Synthesis of Heterobinuclear Cu(II)Ni(II) Complexes with Bis(tetraazamacrocycle)

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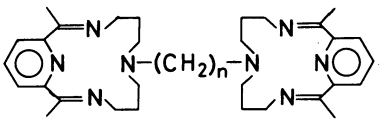
Synopsis. A new series of heterobinuclear Cu(II)Ni(II) complexes with bis(tetraazamacrocycle), i.e., 7,7′-polymethylenebis[2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene]copper(II)nickel(II) perchlorates with polymethylene bridges with a length of 2—6-C, were synthesized by a template reaction.

Metal–metal interactions of homobinuclear Cu(II)-Cu(II)[1-4] and Ni(II)Ni(II)[3-6] complexes with bis(tetraazamacrocycle) have been actively studied by means of the ESR spectroscopical,[1-4] magnetical,[1] and electrochemical methods.[2-6] Recently we synthesized the Ni(II)Ni(II) complexes with several ligands, 7,7′-polymethylenebis[2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene](polymethylene = ethylene (L^2), trimethylene (L^3), tetramethylene (L^4), pentamethylene (L^5), and hexamethylene (L^6)), in which two of the same tetraazamacrocycles are linked by polymethylene bridges of various lengths.[6] Our electrochemical study of the Ni(II)Ni(II) complexes revealed that the metal–metel interaction operates when the polymethylene bridge is shorter than that of tetramethylene.[6]



L^2 : n = 2
L^3 : n = 3
L^4 : n = 4
L^5 : n = 5
L^6 : n = 6

In order to investigate the metal–metal interaction of two different metals, a series of heterobinuclear complexes with L^2—L^6 is required. To the best of our knowledge, however, no such heterobinuclear complex has yet been synthesized except for one compound, $[Cu^{II}Ni^{II}(bis(cyclam))]^{4+}$,[4] which was prepared by the addition of Ni(II) and Cu(II) ions to an aqueous solution of a presynthesized ligand, bis(cyclam), i.e., by a complexation reaction.

In this paper we will describe the synthesis of a series of heterobinuclear Cu(II)Ni(II) complexes with L^2—L^6 by the use of a template reaction; this is the first example of the preparation of heterobinuclear complexes with bis(tetraazamacrocycle) by a template reaction.

In seeking for the proper reaction conditions for the preparation of heterobinuclear Cu(II)Ni(II) complexes, the following characteristic results were obtained. (1) When *N,N,N′,N′*-tetrakis(3-aminopropyl)-1,4-butanediamine, hereafter termed a branched polyamine, was added to a solution containing both Cu(II) and Ni(II) ions and 2,6-diacetylpyridine, the mixture immediately turned blue, indicating that the Cu(II) ion is more favorable for the template reaction than the Ni(II) ion. In fact, after the mixture had been kept at 60 °C for 6 h, the homobinuclear Cu(II)Cu(II)[1] complex was isolated as the major product, and the Cu(II)Ni(II) and Ni(II)Ni(II)[6] complexes, as minor ones. (2) When the template reaction was performed without the Cu(II) ion under the conditions used for the preparation of Cu(II)Ni(II) complexes (see Experimental), the expected monomacrocyclic Ni(II) complex, formed by the template reaction on a single side of the branched polyamine, could not be obtained, but the bismacrocyclic Ni(II)Ni(II) complex was. These results suggest that it is difficult to stop the second cyclization reaction and/or to isolate the monocyclic Ni(II) complex. (3) When a solution including equimolar amounts of the Ni(II)Ni(II) complex and the Cu(II) ion was heated at 50 °C for 3 h, no changes occurred, suggesting that the Ni(II) ion in the complex is not replaced by the Cu(II) ion. On the basis of these results, the procedures described in the experimental section were employed for the preparation of Cu(II)-Ni(II) complexes.

Because the template reaction always afforded a mixture of Cu(II)Cu(II),[1] Cu(II)Ni(II), and Ni(II)-Ni(II)[6] complexes, its products should be separated by column chromatography of SP-Sephadex C-25 ion-exchange resin, followed by elution with an aqueous solution of 0.5 mol dm^{-3} NaCl. In every instance of chromatography, the blue Cu(II)Cu(II) complex was 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 complexes isolated from the second band, the Cu(II)Ni(II) complexes, were characterized as follows.

