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Self-Assembly of Double and Triple Helices Controlled by Metal Ion Stereochemical Preference

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Abstract: The syntheses of the dinucleating bisbidentate ligand bis[5-(1-methyl-2-(6′-methyl-2′-pyridyl)benzimidazolyl)]methane (bismbmp, **3**) and its mononuclear analogue 6-methyl-2-(1-methylbenzimidazol-2-yl)pyridine (mbmp, **1**) are reported. The ligand mbmp (**1**) reacts with copper(I) to give $[Cu(mbmp)_2]ClO_4$ whose crystal structure ($CuC_{28}H_{26}N_6ClO_4$, z = 7.877 (1) Å, b = 13.810 (2) Å, c = 25.090 (7) Å, β = 95.29 (1)°, monoclinic, $P2_1/c$, Z = 4) shows a mononuclear structure with Cu(I) pseudotetrahedrally coordinated by two bidentate α,α'-diimine donor groups. The same chromophore is found for each copper ion in the dinuclear complex $[Cu_2(bismbmp)_2](ClO_4)_2{\cdot}H_2O$ obtained by reaction of copper(I) with bismbmp. Conductivity measurements and UV–visible spectra show that the dinuclear structure is maintained in solution in polar aprotic solvents, and ^{1}H-NMR measurements unambigously establish a double-helical structure for this complex. Mbmp reacts with cobalt(II) to give octahedral $[Co(mbmp)_3](ClO_4)_2{\cdot}CH_3CN$. The same coordination sphere is obtained when bismbmp reacts with cobalt(II), to give the triple-helical dinuclear complex $[Co_2(bismbmp)_3](ClO_4)_4{\cdot}3H_2O$, selectively produced by self-assembly. Spectroscopic results show that the triple-helical structure (D_3 symmetry) observed in the solid state is maintained in polar aprotic solvents. Spectrophotometric titrations show that bismbmp reacts with zinc(II) to give successively a triple-helical complex $[Zn_2(bismbmp)_3]^{4+}$, a double-helical complex $[Zn_2(bismbmp)_2]^{4+}$, and a third complex $[Zn_3(bismbmp)_2]^{6+}$. The influence of metal ion stereochemical preferences on the self-assembly of dinuclear helical complexes is discussed.

Introduction

A theme of considerable interest in supramolecular chemistry is the spontaneous and selective formation of organized supramolecular architectures through the use of self-assembling processes.[1,2] Particular interest has been shown in double-helical structures which may be generated by the complexation of two ligands twisted around metal ions lying on the helical axis. These supermolecules show some structural similarities to nucleic acids,[3] but complexation to the cations is now the binding force which connects the two strands. For nucleic acids, the organized structure arises from a well-defined arrangement of linear hydrogen bonds resulting from stereochemical matching between nucleotide bases,[4] while the equivalent requirement for self-assembly around metal ions is that the coordinating possibilities of the ligand should match the stereochemical preferences of the metal ion. Thus, the reaction of two oligobidentate ligands with cations favoring tetrahedral coordination can lead to double-helical structures. Lehn and his collaborators[5,6] have synthesized a series of oligobipyridyl ligands which form double-helicates containing as many as five Cu(I) ions, while Dietrich-Bücheker and Sauvage[7] have used the double-helical complexes formed by Cu(I) with two oligophenanthroline ligands as a precursor for the synthesis of the first molecular knot. Tetrahedral coordination of copper(I) is not an essential requirement for the formation of double-helical structures and we have recently reported[8] a double-helical complex of Cu(I) with a polydentate ligand which acts essentially as a bis(monodentate) ligand, giving a linear coordination of the two copper ions. Constable and his collaborators have shown how the reaction of a hexadentate polypyridyl ligand with metal ions showing preference for octahedral coordination leads to the expected formation of dinuclear double-helical complexes with Cd(II),[9] Mn(II), Fe(II), or Cu(II)[10] in which the polypyridyl acts as a bis(terdentate) ligand, while the reaction of this ligand with four-coordinate tetrahedral Cu(I) gives a trinuclear double-helical structure containing three copper(I) ions[10] where the ligand is tris(bidentate). Recently, the same workers[11] were able to synthesize a mixed-valence (Cu(I)/Cu(II)) dinuclear double-helical complex by using a quinquedentate ligand which acts as a bidentate ligand toward tetrahedral Cu(I) and as a terdentate donor toward pseudooctahedral Cu(II). However, not every combination of oligomultidentate ligands with metal ions will give helical structures,[6,12] and we showed in a previous paper that one secret of assembling helical structures lies in the design of a ligand with suitable spacer groups between the metal-binding termini.[13]

