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In Situ Synthesis of Trisubstituted Methanol Ligands and Their Potential as One-Pot Generators of Cubane-like Metal Complexes

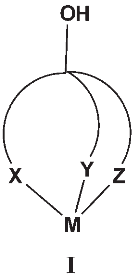
Brendan F. Abrahams, Timothy A. Hudson, and Richard Robson*[a]

Abstract: Two different one pot routes to a variety of metal cubane compounds are reported; one route is based on an in situ benzilic acid type rearrangement and the other involves in situ nucleophilic attack at a ketone. Diketosuccinic acid in basic solution in the presence of certain divalent metal ions undergoes a benzilic acid type rearrangement to generate the carbon oxyanion, $C(CO_2^-)_3O^-$, which serves as a cubane-forming bridging ligand in a series of octanuclear complexes of composition $[M_8\{C(CO_2)_3O\}_4](H_2O)_{12}$ (M = Mg, Mn, Fe, Co, Ni, Zn). At the heart of each of these highly symmetrical aggregates is an M_4O_4 cubane core, each oxygen component of which is provided by the alkoxo centre of a $C(CO_2^-)_3O^-$ ligand. Reaction of 2,2′-pyridil, $(2\text{-}C_5H_4N)COCO(2\text{-}C_5H_4N)$, and calcium nitrate in basic alcoholic solution, which proceeds by a similar benzilic acid type rearrangement, gives the cubane compounds, $[Ca_4L_4(NO_3)_4]$ in which $L = (2\text{-}C_5H_4N)_2C(COOR)O^-$ (R = Me or Et). Nucleophilic attack by bisulfite ion at the carbonyl carbon atom of 2,2′-dipyridyl ketone in the presence of certain divalent metals generates the electrically neutral complexes, $[\{(C_5H_4N)_2SO_3C(OH)\}_2M]$ (M = Mn, Fe, Co, Ni, Zn and Cd). Cubane-like complexes $[M_4\{(C_5H_4N)_2SO_3C(O)\}_4]$ (M = Zn, Mn) can be obtained directly from 2,2′-dipyridyl ketone in one-pot reaction systems (sealed tube, 120 °C) if a base as weak as acetate ion is present to deprotonate the OH group of the initial $[(C_5H_4N)_2SO_3C(OH)]^-$ bisulfite addition compound; the $[(C_5H_4N)_2SO_3C(O)]^{2-}$ ligand in this case plays the same cubane-forming role as the ligands $C(COO^-)_3O^-$ and $(2\text{-}C_5H_4N)_2C(COOR)O^-$ above. When excess sodium sulfite is used in similar one-pot reaction mixtures, the monoanionic complexes, $[M_3Na\{(C_5H_4N)_2SO_3C(O)\}_4]^-$ (M = Zn, Mn, Co) with an M_3NaO_4 cubane core, are formed directly from 2,2′-dipyridyl ketone.

Keywords: alcohols · cubanes · metal clusters · N ligands · self-assembly

Introduction

Cubane-related metal complexes have aroused much interest because of their unusual properties, their potential as single-molecule magnets[1] and their biological relevance—interest considerably intensified recently by the identification of a Mn_3Ca cubane-like core at the active site of photosystem II.[2] Herein we demonstrate that appropriately trisubstituted methanols, which can act as tridentate ligands to form mononuclear complexes, as in **I**, can also, after deprotonation at the alcohol, be "turned inside out", as in **II**, to act as generators of a potentially wide range of cubane-like complexes. We also present two different routes by which these tri-substituted methanols can be generated very simply in the presence of metal ions to yield complexes of types **I** or **II** directly in one-pot reactions, each way offering prospects of wide generality. One of these routes is based on a benzilic acid type rearrangement of an appropriate α-di-



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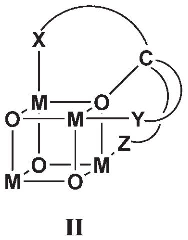

II

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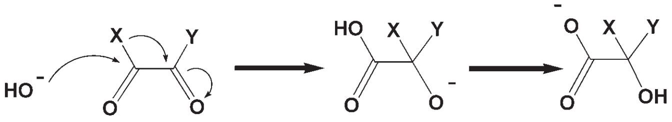
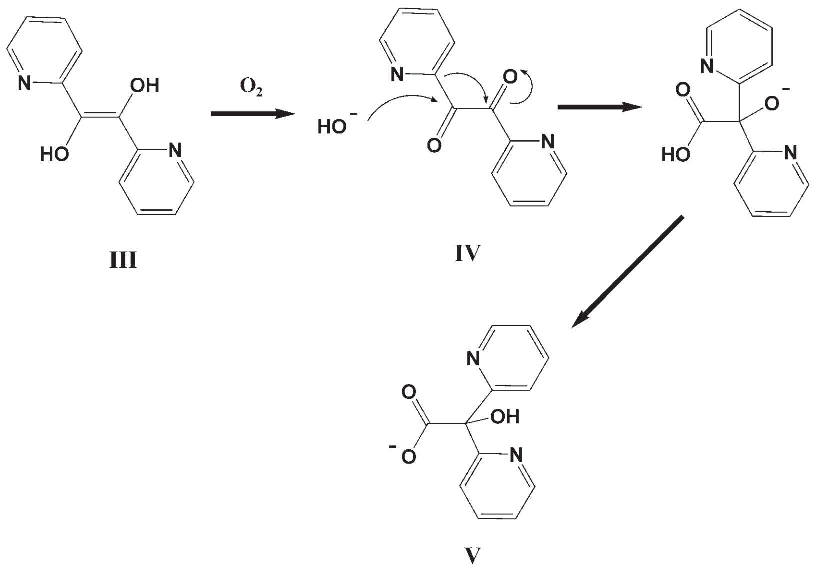
ketone, whilst the other involves attack of an appropriate nucleophile upon an appropriate ketone.

Results and Discussion

Tri-substituted methanol ligands by a benzilic acid type rearrangement: The reaction pathway for the classical base-induced benzilic acid type rearrangement is represented in Scheme 1. The crucial step in the overall process is the migration of the group X from the carbon atom attacked by OH^- to the adjacent carbon atom, whereby the carbon centre initially under attack becomes a carboxylate. It has been demonstrated that the benzilic acid rearrangement can be promoted by transition-metal cations.[3] We have reported that 2,2′-pyridoin, $(2\text{-}C_5H_4N)C(OH)=C(OH)(2\text{-}C_5H_4N)$, structure **III**, undergoes the sequence of oxidation and rearrangement reactions represented in Scheme 2, when treated with nickel nitrate in the presence of air.[4] The product of the benzilic acid type rearrangement, the pyridilate ligand, **V** in Scheme 2, was isolated as the crystalline nickel(II) bis-pyridilate complex, $[Ni\{(C_5H_4N)_2C(OH)(CO_2)\}_2]$, which was shown by X-ray crystallography to have the structure presented in Figure 1.[4]



Scheme 1. The pathway of the hydroxide-promoted benzilic acid rearrangement.



Scheme 2. The Ni^{II}- or Co^{II}- promoted conversion of pyridoin to pyridilate. No doubt the various intermediates are coordinated to the metal cation: this scheme is intended only to indicate the skeletal rearrangements within the organic fragment.

