DALTON
FULL PAPER

Bimetallic reactivity. Preparations, properties and structures of complexes formed by unsymmetrical binucleating ligands bearing 4- and 6-coordinate sites supported by alkoxide bridges

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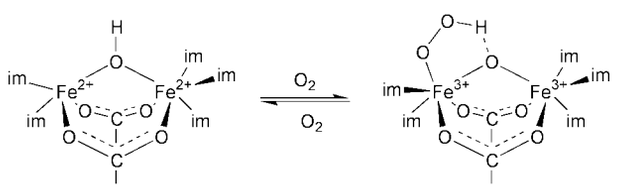
Received 4th April 2001, Accepted 5th September 2001
First published as an Advance Article on the web 14th November 2001

Four binucleating ligands which potentially could provide bimetallic complexes bearing 5- and 6-coordinate sites have been prepared. These ligands, which have alkoxide bridging groups, can be regarded as more elaborate versions of binucleating ligands which have tridentate chelates on each side of the alkoxy bridge. Unlike these previous, less complex ligands, the present series of binucleating ligands have a strong tendency to form oligomers. This has been demonstrated with a series of crystal structures of copper(II) complexes of these ligands. It is probable that oligomers are formed because of the high flexibility of the present ligands. The work serves to illustrate the limits of binuclear ligand design and suggests that, with alkoxide ligand bridges, rigidity is necessary in order to obtain bimetallic complexes with extended multidentate binucleating ligands. One of the ligands gives a mixed valence Mn(II)–Mn(IV) complex after O_2 oxidation of a di-Mn(II) precursor.

Introduction

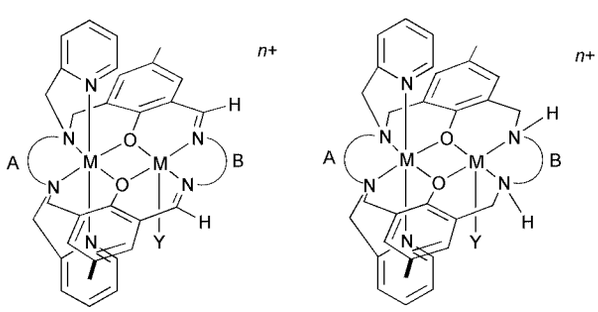
The respiratory protein, hemerythrin,[1] has as its active site two contiguous Fe^{2+} ions bridged by a hydroxide and two carboxylates, one iron is 5-coordinate, the other is 6-coordinate. The remaining ligands are imidazoles, **1**. Dioxygen adds to the 5-coordinate Fe^{2+} ion and is converted to hydroperoxide after two electrons, one from each of the iron atoms, are transferred and the OH proton is delivered to the peroxide, **2**.[2] The proton-coupled electron transfer process, **1** ⟶ **2**, is an example of a one-site addition two-metal oxidation reaction which, as far as we are aware, has not been reproduced in a synthetic system.



1 **2**

im = imidazole

Our previous work on the two bimetallic complex types, **3** and **4**, has revealed certain deactivating factors, peculiar to bimetallic complexes, which control the accessibility of the higher oxidation states.[3] The two monometallic parts of, **3**, namely the 6-coordinate and 5-coordinate sites, readily support the Co^{3+} state but when these two sites are incorporated into the bimetallic complex, **3**, the complex is inert to oxidizing agents which would oxidize the metals in the monometallic parts. This result is independent of chelate ring sizes shown by loops A and B, **3**. The complex, **4**, is somewhat more reactive, in this case the Co^{2+} ion in the 6-coordinate site is readily oxidized but, once this oxidation is achieved, the Co^{2+} in the 5-coordinate site is not readily oxidized even in the presence of added ligands. Similarly, when the Co^{2+} in the 5-coordinate site is oxidized, the 6-coordinate Co^{2+} ion becomes inert to oxidation. Thus, whereas either site of, **4**, can support Co^{3+}, when one site is oxidized, the other becomes deactivated to oxidation. The major source of deactivation appears to be mechanical coupling, a conformational effect which causes one site to be deactivated because of conformational rearrangements which ensue as a consequence of metal oxidation in the other site. We have shown that mechanical coupling can amount to 18 kcal mol^{-1} in certain cases.[3] Thus the design of binucleating ligands which attempt to reproduce the function of hemerythrin must minimize mechanical coupling between sites. It is probable that mechanical coupling is particularly acute in macrocyclic systems such as **3** and **4** because the degrees of freedom are reduced compared to open binucleating ligands.



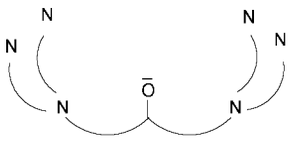
3 **4**

The other feature of hemerythrin is the presence of 6- and 5-coordinate sites. Thus in order to reproduce the binding site and to direct the substrate to the 5-coordinate site, binucleating ligands should incorporate this feature. Finally, an exogenous OH bridge would provide a proton for stabilizing the peroxide group. As yet, no such binucleating ligands incorporating these features have been reported.

Binucleating ligands which provide an alkoxide bridge flanked by multidentate ligands have been the subject of extensive study.[4–15] These ligands are usually symmetrical systems of

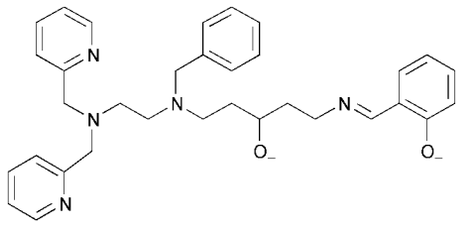
 DOI: 10.1039/b103164n

the type, **I**, where the two metals are coordinated on each side of the alkoxide bridge, and the coordination number is satisfied by exogenous bridging ligands such as acetate, hydroxide, azide or halides. Given this known chemistry, it seemed attractive to prepare unsymmetrical alkoxide bearing binucleating ligands which, upon coordination and the addition of an exogenous bridging ligand, would provide 6- and 4-coordinate metal sites.

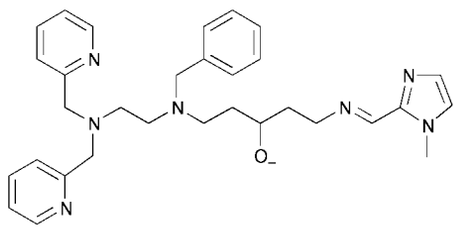


I

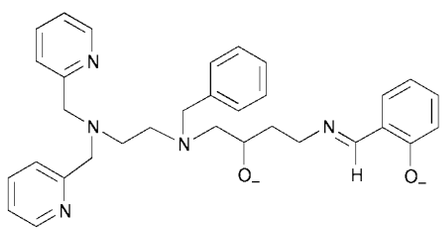
The preparation of four such ligands, **II**, **III**, **IV**, **V**, is described here. They were expected to form the generic complexes of the type, **5**. It will be noted that three variations of these ligands are introduced according to the number of methylene groups linking the alcohol bearing carbon atom and the nearest flanking nitrogen atom. Molecular models suggest that the most stable combination is when there are two pairs of methylene groups in these positions, **II** and **III**. Such ligands were expected to bind in the manner illustrated in, **5**, strainlessly. The other ligands, **IV** and **V**, were expected to introduce strain in the topology, **5**, but simpler versions of these two ligands were found to form stable complexes.[4–14] The benzyl group serves no structural purpose, its presence makes the syntheses easier. These ligands provided unexpectedly complex metal compounds. We report on these here.



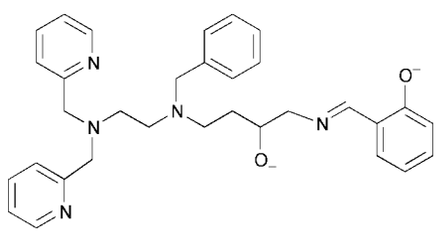
II



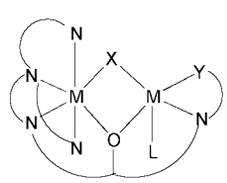
III



IV



V



5

Experimental

General procedures and methods

All reagents were obtained from commercial suppliers and were used without further purification. NMR spectra were taken on Bruker DRX400 or Bruker DMX500 spectrometers. Conductance measurements were made at 25 °C with a YSI Model 35 conductance meter on 1 mM solutions of the complexes, using dry solvents. The UV/VIS solution spectra were obtained on a Perkin-Elmer Lambda 6 spectrophotometer using spectral grade solvents. Infrared spectra were recorded on a Nicolet 20SXB FTIR spectrometer using Nujol mulls on NaCl discs. Magnetic susceptibilities were measured on powdered solid samples using a Johnson–Mathey–Evans magnetic susceptibility balance. Elemental analyses were performed by Desert Analytics, Arizona. Melting points are uncorrected. Ethanol refers to absolute ethanol. Acetonitrile was dried over CaH_2, THF was dried over potassium–benzophenone ketyl and ethyl ether was dried over sodium–benzophenone ketyl. TLC was carried out on precoated silica gel (Whatman, PE SIL G/UV) or aluminium oxide (J. T. Baker, aluminium oxide IB-F). Silica gel 60 Å (Merck, 230–400 mesh) or aluminium oxide 58 Å (Aldrich, activated, basic, 150 mesh) were used for flash chromatography.

Ligand synthesis

Pyridin-2-ylmethylpyridin-2-ylmethyleneamine (VI). To a suspension of anhydrous $MgSO_4$ (82 g, 683 mmol) in CH_2Cl_2 (160 mL) was added 2-pyridinecarboxaldehyde (15 g, 138 mmol), followed by 2-(aminomethyl)pyridine (14.8 g, 138 mmol). The mixture became warm and the color changed to yellow. After being stirred for 3 h at room temperature, the suspension was filtered, washed with CH_2Cl_2 (200 mL), and the solvent was removed under vacuum. A yellow oil (27.4 g, 100%) was obtained. ^{1}H NMR (400 MHz, C_6D_6): δ 8.59 (s, 1H), 8.47 (m, 2H), 8.11 (d, 1H, J = 7.9 Hz), 7.16 (d, 1H, J = 10.1 Hz), 7.09–6.99 (m, 2H), 6.61 (m, 2H), 4.89 (s, 2H).

Bis-pyridin-2-ylmethylamine (VII). The imine **VI** (27.4 g, 138 mmol) was dissolved in CH_3CN (250 mL) and was cooled to −5 °C. Glacial acetic acid (8 mL, 138 mmol) was added in one portion. To the resulting clear yellow solution was added a suspension of sodium borohydride (10.7 g, 276 mmol) in absolute ethanol (300 mL) over a period of 1 h at −5 °C. Vigorous bubbling occurred during the addition, accompanied by the precipitation of a white solid. The color of the solution changed from yellow to bright red by the end of addition. After stirring for 18 h at room temperature, the reaction mixture was quenched with 12 M HCl (160 mL, 1.9 mol), and was heated at 60 °C for 2 h, until no more gas was evolved. The white precipitate was filtered, the filtrate was concentrated *in vacuo*, and then redissolved in water (70 mL). The resulting yellow aqueous solution was basified by addition of solid NaOH pellets (64 g, 1.6 mol) with efficient cooling. A red oil separated immediately. It was extracted with ether (3 × 400 mL). The ether extracts were dried over solid NaOH. Evaporation of the solvent

yielded 30 g of a red oil. Upon distillation, the pure product was obtained as a yellow oil (20 g, 73%). Bp 130–135 °C (0.1 Torr). Lit. 148–149 °C (1.05 Torr).[16] ^{1}H NMR (500 MHz, C_6D_6): δ 8.46 (d, J = 7.5 Hz, 2H), 7.07 (m, 4H), 6.62 (m, 2H), 3.90 (s, 4H), 2.52 (s, br, 1H).

