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The Organization of Two "Soft" (Cu^{2+} , Ni^{2+}) Metal Centers in Heterotrinnuclear Complexes of a Macrocyclic Ligand by Cocomplexation with Ba^{2+} **

By Frank C. J. M. van Veggel, Martinus Bos, Sybolt Harkema, Willem Verboom, and David N. Reinhoudt*

Almost all the reported model compounds for the active site in dicopper metalloproteins like hemocyanin, tyrosinase,

and dopamine β -hydroxylase^[1] contain dinucleating ligands in which a hydroxide, a phenolate, or an alkoxide group acts as a bridge between the two copper sites. As part of our work on the complexation of neutral molecules by macrocyclic receptor molecules,^[2] we have recently reported the complexation of urea and its derivatives by macrocycles in which "soft" cations are immobilized as electrophilic centers.^[3] In addition, we have shown that hard cations, like alkali and alkaline-earth cations, can be cocomplexed in such metallomacrocycles to give heterodinuclear complexes.^[4, 5]

We describe here the synthesis of a barium complex containing a novel type of macrocyclic ligand and its subsequent reaction with copper or nickel acetate to yield heterotrinnuclear complexes in which the arrangement of the two soft metal centers is completely different from that in known dicopper complexes.

The synthesis of the complexes **3b** and **4**, containing the macrocyclic ligand **3a**, is outlined in Scheme 1. Complex **3b** was prepared by simultaneous slow addition of a solution of *o*-phenylenediamine (**2**) and a solution of the dialdehyde **1**^[6] to a refluxing solution of $\text{Ba}(\text{CF}_3\text{SO}_3)_2$ in MeOH and obtained as a red crystalline material in 63% yield.^[7] The FAB mass spectrum of **3b** shows the parent peak at m/z 1123, which corresponds to $[\text{M} - \text{CF}_3\text{SO}_3]^+$.

Ruby red crystals of **3b** were obtained by slow diffusion of petroleum ether into a solution of **3b** in MeOH. The structure of one of the two independent molecules in the asymmetric unit is shown in Figure 1.

The macrocycle is folded around the barium, thereby allowing coordination by all ten oxygen atoms of the macrocycle ($\text{Ba}^{2+} \cdots \text{O}$ 2.69–3.14 Å). The eleventh position around the barium ion is occupied by an oxygen of a triflate ion ($\text{Ba}^{2+} \cdots \text{O}$ 2.82 Å). The two conjugated *N,N'*-*o*-phenylenebis(salicylidenaminato) (salophen) units are not planar, the angles between the two opposite aromatic rings being 17.3 and 29.5°. The mean planes through the four heteroatoms of

Scheme 1.

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[**] We thank Akzo International Research BV for financial support and Prof. N. Nibbering and R. R. Fokkens, Amsterdam, for recording the FAB mass spectra.

the salophen units are approximately parallel, with an angle of 12.6° .

The conversion of the barium complex **3b** into the trinnuclear complexes **4** was carried out by reaction with 2 equivalents of copper or nickel acetate.^[8, 9] The parent peaks in the FAB mass spectra of **4a** (m/z 1245) and

Fig. 1. Crystal structure of **3b**. The asymmetric unit contains two independent molecules, of which one is shown. The noncoordinating triflate ion and hydrogen atoms are omitted for clarity. Green = Ba, red = O, blue = N. Crystal data [16]: triclinic, $a = 21.950(2)$, $b = 16.993(2)$, $c = 14.502(2)$ Å, $\alpha = 84.15(5)$, $\beta = 79.04(5)$, $\gamma = 88.79(5)^\circ$, $V = 5283(8)$ Å³, space group $P\bar{1}$, $Z = 4$, $\rho_{\text{calcd}} = 1.60$ g cm⁻³, $\mu(\text{MoK}\alpha) = 9.18$ cm⁻¹. Final R factor for 4388 significant [$I > 5 \sigma(I)$, $\theta = 3-25^\circ$] reflections is 0.060.

4b (m/z 1234) correspond to $[M-\text{CF}_3\text{SO}_3]^\oplus$ and $[M-\text{CF}_3\text{SO}_3 + \text{H}]^\oplus$, respectively.