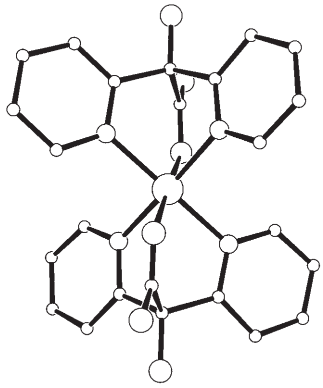
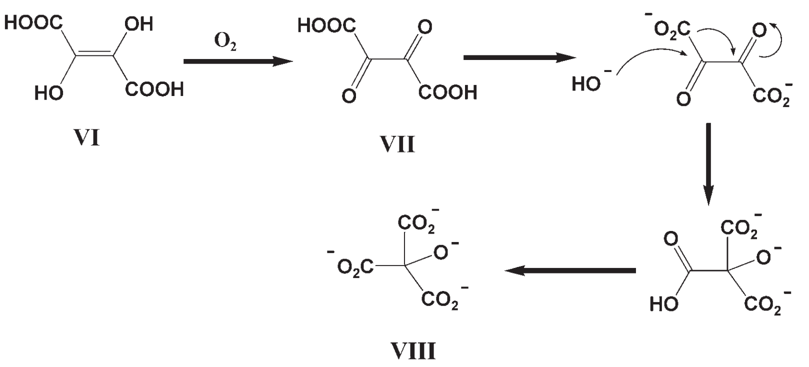


Figure 1. The structure of the nickel(II) bis-pyridilate complex, $[Ni\{(C_5H_4N)_2C(OH)(CO_2)\}_2]$.[4] Circles in order of increasing radius represent C, N, O and Ni respectively.

Dihydroxyfumaric acid, HOOCC(OH)=C(OH)COOH, structure **VI** (see Scheme 3), is a close relative of the 2,2′-pyridoin (**III**) referred to above in that both are ene-diols carrying potential metal-binding terminal substituents. In a recent preliminary communication[5] we reported that dihydroxyfumaric acid, in the presence of certain divalent metal ions in basic aqueous solution at room temperature, undergoes a sequence of aerial oxidation and rearrangement, represented in Scheme 3, closely analogous to the conversion of pyridoin to pyridilate. The tri-substituted methanol derivative arising from the benzilic acid like rearrangement in this case is the previously undocumented oxy-anion of carbon, $C_4O_7^{4-}$, in which the methoxide carbon atom is substituted by three carboxylate residues, that is $^-OC(CO_2^-)_3$, **VIII** in Scheme 3. As reported in our preliminary communication[5] a series of isostructural crystalline solids of composition $[(M^{II})_8(C_4O_7)_4(H_2O)_{12}]\cdot 24H_2O$ can be obtained from simple one-pot reactions using dihydroxyfumaric acid in basic aqueous solution at room temperature for M = Zn, Co, Fe and Mg.[5] We were, however, unable to isolate analogous solids for M = Mn or Ni from reactions with dihydroxyfumaric acid. We now report that when diketosuccinic acid, **VII** in Scheme 3, is used as starting material, Mn and Ni derivatives isostructural with the Zn, Co, Fe and Mg derivatives can be readily obtained; also, the Zn, Co, Fe and Mg derivatives can be obtained equally satisfactorily from either dihydroxyfumaric acid or diketosuccinic acid. The structure of the octanickel molecule in $[(Ni^{II})_8(C_4O_7)_4(H_2O)_{12}]\cdot 24H_2O$ is represented in Figure 2. The $^-OC(CO_2^-)_3$



Scheme 3. The metal ion promoted conversion of dihydroxyfumarate to $C_4O_7^{4-}$. No doubt the various intermediates are coordinated to the metal cation: this scheme is intended only to indicate the skeletal rearrangements within the organic fragment.

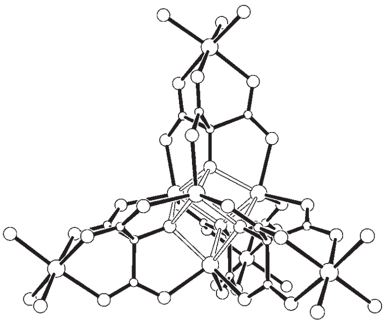


Figure 2. The structure of the octanickel molecule in $[(Ni^{II})_8(C_4O_7)_4(H_2O)_{12}]\cdot 24H_2O$. The Zn, Co, Fe, Mg and Mn derivatives are isostructural). Circles in order of increasing radius represent C, O and Ni respectively.

ligand plays the role seen in **II**. The alkoxo oxygen centres of four $^-OC(CO_2^-)_3$ ligands, acting as μ_3 bridges, provide four corners of a cubane-like core, the other four corners being provided by M^{II} centres, which are forced by the "short reach" of the carboxylate side arms to adopt a trigonal-prismatic coordination environment. This central $[(M^{II})_4(C_4O_7)_4]^{8-}$ unit is then ideally set up to chelate to four other appended metal centres that have an octahedral coordination environment completed by three facially disposed aqua ligands, as can be seen in Figure 2. The hydroxy-tricarboxylic conjugate acid corresponding to $^-OC(CO_2^-)_3$, namely $HOC(COOH)_3$, would be expected to be extremely prone to decarboxylation to give hydroxymalonic acid, $HOCH(COOH)_2$. The $[OC(CO_2)_3]^{4-}$ unit, "frozen" and preserved in the above crystalline metal derivatives, presumably survives in solution without loss of CO_2 because, from the moment of its generation, it is stabilised by chelation to metal centres. In this connection it is interesting to note that at only slightly higher temperatures (40–50 °C) reaction mixtures containing the same components generate crystalline products containing the trianion $^-OCH(CO_2^-)_2$ formed by decarboxylation of $^-OC(CO_2^-)_3$. together with still intact $^-OC(CO_2^-)_3$.[6] These products also contain cubane-related nuclei, similar to but significantly different from those in the above $[(M^{II})_8(C_4O_7)_4(H_2O)_{12}]\cdot 24H_2O$ series of compounds, linked together into an infinite 3D network with the (10,3)-*a* topology.[6]

Cubane-related structures can be obtained in which a pyridilate unit (**V**), generated in situ by benzilic acid rearrangement, has been turned "inside out" as in **II**, but in the systems we have isolated in crystalline form, the carboxylic group has suffered esterification, despite which it is still able to act as a donor to the metal. Solutions containing calcium nitrate, 2,2′-pyridil (**IV**) and triethylamine in either methanol or ethanol in a sealed tube at approximately 90 °C give well-formed crystals, suitable for single-crystal X-ray crystallography, of composition $[Ca_4L_4(NO_3)_4]$, where L^- = the alkoxide ion (2-$C_5H_4N)_2C(COOR)–O^-$, (R = Me or Et). Esterification of the carboxylic group was indicated by elemental analysis, IR spectroscopy (ν_{CO}, 1723 cm^{-1}) and single-crystal X-ray diffraction. Papaefstathiou et al. have also reported metal-promoted reactions of pyridil that result in the generation of unusual pentanuclear complexes.[7]

The structure of the cubane-like molecule (ethyl ester) is shown in Figure 3a from which the nitrate units, which are chelated to the metal centres, are omitted for clarity. The structure of the methyl ester is very similar. Calcium centres are all equivalent and eight-coordinate. The metal coordination environment, shown in Figure 3b, consists of the three cubane-forming μ_3-alkoxo donors (Ca–O 2.423(3) Å), a pyridyl donor from each of two separate ligands (Ca–N 2.497(3), 2.541(3) Å), an ester carbonyl oxygen donor from a third ligand (Ca–O 2.455(3) Å) and a chelating nitrato donor (Ca–O 2.471(3), 2.529(3) Å). One pyridyl residue and the ester unit from each ligand are positionally disordered, the other pyridyl unit being ordered. These ordered pyridyl units, one from each of the four ligands, are shown in Figure 3c, in which the orientations of the four nitrato ligands are also shown. The ordered pyridyl units make close face-to-face contacts with a partner which is somewhat displaced so that the closest contacts are between nitrogen atoms (N···N 3.391(7) Å); such pairs can be seen in Figure 3c. The non-coordinated NO bond of the nitrato ligand is oriented close to parallel with an edge of the cube as is apparent upon inspection of Figure 3c.

