Octanuclear Bis(triple-helical) Metal(II) Complexes

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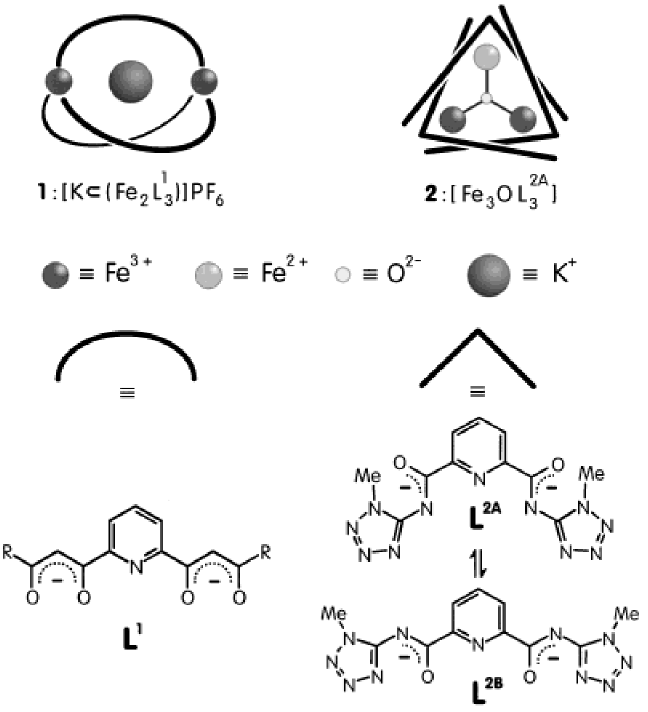
The reaction of H_2L^1 and H_2L^2 with divalent metal ions leads to octanuclear bis(triple-helical) metal(II) complexes of the general composition $[Zn_8O_2L^2{}_6]$ (**3**) and $[M_8O_2L^1{}_6]$ (**4**: M = Cd^{2+}; **5**: M = Mn^{2+}). NMR studies of the diamagnetic cadmium complex **4c** show six equivalent ligands. Unambiguous characterisation of **5b** was achieved by X-ray crystallographic analysis.

There is considerable interest in the design of metallo-supramolecular oligomers containing a defined number of metal ions in a determined spatial arrangement. In principle, it is possible to selectively generate a large variety of structures by choosing the appropriate ligands and metal ions.[1][2] Our interest in polynuclear supramolecular complexes, with two or more Fe^{III} ions bridged by oxygen and nitrogen donor ligands, stems mainly from the importance of oxo-centered polyiron aggregates as model compounds for metalloproteins, oxidation catalysts and corrosion inhibitors.[3]

Complexation of trivalent Fe ions with the doubly negatively charged, pentadentate ligand L^1 leads to the {2}-metallacryptate $[K\subset(Fe_2L^1{}_3)]PF_6$ (**1**).[4] In contrast to L^1, nucleation of iron with the isodentate ligand L^2 yields the triple-helical, oxo-centered, trinuclear mixed-valence iron complex $[Fe_3OL^{2A}{}_3]$ (**2**)[5] but, unexpectedly, no {2}-metallacryptate $[K\subset(Fe_2L^{2B}{}_3)]PF_6$. This result can be explained by the fact that the pentadentate ligand L^2 exists as two different rotamers, L^{2A} and L^{2B} in solution. In the case of L^{2A} the coordination donors are five nitrogen atoms, whereas in the case of L^{2B} the donor atoms are three nitrogen and two oxygen atoms. Due to the topological equivalency of the ligand L^1 and the rotamer L^{2B}, one expects to obtain, using appropriate transition metals, isostructural complexes by nucleation of L^1 and L^2.

Herein we describe the reaction of the pentadentate tritopic ligands L^1 and L^{2B} with divalent metal ions such as zinc, cadmium and manganese. Treatment of 0.75 equiv. of the pyridylene-spacered tetraketone[6] H_2L^1 or the bis(tetrazole)[7] H_2L^2, with one equiv. of zinc acetate, cadmium or manganese dichloride furnishes the coordination compounds **3**−**5** which range from colourless to orange in appearance.