In the IR spectra, all the complexes show distinct bands at about 1620 ($\nu_{C=N}$) and 1580 cm^{-1} (the skeletal vibration of pyridine), but no bands corresponding to $\nu_{C=O}$ and the vibrations of the free amines, indicating a formation of the cyclic ligand by the condensation of diacetylpyridine with branched polyamines.

The presence of Cu(II) and Ni(II) ions in a ratio of 1:1 was determined by polarography. The complexes were decomposed with H_2O_2–H_2SO_4; the subsequent solutions, containing a NH_3–NH_4^+ buffer (pH 10),

showed three waves, at −0.02, −0.32, and −0.87 V vs. Hg-pool, which were assigned to the Cu^{II}/Cu^{I}, Cu^{I}/Cu^{0}, and Ni^{II}/Ni^{0} couples respectively. By a comparison of these wave heights with those of a standard solution containing both Cu(II) and Ni(II) ions, the amounts of the metals were determined (see the elemental analyses in Experimental).

The absorption spectra and differential pulse polarograms (DP) show that the products have two macrocycles of Cu(II) and Ni(II) complexes in the same molecule. Figure 1 shows the absorption spectrum of $[Cu^{II}Ni^{II}(L^4)]^{4+}$ in an aqueous solution; it is practically equal to the sum of the spectrum of $[Ni^{II}_2(L^4)]^{4+}$ and that of $[Cu^{II}_2(L^4)]^{4+}$. The same conclusion was also obtained by differential pulse polarography. Figure 2 shows the DP observed in the oxidation of $[Cu^{II}Ni^{II}(L^4)]^{4+}$ in acetonitrile. The peak of the Ni^{II}/Ni^{III} couple (ca. 1.2 V) is symmetrical, suggesting that the electrode process is quasi-reversible;

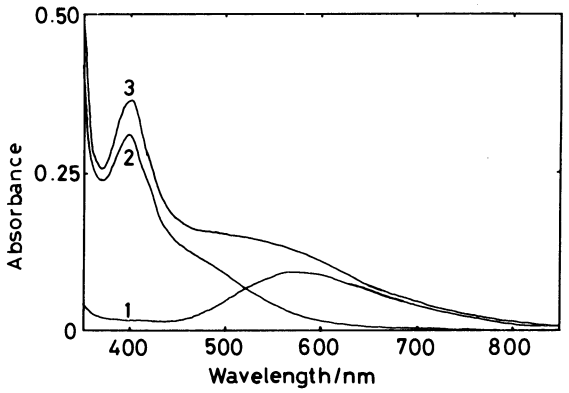


Fig. 1. Absorption spectra of the aqueous solution of $[MM'(L^4)]^{4+}$: 2×10^{-4} mol dm^{-3} M=M'=Cu(II) (1), 2×10^{-4} mol dm^{-3} M=M'=Ni(II) (2), 4×10^{-4} mol dm^{-3} M=Cu(II) and M'=Ni(II) (3). T=25 °C.

