Macrocyclic effects upon isomeric CuII\text{M}^{II} and M^{II}\text{Cu}^{II} cores. Formation with unsymmetric phenol-based macrocyclic ligands

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Abstract. This paper discusses coordination-position isomeric M^{II}\text{Cu}^{II} and Cu^{II}\text{M}^{II} complexes, using unsymmetric dinucleating macrocycles (L_{m;n})_2^{2–} ((L_{2;2})_2^{2–}, (L_{2;3})_2^{2–} and (L_{2;4})_2^{2–}) that comprise two 2-(N-methyl)-aminomethyl-6-iminomethyl-4-bromo-phenonate entities, combined through the ethylene chain (m = 2) between the two amine nitrogens and through the ethylene, trimethylene or tetramethylene chain (n = 2, 3 or 4) between the two imine nitrogens. The macrocycles have dissimilar N(amine)\text{2O}^{2} and N(imine)\text{2O}^{2} metal-binding sites sharing the phenolic oxygens. The reaction of the mononuclear Cu^{II} precursors, [Cu(L_{2;2})], [Cu(L_{2;3})] and [Cu(L_{2;4})], with a M^{II} perchlorate and a M^{II} acetate salt formed (acetato)M^{II}\text{Cu}^{II} complexes: [CoCu(L_{2;2})(AcO)]ClO_4 \cdot 0 \cdot 5\text{H}_2\text{O} (1), [NiCu(L_{2;2})(AcO)]ClO_4 (2), [ZnCu(L_{2;2})(AcO)]ClO_4 (3), [CoCu(L_{2;3})(AcO)]ClO_4 \cdot 0 \cdot 5\text{H}_2\text{O} (4), [NiCu(L_{2;3})(AcO)]ClO_4 (5), [ZnCu(L_{2;3})(AcO)]ClO_4 \cdot 0 \cdot 5\text{H}_2\text{O} (6), [CoCu(L_{2;4})(AcO)(DMF)]ClO_4 (7), [NiCu(L_{2;4})(AcO)]ClO_4 \cdot 2\text{DMF} (8) and [ZnCu(L_{2;4})(AcO)]ClO_4 (9) (the formulation [M_aM_b(L_{m;n})]^{2+} means that M_a resides in the aminic site and M_b in the iminic site). The site selectivity of the metal ions is demonstrated by X-ray crystallographic studies for 2\cdot\text{MeOH}, 3, 5, 7, and 9. An (acetato)Cu^{II}Zn^{II} complex, [CuZn(L_{2;3})(AcO)]ClO_4 (10), was obtained by the reaction of [PbCu(L_{2;3})(ClO_4)_2 with ZnSO_4 \cdot 4\text{H}_2\text{O}, in the presence of sodium acetate. Other complexes of the Cu^{II}M^{II} type were thermodynamically unstable to cause a scrambling of metal ions. The Cu migration from the iminic site to the aminic site in the synthesis of 10 is explained by the ‘kinetic macrocyclic effect’. The coordination-position isomers, 6 and 10, are differentiated by physicochemical properties.

1. Introduction

The design of dinucleating compartmental ligands, whose two metal-binding sites are unsymmetric with respect to the cavity size, coordination number, geometric requirement, or the nature of the donor atom, is important for the study of heterodinuclear complexes. For this purpose, we have developed the unsymmetric phenol-based macrocycles of the type in chart 1, having two dissimilar N(amine)\text{2O}^{2} and N(imine)\text{2O}^{2} metal-binding sites sharing the bridging phenolic oxygens. They are abbreviated as (L_{m;n})^{2–} using the methylene number \textit{m} between the amine nitrogens and the methylene number \textit{n} between the imine nitrogens. Analogous macrocycles bearing a pyridyl auxiliary at the amine nitrogens or doubly bridged...
Chart 1. Chemical structure of \((L^{m;n})_2^-\).

Scheme 1. Synthetic methods for heterodinuclear \(M^{II}Cu^{II}\) and \(Cu^{II}M^{II}\) complexes of \((L^{m;n})_2^-\).

through two ethylene chains between the amine nitrogens\(^6\) were prepared in other laboratories.

Heterodinuclear \(Cu^{II}M^{II}\) or \(M^{II}Cu^{II}\) complexes of \((L^{2,2})_2^-, (L^{2,3})_2^-\) and \((L^{2,4})_2^-\) can be derived by two different methods; (i) the reaction of the mononuclear \(Cu^{II}\) precursors \([Cu(L^{m;n})]\) (having the \(Cu^{II}\) in the iminic site) with \(M^{II}\) salts and (ii) the transmetallation of the \(Pb^{II}\) of the dinuclear \(Pb^{II}Cu^{II}\) precursors \([PbCu(L^{m;n})](ClO_4)_2\) for \(M^{II}\) ions (scheme 1)\(^2,4\). The first method using \(M^{II}\) chloride salts gave \([MCu(L^{m;n})Cl_2]\) \(((L^{m;n})_2^- = (L^{2,2})_2^-, (L^{2,3})_2^-, (L^{2,4})_2^-); M = Mn^{II}, Co^{II}, Ni^{II}, Zn^{II})\(^2,4\) that have the \(M^{II}\) in the \(N(amine)_2O_2\)
site and the Cu\textsuperscript{II} in the Ni(imine)\textsubscript{2}O\textsubscript{2} site: hereafter, the formulation [M\textsubscript{a}M\textsubscript{b}(L\textsubscript{m,n})\textsuperscript{2+}]\textsuperscript{2+} means that M\textsubscript{a} resides in the aminic site and M\textsubscript{b} in the iminic site. The second method using M\textsuperscript{II} sulphate salts gives the Cu\textsuperscript{II}M\textsuperscript{II} perchlorate complexes [CuM(L\textsubscript{m,n})\textsubscript{2}](ClO\textsubscript{4})\textsubscript{2} ((L\textsubscript{m,n})\textsuperscript{2–} = (L\textsubscript{2,2})\textsuperscript{2–}, (L\textsubscript{2,3})\textsuperscript{2–}; M = Co\textsuperscript{II}, Ni\textsuperscript{II}, Zn\textsuperscript{II})\textsuperscript{3}. In this synthesis, the Cu\textsuperscript{II} migrates from the iminic site to the aminic site and the M\textsuperscript{II} is accommodated in the iminic site.

Our previous studies suggest that isomeric M\textsuperscript{III}Cu\textsuperscript{II} and Cu\textsuperscript{II}M\textsuperscript{III} complexes (coordination-position isomers) can be derived from (L\textsubscript{m,n})\textsuperscript{2–} by taking advantage of the two synthetic methods, when an exogenous anionic donor is properly chosen. Coordination-position isomers consisting of two labile metal ions are very limited in spite of the great interest in basic coordination chemistry. In this work our aim was to provide isomeric (acetato)Cu\textsuperscript{II}M\textsuperscript{III} and (acetato)M\textsuperscript{III}Cu\textsuperscript{II} complexes of (L\textsubscript{2,2})\textsuperscript{2–} ~ (L\textsubscript{2,4})\textsuperscript{2–}. One of the latter class, [CuZn(L\textsubscript{2,3})(AcO)](ClO\textsubscript{4})\textsubscript{2}, has been prepared from [PbCu(L\textsubscript{2,3})](ClO\textsubscript{4})\textsubscript{2} by method II in the presence of acetate ion\textsuperscript{3}.

