through hydrogen bonds on the other. The pyrimidine bases are grouped in two kinds of dimers: a cytosine-cytosinium one and a shared-proton pair. The reversible dynamic cytosine-cytosinium conversion is probably responsible of the centrosymmetric loss at low temperature. The electron density (P I at 210 K) was refined using the Hansen-Coppens multipole model [1]. The best results were based on a vanadium  $4s^03d^3$  configuration ( $V^{2+}$ ) leading to the agreement factors  $R = 2.76\%$ ,  $R_w = 2.97\%$  and  $\text{gof} = 1.16$ . The static electron density (figure) displays different V—O overlap and the oxygen polarizations in the decavandate anions.



The atomic charges and the electrostatic potential distribution will be presented and discussed.

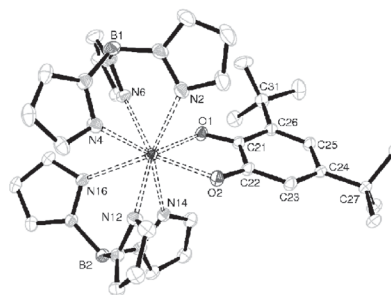
[1] N. Hansen & P. Coppens *Acta Cryst.*, 1978, A34, 909.

**s2.m10.o5 Study of Electronic Interactions in Yttrium and Gadolinium-Semiquinonato Complexes.** Claiser Nicolas<sup>a</sup>, Mohamed Souhassou<sup>b</sup>, Béatrice Gillon<sup>c</sup> and Claude Lecomte<sup>b</sup>, <sup>a</sup>GMCM UMR CNRS 6626, Bât. 11A, Université de Rennes 1, Avenue du Général Leclerc, 35042 Rennes Cedex, France; <sup>b</sup>LCM3B, UMR CNRS 7036, Université Henri Poincaré, Nancy 1, BP 239, 54506 Vandoeuvre-les-Nancy cedex, France; <sup>c</sup>Laboratoire Léon Brillouin, (CEA-CNRS), C.E. Saclay, 91191 Gif-sur-Yvette, France. E-mail: nicolas.claiser@univ-rennes1.fr

**Keywords: Molecular Magnetism; Electronic Density; Spin Density**

Complexes based on ion  $\text{Gd}^{3+}$  ( $S = 7/2$ ) and organic radicals like nitronyle-nitroxide ( $S = 1/2$ ) present usually ferromagnetic couplings [1]. However, in the case of the  $\text{Gd}(\text{HBPz}_3)_2(\text{DTBSQ})$  complex, an antiferromagnetic coupling is observed between the rare earth ion and the semiquinone radical (SQ,  $S = 1/2$ ), corresponding to the spin state  $S = 3$  [2]. This magnetic interaction was interpreted as resulting of two opposite contributions [3]: an antiferromagnetic one due to the direct overlap between the radical  $\pi$  magnetic orbital and the  $4f$  orbital of the central ion, and a second one, ferromagnetic, resulting in the polarization of the  $4f$  electrons consecutively to a partial spin transfer from the radical  $\pi$  orbital to the unoccupied  $5d$  or  $6s$  orbitals of  $\text{Gd}^{3+}$ .

In order to bring new information on the coupling mechanisms, we study the electronic interactions combining two experimental techniques: electron density modeling, based on X-rays diffraction experiment at high resolution and spin density modeling, based on polarized neutron diffraction experiment. We apply this canvass to two isomorphous complexes (Y and Gd-SQ, cf. Figure). Contrary to  $\text{Gd}^{3+}$ , as the  $\text{Y}^{3+}$  cation is spinless ( $S = 0$ ), Y-SQ complex make possible to perceive small charge transfer between central atom and its ligands. Moreover, the topological analysis of the electron density of the yttrium complex allows to obtain precise results such as the integrated charges distribution within the material. The electron density obtained for the gadolinium complex seems to confirm the preceding results, but especially reveals difficulties in modeling the electron density related to the high atomic number of Gd atom.



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