Selective Syntheses of Heterobinuclear Cobalt(III)–Nickel(II) and Cobalt(III)–Copper(II) Complexes with a Bimacrocyclic Ligand *via* 'Lariat Nickel(II) or Cobalt(III) Complexes'

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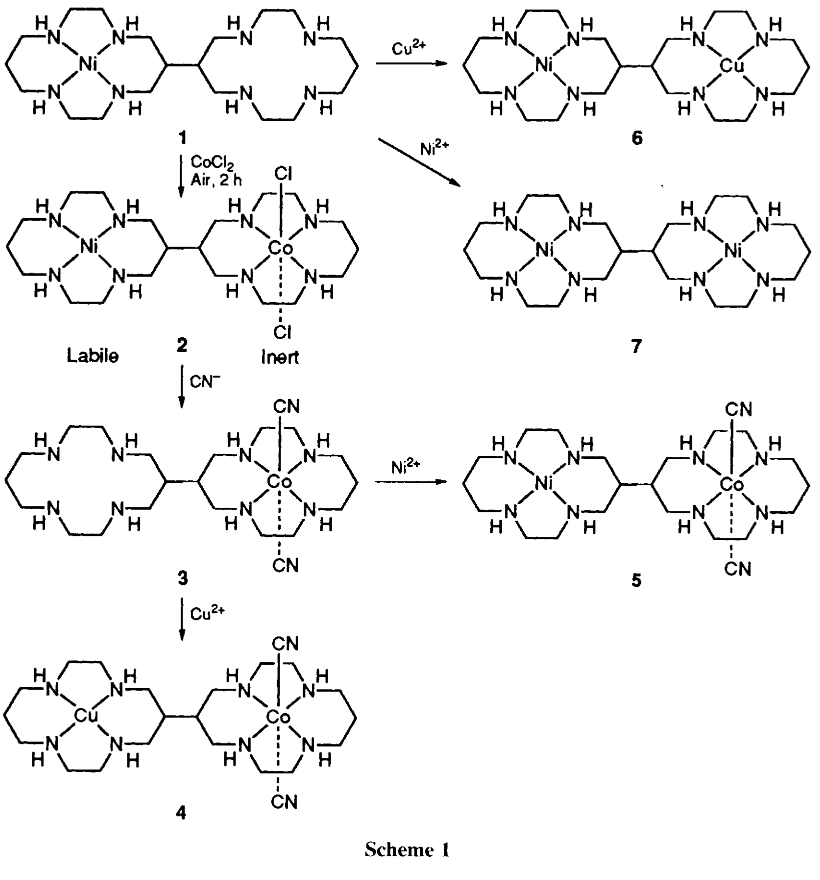
Heterobinuclear Co^{III}–Ni^{II} and Co^{III}–Cu^{II} complexes with bicyclam [6,6'-bis(1,4,8,11-tetraazacyclotetradecane)] **L** are selectively synthesized *via* a mononuclear nickel(II) or cobalt(III) complex with bicyclam 'lariat nickel(II) or cobalt(III) complexes'.

Although a number of homobinuclear complexes with bimacrocyclic ligands have been synthesized and characterized, only a few heterobinuclear complexes[1,2] are known. Only the Cu^{II}–Ni^{II} complex has been reported with a bicyclam ligand.[1] During the synthesis of this Cu^{II}–Ni^{II} complex, dinickel(II) and dicopper(II) complexes are also formed because the complexation follows statistical rules and separation is necessary. We now report a useful method for the selective synthesis of heterobinuclear complexes by using a mononuclear Ni^{II} or Co^{III} complex with bicyclam 'lariat Ni^{II} or Co^{III} complexes' (Scheme 1).

The 'lariat Ni^{II} complex' **1**† can easily incorporate a metal ion in its cavity. Fig. 1(*a*) shows the absorption spectral change during the course of the reaction between Cu^{2+} and complex **1** in aqueous solution. A new absorption band rapidly appeared at *ca.* 500–600 nm with no change in the absorption band due to the Ni^{II} complex. The final spectrum was essentially the same as that of the known Cu^{II}–Ni^{II} complex **6**.[1] This change can be ascribed to the incorporation of Cu^{2+} into the open cavity of **1**. The complexation proceeds quantitatively under the experimental conditions shown in Fig. 1. The reaction of **1** with Ni^{2+} affords the dinickel(II) complex **7**.

