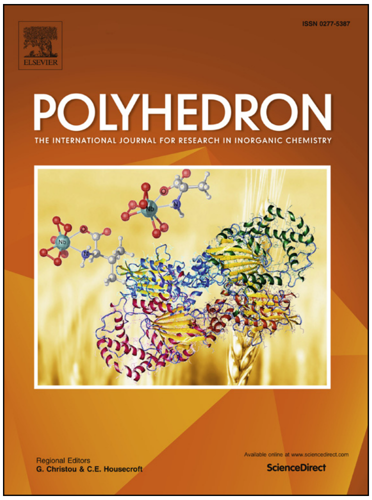

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PII: S0277-5387(17)30553-3
DOI: http://dx.doi.org/10.1016/j.poly.2017.08.022
Reference: POLY 12786

To appear in: *Polyhedron*

Received Date: 26 June 2017
Revised Date: 15 August 2017
Accepted Date: 17 August 2017

Please cite this article as: M. Kołodziejski, A. Jenczak, Z. Hnatejko, J. Harrowfield, A.R. Stefankiewicz, Unsymmetrical Bidentate Ligands as a Basis for Construction of Ambidentate Ligands for Functional Materials: Properties of 4,4-dimethyl-1-phenylpentane-1,3-dionate, *Polyhedron* (2017), doi: http://dx.doi.org/10.1016/j.poly.2017.08.022

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.

Keywords: β-diketonate, structure, supramolecular, isomerism

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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 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 (Figure 1).

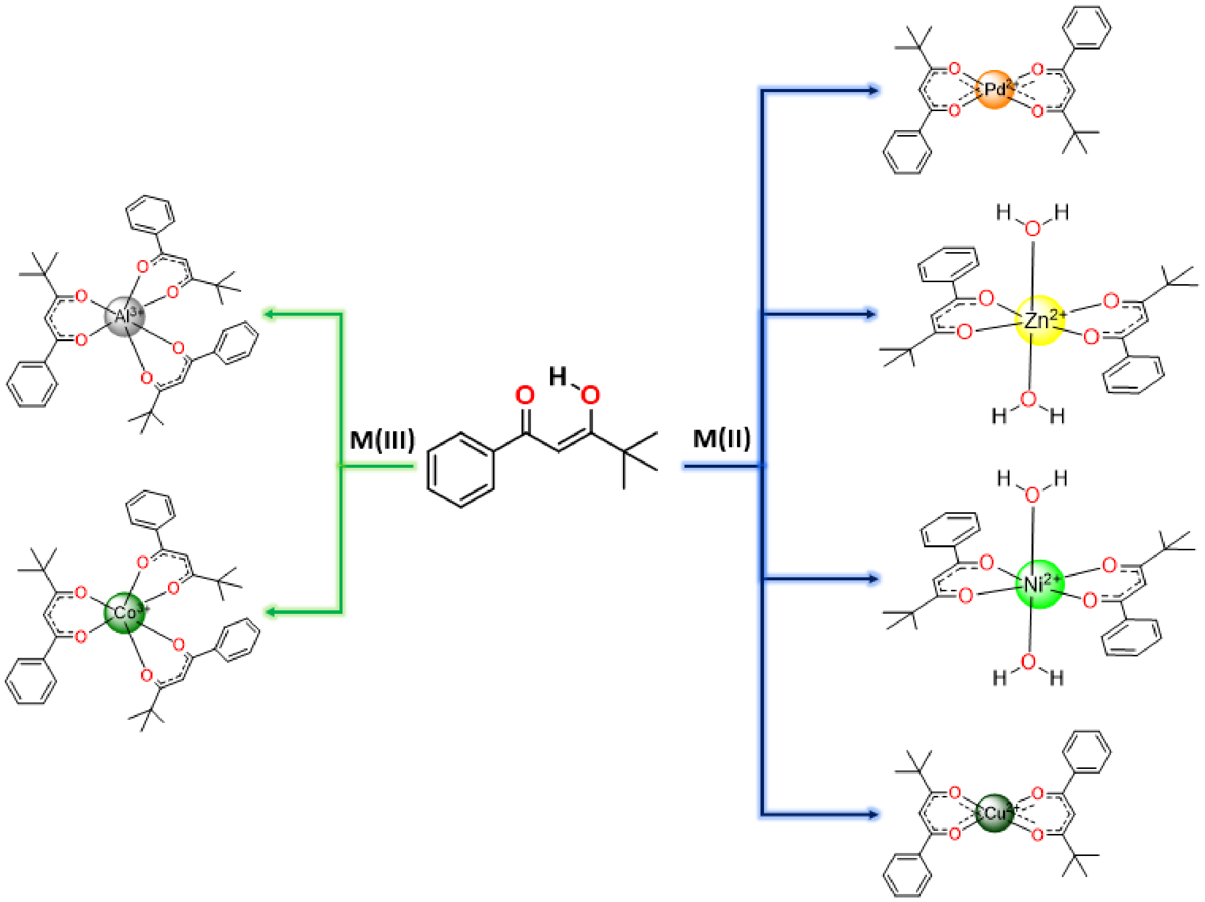

Figure 1. *Complexes obtained in reactions of 4,4-dimethyl-1-phenylpentane-1,3-dione* ***(bpmH)*** *with M(II) and M(III) ions.*