Suitable crystals for an X-ray analysis of the dicopper/barium complex **4a** were obtained by slow diffusion of Et₂O into a solution of **4a** in a mixture of MeOH and CH₃CN (1:1). The structure of the folded macrocycle is shown in Figure 2. It is similar to that of **3b**.

Fig. 2. Crystal structure of **4a** · 2 H₂O. Only the coordinating oxygen atom of the triflate anion (ellipse) is drawn for clarity. The noncoordinating triflate ion, water molecule, and hydrogen atoms are omitted for clarity. Green = Ba, black = Cu, red = O, blue = N. Crystal data [16]: orthorhombic, $a = 28.589(9)$, $b = 27.786(4)$, $c = 13.383(3)$ Å, $V = 10631(6)$ Å³, space group $Pbca$, $Z = 8$, $\rho_{\text{calcd}} = 1.74$ g cm⁻³, $\mu(\text{MoK}\alpha) = 16.9$ cm⁻¹. Final R factor for 2589 significant [$I > 3 \sigma(I)$, $\theta = 3-22.5^\circ$] reflections is 0.078.

The two copper ions in **4a** are complexed in an almost square-planar fashion in the "soft" salophen cavities and the barium ion is complexed in the large polyether cavity. The two conjugated salophen parts of the macrocycle are not completely planar, the angles between the opposite aromatic rings being 8.2 and 8.7°. The mean planes through the coordinating atoms of the copper ions are approximately parallel, with an angle of 5.8°. A view perpendicular to one salophen unit shows that the other unit is not exactly under it but displaced by about 1.4 Å. The barium ion is coordinated

by all ten oxygens of the macrocycle ($\text{Ba}^{2\oplus} \cdots \text{O}$ 2.76–3.63 Å), one water molecule ($\text{Ba}^{2\oplus} \cdots \text{O}$ 3.01 Å), and one triflate ion ($\text{Ba}^{2\oplus} \cdots \text{O}$ 2.89 Å). The metal–metal distances in the cation cluster **4a** are: $\text{Ba}^{2\oplus} \cdots \text{Cu}^{2\oplus}$ 3.70 and 3.85; $\text{Cu}^{2\oplus} \cdots \text{Cu}^{2\oplus}$ 3.50 Å. The angle $\text{Cu}^{2\oplus}-\text{Ba}^{2\oplus}-\text{Cu}^{2\oplus}$ is 55.1°.

Dark red single crystals of the dinickel/barium complex **4b** were similarly obtained by slow diffusion of Et₂O into a solution of **4b** in a mixture of CH₃CN and dimethyl sulfoxide (DMSO). The structure of **4b** resembles that of **4a**. The two nickel ions are complexed in the "soft" salophen cavities in an almost square-planar fashion. The mean planes through the coordinating atoms of the nickel ions are approximately parallel to each other, with an angle of 7.4°. A view perpendicular to one salophen unit shows that the other unit is not exactly under it but displaced by about 0.95 Å. The barium ion is complexed in the "hard" cavity by all crown ether oxygens ($\text{Ba}^{2\oplus} \cdots \text{O}$ 2.72–3.09 Å) and one water molecule ($\text{Ba}^{2\oplus} \cdots \text{O}$ 2.87 Å). The metal–metal distances in the cation cluster **4b** are: $\text{Ba}^{2\oplus} \cdots \text{Ni}^{2\oplus}$ 3.66 and 3.73; $\text{Ni}^{2\oplus} \cdots \text{Ni}^{2\oplus}$ 3.42 Å. The angle $\text{Ni}^{2\oplus}-\text{Ba}^{2\oplus}-\text{Ni}^{2\oplus}$ is 55.1°.