2. Experimental

2.1 Preparation

The mononuclear Cu\textsuperscript{II} precursors, [Cu(L\textsubscript{2,2})], [Cu(L\textsubscript{2,3})] and [Cu(L\textsubscript{2,4})], and the dinuclear Pb\textsuperscript{II}Cu\textsuperscript{II} precursors, [PbCu(L\textsubscript{2,2})](ClO\textsubscript{4})\textsubscript{2}, [PbCu(L\textsubscript{2,3})](ClO\textsubscript{4})\textsubscript{2} and [PbCu(L\textsubscript{2,4})](ClO\textsubscript{4})\textsubscript{2} were prepared by the methods described in our earlier papers\textsuperscript{2}.

2.1a (Acetato)M\textsuperscript{II}Cu\textsuperscript{II} complexes: To a suspension of a mononuclear Cu\textsuperscript{II} precursor [Cu(L\textsubscript{m,n})] (1 \times 10\textsuperscript{–4} mol) in methanol (10 cm\textsuperscript{3}) was added a methanol solution (15 cm\textsuperscript{3}) of a M\textsuperscript{II} perchlorate salt (5 \times 10\textsuperscript{–5} mol) and a M\textsuperscript{II} acetate salt (5 \times 10\textsuperscript{–5} mol), and the mixture was refluxed for 2 h. The resulting product was separated by filtration, washed with ether and dried in vacuo. The following complexes were obtained by this method (method I).

- [CoCu(L\textsubscript{2,2})(AcO)]ClO\textsubscript{4} \cdot 0.5H\textsubscript{2}O (1). Green microcrystals. Found: C 34.74; H 3.29; N 6.85; Cu 8.08; Co 6.94%. Calcd. for C\textsubscript{24}H\textsubscript{28}Br\textsubscript{2}ClCoCuN\textsubscript{4}O\textsubscript{8} \cdot 0.5H\textsubscript{2}O: C 34.89; H 3.42; N 6.78; Co 7.13%. Selected IR [\textsuperscript{n}cm\textsuperscript{–1}] using KBr: 1632, 1583, 1552, 1446, 1425, 1292, 1097, 1082, 764, 623. m\textsubscript{eff} per CoCu: 4.69 m\textsubscript{B} at 290 K. UV-Vis [\textit{l} \textsubscript{max}/nm (\textit{e} M\textsuperscript{–1} cm\textsuperscript{–1})] in DMSO: 356 (8120), 542 (218).

- [NiCu(L\textsubscript{2,2})(AcO)]ClO\textsubscript{4} (2). Green powder. Found: C 35.28; H 3.34; N 6.87; Cu 8.12; Ni 6.98%. Calcd. for C\textsubscript{24}H\textsubscript{27}Br\textsubscript{2}ClCuNiO\textsubscript{8}: C 35.89; H 3.33; N 6.86; Cu 7.78; Ni 7.18%. Selected IR [\textsuperscript{n}cm\textsuperscript{–1}] using KBr: 1632, 1583, 1445, 1292, 1098, 1083, 762, 624. m\textsubscript{eff} per NiCu: 3.58 m\textsubscript{B} at 290 K. UV-Vis [\textit{l} \textsubscript{max}/nm (\textit{e} M\textsuperscript{–1} cm\textsuperscript{–1})] in DMSO: 356 (8290), 555 (170).

- [ZnCu(L\textsubscript{2,2})(AcO)]ClO\textsubscript{4} \cdot MeOH (2\textsuperscript{¢}). Reddish brown crystals. Found: C 34.79; H 3.26; Zn 7.58%. Calcd. for C\textsubscript{23}H\textsubscript{23}Br\textsubscript{2}ClCuZN\textsubscript{4}O\textsubscript{8}: C 35.37; H 3.68; N 6.60; Cu 7.48; Ni 6.91%.

Single crystals of [NiCu(L\textsubscript{2,2})(AcO)]ClO\textsubscript{4} \cdot MeOH (2\textsuperscript{°}) were obtained by slow evaporation of the filtrate. Found: C 35.54; H 3.68; N 6.70; Cu 7.60; Ni 6.52%. Calcd. for C\textsubscript{23}H\textsubscript{23}Br\textsubscript{2}ClCuZN\textsubscript{4}O\textsubscript{8}: C 35.37; H 3.68; N 6.60; Cu 7.48; Ni 6.91%.

- [ZnCu(L\textsubscript{2,2})(AcO)]ClO\textsubscript{4} (3). Reddish brown crystals. Found: C 34.79; H 3.26; N 6.75; Cu 8.07; Zn 7.58%. Calcd. for C\textsubscript{23}H\textsubscript{23}Br\textsubscript{2}ClCuZN\textsubscript{4}O\textsubscript{8}: C 35.00; H 3.30; N 6.80; Cu 7.71; Zn 7.94%. Selected IR [\textsuperscript{n}cm\textsuperscript{–1}] using KBr: 1631, 1592, 1552, 1445, 1293, 1089, 767, 624. m\textsubscript{eff} per CuZn: 1.85 m\textsubscript{B} at 290 K. UV-Vis [\textit{l} \textsubscript{max}/nm (\textit{e} M\textsuperscript{–1} cm\textsuperscript{–1})] in DMSO: 353 (8590), 542 (220).
[CoCu(L\(^{-3}\))(AcO)]\(\text{ClO}_4\)-0.5H\(_2\)O (4). Dark green microcrystals. Found: C 35.50; H 3.53; N 6.53; Cu 8.00; Co 6.91%. Calcd. for C\(_{25}\)H\(_{30}\)Br\(_2\)ClCoCuN\(_4\)O\(_8\): C 35.74; H 3.60; N 6.67; Cu 7.56; Co 7.01%. Selected IR \([\text{cm}^{-1}]\) using KBr: 1619, 1582, 1456, 1402, 1303, 1094, 690, 622. \(\epsilon_{\text{max}}\) per CuCo: 4.82 \(\epsilon_{\text{max}}\) at 290 K. UV-Vis \([\text{nm} (\text{M}^{-1} \text{cm}^{-1})]\) in DMSO: 356 (8810), 636 (120).

[NiCu(L\(^{-3}\))(AcO)]\(\text{ClO}_4\) (5). Green crystals. Found: C 36.14; H 3.63; N 6.70; Cu 7.47; Ni 7.00%. Calcd. for C\(_{25}\)H\(_{30}\)Br\(_2\)ClCuNiN\(_4\)O\(_8\): C 35.46; H 3.57; N 6.62; Cu 7.51; Zn 7.72%. Selected IR \([\text{cm}^{-1}]\) using KBr: 1622, 1609, 1560, 1452, 1302, 1086, 754, 683, 622. \(\epsilon_{\text{max}}\) per CuNi: 3.36 \(\epsilon_{\text{max}}\) at 290 K. UV-Vis \([\text{nm} (\text{M}^{-1} \text{cm}^{-1})]\) in DMSO: 358 (8800), 656 (95).

