Hydrothermal crystal engineering using hard and soft acids and bases: synthesis and X-ray crystal structures of the metal hydroxide-based phases $M_3M'_2(OH)_2[NC_5H_3(CO_2)_2\text{-}2,4]_4(H_2O)_4$ (M = Co, Ni, Zn; M' = Pd, Pt)†

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Solvothermal reaction of $K_2M'Cl_4$ (M' = Pd, Pt) with pyridine dicarboxylate and excess base produces isostructural coordination solids in which 'complex ligands' containing palladium or platinum coordinate to metal hydroxide chains.

The use of solvothermal techniques to prepare hybrid organic–inorganic materials inaccessible by other means is a rapidly expanding area.[1,2] One current challenge is to prepare materials of increasing compositional complexity in which the individual components confer different physical properties or have different structural influences. This goal is exemplified by hydrolytic phases containing oxide or hydroxide moieties in addition to metal ions and ligands.[2] We are particularly interested in this area as judicious choice of ligands can lead to important target materials such as porous solids and low-dimensional magnets. The size of the organic ligand plays an important role in our approach to both of these classes of material as it controls both the size of the pores and the separation between low-dimensional magnetic structures. A logical choice of ligand type to fulfil the role of large 'spacer' would be polycyclic aromatic carboxylates such as 4,4'-biphenyl dicarboxylic acid or 3,4,9,10-perylene tetracarboxylic acid, however, these have proved unsuccessful in our hands,[3] possibly owing to their solubility characteristics. Subsequently we have investigated a strategy based on 'metal complex ligands' which we report here.

A multi-component ligand equivalent in size to those suggested above can be constructed by relying on the principle that hard and soft bases will coordinate to like acids.[4] By coordinating ligands with both hard and soft donor sites to a soft metal we can generate a large but soluble anionic ligand which is terminated by hard (carboxylate) donor groups and as such is analogous to the ligands we have already found to be successful in simpler reactions. Pyridine-2,x-dicarboxylates are known to be stable to solvothermal conditions[2] and also to form stable complexes with soft metals *via* N-coordination.[5] The existence of three isomers also presents the opportunity to study the effect of substitution pattern on product structure. This is actually a very important variable with the 2,4 isomer yielding much more straightforward chemistry hence it is this ligand on which we concentrate here.

The method we have previously developed for preparing hydrolytic phases of the 3d transition metals involves the reaction of a carboxylate salt with $M(OH)_2$ prepared *in situ*, a variation of this technique is used here. Three aqueous solutions are first prepared containing (i) K_2PtCl_4 (0.1 mmol) in H_2O (2.5 ml); (ii) pyridine-2,4-dicarboxylic acid (0.2 mmol) and 1 M KOH (0.7 mmol) in H_2O (5 ml); (iii) MCl_2 hydrate (0.2 mmol) in H_2O (2.5 ml). Solutions (i) and (ii) are first mixed, followed by (iii) which results in formation of $M(OH)_2$. Hydroxide formation is evident for cobalt-containing solutions from the

slight blue colour produced which we have previously observed to be indicative of the onset of Co(II) hydrolysis.[3] This gives a Pt:metal:ligand:base ratio of 1:2:2:7. The mixture was placed in a 23 cm^3 Teflon-lined autoclave and heated at 200 °C for 15 h, followed by slow cooling to room temperature over a period of 8 h. The solid was filtered off and purified by brief ultrasonic treatment of an aqueous slurry followed by decanting. The material was then filtered off, washed with water and air dried. The palladium-containing materials are made in analogous fashion from K_2PdCl_4 on a 0.12 mmol scale with a Pd:metal:ligand:base ratio of 1:2:2:6.

These methods produce $M_3M'_2(OH)_2[NC_5H_3(CO_2)_2\text{-}2,4]_4(H_2O)_4$ as crystalline solids in good yields; **1a**, Co/Pd, pale pink (62 mg, 89%); **1b**, Co/Pt, orange–pink (52 mg, 78%); **2a**, Ni/Pd, pale green (52 mg, 75%); **2b**, Ni/Pt, green (44 mg, 66%); **3a**, Zn/Pd, yellow (57 mg, 82%); **3b**, Zn/Pt, yellow (49 mg, 72%). Satisfactory microanalytical data were obtained for all compounds (ESI†).

IR spectra for the six compounds are essentially super-imposable showing only the slight shifts in frequency expected on isomorphous substitution (ESI†). The band which is indicative of the formation of these materials is the sharp, medium intensity O–H stretch due to the bridging hydroxide ligand: ν_{max}(KBr) = 3598, 3604, 3606, cm^{-1} for Co, Ni and Zn, respectively. The position of the band is insensitive to the presence of Pd or Pt.

