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

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Supplementary information

Synthesis of [Al(L^2)$_3$] 1

$Al(NO_3)_3·9H_2O$ (0.60 g, 1.60 mmol) dissolved in water (5 cm^3) was added dropwise to 1,3-di(4-pyridyl)propane-1,3-dione (H**L**^{2}) (1.131 g, 5.00 mmol) dissolved in water (40 cm^3) containing NaOH (0.206 g, 5.15 mmol). The precipitated material was collected by filtration and washed with water (3 × 10 cm^3). The solid was taken up in dichloromethane (100 cm^3) and the solution dried over Na_2SO_4, filtered, and concentrated by rotary evaporation to *ca.* 20 cm^3. The solution was passed through a short column of Al_2O_3 eluting with dichloromethane –methanol (98:2) then evaporated and the residue taken up in dichloromethane (20 cm^3) and diluted with toluene (100 cm^3). The crystals that formed overnight were harvested and washed sparingly with fresh toluene. Yield 1.099 g (82 %). Found: C, 70.0; H, 4.59; N, 10.2. $C_{47.75}H_{37}AlN_6O_6$ requires C, 70.1; H, 4.56; N, 10.3 %. δ_H ($CDCl_3$): 6.99 (3 H, s), 7.79 (6 H, dd, $J = 4.5, 1.6$ Hz), 8.75 (6 H, dd, $J = 4.5, 1.6$ Hz). δ_C ($CDCl_3$): 95.34, 121.09, 144.01, 150.67, 184.49. *m/z* (ESI) 703.4 ($[M + H]^+$).

Synthesis of [Ga(L^2)$_3$] 2

Di(4-pyridyl)propane-1,3-dione (H**L**^{2}) (0.242 g, 1.1 mmol) was dissolved in water (9 cm^3) with the addition of 1 N NaOH (1.20 cm^3, 1.2 mmol). Ethanol (10 cm^3) was added, and a yellow solution was observed after all the solid has dissolved. $Ga(NO_3)_3·xH_2O$ (0.145 g, 0.4 mmol) dissolved in water (2 cm^3) was added dropwise to this solution. The reaction mixture was stirred for 1 h, then water was added to the solution. The volume of solvent was then reduced using a rotary evaporator, and the reaction vessel was cooled in ice. An off-white solid was collected by filtration, washed with water (2 × 2 cm^3) and ethanol (0.5 cm^3) and dried at 80 °C. Yield 0.076 g (25 %). Found: C, 60.3; H, 3.56; N, 10.7. $C_{39}H_{31}GaN_6O_8$ ([Ga(**L**^{3})$_3$]·2H_2O) requires C, 59.9; H, 4.00; N, 10.8 %. δ_H ($CDCl_3$): 7.26 (3 H, s), 7.79 (6 H, dd, $J = 4.5, 1.6$ Hz), 8.77 (6 H, dd, $J = 4.5, 1.6$ Hz). *m/z* (ESI) 227.08 ([H**L**^{2}]$^+$). ν(CO)/cm^{-1} 1611.

Synthesis of [Al(L^2Ag)$_3$](NO_3)$_3$·4DMSO 3

[Al(**L**^{2})$_3$] (0.053 g, 0.064 mmol) was dissolved in DMSO (4 cm^3) with heating and stirring. To this, a solution of $AgNO_3$ (0.052 g, 50 mmol) in DMSO (1 cm^3) was added. The solution was heated until hot but not boiling. The solid product was allowed to precipitate overnight, this was then filtered and washed sparingly with DMSO and acetone and air dried. Yield 0.042 g. Acetone was then allowed to vapour diffuse into the filtrate, which yielded crystals of **3** of suitable size for single crystal X-ray diffraction. Loss of solvent prevented an accurate microanalysis from being obtained. Unit cell determinations on over 10 crystals suggested homogeneity of the sample, but loss of crystallinity associated with the solvent loss meant that only broad lines were observed in the powder X-ray diffractions patterns.

Synthesis of $[Ga(L^2Ag)_3](NO_3)_3 \cdot 3DMSO$ 4

A solution of $AgNO_3$ (0.051 g, 0.30 mmol) in DMSO (1 cm^3) was added to a solution of **2** (0.049 g, 0.066 mmol) in hot DMSO (4 cm^3). The solution was allowed to cool slowly to room temperature, and a small amount of precipitate was removed by filtration. Acetone was allowed to vapour diffuse into the solution, and after 6 days pale yellow crystals of **4** were harvested. Loss of solvent prevented an accurate microanalysis from being obtained. Unit cell determinations on several crystals suggested homogeneity of the sample, but loss of crystallinity associated with the solvent loss meant that only broad lines were observed in the powder X-ray diffractions patterns.