[ZnCu(L\(^{-3}\))(AcO)]\(\text{ClO}_4\)-0.5H\(_2\)O (6). Green microcrystals. Found: C 35.36; H 3.54; N 6.51; Cu 7.91; Zn 7.75%. Calcd. for C\(_{25}\)H\(_{30}\)Br\(_2\)ClCuZnN\(_4\)O\(_8\): C 35.46; H 3.57; N 6.62; Cu 7.51; Zn 7.72%. Selected IR \([\text{cm}^{-1}]\) using KBr: 1620, 1594, 1565, 1453, 1403, 1085, 776, 689, 623. \(\epsilon_{\text{max}}\) per CuZn: 1.86 \(\epsilon_{\text{max}}\) at 290 K. UV-Vis \([\text{nm} (\text{M}^{-1} \text{cm}^{-1})]\) in DMSO: 352 (8800), 617 (93).

[CoCuL\(^{-4}\)](AcO)(DMF)\(\text{ClO}_4\) (7). Recrystallized from DMF as dark brown crystals. Found: C 38.37; H 4.40; N 7.90; Cu 6.92; Co 6.67%. Calcd. for C\(_{25}\)H\(_{30}\)Br\(_2\)ClCoCuN\(_4\)O\(_8\): C 37.93; H 4.17; N 7.63; Cu 6.92; Co 6.42%. Selected IR \([\text{cm}^{-1}]\) using KBr: 1652, 1622, 1556, 1451, 1450, 1406, 1303, 1097, 1086, 622. \(\epsilon_{\text{max}}\) per CuCo: 4.99 \(\epsilon_{\text{max}}\) at 290 K. UV-Vis \([\text{nm} (\text{M}^{-1} \text{cm}^{-1})]\) in DMSO: 366 (8000), 720 (130).

[NiCu(L\(^{-3}\))(AcO)]\(\text{ClO}_4\)-2DMF (8). Recrystallized from DMF as green microcrystals. Found: C 38.68; H 4.53; N 8.31; Cu 6.16; Ni 5.69%. Calcd. for C\(_{25}\)H\(_{30}\)Br\(_2\)ClCoCuNiN\(_4\)O\(_8\): C 38.78; H 4.58; N 8.48; Cu 6.41; Ni 5.92%. Selected IR \([\text{cm}^{-1}]\) using KBr: 1674, 1652, 1629, 1565, 1447, 1414, 1328, 1102, 1095, 623. \(\epsilon_{\text{max}}\) per CuNi: 3.36 \(\epsilon_{\text{max}}\) at 290 K. UV-Vis \([\text{nm} (\text{M}^{-1} \text{cm}^{-1})]\) in DMSO: 367 (8700), 720 (150).

[ZnCu(L\(^{-3}\))(AcO)]\(\text{ClO}_4\) (9). Green crystals. Found: C 36.63; H 3.66; N 6.48; Cu 7.89; Zn 7.66%. Calcd. for C\(_{25}\)H\(_{30}\)Br\(_2\)ClCuZnN\(_4\)O\(_8\): C 36.66; H 3.67; N 6.58; Cu 7.46; Zn 7.68%. Selected IR \([\text{cm}^{-1}]\) using KBr: 1618, 1592, 1453, 1402, 1302, 1097, 1090, 622. \(\epsilon_{\text{max}}\) per CuZn: 1.83 \(\epsilon_{\text{max}}\) at 290 K. UV-Vis \([\text{nm} (\text{M}^{-1} \text{cm}^{-1})]\) in DMSO: 355 (8900), 740 (74).

2.1b (Acetato)Cu\(^{II}\)M\(^{II}\) complexes: To a suspension of a Pb\(^{II}\) precursor [PbCu(L\(^{-3}\))(AcO)]\(\text{ClO}_4\) \((1 \times 10^{-4} \text{ mol})\) in acetonitrile \((10 \text{ cm}^3)\) was added a methanol solution \(20 \text{ cm}^3\) of a M\(^{II}\) sulphate salt \((1 \times 10^{-4} \text{ mol})\) and sodium acetate \((1 \times 10^{-4} \text{ mol})\), and the mixture was stirred at ambient temperature for 3 h to result in the precipitation of PbSO\(_4\). It was removed by filtration and the filtrate was diffused with ether to give a precipitate.

[CuZn(L\(^{-3}\))(AcO)]\(\text{ClO}_4\) (10) was obtained by this method, but other complexes could not be obtained in pure form.

2.2 Physical measurements

Elemental analyses of C, H, and N were obtained at the Service Center of Elemental Analysis, Kyushu University, Japan. Metal analyses were made on a Shimadzu AA-680 atomic absorption/flame emission spectrophotometer. Infrared spectra were recorded on a JASCO IR-810 spectrophotometer using KBr disks. Electronic absorption spectra in dimethyl sulphoxide (DMSO) were recorded on a Shimadzu UV-3100PC spectrophotometer. Reflectance spectra were recorded on a Shimadzu MPS-2000
spectrophotometer. Magnetic susceptibilities of powdered samples were measured on a quantum design MPMS XL SQUID susceptometer over the temperature range of 2–300 K. Diamagnetic corrections for the constituting atoms were made using Pascal’s constants. Cyclic voltammograms were measured in DMSO solution containing tetra(n-butyl)ammonium perchlorate (TBAP) as the supporting electrolyte, using a BAS CV-50 W electrochemical analyser (Caution! TBAP is explosive and should be handled with great care). A three-electrode cell was used which was equipped with a glassy carbon working electrode, a platinum coil as the counter electrode, and a Ag/Ag⁺ (TBAP/acetonitrile) reference electrode.

2.3 X-ray crystallography

Each single crystal of [NiCu(L²;2)(AcO)]ClO₄·MeOH (2'), [ZnCu(L²;2)(AcO)]ClO₄ (3), [NiCu(L²;3)(AcO)]ClO₄ (5), [CoCu(L²;4)(AcO)(DMF)]ClO₄ (7) and [ZnCu(L²;4)(AcO)]ClO₄ (9) was mounted on a glass fibre and coated with epoxy resin. All the crystallographic measurements were performed on a Rigaku AFC7R diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71069 Å) and a 12 kW rotating anode generator at 20 ± 1 °C. Cell constants and an orientation matrix for the data collection were obtained from 25 reflections in the range 26.84 < 2q < 29.97° for 2', 25 reflections in the range 29.67 < 2q < 29.99° for 3, 24 reflections in the range 26.87 < 2q < 30.01° for 5, 22 reflections in the range 29.59 < 2q < 30.04° for 7, and 20 reflections in the range 6.30 < 2q < 10.59° for 9. For the intensity collections, the w−2q scan mode was used to a maximum 2q value of 55.0° for all the complexes at a scan speed of 16.0°/min (in omega). The octant measured was +h, +k, ±l for all the complexes. Pertinent crystallographic parameters are summarized in table 1.

Three standard reflections were monitored for every 150 measurements. Over the course of the data collection, the standards decreased by 0.7% for 2', 11.8% for 3, 0.7% for 5, 8.2% for 7 and 6.6% for 9. A linear correction factor was applied to the data to account for the phenomena. An empirical absorption correction based on azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.58 to 1.00 for 2', from 0.61 to 1.00 for 3, from 0.89 to 1.00 for 5, from 0.61 to 1.00 for 7 and from 0.70 to 1.00 for 9. Reflection data were corrected for Lorentz and polarization effects.

