# ESI

## Initial employment of di-2-pyridyl ketone as a route to nickel(II)/lanthanide(III) clusters : triangular $Ni_2Ln$ complexes

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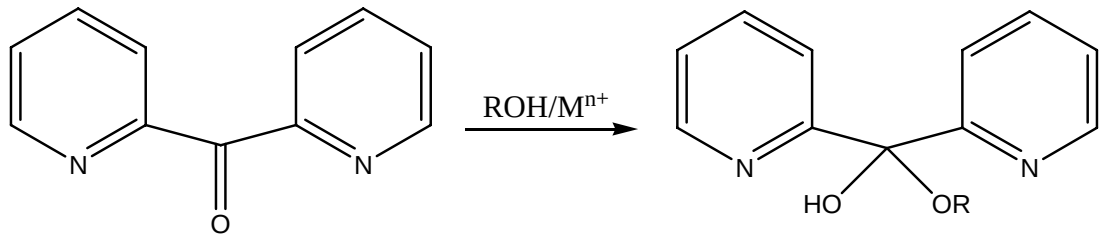


$(py)_2CO$

$(py)_2C(OH)_2$ ; R=H

$(py)_2C(OEt)(OH)$ ; R=Et

**Fig. S1** Di-2-pyridyl ketone-based ligands discussed in the text of the Communication. Note that $(py)_2C(OR)(OH)$ and their anions do not exist as free species but exist only in their respective metal complexes ($M^{n+}$ = metal ion; n = 2 or 3).

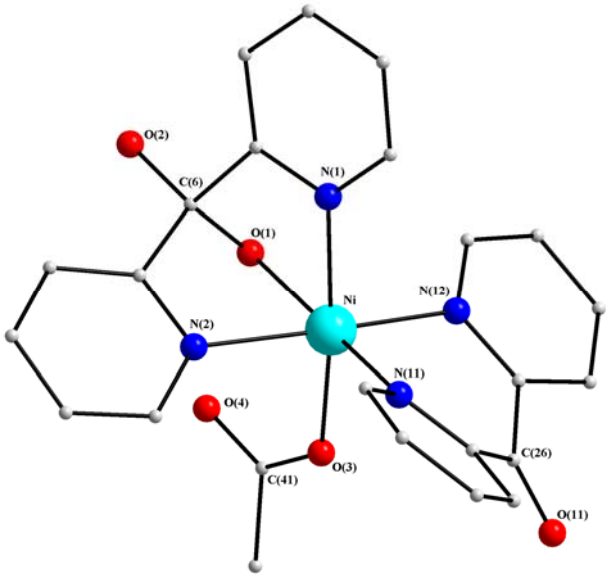


**Fig. S2** The cation $[Ni(O_2CMe)\{(py)_2CO\}\{(py)_2C(OH)_2\}]^+$ that is present in the mononuclear precursor **5**.

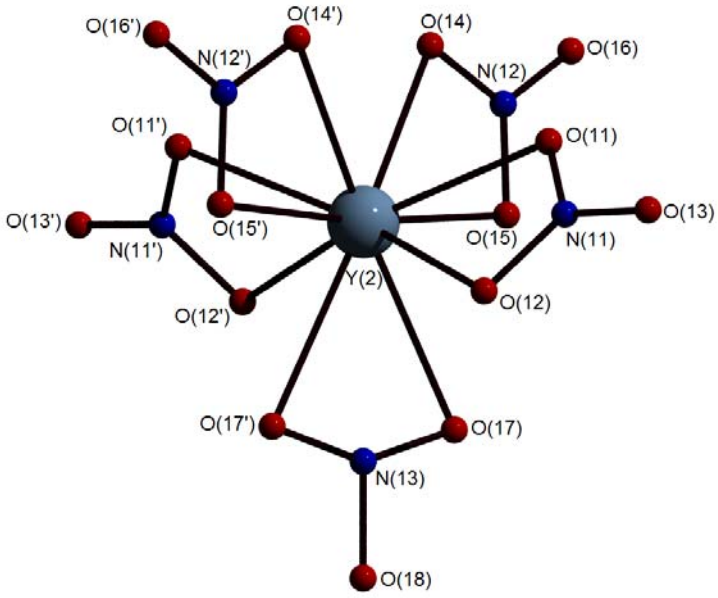


**Fig. S3** Structure of the $[Y(NO_3)_5]^{2-}$ anion that is present in complex **3**. A 2-fold rotation axis passes through Y(2), N(13) and O(18). Unprimed and primed atoms are related by the symmetry operation $-x, y, ½-z$.