2-[2-(Bis-pyridin-2-ylmethyl-amino)ethyl]phthalimide (VIII). This compound was prepared using a modified literature procedure.[17] Anhydrous K_2CO_3 (42 g, 304 mmol) and KI (1.5 g, 0.1 mmol) were suspended in fresh CH_3CN (350 mL). The amine, **VII** (18.3 g, 92 mmol) was added to this suspension, followed by bromoethylphthalimide (25.6 g, 101 mmol). The mixture was refluxed for 24 h, filtered and concentrated under vacuum to yield a red oil. This red oil was dissolved in CH_2Cl_2 (200 mL), and was washed with saturated $NaHCO_3$ solution (3 × 200 mL) and with water (2 × 200 mL). Then the solvent was evaporated *in vacuo*, and to the resulting dark oil was added 2 M HCl (140 mL). The aqueous solution was washed with CH_2Cl_2 (5 × 60 mL), and then it was carefully basified with solid sodium bicarbonate (60 g). An orange solid precipitated. It was extracted into CH_2Cl_2 (4 × 100 mL), and concentrated under vacuum to yield dark brown crystals. These were chromatographed on 50 g of silica-gel (5% CH_2Cl_2 in ethyl acetate as eluant). A tan solid (23.19 g, 68%) was obtained. ^{1}H NMR (400 MHz, C_6D_6): δ 8.36 (d, 2H, J = 4.8 Hz,), 7.44 (dd, 2H, J = 3.1 Hz, J = 5.4 Hz), 7.33 (d, 2H, J = 7.9 Hz), 6.96 (td, 2H, J = 1.8 Hz, J = 7.6 Hz), 6.88 (dd, 2H, J = 3.0 Hz, J = 5.4 Hz), 6.53 (dd, 2H, J = 4.9 Hz, J = 7.3 Hz), 3.59 (t, 2H, J = 5.8), 2.75 (t, 2H, J = 5.8 Hz)

***N,N*-Bis(2-pyridylmethyl)ethane-1,2-diamine (IX).** The protected amine **VIII** (23.19 g, 62.3 mmol) was dissolved in absolute ethanol (80 mL), and was added to a solution of hydrazine monohydrate (3.11 g, 62.3 mmol) in ethanol (60 mL). The solution was diluted with 110 mL of ethanol and was refluxed for 3 h. After 1 h of reflux, a white solid precipitated. The mixture was concentrated under vacuum, and 2 M HCl (200 mL), followed by 12 M HCl (8.5 mL) was added. A white solid separated immediately. The suspension was stirred for 2 h at 50 °C, followed by 24 h at room temperature. Then it was filtered, concentrated under vacuum, and dissolved in water (70 mL). To this aqueous solution was added 15% aqueous NaOH (200 mL). A red oil separated. It was extracted with CH_2Cl_2 (3 × 100 mL). The combined extracts were dried over Na_2SO_4, filtered, and then were concentrated under vacuum to yield a brown oil (15.2 g). Upon distillation, the product was obtained as a pale-yellow oil (10.18 g, 68%). Bp 165–170 °C (0.1 Torr). ^{1}H NMR (400 MHz, C_6D_6): δ 8.47 (d, 2H, J = 4.6 Hz), 7.34 (d, 2H, J = 7.6 Hz), 7.10 (m, 2H), 6.62 (m, 2H), 3.84 (s, 4H), 2.57 (t, 2H, J = 5.9 Hz), 2.46 (t, 2H, J = 5.9 Hz). ^{13}C NMR (125 MHz, C_6D_6): δ 160.55, 149.36, 135.78, 122.89, 121.71, 60.77, 57.76, 40.22.

***N′*-Benzylidene-*N,N*-bis-pyridin-2-ylmethyl-ethane-1,2-diamine (X).** Anhydrous magnesium sulfate (60 g, 500 mmol) was suspended in CH_2Cl_2 (135 mL) with the amine **IX** (10.18 g, 42 mmol) and benzaldehyde (4.46 g, 42 mmol). The mixture was stirred for 3 h at room temperature, filtered, and was concentrated under vacuum to yield a yellow oil (13.8 g, 100%). ^{1}H NMR (400 MHz, C_6D_6): δ 8.46 (d, 2H, J = 4.5 Hz), 7.91 (s, 1H), 7.72 (d, 2H, J = 7.9 Hz), 7.48 (d, 2H, J = 7.8 Hz), 7.10 (m, 5H), 6.59 (dd, 2H, J = 7.2 Hz, J = 5.0 Hz), 4.00 (s, 4H), 3.62 (t, 2H, J = 6.6 Hz), 2.92 (t, 2H, J = 6.3 Hz).

***N′*-Benzyl-*N,N*-bis-pyridin-2-ylmethyl-ethane-1,2-diamine (XI).** Imine, **X** (13.8 g, 42 mmol) was dissolved in acetonitrile (75 mL), and was cooled to −5 °C. Glacial acetic acid (2.2 mL, 42 mmol) was added to this solution, followed by a suspension of sodium borohydride (3.18 g, 84 mmol) in absolute ethanol (70 mL) with continuous cooling. When the bubbling subsided, the white suspension was brought to room temperature, and was stirred for 18 h. Then 12 M HCl (50 mL) was added, and the mixture was stirred for 30 min at 50 °C. The white granular precipitate was filtered off, washed with water, and the filtrate was evaporated *in vacuo*. The white residue was dissolved in 15% NaOH (330 mL). A yellow oil separated. It was extracted with CH_2Cl_2 (5 × 200 mL), dried over anhydrous Na_2SO_4, filtered, and evaporated *in vacuo* to yield the product (12.62 g, 91%) as a yellow oil. ^{1}H NMR (500 MHz, C_6D_6): δ 8.45 (d, 2H, J = 4.0 Hz), 7.33 (m, 4H), 7.20–7.06 (m, 5H), 6.60 (m, 2H), 3.85 (s, 4H), 3.56 (s, 2H), 2.67–2.57 (dt, 4H, J = 37.5 Hz, J = 5.8 Hz).

***N*-(4-Butenyl)phthalimide (XII).** Was prepared as described in the literature.[18] The product was obtained as white crystals in 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (dd, 2H, J = 3.1 Hz, J = 5.4 Hz), 7.71 (dd, 2H, J = 3.0 Hz, J = 5.5 Hz), 5.85–5.75 (m, 1H), 5.09–5.01 (m, 2H), 3.78 (t, 2H, J = 9.2 Hz), 2.45 (m, 2H).

***N*-(3,4-Epoxybutyl)phthalimide (XIII).** The olefin, **XII** (6.12 g, 31.7 mmol) was dissolved in chloroform (90 mL). *m*-Chloroperbenzoic acid (10.56 g, 57%, 34.9 mmol) was added to the olefin solution. The reaction mixture was stirred for 18 h at room temperature and was refluxed for 1 h. The solution was cooled to room temperature and was washed successively with 5% Na_2CO_3 solution (100 mL), water (100 mL), 5% Na_2SO_3 solution (100 mL), 5% Na_2CO_3 solution (50 mL), and water (50 mL). The chloroform fraction was dried over anhydrous $MgSO_4$, and was evaporated under vacuum to yield the pure product as a white crystalline solid (6.46 g, 94%). Mp 84–85 °C. Lit. mp 84–85 °C.[19] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (dd, 2H, J = 2.8 Hz, J = 6.0 Hz), 7.72 (dd, 2H, J = 3.1 Hz, J = 5.5 Hz), 3.95–3.84 (m, 2H), 3.02–2.99 (m, 1H), 2.72 (t, 1H, J = 4.5 Hz), 2.45 (dd, 1H, J = 2.5 Hz, J = 4.9 Hz), 2.03–1.97 (m, 1 H), 1.89–1.82 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.27, 133.98, 123.28, 50.14, 46.38, 35.13, 31.62.

2-(4-{Benzyl[2-(bis-pyridin-2-ylmethylamino)ethyl]amino}-3-hydroxybutyl)phthalimide (XIV). A mixture of the amine **XI** (4.58 g, 13.8 mmol) and the epoxide **XIII** (3 g, 13.8 mmol) in n-butanol (14 mL) was stirred at 100 °C for 8 h. Then the solvent was removed *in vacuo* azeotropically with cyclohexane. The resulting black oil was chromatographed on 140 g of silica-gel with 5% triethylamine in CH_2Cl_2 as an eluant. The product was obtained as a brown oil (6.2 g, 82%). ^{1}H NMR (500 MHz, C_6D_6): δ 8.48 (d, 2H, J = 5.0 Hz), 7.46 (m, 4H), 7.25 (td, 2H, J = 1.7 Hz, J = 7.8 Hz), 7.13 (m, 2H), 7.06–6.99 (m, 3H), 6.85 (dd, 2H, J = 3.0 J = 5.5 Hz), 6.65 (dd, 2H, J = 5.0 Hz, J = 7.0 Hz), 4.87 (s, 1H, br), 4.04 (m, 1H), 3.84–3.50 (m, 6H), 3.49 (d, 1H, J = 13.5 Hz), 3.09 (s, 1H, J = 13.5 Hz), 2.68 (m, 2H), 2.38 (m, 1H), 2.25 (m, 2H), 2.08 (dd, 1H, J = 2.7 Hz, J = 12.7 Hz), 1.77 (m, 1H), 1.60 (m, 1H). ^{13}C NMR (125 MHz, C_6D_6): δ 168.13, 159.76, 149.25, 139.46, 136.1, 133.28, 132.84, 129.37, 128.50, 128.36, 127.16, 123.66, 122.84, 121.90, 66.42, 60.24, 59.89, 51.90, 51 43, 35.87, 33.93.

4-Amino-1-{benzyl[2-(bis-pyridin-2-ylmethyl-amino)ethyl]-amino}butan-2-ol (XV). A solution of the protected amine **XIV** (6.2 g, 11.3 mmol) in 15 mL of absolute ethanol was added to a solution of hydrazine monohydrate (0.56 g, 11.3 mmol) in 10 mL of ethanol. It was diluted with ethanol (15 mL), and refluxed for 3 h. A white precipitate formed after 1 h. The mixture was cooled, and the solvent evaporated *in vacuo*, to yield a brown residue. To this residue was added 2 M HCl (56 mL, 112 mmol), followed by 12 M HCl (5 mL, 60 mmol). The mixture was refluxed for 1.5 h, and was stirred at room temperature for 18 h. A granular white precipitate formed. It was filtered, the filtrate was concentrated *in vacuo* to yield a brown oil. It was dissolved in 60 mL of methanol, and stirred for 1 h with 250 mL of Amberlite-401 ion-exchange resin in the

OH^- form. The suspension was filtered, concentrated under vacuum, redissolved in benzene, and dried over anhydrous $MgSO_4$. After filtration, and evaporation of the solvent, the product was obtained as a brown oil (4.01 g, 85% yield). ^1H NMR (500 MHz, C_6D_6): δ 8.47 (d, 2H, J = 5.0 Hz), 7.45 (d, 2H, J = 8.1 Hz), 7.20–7.05 (m, 7H), 6.62 (dd, 2H, J = 7.5 Hz, J = 5.0 Hz), 3.90–3.76 (m, 5H), 3.52 (d, 1H, J = 13.5 Hz), 3.27 (d, 1H, J = 13.5 Hz), 2.77–2.68 (m, 4H), 2.51 (m, 1H), 2.44–2.37 (m, 2H), 2.19 (dd, 1H, J = 3.8 Hz, J = 12.8 Hz), 1.33 (m, 2H).

