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Metal complexes as potential ligands: The deprotonation of aminephenolate metal complexes.

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Abstract: The cationic nickel, copper and zinc complexes of tris-((2-hydroxybenzyl)-aminoethylamine (H6TrenSal) have been deprotonated using potassium hydroxide. The nickel complex can be sequentially deprotonated to form a series of compounds namely, $[(\text{H6TrenSal})\text{Ni}]^+$, $[(\text{H6TrenSal})\text{Ni}]$ and "$[(\text{H6TrenSal})\text{Ni}]\text{K}$". The latter is isolated as a mixture of species namely $[\{(\text{H6TrenSal})\text{Ni}\}\text{K}(\text{EtOH})]_2$, $[\{(\text{H6TrenSal})\text{Ni}\}\text{K}(\text{EtOH})_2\text{-}\mu\text{-OH}_2]_2$ and $[\{(\text{H6TrenSal})\text{Ni}\}\text{K}(\text{EtOH})_2\text{-}\mu\text{-EtOH}]_2$. which co-crystallise in a roughly 50:27.5:22.5 ratio. In contrast the deprotonation of $[(\text{H6TrenSal})\text{M}]^+$ (M = Cu, Zn) results in the formation of tetrameric complexes $[(\{(\text{H6TrenSal})\text{Ni}\}\text{K}(\text{OH}_2)_2)_4(\mu_4\text{-OH}_2)]$.

We have recently turned our attention to the use of multidentate ligands as a way of constructing multimetallic complexes [1-3]. The synthetic protocols employed to produce these compounds routinely use non-coordinating bases such as triethylamine to deprotonate the ligand during the reaction [3, 4]. Our previous work on Tris-(2-hydroxybenzyl)-aminoethylamine (H6TrenSal**; figure 1, **a**) identified an interesting pair of encapsulated cationic nickel complexes namely [(H6TrenSal)(H$_2$O)Ni]$^+$ and [(H6TrenSal)Ni]$^+$ [3]. Both of these species are six coordinate. The former is a simple cation which utilises one phenoxide from the multidentate ligand leaving a coordination site free for a water molecule. The latter is more interesting as it is devoid of the coordinated water and thus employs two phenols to complete the nickel coordination sphere (figure 1, **b**). However, the second phenol remains protonated and the complex remains cationic. The analogous copper and zinc complexes ([(H6TrenSal)Cu]$^+$; [(H6TrenSal)Zn]$^+$) can also be formed. These are found to be cationic five coordinate species which display two uncoordinated phenolates (figure 1, **c**). It is intriguing that the nickel complexes do not naturally deprotonate to form neutral species as is found for the related tris-((2-hydroxy-5-bromo-benzyl)-aminoethylamine (H6Tren5BrSal; figure 1, **d**) [3]. Our interest in this process stems not just from our desire to design and synthesise further multimetallic complexes but to try an understand why [(H6TrenSal)Cu]$^+$ and [(H6TrenSal)Zn]$^+$ (figure 1, **c**) do not readily form trimetallic lanthanoid complexes similar to the corresponding nickel complex [3-6]. It is likely that the altered reaction pathway stems either from the nature of the uncoordinated phenolates or the manner in which the ligands deprotonate during reaction. We have thus elected to investigate the reaction of caustic base with the cationic metal (M = Ni, Cu, Zn) complexes of H6TrenSal as a model of this process.
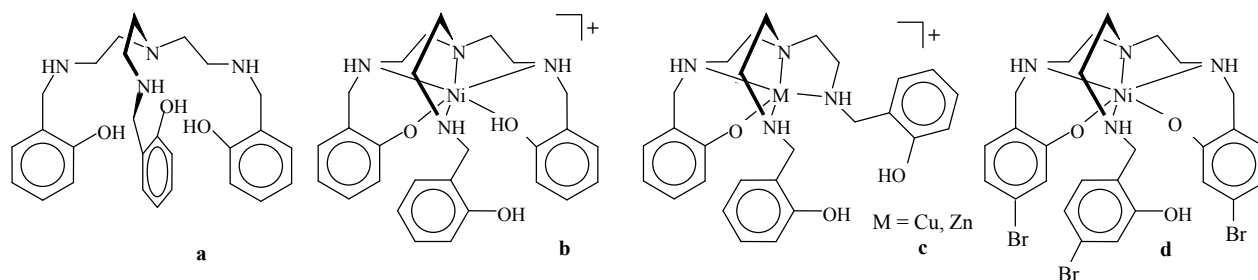
Figure 1. Tris-((2-hydroxybenzyl)-aminoethylamine (H6TrenSal, **a**) and the structures of its corresponding nickel (**b**) copper and zinc (**c**) complexes. The unique neutral motif of tris-((2-hydroxy-5bromo-benzyl)-aminoethylamine ([(H6Tren5BrSal)Ni], **d**) is shown right [3].