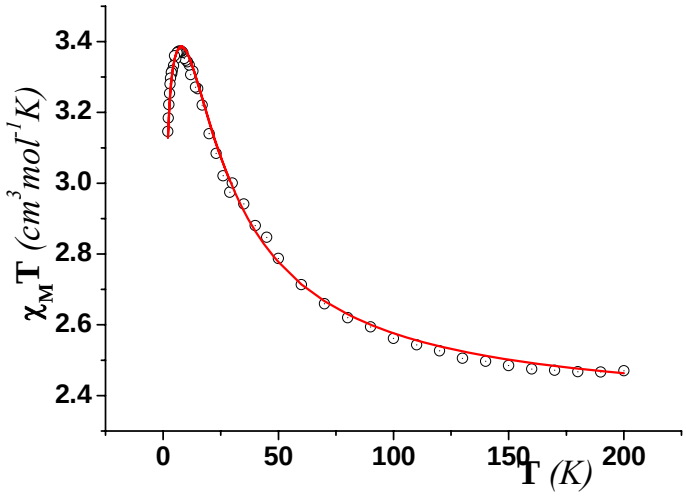


**Fig. S4** Plot of $\chi_M T$ as a function of $T$ for complex **3**; the solid line represents the best fit of the data.

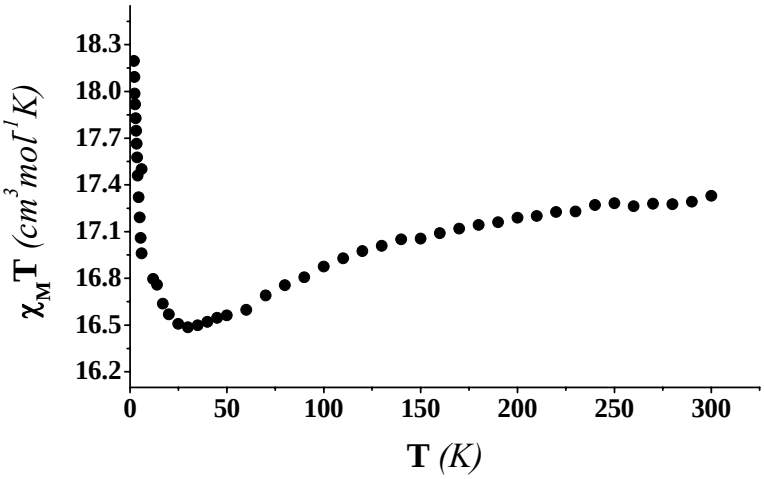


**Fig. S5** Plot of $\chi_M T$ as a function of $T$ for complex **1**.

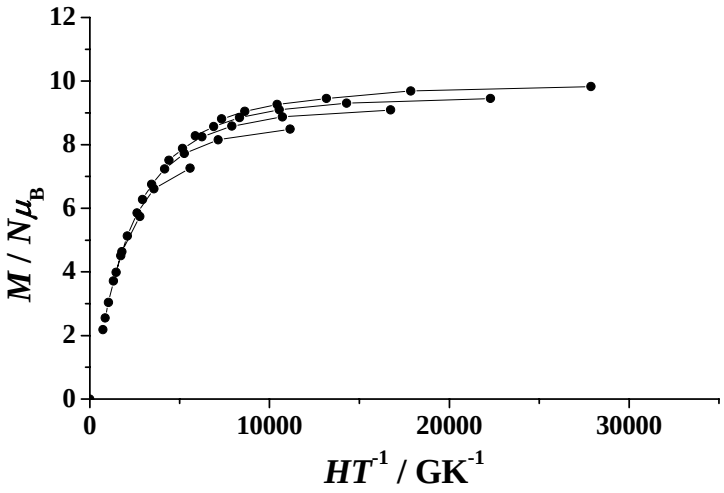


**Fig. S6** Plots of the reduced magnetization, $M/N\mu_B$, *vs* $HT^{-1}$ for complex **1** in the field range 0-5 T. Data were measured for 1 K increments between 1.8 and 6.8 K.

## Syntheses

All manipulations were performed under aerobic conditions using reagents and solvents as received.

**$[Ni_2Tb\{(py)_2C(OEt)O\}_3\{(py)_2C(OH)O\}(NO_3)(H_2O)](ClO_4)_2\cdot 2.3EtOH$ (1·2.3EtOH).** Solid $(py)_2CO$ (0.111 g, 0.60 mmol) was added to a green solution of $Ni(ClO_4)_2\cdot 6H_2O$ (0.109 g, 0.30 mmol) in EtOH (15 mL). The solid soon dissolved to give a brown-red solution. Solid $NaO_2CMe\cdot 3H_2O$ (0.041 g, 0.30 mmol) and solid $Tb(NO_3)_3\cdot 6H_2O$ (0.046 g, 0.10 mmol) were then added sequentially. The resulting solution was stirred under mild heating for 25 min, during which time the colour changed to green. The green solution was allowed to stand undisturbed in a closed flask for a period of 1 week. Emerald green

prismatic crystals appeared which were collected by filtration, washed with $Et_2O$ (2x3 mL) and dried in air. Yield, 75%. The dried solid analyzed as solvent free. Anal. Calc. for $C_{50}H_{50}Ni_2TbN_9O_{20}Cl_2$ : C, 41.58; H, 3.50; N, 8.73. Found : C, 41.70; H, 3.40; N, 8.59%. IR data (KBr, $cm^{-1}$): 3388 sb, 2978 m, 2936 w, 2896 w, 1604 s, 1572 m, 1470 s, 1440 s, 1384 s, 1314 s, 1224 s, 1136 s, 1090 s, 1056 s, 902 w, 774 m, 686 m, 638 m, 626 m, 544 w, 476 m.

