

## Binuclear and Trinuclear Complexes with *exoO*<sub>2</sub>-Cyclam

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### Additional Synthetic Details for other (less pure) salts of the complexes

#### *Co(2,3-dioxo-1,4,8,11-tetraazacyclotetradecane)*

Applying Schlenk techniques, NaOH (8 mg, 0.2 mmol) in methanol (5 ml) was added to 2,3-dioxo-1,4,8,11-tetraazacyclotetradecane (23 mg, 0.1 mmol) in methanol (10 mL) with stirring. Stirring was then stopped and a layer of hexane (6 mL) added. Cobalt (II) nitrate (29 mg, 0.1 mmol) in methanol (10 mL) was then added drop-wise over a period of 30 minutes and left to stand overnight. The solution became a deep red colour and a trace amount of fine precipitate formed. The precipitate was removed by cannular filtration and the filtrate reduced to dryness, washed with acetone and dried to yield a water and alcohol soluble red / brown solid (35 mg, >100 %) containing Co(2,3-dioxo-1,4,8,11-tetraazacyclotetradecane)Na<sup>+</sup>.

(<sup>+</sup>ve FAB) *m/z*: 369 (MNaNO<sub>3</sub>)<sup>+</sup>, 309 (MNa)<sup>+</sup>, 286 (M)<sup>+</sup>, 329 / 176 [matrixNa]<sup>+</sup>.

#### *Zn(2,3-dioxo-1,4,8,11-tetraazacyclotetradecane)*

NaOH (8 mg, 0.2 mmol) in methanol (5 ml) was added to 2,3-dioxo-1,4,8,11-tetraazacyclotetradecane (23.1 mg, 0.1 mmol) in methanol (10 mL) with stirring. Stirring was then stopped and a layer of hexane (4 mL) added. Zinc (II) nitrate (29 mg, 0.1 mmol) in methanol (10 mL) was then added drop-wise via pressure equalised dropping funnel over a period of 40 minutes and left to stir overnight. In the absence of a precipitate, removal of the solvent yielded a water and alcohol soluble white powder - Zn(2,3-dioxo-1,4,8,11-tetraazacyclotetradecane)Na<sup>+</sup> (26 mg, 0.08 mmol, 85 %).

(<sup>+</sup>ve FAB) *m/z*: *m/z* 313 with Zn isotope cluster (MNa)<sup>+</sup>, 251 (MNa-Zn)<sup>+</sup>.

IR (KBr, cm<sup>-1</sup>) (3538m, 3471w, 3403w) br, 3230m, 2922m, 2845m, 2364m, 1638s, 1614s, 1590m, 1383s, 1359m, 1321m, 1181m, 1085m, 1061m, 830s, 806s, 604w.

#### *Cu<sub>2</sub>Mn(2,3-dioxo-1,4,8,11-tetraazacyclotetradecane)<sub>2</sub>.2BF<sub>4</sub>*

Cu[2,3-dioxo-1,4,8,11-tetraazacyclotetradecane] (72.5 mg, 0.25 mmol, 2 equiv) was stirred and suspended in distilled water (5 mL). Manganese (II) dichloride (15.7 mg, 0.125 mmol, 1 equiv) in distilled water (5 mL) was then added drop-wise over 30 minutes. The mixture was allowed to stir for at least 1 hour (or overnight). Sodium tetrafluoroborate (27.5 mg, 0.25 mmol, 2 equiv) in methanol (5 mL) was then added in portions. No precipitate formed over 24 hours. The water was removed and the residue twice taken up into ethanol and filtered. The filtrate was reduced to dryness and the residue dried under vacuum to yield Cu<sub>2</sub>Mn(2,3-dioxo-1,4,8,11-tetraazacyclotetradecane)<sub>2</sub>.2BF<sub>4</sub> (77 mg, 0.098 mmol, 79 %) as a pale purple solid.

