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Ring opening reactions of pyromellitic dianhydride for the synthesis of first row transition metal dicarboxylate complexes

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Abstract

The ring opening reaction of pyromellitic dianhydride by methanol is an effective method to prepare first row transition metal dicarboxylate complexes. The reactions of different first row transition metal salts with pyromellitic dianhydride in the presence of nitrogen donating bidentate ligands such as 1,10-phenanthroline and 2,2′-bipyridine gives different compositions depending on the ligand and the metal salts used. For example, the reaction of nickel(II) acetate with pyromellitic dianhydride in the presence of 1,10-phenanthroline results in the formation of a carboxylato bridged nickel(II) metallacycle through the ring opening reaction of pyromellitic dianhydride (PAH) at the 1 and 3-positions, whereas a mononuclear tetra-aqua 2,2′-bipyridine nickel(II) complex is formed in a similar reaction of nickel(II) acetate through ring opening at the 1,4-position of PAH. Mononuclear cobalt(II) dicarboxylate complexes are formed from the ring opening reaction of pyromellitic dianhydride in methanol in the presence of the nitrogen donor ligands 1,10-phenanthroline or 2,2′-bipyridine. Copper(II) chloride on reaction with PAH and 2,2′-bipyridine gives a mononuclear complex via ring opening at the 1 and 4-positions; having chlorides inside and outside the coordination sphere. Whereas, the reaction of copper(II)acetate gives dinuclear copper complexes having a monodentate carboxylato bridge arising from the carboxylato groups at the 1 and 4-positions on the aromatic ring. The crystal structures of all the complexes have been determined.

Keywords: Ring-opening reactions; Anhydride; Metal carboxylates; Metallacycles; Coordination polymers

1. Introduction

Bonding of carboxylato groups in metallo-organic frameworks has been of great interest to material chemists as well as to synthetic chemists [1]. The complexity involved in such systems is being reviewed from time to time; yet there are big challenges in designed syntheses [2]. An understanding of the binding ability of carboxylate group/s to transition metal ions [3] is useful to delineate the type/s of bonding as well as to have control on directed syntheses. It is also a well known fact that metallacycles containing a carboxylate ligand with a metal like nickel are useful in organic synthesis; however, commonly available nickel metallacycles contain metal–carbon bonds along with the metal carboxylate bond [4]. Many of the first row transition metal complexes can have six coordination, thus to design a coordination polymer or cyclic complexes some of these sites need to be occupied by labile ligands and some by non-labile ligands. One of the ways to generate poly carboxylato anions *in situ* is by ring opening reactions of dianhydrides. Ring opening reactions of anhydrides have been well studied for the synthesis of ordinary esters [5a] as well as chiral esters [5b,5c]. The ring opening reaction of pyromellitic dianhydride by an alcohol can lead to 2,6-dicarbomethoxy benzene 1,4-dicarboxylic acid or 2,4-dicarbomethoxy benzene 1,5-dicarboxylic acid [5a]. In the present study, we have chosen pyromellitic dianhydride as a substrate for the ring opening reactions in order to establish the selectivity of the metal in the ring

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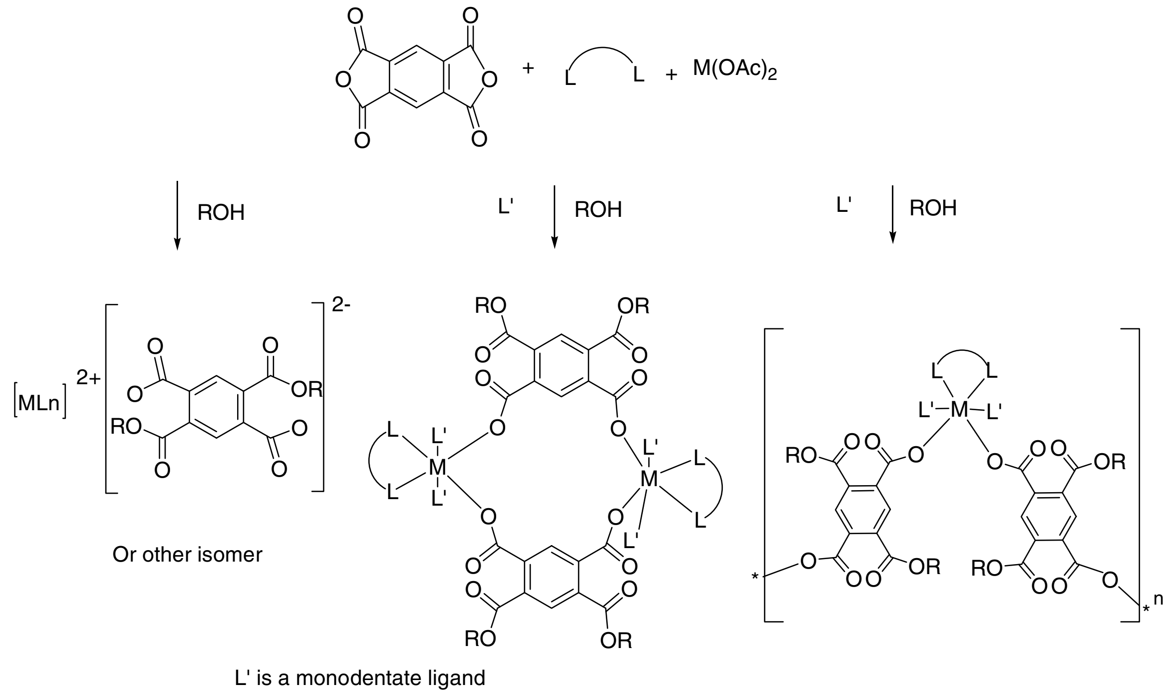