2-(4-{Benzyl[2-(bis-pyridin-2-ylmethyl-amino)ethyl]amino}-3-hydroxybutylimino)methyl]phenol (IV(H)$_2$). A solution of **XV** (500 mg, 1.2 mmol) in benzene (1.7 mL) was added to the suspension of anhydrous $MgSO_4$ (2 g) in benzene (3 mL). Then salicylaldehyde (145 mg, 1.2 mmol) was added. The bright yellow mixture was stirred at room temperature for 20 h, and was filtered. The filtrate was evaporated *in vacuo* to yield the product (90% purity) as a yellow oil (570 mg, 91%). ^1H NMR (500 MHz, C_6D_6): δ 13.86 (s, 1H), 8.47 (dd, 2H, J = 1.6 Hz, J = 4.9 Hz), 7.87 (s, 1H), 7.41 (d, 2H, J = 7.6 Hz), 7.11 (m, 8H), 6.89 (dd, 2H, J = 1.5 Hz, J = 7.5 Hz), 6.67 (m, 3H), 4.57 (s, 1H, br), 3.92–3.68 (m, 5H), 3.50 (m, 3H), 3.16 (d, 1H, J = 13.5 Hz), 2.73 (m, 2H), 2.50 (m, 1H), 2.32 (m, 2H), 2.13 (dd, 1H, J = 2.5 Hz, J = 12.5 Hz), 1.49 (m, 2H). ^{13}C NMR (125 MHz, C_6D_6): δ 165.35, 132.08, 159.71, 149.29, 149.27, 136.01, 132.22, 131.46, 129.38, 128.44, 127.26, 123.58, 121.93, 119.41, 118.42, 117.41, 65.53, 60.63, 60.23, 59.79, 56.58, 52.00 51.83, 36.31.

***N*-α-*tert*-Butoxycarbonyl glycine *N*-methyl-*N*-methoxyamide (XVI).** To a stirred solution of *t*-BOC-glycine (14 g, 80 mmol) in dry THF (85 mL) cooled to 0 °C was added carbonyldiimidazole (12.95 g, 80 mmol) in small portions. After 2 h of stirring at room temperature methoxymethylamine hydrochloride (7.8 g, 80 mmol) was added to the clear solution. A white suspension formed, and was stirred for 3 h. Triethylamine (13 mL, 93 mmol) was added, and the suspension was stirred for 20 h. It was filtered and washed with THF (50 mL). The filtrate was concentrated under reduced pressure to afford white crystals. They were recrystallized from ethyl acetate–hexane to yield the pure product (16 g, 92%). Mp 99–100 °C. Lit. mp 100–101 °C.[20] ^1H NMR (500 MHz, $CDCl_3$): δ 5.27 (s, 1H, br), 4.08 (s, 2H, br), 3.72 (s, 3H), 3.21 (s, 3H), 1.46 (s, 9H).

(2-Oxo-but-3-enyl)carbamic acid *tert*-butyl ester (XVII). This compound was prepared using a modified literature procedure.[21] To a stirred suspension of the Weinreb amide **XVI** (5 g, 23 mmol) in dry ether (60 mL) with cooling to −20 °C was added vinylmagnesium bromide (1 M solution in THF, 92 mL) dropwise. The suspension was warmed to 0 °C and was stirred at this temperature for 2 h. It was poured into an ice-cold mixture of 2 M HCl (240 mL) and ether (100 mL), and the product was extracted into ether. The organic extracts were washed with saturated sodium bicarbonate solution, and were dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* at 25 °C. The product was obtained as a pale-yellow oil with a pungent smell (3.0 g, 70%). The product is unstable, and was used in the next step immediately after its isolation. Higher temperatures than mentioned above, and long exposure to HCl solutions significantly lower the yield of this reaction. ^1H NMR (500 MHz, $CDCl_3$): δ 6.38 (m, 2H), 5.94 (dd, 1H, J = 1.2 Hz, J = 10.1 Hz), 5.37 (s, 1H, br), 4.26 (d, 2H, J = 3.2 Hz), 1.46 (s, 9H).

(4-{Benzyl[2-(bis-pyridin-2-ylmethyl-amino)ethyl]amino}-2-oxo-butyl)carbamic acid *tert*-butyl ester (XVIII). To a stirred solution of amine **XI** (3.15 g, 9.5 mmol) in methanol (5 mL) was added a solution of the Michael acceptor **XVII** (2.73 g, 14.7 mmol) in methanol (15 mL). The reaction is complete after 18 h of stirring at room temperature. The solution was concentrated under reduced pressure to yield a yellow oil (6 g, 100%) which was used in the next step without further purification. ^1H NMR (500 MHz, C_6D_6): δ 8.47 (d, 2H, J = 4.6 Hz), 7.34 (d, 2H, J = 7.8 Hz), 7.18–7.06 (m, 7H), 6.64 (dd, 2H, J = 6.9 Hz, J = 5.0 Hz), 3.85 (s, 4H), 3.68 (d, 2H, J = 5.0 Hz), 3.23 (s, 2H), 2.62 (t, 2H, J = 6.7 Hz), 2.51 (t, 2H, J = 6.9 Hz), 2.45 (t, 2H, J = 6.7 Hz), 2.00 (t, 2H, J = 6.9 Hz), 1.44 (s, 9H).

1-Amino-4-{benzyl-[2-(bis-pyridin-2-ylmethyl-amino)ethyl]-amino}butan-2-ol (XIX). To a stirred solution of ketone **XVIII** (5.23 g, 9.5 mmol) in methanol (20 mL) cooled to 0 °C was added sodium borohydride (1.1 g, 28.5 mmol). The pale yellow solution was stirred for 3 h at 5 °C, and was quenched with 4 M HCl (40 mL). The mixture was stirred for 18 h at room temperature, by which time it turned brown. The acidic solution was washed with ethyl acetate (50 mL). The volume of the aqueous solution was reduced *in vacuo*. The residue was basified with saturated sodium bicarbonate solution (100 mL), and was washed with ethyl acetate (50 mL). The aqueous layer was concentrated to dryness *in vacuo*, and was extracted into hot ethyl acetate (150 mL) with sonication. After filtration, the solvent was removed *in vacuo* to afford pure product as a yellow oil (3.0 g, 75%). ^1H NMR (400 MHz, C_6D_6): δ 8.46 (d, 2H, J = 7.5 Hz), 7.44 (d, 2H, J = 7.9 Hz), 7.23 (d, 2H, J = 8.5 Hz), 7.18–7.04 (m, 5H), 6.62 (dd, 2H, J = 7.5 Hz, J = 4.6 Hz), 3.84 (s, 4H), 3.55 (m, 1H), 3.48 (d, 1H, J = 13.3 Hz), 3.08 (d, 1H, J = 13.3 Hz), 2.72–2.64 (m, 3H), 2.52 (d, 2H, J = 5.7 Hz), 2.39–2.33 (m, 3H), 1.52 (m, 1H), 1.19 (m, 1H).

2-[(4-{Benzyl[2-(bis-pyridin-2-ylmethyl-amino)ethyl]amino}-2-hydroxybutylimino)methyl]phenol (V(H)$_2$). A solution of the amine **XIX** (250 mg, 0.59 mmol) and salicylaldehyde (72 mg, 0.59 mmol) in benzene (1 mL) was stirred at 40 °C for 1 h. The solution was concentrated 4 times under reduced pressure, each time with addition of fresh benzene (15 mL total). The repeated benzene evaporation procedure serves to remove the water formed in the reaction. The product was obtained as a yellow oil (308 mg, 100%). ^1H NMR (500 MHz, C_6D_6): δ 13.93 (s, 1H), 8.44 (d, 2H, J = 6.2 Hz), 7.93 (s, 1H), 7.40 (d, 2H, J = 7.9 Hz), 7.19–7.02 (m, 9H), 6.92 (dd, 1H, J = 1.5 Hz, J = 7.6Hz), 6.67 (t, 1H, J = 7.6 Hz), 6.62 (dd, 2H, J = 7.3 Hz, J = 4.9 Hz), 3.88 (m, 1H), 3.80 (dd, 4H, J = 16.7 Hz, J = 14.3 Hz), 3.43 (d, 1H, J = 13.2 Hz), 3.34 (d, 2H, J = 5.7 Hz), 3.03 (d, 2H, J = 13.3 Hz), 2.64 (m, 3H), 2.38–2.27 (m, 3H), 1.54 (m, 1H), 1.32 (m, 1H).

***N*-α-*tert*-Butoxycarbonyl β-alanine *N*-methyl-*N*-methoxyamide (XX).** To a stirred solution of *N*-*t*-BOC-β-alanine (14.19 g, 75 mmol) in dry THF (100 mL) under N_2 was carefully added solid 1,1′-carbonyldiimidazole (13.38 g, 82.5 mmol). The solution bubbled. It was stirred at room temperature for 4 h. In a separate flask was added a suspension of *N,O*-dimethylhydroxylamine hydrochloride (8.21 g, 82.5 mmol) in dry THF (45 mL) and triethylamine (23 mL, 165 mmol). The mixture was stirred at room temperature for 2 h to give a white turbid solution. The first solution was slowly added to the second under N_2. The white suspension was stirred at room temperature for 20 h. The white solid was filtered, and was washed with THF. The filtrate was evaporated *in vacuo* to yield a yellow liquid (30.1 g). The liquid was dissolved in CH_2Cl_2 (100 mL), was washed with 0.1 M HCl (150 mL), and water (150 mL). It was dried over anhydrous Na_2SO_4. The solvent was evaporated *in vacuo* to afford pure product (17.49 g, 100%). ^1H NMR (400 MHz, $CDCl_3$): δ 5.23 (s, 1H, br), 3.68 (s, 3H), 3.42 (t, 2H, J = 9.2 Hz), 2.64 (s, 2H, br), 1.43 (s, 9H).

(2-Oxo-but-3-enyl)carbamic acid *tert*-butyl ester (XXI). To a solution of **XX** (13.94 g, 60 mmol) in dry ether (150 mL) cooled to 0 °C was added vinylmagnesium bromide (180 mL of 1 M THF solution) over a period of 10 min. The orange mixture was stirred at 0 °C for 70 min. Cold 2 M HCl (150 mL) was added to it in one portion to yield a yellow–orange solution. The product was extracted into ether (450 mL). The ether layer

was washed with saturated sodium bicarbonate solution, and was dried over anhydrous sodium carbonate. After evaporation of the solvent *in vacuo* the product was isolated as an orange oil (11.14 g, 93%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.31 (m, 2H), 5.90 (d, 1H, J = 10.0 Hz), 5.05 (s, 1H, br.), 3.43 (m, 2H), 2.84 (t, 2H, J = 11.1 Hz), 1.43 (s, 9H).