In this paper, we report the preparation of a new bis(bidentate) ligand bis[5-(1-methyl-2-(6′-methyl-2′-pyridyl)benzimidazolyl)]methane (bismbmp, **3**) and its mononuclear equivalent 6-methyl-2-(1-methyl-benzimidazol-2-yl)pyridine (mbmp, **1**). Bismbmp is particularly suitable as a dinucleating ligand since repulsion between the hydrogen atoms at positions 4 and 4′ of the benzimidazole moieties prevents the ligand from adopting a planar configuration and forces the two bidentate ligand groups apart. The chemistry of these ligands with copper(I), cobalt(II), and zinc(II) is presented, and it is shown that the stereochemical preference expressed by the metal ion in the mononuclear complexes is maintained in the dinuclear complexes, leading to the assembly of different dinuclear complexes including the novel triple-helical complex $[Co_2(bismbmp)_3]^{4+}$ whose crystal structure

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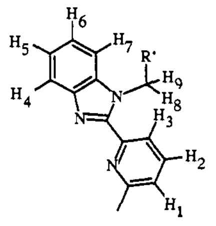
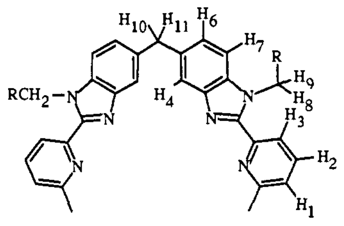


R'=H: mbmp (1)

R'=$(MeO)_2C_6H_3$: dmbbmp (2)



R=H: bismbmp (3)

R=CH_3: bisebmp (4)

has already been described in a preliminary communication.[14] Particular attention is paid to the stability of the dinuclear species in solution, since this point is crucial to the planned synthesis of more complicated systems.

Experimental Section

Materials. Solvents and starting materials were purchased from Fluka AG (Buchs, Switzerland) and used without further purification, unless otherwise stated. Silicagel (Merck 60, 0.040–0.063 mm) and aluminum oxide (Merck act. II–III, 0.063–0.200 mm) were used for preparative column chromatography.

Preparation of the Ligands. The ligand 6-methyl-2-(1-methylbenzimidazol-2-yl)pyridine (mbmp, **1**) was obtained by alkylation of 6-methyl-2-(benzimidazol-2-yl)pyridine[15] according to a previously published method,[16] and purified by column chromatography (Al_2O_3, CH_2Cl_2) and then crystallized from hexane (yield = 88%). Mp 97–99 °C. ^{1}H-NMR in $CDCl_3$: 2.63 (3 H, s), 4.27 (3 H, s), 7.19 (1 H, d, J^3 = 7.5 Hz), 7.3 (3 H, m), 7.72 (1 H, t, J^3 = 7.5 Hz), 7.8 (1 H, m), 8.16 (1 H, d, J^3 = 7.5 Hz). EI-MS: 223 (M^+). 6-Methyl-2-(1-(3,5-dimethoxybenzyl)benzimidazol-2-yl)pyridine (dmbbmp, **2**) was prepared using the same procedure described above with 3,5-dimethoxybenzyl bromide as the alkylating agent[13] (yield = 76%). Mp 108–110 °C. ^{1}H-NMR in $CDCl_3$: 2.55 (3 H, s), 3.66 (6 H, s), 6.08 (2 H, s), 6.29 (1 H, t, J^4 = 2 Hz), 6.36 (2 H, d, J^4 = 2 Hz), 7.18 (1 H, d, J^3 = 8 Hz), 7.3 (3 H, m), 7.50 (1 H, t, J^3 = 8 Hz), 7.8 (1 H, m), 8.20 (1 H, d, J^3 = 8 Hz). EI-MS: 359 (M^+). The ligand 6,6'-dimethyl-2,2'-bipyridine (dmbipy) was obtained according to a literature procedure[17] from 2-bromo-6-methylpyridine.[18]

