X-Ray Crystal Structures of Chiral Spermine-Bridged Cyclophosphazenes. Yunus Zorlu1, Günel Yenilmez Çiftçi2, Simon J. Coles3, Michael B. Hurthouse4, David B. Davies5, Robert A. Shaw6, Adem Kilic7. 1Department of Chemistry, Gebze Institute of Technology, 41400 Gebze-Kocaeli, Turkey. 2School of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, United Kingdom. 3School 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, \([\text{NPXY}]_n \text{n} = 3,4\) 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, \(>\text{P(N-spiro)}\), 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.


Keywords: cyclophosphazene; stereogenicity; single crystal X-ray crystallography
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 \( \text{K}_2\text{NiF}_4 \)-type structure such as \( \text{La}_2\text{MO}_4 \) 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:

\[
\text{La}_2\text{MO}_4 + \delta \text{O}_2^- \leftrightarrow \text{La}_2\text{MO}_{4+\delta} + 2\delta e^-
\]

Among this family of compounds \( \text{La}_2\text{CoO}_4 \) plays - due to the relatively high stability of \( \text{Co}^{2+} \) - a key role in terms of chemical reactivity as it shows with \( \delta \approx 0.25 \) the highest oxygen intercalation rate compared to \( \text{Cu} \) or \( \text{Ni} \) with a \( \delta_{\text{max}} \) of 0.07 and 0.18 respectively. For stoichiometric \( \text{La}_2\text{CoO}_{4+\delta} \) the same octahedral LTO (Low Temperature Orthorhombic) tilting arrangement as the one present for the isostructural \( \text{La}_2\text{CuO}_4 \) compound is observed at 293 K (space group \( \text{Bmab} \)), 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 \( \text{La}_2\text{CoO}_{4+\delta} \) results in a 2D incommensurately modulated structure due to the ordering of the extra oxygen atoms, which at a stoichiometric of \( \text{La}_2\text{CoO}_{4+\delta} \) shows a lock-in transition to a 2D commensurately modulated structure (4\( \times \)4\( \times \)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).

This electrochemically induced ordering of the extra oxygen atoms also strongly influences the physical properties of \( \text{La}_2\text{CoO}_{4+\delta} \) as antiferromagnetic ordering is observed below 35K, whereas all disordered phases do not show any magnetic ordering. \( \text{La}_2\text{CoO}_{4+\delta} \) contains equivalent amount of \( \text{Co}^{2+} \) and \( \text{Co}^{3+} \) (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.


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**Synthesis, Spectroscopic and Structural Characterization Of Bis(Benzimidazolato-κN²) Bis(2-Benzoylbenzoato-κO) Copper(II).** Zerrin Hereň, Hümeýra Paşaoglu, M. Hakki Yıldırım. *Ondokuz Mayıs University Faculty of Arts and Sciences Department of Chemistry, Samsun, Turkey.*

A novel \( \text{Cu}^{2+} \) 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 \( \text{Cu}^{2+} \) 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 monodendate 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⋯O hydrogen bonds. The FT-IR spectra of the complex is also discussed.

**Fig. 1.** The molecular structure of the complex.