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 $CuCl_2•2H_2O$, 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, 2H, *keto*-form -CH_2-, H_2) , 1.26 (s, 9H, *enol*-form –CH_3, H_1), 1.23 (s, 9H, *keto*-form –CH_3, H_1) (Signals assigned according to the figure 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 figure S9). Absorption spectrum (CH_3CN): λ_{max}= 312 nm, ε_{max} = $2.07x10^2$ 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 literature procedures [17], [18], [24], [25]. To a yellow solution of $Al(NO_3)_3•9H_2O$ (65.2 mg; 0.173 mmol) and **bpmH** (106.5 mg; 0.521 mmol) in $MeOH/H_2O$ (1:1, 3 mL), $NaHCO_3$ (51.1 mg; 0.608 mmol) was added. The resulting suspension was stirred for 30 min at room temperature. After removal of the solvents under reduced pressure, the residue was extracted with $CHCl_3$ (2 x 15 mL) and washed with water (2 x 15 mL). The combined organic extracts were dried with Na_2SO_4 after which the solvent was removed to give an oily residue. Addition of EtOAc / hexane (1:1, v/v, 5 mL) resulted in the precipitation of a cream solid, which was filtered off and dried in vacuo to give a white powder which was recrystallized from chloroform, yielded white, hairy small crystals (37.1 mg; 33.4 % yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97, 7.94, 7.92, 7.90, 7.88, 7.86 (sext., 6H, H_3); 7.44, 7.43, 7.41, 7.39, 7.36, 7.35, 7.32 (sept., 9H, H_5, H_4); 7.26 ($CDCl_3$), 6.37, 6.34, 6.32, 6.26 (q, 3H, H_2); 1.23, 1.20, 1.19, 1.17 (q, 27H, H_1) (Signals assigned according to the figure 1). TOF-MS: m/z = 659.2974 - calculated for $C_{39}H_{45}AlNaO_6$ (Na[Al(**bpm**)$_3$]$^+$); found: m/z 659.2929; m/z = 433.1993 - calculated for $C_{26}H_{30}AlO_4^+$ ([Al(**bpm**)$_2$]$^+$); found: m/z = 433.1959. Absorption spectrum (CH_3CN): λ_{max} = 325 nm, ε_{max} = 1.76x10^3 M^{-1} cm^{-1}. Microanalysis: caluclated (%) for $C_{39}H_{45}AlO_6$: C 73.56, H 7.12, O 15.08; found: C 73.72, H 6.98, O 15.23.

*2.2.3 Tris(4,4-dimethyl-1-phenylpentane-1,3-dionato)cobalt(III), [Co(**bpm**)$_3$]*

To a solution of **bpm**H (203 mg; 0.996 mmol) in MeOH (2 ml), TEA (143 µl; 1.03 mmol) was added. After 5 min. of stirring at room temperature, a MeOH solution (2 ml) of $Co(ClO_4)_2$•$6H_2O$ (121.48 mg; 0.332 mmol) with H_2O_2 (11 µl; 0.365 mmol) was added. The resulting mixture was stirred for 30 min. and then H_2O was added to finish precipitation. The voluminous dark green precipitate was filtered off, washed with water, dried and recrystallized from chloroform, yielded dark green flake-shaped crystals (365 mg; 55% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91, 7.88, 7.86, 7.84, 7.81, 7.78 (sext., 6H, H_3); 7.43, 7.41, 7.39, 7.37, 7.34, 7.32, 7.30 (sept., 9H, H_5, H_4); 7.26 ($CDCl_3$), 6.34, 6.30, 6.28, 6.20 (q, 3H, H_2); 1.26, 1.23, 1.21, 1.19 (q, 27H, H_1) (Signals assigned according to the figure S10). TOF-MS: m/z = 669.2626 - calculated for $C_{39}H_{46}CoO_6$ (H[Co(**bpm**)$_3$]$^+$); found: m/z = 669.2626. Absorption spectrum (CH_3CN): λ_{max} = 595 nm, ε_{max} = 183.6 M^{-1} cm^{-1} (the visible region absorption due to d-d transitions). Microanalysis: calculated (%) for $C_{39}H_{45}CoO_6$: C 70.05, H 6.78, O 14.36; found: C 70.19, H 6.63, O 14.27; calculated (%) for $C_{78}H_{90}Co_3O_{12}$: C 67.09, H 6.50, O 13.75; found: C 66.54, H 6.96, O 13,48 (green paramagnetic species, after dehydration by heating).

*2.2.4 Diaqua-bis(4,4-dimethyl-1-phenylpentane-1,3-dionato)nickel(II), [Ni(**bpm**)$_2$(OH$_2$)$_2$]*

To a solution of **bpm**H (124 mg; 0.608 mmol) in MeOH (2 ml), TEA (61 µl; 0.608 mmol) was added. After 5 min. of stirring at room temperature, a MeOH solution (2 ml) of $Ni(CH_3COO)_2$•$4H_2O$ (76 mg; 0.304 mmol) was added. The resulting mixture was stirred for 30 min. and then H_2O was added to finish precipitation. The voluminous light green precipitate was filtered off, washed with water, dried and recrystallized from chloroform, yielded small light green cubes (163 mg; 58% yield). TOF-MS: m/z = 465.1575 - calculated for $C_{26}H_{31}NiO_4$ (H[Ni(**bpm**)$_2$]$^+$); found: m/z = 465.1563. Absorption spectrum (CH_3CN): λ_{max} = 602 nm, ε_{max} = 255.8 M^{-1} cm^{-1} (the visible region absorption due to d-d transitions). Microanalysis: calculated (%) for: $C_{26}H_{34}NiO_6$: C 62.30, H 6.94, O 19.15; found: C 62.08, H 7.12, O 18.99.

