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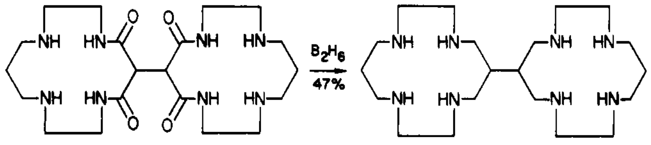
Ditopic Receptors for Transition-Metal Ions: A Heterobimetallic Nickel(II)–Copper(II) Bis(macrocyclic) Complex and Its Stepwise Oxidation to the Tervalent State

Sir:

Several articles have been reported in recent years on the coordination chemistry of bis(macrocycles), i.e. molecules in which two potentially coordinating tetraaza subunits are linked together by bridging the amine nitrogen or carbon atoms of the ligand's backbone.[1–6] Although there are examples of heterobinuclear complexes with Schiff bases[7] and porphyrins,[8] all reported bis(tetraaza macrocyclic) complexes are homobinuclear, incorporating in particular either two nickel(II) or two copper(II) ions. Redox chemistry of some of these dinickel(II)[1] or dicopper(II)[3] complexes has been investigated with regard to the M(II) to M(III) oxidation process. In every case the two metal centers were found to behave almost independently, the potentials of the two redox steps being separated by 100 mV or less, a quantity slightly higher than that expected on a purely statistical base (36 mV).

Interest toward a bimetallic system able to exchange two electrons in two distinctly separated redox steps prompted us to synthesize heterobimetallic bis(macrocyclic) complexes. We report here the synthesis of a mixed nickel(II)–copper(II) bis(macrocyclic) complex and the electrochemical investigation on its oxidation behavior. In the design of the bis(macrocycle) we have chosen the cyclam subunit, which, among polyaza macrocycles, guarantees the greatest thermodynamic[9] and kinetic[10] stability for divalent 3d metal ions and also permits the easiest access to the trivalent state.[11] Biscyclam **2** (C–C linking of the two subunits preferred to the bridging of amine nitrogen atoms in order not to reduce coordinating tendencies) was obtained by reduction of the parent bisdioxocyclam molecule **1**[3] with B_2H_6 and purified through the octahydrochloride.



1 **2**

To prepare the mixed-metal complex, 1 equiv of $Ni(NO_3)_2$ was added to an aqueous solution of biscyclam at pH 7 and the solution was kept at 50 °C for 1 h. Then, 1 equiv of $Cu(NO_3)_2$ was added and the solution again kept at 50 °C for 1 h. On the assumption that the two rings behave independently in the complexation process, the final solution should contain 25% of the dicopper(II) complex, 25% of the dinickel(II) complex and 50% of the mixed nickel(II)–copper(II) complex. Separation of the three dinuclear species was accomplished by ion-exchange chromatography on Sephadex SP 25. On elution with 0.4 M NaCl, three quite distinct bands formed. A violet band (λ_{max} = 510 nm) first eluted, which was ascribed to the dicopper(II) complex. Then elution of a salmon pink band, ascribed to the mixed-metal species, was observed. Finally the yellow (λ_{max} = 460 nm) dinickel(II) complex eluted. Chromatographic separation was monitored through the d–d absorption spectra of the fractions, and its efficiency is demonstrated by the diagram in Figure 1, in which the ratio of the absorbance at 510 nm (corresponding to the Cu(II)–Cu(II) chromophore) and that at 460 nm (corresponding to the Ni(II)–Ni(II) chromophore) measured for every fraction are reported. The middle fractions were collected, concentrated, and treated several times with EtOH in order to eliminate the sodium chloride. On addition of saturated $NaClO_4$ solution to the aqueous solution of the complex, a microcrystalline salmon pink precipitate was obtained, whose elemental analysis corresponds to NiCu(biscyclam)$(ClO_4)_4$.