Tri-substituted methanol ligands formed in situ by nucleophilic attack at a ketone: A very simple one-pot route, of potentially wide applicability, to tridentate methanol ligands of the type seen in **I**, devised by one of us almost forty years ago, consists of metal-promoted attack by appropriate nucleophiles upon an appropriate ketone, such as 2,2′-dipyridyl ketone, as shown in Scheme 4.[8] Our work was focussed on

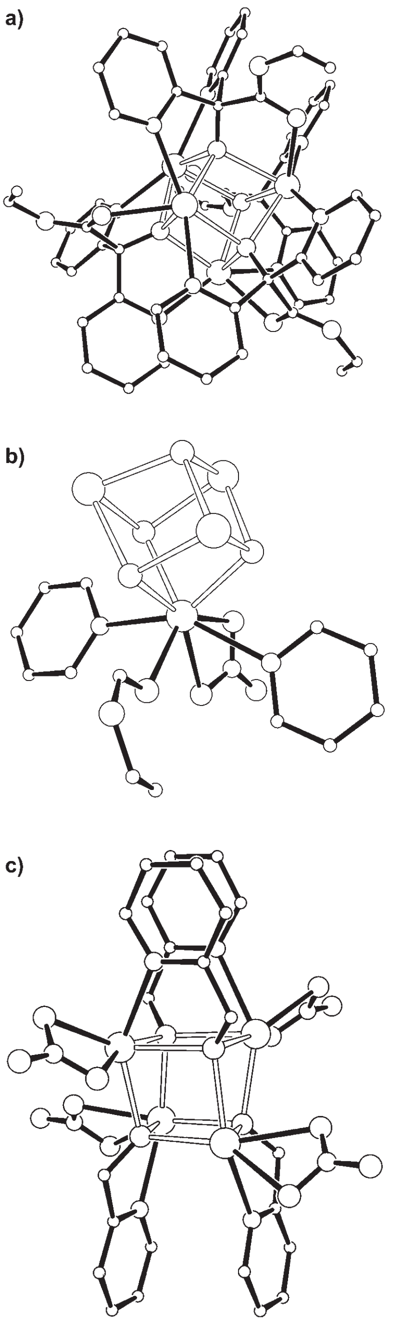
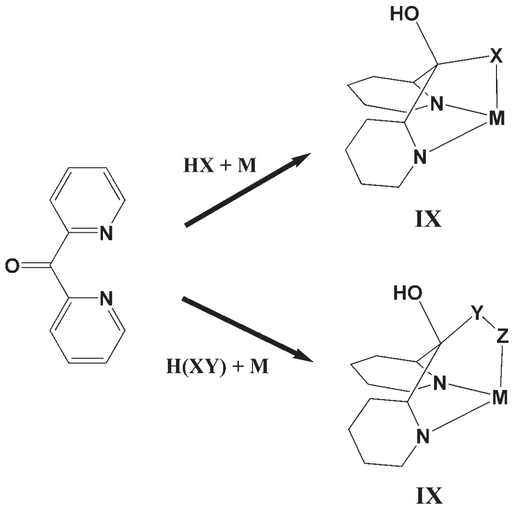


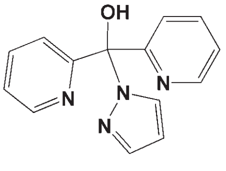
Figure 3. a) The structure of $Ca_4L_4(NO_3)_4$, where L^- = the alkoxide ion $(2\text{-}C_5H_4N)_2C(COOEt){-}O^-$. Circles in order of increasing radius represent C, N, O and Ca respectively. b) The coordination environment of the calcium centre. c) The orientations of the ordered pyridyl residues (one from each ligand) and the nitrato ligands.

2,2′-dipyridyl ketone, but there is every reason to expect that other appropriate ketones could likewise generate facially chelating tridentate tri-substituted methanol ligands. In a preceding paper by the same authors it was shown, for the first time, that when 2,2′-dipyridyl ketone is *N*,*N*′-chelated to Cu^{II} in aqueous solution the ketonic group becomes hydrated to generate the gem-diol $(C_5H_5N)_2C(OH)_2$;[9] this was established by using "sporting" techniques such as vibrational, electronic and ESR spectroscopy.[9] Relief of steric congestion involving the pyridine H atoms adjacent to N was identified as a major driving force for this conversion of the trigonal ketonic carbon atom into a tetrahedral centre, enabling the metal complex product to adopt a configuration in which the two pyridine rings are far from coplanar. This ketone hydrate can be seen as an example of a product of the type **IX** in Scheme 4. In those days "unsporting" crystallographic techniques were time-consuming and relatively infrequently used but in more recent years a very large number of structural studies have been conducted upon complexes of the gem-diol of 2,2′-dipyridyl ketone, $(C_5H_5N)_2C(OH)_2$, first identified by us; in some of these examples the diol is present in the electrically neutral form,[10] whilst in others the coordinated hydroxy group has been deprotonated, and these latter examples include both mononuclear[11] and cubane-like cases.[12]



Scheme 4. Nucleophilic attack at 2,2′-dipyridyl ketone generating tridentate trisubstituted methanol ligands. Products of the type **IX**, which upon coordination yield one six-membered chelate ring and two five-membered rings are generated when the same atom in the nucleophile attacking carbon also provides the dative bond to the metal. In products of the type **X** an atom adjacent to the nucleophilic centre provides the coordinate bond and metal chelates having three six-membered are formed.

In very belated continuation of our earlier work with 2,2′-dipyridyl ketone, we report here unambiguous crystallographic evidence that, upon reaction with pyrazole in the presence of nickel(II) a new C−N bond between the ketonic carbon atom and a nitrogen atom of pyrazole is formed to generate an N3 tridentate ligand, $[(C_5H_4N)_2(C_3H_3N_2)C(OH)]$, (structure **XI**). We emphasise the extreme simplicity of this chemistry: the reaction is conducted in aqueous solution at room temperature. There is no evidence for any reaction whatsoever between pyrazole and 2,2′-dipyridyl ketone in the absence of the metal ion, but when nickel ni-



XI

trate is present, crystals of composition $[Ni\{(C_5H_4N)_2(C_3H_3N_2)C(OH)\}_2(NO_3)_2]\cdot 4H_2O$ separate. X-ray crystallography shows that two $[(C_5H_4N)_2(C_3H_3N_2)C(OH)]$ ligands chelate in a *facial* manner, the two pyrazole units being *trans* to one another, as shown in Figure 4. The electrically neutral dipyridylpyrazolato ligand, forming three six-membered chelate rings as in **X** in Scheme 4, is geometrically almost perfect for *facial* attachment to an octahedral metal centre like Ni^{II}, giving almost exactly right angular N-Ni-N angles.