(5-{Benzyl[2-(bis-pyridin-2-ylmethyl-amino)ethyl]amino}-3-oxo-pentyl)carbamic acid *tert*-butyl ester (XXII). To a stirred solution of amine **XI** (16.04 g, 48.25 mmol) in dry methanol (50 mL) was added a solution of **XXI** (10.97 g, 50.66 mmol) in methanol (100 mL). The clear orange solution was stirred under N_2 atmosphere at room temperature for 24 h. Then more of **XI** was added (2.17 g, 11 mmol) and the solution was stirred at room temperature for a further 20 h. The solution was concentrated under reduced pressure to afford a yellow oil, which was chromatographed on silica-gel with ethyl acetate as an eluant. The pure product was obtained as a yellow oil (24.89 g, 97%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.52 (d, 2H, J = 7.2 Hz), 7.62 (td, 2H, J = 1.8 Hz, J = 5.3 Hz), 7.46 (d, 2H, J = 7.8 Hz), 7.19 (m, 7H), 5.04 (s, 1H, br), 3.81 (s, 4H), 3.49 (s, 2H), 3.28 (m, 2H), 2.67 (m, 6H), 2.48 (m, 4H), 1.42 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 209.40, 159.56, 155.71, 148.84, 138.93, 136.20, 128.63, 128.04, 127.97, 122.75, 121.77, 78.95, 60.65, 58.79, 51.70, 51.50, 48.81, 42.51, 40.82, 34.96, 28.26.

1-Amino-5-{benzyl[2-(bis-pyridin-2-ylmethyl-amino)ethyl]-amino}pentan-3-ol (XXIII). To a stirred solution of **XXII** (22.36 g, 42.14 mmol) in methanol (180 mL) cooled to 0 °C was carefully added solid sodium borohydride (4.78 g, 126.4 mmol) in portions. The pale-yellow solution bubbled, was stirred at room temperature for 3 h, and was quenched with 4 M HCl (100 mL) at 0 °C. After stirring for 20 h at room temperature a brownish solution formed. It was concentrated *in vacuo*, was triturated with ethanol (50 mL), and was filtered. The filtrate was evaporated *in vacuo* to afford a brown oil. The oil was washed with ethyl acetate (100 mL), basified with saturated sodium bicarbonate solution (150 mL) and was washed again with ethyl acetate (300 mL). The aqueous solution was evaporated to dryness under reduced pressure, was extracted into ethyl acetate (300 mL), and was dried over anhydrous Na_2SO_4. After concentration *in vacuo* an orange oil was obtained (20.86 g). Chromatography on neutral alumina with ethyl acetate yielded pure product as an orange oil. (17.74 g, 97%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.46 (d, 2H, J = 4.5 Hz), 7.57 (td, 2H, J = 1.5 Hz, J = 7.8 Hz), 7.41 (d, 2H, J = 8.0 Hz), 7.17 (m, 5H), 7.08 (t, 2H, J = 6.0 Hz), 3.75 (s, 4H), 3.64 (d, 1H, J = 13.5 Hz), 3.27 (d, 1H, J = 13.5 Hz), 2.84–2.44 (m, 9H), 1.59 (m, 1H), 1.44 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.13, 148.69, 137.96, 136.18, 128.83, 128.05, 126.87, 122.80, 121.74, 71.25, 60.36, 58.60, 52.68, 51.17, 50.91, 39.59, 39.11, 32.92.

1-{Benzyl[2-(bis-pyridin-2-ylmethyl-amino)ethyl]amino}-5-[(3-methyl-3*H*-imidazol-4-ylmethylene)amino]pentan-3-ol (III(H)). To a stirred solution of **XXIII** (2.68 g, 6.2 mmol) in benzene (15 mL) was added 1-methyl-2-imidazole carboxaldehyde (0.68 g, 6.2 mmol). The light-orange solution was stirred at room temperature for 30 min. It was evaporated *in vacuo* at 50 °C 4 times, with the addition of fresh benzene each time (30 mL total). The benzene solution was filtered and was evaporated *in vacuo* to yield the product as an orange oil (3.12 g, 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (d, 2H, J = 4.3 Hz), 8.32 (s, 1H), 7.62 (td, 2H, J = 1.7 Hz, J = 7.6 Hz), 7.46 (d, 2H, J = 7.8 Hz), 7.21 (m, 5H), 7.13 (m, 3H), 6.92 (s, 1H), 3.92 (s, 2H), 3.79 (m, 5H), 3.67 (m, 2H), 3.31 (d, 1H, J = 13.2 Hz), 2.77–2.50 (m, 8 H), 1.71 (m, 3H), 1.54 (m, 1H).

2-[(5-{Benzyl[2-(bis-pyridin-2-ylmethyl-amino)ethyl]amino}-3-hydroxypentylimino)methyl]phenol (II(H)$_2$). To a stirred solution of **XXIII** (3.04 g, 7 mmol) in benzene (30 mL) was added salicylaldehyde (0.76 mL, 7 mmol). The intense yellow solution was stirred at room temperature for 30 min. It was evaporated *in vacuo* at 50 °C 4 times, with the addition of fresh benzene each time (45 mL total). The benzene solution was evaporated *in vacuo* to yield the product as a yellow oil (3.74 g, 95% pure, 94% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.65 (s, 1H, br), 8.50 (d, 2H, J = 4.1 Hz), 8.36 (s, 1H), 7.61 (td, 2H, J = 1.7 Hz, J = 7.7 Hz), 7.44 (d, 2H, J = 7.8 Hz), 7.20 (m, 9H), 6.95 (d, 1H, J = 8.2 Hz), 6.86 (t, 1H, J = 7.5 Hz), 5.95 (s, 1H, br), 3.76 (s, 4H), 3.68 (m, 3H), 3.29 (d, 2H, J = 13.2 Hz), 2.74 (m, 3H), 2.64 (m, 2H), 2.50 (m, 1H), 1.69 (m, 3H), 1.49 (m, 1H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 169.85, 164.68, 161.12, 158.87, 148.53, 137.48, 136.06, 131.66, 130.81, 128.81, 128.11, 126.98, 122.66, 121.68, 118.46, 117.97, 116.63, 71.22, 69.60, 60.14, 58.49, 55.37, 52.66, 50.90, 50.77, 38.02, 32.37.

Synthesis of the complexes

[Cu$_2$(IV)(μ-OAc)]PF$_6$ (6). To a stirred solution of **IV**(H)$_2$ (200 mg, 0.38 mmol) in methanol (0.5 mL) was added a suspension of copper acetate monohydrate (168 mg, 0.84 mmol) in methanol (5.2 mL). The resulting dark-green solution was stirred for 15 min. When all of the starting materials dissolved, a solution of triethylamine (77 mg, 0.76 mmol) in methanol (0.3 mL) was added. The dark-green solution was stirred for 2 h. A solution of ammonium hexafluorophosphate (250 mg, 1.5 mmol) in methanol (3 mL) was added. A dark-green precipitate formed within 5 min. The suspension was brought to boiling and the volume of methanol was reduced to 6 mL. The suspension was kept at 5 °C for 24 h. The dark-green precipitate (272 mg, 84%) was collected, was washed with methanol, then ether, and was dried in air. It was recrystallized by vapor diffusion of ether into an acetonitrile solution. [Cu(**IV**)-(μ-OAc)]PF$_6$ was obtained as dark-green needles (192 mg, 62%). Λ_M (CH_3CN) = 119 Ω^{-1} mol^{-1} cm^2. UV [λ_{max}/nm, (ε/L mol^{-1} cm^{-1})]: 639 (178). Selected IR bands (Nujol mull, cm^{-1}): 769, 839, 1377, 1454, 1564, 1577, 1627. μ_{eff} (20 °C) = 2.52 μ_B. Anal. calc. for $C_{34}H_{38}N_5O_4PF_6Cu_2$: C, 47.88; H, 4.49; N, 8.21. Found: C, 48.01; H, 4.62; N, 8.34%.

[Cu$_4$(V)$_2$(μ-OAc)](PF$_6$)$_3$·H$_2$O (7). To a stirred solution of the ligand **V**(H)$_2$ (308 mg, 0.57 mmol) in methanol (10 mL) was added solid copper acetate monohydrate (252 mg, 1.26 mmol). The solution was warmed up to 40 °C, and was filtered. To the clear green filtrate was added triethylamine (116 mg, 1.15 mmol), and the solution was stirred for 15 min at 40 °C. A solution of NH_4PF_6 (373 mg, 2.29 mmol) in methanol (2 mL) was added. A light-Lgreen precipitate formed immediately. The mixture was brought to boiling, and was refluxed for 10 min. It was then cooled to 5 °C. The green precipitate was collected, washed with cold methanol (3 mL) and ether (5 mL) and was dried in air (325 mg, 67%). It was recrystallized by vapor diffusion of ether into an acetonitrile solution. Green needles suitable for X-ray crystallography formed (215 mg, 44%). Λ_M (CH_3CN) = 378 Ω^{-1} mol^{-1} cm^2. UV [λ_{max}/nm, (ε/L mol^{-1} cm^{-1})]: 665 (703). Selected IR bands (Nujol mull, cm^{-1}): 769, 839, 1377, 1454, 1564, 1577, 1627. μ_{eff} (20 °C) = 3.10 μ_B. Anal. calc. for $C_{66}H_{75}N_{10}O_7P_3F_{18}Cu_4$: C, 43.81; H, 4.18; N, 7.74. Found: C, 43.94; H, 4.00; N, 7.51%.

[Cu$_4$(III)$_2$(μ-OAc)$_2$](PF$_6$)$_4$ (8). To a stirred solution of the ligand **III**(H) (0.14 g, 0.27 mmol) in methanol (3 mL) was added a solution of copper acetate monohydrate (107 mg, 0.53 mmol) in methanol (2 mL). A dark-blue solution formed at once. Triethylamine (37.1 μL, 0.27 mmol) was added, and the solution was refluxed for 30 min. A solution of NH_4PF_6 (0.174g, 1.07 mmol) in methanol (2 mL) was added dropwise to the hot reaction mixture, which was refluxed for 20 min. Ethanol (3 mL) was added to the hot solution to induce precipitation. The mixture was refluxed for 30 min. It was cooled

and was kept at 5 °C for 20 h. The pale-blue solid was collected, washed with cold ethanol (2 mL), ether (20 mL), and was dried in air (170 mg, 64%). It was recrystallized by slow diffusion of ether into acetonitrile solution. Bluish-green needles suitable for X-ray crystallography were collected (170 mg, 64%). Λ_M (CH_3CN) = 450 Ω^{-1} mol^{-1} cm^2. UV [λ_{max}/nm, (ε/L mol^{-1} cm^{-1})]: 661 (517). Selected IR bands (Nujol mull, cm^{-1}): 737, 770, 841, 1022, 1091, 1294, 1339, 1406, 1496, 1599, 1601, 2722, 3148, 3161. μ_{eff} (20 °C) = 2.83 μ_B. Anal. calc. for $C_{66}H_{82}N_{14}O_6P_4F_{24}Cu_4$: C, 39.61; H, 4.13; N, 9.80. Found: C, 39.20; H, 4.00; N, 9.68%.

