PhD Seminar II

Daya V P (CY10D028) Date: 31-03-2021

Venue: via Zoom Time: 3:30 pm

Impact of carboxylate alkyl chain length and anions on the structure, spectroscopy and O_2 reactivity of cobalt(II) complexes

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The active-site centers of metalloenzymes containing polynuclear transition metal-ions (Fe, Mn, Ni, Cu) are known to activate small molecules (O_2, H_2O, N_2, N_2O, etc), stabilize high-valent metal-oxygen intermediates and cause oxidation catalysis. This has intrigued bioinorganic chemists to mimic and design industrially useful catalysts.[1] The diiron and tetramanganese active-sites, bridged by carboxylate and supported by histidine ligands, have caught recent attention.[2] Synthetic modelling studies using a combination of tripodal pyridylalkylamine and carboxylate or carboxylate-appended N-ligands, have served as excellent platforms to reproduce some of the active-site features of Fe and Mn centers. The analogous studies with cobalt or other metals are scarce and often produced 1D-polymers.[3] Besides, a systematic study of carboxylate-appended N-ligands with variable alkyl chain length of carboxylate arm and the influence of anions of cobalt(II)-salts, on the structure, spectroscopy and O_2 reactivity is sporadic.[4]

Here, we have synthesized a series of carboxylate-appended bispicolylamine ligands having methylene (L^1), ethylene (L^2) and propylene (L^3) alkyl linkers between the carboxylate and tertiary amine-nitrogen and studied the influence of alkyl chain length and anions (Cl^-, N_3^-, ClO_4^-, BPh_4^-, $BArF_{24}^-$) of different cobalt(II)-salts on the structural diversity, spectroscopy and O_2/H_2O_2 reactivity of Co(II) complexes. The alkyl chain length and anions controlled the metal topology and nuclearity from mono-, di- tri- and tetranuclear structures, as established by X-ray structure and a combination of spectroscopic techniques. O_2 reactivity provided metal- and ligand-based oxidation products, different from a related study.[5] In this presentation, results of these investigations, highlighting the impact of alkyl tether length, anions and solvent, on the structure, nuclearity (Co_n, n = 1-4), spectroscopy (FT-IR, UV-vis, ^{1}H-NMR, ESI-MS) and magnetism of Co(II) complexes, and reactivity studies, will be presented.

1. Jasniewski, A. J.; Que, L., Jr., Chem. Rev. **2018**, 2554.
2. Christou, G., Acc. Chem. Res. **1989**, 328.
3. Lucas, N. T. *et al*., CrystEngComm, **2015**, 2974.
4. McKenzie *et al*., Dalton Trans., **2011**, 10698.
5. Anjana,S.S.; Varghese, B.; Murthy, N.N., Dalton Trans., **2020**, 3187.

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