Preparation of 3,3'-Dinitro-4,4'-bis(*N*-methylamino)diphenylmethane (5) and 3,3'-Dinitro-4,4'-bis(*N*-ethylamino)diphenylmethane (6).[19] 1-Nitro-2-(N-methylamino)benzene (5 g, 32.9 mmol) and 0.493 g (16.4 mmol) of paraformaldehyde were dissolved in concentrated hydrochloric acid (50 mL). After being stirred for 2 h at room temperature, the mixture was slowly heated to 120 °C and maintained at this temperature for 8 h. After being cooled, the solution was poured into water (300 mL) and neutralized with ammonia (pH = 10). The orange precipitate was filtered, washed with water, and recrystallized from ethanol to give 4.38 g (13.84 mmol; yield = 82%) of 3,3'-dinitro-4,4'-bis(*N*-methylamino)diphenylmethane (**5**) as red needles. Mp 187–188 °C. ^{1}H-NMR in DMSO-d_6: 2.90 (6 H, d, J^3 = 5 Hz), 3.80 (2 H, s), 6.92 (2 H, d, J^3 = 9 Hz), 7.40 (2 H, dd, J^3 = 9 Hz, J^4 = 2 Hz), 7.92 (2 H, d, J^4 = 2 Hz), 8.50 (2 H, q, J^3 = 5 Hz). EI-MS: 316 (M^+). The analogous 3,3'-dinitro-4,4'-bis(*N*-ethylamino)diphenylmethane (**6**) was obtained with the same procedure from 1-nitro-2-(*N*-ethylamino)benzene in good yield (81%). Mp 114–115 °C. ^{1}H-NMR in DMSO-d_6: 1.19 (6 H, t, J^3 = 7 Hz), 3.30 (4 H, m), 3.79 (2 H, s), 6.98 (2 H, d, J^3 = 9 Hz), 7.40 (2 H, dd, J^3 = 9 Hz, J^4 = 2 Hz), 7.92 (2 H, d, J^4 = 2 Hz), 8.05 (2 H, t, J^3 = 5 Hz). EI-MS: 344 (M^+).

Preparation of 3,3'-Diamino-4,4'-bis(*N*-methylamino)diphenyl methane (7) and 3,3'-Diamino-4,4'-bis(*N*-ethylamino)diphenylmethane (8).[19,20] 3,3'-Dinitro-4,4'-bis(*N*-methylamino)diphenylmethane (**5**) (10 g, 31.6 mmol) and 16.5 g (252 mmol) of zinc powder were suspended in 150 mL of boiling ethanol under nitrogen. Aqueous 5 M NaOH (20 mL) was slowly added until the solution turned pale yellow. The mixture was then refluxed for 1 h under nitrogen. The hot solution was filtered and the unreacted zinc was washed with four portions of hot ethanol (50 mL). The combined organic phases were evaporated to dryness and the crude residue was partitioned between dichloromethane (500 mL) and water (70 mL). The aqueous layer was separated and extracted with dichloromethane (2 × 100 mL) and the combined organic phases were dried over cellulose and evaporated. The crude product was recrystallized from chloroform to give 7.3 g (28.48 mmol; yield = 90%) of pale yellow 3,3'-diamino-4,4'-bis(*N*-methylamino)diphenylmethane (**7**) which darkened on exposure to air. Mp 105–107 °C. ^{1}H-NMR in $CDCl_3$: 2.84 (6 H, s), 3.20 (6 H, s), 3.74 (2 H, s), 6.52 (2 H, d, J^4 = 2 Hz), 6.60 (2 H, d, J^3 = 8 Hz), 6.70 (2 H, dd, J^3 = 8 Hz, J^4 = 2 Hz). EI-MS: 256 (M^+). The 3,3'-diamino-4,4'-bis(*N*-ethylamino)diphenylmethane (**8**) is prepared in 80% yield from **6** using the same procedure, but the crude product was purified by column chromatography (Silicagel, CH_2Cl_2/MeOH 97:3) to give **8** as a pale brown air-sensitive liquid. ^{1}H-NMR in $CDCl_3$: 1.28 (6 H, t, J^3 = 7 Hz), 3.05 (6 H, s), 3.11 (4 H, q, J^3 = 7 Hz), 3.71 (2 H, s), 6.50 (2 H, d, J^4 = 2 Hz), 6.58 (2 H, d, J^3 = 8 Hz), 6.65 (2 H, dd, J^3 = 8 Hz, J^4 = 2 Hz). EI-MS: 284 (M^+).