[Cu_4(II)$_2$(μ-OAc)$_2$](PF$_6$)$_2$·2EtOH (9). To a stirred solution of the ligand **II**$(H)_2$ (0.27 g, 0.5 mmol) in ethanol (3 mL) was added a solution of copper acetate monohydrate (200 mg, 1 mmol) in ethanol (5 mL). A dark-green solution formed immediately. After the solution was stirred for 10 min at room temperature, triethylamine (139 μL, 1 mmol) was added. After 1.5 h of stirring, a solution of NH_4PF_6 (0.33 g, 2 mmol) in ethanol (3 mL) was added dropwise to the reaction mixture. A pale-green precipitate formed immediately. The mixture was stirred at 80 °C for 30 min, was slowly cooled to room temperature, and was kept at −15 °C for 18 h. The pale-green precipitate was collected, washed with cold ethanol (3 mL), ether (15 mL), and was dried under vacuum (320 mg, 74%). It was recrystallized by slow diffusion of ether into acetonitrile–ethanol solution. Dark-green blocks suitable for X-ray crystallography were collected, washed with ether, and were dried under vacuum (0.27 g, 62%). Λ_M (CH_3CN) = 231 Ω^{-1} mol^{-1} cm^2. UV [λ_{max}/nm, (ε/L mol^{-1} cm^{-1})]: 641 (491), 822 (456). Selected IR bands (Nujol mull, cm^{-1}): 764, 844, 1326, 1617, 2334, 2359. μ_{eff} (20 °C) = 2.62 μ_B. Anal. calc. for $C_{74}H_{92}N_{10}O_{10}P_2F_{12}Cu_4$: C, 48.68; H, 5.08; N, 7.67. Found: C, 48.84; H, 5.02; N, 8.39%.

[Mn_2(II)(OEt)(μ-OAc)(μ-OEt)](PF$_6$)·2EtOH (10). Ligand **II**$(H)_2$ (0.16 g, 0.3 mmol) and manganese(II) acetate tetrahydrate (0.15 g, 0.6 mmol) were dissolved in deaerated ethanol (5 mL) under nitrogen to give a yellow–orange solution. After stirring for 30 min, triethylamine (84 μL, 0.6 mmol) was added. The resulting orange solution was stirred at room temperature for 1.5 h, then it was warmed up to 60 °C, and a solution of NH_4PF_6 (0.2 g, 1.2 mmol) in ethanol (4 mL) was added. The resulting suspension was heated at 80 °C for 1 h. The pale orange–brown suspension was cooled down to room temperature, and then was kept at −15 °C for 18 h. The solid was collected under nitrogen. The filtrate was exposed to air. Brown X-ray quality crystals deposited from the filtrate. They were collected, and were dried in air (110 mg, 39%). They lose solvent of crystallization when dry; for X-ray purposes the crystals were kept in their mother liqor. Λ_M (CH_3CN) = 140 Ω^{-1} mol^{-1} cm^2. UV [λ_{max}/nm, (ε/L mol^{-1} cm^{-1})]: 376 (4000), 520 sh (420). Selected IR bands (Nujol mull, cm^{-1}): 842, 1293, 1376, 1539, 1616, 1652, 1700, 2334, 2361, 3744, 3854. μ_{eff} (20 °C) = 7.31 μ_B. Anal. calc. for $C_{39}H_{50}N_5O_6PF_6Mn_2$: C, 49.85; H, 5.36; N, 7.46. Found: C, 49.58; H, 4.90; N, 7.57%.

Crystallographic structural determination

Crystal, data collection, and refinement parameters are given in Table 1. Suitable crystals for data collection were selected and mounted with epoxy cement on the tips of fine glass fibers. All data were collected with a Siemens P4/CCD diffractometer with graphite-monochromated Mo-K_α X-radiation (λ = 0.71073 Å).

No symmetry higher than triclinic was observed in the diffraction data of **7**–**10**. For each structure the centrosymmetric space group option, $P\bar{1}$, was chosen based on *E*-statistics. The systematic absences in the diffraction data for **6** are uniquely consistent with the reported space group. All structures were solved using direct methods, completed by subsequent difference Fourier syntheses and refined by full-matrix least-squares procedures. Structures **9** and **10** co-crystallized with two molecules of ethanol. Structures **8** and **9** reside on crystallographic inversion centers. Structure **7** co-crystallized with one molecule of water for which the protons could not be located from the electron difference map. Due to the poorly diffracting nature of **7** and **10**, only select atoms were refined with anisotropic displacement coefficients. The two phenyl rings in **7** were constrained to rigid planar hexagons (C–C = 1.39 Å). The asymmetric unit of **6** contains chemically equivalent but crystallographically independent molecules. All non-hydrogen atoms, with the exception of those noted, were refined with anisotropic displacement coefficients and hydrogen atoms were treated as idealized contributions.

The structures of **7** and **10** were both restricted in quality due to the presence of spherically disordered PF_6^- anions. Additionally, there is alkyl group disorder in the EtOH solvent molecules in **10**. These factors contributed to the high residuals obtained, but have not seriously compromised the chemical information concerning the cations.

All software and sources of the scattering factors are contained in the SHELXTL (5.1) program library (G. M. Sheldrick, Siemens XRD, Madison, WI, 1998).

CCDC reference numbers 170793–170797.

See http://www.rsc.org/suppdata/dt/b1/b103164n/ for crystallographic data in CIF or other electronic format.

Results

1 Ligand synthesis

The common element, excluding the Schiff base, in the ligands, **II**, **III**, **IV** and **V**, is the fragment, **XI**, which was prepared by the methods outlined in Scheme 1. The methods follow conventional procedures which provide high yields for each step. Magnesium sulfate suspended in CH_2Cl_2 was used to form the imines. It serves to absorb the water and is a mild Lewis-acid catalyst. The method proved to be simple and effective because we found that other methods gave poor yields and impure products. Ligand, **IV**, was efficiently prepared by the methods outlined in Scheme 2.

Reaction of potassium phthalimide with homoallylic bromide in CH_3CN solution gave **XII** which was epoxidized with *meta*-chloroperbenzoic acid (*m*-CPBA) to give **XIII**. Reaction of **XI** with **XIII** in *n*-butanol at 100 °C for 8 hours gave **XIV**. The presence of the benzyl group in **XI** is necessary, for without it, the primary amine **IX** undergoes multiple additions to the epoxide. The other steps follow conventional procedures.

The preparative procedures for **II**$(H)_2$, **III**(H) and **V**$(H)_2$ are similar and are outlined in Scheme 3.

The *t*-BOC protected amino acids were first activated with carbonyldiimidazole and were then reacted with Weinreb's amine to give the amides, **XVI**, **XX**. These, in turn, were reacted with vinyl Grignard to give the vinyl ketones, **XVII**, **XXI**. They are very sensitive compounds with a tendency to polymerize. These were used immediately for the next step, the Michael addition of **XI** to give **XVIII** and **XXII**. As in the case of the reaction of **XI** with the epoxide in Scheme 2, the absence of the benzyl group led to multiple addition products. Sodium borohydride reduced the ketones and HCl removed the *t*-BOC group to give the amino alcohols, **XIX** and **XXIII**. Schiff base formation in benzene solution gave **II**$(H)_2$, **III**(H) or **V**$(H)_2$ in nearly quantitative yield.

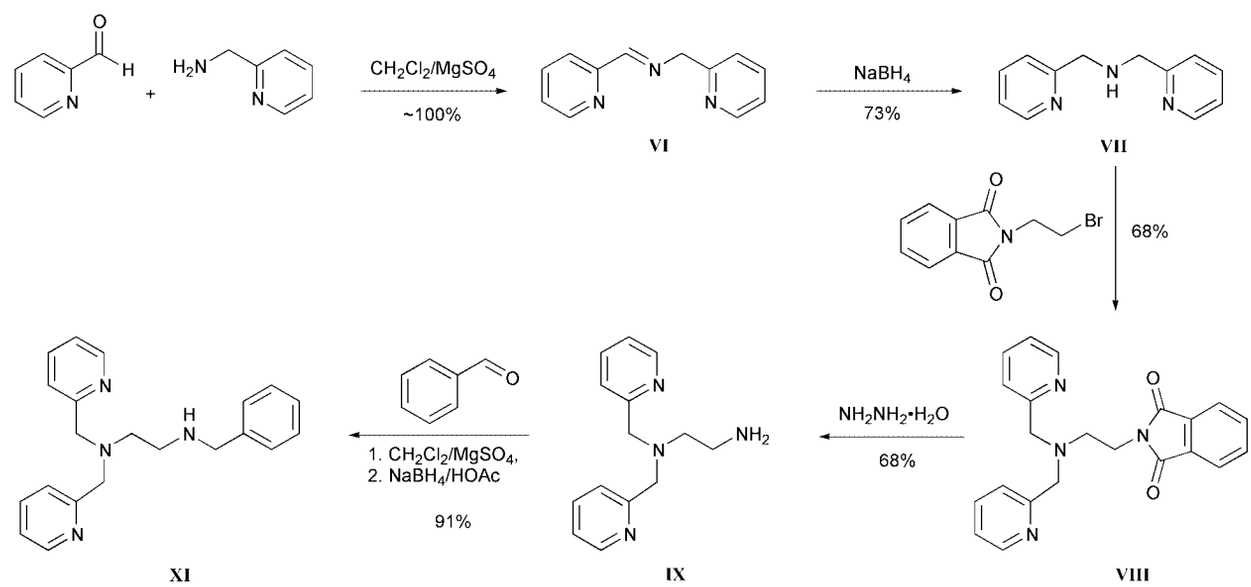
2 Complexes

Described here are five complexes which include all four ligands, **II**, **III**, **IV** and **V**. Four complexes are of Cu^{2+}, one each for the four ligands, and a di-manganese complex of ligand, **II**, is described. The synthesis, properties and structure of each is described separately.

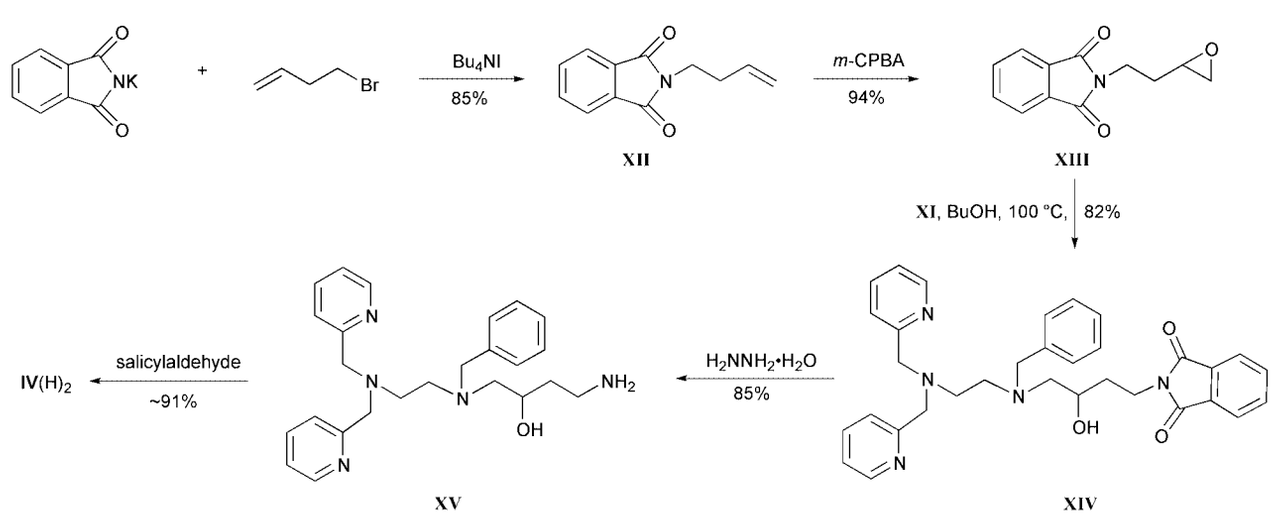
Table 1 Crystallographic data for $[Mn_2(\mathbf{II})(OEt)(\mu\text{-}OAc)(\mu\text{-}OEt)](PF_6)\cdot 2EtOH$ (**10**), $[Cu_4(\mathbf{II})_2(\mu\text{-}OAc)_2](PF_6)_2\cdot 2EtOH$ (**9**), $[Cu_4(\mathbf{III})_2(\mu\text{-}OAc)_2](PF_6)_4$ (**8**), $[Cu_4(\mathbf{V})_2(\mu\text{-}OAc)](PF_6)_3\cdot H_2O$ (**7**), and $[Cu_2(\mathbf{IV})(\mu\text{-}OAc)]PF_6$ (**6**)