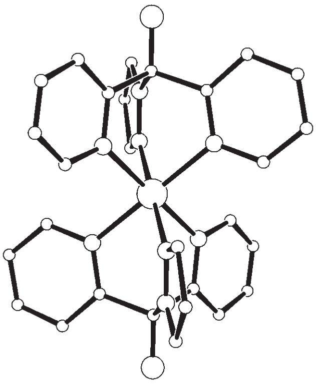
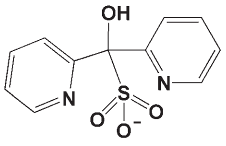


Figure 4. The structure of the $[Ni\{(C_5H_4N)_2(C_3H_3N_2)C(OH)\}_2]^{2+}$ ion in $[Ni\{(C_5H_4N)_2(C_3H_3N_2)C(OH)\}_2](NO_3)_2\cdot 4H_2O$. Circles in order of increasing radius represent C, N, O and Ni.

Aqueous solutions containing 2,2′-dipyridyl ketone, various divalent transition-metal salts and bisulfite ion in 2:1:2 proportions afford, in a one-pot system, crystalline products containing electrically neutral complexes of composition $[M\{(C_5H_4N)_2(SO_3)C(OH)\}_2]$, (M = Mn, Fe, Co, Ni, Zn, Cd) in which the tridentate ligand is the monoanionic $[(C_5H_4N)_2(SO_3)C(OH)]^-$, **XII**, generated by formation of a new C–S bond between the ketonic carbon atom and the sulfite sulfur atom. The structure of the molecule is shown in Figure 5. The very close structural relationship between the pyridilate complexes obtained by the benzilic acid rearrangement route and the complexes obtained by the addition of sulfite to dipyridyl ketone is apparent on comparison of Figure 5 and Figure 1.



XII

We find that it is possible to generate directly from dipyridyl ketone, in a one-pot system, cubane-related complexes of this $[(C_5H_4N)_2(SO_3)C(OH)]^-$ ligand; thus, reaction of $Zn(NO_3)_2$ with 2,2′-dipyridyl ketone, sodium sulfite and sodium acetate (the latter intended to promote formation of the cubane by deprotonation of the alcohol) in 1:1:1:1 proportions in aqueous solution in sealed tubes at 120 °C gives a crystalline product of composition $[Zn_4\{(C_5H_4N)_2(SO_3)C(O)\}_4]\cdot 6H_2O$ containing discrete, electrically neutral cubane-related molecules with the structure shown in Figure 6. The water molecules lie in channels that extend in a direction parallel to the *a* axis.

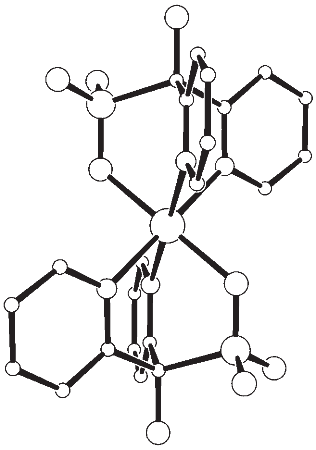


Figure 5. The structure of the electrically neutral complex $[M\{(C_5H_4N)_2(SO_3)C(OH)\}_2]$, (M = Mn, Fe, Co, Ni, Zn and Cd). Circles in order of increasing radius represent C, N, O, S and M.

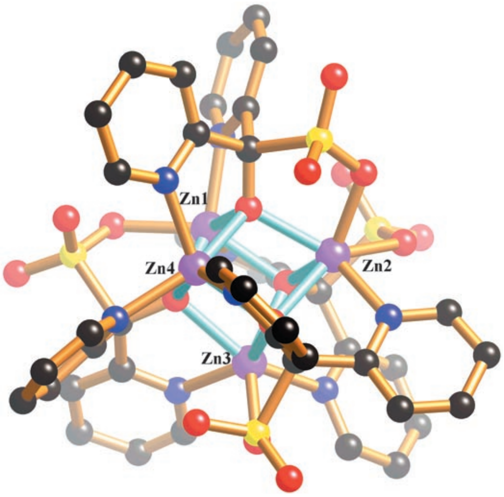


Figure 6. The structure of the $[Zn_4\{(C_5H_4N)_2(SO_3)C(O)\}_4]$ cubane unit. The cubane unit is highlighted in pale blue. Zn atoms labelled Zn1–Zn4 are inequivalent. Color code: C black, N blue, O red, S yellow, Zn purple.

All four zinc centres are different and the molecule is chiral; indeed the crystal as a whole is chiral (space group $P2_12_12_1$), all molecules in the one crystal having the same hand. All four metal centres are six-coordinate with a coordination geometry close to trigonal prismatic, similar to the metal coordination geometries seen in the series of C_4O_7-cubane derivatives referred to above and shown in Figure 2. Zn1 and Zn3 each have two pyridyl donors and one sulfonate donor, Zn2 has one pyridyl donor and two sulfonate donors, whilst Zn4 has three pyridyl donors. Reaction of $Zn(NO_3)_2$ with 2,2′-dipyridyl ketone, sodium sulfite and sodium acetate in 1:2:1:1 proportions (a two-fold increase in the proportion of dipyridyl ketone) in aqueous solution in a sealed tube at 120 °C gives a product of composition $[Zn_4\{(C_5H_4N)_2(SO_3)C(O)\}_4]\cdot 3H_2O\cdot[(C_5H_4N)_2CO]$, containing uncoordinated dipyridyl ketone in the crystal lattice. The packing of the complexes is very similar to that observed in the case of the hydrate, $[Zn_4\{(C_5H_4N)_2(SO_3)C(O)\}_4]\cdot 6H_2O$, and this is reflected in the similarity of the unit cell dimensions. Instead of the intercomplex spaces being occupied by water molecules, dipyridyl ketone molecules are trapped within the crystal lattice. Crystals of an isostructural manganese derivative $[Mn_4\{(C_5H_4N)_2(SO_3)C(O)\}_4]\cdot 3H_2O\cdot[(C_5H_4N)_2CO]$, can be obtained similarly.

Reaction of $Zn(NO_3)_2$, 2,2′-dipyridyl ketone, sodium sulfite and sodium acetate in 1:1:5:1 proportions in aqueous solution in a sealed tube at 120 °C, conditions very similar to those above except that sodium sulfite is present in large excess, affords a crystalline product of composition $[Zn_3Na\{(C_5H_4N)_2(SO_3)C(O)\}_4]\cdot Na\cdot 13.5H_2O$ which contains a monoanionic Zn_3Na cubane-related core with the structure shown in Figure 7.

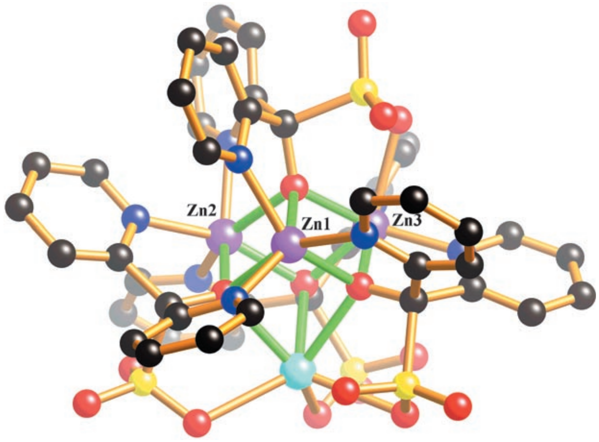


Figure 7. Structure of the monoanionic $[Zn_3Na\{(C_5H_4N)_2(SO_3)C(O)\}_4]^-$ cubane unit in $[Zn_3Na\{(C_5H_4N)_2(SO_3)C(O)\}_4]\cdot Na\cdot 13.5H_2O$. The cubane unit is highlighted in green. Color code: C black, N blue, O red, Zn purple, Na light blue.