The compositions of these complexes were determined by FAB mass spectrometry (FAB = fast-atom bombardment). The FAB-MS spectrum of complex $[Zn_8O_2L^{2B}{}_6]$ (**3**) exhibits the correct molecular peak and isotopic pattern at *m/z* 2519 (Figure 1). According to their FAB-MS data, the corresponding cadmium (**4**) and manganese (**5**) complexes have the same composition.

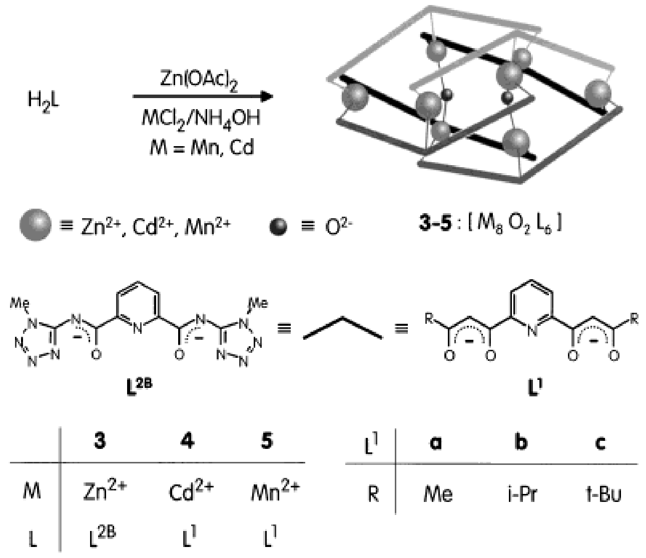
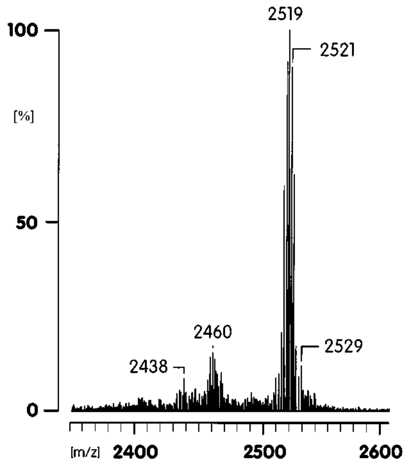


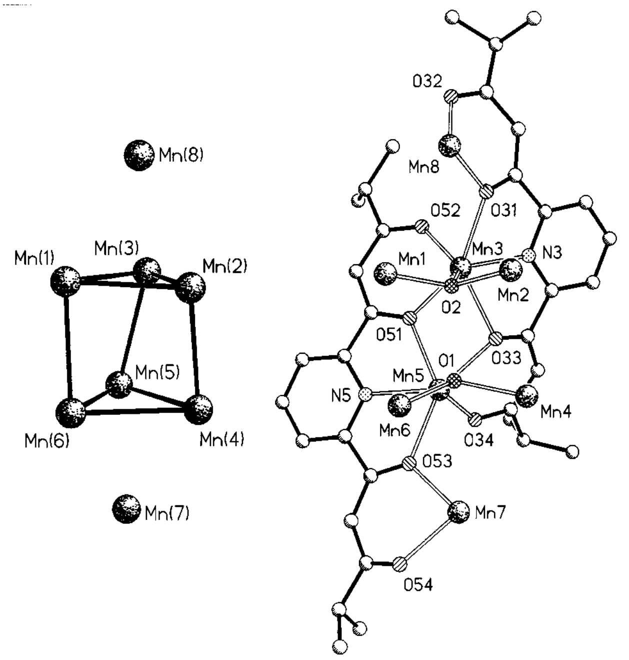
Figure 1. FAB-MS spectrum of zinc complex **3**



^1H- and ^{13}C-NMR studies of the diamagnetic cadmium complex $[Cd_8O_2L_6{}^{1c}]$ (**4c**) reveals that, in solution, all six ligands are chemically identical, but that the two halves of each ligand are in different magnetic environments. Consequently, the ^{13}C-NMR spectrum of **4c** displays a double set of signals in contrast to the single set of the protonated free ligand H_2L^{1c}.