[(H6TrenSal)Ni]Br was prepared using a method reported previously [7] and its structure displays the expected features. The nickel coordinates to all four nitrogens of the Tren moiety and thus sits within (N2-Ni-Nx < 90°) the pocket created by the ligand. Two

phenols complete the N_4O_2 coordination sphere leaving the third phenol and the bromide as non-coordinating entities (figure 2a). The Ni-O bond lengths of the coordinated phenols reflect the protonation of O1, the Ni-O2 distance (2.000(2)Å) being significantly shorter than that found for the corresponding Ni-O(1)H (2.266(3)Å). Treatment of this complex with potassium hydroxide leads to formation of [(H6TrenSal)Ni] [8] (figure 2b). The nickel complex has now di-deprotonated to form a neutral species. Although the gross structures of the neutral and cationic species (figure 2a) look similar the Ni-O bond lengths (Ni-O1, 2.070(4)Å, Ni-O2 2.072(4)Å) found for the neutral species are intermediate between those discussed above and identical to one-another, reflecting the fact that the two donor atoms (O1, O2) now have identical character.
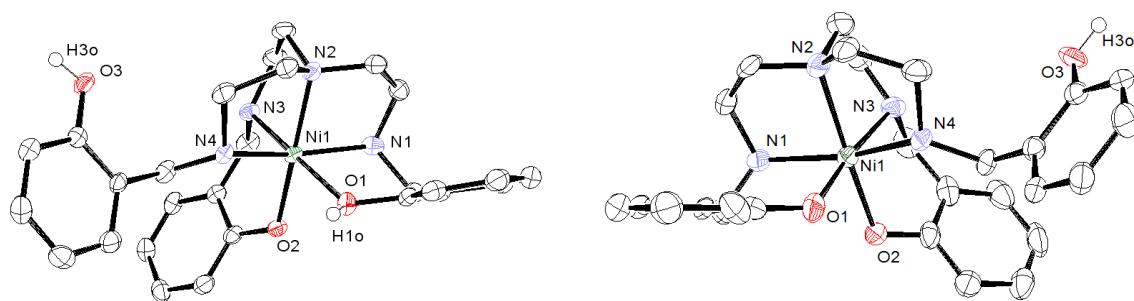

Figure 2. Left: The X-ray crystal structure of [(H6TrenSal)Ni] Br. The non-coordinating bromide counter ion is not shown. The refinement allows the placement of the hydrogens. However only those on O1 and O3 are shown, thus confirming that the H6TrenSal ligand is only mono-deprotonated. Right: The X-ray crystal structure of [(H6TrenSal)Ni]. The refinement allows the placement of the hydrogens. However only the one O3 is shown, thus confirming that the H6TrenSal ligand is now di-deprotonated. The thermal ellipsoids are given at 50% probability. The key metrical parameters of the complexes are given in table 1.