Preparation of Bis[5-(1-methyl-2-(6'-methyl-2'-pyridyl)benzimidazolyl)]methane (bismbmp, 3) and Bis[5-(1-ethyl-2-(6'-methyl-2'-pyridyl)benzimidazolyl)]methane (bisebmp, 4). 3,3'-Diamino-4,4'-bis(*N*-methylamino)diphenylmethane (**7**) (0.5 g, 1.95 mmol) and 0.67 g (4.88 mmol) of 2-carboxy-6-methylpyridine[21] were dissolved in methanol (30 mL). The solvent was evaporated and the solid residue was dried under vacuum. The resulting dry powder was transferred to a glass tube and sealed under vacuum. The tube was then heated at 150 °C for 36 h and cooled to room temperature, and the dark mixture was extracted with dichloromethane (2 × 100 mL). The combined organic phases were dried on cellulose and evaporated. The crude residue was purified by column chromatography (Al_2O_3, CH_2Cl_2/MeOH 99.5:0.5) and then crystallized from acetonitrile to give 0.55 g (1.2 mmol; yield = 62%) of bis[5-(1-methyl-2-(6'-methyl-2'-pyridyl)benzimidazolyl)methane (bismbmp, **3**) as white needles. Mp 169–171 °C. ^{1}H-NMR in $CDCl_3$: 2.61 (6 H, s), 4.23 (6 H, s), 4.26 (2 H, s), 7.16 (2 H, d, J^3 = 8 Hz), 7.19 (2 H, dd, J^3 = 8 Hz, J^4 = 1.5 Hz), 7.30 (2 H, d, J^3 = 8 Hz), 7.68 (2 H, d, J^4 = 1.5 Hz), 7.69 (2 H, t, J^3 = 8 Hz), 8.14 (2 H, d, J^3 = 8 Hz). ^{13}C-NMR in $CDCl_3$: 24.20, 32.68 (primary C); 42.25 (secondary C); 109.67, 119.76, 121.55, 123.00, 124.57, 136.91 (tertiary C); 135.80, 136.29, 142.74, 149.96, 150.47, 157.29 (quaternary C). EI-MS: 458 (M^+). Anal. Calcd for $C_{29}N_{26}N_6$: C, 75.96; N, 18.33; H, 5.72. Found: C, 75.66; N, 18.13; H, 5.67. The same procedure was used to prepare bis[5-(1-ethyl-2-(6'-methyl-2'-pyridyl)benzimidazolyl)]methane (bisebmp, **4**) from **8** in 38% yield. Mp 45–48 °C. ^{1}H-NMR in $CDCl_3$: 1.42 (6 H, t, J^3 = 7 Hz), 2.55 (6 H, s), 4.20 (2 H, s), 4.74 (4 H, q, J^3 = 7 Hz), 7.10 (2 H, d, J^3 = 8 Hz), 7.14 (2 H, dd, J^3 = 8 Hz, J^4 = 1.5 Hz), 7.27 (2 H, d, J^3 = 8 Hz), 7.63 (2 H, d, J^4 = 1.5 Hz), 7.63 (2 H, t, J^3 = 8 Hz), 8.12 (2 H, d, J^3 = 8 Hz). ^{13}C-NMR in $CDCl_3$: 15.24, 24.37 (primary C); 40.59, 42.22 (secondary C); 109.72, 119.85, 121.42, 122.92, 124.51, 136.84 (tertiary C); 134.75, 136.27, 142.92, 149.91, 157.36 (quaternary C). EI-MS: 486 (M^+).

Preparation of Copper(I) Complexes. All manipulations were performed under nitrogen with Schlenk techniques. The complex $[Cu(dmbipy)_2]PF_6$ was obtained from dmbipy and $Cu(CH_3CN)_4PF_6$[22] according to a modified literature procedure.[23]

Preparation of $[Cu(mbmp)_2](ClO_4)$ and $[Cu(dmbbmp)_2](ClO_4)$. Mbmp (**1**) (0.2 g, 0.896 mmol) in dichloromethane (5 mL) was added to a solution of 0.147 g (0.449 mmol) of $Cu(CH_3CN)_4(ClO_4)$[24] in acetonitrile (5 mL). The resulting red mixture was evaporated to dryness and dissolved in acetonitrile (3 mL) and ether was slowly diffused into the solution for 12 h. Red prisms of quality suitable for X-ray diffraction were separated and dried to give 0.18 g (0.295 mmol; yield = 66%) of $[Cu(mbmp)_2](ClO_4)$. ^{1}H-NMR in CD_3NO_2: 2.23 (6 H, s), 4.39 (6 H, s), 7.29 (2 H, t, J^3 = 7 Hz), 7.5 (6 H, m), 7.76 (2 H, d, J^3 = 7 Hz), 8.14 (2 H, t, J^3 = 7 Hz), 8.35 (2 H, d, J^3 = 7 Hz). Anal. Calcd for $CuC_{28}H_{26}N_6ClO_4$: Cu, 10.43; C, 55.17; N, 13.78; H, 4.30. Found: Cu, 11.1; C, 54.55; N, 13.62; H, 4.23. The lipophilic complex $[Cu(dmbbmp)_2](ClO_4)$ was prepared in situ by mixing of stoichiometric amounts of dmbbmp (**2**) and $Cu(CH_3CN)_4(ClO_4)$ in acetonitrile. ^{1}H-NMR in $CDCl_3$: 2.17 (6 H, s), 3.77 (12 H, s), 5.92 (4 H, s), 6.40 (6

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H, s broad), 7.28 (2 H, d, J^3 = 8 Hz), 7.35 (2 H, t, J^3 = 7.5 Hz), 7.40 (2 H, t, J^3 = 7.5 Hz), 7.52 (2 H, d, J^3 = 7.5 Hz), 7.52 (2 H, s), 7.9 (4 H, m).

