The Organization of Two “Soft” (Cu²⁺, Ni²⁺) Metal Centers in Heterotrinuclear Complexes of a Macrocyclic Ligand by Cocomplexation with Ba²⁺**

By Frank C. J. M. van Veggel, Martinus Bos, Sybolt Harmema, 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-hydroxylase⁴¹ 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,⁵² we have recently reported the complexation of urea and its derivatives by macrocycles in which “soft” cations are immobilized as electrophilic centers. 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 heterotrinuclear 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 diisobutylaldehyde 1⁶ into a refluxing solution of Ba(CF₃SO₃)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 [M-CF₃SO₃]⁺.⁸ 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 (Ba²⁺ · · · O 2.69–3.14 Å). The eleventh position around the barium ion is occupied by an oxygen of a triflate ion (Ba²⁺ · · · O 2.82 Å). The two conjugated N,N’-o-phenylenebis(salicyldenaminato) (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 the salophen units are approximately parallel, with an angle of 12.6°.

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

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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 (Ba\(^{2+}\) · · · O 2.76–3.63 Å), one water molecule (Ba\(^{2+}\) · · · O 3.01 Å), and one triflate ion (Ba\(^{2+}\) · · · O 2.89 Å). The metal–metal distances in the cation cluster 4a are: Ba\(^{2+}\) · · · Cu\(^{2+}\) 3.70 and 3.85; Cu\(^{2+}\) · · · Cu\(^{2+}\) 3.50 Å. The angle Cu\(^{2+}\)–Ba\(^{2+}\)–Cu\(^{2+}\) is 55.1°.

Dark red single crystals of the dinickel/barium complex 4b were similarly obtained by slow diffusion of Et\(_2\)O into a solution of 4b in a mixture of CH\(_2\)CN 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 (Ba\(^{2+}\) · · · O 2.72–3.09 Å) and one water molecule (Ba\(^{2+}\) · · · O 2.87 Å). The metal–metal distances in the cation cluster 4b are: Ba\(^{2+}\) · · · Ni\(^{2+}\) 3.66 and 3.73; Ni\(^{2+}\) · · · Ni\(^{2+}\) 3.42 Å. The angle Ni\(^{2+}\)–Ba\(^{2+}\)–Ni\(^{2+}\) 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 Et\(_4\)N\(^{+}\)ClO\(_4\) as supporting electrolyte.\(^{[10]}\) The polarogram of the dicopper/barium complex 4a shows two waves between −0.2 and −1.4 V \([E_{1/2} = −1.065 \text{ and } −1.110 \text{ V (slope 52 and 50 mV, respectively)}]\). 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\(^{2+}\)/M\(^{3+}\) oxidation state to a (formally) M\(^{1+}\)/M\(^{2+}\) oxidation state.\(^{[11]}\)

The polarogram of 4b shows two waves between −0.2 and −1.4 V \([E_{1/2} = −1.036 \text{ and } −1.137 \text{ V (slope 50 and 46 mV, respectively)}]\). The ratio of the limiting currents is about 1. The cyclic voltammograms of 4b at scan rates...
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\(^{11,13}\) but is complicated by reversible intra- and intermolecular C=C coupling of two (reduced) C-N bonds in Ni(salophen) which 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.\(^{11,14}\) 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.\(^{11,15}\) 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.

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Compound 2 was prepared by reaction of 2,3-dihydroxybenzaldehyde and diethylether glycol dioxydate (2-1) in DMSO under basic conditions (NaH); see [3] for the synthesis of analogous dihydroxydienes.

[7] 3b: 63% yield, m.p. 270-280 °C (MeOH/pentane ether 40-60, dec.).

[8] Complex 4a was 4a as a green solid in 74% yield: m.p. > 300 °C (MeOH/CH\(_2\)Cl\(_2\) 1:1, Et\(_2\)O as precipitant). (IR (KBr): \(v = 1605\) cm\(^{-1}\) (N=C). FAB-MS: m/z 1123 [M - CF\(_2\)SO\(_3\)].

A Novel Type of Anionic Cluster Containing a Pt\(_4\)Ag\(_2\) Core **

By Rafael Usón, Juan Fortiés, 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.\(^{11-13}\) Specifically, the anionic binuclear complexes 1 react with AgClO\(_4\) without elimination of AgX to give the trinuclear complexes 2.

The structures of 2a and 2b have been established by single-crystal X-ray studies. In both cases\(^{4,5}\) the bent binuclear [Pt\(_2\)(μ-ξ)(μ-ξ)(μ-ξ)(μ-ξ)]\(^+\) 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 metal (Fig. 1).

However, the analogous binuclear pentachlorophenyl derivatives 3\(^{17}\) behave differently. Upon reaction with AgClO\(_4\) under similar conditions as those used in the syn-