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LETTER

Electrochemical synthesis of a 'lariat' mononuclear Ni(II) complex with a bimacrocyclic ligand from its heterobinuclear Cu(II)Ni(II) complex

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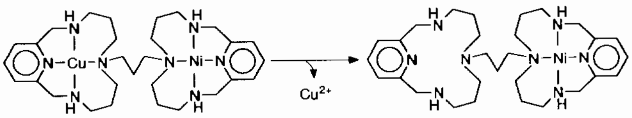
The bimacrocyclic ligands in which two of the same tetraazamacrocycles are linked by a C–C bond or a polymethylene bridge incorporate metal ions into the macrocycles to form a number of binuclear metal complexes. For example, homobinuclear Cu(II)Cu(II) [1, 2] and Ni(II)Ni(II) [2–4] complexes have been synthesized and have served as good systems for studies on the proximate effect of two metal ions. The ligands are anticipated also to afford mononuclear metal complexes, in which one of the two macrocycles enclose a metal ion and the other is vacant, though such complexes have not been synthesized yet.

One very elegant synthesis for the mononuclear metal complexes is by the removal of only one of the metal ions from the binuclear complexes. For this purpose, the use of heterobinuclear complexes has a distinct advantage in that the macrocycles from one another can be distinguished from one another by differences in the properties of the two metal ions accommodated.

In this paper we describe the preparation of the heterobinuclear Cu(II)Ni(II) complex with 7,7′-trimethylenebis[3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene], L, and then the electrochemical synthesis of its mononuclear Ni(II) complex by removal of the Cu(II) ion from the Cu(II)Ni(II) complex; this is the first example, to our knowledge, of the preparation of a mononuclear Ni(II) complex with a bimacrocyclic ligand.



Synthesis of the Cu(II)Ni(II) complex

The ligand L was prepared by the method we reported previously [4]. The Cu(II)Ni(II) complex was prepared by successive complex formation between L and Cu^{2+} and Ni^{2+}. Because the complex formation always affords a mixture of Cu(II)Cu(II), Cu(II)Ni(II) and Ni(II)Ni(II) complexes, its products must be separated by column chromatography using SP-Sephadex C-25 cation-exchange resin, followed by elution with an aqueous solution of 0.5 mol dm^{-3} NaCl. The blue Cu(II)Cu(II) complex was always eluted first, the reddish violet Cu(II)Ni(II) complex second, and the orange Ni(II)Ni(II) complex last. This clear separation of the three bands indicates that the second band is not a mixture of the Cu(II)Cu(II) and Ni(II)Ni(II) complexes.

In fact, the complex, isolated as a perchlorate from the second band, gave a satisfactory elemental analysis for the Cu(II)Ni(II) complex *Anal.* Found: C, 32.71; H, 4.67; N, 10.46. Calc. for $C_{29}H_{48}N_8Cl_4O_{16}CuNi \cdot 2H_2O$: C, 32.71; H, 4.92; N, 10.52%.

The absorption spectra and cyclic voltammograms (CV) prove that the product comprises two macrocycles one of which includes a Cu(II) ion and the other a Ni(II) ion. Figure 1 shows the absorption spectrum of the Cu(II)Ni(II) complex in aqueous solution; it is practically equal to the sum of the spectrum of the Ni(II)Ni(II) complex and that of the Cu(II)Cu(II) complex. The same conclusion was also obtained by cyclic voltammetry. Figure 2 shows the CV observed in the reduction of the Cu(II)Ni(II) complex using a hanging mercury drop electrode (HMDE) in water. The CV of the Cu(II)Ni(II) complex is again equal to

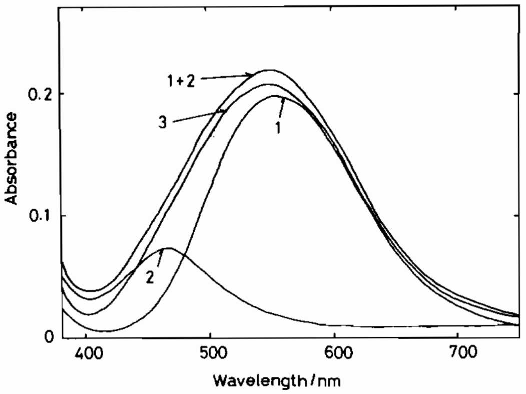


Fig. 1. Absorption spectra of 0.5×10^{-3} mol dm^{-3} Cu(II)Cu(II) (1), 0.5×10^{-3} mol dm^{-3} Ni(II)Ni(II) (2), and 1×10^{-3} mol dm^{-3} Cu(II)Ni(II) (3) complexes with L in water at 25°C.

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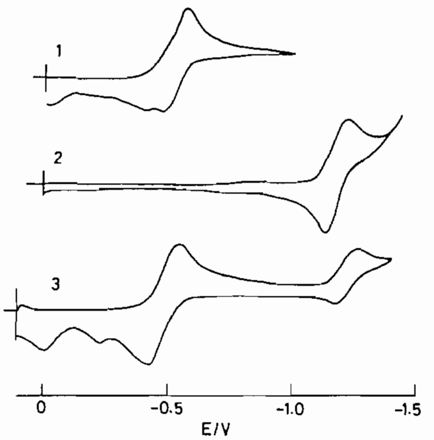

Fig. 2. Cyclic voltammograms of 1×10^{-3} mol dm^{-3} Cu(II)Cu(II) (1), 2×10^{-3} mol dm^{-3} Ni(II)Ni(II) (2), and 2×10^{-3} mol dm^{-3} Cu(II)Ni(II) (3) complexes with L in water at 25 °C. HMDE. E vs. Ag/AgCl. Scan rate = 100 mV s^{-1}.

the sum of the CV of the Cu(II)Cu(II) complex and that of the Ni(II)Ni(II) complex. Thus, the desired heterobinuclear Cu(II)Ni(II) complexes were successfully obtained.