The three inequivalent Zn centres have close to trigonal-prismatic six-coordinate environments. The arrangement of the four ligands around the cubane core is different from that in the Zn_4 and Mn_4 complexes described above. In the Zn_3Na case, two of the zinc centres, Zn1 and Zn2, have three pyridyl donors, whilst Zn3 has two pyridyl donors and one sulfonate. The three remaining sulfonate residues available all associate with the sodium centre. Isostructural Mn_3Na and Co_3Na analogues can likewise be obtained. We note that the cubane core of the Mn_3Na complex shows a striking structural similarity to the Mn_3Ca cubane core recently reported for photosystem II.[2]

Concluding Remarks

In summary, the results presented here support the proposal that appropriately tri-substituted methanols may be effective generators of cubane-related metal complexes; the generality of the proposal receives further support from our observation that citric acid (another tri-substituted methanol, in this case providing three terminal carboxylate donors) affords an isostructural series of cubane-like complexes with a range of divalent metal ions (Mg, Mn, Fe, Co, Ni and Zn).[13] In addition the effectiveness of two different strategies is demonstrated, both simple and of potentially wide applicability, for the in situ generation of the tri-substituted methanols, followed, in the same one-pot reaction system, by the assembly of the targeted cubane. The approaches to cubane-like complexes described here may provide useful models for biological systems and present opportunities for the creation of new chemistry, for example one of our special interests is to use these approaches to provide, again in one-pot reaction systems, new infinite networks constructed from cubane-like building blocks. Since certain cubane nuclei have been shown to undergo facile electron transfer, such networks may have interesting electronic properties. Finally, the results presented here provide striking examples of the spontaneous assembly of targeted systems of very considerable complexity from simple reactants in one pot reaction systems.

Experimental Section

Syntheses and details of X-ray crystallography: Data for all compounds were collected on a Bruker SMART CCDC Area Detector. Structure solutions and refinements were performed by using SHELX programs.[14] Absorption corrections were applied using the SADABS[15] program.

$[M^{II}_8(C_4O_7)_4(H_2O)_{12}]\cdot 24H_2O$ (M = Zn, Mg, Co, Fe, Mn, Ni): To a suspension of disodium diketosuccinic acid (100 mg, 0.45 mmol) in water (30 mL) was added a solution of $M^{II}(OAc)_2$ (0.90 mmol) in water (30 mL). (In the Fe case, $FeSO_4$ (0.90 mmol) was used with NaOAc (1.80 mmol)). The solution was kept at 40 °C overnight. Crystals of $[(M^{II})_8(C_4O_7)_4(H_2O)_{12}]\cdot 24H_2O$ that separated from the solution were collected, washed with water and dried in air. Yields (Zn: 114 mg, 63 %; Co: 128 mg, 67 %; Mg 5 mg, 3 %, Fe: 71 mg, 36 %, Mn: 110 mg, 54 %, Ni: 12 mg, 6 %).

Crystal data for $C_{16}H_{72}Mn_8O_{64}$: 0.20 × 0.18 × 0.18 mm, cubic, space group $I\bar{4}3m$, $a = 15.2889(4)$ Å, $V = 3573.79(16)$ Å^3, $\rho_{calcd} = 1.606\ g\,cm^{-1}$, $2\theta_{max} = 55.0°$, $\lambda = 0.71073$ Å, $T = 130$ K, no. of measured (and independent) reflections: 11207 (797), $\mu = 1.481\ mm^{-1}$, min./max. apparent transmission ratio: 0.851, no. of parameters: 60, $R1\ [I > 2\sigma(I)] = 0.0469$, $wR2$ (all data) = 0.1307, max./min. residual electron density: 0.55/−0.43 e Å^{-3}.

Crystal data for $C_{16}H_{72}Ni_8O_{64}$: 0.15 × 0.15 × 0.15 mm, cubic, space group $I\bar{4}3m$, $a = 14.9208(5)$ Å, $V = 3321.82(19)$ Å^3, $\rho_{calcd} = 1.758\ g\,cm^{-1}$, $2\theta_{max} = 55.0°$, $\lambda = 0.71073$ Å, $T = 130$ K, no. of measured (and independent) reflections: 10446 (747), $\mu = 2.340\ mm^{-1}$, min./max. apparent transmission ratio: 0.9196, no. of parameters: 47, $R1\ [I > 2\sigma(I)] = 0.0535$, $wR2$ (all data) = 0.1633, max./min. residual electron density: 0.76/−0.68 e Å^{-3}.

$[Ca_4\{(C_5H_4N)_2(COOR)C(O)\}_4](NO_3)_4$ (R=Me, Et): Solutions of 2,2′ pyridil (100 mg, 0.47 mmol), triethylamine (0.048 mg, 0.47 mmol) and $Ca(NO_3)_2.4H_2O$ (111 mg, 0.47 mmol) in methanol or ethanol (20 mL) sealed in thick-walled glass tubes were heated at 90 °C for 12 hr. The crystals that separated from the solution were collected, washed with the appropriate alcohol and dried in air. Yields (no attempt was made to optimise): methyl ester, 34 mg, 21 %; ethyl ester, 40 mg, 24 %.

Elemental analysis for $C_{52}H_{44}Ca_4N_{12}O_{24}$ (R = Me) (%) calcd: C 45.2, H 3.2, N 12.2; found: C 45.1, H 3.3, N 12.2; elemental analysis for $C_{56}H_{52}Ca_4N_{12}O_{24}$ (R = Et) calcd: C 46.8, H 3.7, N 11.7; found: C 46.5, H 3.7, N 11.3; FT-IR (R = Me) (KBr 4000–500 cm^{-1}): $\tilde{\nu} = 3433$ (br), 3108 (w), 3072 (w), 2954 (w), 1723 (s), 1696 (s), 1597 (s), 1574 (m), 1474 (m), 1431 (s), 1385 (s), 1325 (s), 1284 (s), 1212 (m), 1156 (w), 1095 (s), 1054 (w), 1013 (m), 972 (w), 931 (w), 824 (w), 772 (s), 750 (m), 705 (m), 662 (m), 636 (m), 586 cm^{-1} (w).

Crystal data for $C_{52}H_{44}Ca_4N_{12}O_{24}$ (R = Me): 0.12 × 0.12 × 0.12 mm, tetragonal, space group $P\bar{4}2_1c$, $a = 14.0022(8)$, $c = 15.3990(17)$ Å, $V = 3019.2(4)$ Å^3, $\rho_{calcd} = 1.520\ g\,cm^{-3}$, $2\theta_{max} = 55.0°$, $\lambda = 0.71073$ Å, $T = 293$ K, no. of measured (and independent) reflections: 15522 (2672), $\mu = 0.225\ mm^{-1}$, no. of parameters: 221, $R1\ [I > 2\sigma(I)] = 0.0442$, $wR2$ (all data) = 0.1188, max./min. residual electron density: 0.38/−0.20 e Å^{-3}.

