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Porphyrinogen tetraanion functioning as a polymetallic assembler: nickel-*meso*-octaethylporphyrinogen binding four transition metal ions at the periphery

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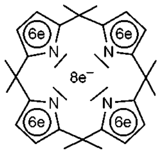
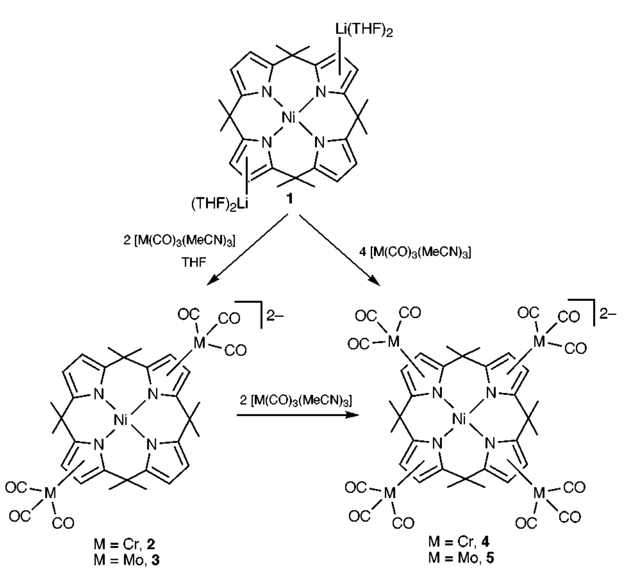
Nickel(II)-*meso*-octaethylporphyrinogen dianion behaves as a π-extended ligand binding four $M(CO)_3$ [M = Cr, Mo] fragments at the periphery, so that the porphyrinogen can assemble five metal centers around itself.

The interest in polymetallic frameworks is exponentially increasing in the domain of discovering cooperative metallic properties, *i.e.* magnetic or chemical reactivity, and, in general, in the context of materials science.[1] One of the molecular approaches to extended polymetallic structures is focused on organic fragments which, by displaying a variety of bonding modes, can assemble the maximum number of metal ions around themselves, as shown in the pioneering work by Constable and co-workers.[2] Such an assembly may function as a building block for extended structures. In this context, we should mention the *meso*-octaalkylporphyrinogen tetraanion,



which binds the metal both by the use of the N_4 core and the pyrroles functioning similarly to cyclopentadienyl anions in the periphery.[3–6] A peculiar property of such dimetallic systems is the electron transfer occurring between the ligand and the peripheral metals.[4] The present report deals with the maximum exploitation of the metal binding ability of the porphyrinogen tetraanion making use of its 32 available electrons for binding up to five metal ions.[3e,5]



Scheme 1

The synthetic sequence is displayed in Scheme 1. The reaction of the nickel-porphyrinogen dianion **1**[6] with 2 mol $[M(CO)_3(MeCN)_3]$[7] [M = Cr, Mo] led to the dimetallated forms **2** and **3**,† which can be further metallated to **4** and **5**,‡ thus forming polymetallic porphyrinogen complexes (65–80%). Each pyrrole functions as an η^5 binding site in the two step reaction and displaces the three labile acetonitriles from the group VI metals. Although the complexes are displayed in Scheme 1 as anions, they occur as ion-pairs in the solid state with lithium cations binding to the oxygens of the carbonyls.[8] The IR spectra in the solid state are somewhat complicated by

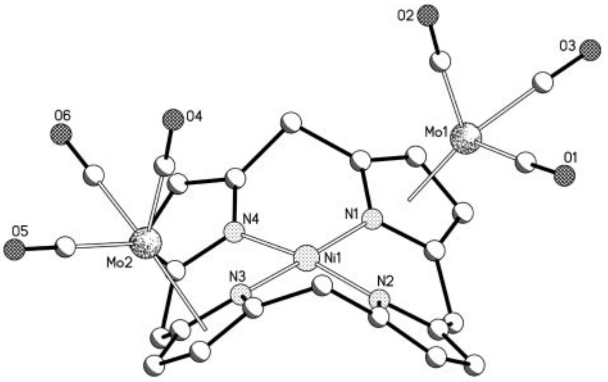


Fig. 1 A plot showing the dianion of compound **3**. Selected bond distances (Å): Ni1–N_{av} 1.877(3), Mo1–η^5(Pyr) 2.087(2), Mo2–η^5(Pyr) 2.091(2), Mo1–C_{av} 1.918(5), Mo2–C_{av} 1.903(6), C–O_{av} 1.177(6), out of plane Ni1–N_4 0.069(2). η^5(Pyr) indicates the centroid.