Electrochemical investigations on the heterobinuclear complex[12] were performed in two different solvents: anhydrous acetonitrile (MeCN) and 70% perchloric acid, which are known to permit the formation of stable Ni(III) and Cu(III) tetraaza macrocyclic complexes in solution.[13,14] Figure 2 reports the differential-pulse polarograms obtained at a platinum-microsphere working electrode of a 10^{-4} M NiCu(biscylam)$(ClO_4)_4$ and 10^{-1} M Et_4NBF_4 solution in CH_3CN (curve b). Curve a refers to a solution 10^{-4} M in both Ni(cyclam)$(ClO_4)_2$ and Cu(cyclam)$(ClO_4)_2$ species. The first peak observed for the mixed-metal complex is ascribed to the Ni(II)/Ni(III) oxidation step, and its potential is coincident with that of the monomeric analogue, Ni(cyclam)$^{2+}$ (see curve a). The second peak in the DPP trace (curve b), ascribed to the one-

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(12) Homodimetallic complexes of biscyclam with nickel(II) and copper(II) display a two-electron-oxidation behavior, analogous to that previously described for bis(macrocyclic) systems.[3,6] In particular, Ni_2(biscyclam)$(ClO_4)_4$ in MeCN undergoes two consecutive oxidation steps, whose potentials are separated by 75 mV. In the case of Cu_2(biscyclam)$(ClO_4)_4$ complex, in concentrated perchloric acid solution, the two one-electron steps are separated by 95 mV.

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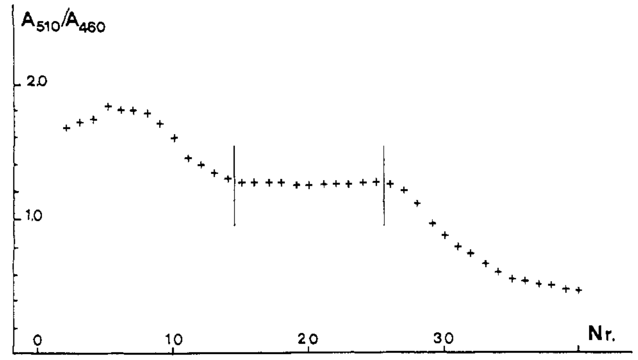

Figure 1. Ratio of the absorbances at 510 nm (A_{510}) and at 460 nm (A_{460}) as a function of the fraction number. The counting of the fraction was started with the elution of the first band.

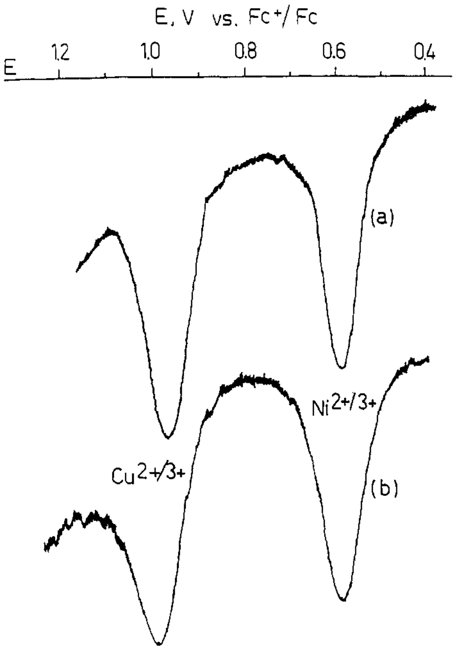

Figure 2. Differential-pulse polarograms for acetonitrile solutions (0.1 M Et_4NBF_4): (a) mixture of 10^{-4} M Ni(cyclam)$(ClO_4)_2$ and 10^{-4} M Cu(cyclam)$(ClO_4)_2$; (b) 10^{-4} M NiCu(biscyclam)$(ClO_4)_4$. Conditions: pulse voltage, 10 mV; potential scan rate, 1 mV s^{-1}; platinum working electrode.