*2.2.5 Bis(4,4-dimethyl-1-phenylpentane-1,3-dionato)copper(II), [Cu(**bpm**)$_2$]*

To a solution of **bpmH** (199 mg; 0.975 mmol) in THF (5 ml), Na_2CO_3 (207 mg; 1.95 mmol) was added. After 5 min. of stirring at room temperature, a THF solution (3 ml) of $Cu(BF_4)_2.6H_2O$ (77.0 mg; 0.325 mmol) was added. The resulting green mixture was stirred for 24 h at room temperature. A small amount of flocculent material was filtered off and green filtrate taken to dryness in vacuo. The solid obtained was dissolved in DCM / EtOH mixture and left to crystallize by slow solvent evaporation (112 mg; 49 % yield). TOF-MS: m/z = 470.1553 - calculated for $C_{26}H_{31}CuO_4$ (H[Cu(**bpm**)$_2$]$^+$); found: m/z = 470.1505. Absorption spectrum (CH_3CN): λ_{maxI} = 663 nm, ε_{maxI} = 52.6 M^{-1} cm^{-1}; λ_{maxII} = 538 nm, ε_{maxII} = 47 M^{-1} cm^{-1} (the visible region absorption due to d-d transitions). Microanalysis: calculated (%) for $C_{26}H_{30}CuO_4$: C 66.43, H 6.43, O 13.61; found: C 66.68, H 6.29, O 13.49.

*2.2.6 Hydrated bis(4,4-dimethyl-1-phenylpentane-1,3-dionato)zinc(II), [Zn(**bpm**)$_2$(OH$_2$)$_n$]*

To a solution of **bpmH** (119 mg; 0.583 mmol) in MeOH (2 mL), NaOH (23.4 mg; 0.583 mmol) was added. After stirring the mixture 5 min, $Zn(CH_3COO)_2{\bullet}2H_2O$ (42.7 mg; 0.194 mmol) was added to give cloudy, yellow solution, which was then stirred for a further 24 h at room temperature. The suspension was filtered and the filtrate taken to dryness to give a yellow solid. This was dissolved in the minimum amount of MeCN and addition of Et_2O/n-hexane (1:1, v/v, 10 ml) used to precipitate the desired product as yellow solid, recrystallized from dichloromethane / diethyl ether mixture, yielded hairy small white crystals (42.3 mg, 32 % yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87, 7.85 (d, 4H, H_3), 7.57, 7.55, 7.53 (t, 2H, H_5), 7.50, 7.48, 7.46 (t, 4H, H_4), 7.26 ($CDCl_3$), 6.30, 6.28 (d, 2H, H_2), 1.26 (s, 18H, H_1) (Signals assigned according to the figure 4). TOF-MS: m/z = 471.1514 – calculated for $C_{26}H_{31}O_4Zn$ (H[Zn(**bpm**)$_2$]$^+$); found: m/z = 471.1508. Absorption spectrum (CH_3CN): λ_{max} = 309 nm, ε_{max} = $2.18x10^3$ M^{-1} cm^{-1}. Microanalysis: calculated (%) for $C_{26}H_{34}ZnO_6$: C 61.48, H 6.75, O 18.90; found: C 61.31, H 6.96, O 18.68.

*2.2.7 Bis(4,4-dimethyl-1-phenylpentane-1,3-dionato)palladium(II), [Pd(**bpm**)$_2$]*

To a solution of **bpmH** (0.156 g; 0.763 mmol) in MeOH (3 mL), NaOH (38.1 mg; 0.953 mmol) was added and the mixture stirred until (1 h) a clear, yellow solution had formed. A solution of $PdCl_2$ (64.4 mg; 0.363 mmol) in MeOH (5 mL) was added, rapidly producing a green precipitate, and the suspension was stirred for 24 h at r.t. The product was isolated by filtration, washing on the filter with with EtOH and Et_2O and recrystallization from chloroform / diethyl ether system, yielded small yellow-green, needle-shaped crystals (109 mg, 55.2 % yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86, 7.83 (d, 4H, H_3); 7.50, 7.47, 7.45 (t, 2H, H_5); 7.42, 7.39, 7.37 (t, 4H, H_4); 7.26 ($CDCl_3$); 6.24 (s, 2H, H_2); 1.26 (s, 18H, H_1) (Signals assigned according to the figure 3). TOF-MS: mz/ = 513.1311 - calculated for $C_{26}H_{31}O_4Pd$ (H[Pd(**bpm**)$_2$]$^+$); found: m/z = 513.1257. Absorption spectrum (CH_3CN): λ_{max} = 589 nm, ε_{max} = 90.2 M^{-1} cm^{-1} (the visible region absorption due to d-d transitions). Microanalysis: calculated (%) for $C_{26}H_{30}PdO_4$: C 60.88, H 5.90, O 12.48; found: C 60.75, H 5.74, O 12.69.

2.3 Crystallography

Crystals of Cu(**bpm**)$_2$ were obtained by slow evaporation of a solution of the complex in a 1:1 dichloromethane/ethanol mixture. Crystals of Pd(**bpm**)$_2$ were obtained by diffusion in a two-phase system of the complex in chloroform as the bottom layer and diethyl ether as the top layer in a closed vial. Diffraction data were collected at room temperature using graphite-monochromated MoK$_\alpha$ radiation (λ = 0.71073 Å) with the ω-scan technique. For data reduction, UB-matrix determination and absorption correction, CrysAlisPro [27] software was used.