Treatment of [(H6TrenSal)Ni]Br with excess potassium hydroxide leads to the formation of a third ([{(H6TrenSal)Ni}K(EtOH)]$_2$, figure 3 top left), a fourth ([{(H6TrenSal)Ni}K(EtOH)$_2$-μ-OH$_2$]$_2$ top right) and a fifth ([{(H6TrenSal)Ni}K(EtOH)$_2$-μ-EtOH]$_2$, bottom), complex in this series which all co-crystallise in a roughly 50:27.5:22.5% ratio [9]. All these species contain a potassium coordinated to an [(H6TrenSal)Ni] moiety and these species are all undoubtedly related, possibly existing in solution as a dynamic equilibrium.*** The major component (50%) in the crystal mixture, [{(H6TrenSal)Ni}K-μ-EtOH]$_2$, is constructed by employing the nickel complexes displayed in figures 2 as ligands with the potassium binding directly with O1 and O2. The motif is completed by the deprotonation of the pendant phenoxide (O3) thus forming the desired anionic nickel moiety (figure 3). The formation of the anionic metalloligand can be further confirmed by inspecting
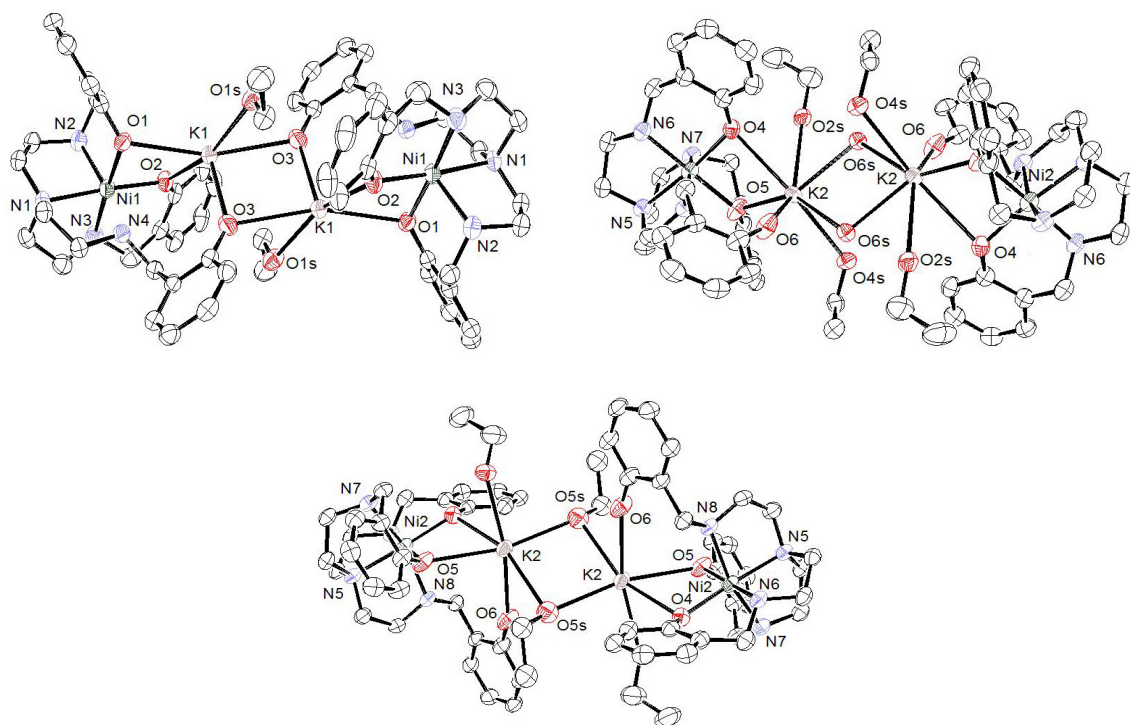
Figure 3. The molecular structure of [{(H6TrenSal)Ni}K(EtOH)]$_2$ (top left), [{(H6TrenSal)Ni}K(EtOH)$_2$-μ-OH$_2$]$_2$ (top right) and [{(H6TrenSal)Ni}K(EtOH)$_2$-μ-EtOH]$_2$ (bottom). These three species co-crystallise in a roughly 50:27.5:22.5% ratio with the latter two species occupying one disordered site. The thermal ellipsoids are given at 50% probability. The key metrical parameters of the major product, [{(H6TrenSal)Ni}K(EtOH)]$_2$ are given in table 1.

the Ni-O distances (Ni-O1, 2.0624(18); Ni-O2, 2.0143(17). These are of the same magnitude and commensurate with those reported for deprotonate phenoxide discussed above (figure 2). [{(H6TrenSal)Ni}K(EtOH)$_2$-μ-OH$_2$]$_2$ and [{(H6TrenSal)Ni}K-μ-EtOH]$_2$ are found occupying the same position in the unit cell with a site occupancy of roughly 1:1 (figure 3). In retrospect, this is understandable as these two complexes differ only in the manner in which the solvents (EtOH, H$_2$O) in the core of the complex are accommodated. Extracting the metrical parameters from the two species on this site is problematic. However, rudimentary distances for Ni-O5 and Ni-O4 have been retrieved (2.062 and 2.056 respectively) which are comparable to those reported for [(H6TrenSal)Ni] above (figure 2) suggesting that metalloligand has been fully deprotonated. By inference the bridging species are thus identified as EtOH and H$_2$O throughout. The positioning of the pendant phenoxide in these complexes which coordinates solely to potassium facilitates the dimerisation of the motif. A similar result is observed for the lanthanoids [3-6]. However, here the lower charge of the potassium fulfils the charge balance on the metalloligand and aggregation thus takes place around a centrosymmetric di-potassium core. With higher charged cations i.e. lanthanoid the charge imbalance drives the reaction such that the ligands nucleate around a single trivalent cation.