	10	**9**	**8**	**7**	**6**
Formula	$C_{43}H_{62}F_6Mn_2N_5O_8P$	$C_{74}H_{92}Cu_4F_{12}N_{10}O_{10}P_2$	$C_{66}H_{82}Cu_4F_{24}N_{14}O_6P_4$	$C_{66}H_{75}Cu_4F_{18}N_{10}O_7P_3$	$C_{34}H_{38}Cu_2F_6N_5O_4P$
Formula weight	1031.82	1825.68	2001.49	1809.43	852.74
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a/Å	12.1741(2)	10.3158(2)	11.5418(6)	11.7811(2)	18.0761(2)
b/Å	13.5908(2)	12.0891(2)	13.7097(7)	16.6703(3)	21.1395(2)
c/Å	16.5007(2)	17.6124(2)	14.0734(8)	19.1074(2)	19.3919(2)
α/°	79.2919(8)	74.0125(2)	69.5232(11)	96.1665(2)	—
β/°	68.9785(3)	81.8911(5)	83.0061(13)	96.5247(6)	97.9872(2)
γ/°	79.8058(8)	71.7472(7)	77.5450(11)	96.2454(5)	—
V/Å^3	2485.88(3)	2001.61(5)	2034.5(3)	3678.78(12)	7338.14(3)
Z, $\overline{Z}$	2, 1	1, 1/2	1, 1/2	2, 1	8, 2
Crystal color, habit	Brown, plate	Green, plate	Blue, needle	Green, plate	Green, rod
D_{calc}/g cm^{-3}	1.378	1.515	1.633	1.633	1.544
μ(Mo-Kα)/cm^{-1}	6.16	11.78	12.23	13.11	12.78
T/K	223(2)	173(2)	223(2)	173(2)	173(2)
$R(F)$ (%)[a]	9.55	6.37	7.27	10.70	4.67
$R(wF^2)$ (%)[a]	31.49	19.22	17.51	27.43	15.49

[a] Quantity minimized = $R(wF^2) = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[(wF_o^2)^2]^{\frac{1}{2}}$; $R = \Sigma\Delta/\Sigma(F_o)$, $\Delta = |(F_o - F_c)|$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + \mathrm{Max}(F_o, 0)]/3$.

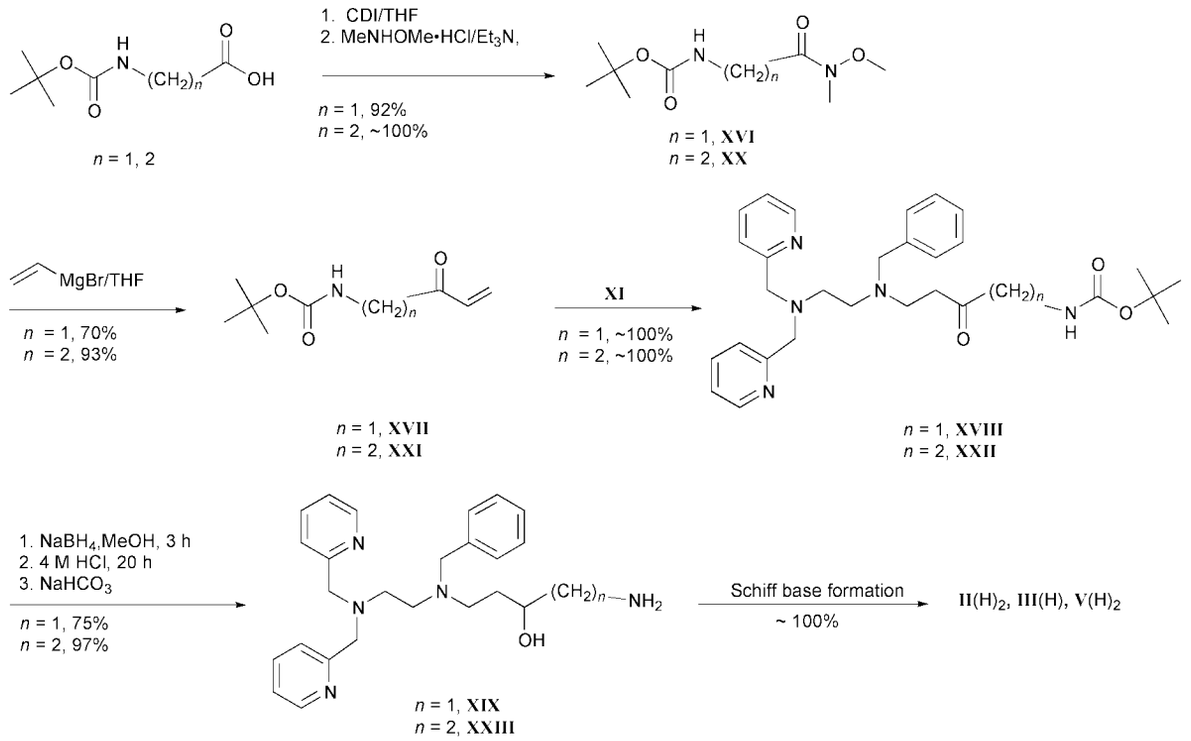


Scheme 1



Scheme 2

$[Cu_2(IV)(\mu\text{-}OAc)]PF_6$ (6). When $\mathbf{IV}(H)_2$ is allowed to react with copper acetate in methanol solution, a green solution is formed after the addition of triethylamine. Dark green crystals are formed upon the addition of NH_4PF_6, and deep green needles are obtained by ether diffusion into an acetonitrile solution. The product is a 1 : 1 electrolyte in acetonitrile solution and its solid state magnetic moment at 25 °C is 2.52 μ_B based on the formula above.



Scheme 3

Table 2 Selected bond lengths (Å) and angles (°) for [Cu_2(**IV**)-(μ-OAc)]PF_6 (**6**)

Cu(1)–O(1)	1.903(3)	Cu(2)–O(2)	1.949(2)
Cu(1)–O(2)	1.932(3)	Cu(2)–O(3)	1.964(2)
Cu(1)–N(1)	1.992(3)	Cu(2)–N(4)	2.006(3)
Cu(1)–O(4)	2.139(3)	Cu(2)–N(3)	2.089(3)
Cu(1)–N(5)	2.260(3)	Cu(2)–N(2)	2.400(3)
O(1)–Cu(1)–O(2)	174.68(11)	O(2)–Cu(2)–O(3)	93.82(10)
O(1)–Cu(1)–N(1)	93.64(12)	O(2)–Cu(2)–N(4)	161.87(12)
O(2)–Cu(1)–N(1)	89.68(12)	O(3)–Cu(2)–N(4)	92.58(12)
O(1)–Cu(1)–O(4)	91.66(12)	O(2)–Cu(2)–N(3)	89.60(11)
O(2)–Cu(1)–O(4)	89.81(10)	O(3)–Cu(2)–N(3)	174.34(12)
N(1)–Cu(1)–O(4)	125.22(12)	N(4)–Cu(2)–N(3)	82.85(12)
O(1)–Cu(1)–N(5)	85.69(12)	O(2)–Cu(2)–N(2)	77.26(11)
O(2)–Cu(1)–N(5)	89.10(11)	O(3)–Cu(2)–N(2)	103.03(12)
N(1)–Cu(1)–N(5)	140.16(12)	N(4)–Cu(2)–N(2)	117.67(12)
O(4)–Cu(1)–N(5)	94.60(11)	N(3)–Cu(2)–N(2)	82.13(13)
Metal–metal distance			
Cu(1)–Cu(2)	3.128(5)		

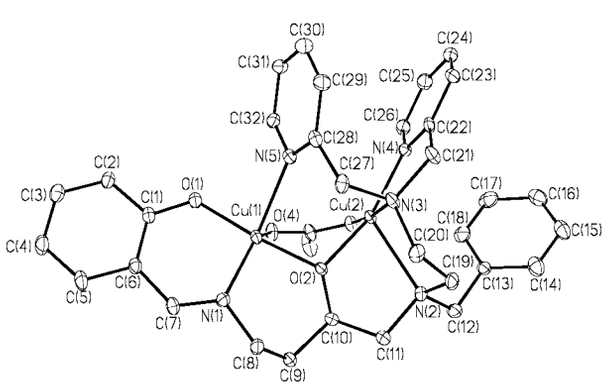


Fig. 1 ORTEP[25] structure of [Cu_2(**IV**)(μ-OAc)]PF_6 (**6**). Thermal ellipsoids are at 30% probability, counter-ion omitted for clarity.

The solid state structure was determined by X-ray diffraction. Table 1 contains diffraction data, Table 2 contains selected bond length and angle data and the structure is shown in Fig. 1.

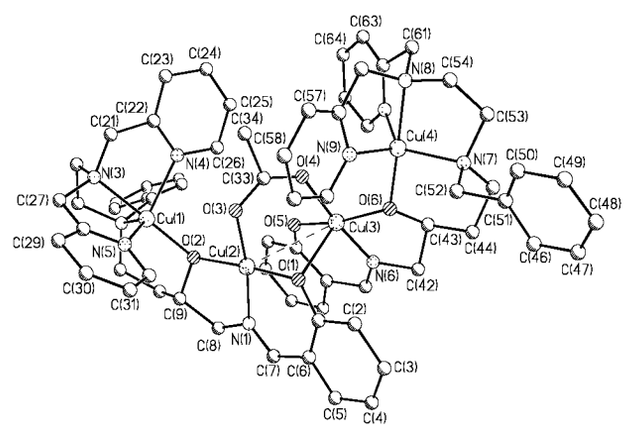


Fig. 2 Structure of [Cu_4(**V**)$_2$(μ-OAc)]$(PF_6)_3$·H_2O (**7**). Hydrogen atoms, counter-ions, and lattice solvent are omitted for clarity.

The Cu^{2+} ions (Cu(1), Cu(2)) are bridged by the alkoxide oxygen atom (O(2)) and by an acetate ion. Each Cu^{2+} ion is 5-coordinate, (Cu(1)) is in a distorted trigonal bipyramidal geometry and the other (Cu(2)) is a distorted square pyramid with an elongated axial (Cu(2)–N(2)) bond length. The pyridine ligand bearing N(5) is bonded to Cu(1) rather than to Cu(2) in which case Cu(2) would have become 6-coordinate, a coordination number disfavored by Cu^{2+}. The Cu(1)–N(5) bond length is longer than the others which surround Cu(1). To some extent, this structure probably reflects the inability of Cu^{2+} to form stable 6-coordinate complexes.

[Cu_4(V**)$_2$(μ-OAc)]$(PF_6)_3$ (7).** This complex was prepared in a similar manner to that described for the previous complex. The complex forms crystals which are green needles, it has a solid state magnetic moment at room temperature of 3.10 μ_B and is a 3 : 1 electrolyte in acetonitrile solutions.