Using Olex2 [28], the structures were solved by direct methods using SHELXL [29] and refined by full-matrix least-squares against F^2 utilizing SHELXL. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated at ideal positions by molecular geometry and refined as rigid groups. U_{iso} of hydrogen atoms were set as 1.2 (for C-carriers) times U_{eq} of the corresponding carrier atom. Crystal and refinement data are summarised in Table 1 and selected structural parameters are reported in Tables S1-S4. The data have been deposited in the form of cifs with the Cambridge Crystallographic Data Centre (CCDC), deposition numbers CCDC 1558066 (for [Cu(**bpm**)$_2$]) and CCDC 1558067 (for [Pd(**bpm**)$_2$]). These can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge

Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Table 1 Crystal and refinement data

Complex	**[Cu(bpm)$_2$]**	**[Pd(bpm)$_2$]**
Empirical formula	$C_{26}H_{30}CuO_4$	$C_{26}H_{30}O_4Pd$
Formula weight	470.04	512.90
Temperature/K	293(2)	293(2)
Crystal system	triclinic	monoclinic
Space group	P-1	$P2_1/n$
a/Å	6.4306(7)	10.6894(2)
b/Å	9.5411(12)	12.0326(2)
c/Å	10.3037(9)	18.8931(4)
α/°	82.414(9)	90
β/°	86.448(8)	97.597(2)
γ/°	72.626(10)	90
Volume/Å^3	597.89(12)	2408.72(8)
Z	1	4
ρ_{calc}g/cm^3	1.305	1.414
μ/mm^{-1}	0.941	0.798
F(000)	247.0	1056.0
Crystal size/mm^3	0.25 × 0.2 × 0.02	0.2 × 0.15 × 0.1
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.64 to 48.798	4.158 to 56.69
Index ranges	$-7 \leq h \leq 7$, $-11 \leq k \leq 10$, $-11 \leq l \leq 11$	$-14 \leq h \leq 14$, $-15 \leq k \leq 15$, $-24 \leq l \leq 25$
Reflections collected	5575	117908
Independent reflections	1873 [R_{int} = 0.0595, R_{sigma} = 0.0702]	5768 [R_{int} = 0.0690, R_{sigma} = 0.0309]
Data/restraints/parameters	1873/0/145	5768/0/289
Goodness-of-fit on F^2	1.032	1.182
Final R indexes [I>=2σ (I)]	R_1 = 0.0448, wR_2 = 0.0943	R_1 = 0.0454, wR_2 = 0.0819
Final R indexes [all data]	R_1 = 0.0665, wR_2 = 0.1027	R_1 = 0.0823, wR_2 = 0.0895
Largest diff. peak/hole / e Å^{-3}	0.22/-0.21	0.39/-0.36

3. Results and discussion

3.1 Synthesis: Both the diketone and diketonate complex syntheses were based on very familiar literature procedures for the same or closely related species and provided no surprising results. Methanol proved to be a convenient solvent for all the complex ion syntheses, although various other solvents such as ethanol, acetonitrile or tetrahydrofuran could be used with equal success.

3.2 Composition, structure and stereochemistry of the complexes: Although the syntheses were designed to produce just the neutral, homoleptic species M(**bpm**)$_n$ (possibly as solvates) and were successful in this regard, it is of course possible that such species could oligomerise [8-10]. Mass spectra of the complexes (see experimental) provided no evidence for the presence of oligomers but the necessary use of ion association to obtain charged species appeared in several cases to result in partial breakdown by dissociation of **bpm**$^-$, so that depolymerisation of initially weakly associated species cannot be excluded. However, it is known [8-10], [30] that oligomerisation is inhibited by bulky substituents on the diketonate unit and complexes of Ni(II) [30] are of particular significance in this regard, as the colour (*i.e.* the absorption spectrum) of diamagnetic square-planar mononuclear species is quite different to that of paramagnetic octahedral oligomers such as formed, for example, by dehydration of octahedral *trans*-[Ni(acac)$_2$(OH$_2$)$_2$]. While the square- planar form of the Ni(II) complex of the symmetrical dipivaloylmethanate (dpm$^-$) ligand was established long ago by an X-ray structure determination [31] and shown to be maintained in solution [32], there is, however, evidence [17], [24] largely based on solution molecular weight estimates, that benzoylpivaloylmethanate is a less restrictive ligand in regard to oligomerisation. This conclusion is supported by the present observations on the Ni(II) complex, which was isolated as the green, octahedral [Ni(**bpm**)$_2$(OH$_2$)$_2$] complex that, on heating, underwent dehydration to give a green, paramagnetic species analogous to [Ni$_3$(acac)$_6$] (see experimental).

An alternative index of ligand-ligand interactions within the coordination sphere of a complex can be provided in the case of an unsymmetrical ligand such as **bpm**$^-$ in the distribution of isomeric forms of bis- or tris-ligand complexes. In complexes of sufficient stability and stereochemical rigidity, this isomer distribution can be monitored by NMR spectroscopy. Thus, in the present work the ^{1}H spectra of the diamagnetic complexes [Al(**bpm**)$_3$], [Co(**bpm**)$_3$], [Zn(**bpm**)$_2$(OH$_2$)$_n$] and [Pd(**bpm**)$_2$] provided clear evidence for the presence of two species in each case. For the expected octahedral form of the Al(III) (Figure 2) and Co(III) (Figure S10) complexes, the C_3-symmetric *fac* isomer should give rise to a single peak for the methine and methyl group protons, while the C_1-symmetric *mer* isomer should show three peaks of equal intensity for each type of proton, enabling ready identification of the separate isomers and therefore a direct establishment of the *fac:mer* ratio (equilibrium constant). For the Al(III) and Co(III) complexes, this ratio was essentially identical at 1.65, a value little different from that expected for the statistical distribution (2:1 *fac:mer*).