This procedure of incorporating another metal ion enables us to prepare a heterobinuclear Co^{III}–Ni^{II} complex **2**. The complex **1** was treated with $CoCl_2$ in H_2O followed by oxidation with air. Addition of hydrochloric acid affords the chloride $[Co^{III}Cl_2Ni^{II}L]Cl_3{\cdot}3H_2O$‡ as yellowish green needles. The isolated complex was not a mixture of dicobalt and dinickel complexes but the heterobinuclear complex, as confirmed by MS. The FAB-MS of the complex showed the $[M-Cl]^+$ peak at *m/z* = 657, of which the isotope splitting pattern practically agreed with the theoretical one [Fig. 2(*a*)]; peaks corresponding to dicobalt and dinickel complexes were not observed. The VIS absorption spectrum of the heterobinuclear complex has two absorption bands [λ_{max} = 442 nm (ε/dm^3 mol^{-1} cm^{-1} = 77), 618 (27); H_2O, 25 °C] and is very similar to the sum of the absorption spectra of the complex **1** and $[Co^{III}{}_2Cl_4L]Cl_2$.¶ The CV shows two waves ascribable to Ni$^{II/III}$ (E_{pc} = +0.59, E_{pa} = +0.67, $E_{1/2}$ = +0.63 V *vs.* Ag/AgCl in 0.2 mol dm^{-3} KCl, glassy carbon) and Co$^{II/III}$ (E_{pc} = −0.07, E_{pa} = +0.08, $E_{1/2}$ = +0.01 V), which are again similar to the sum of the CV of the complex **1** and $[Co^{III}{}_2Cl_4L]Cl_2$.

As the Co^{III} ion is much less reactive than the Ni^{II} ion, the use of an appropriate strong ligand should only remove the Ni^{II} ion from the complex. Indeed, treatment of complex **2** with NaCN yielded the mononuclear Co^{III} complex **3**, isolated as the perchlorate, $[Co^{III}(CN)_2LH_2](ClO_4)_3{\cdot}2H_2O$,|| where one of the macrocycles encloses the Co^{III} ion and the other is protonated. The isotope splitting pattern of the FAB-MS (*m/z* = 709 $[M-ClO_4]^+$) [Fig. 2(*b*)] and the elemental analysis confirmed the mononuclear Co^{III} complex. The diamagnetic



Scheme 1

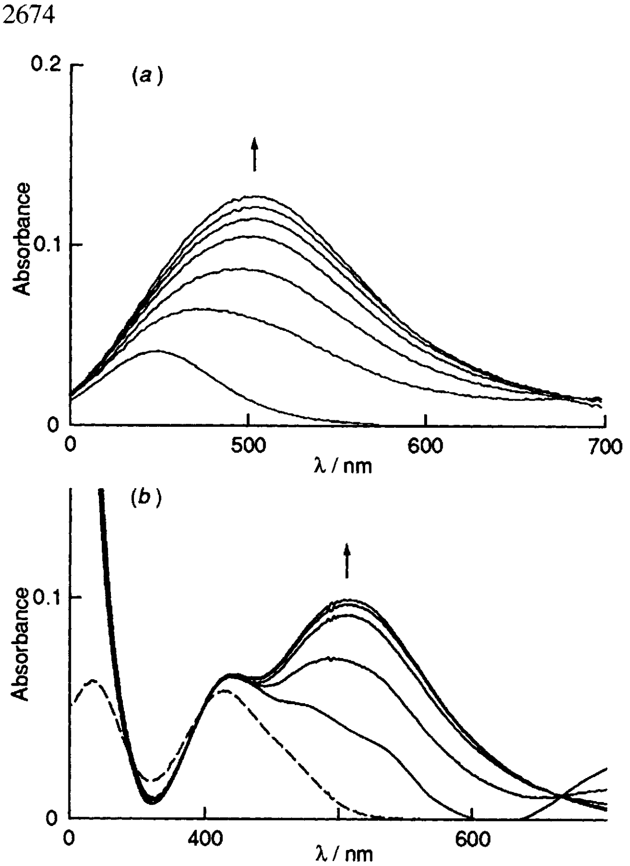


Fig. 1 Absorption spectral changes in the reactions of 1 mmol dm^{-3} $Cu(ClO_4)_2$ with (*a*) 1 mmol dm^{-3} **1** and (*b*) 1 mmol dm^{-1} **3** in 0.1 mol dm^{-3} aqueous acetate buffer (pH = 4.1) at 26 °C

