

MS29-P10 Halogen-halogen, halogen-oxygen, and dipolar interactions in a series of $\text{Re(I)}(\text{CO})_3$ complexes with halogen-substituted nitrogen-donor ligands

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Intermolecular interactions are of significant interest in chemistry, mainly because they are responsible for stabilization of many important molecules such as DNA and proteins [1]. They have also important roles in the arrangement of molecular species in crystal packing. Therefore, they are one of the main foci in the field of crystal engineering because of their structural role on the physical properties of crystalline materials such as nonlinear optics, electrical, and magnetic properties [2]. In this study, the effect of different intermolecular interactions such as halogen-halogen, halogen-oxygen, and π - π interactions has been investigated on the crystal packing of $\text{Re}(\text{CO})_3$ complexes with halogen-substituted nitrogen-donor ligands.

References

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Keywords: Intermolecular interactions, Halogen interactions, Re(I) complexes

MS29-P11 Insights into solution and solid-state coordinative properties of tantalum(V) and niobium(V) metal centres.

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Tantalum(V) and niobium(V) are two transition metals found in the vanadium triad in the periodic table, with very similar chemical properties, and always occur together in nature. Both elements have hard metal centres and the halido species are known to readily hydrolyse to form relatively unreactive oxido species, which severely inhibit bidentate ligand coordination to these metal centres.[1] Accordingly, in-depth investigations of the coordinative preferences of these elements remain elusive.

In this present investigation of tantalum(V) and niobium(V) complexes, a range of functionalized mono-charged bidentate ligands (L,L' -*Bid*) has been used in synthesis, in an attempt to study the variation in activity and selectivity of coordination of L,L' -*Bid* to the metal halides in both solid- and solution state. [L,L' -*Bid*H = functionalized acetylaceton- (acacH), 8-hydroxyquinoline- (oxH) and tropolone (tropH) derivatives].

Two new stable (relatively hydrolysis resistant) synthons $(\text{Et}_3\text{N})[\text{NbCl}_6]$ (see Figure 1 a) and $(\text{Et}_3\text{N})[\text{TaCl}_6]$ have been instrumental in the success of β -diketone and tropolone ligand coordination to tantalum and niobium metal centres.[2] Crystal structures have been obtained for numerous complexes, with examples including: $[\text{Nb}(\text{trop})_2\text{Cl}]$, $[\text{Ta}(\text{trop})_2\text{Cl}]$, $(\text{Et}_3\text{N})[\text{NbOCl}_2(\text{tfa})]$ (see Figure 1 b), $(\text{Et}_3\text{N})[\text{NbOCl}_2(\text{hfaa})]$ and $(\text{Et}_3\text{N})[\text{NbOCl}_2(\text{bfa})]$, where tropH = tropolone, tfaH = thenoyltrifluoroacetone, hfaaH = hexafluoroacetylacetonone, bfaH = benzoyltrifluoroacetone and tffaH = trifluorofurylacetonone. Differences in coordination modes and crystal packing of these isostructural complexes have been identified in an attempt to gain insight into these compounds to assist in predictions of properties for future use.

Additionally, to further evaluate the electronic environment experienced by the niobium(V) and tantalum(V) centres in these complexes, a solution-state kinetic study of the substitution reactions of $[\text{NbCl}_6]^-$ and $[\text{TaCl}_6]^-$ with a range of β -diketones as entering ligands was undertaken. These results will also be reported and correlated to entering ligand electronic characteristics.

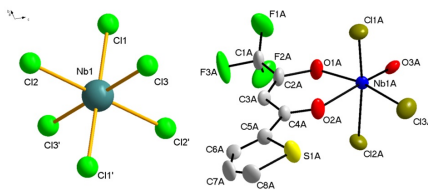


Figure 1. (a) Ball-and-stick representation of $(\text{Et}_3\text{N})[\text{NbCl}_6]$ (tetraethylammonium counter-ion omitted) (b) Ball-and-stick

representation of (Et₄N)[NbOCl₃(tfa)] (tetraethylammonium counter-ion omitted).

Keywords: hydrolysis, bidentate, kinetics, crystallization

MS29-P12 Temperature structural studies of spin crossover 1D coordination polymer [Fe(4-amino-1,2,4-triazole)₃]SO₄

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Spin crossover (SCO) usually occurs in octahedral 3d⁴-d⁷ transition metal complexes. SCO can be induced by change of temperature, application of pressure or by light irradiation and is accompanied by change of magnetic, optical and dielectric properties. What is important, transition from high spin (HS, t_{2g}⁴e_g², S=2) to low spin (LS, t_{2g}⁶e_g⁰, S=0) form in iron(II) complexes is accompanied by shortening of Fe-ligand distance at about 0.2 Å. Although SCO phenomenon is of molecular nature, a perturbation produced by shrinkage of complex molecule (as a result of Fe-ligand bond shortening) spreads on the whole crystal lattice through intermolecular interactions. Therefore it was postulated that an incorporation of direct linkage between metal ions should enhanced transmission of perturbation. Thus it should lead to the more cooperative spin transitions. Indeed, in the coordination polymers in which iron(II) ions are bridged by small and rigid ligands, SCO very often proceeds in narrow temperature range. In particular iron(II) complexes based on 1H,2,4-triazole or 4-amino-1,2,4-triazole (NH₄trz) exhibit very abrupt spin transitions accompanied by hysteresis loops [1]. Unfortunately, synthesis of these type of complexes does not lead to the formation of crystalline samples suitable for single crystal X-Ray diffraction studies. Initially, postulated structure of one dimensional (1D) polymeric chains in which metal ions are bridged by three 1,2,4-triazole rings was supported by elucidation of crystal structure of copper(II) complexes [2].

The subject of performed studies are spin crossover 1D coordination polymers [Fe_{1-x}Zn_x(4-amino-1,2,4-triazole)₃]SO₄ (for x=0.0, 0.09, 0.20, 0.40, 0.60, 1.00) that represent an examples of NH₄trz based SCO systems containing divalent anion [3]. The complex exhibits complete one step, abrupt spin crossover slightly above room temperature and is accompanied by the hysteresis loop. Based on the synchrotron powder diffraction measurements we have determined the crystal structure of the studied compounds.

Literature

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Keywords: Spin crossover, synchrotron powder diffraction study, Fe(II) compounds