Preparation of [Cu$_2$(bismbmp)$_2$](ClO$_4$)$_2$·H$_2$O and [Cu$_2$(bisebmp)$_2$](ClO$_4$)$_2$. Bismbmp (**3**) (50 mg, 0.109 mmol) in dichloromethane (5 mL) was added to a solution of 35.6 mg (0.109 mmol) of Cu(CH$_3$CN)$_4$(ClO$_4$) in acetonitrile (10 mL). The resulting red mixture was concentrated to 5 mL and crystallized at −20 °C. The orange precipitate was filtered and dissolved in acetonitrile, and ether was allowed to diffuse into the solution for 2 days. The thin orange needles were separated and dried to give 60 mg (0.476 mmol; yield = 87%) of [Cu$_2$(bismbmp)$_2$](ClO$_4$)$_2$. ^{1}H-NMR in CD$_3$NO$_2$: 2.09 (12 H, s), 4.02 (12 H, s), 4.13 (4 H, s), 7.17 (4 H, s), 7.3 (8 H, m), 7.46 (4 H, d, J^3 = 8 Hz), 8.02 (4 H, t, J^3 = 8 Hz), 8.13 (4 H, d, J^3 = 8 Hz). FAB-MS: 1143 ([Cu$_2$(bimbmp)$_2$(ClO$_4$)]$^+$). Anal. Calcd for Cu$_2$C$_{58}$H$_{52}$N$_{12}$Cl$_2$O$_8$·H$_2$O: Cu, 10.08; C, 55.23; N, 13.33; H, 4.32. Found: Cu, 10.2; C, 54.83; N, 13.26; H, 4.29. The related complex [Cu$_2$(bisebmp)$_2$](ClO$_4$)$_2$ was prepared in situ by stoichiometric mixing of bisebmp (**4**) and Cu(CH$_3$CN)$_4$(ClO$_4$) in acetonitrile/dichloromethane. ^{1}H-NMR in DMF-d_7: 1.59 (12 H, t, J^3 = 7 Hz), 2.02 (12 H, s), 4.29 (4 H, s), 4.86 (8 H, q, J^3 = 7 Hz), 7.12 (4 H, s broad), 7.48 (4 H, d, J^3 = 8 Hz), 7.60 (4 H, d, J^3 = 8 Hz), 7.87 (4 H, d, J^3 = 8 Hz), 8.17 (4 H, t, J^3 = 8 Hz), 8.31 (4 H, d, J^3 = 8 Hz).

Preparation of Cobalt(II) Complexes. The orange brown complex [Co(mbmp)$_3$](ClO$_4$)$_2$·CH$_3$CN was obtained in good yield (89%) using the same procedure described for [Cu(mbmp)$_2$](ClO$_4$), but with 3.0 equiv of mbmp (**1**) and 1.0 equiv of Co(H$_2$O)$_6$(ClO$_4$)$_2$. Anal. Calcd for CoC$_{42}$H$_{39}$N$_9$Cl$_2$O$_8$·CH$_3$CN: Co, 6.08; C, 54.55; N, 14.46; H, 4.37. Found: Co, 6.4; C, 54.17; N, 14.29; H, 4.26.

Preparation of [Co$_2$(bismbmp)$_3$](ClO$_4$)$_4$·3H$_2$O and [Co$_2$(bisebmp)$_3$](ClO$_4$)$_4$. Bismbmp (**3**) (0.3 g, 0.654 mmol) in 30 mL of acetonitrile/dichloromethane (1:1) was added to 0.16 g (0.436 mmol) of Co(H$_2$O)$_6$(ClO$_4$)$_2$ in acetonitrile (5 mL). The dichloromethane was distilled off and the resulting clear solution was slowly evaporated at 60 °C to a final volume of 5 mL. The red orange crystals were separated and dried to give 0.348 g (0.179 mmol; yield = 82%) of [Co$_2$(bismbmp)$_3$](ClO$_4$)$_4$·3H$_2$O. ^{1}H-NMR in CD$_3$CN: −58.1 (18 H, s), −43.5 (6 H, s), −1.5 (6 H, s), 3.6 (6 H, s), 15.2 (6 H, s), 18.7 (18 H, s), 33.1 (6 H, s), 47.6 (6 H, s), 62.0 (6 H, s). FAB-MS: 1791.3 ([Co$_2$(bismbmp)$_3$(ClO$_4$)$_3$]$^+$). Anal. Calcd for Co$_2$C$_{87}$H$_{78}$N$_{18}$Cl$_4$O$_{16}$·3H$_2$O: Co, 6.06; C, 53.71; N, 12.96; H, 4.35. Found: Co, 6.6; C, 53.77; N, 12.89; H, 4.21. The complex [Co$_2$(bisebmp)$_3$](ClO$_4$)$_4$ was prepared in situ by mixing of stoichiometric amounts of bisebmp and Co(H$_2$O)$_6$(ClO$_4$)$_2$ in acetonitrile. ^{1}H-NMR in CD$_3$CN: −56.1 (18 H, s), −45.8 (6 H, s), −0.8 (6 H, s), 4.0 (6 H, s), 9.2 (18 H, s), 14.3 (6 H, s), 17.1 (6 H, s), 22.8 (6 H, s), 33.3 (6 H, s), 48.6 (6 H, s), 62.5 (6 H, s).