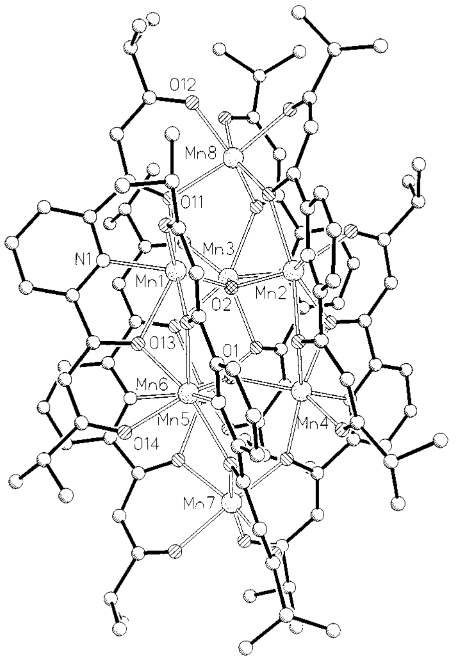
In order to unequivocally establish the structure of the polynuclear systems **3**−**5**, the manganese complex **5b** was taken as a representative example and we carried out an X-ray crystallographic analysis.[8] According to this analysis, **5b** is present in the crystal as a neutral, octanuclear bis(triple-helical) chelate complex. The core of **5b** consists of eight manganese(II) ions, forming a twofold capped, slightly twisted trigonal prism with a μ_3-O^{2-} ion centered in each of the two inner faces (Figure 2.). All the six doubly negatively charged pentadentate ligands L^{1b} link to three manganese atoms. The two antipodal manganese(II) ions are coordinated by three μ_1- and three μ_2-oxygen chelate atoms of three ligands. However, the six metal centers, constituting the trigonal prism, are coordinated by one pyridylene nitrogen and two μ_2-chelate oxygen atoms. Distorted octahedral coordination of these six manganese(II) ions is achieved by two extra μ_3-O^{2-} ions.

Figure 2. Left: Core of the octanuclear complex **5b** to highlight the bicapped distorted trigonal prism; right: Octanuclear core of **5b** showing two ligands and the μ_3-O^{2-} ions; H atoms omitted for clarity, O atoms hatched, C atoms shaded, N atoms empty, Mn atoms dotted



Consequently, in the neutral, octanuclear, bis(triple-helical) complex **5b** all the manganese(II) ions are octahedrally coordinated (Figure 3).

Figure 3. Molecular structure of the octanuclear complex **5b** in the crystal; H atoms omitted for clarity, O atoms hatched, C atoms shaded, N atoms empty, Mn atoms dotted



As shown by X-ray crystallographic analysis[12], the zinc complex **3** is isostructural with **5b**. The space-filling model of **3** (Figure 4) illustrates the bis(triple-helical) arrangement of the ligands.

Figure 4. Space-filling model of bis(triple-helical) octanuclear [$Zn_8O_2L^{2B}{}_6$] (**3**); top: view along the C_3 axis; bottom: view along the C_2 axis