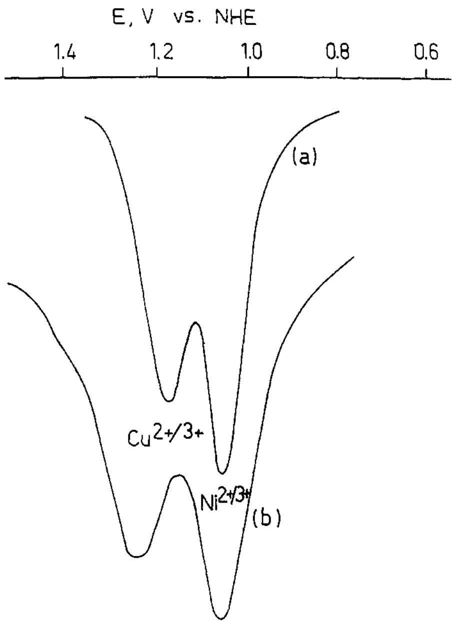

Figure 3. Differential-pulse polarograms for 70% $HClO_4$ solutions: (a) mixture of 5×10^{-4} M Ni(cyclam)$(ClO_4)_2$ and 5×10^{-4} M Cu(cyclam)$(ClO_4)_2$; (b) 5×10^{-4} M NiCu(biscyclam)$(ClO_4)_4$. Conditions: pulse voltage, 10 mV; potential scan rate, 1 mV s^{-1}; platinum working electrode. A silver wire calibrated vs. the Fe^{3+}/Fe^{2+} couple was used as a quasi-reference electrode. Potentials were referred to the NHE by using the formula of Ciavatta.[16]

electron oxidation of the Cu(II) center, occurs at a potential 30 mV more positive than that observed for the monomeric reference system, Cu(cyclam)$^{2+}$ (curve a). Figure 3 reports the DPP in concentrated (11.6 M) $HClO_4$ solution for both the equimolar Ni(cyclam)$^{2+}$/Cu(cyclam)$^{2+}$ mixture and the NiCu(biscyclam)$^{4+}$ complex. In this medium the second peak (Cu(II)/Cu(III)) is much closer to the first one (Ni(II)/Ni(III)), as compared to MeCN. This reflects the well-known effect of the "inert electrolyte" (11.6 M ClO_4^-), which stabilizes Cu(III) and destabilizes Ni(III) in tetraaza macrocyclic complexes.[16] Also in this case, the potential separation for the biscyclam complex is 60 mV greater than that observed for the solution containing the monomeric cyclam complexes. This generally reflects the increased difficulty in oxidizing Cu(II) to Cu(III) in the presence of a tripositive cation Ni(III) at a distance of about 8 Å (as estimated by molecular models), compared to a situation in which the metal centers are far apart. The fact that the difference between the Ni(II)/Ni(III) and Cu(II)/Cu(III) peaks for the biscyclam complex is greater in 70% $HClO_4$ than in MeCN (60 and 30 mV, respectively) could be interpreted in terms of solvent-moderated interaction between the metal centers. In the $HClO_4$ solution the massive amount of electrolyte strongly competes for the solvent molecules, so that the bimetallic species is poorly solvated, and the repulsive electrostatic effect exerted by Ni(III) on the proximate redox center is particularly large.

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Registry No. **1**, 84507-37-9; **2**, 102632-51-9; Cu_2(biscyclam)$^{4+}$, 102649-29-6; Ni_2(biscyclam)$^{4+}$, 102649-30-9; CuNi(biscyclam)$^{4+}$, 102649-31-0.

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Generation and Reactions of Chiral, Pyramidal, Transition-Metal Lewis Acids of the Formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+X^-$

Sir:

Transition-metal complexes of weakly coordinating ligands such as BF_4^- and PF_6^- are currently the focus of much synthetic, structural, and mechanistic interest.[1-5] Such complexes are often

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