Crystal data for $C_{56}H_{52}Ca_4N_{12}O_{24}$ (R = Et): 0.10 × 0.10 × 0.10 mm, tetragonal, space group $P\bar{4}2_1c$, $a = 14.2373(6)$, $c = 15.5039(13)$ Å, $V = 3142.7(3)$ Å^3, $\rho_{calcd} = 1.519\ g\,cm^{-1}$, $2\theta_{max} = 55.0°$, $\lambda = 0.71073$ Å, $T = 293$ K, no. of measured (and independent) reflections: 19412 (3599), $\mu = 0.436\ mm^{-1}$, Flack parameter: 0.05, no. of parameters: 169, $R1\ [I > 2\sigma(I)] = 0.0861$, $wR2$ (all data) = 0.2395, max./min. residual electron density: 0.79/−0.57 e Å^{-3}.

$[Ni\{(C_5H_4N)_2(C_3H_3N_2)C(OH)\}_2](NO_3)_2\cdot 4H_2O$: Crystal data for $C_{28}H_{32}N_{10}O_{12}Ni$: 0.11 × 0.08 × 0.06 mm, triclinic, space group $P\bar{1}$, $a = 8.4969(9)$, $b = 9.8555(11)$, $c = 10.8443(12)$ Å, $\alpha = 106.183(2)°$, $\beta = 101.154(2)°$, $\gamma = 98.246(3)°$, $V = 836.68(16)$ Å^3, $\rho_{calcd} = 1.507\ g\,cm^{-1}$, $2\theta_{max} = 45.0°$, $\lambda = 0.71073$ Å, $T = 293$ K, no. of measured (and independent) reflections: 3446 (2137), $\mu = 0.657\ mm^{-1}$, min./max. apparent transmission ratio: 0.851, no. of parameters: 232, $R1\ [I > 2\sigma(I)] = 0.0746$, $wR2$ (all data) = 0.1986, max./min. residual electron density: 0.53/−0.55 e Å^{-3}.

$[M^{II}\{(C_5H_4N)_2(SO_3)C(OH)\}_2]$, (M = Zn, Fe, Ni, Cd, Co,[16] Mn): To a solution of di-2-pyridyl ketone (100 mg, 0.54 mmol) in water (20 mL) was added a solution of $M(NO_3)_2$ (0.27 mmol) in water (10 mL) followed by solution of $NaHSO_3$ (58 mg, 0.54 mmol). Crystals of $[M^{II}\{(C_5H_4N)_2(SO_3)C(OH)\}_2]$ separated from the solution overnight, which were collected, washed with water and dried in air. In all cases, X-ray powder patterns of the bulk solid were in good agreement with those calculated on the basis of the single crystal data. Yields: M = Zn, (137 mg, 85 %); M = Co, (146 mg, 91 %); M = Cd, (118 mg, 67 %); M = Mn, (41 mg, 26 %); M = Fe (132 mg, 83 %); elemental analyses for $C_{22}H_{18}N_4O_8S_2M^{II}$ (%): M = Zn, calcd: C 44.3, H 3.0, N 9.4; found: C 43.7, H 3.0, N 9.3; M = Cd, calcd: C 41.1, H 2.8, N 8.7; found: C 40.8, H 3.1, N 9.3; M = Fe, C 45.1, H 3.1, N 9.6; found: C 43.8, H 3.1, N 9.4; M = Mn, calcd: C 45.1, H 3.1, N 9.6; found: C, 44.3, H, 3.1, N 9.4; M = Co, calcd: C 43.8, H 3.1, N 9.5; found: C 43.7, H 3.1, N 9.4; FT-IR (M = Fe) (KBr 4000–500 cm^{-1}): 3309 (br), 3111 (w), 1603 (m), 1577 (w), 1475 (w), 1465 (m), 1365 (w), 1268 (s), 1221 (w), 1203 (m), 1172(s), 1143 (m), 1099 (w), 1060 (w), 1037 (s), 1020 (m), 919 (w), 910 (w), 779 (m), 757 (m), 715 (w), 666 (w), 650 (s), 638 (s), 540 (w), 518 cm^{-1} (m).

Crystal data for $C_{22}H_{18}N_4O_8S_2Zn$: 0.18 × 0.15 × 0.10 mm, monoclinic, space group $P2_1/c$, $a = 7.8126(14)$, $b = 9.3835(17)$, $c = 15.743(3)$ Å, $\beta = 98.052(4)°$, $V = 1142.8(4)$ Å^3, $\rho_{calcd} = 1.732\ g\,cm^{-1}$, $2\theta_{max} = 55.0°$, $\lambda = 0.71073$ Å, $T = 293$ K, no. of measured (and independent) reflections: 6865 (2557), $\mu = 1.317\ mm^{-1}$, min./max. apparent transmission ratio: 0.886, no. of parameters: 177, $R1\ [I > 2\sigma(I)] = 0.0393$, $wR2$ (all data) = 0.1039, max./min. residual electron density: 0.59/−0.26 e Å^{-3}.

Crystal data for $C_{22}H_{18}FeN_4O_8S_2$: 0.3 × 0.3 × 0.2 mm, monoclinic, space group $P2_1/c$, $a = 7.8027(6)$, $b = 9.3800(7)$, $c = 15.6874(11)$ Å, $\beta = 98.3700(10)°$, $V = 1135.92(15)$ Å^3, $\rho_{calcd} = 1.714\ g\,cm^{-1}$, $2\theta_{max} = 55.0°$, $\lambda = 0.71073$ Å, $T = 293$ K, no. of measured (and independent) reflections: 6972 (2580), $\mu = 0.908\ mm^{-1}$, min./max. apparent transmission ratio: 0.898, no. of parameters: 170, $R1\ [I > 2\sigma(I)] = 0.0301$, $wR2$ (all data) = 0.0842, max./min. residual electron density: 0.32/−0.49 e Å^{-3}.

Crystal data for $C_{22}H_{18}N_4NiO_8S_2$: 0.6 × 0.4 × 0.4 mm, monoclinic, space group $P2_1/c$, $a = 7.764(2)$, $b = 9.322(3)$, $c = 15.729(4)$ Å, $\beta = 97.150(4)°$, $V = 1129.6(5)$ Å^3, $\rho_{calcd} = 1.732\ g\,cm^{-1}$, $2\theta_{max} = 46.6°$, $\lambda = 0.71073$ Å, $T = 293$ K, no. of measured (and independent) reflections: 4496 (1624), $\mu = 1.104\ mm^{-1}$, min./max. apparent transmission ratio: 0.748, no. of parameters: 173, $R1\ [I > 2\sigma(I)] = 0.0527$, $wR2$ (all data) = 0.1269, max./min. residual electron density: 0.74/−0.56 e Å^{-3}.

Crystal data for $C_{22}H_{18}CdN_4O_8S_2$: 0.25 × 0.25 × 0.1 mm, monoclinic, space group $P2_1/c$, $a = 7.9227(7)$, $b = 9.4701(8)$, $c = 15.6967(14)$ Å, $\beta = 101.506(2)°$, $V = 1154.04(17)$ Å^3, $\rho_{calcd} = 1.850\ g\,cm^{-1}$, $2\theta_{max} = 55.0°$, $\lambda = 0.71073$ Å, $T = 293$ K, no. of measured (and independent) reflections: 7006 (2608), $\mu = 1.187\ mm^{-1}$, min./max. apparent transmission ratio: 0.866, no. of parameters: 173, $R1\ [I > 2\sigma(I)] = 0.0241$, $wR2$ (all data) = 0.0663, max./min. residual electron density: 0.54/−0.26 e Å^{-3}.