(<sup>+</sup>ve FAB) *m/z*: 670 (M+2H<sub>2</sub>O)<sup>+</sup>, 633 (M)<sup>+</sup>, trace 345 (M-(CuL)<sup>+</sup>, 329 [(matrix)<sub>2</sub>Na]<sup>+</sup>, 290 (M-LCuMn)<sup>+</sup>, 176 [matrixNa]<sup>+</sup>.

#### *Cu<sub>2</sub>Ni(exoO<sub>2</sub>-cyclam)<sub>2</sub>.2BF<sub>4</sub>*

Cu[2,3-dioxo-1,4,8,11-tetraazacyclotetradecane] (72.5 mg, 0.25 mmol, 2 equiv), nickel (II) nitrate (36.8 mg, 0.125 mmol, 1 equiv) and sodium tetrafluoroborate (27.5 mg, 0.25 mmol, 2 equiv) were reacted as described for compound **5** to yield a pale purple powder (92 mg, 0.11 mmol, 91 %). (<sup>+</sup>ve FAB) *m/z*: 700, 637 (M)<sup>+</sup>, trace 347 (M-(CuL)<sup>+</sup>, 329 [(matrix)<sub>2</sub>Na]<sup>+</sup>, 290 (M-LCuNi)<sup>+</sup>, 176 [matrixNa]<sup>+</sup>.

#### Alternative route to **6**

Iron(II) chloride (60 mg, 0.3 mmol) in methanol (20 mL) was added drop-wise to 2,3-dioxo-1,4,8,11-tetraazacyclotetradecane (46 mg, 0.2 mmol) in mixture of distilled water (10 mL) and methanol (5 mL) with stirring. A gradual yellow to greenish colour change was observed and upon stirring for a further 48 hours a

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red/brown suspension formed. A third of the suspension was taken and copper(II) nitrate (15.8 mg, 0.07 mmol) added drop-wise as a methanolic solution. Subsequent addition of sodium tetraphenyl-borate (0.14 mmol, 2 equiv) caused immediate precipitation. The solution was removed by cannular filtration and the solid residue washed with distilled water and dried. The product was then dissolved in acetone, filtered and the solvent removed under vacuum to yield  $\text{Cu}_2\text{Fe}(\text{2,3-dioxo-1,4,8,11-tetraazacyclotetradecane})_2\cdot 2\text{BPh}_4$  (35 mg, 0.028 mmol, 42 %).

(<sup>+</sup>ve FAB) *m/z*: 666, 632 + isotopes (M)<sup>+</sup>, 531, 509 (M-2Fe)<sup>+</sup>, 391, 290 (M-LCuFe)<sup>+</sup>.

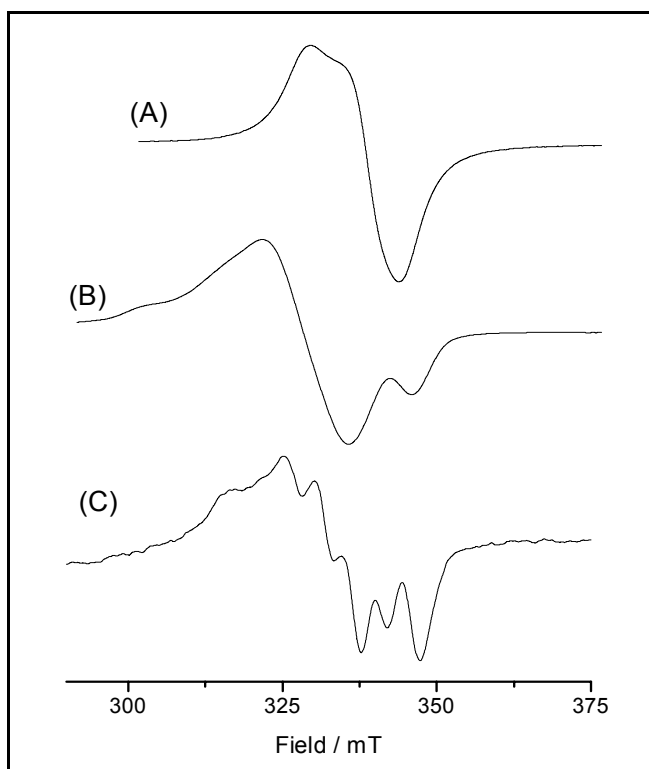
$\text{Cu}_2\text{Fe}(\text{2,3-dioxo-1,4,8,11-tetraazacyclotetradecane})_2\cdot 2\text{BF}_4$