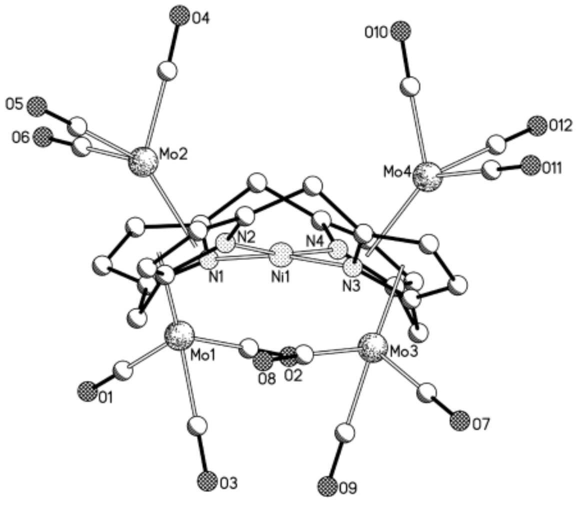


Fig. 2 A plot showing the dianion of compound **5**. Selected bond distances (Å): Ni1–N_{av} 1.874(3), Mo1–η^5(Pyr) 2.079(2), Mo2–η^5(Pyr) 2.086(2), Mo3–η^5(Pyr) 2.084(2), Mo4–η^5(Pyr) 2.087(2), Mo1–C_{av} 1.929(5), Mo2–C_{av} 1.926(5), Mo3–C_{av} 1.921(5), Mo4–C_{av} 1.922(5), C–O_{av} 1.173(6), out of plane Ni1–N_4 0.002(2). η^5(Pyr) indicates the centroid.

the lowering of the local symmetry due to solid state effects and the lithium–oxygen interactions, while in solution all complexes have C–O stretching vibrations according to a C_{3v} symmetry or very close to it. Further characterization has been carried out using ^{1}H NMR and X-ray analysis for both **3** and **5**, the structures being displayed in Figs. 1 and 2, respectively, with some relevant structural parameters provided in the captions.[§]

The first two M(CO)$_3$ fragments bind η^5 to two *trans*-pyrroles and are arranged *syn* to each other. The porphyrinogen displays a saddle-shape conformation, with the usual trend in the structural parameters. The overall conformation of the ligand does not change significantly moving from **3** to **5**, with the four M(CO)$_3$ fragments η^5-bonded to the four pyrroles. The sequence is up and down, so that two are bonded at the upper face and two at the bottom face. The structural parameters of the Ni-porphyrinogen moiety[6a] are not particularly affected by the presence of the Mo(CO)$_3$ fragments. In both complexes some of the lithium cations are associated with the carbonyl oxygens O1 and O4 in **3**, and O9 in **5**. Complexes **2**–**5** show how the nickel-porphyrinogen complex is a very versatile π-ligand for a variety of M(0) complexes, and how one can proceed from **2**–**5** to build up extended polymetallic structures.

