

This work has been supported by Slovak Grant Agency APVV (APVV-0202-10) and VEGA (1/0679/11).

[1] J. Kožíšek, L. Perašinová, M. Breza, *Acta Crystallogr.* **2008**, *64*, C128. [2] L. Perašinová, M. Fronc, L. Bučinsky, M. Gall, M. Breza, J. Kožíšek, submitted to *Inorg. Chem.* [3] R. Boča, M. Hvastijová, J. Kožíšek, M. Valko, *Inorg. Chem.* **1996**, *35*(16), 4794-4797. [4] J. Kožíšek, M. Hvastijová, J. Kohout, *Inorg. Chim. Acta* **1990**, *168*(2), 157-158.

Keywords: Cu-complex, electronic structure, d-orbitals

MS34.P25

Acta Cryst. (2011) **A67**, C453

First principle calculation of perovskite type oxide LaMO_3 ($M = \text{Cr, Mn, Fe, Co, Ni, Cu}$): Correlation of electron density at the $M\text{-O}$ bond with structure

Kazuki Omoto,^a Masatomo Yashima,^{a,b} ^a*Department of Materials Science and Engineering, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Nagatsuta-cho 4259, Midori-ku, Yokohama, 226-8502, (Japan).* ^b*Department of Chemistry and Materials Science, Tokyo Institute of Technology, (Japan).* E-mail: kazuki.o.aa@m.titech.ac.jp

Perovskite-type oxide LaMO_3 ($M = \text{Cr, Mn, Fe, Co, Ni, Cu}$)-based materials are utilized in a wide variety of applications such as solid-oxide fuel cells, catalysts, and gas sensors. Electronic structure and chemical bonding are important, because almost all the properties are governed by them. The covalency at the $M\text{-O}$ bond may influence on the material properties. But, the covalency of $M\text{-O}$ bond has not been investigated in the literature. The covalency at the $M\text{-O}$ bond can be studied by the minimum electron density (MED). In the present work, the MED at the $M\text{-O}$ bond in was studied through the density functional theory (DFT).

The *ab initio* total energy program VASP (Vienna *Ab initio* Simulation Package) [1] was employed to calculate the valence electron-density distribution of LaMO_3 ($M = \text{Cr, Mn, Fe, Co, Ni, Cu}$). Unit-cell parameters and atomic coordinates of LaMO_3 were optimized with the convergence condition of 0.02 eV/Å. Projector augmented-wave (PAW) potentials were used for M , O, and La atoms [2]. A plane-wave basis set with a cutoff of 500 eV was used. The Perdew-Burke-Ernzerhof (GGA) was employed for the exchange and correlation functional. Sums over occupied electronic state were performed using the Monkhorst-Pack scheme [3] on $5 \times 5 \times 5$, $5 \times 5 \times 5$ and $7 \times 7 \times 7$ sets of k -point meshes for $M = \text{Cr, Mn, Fe, Co, Ni, Cu}$, respectively. Optimized crystal structure and valence electron density distribution were drawn with a computer program VESTA [4].

Calculated valence electron density distributions clearly indicate that the $M\text{-O}$ bond is covalent, while the La atom is more ionic. The MED of Cu-O bond in LaCuO_3 (0.61 \AA^{-3}) is higher than that of Mn-O bond in LaMnO_3 (0.50 \AA^{-3}), which is ascribed to the shorter Cu-O bond (1.938 Å) compared to the Mn-O one (1.9904 Å). The MED of $M\text{-O}$ bond in LaMO_3 ($M = \text{Cr, Mn, Fe, Co, Ni, Cu}$) decreases with an increase of $M\text{-O}$ bond length.

[1] G. Kresse, D. Joubert, *Phys. Rev.* **1999**, *B 59* 1758. [2] J. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865. [3] H.J. Monkhorst, J.D. Pack, *Phys. Rev.* **1976**, *B 13*, 5188. [4] K. Momma, F. Izumi, *J. Appl. Crystallogr.* **2008**, *41*, 653-658.

Keywords: first principles calculation, perovskite-type oxide, electron density, density functional theory (DFT)

MS34.P26

Acta Cryst. (2011) **A67**, C453

Evaluating electron delocalization: the need for aromaticity descriptors

Jakob Hey, Dirk Leusser, Daniel Kratzert, Christian Kling, Dietmar Stalke *Institut für Anorganische Chemie, Georg-August-Universität, Göttingen, (Germany).* E-mail: jhey@chemie.uni-goettingen.de

Our aim is to derive chemical properties such as reactivity, coordination behaviour and bond strengths from experimental charge density analysis. Currently, our research is focused on the understanding of catalytically active compounds. In the rapidly progressing field of homogenous organometallic catalysis, the large group of phosphanes can be considered to be one of the most important variables in catalyst design.

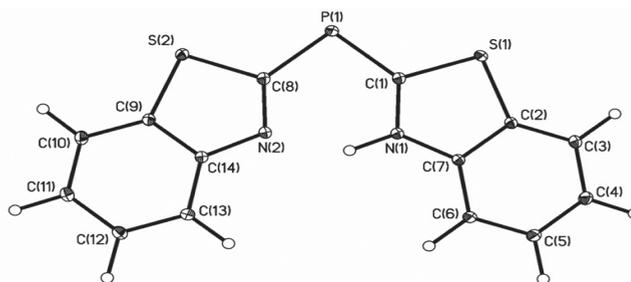
The secondary phosphane $\text{P}[\text{Hbth}][\text{bth}]$ ($[\text{bth}] = \text{benzothiazol-2-yl}$) with phosphorus, sulfur, and nitrogen donor sites provides coordination site selectivity in heterobimetallic complexes.[1,2] Its unusual structure can be explained by tautomerism.

After multipole structure refinement on a high-resolution dataset of the compound obtained at a temperature of 15 K, we showed that two Lewis lone pairs are located at each of the phosphorus and the sulfur atoms, giving them approximately tetrahedral environments according to VSEPR theory.

This conflicts with common textbook concepts employed to describe aromaticity since one of the two sulfur lone pairs is believed to be delocalized in the case of sulfur-containing heteroaromatic rings, which would lead to trigonal-planar symmetry.

There is no direct method to measure the amount of aromaticity and no unambiguous aromaticity descriptors are applicable to results from multipole refinements.

We are combining results from approved methods derived from Bader's Quantum Theory of Atoms in Molecules [3] with new approaches including the Source Function [4] to explain the observed ambiguity. Our results lead to the conclusion that the established rules for delocalization that strictly apply to elements of the second period may not be as compelling to the heavier elements.



[1] T. Stey, J. Henn, D. Stalke, *Chem. Commun.* **2007**, 413-415. [2] J. Henn, K. Meindl, A. Oechsner, G. Schwab, T. Koritsanszky, D. Stalke *Angew. Chem.* **2010**, *122*, 2472; *Angew. Chem. Int. Ed.* **2010**, *49*, 2422. [3] R.F.W. Bader, *Atoms in Molecules - A Quantum Theory*. Oxford University Press, New York, **1990**. [4] C. Gatti, *The Source Function Descriptor as a Tool to Extract Chemical Information from Theoretical and Experimental Electron Density in Electron Density and Chemical Bonding II (Theoretical)* in *Structure and Bonding*, Volume Editors: U. Flierler, D. Stalke, Springer, Berlin, New York, **2011**, online, DOI: 10.1007/430_2010_31.

Keywords: aromaticity, catalysis, high resolution data.