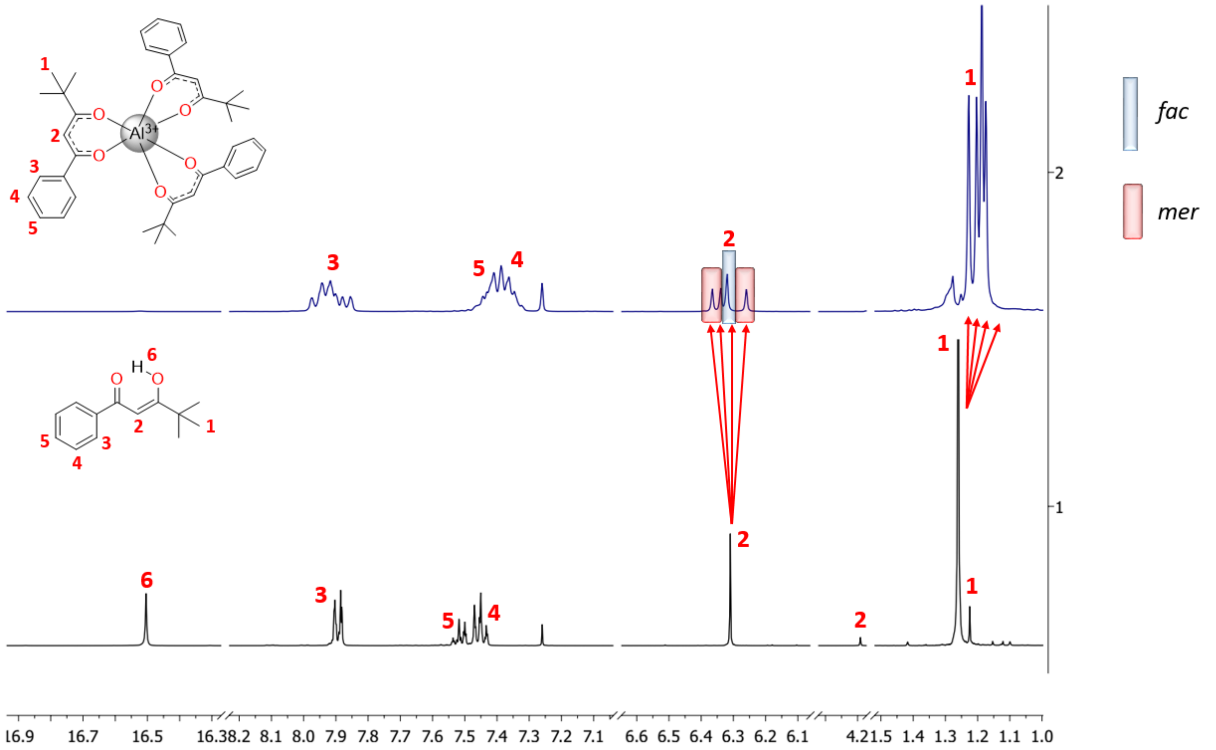

***Figure 2.** Comparison of the ^{1}H NMR (300 MHz) spectra of **bpm**H (bottom, black) and the complex [Al(**bpm**)$_3$] (top, blue) in $CDCl_3$ at room temperature.*

For the expected square-planar form of [Pd(**bpm**)$_2$], *cis* and *trans* isomers are possible. On recording the ^{1}H NMR spectrum of [Pd(**bpm**)$_2$] immediately after dissolving crystals of the bulk recrystallized complex, only one methine signal was observed and thus assigned to the *trans* form, given that this is the species found in the crystal lattice. For the same sample after an hour, signals consistent with the presence of a mixture of *cis* and *trans* isomers were observed indicating a *cis:trans* ratio of 1:1.66 (Figure 3), in this case differing more significantly from the statistical value (of 1:1). In any case, both these spectroscopic results and the nature of the Ni(II) complex indicate that ligand-ligand interactions in complexes of **bpm**$^-$ are not strong, making this ligand somewhat closer to acac$^-$ than to dpm$^-$ (dipivaloylmethanate) in its coordinative properties.