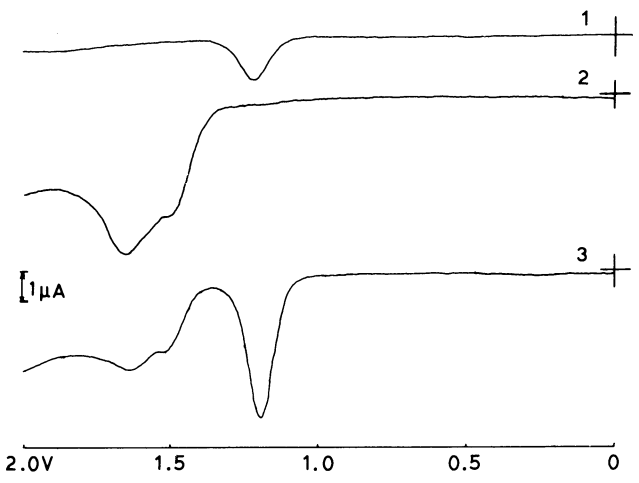


Fig. 2. Differential pulse polarograms (scan rate: 1 mV s^{-1}; pulse amplitude: 10 mV) of $[MM'(L^4)]^{4+}$ in acetonitrile: M=M'=Ni(II) (1), M=M'=Cu(II) (2), M=Cu(II) and M'=Ni(II) (3). V vs. $Ag-Ag^{+}$ (0.01 mol dm^{-3} $AgNO_3$). Glassy carbon electrode.[11] T= 25 °C.

also, it is well-separated from that of the Cu^{II}/Cu^{III} couple. The DP of $[Cu^{II}Ni^{II}(L^4)]^{4+}$ is again equal to the sum of the DP of $[Cu^{II}_2(L^4)]^{4+}$ and that of $[Ni^{II}_2(L^4)]^{4+}$. Similar results in the absorption spectra and DPs were obtained for the other binuclear complexes prepared herewith.

Thus, the desired heterobinuclear Cu(II)Ni(II) complexes were successfully obtained.[7]

Experimental

Materials. A typical procedure for the preparation of the heterobinuclear complexes was as follows.

2,6-Diacetylpyridine (3.26 g, 0.02 mol) and nickel(II) acetate tetrahydrate (2.49 g, 0.01 mol) were dissolved in 200 cm^3 of ethanol–water (1:1, v/v). To this solution we then added 100 cm^3 of ethanol–water (1:1, v/v) containing *N,N,N',N'*-tetrakis(3-aminopropyl)-1,4-butanediamine (3.22 g, 0.0102 mol) which had been neutralized with acetic acid just before the addition. After the solution had then been stirred for 3.5 h at 60 °C, 100 cm^3 of an ethanol–water (1:1, v/v) solution containing copper(II) acetate monohydrate (2.00 g, 0.01 mol) was added. The mixture was stirred for 4.5 h at 60 °C, left to stand at room temperature for 1 h, evaporated to half of its original volume, and then filtered. To the filtrate we added a saturated aqueous sodium perchlorate solution to obtain dark brown precipitates. The precipitates were suspended in a small amount of water and then the suspension was passed through a column of Cl-form anion-exchange resin (Amberlite IRA410, ϕ=30 mm, l=300 mm) to exchange the counter ions. The resulting clear solution was chromatographed with a cation-exchange column (SP-Sephadex C-25, ϕ=30 mm, l=1250 mm), with 0.5 mol dm^{-3} sodium chloride solution as the eluant, to give three well-separated bands. The first, blue-violet band and the third, reddish-yellow one were assigned to the homobinuclear Cu(II)Cu(II)[1] and Ni(II)Ni(II)[6] complexes respectively by comparison with authentic samples. The second, dark-reddish-purple eluate was concentrated to ca. 20 cm^3. The sodium chloride then precipitated by the addition of ethanol to the solution was filtered off. The same procedure was repeated five times in order to remove all the sodium chloride. The residue thus obtained was dissolved in a minimum amount of water, to which was added a saturated aqueous sodium perchlorate solution to yield microcrystalline precipitates. After dissolving the precipitates in a small amount of hot water, the addition of a small amount of $HClO_4$ gave crystals, which were then washed well with water and dried over P_2O_5 in a vacuum. The absence of chloride ions in the complex was checked by the use of $AgNO_3$.

The physical data of the new compounds are given below. $[Cu^{II}Ni^{II}(L^4)](ClO_4)_4\cdot2H_2O$: Yield: 8%.[8] Found: C, 36.28; H, 4.49; N, 9.91; Cu, 5.5; Ni, 5.1%. Calcd for $C_{34}H_{50}N_8CuNiCl_4O_{16}\cdot2H_2O$: C, 36.24; H, 4.83; N, 9.94; Cu, 5.64; Ni, 5.21%. IR (KBr): 1619 (C=N) and 1580 cm^{-1} (py).