Scheme 1. Some possibilities for metal carboxylate complex formation by ring opening reactions of pyromellitic dianhydride by alcohols.

opening, as illustrated in Scheme 1 and also to use the ring opening reactions for formation of metal complexes of first row transition metals.

2. Experimental

2.1. General

The reagents used here were purchased from commercial sources (Sigma–Aldrich or Fluka) and were used as received unless otherwise stated. The X-ray diffraction data were collected at 296 K with Mo Kα radiation ($\lambda = 0.71073$ Å) using a Bruker Nonius SMART CCD diffractometer equipped with a graphite monochromator. SMART software was used for data collection and also for indexing the reflections and determining the unit cell parameters; the collected data were integrated using SAINT software. The structures were solved by direct methods and refined by full-matrix least-squares calculations using SHELXTL software. All the non-H atoms were refined in the anisotropic approximation. The crystallographic parameters of the compounds studied are given in Table 1.

2.2. Synthetic procedures for the complexes

2.2.1. Synthesis of (2,2′-bipyridyl)dibenzoato nickel(II) [A]

Benzoic acid (733 mg, 6 mmol) and potassium hydroxide (337 mg, 6 mmol) were mixed together with nickel(II) chloride hexahydrate (710 mg, 3 mmol) in a mortar. The whole content was heated at 100 °C for 30 min. The mixture was cooled and transferred to a solution of 2,2′-bipyridine (234 mg, 3 mmol) in 10 ml of methanol. The mixture was stirred for half an hour, after which time a green colored solution was obtained and filtered. The filtrate was kept undisturbed for crystallization to give crystals of **A** (isolated yield 87%). Elemental *Anal.* Calc. for $C_{24}H_{18}N_2NiO_4$: C, 63.01; H, 3.94. Found C, 63.03; H, 3.96%. IR (KBr, cm^{-1}): 3434(b), 1593(m), 1523(s), 1426(s), 1073(w), 1026(w), 857(m), 726(m), 734(m), 685(m). Visible λ_{max}, 645 nm ($\varepsilon_{ethanol} = 9.11$ M^{-1} cm^{-1}).

2.3. The ring opening reactions of pyromellitic dianhydride

The complexes with different compositions are prepared by reactions of *in situ* generated 2,5-dicarbomethoxy benzene 1,4-dicarboxylic acid or its isomer 2,4-dicarbomethoxy benzene 1,5-dicarboxylic acid (abbreviated as LH_2) with different metal salts and nitrogen containing heterocycles such 1,10-phenanthroline (phen) or 2,2′-bipyridine (bpy) as follows:

2.3.1. Synthesis of dicarboxylate complexes

$[Ni_2L_2(phen)_2(CH_3OH)_2(H_2O)_2]\cdot 2CH_3OH$ [**B**]: To a solution of pyromellitic dianhydride (218 mg, 1 mmol) in methanol (15 ml) a solution of nickel(II) acetate tetrahydrate (248 mg, 1 mmol in 5 ml methanol) was added, giving a green cloudy solution. To this solution a solution of 1,10-phenanthroline (200 mg, 1 mmol in 5 ml methanol) was added, followed by stirring at room temperature for 1 h. The solution was refluxed for 8 h and filtered, the filtrate on standing gave complex **B** (isolated yield of pure crystals 14%). Elemental *Anal.* Calc. for $C_{54}H_{60}N_4Ni_2O_{24}$: C, 51.21;