The structures were solved by the direct method and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically except for the case of 7. The perchlorate ion in 7 was positioned at a special equivalent position in the crystal lattice (occupancy factor 0.5) and its oxygens were disordered. The refinement of 7 was performed by assuming the perchlorate ion as a rigid ball. Hydrogen atoms were included in the structure factor calculation but were not refined. Neutral atom scattering factors were taken from Cromer and Waber. Anomalous dispersion effects were included in the final calculations; the values for Δf' and Δf'' were taken from reference [10] and those for the mass-attenuation coefficients from reference [11]. Computations were carried out on an IRIS Indigo computer using the TEXSAN crystallographic software package of the Molecular Structure Corporation.
## Table 1. Crystallographic data of [NiCu(L\textsubscript{2,5})(AcO)]ClO\textsubscript{4} \cdot MeOH (2), [ZnCu(L\textsubscript{2,5})(AcO)]ClO\textsubscript{4} (3), [NiCu(L\textsubscript{2,3})(AcO)]ClO\textsubscript{4} (5), [CoCu(L\textsubscript{2,4})(AcO)(dmf)]ClO\textsubscript{4} (7) and [ZnCu(L\textsubscript{2,4})(AcO)]ClO\textsubscript{4} (9).

| Complex | formula | f.w. | Crystal colour | Crystal size/mm\textsuperscript{3} | Crystal system | Space group | a/Å | b/Å | c/Å | α/deg | β/deg | γ/deg | V/Å\textsuperscript{3} | Z | D\textsubscript{calc}/g cm\textsuperscript{-3} | r(Mo-K\textsubscript{α})/cm\textsuperscript{-1} | No. of reflections | F(000) | R = ∑[|F\textsubscript{obs}|-|F\textsubscript{calc}|]/∑|F\textsubscript{calc}| | w = 1/σ(|F\textsubscript{calc}|)\textsuperscript{2} | R\textsubscript{w} = ∑w(|F\textsubscript{obs}|-|F\textsubscript{calc}|)/∑w|F\textsubscript{calc}|\textsuperscript{2} |
|---------|---------|------|----------------|-------------------------|---------------|-------------|------|------|------|-------|-------|-------|----------------|---|-------------------|----------------|----------------|--------|-------------------|----------------|------------------|---------|
| 2       | C\textsubscript{2}H\textsubscript{13}Br\textsubscript{2}ClCuN\textsubscript{4}NiO\textsubscript{3} | 849.05 | Dark green     | 0.40 × 0.25 × 0.20     | Triclinic     | P1 (#1)     | 7.962 | 13.797(3) | 15.060(4) | 109.23(2) | 105.69(2) | 89.60(2) | 1497(1)          | 2 | 1.882             | 41.62          | 5144             | 850    | 0.052             | 0.040             |
| 3       | C\textsubscript{2}H\textsubscript{12}Br\textsubscript{2}ClCuN\textsubscript{4}ZnO\textsubscript{3} | 823.69 | Purple brown   | 0.60 × 0.60 × 0.60     | Triclinic     | P1 (#2)     | 11.526(2) | 14.815(3) | 9.039(2)  | 97.98(2)  | 104.23(2) | 77.03(1) | 1452.3(5)        | 4 | 1.883             | 44.63          | 4805             | 818    | 0.072             | 0.097             |
| 5       | C\textsubscript{2}H\textsubscript{12}Br\textsubscript{2}ClCuN\textsubscript{4}NiO\textsubscript{3} | 831.03 | Green          | 0.30 × 0.30 × 0.18     | Monoclinic    | P\textsubscript{2}1\textsubscript{1} (#14) | 9.301(4) | 18.83(4)  | 17.274(3) | 102.48(6) | 98.55(3)  | 81.18(6) | 2992(1)          | 2 | 1.844             | 41.61          | 4805             | 1660   | 0.039             | 0.025             |
| 7       | C\textsubscript{2}H\textsubscript{13}Br\textsubscript{2}ClCoCuN\textsubscript{5}O\textsubscript{9} | 918.39 | Green          | 0.25 × 0.25 × 0.25     | Triclinic     | P1 (#2)     | 10.390(9) | 20.32(1)  | 9.496(8)  | 107.26(6) | 97.25(3)  | 3206(1) | 1860(2)          | 2 | 1.639             | 32.98          | 4805             | 924    | 0.101             | 0.077             |
| 9       | C\textsubscript{2}H\textsubscript{13}Br\textsubscript{2}ClCuN\textsubscript{4}ZnO\textsubscript{3} | 851.74 | Green          | 0.30 × 0.30 × 0.25     | Monoclinic    | P\textsubscript{2}1\textsubscript{1} (#14) | 9.658(2) | 19.493(5) | 17.225(7) | 97.84(2)  | 97.18(6)  | 1.764          | 1700           | 0.068             | 40.46             |

\(^aR = \sum||F\textsubscript{obs}|-|F\textsubscript{calc}||/\sum|F\textsubscript{calc}|, ^bR\textsubscript{w} = \sum(w(|F\textsubscript{obs}|-|F\textsubscript{calc}|)/\sum|F\textsubscript{calc}|)\textsuperscript{2}, ^cw = 1/\sigma(|F\textsubscript{calc}|)\textsuperscript{2}\)
3. Results and discussion

3.1 Synthesis

A series of the (acetato)M$^{II}$Cu$^{II}$ complexes, $[MCu(L_{m;n})(AcO)]ClO_4$ ((L$_{m;n}$)$_2^-$ = (L$_2$)$_2^-$ $\sim$ (L$_2$)$_4^-$; 1 $\sim$ 9), were obtained when the mononuclear Cu$^{II}$ precursors $[Cu(L_{2,2})]$ $\sim$ $[Cu(L_{2,3})]$ were treated with a M$^{II}$ perchlorate salt and a M$^{II}$ acetate salt in methanol at the refluxing temperature (method I). In our attempt to prepare the (acetato)Cu$^{II}$M$^{II}$ complexes by method II, on the other hand, only $[CuZn(L_{2,3})(AcO)]ClO_4$ (10) could be obtained in a pure form. In other cases, the resulting products contained a large copper content relative to the M content. FAB mass spectrometric studies indicated the presence of $[CuCu(L_{m;n})(AcO)]^+$ as the main species along with a small amount of $[CuM(L_{m;n})(AcO)]^+$. It appears that the (acetato)Cu$^{II}$M$^{II}$ complexes, except for 10, are thermodynamically unstable to cause a scrambling of metal ions.

3.2 Crystal structures

X-ray crystallographic studies were carried out for 2', 3, 5, 7 and 9 to see the site selectivity of metal ions and their core structures. $[NiCu(L_{2,3})(AcO)]ClO_4\cdot MeOH$ (2'). An ORTEP$^{13}$ view of the cationic part of 2' is shown in figure 1 together with the numbering scheme. Selected bond distances and angles are summarized in table 2.