The electrochemical properties of the trinuclear complexes **4a** and **4b** were investigated by polarography and cyclic voltammetry at a mercury drop electrode in DMSO with 0.1 M Et₄N⁺ClO₄⁻ as supporting electrolyte.^[10]

The polarogram of the dicopper/barium complex **4a** shows two waves between -0.2 and -1.4 V [$E_{1/2} = -1.065$ and -1.110 V (slope 52 and 50 mV, respectively)].^[11] The ratio of the limiting currents is 1, which indicates two one-electron reductions.^[12] Cyclic voltammograms of **4a** were recorded at scan rates of 0.5 to 6 V s⁻¹. At these scan rates the two-step process is reflected as a shoulder on a peak in the reductive as well as in the oxidative sweep. This two-electron reduction/oxidation is *chemically* reversible, because, when five scans at scan rates of 0.5 and 6 V s⁻¹ were applied, five identical cyclic voltammograms were recorded. This reduction can be regarded as taking place by a simple EE mechanism, that is, two one-electron transfers via a (formally) M^{II}₁/M^I₁ oxidation state to a (formally) M^I₁/M^I₁ oxidation state.

The polarogram of **4b** shows two waves between -0.2 and -1.4 V [$E_{1/2} = -1.036$ and -1.137 V (slope 50 and 46 mV, respectively)].^[11] The ratio of the limiting currents is about 1. The cyclic voltammograms of **4b** at scan rates

Fig. 3. Cyclic voltammograms of **4b** in DMSO, with 0.1 M Et₄N⁺ClO₄⁻ as supporting electrolyte, at scan rates of 0.5 to 6 V s⁻¹ (shown on the curves); vs. Ag/AgCl.

of 0.5 to 6 V s⁻¹ between -0.2 and -1.4 V are shown in Figure 3.

Cyclic voltammetry showed that the reduction/oxidation of **4b** is also *chemically* reversible, because, when 30 scans were applied at scan rates of 2 and 6 V s⁻¹ between -0.2 and -1.4 V, 30 identical voltammograms were recorded. However, this reduction/oxidation cannot be regarded as two simple one-electron transfers^[13] but is complicated by reversible intra- and intermolecular C-C coupling of two (reduced) C=N bonds. This reductive C-C coupling of two C=N bonds in Ni(salophen) units has also been observed in the solid state by Floriani et al. upon reduction of Ni(salophen) with one equivalent of lithium and sodium metal.^[14] They showed that the C-C coupling product could be oxidized to give the original Ni(salophen), which demonstrates the reversibility of this reductive C-C coupling. The reduced Ni(salophen) can be regarded as a complex of Ni^{II} with a radical anion ligand, as was demonstrated by Gosden et al.^[15] by ESR measurements of reduced Ni(salophen) at 77 K.

Currently we are studying the interaction of the trinuclear complexes **4** with small anions and neutral molecules.

Received: January 26, 1989 [Z 3142 IE]
German version: *Angew. Chem.* 101 (1989) 800

CAS Registry numbers:

1, 121073-78-7; **2**, 95-54-5; **3b**, 121073-80-1; **4g**, 121073-84-5; **4a**·2H₂O, 121073-85-6; **4b**, 121073-82-3.