Caution! Perchlorate salts with organic ligands are potentially explosive and should be handled with the necessary precautions.[25]

Crystal Structure Determinations of [Cu(mbmp)$_2$](ClO$_4$). CuC$_{28}$H$_{26}$N$_6$ClO$_4$, M_r = 609.6, μ = 0.946 mm^{-1}, F_{000} = 1256, d_x = 1.49 g·cm^{-3}, monoclinic, $P2_1/c$, $Z = 4$, a = 7.8774 (11) Å, b = 13.810 (2) Å, c = 25.090 (7) Å, β = 95.29 (1)°, V = 2721.3 (9) Å^3 from 29 reflections ($17° < 2\theta < 25°$). Crystal form: red prism 0.17 × 0.20 × 0.20 mm mounted on a quartz fiber. Cell dimensions and intensities were measured at room temperature on a Philips PW1100 diffractometer with graphite-monochromated Mo Kα radiation, ω–2θ scans, scan width 1.2 + 0.25 tan (θ)°, and scan speed 0.06°/s; two reference reflections measured every 60 min showed variations less than 3.5$\sigma(I)$. $-8 < h < 8$; $0 < k < 14$; $0 < l < 26$; $6° < 2\theta < 44°$. 3444 measured reflections, 3361 unique reflections, of which 2030 were observable ($|F_o| > 4\sigma(F_o)$); R_{int} for equivalent reflections 0.077. Data were corrected for anomalous dispersion, Lorentz polarization, and absorption effects (absorption coefficient A^*, min 1.155, max 1.183). The structure was solved by direct methods using MULTAN 87,[26] all other calculations used the XTAL[27] system and ORTEP II[28] programs. Atomic scattering factors and anomalous dispersion terms were taken from ref 29. Full-matrix least-squares refinement based on F using weights of $1/\sigma^2(F_o)$ gave final values R = 0.091, R_w = 0.041, S = 2.73 for 361 variables and 1972 contributing reflections. The mean shift/error on the last cycle was 0.016 and the maximum was 0.234. Hydrogen atoms were placed in calculated positions and the 40 non-hydrogen atoms were refined with anisotropic displacement parameters. The final difference electron density map showed +1.06 and −1.13 e Å^{-3} as a maximum and a minimum.

Physical Measurements. Electronic spectra in the UV–visible range were recorded in solution with Perkin-Elmer Lambda 5 and Perkin-Elmer Lambda 2 spectrophotometers at 20 °C using quartz cells of 1, 0.1, and 0.01 cm path length. Spectrophotometric titrations were performed with a Perkin-Elmer Lambda 5 spectrophotometer connected to a personal computer. In a typical experiment, 50 mL of ligand bismbmp in acetonitrile (2 × 10^{-4} M) were titrated with a 10^{-2} M solution of the perchlorate salt of the appropriate metal ion (Co(II), Cu(I), Zn(II)) in acetonitrile. After each addition of 0.15 mL, the absorbances at different wavelengths were recorded using a 0.1-cm quartz cell and transferred to the computer. Ten to fifteen different wavelengths were used for each titration, and the ten wavelengths which showed the greatest change in absorbance were used for further analysis. Plots of extinction as a function of the metal/ligand ratio gave a first indication of the number and stoichiometry of the complexes formed: factor analysis[30] was then applied to the data to confirm the number of different absorbing species. Finally, a model for the distribution of species was fitted with a nonlinear least-squares algorithm to the observed absorbances. The model comprised a set of complexes with fixed stoichiometry and variable stability constants: from the (known) total concentrations of metal and ligand and the estimated stability constants a speciation was calculated, and unknown extinction coefficients of absorbing species were obtained by a linear least-squares treatment; the extinction coefficients and the concentrations may then be used to obtain calculated absorbances, and the stability constants are refined by a least-squares algorithm. The mathematical treatment used was that published by Gampp et al.[31] In all three cases convergence was obtained, with a root-mean-square difference between observed and calculated absorbances of 0.005 absorbance units or less. This method gave a good measure of the merits of different models for complex stoichiometry, and the individual results are discussed below.