Figure 1. An ORTEP view of $[NiCu(L_{2,3})(AcO)]ClO_4\cdot MeOH$ (2') with the atom numbering scheme.
Table 2. Selected bond distances and angles for \([\text{NiCu(L}^{2-2}](\text{AcO})\text{ClO}_4 \cdot \text{MeOH (2')}.\]

**Bond distances (Å)**

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**Bond angles (deg)**

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**Dihedral angles (deg)**

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The cation has a heterodinuclear core with the Ni\(^{II}\) in the aminic site and the Cu\(^{II}\) in the iminic site with the Ni–Cu intermetallic separation of 2.972(1) Å. The acetate group coordinates to the Ni\(^{II}\) as a chelating ligand to provide a distorted six-coordinate geometry about the metal; the methanol molecule is free from coordination and is captured in the crystal lattice. The Ni-to-donor bond distances range from 2.058(5) to 2.120(4) Å. The Ni is displaced by 0.721 Å from the basal N(amine)\(_2\)O\(_2\) least-squares plane toward the acetate ion. The geometry around the Cu\(^{II}\) is essentially planar with the Cu-to-donor bond distances ranging from 1.890(4) to 1.921(4) Å. The Ni-O1-Cu and Ni-O2-Cu angles are 95.0(1)° and 97.1° respectively. The N(amine)\(_2\)O\(_2\) least-squares plane and the N(imine)\(_2\)O\(_2\) least-squares plane are bent at the O1–O2 edge with a dihedral angle of 11.96°.

The asymmetric nitrogens N1 and N2 have the same confirmation (S and S), and the two methyl groups attached to the nitrogens are situated trans to each other and axially oriented with respect to the mean N(amine)\(_2\)O\(_2\) plane. In the M\(^{II}\)Cu\(^{II}\) complexes of (L\(_{2-2}\))^\(2-\) and (L\(_{2-3}\))^\(2-\) so far characterized, the M\(^{II}\) assumes a five-coordinate geometry where the aminic nitrogens have different configurations (R and S) with the cis arrangement of the two methyl groups with respect to the en-chelate \(^2\)-4.

[ZnCu(L\(_{2-2}\))(AcO)]ClO\(_4\) (3). An ORTEP drawing of the cationic part of 3 is shown in figure 2 together with the numbering scheme. Selected bond distances and angles are given in table 3.
Figure 2. An ORTEP view of [ZnCu(L^2:2)(AcO)]ClO_4 (3) with the atom numbering scheme.

Table 3. Selected bond distances and angles for [ZnCu(L^2:2)(AcO)]ClO_4 (3).

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The cation has a dinuclear core with the Zn$^{II}$ in the aminic site and the Cu$^{II}$ in the iminic site. The acetate ion bridges the Zn$^{II}$ and Cu$^{II}$ ions to afford a five-coordinate environment for the two metal ions. The Zn–Cu intermetallic separation is 2.872(1) Å. The geometry about the Zn can be regarded as a distorted square-pyramid with the N$_2$O$_2$ donor atoms on the base and the acetate oxygen at the apex. The geometric discrimination factor $t^{14}$ between square-pyramid ($t = 0$) and trigonal-bipyramid ($t = 1$) is 0.16. The Zn is displaced by 0.66 Å from the basal least-squares plane toward the acetate oxygen. The basal Zn–N and Zn–O bond distances range from 2.078(4) to 2.122(5) Å. The axial Zn–O3 (acetate) bond distance is shorter (1.924(5) Å). The geometry about the Cu$^{II}$ is also square-pyramidal ($t = 0.01$). The basal Cu–N and Cu–O bond distances (1.894(4) ~ 1.911(6) Å) are significantly short, relative to the basal Zn–N and Zn–O bond distances. The axial Cu–O4(acetate) bond is elongated (2.493(5) Å) owing to the Jahn-Teller effect for the d$^9$ electronic configuration. The Cu is displaced by 0.007 Å from the basal least-squares plane toward O4. The N(amine)$_2$O$_2$ and the N(imine)$_2$O$_2$ least-squares planes are bent at the O1–O2 edge with a dihedral angle of 24.93°. The asymmetric nitrogens N1 and N2 have different configurations ($S$ and $R$); the two methyl substituents on the aminic nitrogens are situated cis to each other and are axially oriented with respect to the mean N(amine)$_2$O$_2$ plane.

$[\text{NiCu(L}^{2+})(\text{AcO})]\text{ClO}_4$ (5). An ORTEP drawing of the cationic part of 5 is shown in figure 3 together with the numbering scheme. Selected bond distances and angles are given in table 4.

The X-ray crystallography demonstrates a dinuclear core with the Ni$^{II}$ in the aminic site and the Cu$^{II}$ in the iminic site. The acetate group bridges the two metal ions in the Ni–Cu intermetallic separation of 2.935(1) Å. The geometry about the Ni can be regarded...
Table 4. Selected bond distances and angles for [NiCu(L²⁻³)(AcO)]ClO₄ (5).

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Dihedral angles (deg)

| O(1)O(2)N(1)N(2)–O(1)O(2)N(3)N(4) | 15.77    |

as a square-pyramid with the acetate oxygen (O3) at the apex (t: 0.152). The basal Ni–N and Ni–O bond distances fall in the range of 1.963(3) – 2.054(4) Å. The axial Ni–O3 bond is shorter (1.962(3) Å). The Ni is displaced by 0.407 Å from the basal least-squares plane towards the axial site. The geometry about the Cu is square-pyramidal with the acetate oxygen O4 at the apex (t: 0.013). The basal Cu–N and Cu–O bond distances range from 1.936(3) to 1.978(3) Å. The axial Cu–O4 bond distance is elongated (2.05(4) Å). The displacement of the Cu from the basal N₃O₂ least-squares plane toward O4 is 0.170 Å. The bending between the N(amine)₂O₂ and N(imine)₂O₂ least-squares planes at the O1–O2 edge is 15.77º. The asymmetric nitrogens N1 and N2 have different configurations (S and R); the two methyl substituents on the aminic nitrogens are situated cis to each other and are axially oriented with respect to the mean N(amine)₂O₂ plane.

[CoCu(L²⁻³)(AcO)(DMF)]ClO₄ (7). An ORTEP drawing of the cationic part of 7 is shown in figure 4. Selected bond distances and angles are given in table 5.

The dinuclear core has the CoⅡ in the aminic site and the CuⅡ in the iminic site and the acetate group bridges the metal ions in the Co–Cu separation of 3.023(3) Å. The O1–N1–N2–O2 entity assumes a non-planar configuration providing a cis-b octahedral geometry about the Co with the acetate oxygen O3 and the DMF oxygen O5 in cis positions. The Co–N and Co–O bond distances range from 2.005(8) to 2.17(1) Å.

The CuⅡ assumes a distorted trigonal-bipyramidal geometry with O1 and N3 of the macrocycle at the axial sites and with O2 and N4 of the macrocycle and the O4 of the bridging acetate group on the equatorial base. The axial Cu–O1 and Cu–N3 bond distances are 1.929(9) and 1.97(1) Å respectively and the O1–Cu–N3 angle is 169.1(5)º. The equatorial Cu–O2, Cu–N4 and Cu–O4 bond distances are longer (2.11(1), 1.98(1)
Figure 4. An ORTEP view of [CoCu(L\textsuperscript{2,4})(AcO)(DMF)]\textsubscript{4}ClO\textsubscript{4} (7) with the atom numbering scheme.

Table 5. Selected bond distances and angles for [CoCu(L\textsuperscript{2,4})(AcO)(DMF)]\textsubscript{4}ClO\textsubscript{4} (7).