Table 1 contains the crystallographic data. Table 3 lists selected bond lengths and angles and the structure is shown in Fig. 2.

The structure consists of two different di-Cu^{2+}-ligand units, a unit consisting of Cu(1) and Cu(2) and the other is Cu(3) and

Table 3 Selected bond lengths (Å) and angles (°) for $[Cu_4(\mathbf{V})_2(\mu\text{-}OAc)](PF_6)_3\cdot H_2O$ (**7**)

Cu(1)–O(2)	1.927(11)	Cu(3)–O(5)	1.918(12)
Cu(1)–N(3)	2.023(14)	Cu(3)–O(4)	1.923(11)
Cu(1)–N(5)	2.068(11)	Cu(3)–O(6)	1.988(12)
Cu(1)–N(2)	2.138(13)	Cu(3)–O(1)	2.382(8)
Cu(1)–N(4)	2.144(9)	Cu(4)–O(6)	1.932(10)
Cu(2)–N(1)	1.891(11)	Cu(4)–N(10)	2.058(13)
Cu(2)–O(3)	1.941(9)	Cu(4)–N(8)	2.089(14)
Cu(2)–O(1)	1.957(11)	Cu(4)–N(9)	2.116(12)
Cu(2)–O(2)	2.001(11)	Cu(4)–N(7)	2.138(15)
Cu(3)–N(6)	1.906(15)		
O(2)–Cu(1)–N(3)	177.7(5)	O(5)–Cu(3)–O(4)	90.1(5)
O(2)–Cu(1)–N(5)	101.1(5)	N(6)–Cu(3)–O(6)	84.7(6)
N(3)–Cu(1)–N(5)	80.8(5)	O(5)–Cu(3)–O(6)	164.6(4)
O(2)–Cu(1)–N(2)	93.6(5)	O(4)–Cu(3)–O(6)	92.1(5)
N(3)–Cu(1)–N(2)	84.2(5)	N(6)–Cu(3)–O(1)	96.4(4)
N(5)–Cu(1)–N(2)	132.8(4)	O(5)–Cu(3)–O(1)	92.3(3)
O(2)–Cu(1)–N(4)	100.7(4)	O(4)–Cu(3)–O(1)	88.8(3)
N(3)–Cu(1)–N(4)	79.4(5)	O(6)–Cu(3)–O(1)	102.9(4)
N(5)–Cu(1)–N(4)	119.8(5)	O(6)–Cu(4)–N(10)	98.2(5)
N(2)–Cu(1)–N(4)	100.8(4)	O(6)–Cu(4)–N(8)	177.7(5)
N(1)–Cu(2)–O(3)	169.2(4)	N(10)–Cu(4)–N(8)	83.2(5)
N(1)–Cu(2)–O(1)	92.1(5)	O(6)–Cu(4)–N(9)	98.7(4)
O(3)–Cu(2)–O(1)	89.6(4)	N(10)–Cu(4)–N(9)	122.5(5)
N(1)–Cu(2)–O(2)	86.3(5)	N(8)–Cu(4)–N(9)	79.0(5)
O(3)–Cu(2)–O(2)	91.2(4)	O(6)–Cu(4)–N(7)	95.3(5)
O(1)–Cu(2)–O(2)	175.7(3)	N(10)–Cu(4)–N(7)	129.2(5)
N(6)–Cu(3)–O(5)	91.7(6)	N(8)–Cu(4)–N(7)	85.2(6)
N(6)–Cu(3)–O(4)	174.4(4)	N(9)–Cu(4)–N(7)	103.2(5)
Metal–metal distances			
Cu(1)–Cu(2)	3.482(5)		
Cu(2)–Cu(3)	3.045(3)		
Cu(3)–Cu(4)	3.398(5)		

Table 4 Selected bond lengths (Å) and angles (°) for $[Cu_4(\mathbf{III})_2(\mu\text{-}OAc)_2](PF_6)_4$ (**8**)

Cu(1)–O(3)	1.914(5)	Cu(2)–O(1)#1	1.924(4)
Cu(1)–N(5)	2.045(5)	Cu(2)–O(1)	1.933(4)
Cu(1)–N(6)	2.079(5)	Cu(2)–N(3)	2.011(5)
Cu(1)–N(7)	2.079(6)	Cu(2)–N(1)	2.019(5)
Cu(1)–N(4)	2.187(5)	Cu(2)–O(2)	2.243(5)
O(3)–Cu(1)–N(5)	168.7(2)	O(1)#1–Cu(2)–O(1)	77.16(18)
O(3)–Cu(1)–N(6)	107.0(2)	O(1)#1–Cu(2)–N(3)	170.3(2)
N(5)–Cu(1)–N(6)	81.0(2)	O(1)–Cu(2)–N(3)	104.46(18)
O(3)–Cu(1)–N(7)	87.8(2)	O(1)#1–Cu(2)–N(1)	93.55(19)
N(5)–Cu(1)–N(7)	81.4(2)	O(1)–Cu(2)–N(1)	163.0(2)
N(6)–Cu(1)–N(7)	116.9(2)	N(3)–Cu(2)–N(1)	82.4(2)
O(3)–Cu(1)–N(4)	96.9(2)	O(1)#1–Cu(2)–O(2)	94.82(18)
N(5)–Cu(1)–N(4)	84.3(2)	O(1)–Cu(2)–O(2)	107.87(19)
N(6)–Cu(1)–N(4)	125.3(2)	N(3)–Cu(2)–O(2)	93.7(2)
N(7)–Cu(1)–N(4)	112.4(2)	N(1)–Cu(2)–O(2)	86.9(2)
Metal–metal distances			
Cu(2)–Cu(2A)	3.0154(14)		

[a] Symmetry transformation used: #1 $-x + 1, -y + 1, -z + 1$.

Cu(4). These two units are bridged by an acetate ligand joining Cu(2) and Cu(3) and a phenolate oxygen atom O(1). The pairs of Cu^{2+} ions of each unit are bridged by alkoxide oxygen atoms, namely, Cu(1)–O(2)–Cu(2) and Cu(3)–O(6)–Cu(4). The two Cu^{2+} ions, Cu(1) and Cu(4) are in a distorted trigonal bipyramidal geometry, whereas Cu(2) is square-planar and Cu(3) is square pyramidal. In the last, the axial bond Cu(3)–O(1) is elongated. The other bond lengths vary but are within the range expected for the individual Cu^{2+} geometries. As in the previous structure, this structure adopts favorable Cu^{2+} geometries.

$[Cu_4(\mathbf{III})_2(\mu\text{-}OAc)_2](PF_6)_4$ (8). This compound was prepared in a manner similar to that for the two previous compounds. It crystallizes from acetonitrile–ether as blue-green needles, it has

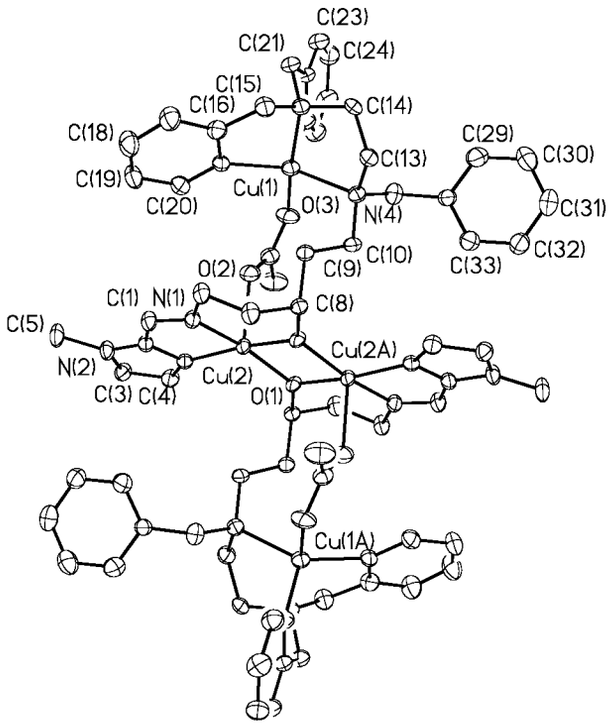


Fig. 3 ORTEP structure of $[Cu_4(\mathbf{III})_2(\mu\text{-}OAc)_2](PF_6)_4$ (**8**). Thermal ellipsoids are at 30% probability and counter-ions are omitted for clarity.

a room temperature, solid state magnetic moment of 2.83 μ_B, and is a 4 : 1 electrolyte in acetonitrile solutions. The crystallographic data is collected in Table 1, selected bond lengths and angles are listed in Table 4 and the structure is shown in Fig. 3.

The molecule lies on a center of inversion. The central two Cu^{2+}ions are bridged by the alkoxide groups of the two ligands and the terminal Cu^{2+} ions are bridged to the two central ions by acetate ligands. All Cu^{2+} ions are 5-coordinate, the central two Cu^{2+} ions are distorted square pyramids with an elongated Cu–O acetate bond whereas the terminal Cu^{2+} ions are in a distorted trigonal bipyramidal geometry.

$[Cu_4(\mathbf{II})_2(\mu\text{-}OAc)_2](PF_6)_2\cdot 2EtOH$ (9). By similar methods to those above, this complex was isolated as dark green blocks, it has a solid state magnetic moment at room temperature of 2.62 μ_B and is a 2 : 1 electrolyte in acetonitrile solutions. Crystallographic data is provided in Table 1, selected bond lengths and angles are collected in Table 5 and the structure is illustrated in Fig. 4.

As for the previous structure, the present molecule has a center of inversion and generally resembles the tetramer formed by **III**. The major difference is associated with the acetate ligands which, in this case, are terminally bonded to the outer Cu^{2+} ions. As a consequence, the inner two Cu^{2+} ions are square planar and are bridged to each other by the alkoxide groups of the two ligands. The terminal Cu^{2+} ions are in a distorted trigonal bipyramidal geometry.

$[Mn_2(\mathbf{II})(OEt)(\mu\text{-}OAc)(\mu\text{-}OEt)](PF_6)\cdot 2EtOH$ (10). The ligand, $\mathbf{II}(H)_2$, was reacted with $Mn(OAc)_2\cdot 4H_2O$ in ethanol under an inert atmosphere to give a yellow-orange solution which turned orange upon the addition of one equivalent of triethylamine. Heating this solution and the addition of NH_4PF_6 led to the formation of a brown suspension. After filtration, the filtrate was exposed to air. Orange-brown crystals of $[Mn_2(\mathbf{II})(OEt)(\mu\text{-}OAc)(\mu\text{-}OEt)](PF_6)\cdot 2EtOH$ slowly formed which effloresce when the solvent is removed. The material has a room temperature magnetic moment of 7.31 μ_B and is a 1 : 1 electrolyte in acetonitrile solutions. Thus the complex could

Table 5 Selected bond lengths (Å) and angles (°) for $[Cu_4(\mathbf{II})_2(\mu\text{-}OAc)_2](PF_6)_2\cdot 2EtOH$ (**9**)

Cu(1)–O(1)	1.898(4)	Cu(2)–N(3)	2.063(4)
Cu(1)–O(2)	1.925(3)	Cu(2)–N(5)	2.086(4)
Cu(1)–O(2)#1	1.956(3)	Cu(2)–N(4)	2.133(4)
Cu(1)–N(1)	1.977(4)	Cu(2)–N(2)	2.154(4)
Cu(2)–O(3)	1.956(4)		
O(1)–Cu(1)–O(2)	166.48(15)	N(3)–Cu(2)–N(5)	80.85(18)
O(1)–Cu(1)–O(2)#1	91.77(14)	O(3)–Cu(2)–N(4)	100.42(16)
O(2)–Cu(1)–O(2)#1	75.56(15)	N(3)–Cu(2)–N(4)	81.01(16)
O(1)–Cu(1)–N(1)	95.38(16)	N(5)–Cu(2)–N(4)	117.05(15)
O(2)–Cu(1)–N(1)	97.72(16)	O(3)–Cu(2)–N(2)	102.90(16)
O(2)#1–Cu(1)–N(1)	170.83(15)	N(3)–Cu(2)–N(2)	85.29(15)
O(3)–Cu(2)–N(3)	170.43(17)	N(5)–Cu(2)–N(2)	127.46(15)
O(3)–Cu(2)–N(5)	90.15(17)	N(4)–Cu(2)–N(2)	110.25(14)
Metal–metal distance			
Cu(1)–Cu(1A)	3.067(5)		

[a] Symmetry transformation used: #1 $-x+1, -y+1, -z+1$.