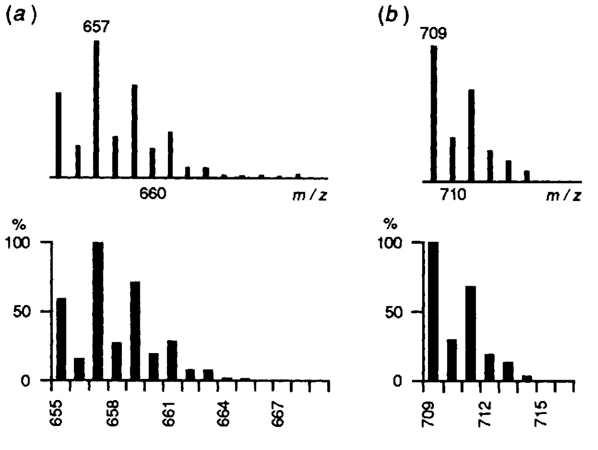


Fig. 2 The observed (upper) and theoretical (lower) mass peaks for (*a*) **2** $[M-Cl]^+$ and (*b*) **3** $[M-ClO_4]^+$

complex **3** shows the 12 expected signals (2 doublets and 10 triplets) in its ^{13}C NMR spectrum, indicating each macrocycle is chemically unequivalent. The VIS absorption spectrum of **3** [λ_{max} = 414 nm (ε = 78), 317 (87), H_2O] is very similar to that of $[Co^{III}(CN)_2(cyclam)]ClO_4$.||

The 'lariat Co^{III} complex' **3** also has the property of incorporating another metal ion into its open cavity. The reactions of **3** with $Cu(ClO_4)_2$ and $Ni(ClO_4)_2$ almost quantitatively afford the heterobinuclear complexes **4** and **5** respectively, isolated as the perchlorates $[Co^{III}(CN)_2Cu^{II}L](ClO_4)_3 \cdot 3H_2O$** and $[Co^{III}(CN)_2Ni^{II}L](ClO_4)_3 \cdot 3H_2O$.†† Fig. 1(*b*) shows the absorption spectral change during the course of the reaction between **3** and Cu^{2+} in aqueous solution. A similar change to that observed in the reaction of **1** with Cu^{2+} occurs at *ca.* 500–600 nm. The final spectrum [λ_{max} = 502 nm (ε = 108), 419 (86), H_2O] as very similar to the sum of the spectra of complex **3** and $[Cu(cyclam)]^{2+}$.[1] The ESR spectrum of **4** (DMF glass, 77 K) is typical of axial symmetry, with $g_{\|}$ split by the hyperfine coupling constant into a quartet; it is practically identical to that of $[Cu(cyclam)]^{2+}$.[1]

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Footnotes

† **1** was prepared from the reaction between **L** (5 mmol dm^{-3}) and $NiCl_2$ (3.5 mmol dm^{-3}) in aqueous solution. Purification by column chromatography with SP-Sephadex C-25, yielded the perchlorate (37%). FAB-MS: $[M-ClO_4]^+$ *m/z* = 757. VIS (H_2O, 25 °C): 452 nm (ε = 40). CV (Ag/AgCl, GC, 0.2 mol dm^{-3} KCl): $Ni^{II/III}$: E_{pc} = +0.58, E_{pa} = +0.66 V. The preliminary X-ray structure was obtained as well as that of the dinickel(II) complex **7**.

‡ Although it is still unclear whether Cl^- or H_2O coordinates to the Ni^{II} ion in the solid state of the isolated complex, the formula is provisionally used here.

§ The VIS absorption spectra of the Ni^{II} complexes **1**, **2**, **5**, **6** and **7** in water are temperature-dependent, because of the presence of an equilibrium between the square planar and water-coordinated octahedral Ni^{II} species.

¶ The dicobalt(III) complex was prepared according to the similar method reported for $[Co^{III}Cl_2(cyclam)]Cl$.[3] FAB-MS: $[M-Cl)^+$ *m/z* = 693. VIS (H_2O): 626 nm (ε = 58), 430 (85). CV (Ag/AgCl, GC, 0.2 mol dm^{-3} KCl): $Co^{II/III}$: E_{pc} = −0.10, E_{pa} = + 0.05 V.

|| $[Co^{III}(CN)_2(cyclam)]ClO_4$ was prepared by the reaction of $[Co^{III}Cl_2(cyclam)]Cl$ with NaCN. FAB-MS: $[M-ClO_4]^+$ *m/z* = 311. VIS (H_2O): 412 nm (ε = 79), 315 (91).

** FAB-MS: $[M-ClO_4]^+$ *m/z* = 772.

†† FAB-MS: $[M-ClO_4]^+$ *m/z* = 767. VIS (H_2O, 25 °C): 422 nm (ε = 101), 315 (95).

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