The nickel complexes isolated have a remarkably similar configuration. A comparison of the metrical parameters for the three complexes together with those of [{(H6TrenSal)Ni}$_2$La(MeOH)]$^+$ and [(H6Tren5BrSal)Ni] create a picture of a nickel in an environment which does not change markedly in response to charge or the presence of external metal centres (table 1). In this sense the [(H6TrenSal)Ni)] moiety would seem to be behaving as an univalent anion. However the importance of the metal centre to the manner in which the donors sites are arranged is somewhat different to metalloligands where the metal (Cd, Hg, Ga, In) is an intrinsic part of the ligand rather than the framework around which it wraps [10-12].

	N_{apex}-Ni (Å)	<Ni2-Ni-N (^{o})
[(H6TrenSal)Ni]$^+$	2.092(3)	82.9(1)
		84.1(1)
		84.4(1)
[(H6TrenSal)Ni]	2.128(5)	81.8(2)
		83.2(2)
		83.7(2)
[{(H6TrenSal)Ni}K(EtOH)]$_2$	2.115(2)	81.20(8)
		83.78(8)
		83.98(8)
[(H6Tren5BrSal)Ni] [3]	2.127	81.33
		81.04
		84.00
[{(H6TrenSal)Ni}$_2$La(MeOH)]$^+$ [3]	2.103	80.92
		83.39
		85.47
	2.108	84.68
		84.15
		80.34

Table 1. The key metrical parameters for [(H6TrenSal)Ni]$^+$ (figure 1**a**), [(H6TrenSal)Ni], [{(H6TrenSal)Ni}K(EtOH)]$_2$, [(H6Tren5BrSal)Ni] and [{(H6TrenSal)Ni}$_2$La(MeOH)]$^+$ [3]. [{(H6TrenSal)Ni}K(EtOH)$_2$-μ-OH$_2$]$_2$ and [{(H6TrenSal)Ni}K-μ-EtOH]$_2$ are not included as there is greater uncertainty regarding the metrical data.

The analogous copper and zinc complexes ([(H6TrenSal)M]$^+$, M= Cu, Zn) have also been prepared (figure 1 **c**). However, they are both five coordinate complexes employing an N$_4$O motif with two phenolates rotated away from the metal binding pocket [3]. If the
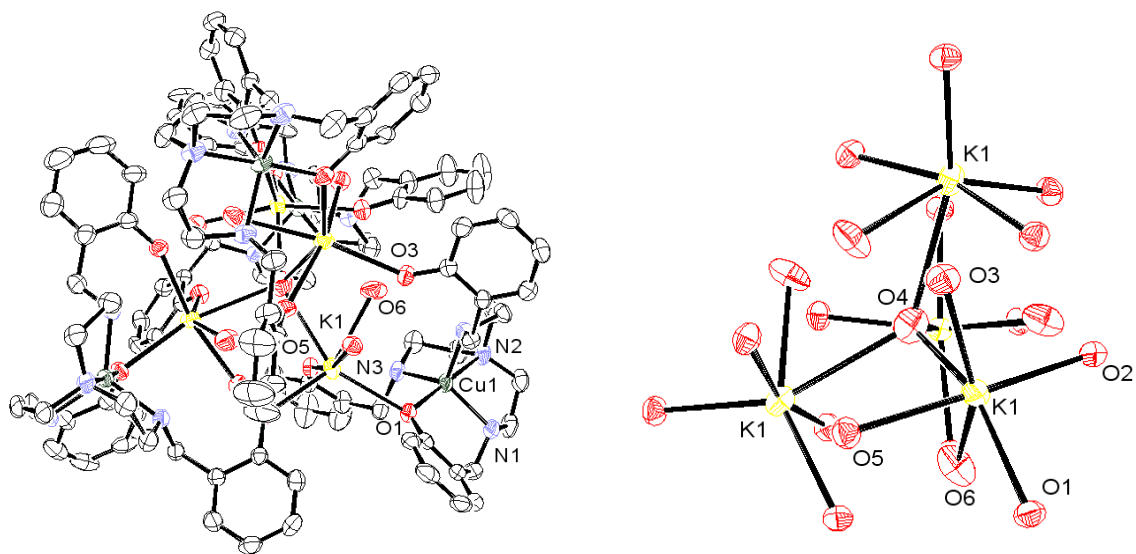
Figure 4. (left) The X-ray crystal structure of $[(\{(H6TrenSal)Cu\}K)(OH_2)_2)_4\text{-}\mu_4\text{-}OH_2]$. The expansion of the motif from monopotassiate to tetrapotassiate is supported by the bridging nature of the two pendant phenolates (cf nickel figure 2). (right) The alkali metal core of the complex. The unique μ_4-water molecule at the core of the complex is more clearly seen. The zinc complex is not shown as it is isostructural to the copper species presented. The thernal ellipsoids are given at probability 50%.