IR spectra were obtained from KBr pellets with a Perkin-Elmer IR 883 spectrophotometer. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on Varian XL 200 and Bruker AMX 400 spectrometers. Chemical shifts are given in ppm with respect to TMS (abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet). Conductivity measurements were made with a Metrohm E527 Wheastone bridge connected to a Metrohm EA240 cell (f = 0.61 cm^{-1}) immersed in a thermostated vessel at 25 °C. DMF was distilled under reduced pressure (10^{-2} Torr) from CaH$_2$. EI-MS (70 eV) were recorded with VG 7000E and Finnigan 4000 instruments. FAB-MS (positive mode from nitrobenzyl alcohol matrix) were recorded at the Laboratories of Mass Spectrometry of the University of Fribourg (Switzerland) and University of Strasbourg (France). Cyclic voltammograms were recorded using a Tacussel PRGE-DEC potentiostat connected to a function generator and a XY plotter. A 3-electrode system consisting of a stationary Pt disk working electrode, a Pt counter electrode, and a non-aqueous Ag/Ag$^+$ reference electrode was used. NBu$_4$ClO$_4$ (0.1 M in CH$_3$CN) served as inert electrolyte and CH$_3$CN was distilled from P$_2$O$_5$ and then passed through an Alox column (activity I). The reference potential ($E°$ = 0.39 (V) vs SCE) was standardized against the known complex [Ru(bipy)$_3$](ClO$_4$)$_2$.[32] The scan speed used was 0.2 V/s and voltammograms were analyzed according to established procedures.[32] All potentials are expressed vs SCE. Coulometry at controlled potential was performed using an Amel Integrator 731 connected to a ENNG 362 potentiostat and a polarographic recorder. The 3-electrode system described above was used in a Metrohm two-compartment cell with working and reference electrode in the main compartment and the auxiliary electrode in the secondary compartment separated by a Nafion 117 membrane. Elemental analyses were performed by Dr. H. Eder of the Microchemical Laboratory of the University of Geneva. Copper and cobalt content was determined by atomic absorption (Pye Unicam SP9) after acidic oxidative mineralization of the complex.

Results

1. Preparation of Ligands.

The bidentate ligands 6-methyl-2-(1-methylbenzimidazol-2-yl)pyridine (mbmp, **1**)[15] and 6-methyl-2-(1-(3,5-dimethoxybenzyl)benzimidazol-2-yl)pyridine (dmbbmp, **2**) are obtained in three steps according to a strategy used previously for the preparation of analogous terdentate lig-

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Table I. Selected Bond Distances (Å), Angles (deg), and Least-Squares-Plane Data for $[Cu(mbmp)_2]ClO_4$ (**9**)

	distances (Å)		angles (deg)
Cu–N(1)	2.010 (9)	N(1)–Cu–N(3)	81.5 (4)
Cu–N(3)	2.04 (1)	N(01)–Cu–N(03)	80.4 (5)
Cu–N(01)	1.91 (1)	N(1)–Cu–N(01)	121.8 (4)
Cu–N(03)	2.11 (1)	N(1)–Cu–N(03)	123.2 (4)
C(1)–C(8)	1.47 (2)	N(3)–Cu–N(01)	124.0 (4)
C(01)–C(08)	1.47 (2)	N(3)–Cu–N(03)	131.8 (4)

least-squares planes			
plane	description	max deviation, Å	atom
1	pyridine, N(3)	0.016	C(10)
2	benzimidazole, N(1), N(2)	0.020	C(4)
3	pyridine, N(03)	0.012	C(011)
4	benzimidazole, N(01), N(02)	0.029	C(03)

	interplane angles (deg)		
	2	3	4
1	7.7 (4)	90.2 (5)	85.4 (4)
2		91.8 (5)	88.0 (3)
3			9.2 (4)

ands[13,16] (Scheme I). The bis(bidentate) ligands bis[5-(1-methyl-2-(6′-methyl-2′-pyridyl)benzimidazolyl)]methane (bismbmp, **3**) and bis[5-(1-ethyl-2-(6′-methyl-2′-pyridyl)benzimidazolyl)]methane (bisebmp, **4**) are synthesized using a convergent strategy based on a modified double Philips reaction[33] between the tetraamine compounds **7**, **8**,[19] and 2-carboxy-6-methylpyridyne.[21] The introduction of the methylene group between the two aromatic bidentate donor groups of the ligand is achieved through a Friedel-Crafts type reaction of paraformaldehyde with N-substituted *o*-nitroaniline.[19] For the alkyl substituents on the benzimidazole moieties in **3** and **4** to occupy exo positions they must be present in the nitroamine before the introduction of the methylene bridge.