Notes and references

† *Synthesis* of **3**. [Mo(CO)$_3$(MeCN)$_3$] (6.10 g, 20.14 mmol) was added to a solution of **1** (9.03 g, 10.07 mmol) in THF (220 cm^3), resulting in a yellow–brown solution which was stirred at room temperature for 24 h. The solvent was evaporated and Et$_2$O (200 cm^3) was added to the obtained orange oily residue. The mixture was stirred overnight to give a yellow powder which was collected and dried *in vacuo* (9.60 g, 80%). Crystals suitable for X-ray diffraction were grown in Et$_2$O. (Found: C, 55.05; H, 5.41; N, 4.35. **2**·Li$_2$(THF)$_3$, $C_{54}H_{72}N_4Li_2Mo_2NiO_9$, requires: C, 54.70; H, 6.12; N, 4.35%). ^{1}H NMR (d$_8$-THF, 400 MHz, 298 K) δ 6.08 (d, J = 2.93 Hz, 2H, C_4H_2N), 6.01 (d, J = 2.93 Hz, 2H, C_4H_2N), 5.50 (d, J = 2.93 Hz, 2H, C_4H_2N), 5.41 (d, J = 2.93 Hz, 2H, C_4H_2N), 4.98 (dq, J_{gem} = 13.2 Hz, J_{vic} = 7.34 Hz, 2H, CH$_2$), 3.82 (dq, J_{gem} = 13.6 Hz, J_{vic} = 7.34 Hz, 2H, CH$_2$), 3.55 (m, 12H, THF), 2.87 (dq, J_{gem} = 12.8 Hz, J_{vic} = 7.34 Hz, 2H, CH$_2$), 2.72 (dq, J_{gem} = 13.2 Hz, J_{vic} = 7.34 Hz, 2H, CH$_2$), 2.32 (m, 4H, CH$_2$), 2.18 (m, 4H, CH$_2$), 1.46 (m, 18H, THF + CH$_3$), 1.32 (t, J = 7.34 Hz, 6H, CH$_3$), 1.20 (t, J = 7.34 Hz, 6H, CH$_3$), 0.89 (t, J = 7.34 Hz, 6H, CH$_3$). IR (Nujol, ν_{max}/cm^{-1}) 1916 (s), 1910 (s), 1822 (s), 1789 (s); 1767 (s), 1734 (s). IR (THF, ν_{max}/cm^{-1}) 1914 (sh), 1810 (sh), 1750 (sh). UV/vis(THF) λ_{max}/nm (ε/M^{-1} cm^{-1}) = 230 (34945), 254 (27842), 310 (12981), 444 (702).

‡ *Synthesis* of **5**. [Mo(CO)$_3$(MeCN)$_3$] (5.0 g, 16.6 mmol) was added to a solution of **1** (3.72 g, 4.15 mmol) in THF (200 cm^3). The resulting red solution was stirred overnight at room temperature. The solvent was removed under reduced pressure, and the solid collected with Et$_2$O (150 cm^3). The mother liquor was concentrated, and the violet powder was filtered and dried *in vacuo* (4.24 g, 66%). Crystals suitable for X-ray diffraction were grown in a mixture of DME–benzene. (Found: C, 46.64; H, 5.18; N, 3.24. **3**·Li$_2$(THF)$_3$, $C_{60}H_{72}N_4Li_2Mo_4NiO_{15}$, requires: C, 46.63; H, 4.69; N, 3.62. ^{1}H NMR: (d$_8$-THF, 400 MHz, 298 K) δ 5.52 (d, J = 2.93 Hz, 4H, C_4H_2N), 5.27 (d, J = 2.93 Hz, 4H, C_4H_2N), 4.19 (dq, J_{gem} = 13.6 Hz, J_{vic} = 7.34 Hz, 4H, CH$_2$), 3.58 (m, 12H, THF), 2.78 (dq, J_{gem} = 13.6 Hz, J_{vic} = 7.34 Hz, 4H, CH$_2$), 1.94 (dq, J_{gem} = 15.2 Hz, J_{vic} = 7.34 Hz, 4H, CH$_2$), 1.82 (dq, J_{gem} = 15.2 Hz, J_{vic} = 7.34 Hz, 4H, CH$_2$), 1.74 (m, 12H, THF), 1.11 (t, J = 7.34 Hz, 12H, CH$_3$), 1.09 (t, J = 7.34 Hz, 12H, CH$_3$). IR (Nujol, ν_{max}/cm^{-1}) 1919 (sbd), 1825 (sbd), 1746 (sbd). IR (THF, ν_{max}/cm^{-1}) 1917 (sh), 1813 (sh). UV/vis(THF) λ_{max}/nm (ε/M^{-1} cm^{-1}) = 232 (51596), 256 (38660), 308 (17107), 404 (4407).