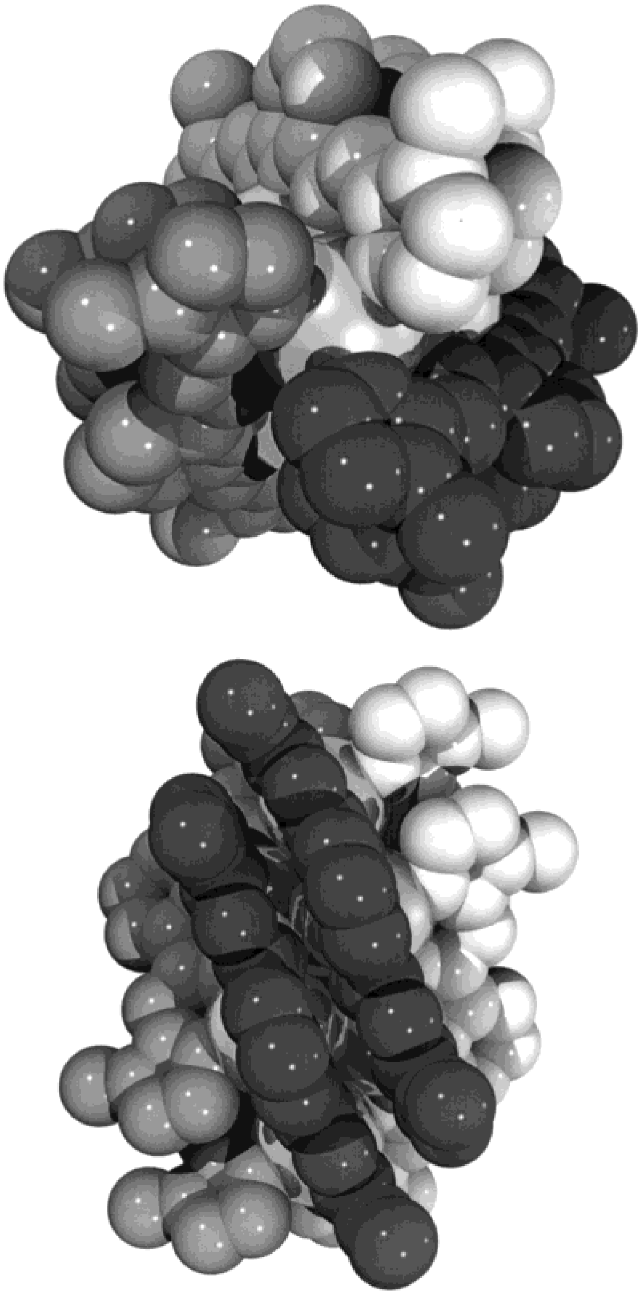
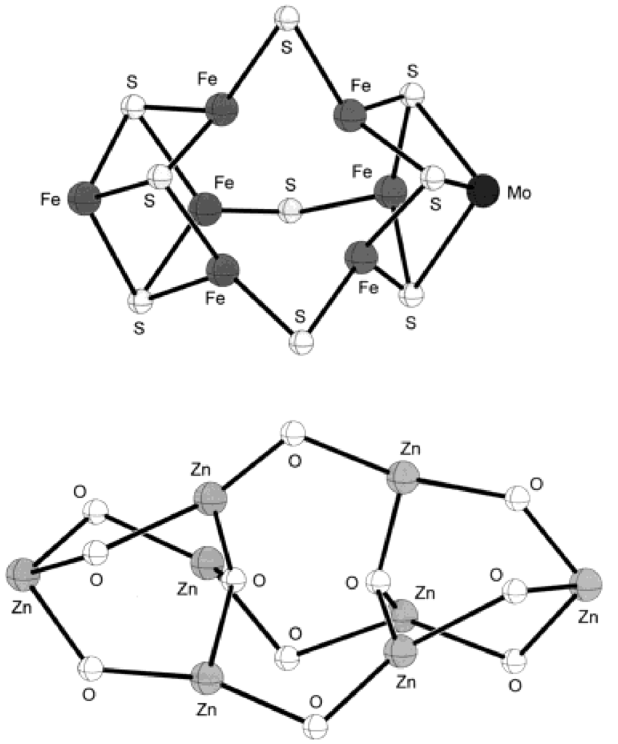


Figure 5. Top: Core of the iron-molybdenum co-factor of nitrogenase[13]; bottom: torso of [$Zn_8O_2L^{2B}{}_6$] (**3**)



The similarity between the core of the octanuclear complex **3** and the metal framework of the iron-molybdenum co-factor of the nitrogenase MoFe protein[13] is noteworthy (Figure 5).

In conclusion these results demonstrate clearly that the formation of metalla-supramolecular structures is highly sensitive with respect to the metal ions, the ligands and their conformation. In contrast to the {2}-iron(III) cryptate **1** and the oxo-centered iron(III) complex **2,** both ligands $(L^1)^{2-}$ and $(L^{2A}/L^{2B})^{2-}$ lead to the isostructural bis(triple-helical) octanuclear complexes, i.e. [$Zn_8O_2L^{2B}{}_6$] (**3**), [$Cd_8O_2L^1{}_6$] (**4**) and [$Mn_8O_2L^1{}_6$] (**5**).

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Experimental Section

^{1}H- and ^{13}C-NMR spectra: Jeol JNM-GX-400 (400 MHz; 100 MHz) spectrometer with TMS as internal standard, chemical shifts are given in ppm. − Mass spectra: Varian MAT 3rA (EIMS) or a Finnigan MAT TSQ 70 instrument (ion desorption from *m*-NBA matrix: 10 keV xenon atoms, FAB MS). − Microanalyses: Heraeus CHN-Mikroautomat. − IR: Perkin−Elmer 1420 Ratio-Recording Infrared Spectrophotometer.