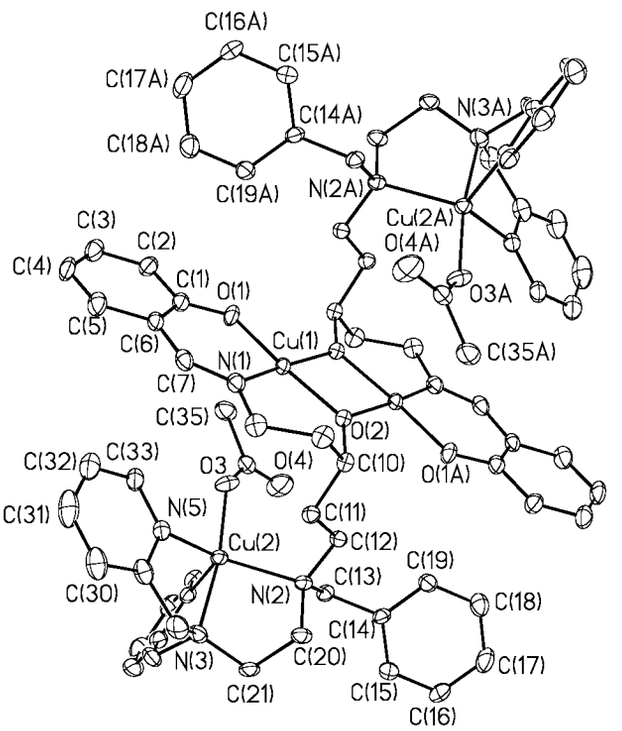


Fig. 4 ORTEP structure of $[Cu_4(\mathbf{II})_2(\mu\text{-}OAc)_2](PF_6)_2\cdot 2EtOH$ (**9**). Thermal ellipsoids are at 30% probability and hydrogen atoms, counter-ions, and lattice solvent are omitted for clarity.

be a $Mn^{3+}Mn^{3+}$ or $Mn^{2+}Mn^{4+}$ complex where, in either case, the metals are antiferromagnetically coupled which decreases the moment from the spin-only value of 8.9 μ_B. One, poorly resolved, d–d electronic absorption band is observed at 520 nm (ε, 420 L mol^{-1} cm^{-1}). The crystal structure of this complex suggests that it is a mixed valence $Mn^{2+}Mn^{4+}$ compound. Crystallographic data is provided in Table 1, selected bond lengths and angles are given in Table 6 and the structure is shown in Fig. 5.

In the structure, the two manganese ions are bridged by the alkoxide group of the ligand, by an exogenous ethoxide ion and by an acetate ligand. Both manganese ions are 6-coordinate with Mn(1) bonded to a terminal ethoxide ligand. Of the two molecules of ethanol of crystallization, one appears to be hydrogen bonded to the oxygen atom of the terminal ethoxide ligand and the other seems to be bonded to one of the oxygen atoms of the acetate bridge. The bond lengths of Mn(1) are generally shorter than those of Mn(2) although the axial (O(6)–

Table 6 Selected bond lengths (Å) and angles (°) for $[Mn_2(\mathbf{II})(OEt)(\mu\text{-}OAc)(\mu\text{-}OEt)](PF_6)\cdot 2EtOH$ (**10**)

Mn(1)–O(1)	1.896(7)	Mn(2)–O(5)	2.117(5)
Mn(1)–O(3)	1.901(6)	Mn(2)–O(3)	2.130(7)
Mn(1)–O(2)	1.912(6)	Mn(2)–O(2)	2.136(6)
Mn(1)–N(1)	2.010(8)	Mn(2)–N(4)	2.270(9)
Mn(1)–O(4)	2.220(6)	Mn(2)–N(3)	2.333(5)
Mn(1)–O(6)	2.326(6)	Mn(2)–N(2)	2.354(9)
O(1)–Mn(1)–O(3)	93.2(3)	O(5)–Mn(2)–O(3)	96.8(2)
O(1)–Mn(1)–O(2)	176.6(2)	O(5)–Mn(2)–O(2)	93.0(2)
O(3)–Mn(1)–O(2)	83.8(3)	O(3)–Mn(2)–O(2)	73.3(3)
O(1)–Mn(1)–N(1)	88.8(3)	O(5)–Mn(2)–N(4)	93.9(2)
O(3)–Mn(1)–N(1)	174.4(2)	O(3)–Mn(2)–N(4)	91.7(3)
O(2)–Mn(1)–N(1)	94.1(3)	O(2)–Mn(2)–N(4)	164.1(3)
O(1)–Mn(1)–O(4)	93.1(3)	O(5)–Mn(2)–N(3)	163.8(3)
O(3)–Mn(1)–O(4)	93.7(3)	O(3)–Mn(2)–N(3)	93.5(2)
O(2)–Mn(1)–O(4)	88.6(2)	O(2)–Mn(2)–N(3)	101.8(2)
N(1)–Mn(1)–O(4)	91.4(3)	N(4)–Mn(2)–N(3)	73.4(2)
O(1)–Mn(1)–O(6)	85.8(3)	O(5)–Mn(2)–N(2)	95.2(3)
O(3)–Mn(1)–O(6)	85.6(3)	O(3)–Mn(2)–N(2)	161.9(3)
O(2)–Mn(1)–O(6)	92.4(2)	O(2)–Mn(2)–N(2)	92.5(3)
N(1)–Mn(1)–O(6)	89.3(3)	N(4)–Mn(2)–Mn(1)	128.4(2)
O(4)–Mn(1)–O(6)	178.7(3)	N(3)–Mn(2)–Mn(1)	112.2(2)
Metal–metal distance			
Mn(1)–Mn(2)	3.0367(19)		

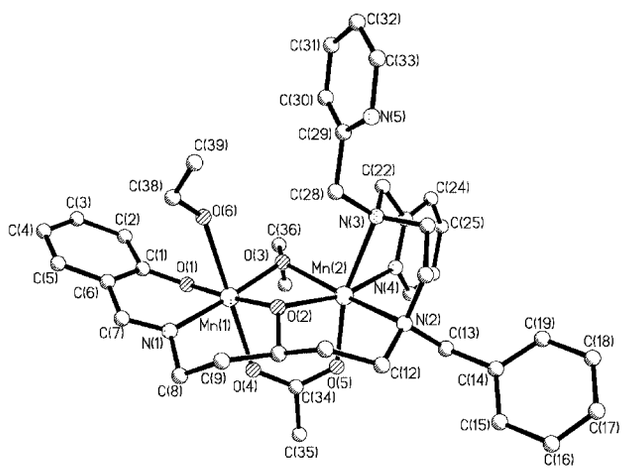


Fig. 5 Structure of $[Mn_2(\mathbf{II})(OEt)(\mu\text{–}OAc)(\mu\text{-}OEt)](PF_6)\cdot 2EtOH$ (**10**). Hydrogen atoms, counter-ion, and lattice solvent omitted for clarity.

Mn(1)) and (O(4)–Mn(1)) bond lengths are longer than the bond lengths in the Mn(1) plane. The axial bond lengths of Mn(1) are comparable to the bond lengths found for Mn(2). The crystal structure contains two ethanol molecules which are oriented and positioned for hydrogen bonding with O(6) and O(4). If this is so, the elongation of the axial bonds may be caused by hydrogen bonding. The two ethanols of crystallization are omitted from Fig. 5 for clarity. It is perhaps significant that the bridge bonds are of different lengths, that is, the Mn(1)–O(3) and Mn(1)–O(2) bond lengths are much shorter than the analogous bonds, Mn(2)–O(3) and Mn(2)–O(2). This asymmetry and the average bond lengths of the two metals suggest that Mn(1) is in the Mn^{4+} oxidation state and that Mn(2) is in the Mn^{2+} level. Consistent with this mixed valence assignment is the presence of four negative oxygen ligands coordinated to the Mn^{4+} ion. The ability of O_2 to oxidize Mn^{2+} to Mn^{4+} probably depends on the presence of these oxygen donors. It will be noted that one of the pyridine ligands of the binucleating ligand is not coordinated.

Discussion

This series of crystal structures indicates that the present set of ligands does not readily form the desired bimetallic complexes,

5. Rather oligomeric complexes or otherwise unexpected structures are formed when the structure is not oligomeric. It is not clear that the structures reported, particularly for the oligomeric Cu^{2+} complexes, are not a consequence of solubility where the least soluble solution species crystallizes. If this were the case for some of the complexes, the structure would depend on the solvent and the counter-ion. It could be argued that the Cu^{2+} oligomers form in part because of the instability of the octahedral geometry and that oligomerization leads to stable 4- and 5-coordination numbers as observed. This may be a factor for the copper complexes but it is probably not the only factor. Attempts to prepare Co^{2+}, Ni^{2+} and Mn^{2+} complexes with these ligands led to the formation of ill-defined species which appeared to be oligomeric. Since these metals were expected to accommodate 6-coordination, the formation of oligomers suggests that the ligands carry an inherent proclivity to oligomerize. The tendency of this set of ligands to form oligomers is perhaps surprising, given the observations reported on ligands of type **I**. Binucleating ligands of this type, whether possessing a phenolate bridge[22–24] or an alkoxide bridge[4–15] are reported to form binuclear complexes with nearly all first row transition metals, including a number of di-Cu^{2+} complexes.[4–8] There are examples where tetrametallic complexes are formed when two bimetallic complexes are joined by exogenous bridges, but in these cases the ligand in each bimetallic unit binds in the expected way.[15] In this respect the present ligands are unique in not forming the expected bimetallic structures, **5**. The binuclear complexes formed by type **I** ligands represent a part of the structure, **5**, and it might be anticipated that the final extension of the type **I** complexes to **5** would not represent a complication. This, of course, was the assumption, which provided the impetus for the present work. The tendency for the formation of oligomers with ligands, **II**, **III**, **IV** and **V**, is probably connected with the flexibility of these ligands. The traditional ligands of type **I** have fewer degrees of freedom to form oligomers than do the present ligands. The possibility that alkoxides are poor bridging ligands and thus allow for oligomerization is unlikely because the present oligomeric complexes display extensive dimetal alkoxide bridging. It thus appears that the major reason for oligomerization is the flexibility of the ligands. The present work serves to illustrate the limits of binucleating ligand design.

Acknowledgements

This work was supported by grants from the NSF, NIH and PRF.

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