$\text{Cu}[\text{2,3-dioxo-1,4,8,11-tetraazacyclotetradecane}]$  (72.5 mg, 0.25 mmol, 2 equiv), iron (II) dichloride (17 mg., 0.125 mmol, 1 equiv) and sodium tetrafluoroborate (27.5 mg, 0.25 mmol, 2 equiv) were reacted as described for compound **20** to yield  $\text{Cu}_2\text{Fe}(\text{2,3-dioxo-1,4,8,11-tetraaza-cyclotetradecane})_2\cdot 2\text{BPh}_4$  (82 mg, 0.1 mmol, 82 %) as a yellow-brown powder.

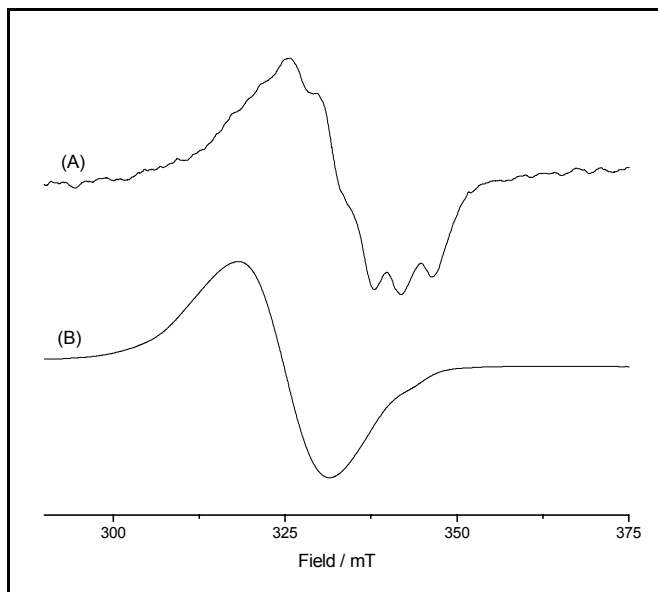
(<sup>+</sup>ve FAB) *m/z*: 869, 633 (M)<sup>+</sup>, 329 [(matrix)<sub>2</sub>Na]<sup>+</sup>, 290 (M-LCuFe)<sup>+</sup>, 176 [matrixNa]<sup>+</sup>.

$\text{Cu}_2\text{Mn}(\text{2,3-dioxo-1,4,8,11-tetraazacyclotetradecane})_2\cdot 2\text{PF}_6$  (8.3 mg, 0.01 mmol, 44%) was produced as above except with tetrabutyl-ammonium hexafluorophosphate (TBA PF<sub>6</sub>) (2 equiv). [(<sup>+</sup>ve FAB) *m/z*: 635/3 (M)<sup>+</sup>, 344 (M-(CuL)<sup>+</sup>, 290 (M-LCuMn)<sup>+</sup>, 242(TBA)<sup>+</sup>]. Likewise,  $\text{Cu}_2\text{Mn}(\text{1,4,8,11-tetraazatetracyclododecane-2,3-dione})_2\cdot 2\text{CF}_3\text{SO}_3^-$  was produced as above except with silver triflate (light sensitive compound).

