Dipyridyl beta-diketonate complexes: versatile polydentate metalloligands for metal-organic frameworks and hydrogen-bonded networks

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Abstract
The Group 13 metal complexes [M(L-2)(3)], where M is Al or Ga and L-2 is 1,3-di(4-pyridyl)-1,3-propanedionato, are hexatopic metalloligands that have been used to prepare mixed-metalorganic frameworks containing interpenetrated primitive cubic networks. In contrast, the europium complex [Eu(HL2)(3)-(H2L2)]Cl-4 center dot EtOH forms a hydrogen-bonded network following partial protonation of the pyridyl groups.

Keywords
complexes, diketonate, dipyridyl, hydrogen, frameworks, networks, organic, bonded, metal, metalloligands, polydentate, versatile, beta, CMMB

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The Group 13 metal complexes [M(L2)3], where M is Al or Ga and L 2 is 1,3-di(4-pyridyl)-1,3-propanedionato, are hexatopic metalloligands that have been used to prepare mixed-metal–organic frameworks containing interpenetrated primitive cubic networks. In contrast, the europium complex [Eu(HL2)3]Cl4-(H2L2)Cl4·EtOH forms a hydrogen-bonded network following partial protonation of the pyridyl groups.

Metal–organic frameworks (MOFs) have attracted considerable attention recently, largely as a consequence of their porosity and subsequent use as materials for applications such as gas storage, separations and catalysis.1 Mixed–metal–organic frameworks (MMOFs) are an interesting sub-class of these materials, and given that two types of metal ions may have different structural and/or functional roles within a network structure, these are likely to attract increasing attention. While it is possible to prepare MMOFs in a one-pot reaction, it is often difficult to control the nature of the products in this way. This has led to the development of a stepwise synthetic approach to these materials. Thus, a metal centre is reacted with a bifunctional ligand to give an isolable intermediate complex, which itself can act as a building block in network formation.2 The reaction of this metalloligand with a second metal centre can then be used to form the desired MMOF.

A number of metalloligands have been used in this way, including complexes of pyridinedicarboxylates,3 Schiff bases4 and bis(oxamato) ligands,5 that function as ditopic O-donors, and pyridyl-functionalised porphyrins,6 dipyrinimato ligands,7 terpyridines8 and tris(triazolyl)borates9 that function as polytopic N-donors.

Bifunctional ligands based on acetylacetanotes are attractive for use in construction of mixed-metal networks. The chelating nature of the bidentate O,O-donor ensures relatively low lability, and the negative charge on the ligand allows access to neutral complexes. We have recently reported MMOFs based on 3-cyanoacetylacetonate,10 whereas the Domasevitch11,12 and Maverick13 groups have prepared MMOFs based on 3-(4-pyridyl)acetylacetonate (L1).

A limitation of functionalising at the central carbon of a β-diketonate is the inherent restriction on the number of exotopic donor groups per ligand. Thus, an octahedral complex of the general formula [M(L1)3] functions as a tritopic ligand. In addition, there is an issue with the stability of HL1, since it decomposes via a reverse-Claisen condensation.14 We reasoned that by functionalising with 4-pyridyl groups at both ends of the β-diketonate, we could remove the stability limitation, whilst at the same time increasing the number of exotopic donor sites. This would be expected to lead to an increase in the connectivity of the resultant MMOFs. 1,3-Di(4-pyridyl)propane-1,3-dione (HL2) seemed an ideal candidate for this, with octahedral complexes of the form [M(L2)3] expected to contain six remote N-donor sites, approximately orientated at the vertices of an octahedron. HL2 has previously been used to prepare pyrazoles,15 and shown to exist in solution predominantly as the enol tautomer.16 Gadolinium and holmium complexes have also been reported very recently.17

The reaction of hydrated aluminium or gallium nitrate with HL2 and NaOH in aqueous solution gave the complexes [M(L2)3] (I, M = Al; 2, M = Ga) in high yield. Following crystallisation from dichloromethane–toluene, crystals of 1 suitable for X-ray single-crystal analysis were obtained. The crystal structure determination† revealed that the crystals were the toluene solvate I·1.25C6H5Me, with the asymmetric unit consisting of one molecule of I, one full molecule of toluene, and half of a toluene fragment at 50% occupancy, proximate to the crystallographic inversion centre.