**$[Ni_2Gd\{(py)_2C(OEt)O\}_3\{(py)_2C(OH)O\}(NO_3)(H_2O)](ClO_4)_2\cdot 2.3EtOH$ (2·2.3EtOH).** Solid $(py)_2CO$ (0.147 g, 0.80 mmol) was added to a green solution of $Ni(ClO_4)_2\cdot 6H_2O$ (0.146 g, 0.40 mmol) in EtOH (15 mL). The solid dissolved immediately followed by an abrupt colour change to brown-red. Solid $LiOH\cdot H_2O$ (0.017 g, 0.40 mmol) and solid $Gd(NO_3)_3\cdot 6H_2O$ (0.063 g, 0.14 mmol) were then added sequentially. The resulting solution was stirred under mild heating for 25 min, during which time the colour changed to green. The green solution was allowed to stand undisturbed in a closed flask for a period of 1 week. Emerald green prismatic crystals appeared which were collected by filtration, washed with $Et_2O$ (2x3 mL) and dried in air. Yield, 75%. The dried solid analyzed as solvent free. Anal. Calc. for $C_{50}H_{50}Ni_2GdN_9O_{20}Cl_2$ : C, 41.63; H, 3.50; N, 8.74. Found : C, 41.58; H, 3.40; N, 8.88%. IR data (KBr, $cm^{-1}$): 3388 sb, 2978 m, 2936 w, 2896 w, 1604 s, 1573 m, 1469 s, 1440 s, 1384 s, 1313 s, 1224 s, 1136 s, 1090 s, 1055 s, 902 w, 775 m, 686 m, 638 m, 625 m, 542 w, 475 m.

**$[Ni_2Y\{(py)_2C(OEt)O\}_4(NO_3)(H_2O)]_2[Y(NO_3)_5](ClO_4)_2\cdot 2.6EtOH\cdot 3H_2O$ (3·2.6EtOH·3H$_2$O).** Solid $Y(NO_3)_3\cdot 6H_2O$ (0.039 g, 0.10 mmol) was added to a brown solution of $[Ni(O_2CMe)\{(py)_2CO\}\{(py)_2C(OH)_2\}](ClO_4)$ (**5**, 0.060 g, 0.10 mmol) in EtOH (20 mL). The solid dissolved immediately and the resulting solution was stirred under mild heating for 30 min. During the stirring period the colour of the solution changed gradually to green. The green solution was allowed to stand undisturbed in a closed flask for a period of 1 week. Emerald green prismatic crystals appeared which were collected by filtration, washed with $Et_2O$ (2x3 mL) and dried in air. Yield, 70%.

The dried solid analyzed as EtOH-free (**3**·3$H_2O$). Anal. Calc. for $C_{104}H_{114}Ni_4Y_3N_{23}O_{50}Cl_2$ : C, 40.83; H, 3.76; N, 10.53. Found : C, 40.94; H, 3.63; N, 10.60%. IR data (KBr, $cm^{-1}$): 3394 sb, 2974 m, 2930 w, 2896 w, 1604 m, 1570 w, 1472 s, 1442 m, 1384 s, 1316 s, 1224 m, 1089 s, 1054 s, 904 w, 780 m, 686 m, 636 m, 626 m, 542 w, 474 m.

**$[Ni_2Dy\{(py)_2C(OEt)O\}_4(NO_3)(H_2O)]_2[Dy(NO_3)_5](ClO_4)_2$·2.6EtOH·3$H_2O$**

**(4·2.6EtOH·3$H_2O$).** Solid $Dy(NO_3)_3$·6$H_2O$ (0.046 g, 0.10 mmol) was added to a brown solution of $[Ni(O_2CMe)\{(py)_2CO\}\{(py)_2C(OH)_2\}](ClO_4)$ (**5**, 0.060 g, 0.10 mmol) in EtOH (15 mL). The solid dissolved immediately and the resulting solution was stirred under mild heating for 30 min. During the stirring period the colour of the solution changed gradually to green. The green solution was allowed to stand undisturbed for a period of 1 week. Emerald green prismatic crystals appeared which were collected by filtration, washed with $Et_2O$ (2x3 mL) and dried in air. Yield, 65%. The dried solid analyzed as **4**·2$H_2O$. Anal. Calc. for $C_{104}H_{112}Ni_4Dy_3N_{23}O_{49}Cl_2$ : C, 38.29; H, 3.47; N, 9.88. Found : C, 38.40; H, 3.51; N, 10.01%. IR data (KBr, $cm^{-1}$): 3394 sb, 2974 m, 2930 w, 2897 w, 1604 m, 1570 w, 1472 s, 1443 m, 1384 s, 1316 s, 1225 m, 1090 s, 1054 s, 904 w, 780 m, 686 m, 635 m, 625 m, 542 w, 472 m.