#### EPR and Magnetic Data



(a)



(b)

Fig. S1: (a) X-Band EPR spectra of (A) a powder sample of **1** (9.81 GHz) and of **1** in an 0.01M LiClO<sub>4</sub> solution in acetonitrile at (B) 77 K (9.48 GHz) and (C) room temperature (9.70 GHz). The LiClO<sub>4</sub> is necessary to increase the solubility of the complex by interaction with the chelating oxygen atoms. Spectrum C clearly indicates the presence of more than one species. (b) X-band EPR spectrum of an acetonitrile solution of **9** (A) at room temperature (9.71 GHz) and (B) at 77 K (9.48 GHz).

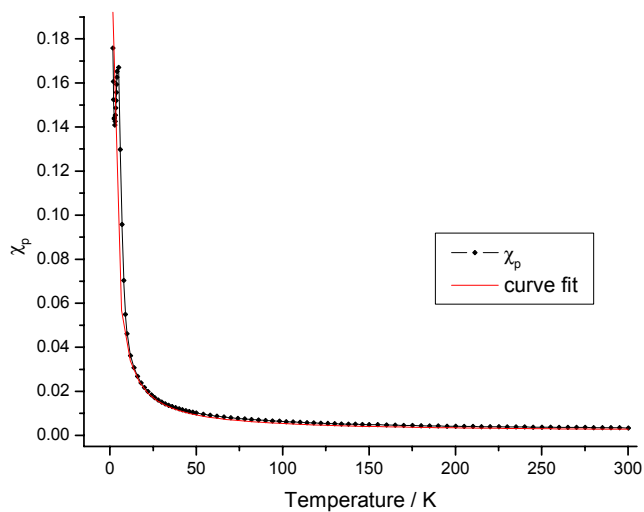


Fig. S2: Fit to trinuclear isotropic exchange model for complex **3**