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and 2.06 Å, respectively). The equatorial plane shows a large distortion from the triangle; the O2–Cu–N4, O2–Cu–O4 and N4–Cu–O4 angles are 130.9(5), 93.6(4) and 135.4(5)º respectively. The bridging phenolic oxygen O2 shows a distortion to tetrahedron as seen in the sum of the angles of Co–O2–Cu, Co–O2–C13 and Cu–O2–C13 (345.2º). The asymmetric amino nitrogens N1 and N2 have the same configuration (R), and the two methyl groups attached to the nitrogens are situated trans with respect to the enchelate ring.

[ZnCu(L2;4)(AcO)]ClO4 (9). An ORTEP drawing of the cationic part of 9 is shown in figure 5 together with the numbering scheme. Selected bond distances and angles are given in table 6.

The dinuclear core has the ZnII in the aminic site and the CuII in the iminic site. The acetate group bridges the two metal ions in the Cu–Zn intermetallic separation of 2.980(2) Å. The geometry about the Zn is square-pyramidal with the N2O2 donor atoms on the base and the acetate oxygen O3 at the apex (t: 0.14). The axial Zn–O3 bond distance (1.912(6) Å) is short, relative to the basal bond distances (2.107(7) – 2.086(5) Å). The displacement of the Zn from the basal least-squares plane is 0.621 Å. The geometry about the Cu in the iminic site is also square-pyramidal with an acetate oxygen O4 at the apex (t: 0.03). The basal bond distances fall in the range of 1.937(5) – 2.004(7) Å. The axial Cu–O4 bond distance is elongated (2.270(7) Å). The Cu is

![Figure 5. An ORTEP view of [ZnCu(L2;4)(AcO)]ClO4 (9) with the atom numbering scheme.](image-url)
Table 6. Selected bond distances and angles for [ZnCu(L2;4)(AcO)ClO4 (9)].

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Displaced by 0.163 Å from the basal least-squares plane toward O4. The N(amine)2O2 and the N(imine)2O2 least-squares planes are bent at the O1–O2 edge with a dihedral angle of 10.0º. The asymmetric amino nitrogens N1 and N2 have different configurations (S and R), and the two methyl substituents on the aminic nitrogens are situated cis to each other and are axially oriented with respect to the mean N(amine)2O2 plane.

[CuZn(L2;3)(AcO)]ClO4 (10). The crystal structure of this complex was previously determined. It has the CuII in the aminic site and the ZnII in the iminic site, bridged by an acetate group in the syn: syn mode. The result demonstrates the migration of the CuII from the iminic site to aminic site in the transmetallation process. The assignment of the positions of the metal ions is based on the relative metal-N and M–O bond distances and the geometric features of the two chromophores. The {CuN(amine)2O2} site assumes a square-pyramidal geometry. The basal Cu–N and Cu–O bond distances range from 1.973(6) to 2.026(8) Å, and the axial Cu–O(acetate) bond (2.093(7) Å) is slightly elongated owing to the Jahn-Teller effect. The {ZnN(imine)2O2} site also assumes a square-pyramidal geometry. The basal Zn–N and Zn–O bond distances (2.029(8) – 2.061(6) Å) are longer than the corresponding bond distances of {CuN(amine)2O2}. Instead, the axial Zn–O(acetate) distance is short (2.018(6) Å).

3.3 Kinetic and thermodynamic macrocyclic effect

From the above crystallographic studies, it is evident that (L2;2)2–, (L2;3)2– and (L2;4)2– show a site selectivity of metal ions, providing the (acetato)MIICuII complexes (M = Co, Ni, Zn). The acetate group acts as a bidentate chelating ligand to the MII or a bridging ligand between the CuII and MII ions. In both the chelating and bridging functions, the acetate group probably plays an important role in stabilizing the MIICuII core.
It is interesting to see the core structures of the complexes with respect to the MII in the aminic site and the ring size of the macrocyclic ligands. In the NiII-CuII complex 2 of (L2;2)2–, the NiII cannot reside within the aminic cavity and is largely displaced from the N(amino)2O2 least-squares plane (0.721 Å). The bidentate chelation of the acetate ion to the NiII is preferred in this case. In the ZnII-CuII complex 3 of (L2;2)2–, the acetate-bridged core is formed because the Zn displacement from the N(amino)2O2 least-squares plane is smaller (0.66 Å) and ZnII prefers five-coordination to six-coordination. In the NiII-CuII complex 5 of (L2;3)2–, the elongation of the lateral chain in the iminic site gives rise to a considerable adaptability for the aminic site to accommodate the NiII ion. The displacement of the Ni in this complex is small (0.407 Å) so that the acetate-bridged core is preferred. The macrocycle (L2;4)2– has a higher adaptability for complexation due to further elongation in the lateral chain in the iminic site. In the CoII-CuII complex 7, the N2O2 donor atoms in the aminic site are arranged in a non-polar manner, providing a cis-b six-coordination about the CoII with an acetate oxygen and a DMF oxygen in cis positions. This accompanies a significant distortion about the CuII in the iminic site as previously discussed.

Of particular interest is the Cu migration in the transmetallation to convert [PbCu(L2;3)](ClO4)2 into [CuM(L2;3)(AcO)]ClO4. Previously, this site-selectivity for metal ions was explained by the relative sizes of the metal ions and the metal-binding cavities (thermodynamic macrocyclic effect) 3. However, the present study strongly suggests that the formation of [CuM(L2;3)(AcO)]ClO4 is kinetically controlled and is known as the kinetic macrocyclic effect. A mechanistic scheme for the Cu migration is discussed here.

A mechanism involving the dissociation of PbII prior to the attack of MII is ruled out because this may provide the (acetato)MII-CuII form. Instead, the transmetallation may occur through an association mechanism. Based on the X-ray structure analysis for a PbII-CuII complex of (L2;2)2–3 the aminic and iminic least-squares planes are bent at the O–O edge with a dihedral angle of 14.87°. This means that the bridging phenolic oxygens have sp2 hybridization character. Thus, the PbII-CuII complex can bind an MII ion through the phenolic oxygens to form a di((phenoxo)PbII-CuII-MII complex (scheme 2). Two paths are considered for the transmetallation. Path A is a concerted mechanism involving the approach of the M to the iminic site, the migration of the Cu to the aminic site and the release of the Pb from the aminic site. This can be performed without the cleavage of the O–Cu and O–M bonds, by rotating the O–Cu and O–M linkages with respect to the O–O axis (see scheme 2). When the M approaches the aminic site to eject the Pb (path B), the MII-CuII core may be formed. This is not the case with the transmetallation observed. In fact, path B can be ruled out because the [MN(amino)2O2] entity assumes, at least transiently, an energetically unfavourable configuration with a Cu displacement toward the ethylene chain side. It must be noted that in all the MII-CuII complexes so far characterized, the [MN(amino)2O2] entity has the M displacement toward the N-methyl substituent side. Thus, path A can explain the result observed. Such a Cu migration probably occurs in other transmetallations of [PbCu(Lm;n)](ClO4)2 to form (acetato)CuII-MII complexes. The latter are however thermodynamically unstable and are not isolated.