General Procedure for the Synthesis of the Bis(tetrazole) Ligand $\mathbf{H_2L^2}$: A cooled suspension of 2.0 g (20 mmol) *N*-methylaminotetrazole and 2.0 g (47 mmol) of dry lithium chloride was placed in a three-necked, round-bottom flask, fitted with a condenser. The contents of the flask were stirred, while 2.03 g (10 mmol) of 2,6-pyridinedicarboxylic dichloride was slowly added. The solution was poured into ice-cold water (400 ml), stirred for 2 h and the white precipitate was filtered off, washed with water and dried in vacuo (oil pump).

N,N'-Bis(1-methyl-1H-tetrazol-5-yl)pyridyl-2,6-dicarboxamide ($\mathbf{H_2L^2}$): Yield 2.77 g (84%), white powder, m.p. > 250°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3340 cm^{-1}, 3120 (NH), 3020 (=CH), 2920 (CH_3), 1690 (C=O), 1550 (C=C). − ^{1}H NMR (CD_3CN/CF_3COOD): δ = 4.25 (s, 6 H, 2 CH_3), 8.39 (t, $^3J_{H,H}$ = 7.7 Hz, 1 H, 4-pyridyl-CH), 8.63 (d, $^3J_{H,H}$ = 7.7 Hz, 2 H, 3,5-pyridyl-CH). − ^{13}C NMR

(CD_3CN/CF_3COOD): δ = 37.08 (2 CH_3), 129.84 (3,5-pyridyl-CH), 142.56 (4-pyridyl-CH), 148.13 (2,6-pyridyl-C=), 150.25 (2 CN_2), 164.19 (2 C=O). − MS (EI, 70 eV); *m/z*: 330 [M^+]. − $C_{11}H_{11}N_{11}O_2$ (329.32): calcd. C 40.12, H 3.37, N 46.80; found C 39.55, H 3.74, N 45.93.

General Procedure for the Synthesis of the Octameric Zinc Complex **3**: A solution of 293 mg (1.33 mmol) of $Zn(OAc)_2 \cdot 2\ H_2O$ in methanol (50 ml) was added to a solution of 329 mg (1.0 mmol) bis(tetrazole) H_2L^2 in acetonitrile (400 ml). The reaction mixture was stirred and heated under reflux for 24 h. The resulting precipitate was filtered off washed with diethyl ether and dried in vacuo. The resulting solid was recrystallized from hot acetonitrile.

[$Zn_8O_2L^{2b}{}_6$]$_2$ (**3**): Yield 365 mg (87%) of colourless crystals from acetonitrile, m.p. > 250°C (decomp.). − IR (KBr): ṽ = 1640 cm^{-1} (C=O), 1550 (C=C), 1450 (C=N). − MS (FAB, *m*-NBA); *m/z*: 2519 [M^+]. − $C_{66}H_{54}N_{66}O_{14}Zn_8$ (2518.70): calcd. C 31.48, H 2.16, N 36.70; found C 31.53, H 2.98, N 36.16.

General Procedure for the Synthesis of the Pyridyl-Spacered Tetraketones (**H_2L^1**): A suspension of 1.0 g (44 mmol) of freshly cut sodium and diethyl 2,6-pyridinedicarboxylate (4.90 g, 22 mmol) in dry benzene (50 ml) was placed in a three-necked, round-bottom flask, fitted with a condenser. The contents of the flask were stirred, while a solution of the corresponding methyl ketone (44 mmol) in benzene (25 ml) was added dropwise. Stirring at room temp. was continued for 30 min until the yellow sodium salt had precipitated out of the solution. The reaction mixture was heated gently for about 2−4 h. The sodium salt was collected by filtration and washed thoroughly with petroleum ether before drying. The dry solid was added to dilute hydrochloric acid (2 N, 50 ml) and the resulting solid was collected by filtration. The crude products were recrystallized from the mentioned solvents.

