

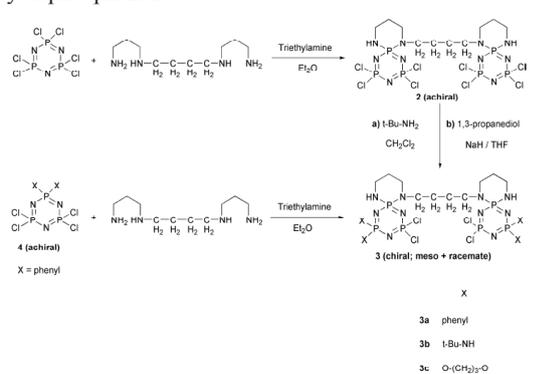
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X-Ray Crystal Structures of Chiral Spermine-Bridged Cyclophosphazenes. Yunus Zorlu^a, Gönül Yenilmez Çiftçi^a, Simon J. Coles^b, Michael B. Hursthouse^b, David B. Davies^c, Robert A. Shaw^c, Adem Kılıç^a. ^aDepartment of Chemistry, Gebze Institute of Technology, 41400 Gebze-Kocaeli, Turkey. ^bSchool of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, United Kingdom. ^cSchool of Biological and Chemical Sciences, Birkbeck College (University of London), Malet Street, London WC1E 7HX, United Kingdom.

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Tetra-coordinated phosphorus atoms in cyclophosphazenes are pentavalent and potential stereocentres. Although the possibility of optical isomerism in cyclophosphazene derivatives, [(NPXY)_n n = 3,4] was first discussed many years ago [1], chiral properties of molecules have recently been elucidated [2–5]. The spermine-bridged cyclophosphazene compound **2** has been prepared previously [6] by reaction of cyclotriphosphazene with the tetrafunctional amine, spermine. Compound **2** is achiral because the substitution pattern of each cyclophosphazene ring is the same and each cyclophosphazene ring has a plane of symmetry. However, singly-bridged analogues with gem disubstituted cyclophosphazene rings (e.g., **3**) exhibit stereoisomerism [3], because the three phosphorus atoms of each cyclophosphazene ring have different substitution patterns and those that are part of the bridge, >P(N-spiro), are stereogenic, i.e., there are R and S forms.

X-ray crystallographic studies have provided definite proof of stereogenic properties of chiral spermine-bridged cyclophosphazenes.



[1] R.A. Shaw, B.W. Fitzsimmons, B.C. Smith, *Chem. Rev.* **62**, 1962, 247. [2] D.B. Davies, T.A. Clayton, R.J. Eaton, R.A. Shaw, A. Egan, M.B. Hursthouse, G. Sykara, I. Porwolick-Czomperlik, M. Siwy, K. Brandt, *J. Am. Chem. Soc.* **122**, 2000, 12447. [3] S.J. Coles, D.B. Davies, R.J. Eaton, M.B. Hursthouse, A. Kılıç, T.A. Mayer, R.A. Shaw, G. Yenilmez, *J. Chem. Soc. Dalton*, **2001**, 365. [4] S. Bešli, S.J. Coles, D.B. Davies, R.J. Eaton, M.B. Hursthouse, A. Kılıç, R.A. Shaw, G. Yenilmez Çiftçi, S. Yesilot, *J. Am. Chem. Soc.* **125**, 2003, 4943. [5] S.J. Coles, D.B. Davies, R.J. Eaton, A. Kılıç, M.B. Hursthouse, R.A. Shaw, G. Yenilmez Çiftçi, *Polyhedron* **25**, 2005, 953-962. [6] (a) J.-F. Labarre, G. Guersch, F. Sournies, R. Lahana, R. Enjalbert, J. Galy, *J. Mol. Struct.* **116**, 1984, 75.

Keywords: cyclophosphazene; stereogenicity; single crystal X-ray crystallography

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Synthesis, X-ray Molecular Structure, and Computational Study of (E)-2-[tris(hydroxymethyl)methyl]aminomethylen-4-methylphenol. Gonca Özdemir Tarı^a, Şamil Işık^a, Hasan Tanak^a, Ferda Erşahin^b, Erbil Ağar^c. ^aDepartment of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, Kurupelit, 55139 Samsun, Turkey. ^bGerze Sinop Vocational School, Sinop University, Sinop, Turkey. ^cDepartment of Chemistry, Faculty of Arts and Sciences, Ondokuz Mayıs University, Kurupelit, 55139 Samsun, Turkey.