Crystal data for $C_{22}H_{18}MnN_4O_8S_2$: 0.2 × 0.2 × 0.15 mm, monoclinic, space group $P2_1/c$, $a = 7.8077(7)$, $b = 9.4162(8)$, $c = 15.6681(14)$ Å, $\beta = 100.2980(10)°$, $V = 1133.35(17)$ Å^3, $\rho_{calcd} = 1.716\ g\,cm^{-1}$, $2\theta_{max} = 55.0°$, $\lambda = 0.71073$ Å, $T = 293$ K, no. of measured (and independent) reflections: 6914 (2564), $\mu = 1.716\ mm^{-1}$, min./max. apparent transmission ratio: 0.827 no. of parameters: 173, $R1\ [I > 2\sigma(I)] = 0.0301$, $wR2$ (all data) = 0.0817, max./min. residual electron density: 0.42/−0.32 e Å^{-3}.

$[Zn_4\{(C_5H_4N)_2(SO_3)C(O)\}_4]\cdot 3H_2O$: Mixtures of di-2-pyridyl ketone (300 mg, 1.63 mmol), $Zn(NO_3)_2.6H_2O$ (485 mg, 1.63 mmol), Na_2SO_3 (205 mg, 1.63 mmol) and NaOAc (134 mg, 1.63 mmol) in water (10 mL) were sealed in thick-walled glass tubes and heated at 120 °C for 12 h. Crystals of hydrated $[Zn_4\{(C_5H_4N)_2(SO_3)C(O)\}_4]$ that separated from the solution were collected, washed with water and dried in air. Yield: (335 mg, 60 %). The X-ray powder pattern of the bulk solid was in good agreement with that calculated on the basis of the single crystal data. Elemental analysis for $[Zn_4\{(C_5H_4N)_2(SO_3)C(O)\}_4]\cdot 3H_2O$ ($C_{44}H_{4438}N_8O_{19}S_4Zn_4$) (%): calcd: C 38.5, H 2.9, N 8.2; found: C 38.7, H 2.9, N 8.3; FT-IR (KBr 4000–500 cm^{-1}): $\tilde{\nu} = 3505$ (br), 3121 (m), 3081 (m), 1685 (w), 1607 (s), 1576 (m), 1473 (s), 1438 (s), 1300 (w), 1261 (s), 1213 (w), 1178 (s), 1122 (m), 1106 (s), 1063 (s), 1036 (s), 1018 (s), 948 (w), 907 (w), 770 (s), 720 (w), 677 (m), 639 (s), 543 cm^{-1} (s).

Crystal data for $[Zn_4\{(C_5H_4N)_2(SO_3)C(O)\}_4]\cdot 6H_2O$ ($C_{44}H_{44}N_8O_{22}S_4Zn_4$): 0.60 × 0.60 × 0.40 mm, orthorhombic, space group $P2_12_12_1$, $a = 12.6826(8)$, $b = 16.5800(10)$, $c = 27.0364(17)$ Å, $V = 5685.1(6)$ Å^3, $\rho_{calcd} = 1.671\ g\,cm^{-1}$, $2\theta_{max} = 55.0°$, $\lambda = 0.71073$ Å, $T = 130$ K, no. of measured (and independent) reflections: 35248 (12850), $\mu = 1.898\ mm^{-1}$, min./max. apparent transmission ratio: 0.913, Flack parameter: 0.028, no. of parameters: 748, $R1\ [I > 2\sigma(I)] = 0.0554$, $wR2$ (all data) = 0.1579, max./min. residual electron density: 0.79/−1.60 e Å^{-3}.

$[Zn^{II}_4\{(C_5H_4N)_2(SO_3)C(O)\}_4]\cdot 3H_2O\cdot[(C_5H_4N)_2C(O)]$: Mixtures of di-2-pyridyl ketone (300 mg, 1.63 mmol), $Zn(NO_3)_2\cdot 6H_2O$ (243 mg, 0.82 mmol), Na_2SO_3 (205 mg, 1.63 mmol) and NaOAc (134 mg, 1.63 mmol) in water (10 mL) were sealed in thick-walled glass tubes and heated at 120 °C for 12 h. Crystals of $[Zn_4\{(C_5H_4N)_2(SO_3)C(O)\}_4]\cdot 3H_2O\cdot$-$[(C_5H_4N)_2CO]$ that separated from the solution were collected, washed with water and dried in air. Yield: (84 mg, 26 %). Elemental analysis calcd (%) for $C_{55}H_{46}N_{10}O_{20}S_4Zn_4$: C 42.4, H 3.0, N 8.8; found: C 41.8, H 3.0, N 9.0. FT-IR (KBr 4000–500 cm^{-1}): $\tilde{\nu} = 3514$ (br), 3118 (m), 3080 (m), 1685 (m), 1639 (w)m 1607 (s), 1575 (m), 1473 (s), 1437 (s), 1384 (w), 1321 (m), 1263 (s), 1212 (m), 1180 (S), 1122 (m), 1106 (s), 1063 (s), 1035 (s), 1018 (s), 828 (w), 947 (w), 770 (s), 720 (w), 677 (m), 639 (s), 543 cm^{-1} (m).

Crystal data for $C_{55}H_{46}N_{10}O_{20}S_4Zn_4$: 0.13 × 0.08 × 0.08 mm, orthorhombic, space group $P2_12_12_1$, $a = 12.585(5)$, $b = 16.968(6)$, $c = 27.128(9)$ Å, $V = 5793(4)$ Å^3, $\rho_{calcd} = 1.785\ g\,cm^{-1}$, $2\theta_{max} = 55.0°$, $\lambda = 0.71073$ Å, $T = 130$ K, no. of measured (and independent) reflections: 34668 (12964), $\mu = 1.870\ mm^{-1}$, min./max. apparent transmission ratio: 0.828, Flack parameter: 0.04, no. of parameters: 767, $R1\ [I > 2\sigma(I)] = 0.0832$, $wR2$ (all data) = 0.2068, max./min. residual electron density: 0.86/−1.1 e Å^{-3}.

$[Mn^{II}_4\{(C_5H_4N)_2(SO_3)C(O)\}_4]\cdot 3H_2O\cdot[(C_5H_4N)_2C(O)]$: Mixtures of di-2-pyridyl ketone (300 mg, 1.63 mmol), $Mn(NO_3)_2\cdot xH_2O$ (292 mg, 1.63 mmol), Na_2SO_3 (205 mg, 1.63 mmol) in water (10 mL) were sealed in thick-walled glass tubes and heated at 120 °C for 12 h. Crystals of $[Mn_4\{(C_5H_4N)_2(SO_3)C(O)\}_4]\cdot 3H_2O$. $[(C_5H_4N)_2C(O)]$ that separated from the solution were collected, washed with water and dried in air. Yield: (184 mg, 30 %). Elemental analysis calcd (%) for $C_{55}H_{46}Mn_4N_{10}O_{20}S_4$: C 43.6, H 3.1, N 9.3; found: C 43.5, H 3.1, N 9.2; FT-IR (KBr 4000–500 cm^{-1}): $\tilde{\nu} = 3515$ (br), 3114 (m), 3077 (m), 1685 (s), 1637 (w), 1603 (s), 1574 (s), 1471 (s), 1433 (s), 1322 (s), 1299 (w), 1254 (s), 1210 (s), 1176 (s), 1156 (s), 1093 (s), 1060 (s), 1029 (s), 1014 (s), 946 (m), 905 (w), 828 (w), 769 (s), 718 (m), 675 (s), 636 (s), 543 cm^{-1} (m).