1,1′-(2,6-Bispyridyl)bis-1,3-butanedione (**H_2L^{1a}**): [The ^{1}H-NMR spectrum shows the presence of keto-enol tautomers. In the following we describe only the main tautomer (90%), the bis(keto-enol) system.] Yield 2.30 g (42%), yellow microcrystals from methanol, m.p. 60°C. − IR (KBr): ṽ = 3450 cm^{-1} (OH), 2920 (CH), 1720 (C=O), 1620 (C=C). − ^{1}H NMR ($CDCl_3$): δ = 2.30 (s, 6 H, 2 CH_3), 6.87 (s, 2 H, 2 =CH), 7.99 (t, $^3J_{H,H}$ = 7.7 Hz, 1 H, 4-pyridyl-CH), 8.24 (d, $^3J_{H,H}$ = 7.7 Hz, 2 H, 3,5-pyridyl-CH), 15.75 (br. s, 2 H, 2 =C−OH). − ^{13}C NMR ($CDCl_3$): δ = 26.13 (2 CH_3), 97.27 (2 =CH), 124.29 (3,5-pyridyl-CH), 138.16 (4-pyridyl-CH), 151.71 (2,6-pyridyl-C=), 180.43 (2 =C−OH), 194.92 (2 C=O). − MS (EI, 70 eV); *m/z*: 247 [M^+]. − $C_{13}H_{13}NO_4$ (247.25): calcd. C 63.15, H 5.31, N 5.67; found C 63.23, H 5.49, N 5.63.

1,1′-(2,6-Bispyridyl)bis-4-methyl-1,3-pentanedione (**H_2L^{1b}**): [The ^{1}H-NMR spectrum shows the presence of keto-enol tautomers. In the following we describe only the main tautomer (75%), the bis(keto-enol) system.] Yield 2.40 g (36%), yellow microcrystals from methanol, m.p. 44°C. − IR (l, $CHBr_3$): ṽ = 3480 cm^{-1} (OH), 2950 (CH), 1600 (C=O), 1550 (C=C). − ^{1}H NMR ($CDCl_3$): δ = 1.27 (d, $^3J_{H,H}$ = 7.0 Hz, 12 H, 4 CH_3), 2.37 [sept, 2 H, 2 C*H*(CH_3)$_2$], 6.92 (s, 2 H, 2 =CH), 7.98 (t, $^3J_{H,H}$ = 7.7 Hz, 1 H, 4-pyridyl-CH), 8.19 (d, $^3J_{H,H}$ = 7.7 Hz, 2 H, 3,5-pyridyl-CH), 15.81 (br. s, 2 H, 2 =C−OH). − ^{13}C NMR ($CDCl_3$): δ = 19.23 (4 CH_3), 37.55 [2 *C*H(CH_3)$_2$], 94.67 (2 =CH), 124.63 (3,5-pyridyl-CH), 138.40 (4-pyridyl-CH), 151.80 (2,6-pyridyl-C=), 181.61 (2 =C−OH), 201.79 (2 C=O). − MS (EI, 70 eV); *m/z*: 303 [M^+]. − $C_{17}H_{21}NO_4$ (303.36): calcd. C 67.31, H 6.98, N 4.62; found C 67.02, H 6.88, N 4.69.

1,1′-(2,6-Bispyridyl)bis-4,4′-dimethyl-1,3-pentanedione (**H_2L^{1c}**): Yield 0.93 g (13%), colourless needles from methanol, m.p. 124°C: − IR (l, $CHBr_3$): ṽ = 3440 cm^{-1} (OH), 2970 (CH), 1610 (C=O), 1570 (C=C). − ^{1}H NMR ($CDCl_3$): δ = 1.30 (s, 18 H, 6 CH_3), 7.13 (s, 2 H, 2 =CH), 7.99 (t, $^3J_{H,H}$ = 7.8 Hz, 1 H, 4-pyridyl-CH), 8.19 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H, 3,5-pyridyl-CH), 15.90 (br. s, 2 H, 2 = C−OH). − ^{13}C NMR ($CDCl_3$): δ = 27.24 (6 CH_3), 39.87 [2 *C*(CH_3)$_2$], 92.59 (2 =CH), 123.98 (3,5-pyridyl-CH), 138.21 (4-pyridyl-CH), 151.86 (2,6-pyridyl-C=), 182.39 (2 =C−OH), 202.78 (2 C=O). − MS (EI, 70 eV); *m/z*: 331 [M^+]. − $C_{19}H_{22}NO_4$ (331.41): calcd. C 68.86, H 7.58, N 4.23; found C 68.34, H 7.56, N 4.24.