uncoordinated phenolate is critical to the structures adopted (figure 2) then the presence of a second pendant phenolate might be expected to expand the structural catalogue of these potassiated metal complexes further. Thus reactions of the metal nitrates, H6TrenSal and KOH or the treatment of $[(H6TrenSal)M]^+$ (M= Cu, Zn) with potassium hydroxide leads to the formation of the tetranuclear system $[(\{(H6TrenSal)M\}K)(OH_2)_2)_4(\mu_4\text{-}OH_2)]$ (M= Cu, Zn) (figure 4) [13]. These complexes are viewed as a series of concentric layers of atoms starting from the unique water molecule (O4) at the core of the complex. This is surrounded by four equidistant potassium atoms (K-O 3.0821(8), Cu; 3.0870(11), Zn) arranged relative to one another as a distorted tetrahedron. In turn the coordination sphere of the potassium atoms are completed by five further oxygen donors; two from water molecules and three from the H6TrenSal ligands (O1, O2, O3). Crucially the potassium is didentate to one of the [(H6TrenSal)Cu] species (O1, O2) and monodentate to the phenolate (O3) on an adjacent [(H6TrenSal)Cu] unit. The expansion of the motif from monometallic (figure 2) to octametallic (M_4K_4, figure 4) undoubtedly hinges on the exposed nature of the additional pendant phenolate on the parent [(H6TrenSal)Cu] complex.

In the established nickel-lanthanoid complexes of H6TrenSal [3, 4] phenolate pairs bridge the lanthanoid and nickel leaving only a single pendant phenolate to coordinate exclusively to the rare earth. This facilitates the formation of a compact trimetallic motif, the lanthanoid being held close to the nickel centre. However, for copper and zinc complexes (figure 4) two phenolates bind solely to the potassium creating a more open and complex structure. This observation goes some way to explain why we have had difficulty in generating mixed lanthanoid complexes with $[(H6TrenSal)Cu]^+$ and $[(H6TrenSal)Zn]^+$ [3, 4]. Although there is sufficient space within the core of $[(\{(H6TrenSal)Cu\}K)(OH_2)_2)_4(\mu_4-OH_2]$ to accommodate an atom with lanthanoid dimensions, the build up of charge within the core as a result of the aggregation of four trivalent cations will destabilise the trimetallic motif.
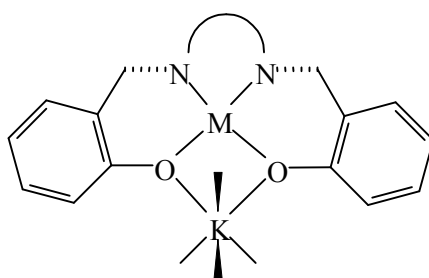

Figure 5. A schematic of the manner in which potassium chelates to tetradentate N_2O_2 Schiff base complexes and their modified amine complexes [14–17]. Dotted lines denote -CH=N- and -CH$_2$-NH- respectively

Potassiated tetradentate Schiff base and modified Schiff base complexes have been reported previously [14-17]. In these compounds the alkali metal is chelated between the phenoxide donors of the neutral metal complex (figure 5). The third phenolate present in the heptadentate ligands discussed here provides the alkali metal with a selection of potential donor sites and the resulting structures indicate that binding to the pendant phenol and a metal bound bridging phenolate is preferential to chelation to phenolate pairs.