Synthesis of the mononuclear Ni(II) complex

In the CV of the Cu(II)Ni(II) complex the cathodic peak current, i_{pc}, of the copper wave (−0.55 V) is *c.* twice that of the nickel wave (−1.26 V). Because a one electron process is most probable in the oxidation–reduction of the Ni(II) ion (Ni^{II}/Ni^{I}), two electrons should be consumed at the Cu(II) wave. We hence speculated that at the HMDE, disproportionation of Cu^{I} ($2Cu^{I} \rightleftharpoons Cu^{0} + Cu^{II}$), an apparent two electron process ($Cu^{II} + 2e \rightleftharpoons Cu^{0}$), should occur after the reduction of the Cu^{II} to Cu^{I} ion; Cu^{0} thus formed may be released from the macrocyclic complex to form amalgam with Hg. The CV and the above speculation led to the electrochemical removal of the Cu(II) ion from the Cu(II)Ni(II) complex.

The electrolytic reduction of the Cu(II)Ni(II) complex (0.1 g in 30 ml of 0.1 mol dm^{-3} KCl) was performed at −0.6 V, where the Cu(II) ion could be reduced but the Ni(II) ion could not, using a Hg pool (14 cm^2) as a working electrode with vigorous stirring. As the reduction proceeded, the solution turned gradually from violet to yellow. Electrolysis was continued until the solution was totally yellow. The electrolyzed solution was chromatographed using a cation-exchange resin column (SP-Sephadex C25, $\phi = 26$ mm, $l = 200$ mm), followed by elution with an aqueous solution of 0.5 mol dm^{-3} NaCl. An orange main band was collected. After NaCl had been removed, the product was isolated as a perchlorate salt. The perchlorate thus obtained was recrystallized from hot water to give crystals, which were dried over P_2O_5 in a vacuum (yield *c.* 70%). The elemental analysis of the product agreed well with that expected for a perchlorate of a mononuclear Ni(II) complex with L. *Anal.* Found: C, 34.32; H, 5.00; N, 10.89. Calc. for $C_{29}H_{50}N_8Cl_4O_{16}Ni \cdot 2H_2O$: C, 34.72; H, 5.43; N, 11.17%.

In the CV of the complex obtained by electrolysis, the Cu(II) wave was not observed but the Ni(II) wave was. An analogous situation was found in the absorption spectrum. The electrolyzed complex only shows the absorption band at 465 nm ascribable to a Ni(II) complex; it is very similar to the binuclear Ni(II)Ni(II) complex with L, though its intensity (ϵ: 86) is *c.* 60% of that of the Ni(II)Ni(II) complex.

Definite evidence for the formation of the mononuclear Ni(II) complex with L was obtained from the FAB-mass spectrum of the reduced complex (Fig. 3).

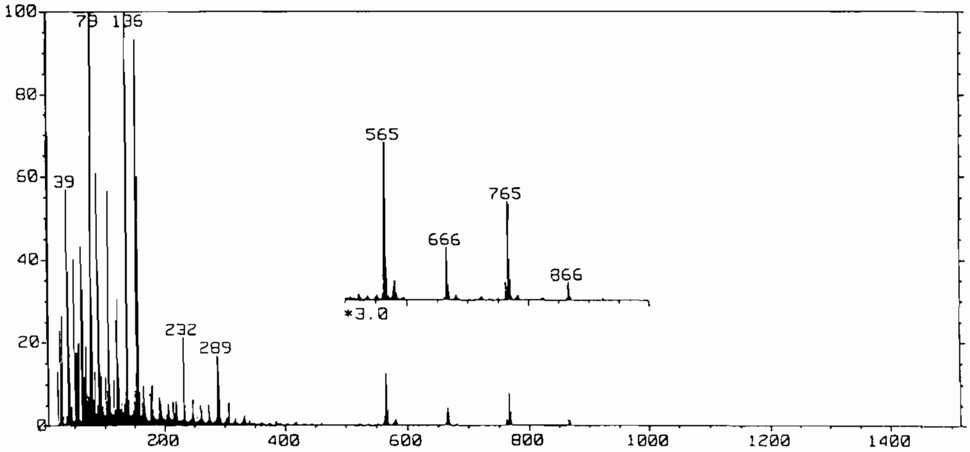

Fig. 3. The FAB-mass spectrum of the mononuclear Ni(II) complex with L. Matrix: *m*-nitrobenzyl alcohol.

Four groups of peaks were observed around m/z 866, 765, 666 and 565, which were due to the complexes produced by liberation of one, two, three and four perchlorate ions, respectively, from $[NiLH_2](ClO_4)_4$ (964): i.e. the two secondary amines on the vacant macrocycle should be protonated in the isolated complex.

The complex thus confirmed has one vacant macrocycle to incorporate another metal ion; the complex formation with Cu^{2+} was investigated spectrophotometrically. Upon addition of Cu^{2+} to an aqueous solution containing the mononuclear Ni(II) complex, the solution turned from yellow to violet immediately. The final absorption spectrum coincided with that of the Cu(II)Ni(II) complex with L. On the other hand, no change occurred for the solution containing the Ni(II)Ni(II) complex with L. These results undoubtedly indicate that the mononuclear Ni(II) complex incorporates metal ions into the vacant hole, like a 'lariat'.

The 'lariat' complex, a mononuclear Ni(II) complex with a bimacrocyclic ligand, L, was thus successfully prepared by the electrochemical removal of Cu(II) ions from the Cu(II)Ni(II) complex. This complex is expected to be a starting complex for convenient and selective preparation of other heterobinuclear metal complexes; the study is now in progress.

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