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- [6] Compound **2** was prepared by reaction of 2,3-dihydroxybenzaldehyde and diethylene glycol ditosylate (2:1) in DMSO under basic conditions (NaH); see [3] for the synthesis of analogous dialdehydes.
- [7] **3b**: 63% yield; m.p. 270–280 °C (MeOH/petroleum ether 40–60, dec.). ¹H NMR ([D₆]DMSO): δ = 13.37 (s, 4H, OH), 8.92 (s, 4H, N=CH), 7.45 (s, 8H, arylH), 7.3–7.1 (m, 8H, arylH), 6.9–6.7 (m, 4H, arylH), 4.1–4.0 (m, 8H, aryl OCH₂), 4.0–3.9 (m, 8H, OCH₂). ¹³C NMR ([D₆]DMSO): δ = 163.5 (d, N=C), 151.4 (s, C-3), 146.4 (s, C-2), 140.7 (s, C-1'), 127.3, 124.2, 118.7, 117.6, 117.3 (d, C-4–C-6, C-2', C-3'), 118.6 (s, C-1), 68.5, 67.8 (t, OCH₂). IR (KBr): ν̄ = 1620 cm⁻¹ (N=C). FAB-MS: m/z 1123 [M–CF₃SO₃]⁺. Satisfactory C, H, N analysis for C₄₈H₄₄BaF₆N₄O₁₆S₂.
- [8] Complex **4a** was obtained as a green solid in 74% yield: m.p. > 300 °C [MeOH/CH₃CN (1:1), Et₂O as precipitant]. IR (KBr): ν̄ = 1608 cm⁻¹ (N=C). FAB-MS: m/z 1245 [M–CF₃SO₃]⁺. Satisfactory C, H, N analysis for C₅₀H₄₀BaCu₂F₆N₄O₁₆S₂·2 H₂O. Complex **4b** was obtained as a dark red solid in 64% yield: m.p. > 300 °C [MeOH/CH₃CN (1:1), Et₂O as precipitant]. ¹H NMR ([D₆]DMSO): δ = 8.39 (s, 4H, N=CH), 7.7–7.5 (m, 4H, arylH), 7.2–7.0 (m, 4H, arylH), 7.0–6.6 (m, 4H, arylH), 6.5–6.3 (m, 8H, arylH), 4.9–3.6 (m, 16H, OCH₂). ¹³C NMR ([D₆]DMSO): δ = 156.9 (d, N=C), 151.6 (s, C-3), 147.3 (s, C-2), 140.7 (s, C-1), 127.7, 125.1, 115.6, 115.3, 113.7 (d, C-4–C-6, C-2', C-3'), 119.4 (s, C-1), 67.3, 66.2 (t, OCH₂). IR (KBr): ν̄ = 1610 cm⁻¹ (N=C). FAB-MS: m/z 1234 [M–CF₃SO₃ + H]⁺. Satisfactory C, H, N analysis for C₅₀H₄₀BaF₆N₄Ni₂O₁₆S₂·2 H₂O.

- [9] The barium-free dicopper and dinickel complexes could be made by reaction of **3a** with two equivalents of copper and nickel acetate, respectively, but these complexes are insoluble in all normal organic solvents.
- [10] Measurements were performed in 0.1 M Et₄N⁺ClO₄⁻ solution in DMSO at 20 °C. The apparatus was operated in a three-electrode mode with a mercury drop as cathode, a platinum wire as auxiliary electrode, and an Ag/AgCl electrode as reference. The reference electrode (Ag/AgCl) was filled with 1 M Et₄NCl in MeOH and brought into contact via a salt bridge, filled with 0.1 M Et₄N⁺ClO₄⁻ in DMSO, with the sample solution. See [4,5] for a more detailed description of the apparatus and procedures.
- [11] Determination of the half-wave potentials (E_{1/2}) was done manually. The slopes were estimated with E_{3/4} – E_{1/4}. The peak at about -0.3 V, which occurs at higher scan rates, is due to capacitance effects. This peak is also found in the blank.
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A Novel Type of Anionic Cluster Containing a Pt₄Ag₂ Core**

By Rafael Usón, Juan Forniés, Milagros Tomás, and José M. Casas

The electron-rich metal centers in mono- and binuclear platinum(II) complexes containing perhalophenyl ligands are able to donate electron density to suitable Lewis acids, such as Ag⁺ and (AgL)⁺, to afford unusual polynuclear complexes containing Pt→Ag bonds.^[1–6] Specifically, the anionic binuclear complexes **1** react with AgClO₄ without elimination of AgX to give the trinuclear complexes **2**.

a, X = Cl; b, X = Br; c, X = C₆F₅

The structures of **2a** and **2c** have been established by single-crystal X-ray studies. In both cases^[4, 5] the bent binuclear [Pt₂(μ-X)₂(C₆F₅)₄] fragment acts as a bidentate chelating ligand with both platinum donor atoms bonded to the silver atom through otherwise unsupported Pt→Ag bonds. The diethyl ether molecule is coordinated to the silver atom (Fig. 1).

However, the analogous binuclear pentachlorophenyl derivatives **3**^[7] behave differently. Upon reaction with AgClO₄ (under similar conditions as those used in the syn-

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** This work was supported by the Spanish Comisión Asesora de Investigación Científica y Técnica (CAICYT) (project PB85-0128).