§ *Crystal data*: for **3**: $C_{62}H_{88}Li_2Mo_2N_4NiO_{11}\cdot C_4H_8O$, M = 1401.94, monoclinic, space group $C2/c$, a = 50.392(4), b = 11.6140(8), c = 23.8148(12) Å, β = 105.537(5)°, V = 13428.3(15) Å^3, Z = 8, D_c = 1.387 g cm^{-3}, $F(000)$ = 5872, λ(Mo-Kα) = 0.71073 Å, μ = 0.707 mm^{-1}, crystal dimensions 0.29 × 0.25 × 0.21. Diffraction data were collected on a KUMA CCD at 143 K. For 9809 observed reflections [$I > 2\sigma(I)$] and 760 parameters, the final R is 0.0536 ($wR2$ = 0.1411 for 11199 independent reflections). For **5**: $C_{60}H_{72}LiMo_4N_4NiO_{15}\cdot Li(C_4H_8O)_4\cdot C_6H_6$, M = 1912.09, monoclinic, space group $P2_1/c$, a = 27.300(6), b = 17.269(2), c = 18.076(2) Å, β = 96.17(2)°, V = 8473(2) Å^3, Z = 4, D_c = 1.499 g cm^{-3}, $F(000)$ = 3936, λ(Mo-Kα) = 0.71070 Å, μ = 0.863 mm^{-1}, crystal dimensions 0.35 × 0.27 × 0.20. Diffraction data were collected on a mar345 Imaging Plate Detector System at 143 K. For 11822 observed reflections [$I > 2\sigma(I)$] and 1010 parameters, the final R is 0.0473 ($wR2$ = 0.1340 for 13785 independent reflections). CCDC 182/1445. See http://www.rsc.org/suppdata/cc/1999/2319/ for crystallographic files in .cif format.

1 *Early Transition Metal Clusters with π-Donor Ligands*, ed. M. H. Chisholm, VCH, New York, 1995; *Advances in Supramolecular Chemistry*, ed. G. W. Gokel, Jai Press, Hampton Hill, England, 1995; F. Vögtle, *Supramolecular Chemistry*, Wiley, New York, 1991; *Transition Metals in Supramolecular Chemistry*, ed. L. Fabbrizzi and A. Poggi, Nato ASI Series, Kluwer, Dordrecht, 1994; E. Tsuchida, *Macromolecular Complexes, Dynamic Interactions and Electronic Processes*, VCH, New York, 1991; *Magnetism, a Supramolecular Function*, ed. O. Kahn, Nato ASI Series, Kluwer, Dordrecht, 1996; *Inorganic Materials*, ed. D. W. Bruce and D. O'Hare, Wiley, New York, 1992.

2 E. C. Constable and C. E. Housecroft, *Chimia*, 1998, **52**, 533; E. C. Constable, *Oligomeric Metal Complexes* in *Electronic Materials: the Oligomer Approach*, ed. K. Müllen and G. Wegner, Wiley–VCH, Weinheim, 1998, p. 273; E. C. Constable, *Chem. Commun.*, 1997, 1073; E. C. Constable, C. E. Housecroft, B. Krattinger, M. Neuburger and M. Zehnder, *Organometallics*, 1999, **18**, 2565.

3 General references are made to: (*a*) C. Floriani, *Pure Appl. Chem.*, 1996, **68**, 1; (*b*) C. Floriani, *Chem. Commun.*, (Feature article), 1996, 1257; (*b*) D. Jacoby, S. Isoz, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *J. Am. Chem. Soc.*, 1995, **117**, 2793; (*c*); 2805; (*d*) C. Floriani, in *Stereoselective Reactions of Metal-Activated Molecules*, ed. H. Werner and J. Sundermeyer, Vieweg, Wiesbaden, 1995, pp. 97–106; (*e*) S. De Angelis, E. Solari, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1092; (*f*) C. Floriani, E. Solari, G. Solari, A. Chiesi-Villa and C. Rizzoli, *Angew. Chem., Int. Ed.*, 1998, **37**, 2245 and references therein.

4 L. Bonomo, E. Solari, M. Latronico, R. Scopelliti and C. Floriani, *Chem. Eur. J.*, 1999, **5**, 2040.

5 For the relevance of the π-bonding ability of the polypyrrole structure see: M. O. Senge, *Angew. Chem., Int. Ed. Engl.* 1996, **35**, 1923 and references therein. For π-binding between aromatic metalla-porphyrins and a metal see: K. Koczaja Dailey, G. P. A. Yap, A. L. Rheingold and T. B. Rauchfuss, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1833.

6 (*a*) S. De Angelis, E. Solari, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *J. Am. Chem. Soc.*, 1994, **116**, 5691; (*b*) J. Jubb, D. Jacoby, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Inorg. Chem.*, 1992, **31**, 1306.

7 D. P. Tate, W. R. Knipple and J. M. Augl, *Inorg. Chem.*, 1962, **1**, 433; H. Werner, K. Deckelmann and U. Schönenberger, *Helv. Chim. Acta*, 1970, **53**, 2002.

8 D. F. Shriver and M. J. Sailor, *Acc. Chem. Res.*, 1988, **21**, 374.

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