Synthesis of $[Eu(HL^2)_3(H_2L^2)]Cl_4 \cdot EtOH$ 5

H**L**^{2} (0.113 g, 0.5 mmol) was dissolved in ethanol (10 cm^3) with heating and stirring. Whilst hot, a solution of $EuCl_3 \cdot 6H_2O$ (0.046 g, 0.12 mmol) in ethanol (10 cm^3) was added. Crystals of suitable size for single crystal X-ray diffraction grew over several days. Yield 0.065 g (43 %). *m/z* (ESI) 1053.2 $[Eu(\mathbf{L}^2)_4]^-$. The powder X-ray diffraction pattern showed phase purity when compared against a simulated pattern for the single crystal (Fig. S1).

Compound **5** was also produced from the reaction between $EuCl_3 \cdot 6H_2O$ and H**L**^{2} in the presence of NaOH, but with a lower isolated yield.

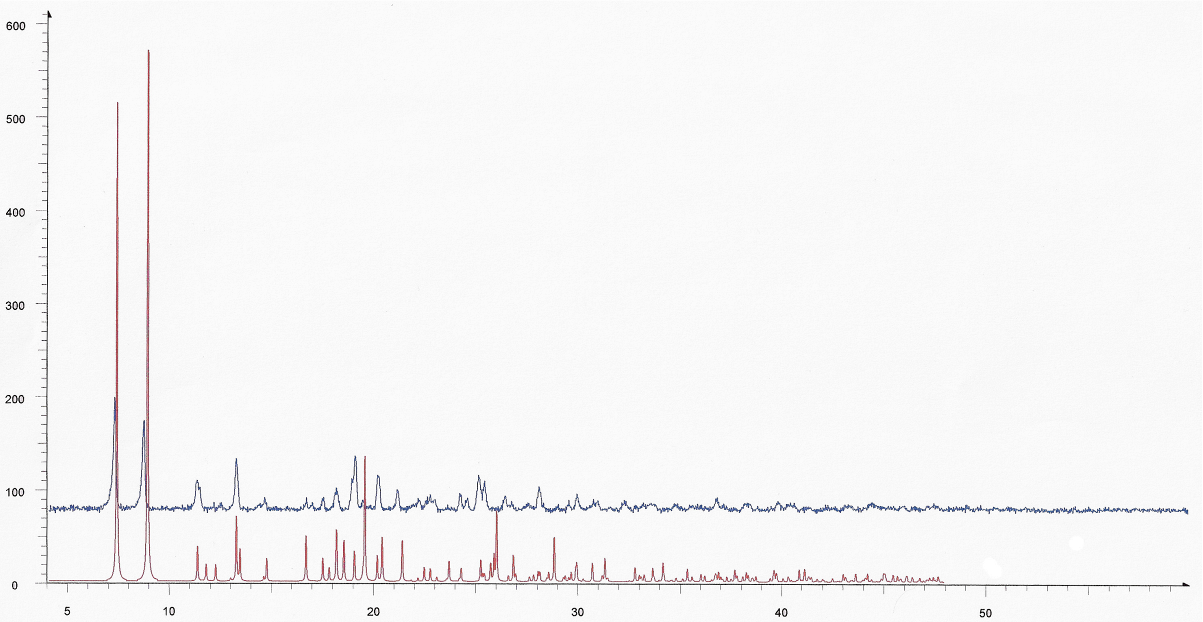

Figure S1. Experimental (blue) and simulated (red) powder X-ray diffraction patterns for $[Eu(HL^2)_3(H_2L^2)]Cl_4 \cdot EtOH$ **5**.

Crystallography

Compounds **1**, **4** and **5** were analysed on a Nonius KappaCCD diffractometer using Mo-K_α radiation (λ = 0.71073 Å), whereas compound **3** was analysed on a Oxford Diffraction instrument using Cu-K_α radiation (λ = 1.54184 Å). Crystallographic data for **1** and **3-5** are given in Table S1.

The asymmetric unit of **1** consists of one molecule of [Al($\mathbf{L}^2$)$_3$], one full molecule of toluene, and half of a toluene fragment at 50% occupancy, proximate to the crystallographic inversion centre at 0.5, 0.5, 0.5. The methyl group from this latter fragment is consequently disordered with respect to the crystallographic symmetry, and therefore exhibits 25% site occupancy. Residual electron density in the difference Fourier map is proximate to this solvent fragment, which was refined subject to restraints in the final least-squares cycles.