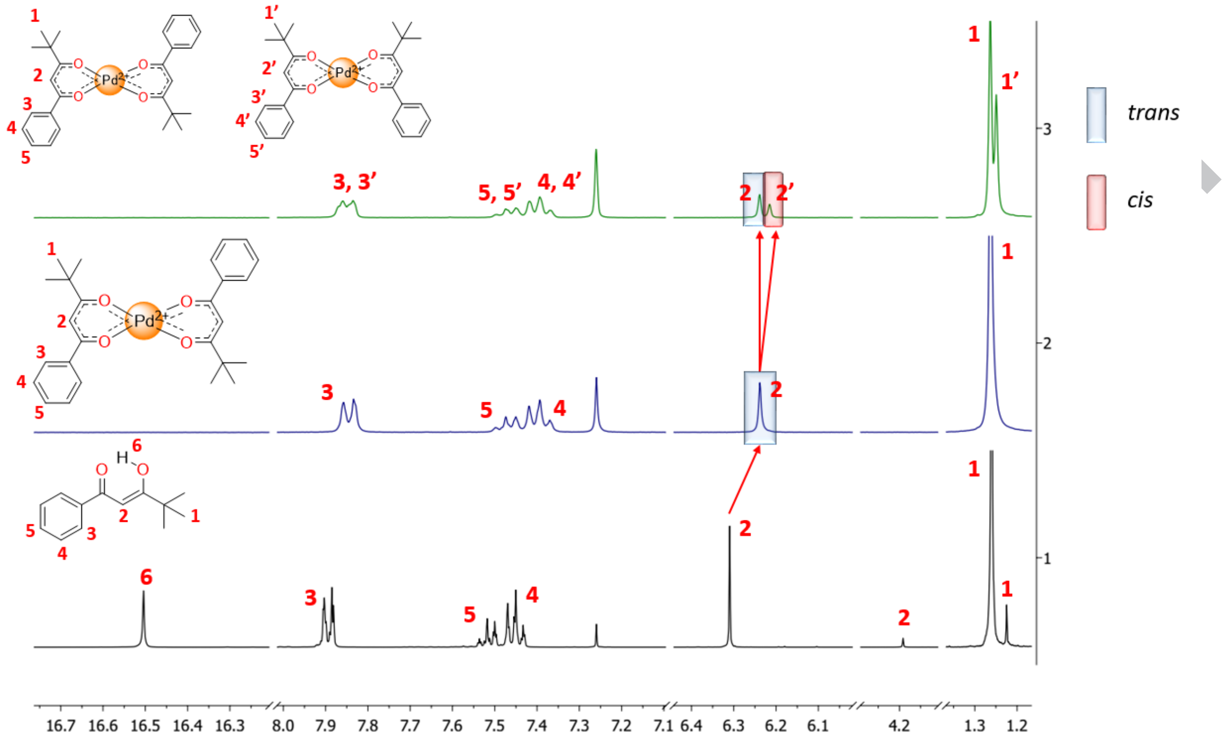

*Figure 3. Comparison of the ^{1}H NMR (300 MHz) spectra of **bpm**H (bottom, black), the complex [Pd(**bpm**)$_2$] immediately after preparing the solution (middle, blue) and the complex [Pd(**bpm**)$_2$] after one hour in solution (top, green) in CDCl$_3$ at room temperature.*

Elemental analyses for the Zn(II) complex indicated the presence of two water molecules per Zn and thus were consistent with different formulations such as [Zn(**bpm**)$_2$(OH$_2$)]•H$_2$O or [Zn(**bpm**)$_2$(OH$_2$)$_n$]. The former is consistent with the square-pyramidal structure known for the acetylacetonate analogue [33], but in either case *cis* and *trans* isomeric forms would be possible. At room temperature, the ^{1}H NMR spectrum of this complex shows two methine peaks with an intensity ratio of 1:1.5 (Figure 4) but in this case their assignment to particular isomers is not possible, although the fact that a single methine peak is apparent for each species does not exclude the possibility that any [Zn(**bpm**)$_2$(OH$_2$)$_n$] species could be a *cis* isomer. The nature of the Zn(II) complex in chloroform solution, however, is perhaps, more complicated than expected, as its spectrum shows a significant temperature dependence (Figure 5) in which the higher-field methine resonance shifts upfield and broadens considerably as the temperature is lowered. This possibly indicative of an equilibrium between five- and six-coordinate species rather than or as well as *cis/trans* isomerism.