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Schiff bases can be classified by their photochromic and thermochromic properties [1]. Photo- and thermochromism arise via H-atom transfer from the hydroxy O atom to the N atom. There are two possible types of intramolecular hydrogen bonds in Schiff bases, viz. the keto-amine (N-H...O) and enol-imine (N...H-O) tautomeric forms. The present x-ray investigation shows that the title compound, prefers the enol-imine tautomeric form rather than the keto-amine tautomerism.

The crystal and molecular structure of the title compound, C₁₂H₁₇NO₄, has been synthesized and characterized by elemental analysis and x-ray single crystal determination. The compound crystallizes in the triclinic, space group P-1 with unit cell dimensions a=6.7501(6), b=8.5036(8), c=11.1290(11), M_r=239.27, V=611.91(10), Z=2, and wR₂=0.1372. The title compound C₁₂H₁₇NO₄ adopts the enol-imine tautomeric form. The structure is stabilized by intramolecular O-H...N and intermolecular O-H...O hydrogen bonds.

Geometric optimization based on x-ray diffraction technique and semi-empirical quantum mechanical calculations were performed. The calculated geometric parameters were compared to the corresponding x-ray determination results of the compound. The x-ray crystallographic data have been compared with AM1, PM3 and DFT molecular orbital methods. To inform minimum energy conformation of the title compound, selected torsion angle are varied from -180 to +180 in every 10° and then molecular energy profile is calculated by AM1 and PM3 semi-empirical method.

[1] Cohen, M. D., Schmidt, G.M.J. & Flavian, S., 1964. *J. Chem. Soc.*

Keywords: schiff base; X-ray diffraction; computational techniques

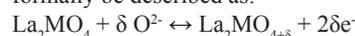
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Understanding the Oxygen Diffusion Process in Ruddlesden-Popper Phases at Room Temperature: The Special Case of La₂CoO_{4+δ}. L. Le Dréau^a, W. Paulus^a, J. Schefer^b, K. Conder^c. ^aUniversité Rennes I, Sciences Chimiques de Rennes UMR 6226, Campus Beaulieu bat 10B 35042 Rennes, France. ^bETH Zürich & Paul Scherrer Institute, Laboratory for Neutron Scattering, 5232 Villigen PSI, Switzerland. ^cPaul

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The understanding of chemical reactivity of solids at low temperatures in terms of structural modifications and disorder occurring during the reaction process is still a relatively unknown and poorly understood field. Due to the strong applied character of this discipline this is a rather surprising fact, as this knowledge is necessary e.g. for the tailoring of new high-current and non-toxic battery systems; In this context we are interested to better understand the reaction mechanism of oxygen intercalation into solid oxides, i.e. oxides with K_2NiF_4 -type structure such as $La_2MO_{4+\delta}$ showing very high oxygen diffusion rates already present at low temperature which are therefore promising candidates for being used e.g. as oxygen membrane in solid oxide fuel cells. The reaction which can be performed in an aqueous alkaline electrolyte at ambient temperature can formally be described as:



Among this family of compounds La_2CoO_4 plays - due to the relatively high stability of Co^{3+} - a key role in terms of chemical reactivity as it shows with $\delta = 0.25$ the highest oxygen intercalation rate compared to Cu or Ni with a δ_{max} of 0.07 and 0.18 respectively. For stoichiometric $La_2CoO_{4.00}$ the same octahedral LTO (Low Temperature Orthorhombic) tilting arrangement as the one present for the isostructural La_2CuO_4 compound is observed at 293 K (space group Bmab), but small quantities of intercalated oxygen are sufficient to induce local lattice distortions as the extra oxygen atoms are located on interstitial sites [2]. Applying electrochemical oxidation we were, however, able to intercalate relatively high extra oxygen contents up to $\delta = 0.25$, which for $La_2CoO_{4.19}$ results in a 2D incommensurately modulated structure due to the ordering of the extra oxygen atoms, which at a stoichiometry of $La_2CoO_{4.25}$ shows a lock-in transition to a 2D commensurately modulated structure ($4a \times 4a \times c$ unit cell) which is directly related to the ordered distribution of the extra oxygen atoms. These two ordered phases show weak but sharp satellite or superstructure reflections up to high $\sin\theta/\lambda$ values which are completely unexpected as the reaction performs at 293 K i.e. far away from thermal equilibrium where complete relaxation of lattice hindered (see Fig 1).