General Procedure for the Synthesis of the Octameric Cadmium (**4a−c**) *and Manganese* (**5a−c**) *Complexes:* Aqueous ammonia (2 ml, 12%) was added dropwise to a solution of 184 mg (1.0 mmol) cadmium chloride or 126 mg (1.0 mmol) manganese(II) chloride and the appropriate pyridyl-spacered ligand H_2L^1 (0.75 mmol) in ethanol (100 ml), until no more turbidity was seen. To achieve complete precipitation of the products, water (100 ml) was added. The products were filtered off and dried in vacuo (oil pump) and recrystallized from the solvents described above.

[$Cd_8O_2L^{1a}{}_6$] (**4a**): Yield 180 mg (60%), yellow microcrystals from ethanol, m.p. 290°C (decomp.). Because of the total insolubility in all available solvents, detailed NMR investigations could not be carried out. − IR (KBr): ṽ = 2970 cm^{-1} (CH), 1610 (C=O), 1585 (C=C). − MS (FAB, *m*-NBA); *m/z*: 2402 [M^+]. − $C_{77}H_{66}Cd_8N_6O_{26}$ (2402.69): calcd. C 38.99, H 2.77, N 3.50; found C 41.60, H 3.99, N 3.61.

[$Cd_8O_2L^{1b}{}_6$] (**4b**): Yield 320 mg (94%), yellow microcrystals from ethanol, m.p. 275°C (decomp.). Because of the total insolubility in all available solvents, detailed NMR investigations could not be carried out. − IR (l, $CHBr_3$): ṽ = 2960 cm^{-1} (CH), 1610 (C=O), 1500 (C=C) − MS (FAB, *m*-NBA); *m/z*: 2740 [M^+]. − $C_{102}H_{114}Cd_8N_6O_{26}$ (2739.34): calcd. C 44.72, H 4.20, N 3.07; found C 43.55, H 4.48, N 3.07.

[$Cd_8O_2L^{1c}{}_6$] (**4c**): Yield 280 mg (77%), yellow microcrystals from ethanol, m.p. 285°C (decomp.). − IR (KBr): ṽ = 2950 cm^{-1} (CH), 1610 (C=O), 1450 (C=C). − ^{1}H NMR ($CDCl_3$): δ = 0.71, 1.24 (s, 54 H, 18 CH_3), 5.35, 6.22 (s, 6 H, 6 =CH), 7.57 (d, $^3J_{H,H}$ = 6.4 Hz, 6 H, 3-pyridyl-CH), 7.79 (d, $^3J_{H,H}$ = 7.3 Hz, 6 H, 5-pyridyl-CH), 7.89 (t, $^3J_{H,H}$ = 7.5 Hz, 6 H, 4-pyridyl-CH). − ^{13}C NMR ($CDCl_3$): δ = 27.92, 27.99 (18 CH_3), 42.50, 43.01 [6 *C*(CH_3)$_3$], 89.82, 94.20 (6 =CH), 121.11, 122.89 (3,5-pyridyl-CH), 138.98 (4-pyridyl-CH), 152.85, 155.99 (2,6-pyridyl-C), 172.05, 174.61, 207.62, 207.66 (24 C=O). − MS (FAB, *m*-NBA); *m/z*: 2908 [M^+]. − $C_{114}H_{138}Cd_8N_6O_{26}$ (2907.66): calcd. C 47.09, H 4.78, N 2.89; found C 40.07, H 4.50, N 2.51.

[$Mn_8O_2L^{1a}{}_6$] (**5a**): Yield 144 mg (59%), orange microcrystals from ethanol, m.p. 215°C (decomp.). − IR (KBr): ṽ = 2920 cm^{-1} (CH), 1620 (C=O), 1510 (C=C). − MS (FAB, *m*-NBA); *m/z*: 1942 [M^+]. − $C_{78}H_{66}Mn_8N_6O_{26}$ (1942.91): calcd. C 48.22, H 3.42, N 4.33; found C 48.93, H 4.63, N 5.22.