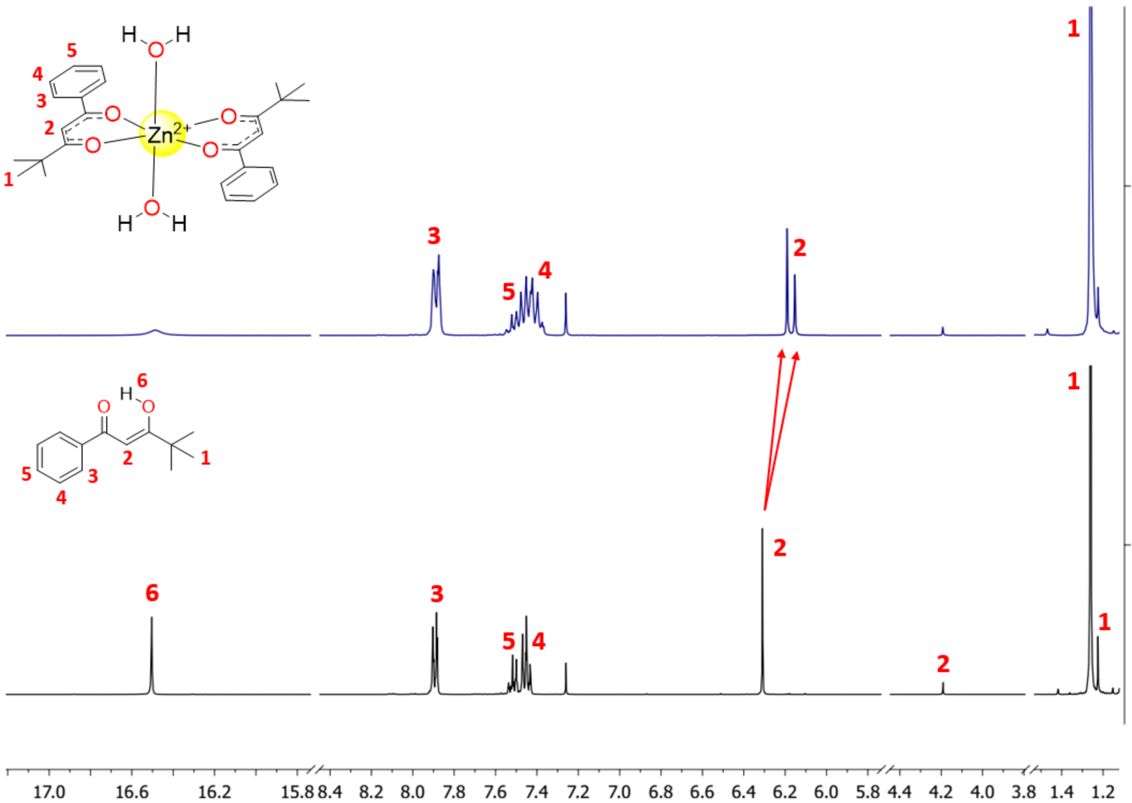

Figure 4. *Comparison of the* ^{1}*H NMR (300 MHz) spectra of* ***bpm****H (bottom, black) and the complex [Zn(****bpm****)*$_2$*(OH*$_2$*)*$_n$*] immediately after preparing the solution (top, blue) in CDCl*$_3$ *at room temperature.*

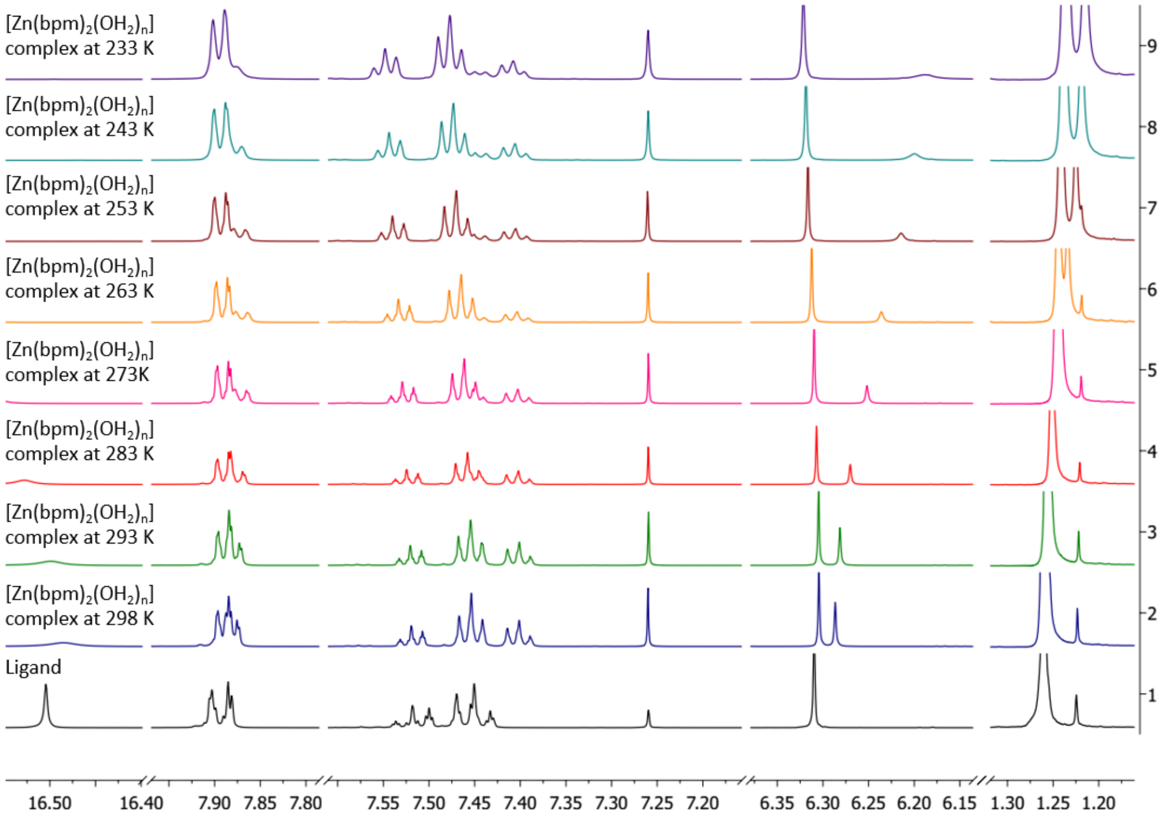

Figure 5. *Variable Temperature NMR (600 MHz) spectra for [Zn(**bpm**)$_2$(OH$_2$)$_n$] recorded in CDCl$_3$.*

While electronic absorption spectra in the visible region of the coloured complexes show d-d absorption bands at positions consistent with O-donor environments (and essentially identical to those in their acetylacetonate analogues [8-10]), these bands are broad and not readily resolved into separate isomer contributions. The much stronger UV absorptions seen in all complexes are also broad and not deconvolutable but they do illustrate the dramatic spectral changes that result from replacement of the acidic ligand proton by a metal ion (Figure S1).

Given that at least under the conditions of synthesis and crystallisation presently applied, all the metal ions used could be considered to be labile, slow crystallisation was considered as a potential means of isolating a single species from a solution mixture. The paramagnetic [Cu(**bpm**)$_2$] crystals (reported before by S.V.Borisov et al. [34]) were obtained by slow evaporation of solvent from solution of complex in a 1:1 dichloromethane/ethanol mixture. Crystals of diamagnetic [Pd(**bpm**)$_2$] were obtained by diffusion in two-phase system of the complex in chloroform as the bottom layer and diethyl ether as the top layer in a closed vial. The X-Ray structure of the [Cu(**bpm**)$_2$] complex was the sole means of establishing its stereochemistry because its paramagnetism excluded the use of ^{1}H NMR spectroscopy. Both complexes proved to be the expected *bis*(diketonate) species and to have a square-planar, *trans* geometry in the solid state [35], [36]. X-ray structures of the complex units within their lattices are shown below (Figure 6) and crystallographic data for both structures are summarised in Table 1.