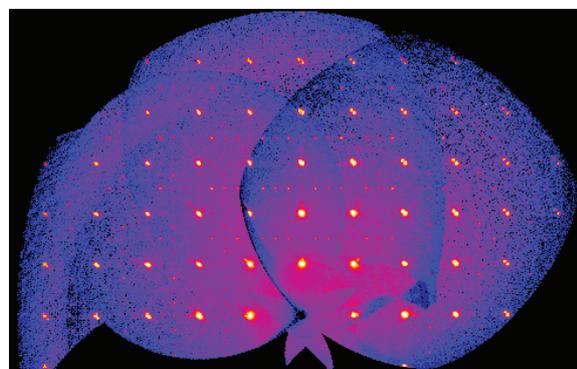


Fig. 1 Section of the (hk1) diffraction plane obtained on an electrochemically oxidized single-crystal by laboratory X-ray

diffraction with the use of a CCD detector. The sharp superstructure reflections of the twinned crystal correspond to a $4a \times 4a \times c$ unit cell.

This electrochemically induced ordering of the extra oxygen atoms also strongly influences the physical properties of $La_2CoO_{4.25}$ as antiferromagnetic ordering is observed below 35K, whereas all disordered phases do not show any magnetic ordering.

$La_2CoO_{4.25}$ contains equivalent amount of Co^{2+} and Co^{3+} (the latter is non-magnetic in the low spin state) and the interstitial oxygen stoichiometry correspond to one extra oxygen atom per unit cell. This gives a complex scenario between charge separation, magnetic ordering and long range ordering of interstitial oxygen atoms which crucial for the interpretation of the chemical reactivity and the physical properties of these compounds.

[1] W. Paulus *et al.* *Solid State Sciences* 4, **2001**, 565. [2] R. Le Toquin, W. Paulus^a, A. Cousson, G. Dhalenne, A. Revcolevschi, *Physica B* 350, **2004**, 269. [3] J.M. Tranquada, *J. Phys. Chem. Solids* 59, **1998**, 2150 ; *Nature*, 375, **1995**, 561.

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Synthesis, Spectroscopic and Structural Characterization Of Bis(Benzimidazole- κN^3) Bis(2-Benzoylbenzoato- κO)Copper(II).

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A novel Cu^{II} complex of the 2-benzoylbenzoato ligand (2-byba) with benzimidazole (bim) was synthesized and characterized by elemental analysis, FT-IR spectroscopy, and X-ray diffraction. In the complex, the Cu^{II} ion lying on a centre of symmetry, is in a square-planar coordination geometry formed by two symmetry related 2-byba and two symmetry related bim ligands (Fig. 1). Both ligands are monodentate with 2-byba coordinates carboxylate O atom and bim coordinates through the aromatic N atom. The molecular packing is mainly stabilized by strong intermolecular $N-H\cdots O$ hydrogen bonds. The FT-IR spectra of the complex is also discussed.

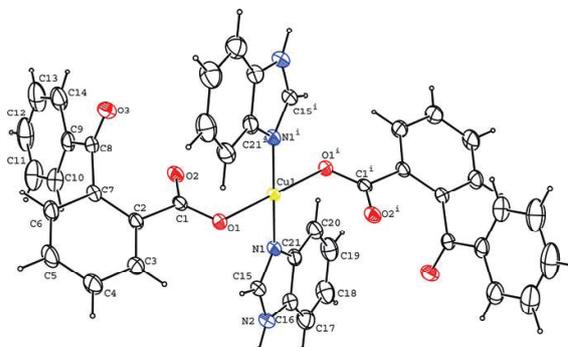


Fig. 1. The molecular structure of the complex.