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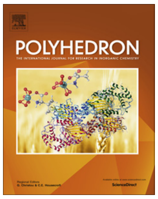

Unsymmetrical bidentate ligands as a basis for construction of ambidentate ligands for functional materials: Properties of 4,4-dimethyl-1-phenylpentane-1,3-dionate

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ABSTRACT

To establish a background to the possible use of its ambidentate derivatives as stimulus-responsive ligands in functional complexes, the basic coordination chemistry of the anion derived from 4,4-dimethyl-1-phenylpentane-1,3-dione (benzoylpivaloylmethane, **bpm**H) has been re-examined with selected main group and transition metal M(II) and M(III) species. There is evidence that the steric bulk of the 1,3-dione substituents is not sufficient to prevent oligomerisation of the Ni(II) complex and equilibrium mixtures of geometric isomers can be detected in solution for at least the Al(III), Co(III) and Pd(II) complexes. Crystal structure determinations on both [Cu(**bpm**)$_2$] and [Pd(**bpm**)$_2$] show, however, that a single isomer can be isolated in the solid state.

1. Introduction

Supramolecular chemistry is based upon the use of labile intermolecular interactions to assemble complex structures with specific functionality [1]. While the nature and energy of these labile interactions are both extremely varied, a particularly useful type of interaction is that involving coordinate bonding to metal ions. A coordinate bond is not necessarily labile but this is commonly the case and one feature of the coordinate bond that greatly enhances its utility is that it can be converted from a labile to an inert state by the appropriate choice of donor atoms and/or ligand structure. This can even be done selectively within the coordination sphere of a single metal ion by the introduction of multidentate chelate or, particularly, macrocyclic ligands [2]. An aspect of multidentate ligand design which has been little explored to date in relation to the multifunctionality of complexes is the deliberate introduction of ambidentate character. In principle, this should allow the complex of an appropriate ligand to switch, under a particular stimulus [3], between forms with various functions such as different degrees of catalytic activity. Thus, we have begun a programme of research concerned with divergent multitopic ligands and the properties of their isomeric complexes.

An especially versatile and long-studied group of chelate ligands is that based on 1,3-diketones [4–14], acetylacetone (acacH) or pentane-2,4-dione being the best-known of such molecules. While the neutral species can act as O,O′-chelates towards metal ions, provided the carbon atom linking the carbonyl groups has at least one H-substituent, enabling tautomerism with an enol form, these molecules are weak acids and the coordination chemistry of their conjugate-base, delocalised diketonate anion derivatives is far more extensive and includes examples of C-donor bonding as well as O,O′ chelation [4–14]. The ease of synthesis of 1,3-diketones, not necessarily directed solely towards metal ion complexation [15], means that an exceptional range of such species is accessible and relatively recent work has provided examples of pyridyl derivatives which could indeed function as ambidentate species [16]. Particularly useful as a means of introducing extra functionality is a phenyl substituent and a variety of derivatives of benzoylpivaloylmethane (**bpm**H) are known which illustrate this approach [17–19], although the substituents known in this case, with one exception [19], do not provide metal-binding sites competitive with the diketonate unit. A phenyl group or larger aromatic unit can also be employed in the generation of poly-1,3-diketonate ligands, such species having been the basis of some

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remarkable recent extensions of diketonate coordination chemistry [20–23]. In our focus on the possibility of generating ambidentate ligands from a phenyl-substituted 1,3-diketone, we were confronted with two issues potentially complicating their application: aggregation and isomerism of the complexes. The diketone benzoylpivaloylmethane (**bpm**H) being a readily available "parent" species for ambidentate ligand construction, we sought to make specific expansions of the rather limited knowledge [17–19,24–26] of the coordination chemistry of the derived diketonate in relation to these potential complications using transition metal M(II) and M(III) species, plus Al(III) as a main group representative (Fig. 1).

2. Experimental

2.1. Reagents and instrumentation

All reagents were purchased from commercial sources (Sigma, Fluorochem, AlfaAesar). High purity solvents were purchased from POCH and anhydrous THF was dried over molecular sieves under argon. NMR spectra were measured on a Bruker Ultrashield™ 300 + 300 Fourier-Transform spectrometer using deuterated solvents ($CDCl_3$, CD_3CN). TOF-MS spectra were measured using chloroform solutions on a BRUKER Impact HD ESI-Q-TOF mass spectrometer. Solution electronic absorption and luminescence spectra were recorded in 1 cm quartz cells at ambient temperature in MeCN on Shimadzu UV-2401 PC and Hitachi F-7000 Fluorescence instruments, respectively. Luminescence spectra were also recorded on the solid complexes.

X-ray diffraction data were obtained on a 4-circle Xcalibur EosS2 diffractometer (Agilent Technologies) equipped with a CCD detector.