The hexamethylene, pentamethylene, and trimethylene derivatives were prepared by the same procedure except that for using *N,N,N',N'*-tetrakis(3-aminopropyl)-1,6-hexanediamine, *N,N,N',N'*-tetrakis(3-aminopropyl)-1,5-pentanediamine, and *N,N,N',N'*-tetrakis(3-aminopropyl)-1,3-propanediamine were used instead of *N,N,N',N'*-tetrakis(3-aminopropyl)-1,4-butanediamine. In the case of ethylene derivative (*N,N,N'N'*-tetrakis(3-aminopropyl)-1,2-ethanediamine), however, a longer reaction time (8 and 9 h after the addition of the Ni(II) and Cu(II) ions respectively) was required, because only small amounts of macrocyclic products were obtained under the conditions described

above.

$[Cu^{II}Ni^{II}(L^6)](ClO_4)_4 \cdot 2H_2O$: Yield: 10%.[8] Found: C, 37.53; H, 4.72; N, 9.65; Cu, 5.8; Ni, 4.8%. Calcd for $C_{36}H_{54}N_8CuNiCl_4O_{16} \cdot 2H_2O$: C, 37.44; H, 5.06; N, 9.70; Cu, 5.50; Ni, 5.08%. IR (KBr): 1615 (C=N) and 1575 cm^{-1} (py).

$[Cu^{II}Ni^{II}(L^5)](ClO_4)_4 \cdot 2H_2O$: Yield: 8%.[8] Found: C, 36.51; H, 4.64; N, 9.58; Cu, 5.8; Ni, 5.1%. Calcd for $C_{35}H_{52}N_8CuNiCl_4O_{16} \cdot 2H_2O$: C, 36.85; H, 4.95; N, 9.82; Cu, 5.57; Ni, 5.14%. IR (KBr): 1615 (C=N) and 1575 cm^{-1} (py).

$[Cu^{II}Ni^{II}(L^3)](ClO_4)_4 \cdot 2H_2O$: Yield: 8%.[8] Found: C, 35.63; H, 4.44; N, 10.04; Cu, 5.3; Ni, 4.9%. Calcd for $C_{33}H_{48}N_8CuNiCl_4O_{16} \cdot 2H_2O$: C, 35.62; H, 4.71; N, 10.07; Cu, 5.71; Ni, 5.27%. IR (KBr): 1620 (C=N) and 1580 cm^{-1} (py).

$[Cu^{II}Ni^{II}(L^2)](ClO_4)_4$: Yield 27%.[8,9] Found: C, 36.19; H, 4.29; N, 10.38; Cu, 5.5; Ni, 5.1%. Calcd for $C_{32}H_{46}N_8CuNiCl_4O_{16}$: C, 36.16; H, 4.36; N, 10.54; Cu, 5.78; Ni, 5.34%. IR (KBr): 1615 (C=N) and 1585 cm^{-1} (py).

Measurements. The infrared and visible absorption spectra were measured with Hitachi 260-10 and Hitachi 340 spectrophotometers respectively. The electrochemical measurements were performed according to the method described in our previous paper.[10]

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7) The product ratios of the Cu(II)Cu(II):Cu(II)Ni(II):Ni(II)Ni(II) complexes were as follows: 0.30:1:0.18 (L^2); 0.12:1:1.1(L^3); 0.23:1:1.0(L^4); 0.48:1:1.2(L^5); 0.28:1:1.4(L^6). If there is no difference in reactivity between Cu(II) and Ni(II) ions, the product ratio can be expected to be 1:2:1. However, the experimental results did not agree with this surmise.

8) The overall yield (isolated after recrystallization) is calculated by assuming that the reaction gave the Cu(II)-Ni(II) complex only.

9) The conditions employed for the preparation of the complexes with L^3—L^6 gave only small amounts of the macrocyclic products. Prolonging the reaction time considerably increased the yield of $[Cu^{II}Ni^{II}(L^2)]^{4+}$. These results might be explained as indicating that the electrostatic repulsion between two metal ions which are located close to each other during the reactions is serious in the case of the ethylene derivatives, thus retarding the template reaction.

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11) Similar results were obtained with the Pt-electrode.