[$Mn_8O_2L^{1b}{}_6$] (**5b**): Yield 250 mg (88%), red crystals from toluene/pyridine, m.p. > 300°C. − IR (l, $CHBr_3$): ṽ = 2975 cm^{-1} (CH), 1625 (C=O), 1575 (C=C). − MS (FAB, *m*-NBA); *m/z*: 2280 [M^+]. − $C_{102}H_{114}Mn_8N_6O_{26}$ (2279.56): calcd. C 53.74, H 5.04, N 3.66; found C 55.53, H 4.64, N 3.44.

[$Mn_8O_2L^{1c}{}_6$] (**5c**): Yield 260 mg (85%), orange microcrystals from ethanol, m.p. > 300°C. − IR (KBr): ṽ = 2950 cm^{-1} (CH), 1610 (C=O), 1500 (C=C). − MS (FAB, *m*-NBA); *m/z*: 2448 [M^+]. − $C_{114}H_{138}Cd_8N_6O_{26}$ (2447.88): calcd. C 55.94, H 5.68, N 3.43; found C 57.03, H 6.30, N 3.68.

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[8] Crystal structure determination of compound **5b**: $C_{102}H_{114}Mn_8N_6O_{26}$ + 6 C_5H_5N + LiCl (captured during crystallisation), M_r = 2279.56 + 6·79.10 + 42.39, monoclinic, space group $P2_1/c$, a = 1604.9(3), b = 4354.9(8), c = 1978.1(4) pm, β = 110.28(2)°, V = 12.968(4) nm^3, Z = 4, $\rho_{calcd.}$ = 1.432 Mg/m^3, F(000) = 5792, λ = 71.073 pm, T = 153 K, μ(Mo-K_α) = 0.849 mm^{-1}, min/max transmission 0.630/0.883, crystal dimensions 0.60 × 0.35 × 0.15 mm, 6.54° ≤ 2Θ ≤ 46.52°; 103087 measured reflections of which 18490 were independent (R_{int} = 0.0671) and employed in the structure refinement (1779 parameters, 802 restraints). The R values are: $R1 = \Sigma|F_o - F_c|/\Sigma F_o = 0.0552$ [$I > 2\sigma(I)$]; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$ = 0.1126 (all data); min/max residual electron density −407 e nm^{-3}/596 e nm^{-3}. Four isopropyl groups and one pyridine solvent molecule are disordered over two sites. The electron density at two pyridine nitrogen atoms was modelled as a lithium atom. A hydrogen atom attached to a bridging oxygen atom could not be located in the difference Fourier synthesis. In view of the possibility of disorder, X-ray analysis cannot provide a definite assignment in such a case. Crystallographic data for **5b** were collected with a Stoe-Siemens-Huber four-circle diffractometer with Siemens CCD area detector by using φ-scans on a shock-cooled crystal in an oil drop[9]. Data integration was performed with the program SAINT. A semiempirical absorption correction was applied. The structure was solved by direct methods (SHELXS-97)[10] and refined against F^2 by the least squares[11]. All non-hydrogen atoms were refined anisotropically. For the hydrogen atoms a riding model was employed. All disordered components were refined anisotropically with the assistance of distance and *ADP* restraints. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100830. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + (1223) 336-033; E-mail: deposit@ccds.cam.ac.uk].

[9] T. Kottke, D. Stalke, *J. Appl. Crystallogr.* **1993**, *26*, 615.

[10] G.M. Sheldrick, "SHELXS-97, Program for structure solution", *Acta Crystallogr.* **1990**, *A46*, 467.

[11] G.M. Sheldrick, *SHELXL-97*, *Program for structure refinement*, University of Göttingen, **1997**.

[12] The Zn complex **3** co-crystallises with ZnL^{2A}_2 (**6**). The asymmetric unit is composed of disordered **3** and **6**. The position of **6** is close to a C_2 axis which leads to two superimposed structures. The reason for that may be found in twinning. The reliability criteria for **3** are R_1 = 0.093 and wR_2 = 0.27. For red-green stereo presentations of **3** and **5b** see: http://www.organik.uni-erlangen.de/saalfrank/index/html

[13] J. B. Howard, D. C. Rees, *Chem. Rev.* **1996**, *96*, 2965−2982; B. K. Burgess, D. L. Lowe, *Chem. Rev.* **1996**, *96*, 2983−3011.

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