2.2. Synthesis

2.2.1. 4,4-dimethyl-1-phenylpentane-1,3-dione (benzoylpivaloylmethane), **bpmH**

The ligand was prepared according to a literature procedure [15], although it is also available commercially. Pinacolone (5.54 g; 0.055 mol) was added to a suspension of NaH (6.65 g; 0.166 mol) in dry THF (50 mL). After 30 min. of stirring, methyl benzoate (3.5 mL; 0.277 mol) was added to the grey-yellow suspension. The mixture was heated at 47 °C for 24 h. Reaction was quenched by the addition of water, followed by aqueous HCl to reduce the pH to ~4. The product was extracted into ethylacetate and the extract evaporated down after drying over Na_2SO_4. The crude product was purified by addition of $CuCl_2{\cdot}2H_2O$, isolation of the solid complex formed and then dissociating the ligand from this by treatment with hot aqueous H_2SO_4. Extraction into DCM, drying and evaporation of the extract yielded the desired product as a yellow oil (2.81 g; 50.0% yield). ^1H NMR (300 MHz, $CDCl_3$) δ 16.53 (s, 1H, *enol*-form -OH, H_6); 7.90, 7.89 (d, 2H, H_3); 7.54, 7.52, 7.50 (t, 1H, H_5); 7.47, 7.45, 7.43 (t, 2H, H_4), 7.26 ($CDCl_3$), 6.31 (s, 1H, *enol*-form –CH_2–, H_2), 4.19 (s, 2 H, *keto*-form –CH_2–, H_2), 1.26 (s, 9 H, *enol*-form –CH_3, H_1), 1.23 (s, 9 H, *keto*-form –CH_3, H_1) (Signals assigned according to the Fig. S8). ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.97 (C_9), 184.65 (C_8), 135.59 (C_7), 132.20 (C_6), 128.65 (C_5), 127.05 (C_4), 92.17 (C_3), 77.58, 77.16, 76.74 (Solvent, $CDCl_3$), 39.93 (C_2), 27.47 (C_1) (Signals assigned according to the Fig. S9). Absorption spectrum (CH_3CN): $\lambda_{max} = 312$ nm, $\varepsilon_{max} = 2.07 \times 10^2\ M^{-1}\ cm^{-1}$. Microanalysis: calculated (%) for $C_{13}H_{16}O_2$: C 76.44, H 7.90, O 15.66; found: C 76.31, H 8.11, O 15.58.

2.2.2. Tris(4,4-dimethyl-1-phenylpentane-1,3-dionato)aluminium(III), [Al(**bpm**)$_3$]

As for the free diketone, the syntheses of the Al(III) diketonate and of the other complexes described herein were based on litera-

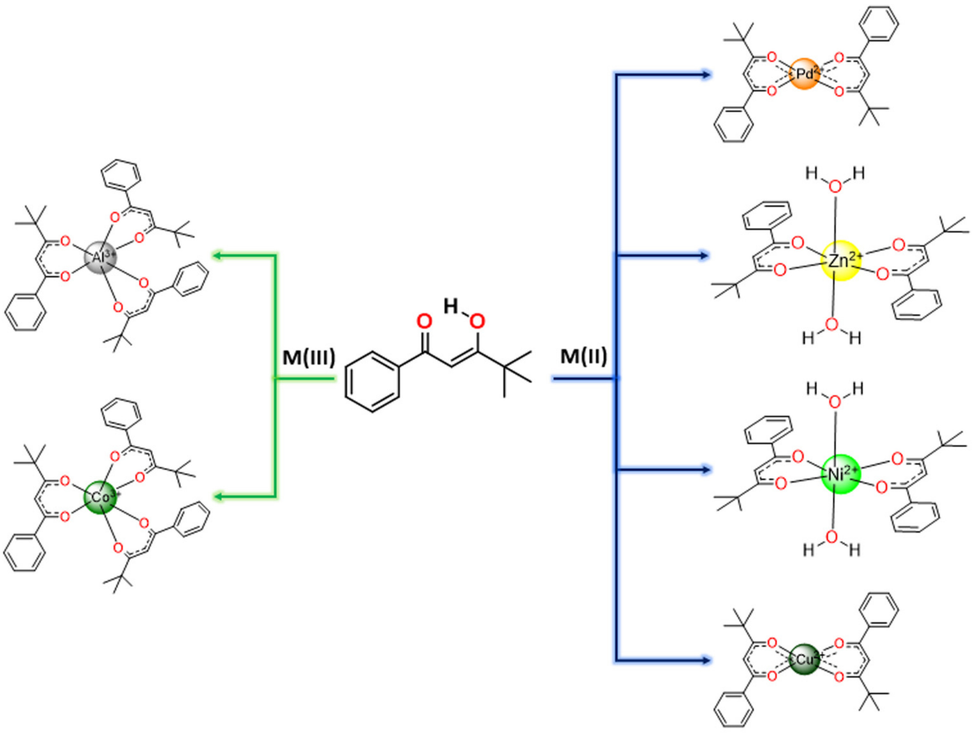

Fig. 1. Complexes obtained in reactions of 4,4-dimethyl-1-phenylpentane-1,3-dione (bpmH) with M(II) and M(III) ions.