Supporting information

Details of the X-ray crystal structure determinations may be obtained from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax +44-1223-336033; e-mail deposit@ccdc.cam.ac.uk or www:http://ccdc.cam.ac.uk) on request quoting the depository numbers ccdc 693152 – 693156 and 761468

Footnotes

** H6TrenSal: tris-((2-hydroxybenzyl)-aminoethylamine. This compound is derived from a Schiff base species (TrenSal). The H6 prefix is used to show that the three imine groups have been fully hydrogenated

*** Numerous attempts to generate crystals of independent complexes were attempted. Many were badly disordered. One such structure ccdc993154 has been deposited in the database. It would seem that the method reported here used to prepare this complex generates a mixture. There are parallels with the syntheses of [(H6TrenSal)Ni] NO_3 and [(H6TrenSal)Ni(OH$_2$)] NO_3 [3].

**** the formula given is for a 50:25:25 ratio of the three complexes

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7. **Synthesis of [(H6TrenSal)Ni] Br**; H6TrenSal (1.10 g, 2.37 mmol) was dissolved in methanol (20 ml) and then added to a methanolic solution (5 ml) of NiBr$_2$.3H$_2$O (0.65 g, 2.37 mmol). The mixture was stirred for 5 minutes whereupon a deep purple colour

forms. The solution was stirred at 50°C for further 15 minutes, then hot filtered and allowed to cool. A purple product forms which can be collected. Crystals were grown from slow evaporation of the saturated solution of the complex. Yield 72%. Found: C, 44.02; H, 6.10; N, 7.85 % Expected for $C_{27}H_{34}N_4BrNiO_3$ $7H_2O$: C, 44.65; H, 6.52; N, 7.71%. λmax (solid) 568 nm. IR ν/cm^{-1} 3405 (br OH, 2850-2950 (NH), 1465 (C=C), 1295 (C-O), 760 (arom). Mass spec. (ESI) *m/z* 521. Crystal data: [(H6TrenSal)Ni] Br .MeOH, Orthorhombic Pbca, a = 18.4509(4) Å, b = 15.3424(3) Å, c = 19.9382(4) Å, V = 5644.1(2) $Å^3$, Z = 8, independent reflections = 6219, R_{obs} = 0.0488, wR2 = 0.1026, GOF = 1.012, No of parameters = 350.

8. **Synthesis of [(H6TrenSal)Ni]:** [(H6TrenSal)Ni] Br (0.50 g, 0.81 mmol) and KOH (0.10 g, 1.8 mmol) were placed in methanol (20 ml). As the solution was heated to reflux the reagents dissolved with the solution changing from purple to blue in colour. The reflux was maintained for 90 mins. The solvent was removed and the resulting very pale blue material extracted with hot methanol. The solution was filtered and allowed to cool and evaporate whereupon a pale blue powder forms. Crystals were grown by vapour diffusion of diethyl-ether into a solution of the product in methanol. Yield 52%. Found: C, 57.57; H, 6.21; N, 9.73 % Expected for $C_{27}H_{34}N_4NiO_3$ $MeOH$ $2H_2O$: C, 57.06; H, 7.18; N, 9.50 %. λmax (solid) 595, 980 (shoulder) nm. IR ν/cm^{-1} 1475, 1440, 1290, 755. Mass spec. (ESI) *m/z* 521 $[MH]^+$. Crystal data: [(H6TrenSal)Ni]. 0.65 MeOH. 1.15 H_2O, Orthorhombic Pna2$_1$, a = 15.9243(8) Å, b = 11.7363(5) Å, c = 15.4517(7) Å, V ($Å^3$) 2887.8(2), Z = 4, independent reflections = 6334, R_{obs} = 0.0653, wR2 = 0.1367, GOF = 0.945, No of parameters = 364.

9. **Synthesis of [{(H6TrenSal)Ni}K(EtOH)]$_2$/ [{(H6TrenSal)Ni}K(EtOH)$_2$-μ-OH$_2$]$_2$/ [{(H6TrenSal)Ni}K(EtOH)-μ-EtOH]$_2$** [(H6TrenSal)Ni] Br (1.10 g, 1.8 mmol) was refluxed in ethanol (25 ml) with KOH (0.65 g,).12 mmol) for 2hr. The solvent was removed and the blue material extracted into the minimum amount of ethanol, filtered through celite and crystallised by vapour diffusion with diethyl ether. Yield 30% Found: C, 56.14; H, 6.99; N, 8.50% Expected for $C_{60}H_{85}K_2N_8Ni_2O_{9.5}$****: C, 56.92; H, 6.77; N, 8.85%. λmax (solid) 575, 980 (shoulder) nm. Mass spec. (ESI) *m/z* 521, $[(H6TrenSal)Ni]^+$ (100%), 1117, $[{(H6TrenSal)Ni}_2K_2]^+$. IR ν/cm^{-1} 1590, 1475, 1455, 1295, 755. Crystal data; 0.5 [{(H6TrenSal)Ni}K(EtOH)]$_2$ 0.275 [{(H6TrenSal)Ni}K(EtOH)$_2$-μ-OH$_2$]$_2$ 0.225 [{(H6TrenSal)Ni}K(EtOH)-μ-EtOH]$_2$ .0.45Et$_2$O, Triclinic, P-1, a = 10.3775(9) Å, b = 16.8281(14), c = 18.6220(13), α =