The molecular structure of I is shown in Fig. 1. As expected, the complex has distorted octahedral geometry around the

Fig. 1 The molecular structure of [Al(L2)3] 1, from the crystal structure of I·1.25C6H5Me.
aluminium centre, with ligand bite angles ranging from 88.84(6°) to 91.27(6°). The $\text{AlO}_2\text{C}_3$ chelate rings are non-planar, with the aluminium atom sitting out of the plane defined by the ligand atoms in the ring. This distortion can be quantified by the angle between the $\text{AlO}_2$ plane and the $\text{O}_2\text{C}_3$ plane defined by the ligand atoms in the chelate ring. These inter-plane ‘fold angles’ are 18°, 16° and 26° for the three ligands.

Together with the constraints imposed by the bidentate nature of $\text{L}^2$, this folding has a significant impact on the relative orientations of the pyridyl groups. For an ideal octahedral hexatopic metalloligand, the lone pairs on the pyridyl groups would be orientated at 90° and 180° from each other. For $[\text{Al(L}^2\text{)}_3]$, the angles between nitrogen lone pair vectors within the same ligand lie in the range 117° to 122°. The angles between lone pair vectors involving two different ligands range from 69° to 113° for the cis positions of the octahedron, and between 155° and 175° for the trans positions. The distortions from a regular octahedron can further be quantified by the N···N distances, which range from 7.43 to 11.40 Å for the cis positions of the octahedron and from 13.39 to 13.59 Å for the trans positions.

Studies on complexes of 3-(4-pyridyl)acetylacetionate ($\text{L}^1$) have also revealed distortions, which affect the angles between the three exotopic donor groups, and introduce variation from the ‘regular’ angle of 120°. Distortions present in the metalloligands have been shown to be reproduced in MIMOFs derived from them, and the angles between the lone pairs of the pyridyl groups have been used to control the network topology.12

Given the distortions from a regular octahedral arrangement of the pyridyl groups in $[\text{Al(L}^2\text{)}_3]$, we reasoned that linking these metalloligands together to produce a regular cubic network would require use of a metal centre with inherent coordinative flexibility. Silver(i) is well known to exhibit a coordinative flexibility. Silver(i) is well known to exhibit a

Given the success in preparing a network structure based on the [M($\text{L}^2$)$_3$] hexatopic metalloligand, we reasoned that it might be possible to prepare metalloligands with even higher numbers of donor atoms. Accordingly, EuCl$_3$ was reacted with $\text{HL}^2$ in ethanol in the presence and absence of base. The reactions yielded the same product as yellow crystals suitable for a single crystal X-ray analysis. This analysis enabled the product to be characterised as $[\text{Eu(\text{HL}^2)(\text{H}_2\text{L}^2)}]\text{Cl}_2\text{EtOH}$. In this complex, the $\beta$-diketonates remain chelating and anionic, whereas the exodentate pyridine groups of the ligands are in two states of protonation. The $\text{HL}^2$ ligand is zwitterionic, with one of the pyridyl groups protonated, whereas the $\text{H}_2\text{L}^2$ ligand is cationic, due to protonation of both pyridyl groups.

The asymmetric unit of 5 consists of one-quarter of a europium centre (located at a special position in the space group), a partially protonated $\text{L}^2$ ligand, a chloride ion and some diffuse solvent. The europium centre in 5 is 8-coordinate

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**Fig. 2** The structure of $[\text{Al(L}^2\text{Ag)}_3]_4\text{NO}_3$ 3. Part (a) shows a single primitive cubic network, and part (b) shows the triply-interpenetrated networks. Solvent molecules, nitrate ions and hydrogen atoms have been omitted for clarity.
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Notes and references