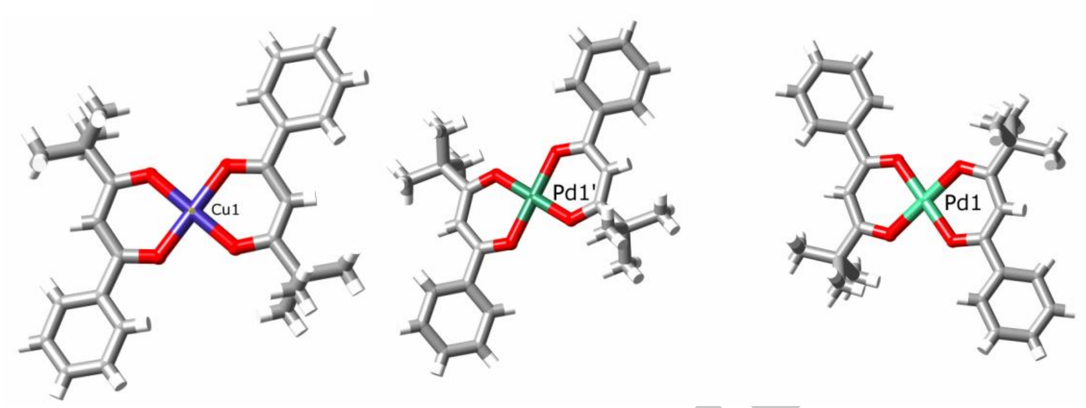

Figure 6. *Views of (left) the unique molecular unit present in the lattice of [Cu(**bpm**)$_2$] and (right) the two inequivalent but very similar molecular units present in the lattice of [Pd(**bpm**)$_2$].*

Unlike their acetylacetonate analogues [37], [38], [Cu(**bpm**)$_2$] and [Pd(**bpm**)$_2$] are not isomorphous but their lattices are nonetheless quite similar, with stacked columns of M(**bpm**)$_2$ units lying parallel to *a* in both (Figures S2, S3). Consideration of the Hirshfeld surfaces [39], [40] (Figures S4, S5) shows that interactions between the unique [Cu(**bpm**)$_2$] units do not exceed dispersion forces whereas interactions of the two, inequivalent [Pd(**bpm**)$_2$] units involve, in addition to dispersion, both aromatic-CH...O and aromatic-C...O interactions that link Pd1 and Pd1' in a reciprocal manner (H5...O2' 2.670(3) ; C5...O1' 3.141(5) Å) along the *a* direction (Figure S6), and aliphatic-CH...C (H13E...C3 2.872(6) Å) interactions, again reciprocal (Figure S6) that link the Pd1 units into a two-dimensional sheet parallel to the (1 0 -1) plane (Figure S7). These differences between the Cu(II) and Pd(II) complexes must reflect differences in the electronic influence of the two metal ions, although the two Pd units are involved in quite different interactions, indicating that a delicate balance of factors may be operative. An interesting feature of the slipped-stack column in the Cu(II) complex lattice is that it places each Cu(II) symmetrically in between two phenyl rings, indicating that there may be some axial interaction, even if it does not exceed dispersion, and this could well explain the preference for the *trans* configuration of each complex unit. A similar situation clearly does not apply in the Pd(II) complex lattice, where the preference for the *trans* isomer is presumably to be associated with the weak interactions beyond dispersion revealed in the Hirshfeld surface.

Conclusions

Despite the relatively bulky nature and different electronic character of the substituents attached to the dionate unit of **bpm**H, there appears to be little preference in regard to the isomeric form of its homoleptic complexes in solution, although individual species can be isolated in the crystalline state. In the two cases structurally characterised, the solid state interactions associated with the preferred isomeric form are quite different, indicating that the bound metal ion has a significant and unique influence on the peripheral properties of its complex. In relation to the possible use of the phenyl ring of **bpm**$^-$ as a site for the introduction of an alternative metal ion binding site, it would seem that the evaluation of the resultant complexes as heterogeneous catalysts containing a single isomeric species is the most obvious starting point.

Appendix A. Supplementary data

CCDC 1558066 contains the supplementary crystallographic data for [Cu(bpm)2].
CCDC 1558067 contains the supplementary crystallographic data for [Pd(bpm)2].
These can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or e-mail: deposit@ccdc.cam.ac.uk

Acknowledgments

We thank the National Centre for Research and Development for funding – LIDER 024/391/L-5/13/NCBR/2014.

Conflicts of interests

The authors declare no conflict of interests.

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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) ions. The mixture of isomers of Al(III), Co(III), Pd(II), Zn(II), Ni(II) and Cu(II) is present in solution. For Al(III), Co(II) and Pd(II) *cis/trans* equilibrium can be well described by ^{1}NMR measurements in solution. Crystal structure determinations on Cu(II) and Pd(II) complexes showed that only one isomer can be isolated from the mixture in solution in the solid state. Zn-complex made us realize that water molecules also can lead to competition between five- and six- coordinated species. Ni(II) complex is evidence that the steric bulk of 1,3-dione substituents is not sufficient to prevent oligomerisation.