85.761(6), β = 78.459(6), γ = 85.312(7), V 3170.1(4) (Å^3), Z = 1, independent reflections = 9785, R_{obs} = 0.0388, wR2 = 0.1016, GOF = 1.002, No of parameters = 805.

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13. **Synthesis of [({(H6TrenSal)M}K)(OH$_2$)$_2$)$_4$(μ_4-OH$_2$)] (M = Cu, Zn):** H6TrenSal (0.1 g, 0.22 mmol) was dissolve in 15ml methanol. An equimolar amount of the required metal nitrate was added and the mixture was stirred at 50 °C for 5 minutes. To this solution was added a methanolic (10ml) solution of potassium hydroxide KOH (0.012 g, 0.22 mmol). The solution was stirred for further 5minutes, allowed to cool and filtered. For M = Cu: Crystals were grown by slow evaporation of the saturated solution. Yield 48%. Found: C, 52.13; H, 5.93; N, 8.86 %. Expected for $C_{108}H_{150}Cu_4K_4N_{16}O_{21}$. $4H_2O$: C, 52.07; H, 6.39; N, 9.00 %. λmax (solid) 440, 680, 780 nm. IR ν/cm^{-1} 1595 (s), 1460 (s), 1445 (s), 1295 (m), 765 (w). Mass spec. (ESI) m/z 526, [(H6TrenSal)Cu]$^+$ (100%). Crystal data: [({(H6TrenSal)Cu}K)(OH$_2$)$_2$)$_4$(μ_4-OH$_2$)], Cubic, I-43d, a = 32.9427(9) Å, V (Å^3) 35750.1(17), Z = 12, independent reflections = 6833,R_{obs} = 0.0427, wR2 = 0.1004,GOF = 1.038, No of parameters = 366. For M = Zn: The solution was reduced in volume (~5 ml), refiltered and crystallised by vapour diffusion using diethyl-ether. Found: C, 52.22; H, 6.15; N, 8.63 %. Expected for $C_{108}H_{150}K_4N_{16}O_{21}Zn_4$.$4H_2O$: C, 51.92; H, 6.37; N, 8.96 %. ν/cm^{-1} 1590 (s), 1480 (s), 1450 (s), 1300 (m), 765 (m). Crystal data: [({(H6TrenSal)Zn}K)(OH$_2$)$_2$)$_4$(μ_4-OH$_2$)]: Cubic, I-43d, a = 33.0490(2) Å, V (Å^3) 36097.3(4), Z = 12, independent reflections = 5922, R_{obs} = 0.0463, wR2 = 0.1315, GOF = 1.120, No of parameters = 357. Mass spec. (ESI) m/z 527, [(H6TrenSal)Zn]$^+$ (100%), 1110, [{(H6TrenSal)Zn}KOH$_2$]$^+$ (18%). Alternatively: [(H6TrenSal)M] NO$_3$ (M = Cu, Zn: 0.50 g, ~0.81 mmol) and KOH (0.10 g, 1.8 mmol) were placed in methanol (20 ml). As the solution was heated to reflux the reagents dissolved. The reflux was maintained for 1 hr. The solvent was removed and the resulting material extracted. Crystallisation was effected as stated above. The spectroscopic data retrieved from these materials matched those given above. . Found: C, 52.60; H, 6.31; N, 9.01 %. Expected for $C_{108}H_{150}K_4N_{16}O_{21}Zn_4$.$4H_2O$: C, 51.92; H, 6.37; N, 8.96 %. Found: C, 51.70; H, 5.95; N, 8.73 %. Expected for $C_{108}H_{150}Cu_4K_4N_{16}O_{21}$. $4H_2O$: C, 52.07; H, 6.39; N, 9.00 %.

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