Crystal data for $C_{55}H_{46}Mn_4N_{10}O_{20}S_4$: 0.25 × 0.20 × 0.20 mm, orthorhombic, space group $P2_12_12_1$, $a = 12.6940(12)$, $b = 16.9130(16)$, $c = 27.232(3)$ Å, $V =$

5846.6(10) Å^3, $\rho_{calcd}=1.721$ g cm^{-1}, $2\theta_{max}=55.0°$, $\lambda=0.71073$ Å, $T=130$ K, no. of measured (and independent) reflections: 36544 (13236), $\mu=1.075$ mm^{-1}, min./max. apparent transmission ratio: 0.870, Flack parameter: no. of parameters: 782, $R1$ $[I>2\sigma(I)]=0.0589$, $wR2$ (all data)$=0.1469$, max./min. residual electron density: 0.82/−0.69 e Å^{-3}.

$Na[NaZn^{II}_3\{(C_5H_4N)_2(SO_3)C(O)\}_4]\cdot 13.5\,H_2O$: To a solution of di-2-dipyridil ketone (100 mg, 0.54 mmol) in water (5 mL) was added solutions of $Zn(NO_3)_2.6H_2O$ (162 mg, 0.54 mmol) in water (5 mL) and NaOAc (45 mg, 0.54 mol) followed by a solution of Na_2SO_3 (1.025 g, 2.7 mmol) in water (10 mL). upon which an immediate precipitate formed. The suspension was then transferred to a thick walled sealed glass tube and heated to 120° for 12 h. Crystals of $Na[NaZn_3\{(C_5H_4N)_2(SO_3)C(O)\}_4].13.5H_2O$ that separated from the solution were filtered, washed with water, and dried in air. Yield: (60 mg, 28 %).

Crystal data for $C_{44}H_{59}N_8Na_2O_{29.50}S_4Zn_3$: 0.15 × 0.15 × 0.1 mm, monoclinic, space group $P2_1/n$, $a=11.3225(12)$ Å, $b=20.685(2)$ Å, $c=25.961(3)$ Å, $\beta=98.195(2)°$, $V=6018.3(11)$ Å^3, $\rho_{calcd}=1.702$ g cm^{-1}, $2\theta_{max}=55.0°$, $\lambda=0.71073$ Å, $T=130$ K, no. of measured (and independent) reflections: 30171 (10651), $\mu=1.436$ mm^{-1}, min./max. apparent transmission ratio: 0.832, no. of parameters: 849, $R1$ $[I>2\sigma(I)]=0.0630$, $wR2$ (all data)$=0.1420$, max. min^{-1}. residual electron density: 1.00/-0.60 e Å^{-3}.

$Na[NaMn^{II}_3\{(C_5H_4N)_2(SO_3)C(O)\}_4]\cdot 13\,H_2O$: To a solution of di-2-dipyridil ketone (300 mg, 1.63 mmol) in water (10 mL) was added solutions of $Mn(NO_3)_2\cdot xH_2O$ (290 mg, 1.63 mmol) in water (10 mL) and NaOAc (134 mg, 1.63 mmol) in water (5 mL) followed by a solution of Na_2SO_3 (1.03 g, 8.15 mmol) in water (10 mL). The crystals of $Na[NaMn_3\{(C_5H_4N)_2(SO_3)C(O)\}_4]\cdot 13\,H_2O$ that separated from the solution at room temperature after two days were filtered, washed with water, and dried in air. Yield: (295 mg, 48 %). Elemental analysis calcd (%) for $C_{44}H_{58}N_8O_{29}S_4NaMn_3$ (%): C 35.8, H 3.4, N 7.6; found: C 35.2, H 3.8, N 7.4.

Crystal data for $C_{44}H_{58}N_8O_{29}S_4NaMn_3$: 0.20 × 0.18 × 0.18 mm, monoclinic, space group $P2_1/n$, $a=11.3955(8)$, $b=20.7433(14)$, $c=25.9614(18)$ Å, $\beta=98.2580(10)°$, $V=6073.1(7)$ Å^3, $\rho_{calcd}=1.643$ g cm^{-1}, $2\theta_{max}=55.0°$, $\lambda=0.71073$ Å, $T=130$ K, no. of measured (and independent) reflections: 37176 (13772), $\mu=0.860$ mm^{-1}, min./max. apparent transmission ratio: 0.842, no. of parameters: 817, $R1$ $[I>2\sigma(I)]=0.0508$, $wR2$ (all data)$=0.1331$, max./min. residual electron density: 0.81/−0.36 e Å^{-3}.

$Na[NaCo^{II}_3\{(C_5H_4N)_2(SO_3)C(O)\}_4]\cdot 9.5\,H_2O$: To a solution of di-2-dipyridil ketone (100 mg, 0.54 mmol) in water (10 mL) was added solutions of $Co(NO_3)_2.6H_2O$ (158 mg, 0.54 mmol) in water (10 mL) and NaOAc (45 mg, 0.54 mmol) in water (5 mL) followed by a solution of Na_2SO_3 (342 mgg, 2.72 mmol) in water (10 mL). The solution was then transferred to a thick-walled sealed-glass tube and heated to 120 °C for three days. The crystals of $Na[NaCo_3\{(C_5H_4N)_2(SO_3)C(O)\}_4]\cdot 9.5\,H_2O$ that separated from the solution at room temperature after two days were filtered, washed with water, and dried in air. Yield: (22 mg, 11 %). FT-IR (KBr 4000–500 cm^{-1}): $\tilde{\nu}=3467$ (br), 3145 (w), 3079 (w), 1652 (m), 1605 (s), 1571 (m), 1467 (s), 1434 (s), 1384 (w), 1295 (w), 1189 (s), 1124 (w), 1106 (s), 1048 (s), 1022 (s), 952 (w), 915 (w), 891 (w), 771 (s), 721 (m), 679 (m), 635 (s), 539 cm^{-1} (m).

Crystal data for $C_{44}H_{51}Co_3N_8Na_2O_{25.50}S_4$: 0.30 × 0.25 × 0.25 mm, monoclinic, space group $P2_1/c$, $a=11.290(4)$, $b=20.730(8)$, $c=24.215(10)$ Å, $\beta=91.450(7)°$, $V=5666(4)$ Å^3, $\rho_{calcd}=1.701$ g cm^{-1}, $2\theta_{max}=55.0°$, $\lambda=0.71073$ Å, $T=130$ K, no. of measured (and independent) reflections: 32494 (12642), $\mu=1.124$ mm^{-1}, min./max. apparent transmission ratio: 0.597, no. of parameters: 815, $R1$ $[I>2\sigma(I)]=0.0930$, $wR2$ (all data)$=0.2154$, max./min. residual electron density: 1.65/−0.89 e Å^{-3}.

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