3.4 Physicochemical properties

3.4a Infrared spectra: All the complexes show the ν(C=N) vibration of azomethine group at 1632 ~ 1618 cm⁻¹. Complex 2 shows the νs(COO) and νas(COO) vibrations of
the acetate group at 1583 and 1445 cm$^{-1}$ respectively. The separation between the two vibrations is smaller than 200 cm$^{-1}$, in accord with the chelating mode of the acetate group$^{15}$. Similarly, the separation between the $\nu_{as}(\text{COO})$ and $\nu(\text{COO})$ vibrations for the other complexes is less than 200 cm$^{-1}$, in agreement with the bridging function of the acetate group proved for $3$, $5$, $7$ and $9$. The $\nu(\text{C}=\text{O})$ mode of the perchlorate group at $1100 \sim 1080$ cm$^{-1}$ shows no appreciable splitting. Complex $7$ shows an intense band at $1652$ cm$^{-1}$ that can be attributed to the $\nu(\text{C}=\text{O})$ vibration of the coordinated DMF molecule. Complex $8$ has two IR bands at $1674$ and $1652$ cm$^{-1}$ attributable to the $\nu(\text{C}=\text{O})$ modes of DMF.

It must be emphasized that isomeric $[\text{ZnCu}(\text{L}^{2-3})(\text{AcO})]\text{ClO}_4$ ($6$) and $[\text{CuZn}(\text{L}^{2-3})\text{(AcO)})\text{ClO}_4$ ($10$) are differentiated by IR spectra. For example, the former shows the $\nu_{as}(\text{COO})$ and $\nu_s(\text{COO})$ vibrations at $1594$ and $1453$ cm$^{-1}$ respectively, whereas the latter shows the corresponding vibrations at $1575$ and $1450$ cm$^{-1}$ respectively.

3.4b Electronic spectra: Absorption spectra of $1 \sim 9$ in DMSO are characterized by an intense absorption in the near ultraviolet region and a weak broad absorption in the visible region. The former band at $352 \sim 367$ nm is assigned to the intraligand $\pi-\pi^*$ band associated with the azomethine linkage $^{16,17}$ and the latter band to a superposition of Cu$^{II} d-d$ transition bands. The superposed $d-d$ bond is located at $542 \sim 555$ nm for $1 \sim 3$ of $(\text{L}^{2-3})^2$, at $617 \sim 656$ nm for $4 \sim 6$ of $(\text{L}^{2-3})^2$, and at $720 \sim 740$ for $7 \sim 9$ of $(\text{L}^{2-4})^2$. This is in accord with the decreasing ligand field strength of the $\{\text{CuN(imine)}_2\text{O}_2\}$ chromophore with the elongation in the lateral chain $^{18-20}$. The $d-d$ transition bands due to the Co$^{II}$ or Ni$^{II}$ ion in $1$, $2$, $4$, $5$, $7$ and $8$ are not resolved.

Isomeric $6$ and $10$ are differentiated by visible spectra. The former has the superposed $d-d$ band of Cu$^{II}$ at $617$ nm ($\epsilon$ $93$ M$^{-1}$ cm$^{-1}$), whereas the latter has the corresponding band maximum at $624$ nm ($\epsilon$ $103$ M$^{-1}$ cm$^{-1}$) $^{3}$.

3.4c Cyclic voltammetry: The electrochemical properties of $1 \sim 9$ were studied by cyclic voltammetry. Typical examples of cyclic voltammograms are given in figure 6, and the numerical data are summarized in table 7.
Figure 6. Cyclic voltammograms for 4, 5 and 6. Conditions for measurements are given in table 7.

Table 7. Electrochemical data for 1–10.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>$E_{pa}$</th>
<th>$E_{pc}$</th>
<th>$E_{1/2}(\Delta E)$</th>
<th>$E_{pa}$</th>
<th>$E_{pc}$</th>
<th>$E_{1/2}(\Delta E)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[CoCu(L$_{2;2}$(AcO))$_2^+$ (1)</td>
<td>–1.08</td>
<td>–1.19</td>
<td>–1.14 (0.11)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[NiCu(L$_{2;2}$(AcO))$_2^+$ (2)</td>
<td>–1.10</td>
<td>–1.21</td>
<td>–1.16 (0.11)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[ZnCu(L$_{2;2}$(AcO))$_2^+$ (3)</td>
<td>–1.26</td>
<td>–1.09</td>
<td>–1.18 (0.17)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[CoCu(L$_{2;3}$(AcO))$_2^+$ (4)</td>
<td>–0.88</td>
<td>–0.96</td>
<td>–0.92 (0.08)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[NiCu(L$_{2;3}$(AcO))$_2^+$ (5)</td>
<td>–0.92</td>
<td>–1.01</td>
<td>–0.95 (0.09)</td>
<td>–1.61</td>
<td>–1.71</td>
<td>–1.66 (0.10)</td>
</tr>
<tr>
<td>[ZnCu(L$_{2;3}$(AcO))$_2^+$ (6)</td>
<td>–0.95</td>
<td>–1.03</td>
<td>–0.99 (0.08)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[CoCu(L$_{2;4}$(AcO))$_2^+$ (7)</td>
<td>–0.98</td>
<td>–1.07</td>
<td>–1.02 (0.09)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[NiCu(L$_{2;4}$(AcO))$_2^+$ (8)</td>
<td>–0.97</td>
<td>–1.08</td>
<td>–1.03 (0.11)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[ZnCu(L$_{2;4}$(AcO))$_2^+$ (9)</td>
<td>–0.91</td>
<td>–1.00</td>
<td>–0.96 (0.09)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[CuZn(L$_{2;3}$(AcO))$_2^+$ (10)</td>
<td>–0.77</td>
<td>–0.85</td>
<td>–0.81 (0.08)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Unit: V vs Ag/Ag$. Conditions: Glassy-carbon working, Pt auxiliary, and Ag/Ag$^+$ (TBAP/MeCN) reference electrodes. Supporting electrolyte: TBAP. Scan rate: 100 mV/s. Concentration: Complex (1×10$^{-3}$ M), TBAP (1×10$^{-1}$ M) in DMSO. $\Delta E = |E_{pa} - E_{pc}|$

In the sweep to negative potential, the complexes show a reversible or quasi-reversible couple at –1.05 ± 0.13 V (vs Ag/Ag$^+$) that is attributable to the Cu$^{II}$/Cu$^{I}$ process in the iminic site$^{21}$. Complex 5 (NiCu) with (L$_{2;3}$)$_2^-$ showed another reduction couple at –1.66 V that is attributed to the Ni$^{II}$/Ni$^{I}$ reduction in the aminic site. For the other complexes, the reduction of the M$^{II}$ was not observed in the available potential.
It must be emphasized that isomeric 6 and 10 differ in electrochemical property when compared under the same conditions. The former has the Cu^{II}/Cu^{I} couple at –0.99 V, whereas the latter has the corresponding couple at –0.81 V. The high Cu^{II}/Cu^{I} potential for the latter implies that the aminic site is more flexible to provide a non-planar environment preferred for Cu^{I}.22.

3.4d Magnetic properties: The Zn^{II}Cu^{II} complexes (3, 6 and 9) have a magnetic moment common for one unpaired electron (1.85, 1.86 and 1.83 μB, respectively). The magnetic moment of the Cu^{II}Zn^{II} complex 10 is reported to be 1.78 μB. The magnetic moments of the Co^{II}Cu^{II} complexes (1, 4 and 7) and the Ni^{II}Cu^{II} complexes (2, 5 and 8) are temperature-dependent, suggesting an antiferromagnetic spin-exchange interaction within each dinuclear unit. The cM_T vs T plots for 1 and 2 are illustrated in figure 7.