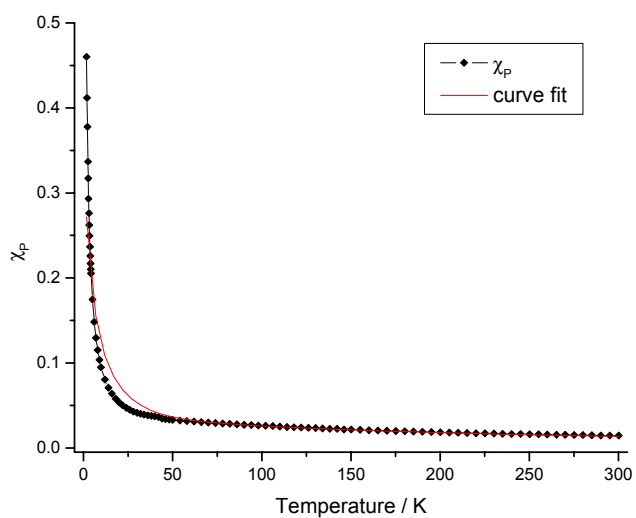


Fig. S3: Fit to trinuclear isotropic exchange model for complex 5

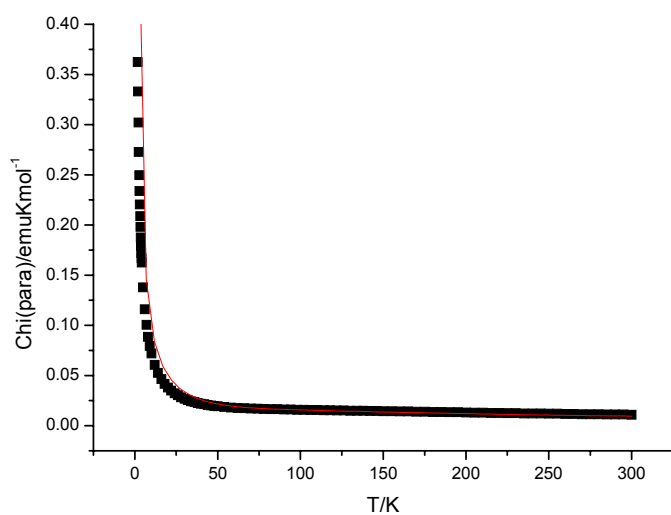


Fig. S4: Fit to trinuclear isotropic exchange model for complex 6

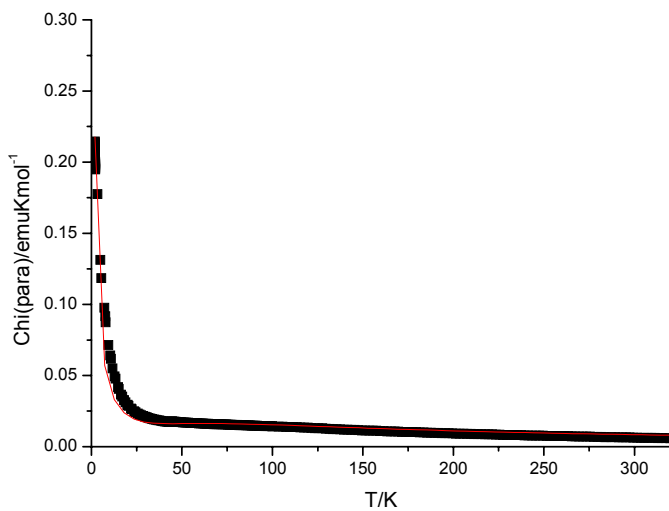


Fig. S5: Fit to trinuclear isotropic exchange model for complex 7 with  $S = 3/2$  for the central  $\text{Co(II)}$ .

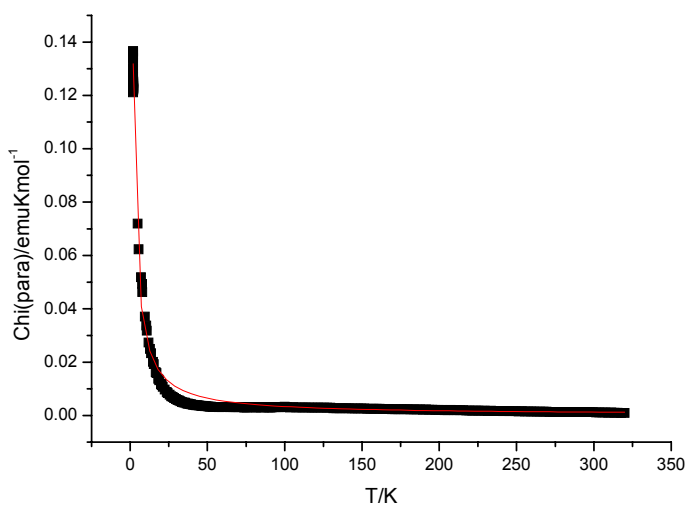


Fig. S6: Fit to Curie-Weiss law for complex 8 giving  $C = 0.32 \text{ emuKmol}^{-1}$  and  $\theta = -0.5 \text{ K}$

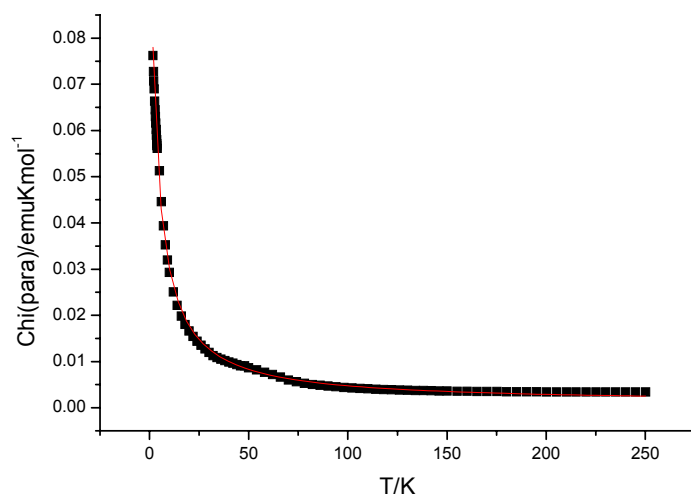


Fig S7: Fit to Curie-Weiss model for complex **10**