Compound **3** exhibits high symmetry and considerable disorder. Several data collections were made, in an effort to be completely certain about the space group assignment, and to model the disorder if possible. Ultimately, in this eighth instance an excellent data set (R_{int} = 0.0275, R_{sigma} = 0.0189, prior to SQUEEZE) was collected, which afforded good statistics and, equally importantly, bore none of the usual signs of merohedral/pseudo-merohedral twinning. The space groups possible were *R*–3*c* and *R*3*c*. The former did not afford a credible solution which, when the structure was solved, could be easily rationalised as there is no centre of inversion present either in the Al($\mathbf{L}^2$)$_3$ moieties or in the gross structure. The asymmetric unit then, as presented, consists of three Al$_{1/3}$($\mathbf{L}^2$Ag) fragments, three nitrate ions and some disordered solvent of recrystallisation. The nitrates were hopelessly disordered, which suggests that they do not bind in any periodic way to the silvers, if indeed they bind at all. Thus, the anions and the disordered solvent were treated with the PLATON SQUEEZE routine and given the diffuse nature of the solvent and the available volume, four molecules of DMSO have been included in the asymmetric unit. A correction for racemic twinning was also included in the refinement.

The structure of **4** suffered from the same issues as that of the isostructural aluminium analogue **3**. It was notable in this case that suitably sized samples for crystallography all contained an internal flaw, which has impacted on the R(int) of the data collected. Diffraction fall-off resulted in the using data to a maximum resolution of 0.9 Å in the final least squares. To minimize the esd on that data, a 3-day data collection was undertaken. The asymmetric unit then, as presented, consists of three Ga$_{1/3}$($\mathbf{L}^2$Ag) fragments, three nitrates and some disordered solvent of recrystallisation. The nitrates were hopelessly disordered, which suggests that they do not bind in any periodic way to the silvers. Thus, the anions and the disordered solvent were treated with the PLATON SQUEEZE routine and given the diffuse nature of the solvent and the available volume, three molecules of DMSO have been included in the asymmetric unit. A correction for racemic twinning was also included in the refinement. 6-membered rings were treated as rigid hexagons, and the ADPs in each were refined subject to similarity restraints.

The asymmetric unit of **5** consists of a quarter of a europium atom, located at a special position in the space group, one $\mathbf{L}^2$ ligand, one chloride anion and a diffuse region of solvent. The $\mathbf{L}^2$ ligand is neutral for 75% of the time (*i.e.* one of the ligand nitrogen atoms is protonated), and positively charged for the remaining 25% of the time (*i.e.* both nitrogen atoms are protonated). The nitrogen-bound ligand hydrogen atoms are disordered such that a proton is located on N(1) in 65% of the structure, and another on N(2) in 60% of the structure. These partial occupancy atoms – H(1) and H(2) – were located and refined at a distance of 0.9 from the parent atoms. The solvent is proximate to crystallographic symmetry and could not be successfully resolved. Hence, PLATON SQUEEZE was utilized, which gave an estimate of one molecule of ethanol per europium, which has been included in the formulation.

Table S1 Crystallographic data for compounds **1** and **3-5**

	1	**3**	**4**	**5**
Formula	$C_{47.75}H_{37}AlN_6O_6$	$C_{47}H_{51}Ag_3AlN_9O_{19}S_4$	$C_{45}H_{45}Ag_3GaN_9O_{18}S_3$	$C_{54}H_{47}Cl_4EuN_8O_9$
M	817.81	1524.80	1489.42	1245.76
T / K	150(2)	173(2)	150(2)	150(2)
Crystal system	Triclinic	Trigonal	Trigonal	Orthorhombic
Space group	*P*–1	*R*3*c*	*R*3*c*	*Fddd*
a / Å	11.9780(1)	22.4562(3)	22.9930(6)	15.1070(4)
b / Å	12.5850(1)	22.4562(3)	22.9930(6)	27.3860(7)
c / Å	14.3390(2)	72.1481(4)	71.297(2)	29.0380(7)
α / °	87.816(1)	90	90	90
β / °	84.052(1)	90	90	90
γ / °	79.823(1)	120	120	90
U / $Å^3$	2115.61(4)	31508.5(6)	32643.2(16)	12013.6(5)
Z	2	18	18	8
$\mu(Mo-K_\alpha)/mm^{-1}$	0.105	8.419	1.310	1.279
Reflections collected	39978	57004	90151	47751
Independent reflections	12287	12792	10267	2638
R(int)	0.0539	0.0738	0.1249	0.1149
Reflections observed (>2σ)	8909	10519	6998	2424
*R*1, w*R2* [*I*>2σ(*I*)]	0.0633, 0.1713	0.0719, 0.1893	0.0883, 0.2698	0.0502, 0.1079
R indices (all data)	0.0933, 0.1945	0.0767, 0.1945	0.1102, 0.2856	0.0602, 0.1123
Largest diff. peak and hole / e $Å^{-3}$	0.951, –0.423	2.332, –0.432	0.916, –0.919	0.513, –0.353
Absolute structure parameter		0.478(9)	0.39(3)	