The X-ray crystal structures‡ of a representative sample of the compounds (**1a** and **3a**) along with the unit cell dimensions for **1b**, **2a**, **2b** and **3b**, were determined showing that the materials are indeed isostructural (ESI†). The secondary building unit (SBU) is the $M'M_2L_2$ fragment (Fig. 1) which has two environments for the hard (octahedral) metal. The SBUs are held together by two different types of linkage, the overall effect of which is to produce layers lying parallel to [0 1 −1]. The first type of linkage consists of infinite chains with a –MLM'LMLM'– repeat unit running parallel to the *bc* bisector. The second type is a series of metal hydroxide strips containing chains of edge- and vertex-sharing $M_3(\mu_3\text{-OH})$ triangles which run parallel to the *a* axis (Fig. 2). Each individual layer has metal hydroxide 'ribs' which are linked to their nearest neighbours by a row of LM'L moieties. The ligands form the upper and lower faces of the layer (Fig. 3) with an average intra-
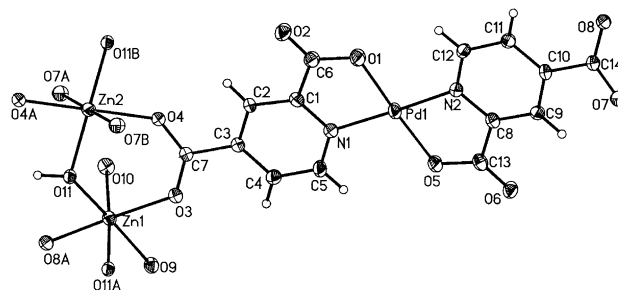

Fig. 1 The basic building block of the title complexes (illustrated here for **3a**) showing the atom numbering scheme. Ellipsoids are drawn at the 30% probability level.
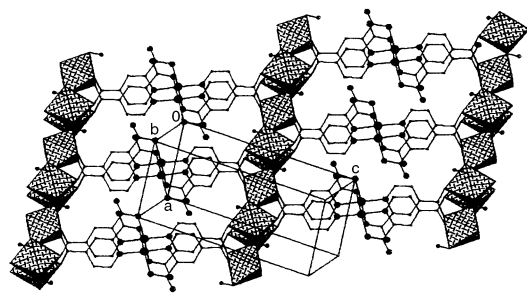
Fig. 2 View showing the chains of vertex sharing metal octahedra (running down the crystallographic *a* axis) and their linkage *via* the LML moiety.
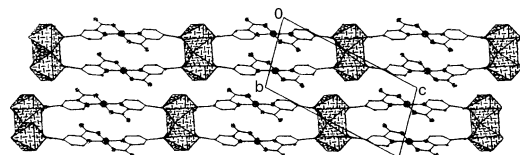

Fig. 3 View down the crystallographic *a* axis showing the packing of layers.

layer distance of 3.42(1) Å. There is a second π-stacking interaction between the sheets with an average separation of 3.56(1) Å. The π stacks and metal hydroxide strips run along orthogonal axes, this leads to the formation of a tightly packed three-dimensional structure. We believe that the stacking interaction hampers the formation of pores within these materials. It is also noteworthy that when porous materials have been prepared[3] the ligands bridge in the plane of the metal triangles, rather than above and below as seen here. All bond lengths and angles are normal with the metal–ligand distances showing small deviations from ideal square and octahedral geometry (ESI†). For example the palladium square planar angles range from 82.5(2) to 100.1(2)°. The two octahedral zinc geometries show a greater distortion for the metal that is not on an inversion centre, Zn(1). The angles range from 82.2(2) to 96.9(2)° and 172.1(2) to 176.8(2)° for Zn(1) in comparison with 86.6(1) to 93.2(1)° and exactly 180° for Zn(2). The formation of the particularly stable five-membered chelate ring for the soft metal helps to stabilise it against decomposition to intractable material, which we believe to be oxide, at the relatively high pH required for hydrolysis of the divalent 3d metal ions.

This material can be synthesised using a range of metal : metal′ : ligand : base ratios provided that the pH is kept relatively high. The optimum reaction conditions found for the platinum compounds require a ratio of 1 : 2 : 2 : 7 resulting in a pH in the range 7.7–8.8 depending on the metal. The palladium compounds can be obtained in pure form from a ratio of 1 : 2 : 2 : 6 which gives pH values in the range 6.7–7.8. In general the production of the platinum compounds requires more base than is needed for the palladium-containing materials. Hydrolysis of the metal salts occurs prior to heating and therefore the pH values measured for the reaction mixtures are lower than expected considering the excess base used. Accurate control of hydroxide content is essential as there is a very narrow range in which these materials may be formed. There is little overlap between the conditions required for the formation of M(OH)-containing materials and those required for stabilisation of the soft metal complex.

The reactions are also sensitive to temperature and duration. To obtain an optimum yield of pure product the reactions should be performed at temperatures in the range 180–220 °C for 15 h. Lower temperatures result in contamination by other products whilst higher temperatures result in decomposition. We have also investigated the chemistry of isomeric ligands under similar conditions. Reactions with pyridine-2,3-dicarboxylate yield only decomposition products whilst pyridine-2,5-dicarboxylate gives a range of highly complex products with structures sensitive to both the hard and soft metal.

We have shown that hard and soft donor sites on a metal can preferentially bind hard and soft metal ions from a binary mixture. This provides another tool in our armoury for engineering materials with specific properties such as magnetism and porosity.

Notes and references

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