The cM_T value for 1 at room temperature is 2.68 K cm^3 mol^{-1} (4.63 μB) that decreased with decreasing temperature to 0.27 cm^3 mol^{-1} (1.48 μB) at 2.0 K. The moment at 2.0 K is lower than the spin-only value for S_T = 1 arising from the spin-coupling between Cu^{II} (S =1/2) and Co^{II} (S = 3/2). This fact means the operation of secondary contribution(s) such as orbital effect and/or zero-field splitting of Co^{II}.

Magnetic simulations for 1 were carried out by the magnetic susceptibility equation for the (SCo = 3/2) – (SCu = 1/2) system,

\[ c_M = \frac{N b^2}{k (T + q)} \left[ \frac{2 g_1^2 + 2 g_1^2 \exp(-4 J/kT)}{5 + 3 \exp(-4 J/kT)} \right] + N a, \]

where N is Avogadro’s number, b is the Bohr magneton, k is the Boltzmann constant, J is the exchange integral, T is the absolute temperature, q is the correction term for the

Figure 7. cM_T vs T curves for 1 (trace a) and 2 (trace b). The solid curves are drawn based on the magnetic susceptibility expressions using the magnetic parameters given in the text.
secondary contribution(s), \( Na \) is the temperature-independent paramagnetism, and \( g_1 \) and \( g_2 \) are \( g \) factors associated with the total spin-states \( S_T = 1 \) and \( 2 \), respectively. The \( g \) factors are expressed using local \( g \) values (\( g_{Co} \) and \( g_{Cu} \)) as follows:

\[
g_1 = \frac{5g_{Co} - g_{Cu}}{4} \quad \text{and} \quad g_2 = \frac{3g_{Co} + g_{Cu}}{4}.
\]

A good simulation was obtained as indicated by the solid line in figure 7, using the magnetic parameters \( J = -10.0 \, \text{cm}^{-1}, \, g_{Co} = 2.20, \, g_{Cu} = 2.10, \, q = -5.0 \, \text{K}, \, Na = -300 \, \text{\textmu} \text{m}^{-1}. \)

Similar magnetic simulations for 4 and 7 gave a negative exchange integral of \(-20.0 \, \text{cm}^{-1}\) and \(-9.0 \, \text{cm}^{-1}\), respectively. It is notable that the \(-J\) value for 7 is small relative to the values for 1 and 4. The weak antiferromagnetic interaction for 7 is probably related to the distorted configuration about the CuII as previously discussed (see figure 4).

The \( c_M T \) value for 2 at room temperature is \( 1.60 \, \text{K} \, \text{cm}^{-1} \, \text{mol}^{-1} \) (= 3.46 \( r\text{g} \)) that decreased with decreasing temperature to \( 0.45 \, \text{K} \, \text{cm}^{-1} \, \text{mol}^{-1} \) at 2.0 K (figure 7, trace b). The magnetic moment at 2.0 K corresponds to the value for \( S_T = 1/2 \) resulting from spin-coupling between CuII (\( S = 1/2 \)) and NiII (\( S = 1 \)). Magnetic simulations were carried out using the magnetic susceptibility equation for the \((S_{Ni} = 1) - (S_{Cu} = 1/2)\) system,

\[
c_M = \left\{ \frac{Ng_{1/2}^2 + g_{3/2}^2 \exp(-3J/kT)}{2 + \exp(-3J/kT)} \right\} + Na,
\]

where, \( g_{1/2} \) and \( g_{3/2} \) indicate the \( g \) factors associated with the total spin-states \( S_T = 1/2 \) and \( 3/2 \), respectively, and other symbols have the same meanings as equation (1). The \( g \) factors are expressed using local \( g \) values as \( g_{1/2} = (4g_{Ni} - g_{Cu})/3 \) and \( g_{3/2} = (2g_{Ni} + g_{Cu})/3 \). The cryomagnetic property of 2 could be well reproduced by (2) as shown in figure 7, using the magnetic parameters of \( J = -18 \, \text{cm}^{-1}, \, g_{Ni} = 2.17, \, g_{Cu} = 2.10 \) and \( Na = 280 \, \text{\textmu} \text{m}^{-1} \). Similarly, the exchange integrals for 5 and 8 were evaluated to be \(-25 \) and \(-33 \, \text{cm}^{-1}\), respectively. Complex 2 shows a weak antiferromagnetic interaction compared with 5. This can be explained by the large Ni displacement from the basal least-squares plane in 2 (0.721 Å) compared with that for 5 (0.407 Å).

4. Conclusions

A series of the (acetato)MII\textsuperscript{II}Cu\textsuperscript{II} complexes, \([MCu(L_{m;n})(AcO)]ClO_4 (L_{2;2} \sim L_{2;4})\), were obtained from the mononuclear Cu\textsuperscript{II} precursors, \([Cu(L_{m;n})] \), and the site selectivity of metal ions was demonstrated by X-ray crystallography. The isomeric (acetato)Cu\textsuperscript{III}Cu\textsuperscript{II} complexes, \([CuM(L_{m;n})(AcO)]ClO_4 \), could be prepared from the Pb\textsuperscript{II}Cu\textsuperscript{II} precursors by taking advantage of the ‘kinetic macrocyclic effect’, but they were unstable to cause a scrambling of metal ions except for the case of \([ZnCu(L_{2;3})(AcO)]ClO_4 \). The coordination-position isomers, \([ZnCu(L_{2;3})(AcO)]ClO_4 \) and \([CuZn(L_{2;3})(AcO)]ClO_4 \), were differentiated by different physicochemical properties.

The core structures of \([MCu(L_{m;n})(AcO)]ClO_4 \) were studied in view of the ring-size of the macrocycle and the nature of the M\textsuperscript{II} ion. In \([NiCu(L_{2;2})(AcO)]ClO_4 \cdot \text{MeOH} \), the Ni is largely displaced from the N(amine)\textsubscript{2}O\textsubscript{2} least-squares plane (0.721 Å) and assumes a distorted six-coordination with a chelating acetate group. In \([ZnCu(L_{2;2})(AcO)]ClO_4 \), the acetate group bridges the metal ions because the Zn assumes five-coordination and the Zn displacement is smaller (0.66 Å). The elongation of the lateral chain in the iminic site gives rise to a considerable adaptability for complexation not only for the iminic site but also for the aminic site. In \([NiCu(L_{2;3})(AcO)]ClO_4 \), the displacement of the Ni becomes small (0.407 Å) to allow an acetate bridge between the metal ions. The macrocycle
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... has a higher adaptability for complexation as demonstrated for [CoCu(L\textsuperscript{2,4})(AcO)(DMF)]ClO\textsubscript{4}, where the N(amine)\textsubscript{2}O\textsubscript{2} moiety adopts a non-planar coordination mode providing a cis-\textit{b}octahedral configuration about the Co. On the other hand, [ZnCu(L\textsuperscript{2,4})(AcO)]ClO\textsubscript{4} has a (\textit{m}-acetato)Zn\textsuperscript{II}Cu\textsuperscript{II} core similar to that of [NiCu(L\textsuperscript{2,3})(AcO)]ClO\textsubscript{4} because Zn\textsuperscript{II} prefers five-coordination.

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