2. Copper(I) Complexes. The Cu(I) complexes are obtained by mixing ligands **1**–**4** with stoichiometric amounts of $[Cu(CH_3CN)_4]^+$ in acetonitrile or dichloromethane/acetonitrile under an inert atmosphere. The perchlorate salts of the copper(I) complexes with ligands **1** and **3** can easily be crystallized in good yield by slow diffusion of ether into the solution to give red orange crystals whose elemental analyses are compatible with the formulations $[Cu(mbmp)_2](ClO_4)$ and $[Cu(bismbmp)](ClO_4)\cdot 0.5H_2O$. The FAB-MS spectrum of this latter complex exhibits peaks centered at m/z = 1143 and 1043 whose isotopic distributions correspond respectively to the species $[Cu_2(bismbmp)_2(ClO_4)]^+$ and $[Cu_2(bismbmp)_2]^+$. These results imply a dimeric formulation for the complex $[Cu_2(bismbmp)_2](ClO_4)_2\cdot H_2O$. The IR spectra show that the characteristic ligand vibration at 1575 cm^{-1} for **1** and **3** (C=C, C=N stretching) is split upon complexation to Cu(I) into two components at 1570 and 1600 cm^{-1} for the complexes. The ClO_4^- anions all show the two expected symmetrical vibrations (1095, 625 cm^{-1}) typical of ionic perchlorates.[34] In order to investigate the properties of the chromophore $[Cu(mbmp)_2]^+$, which is also found in $[Cu_2(bismbmp)_2](ClO_4)_2\cdot H_2O$, X-ray quality crystals of $[Cu(mbmp)_2](ClO_4)$ were grown from a concentrated acetonitrile solution by slow diffusion of ether. Unfortunately, we were unable to obtain X-ray quality crystals of $[Cu_2(bismbmp)_2](ClO_4)_2\cdot H_2O$.

The lipophilic complexes of Cu(I) with the ligands **2** and **4** are designed to investigate the structure of the complexes in solution (vide infra), but they are very difficult to crystallize. Therefore, $[Cu(dmbbmp)_2]^+$ and $[Cu_2(bisebmp)_2]^{2+}$ were prepared in situ in an appropriate solvent.

X-ray Crystal Structure of $[Cu(mbmp)_2]ClO_4$. Selected bond distances, angles, and least-squares plane data are given in Table I. Figure 1 shows the atomic numbering scheme. Figure 2 gives an ORTEP[28] stereoview of the complex roughly perpendicular to the pseudo-C_2 axis of the complex.

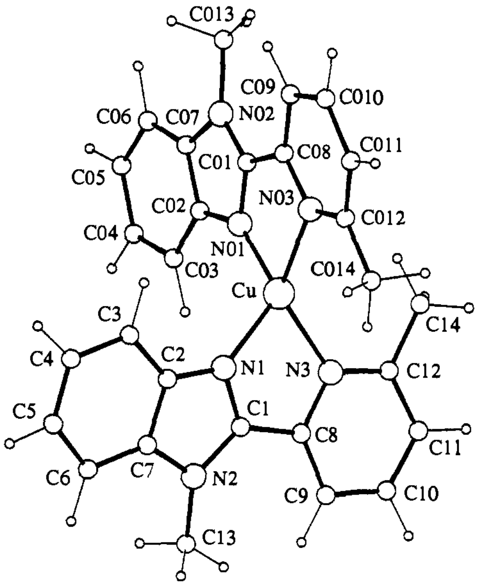

Figure 1. Atomic numbering scheme for $[Cu(mbmp)_2]^+$.

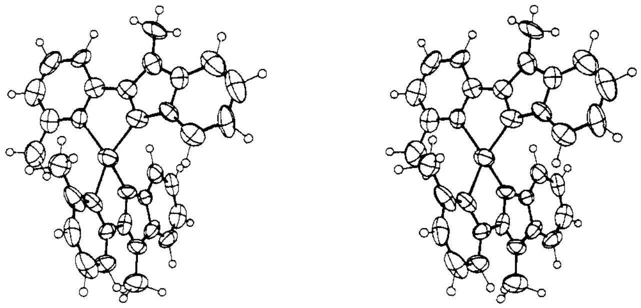

Figure 2. ORTEP[28] stereoscopic view of $[Cu(mbmp)_2]^+$ roughly perpendicular to the pseudo-C_2 axis.

In agreement with the IR results, the crystal structure determination shows the presence of a cation $[Cu(mbmp)_2]^+$ and one uncoordinated perchlorate anion. The perchlorate anion is slightly disordered, and this is assumed to be responsible for the relatively high unweighted residual factor R = 0.091; otherwise, the anion shows no feature of interest. The $[Cu(mbmp)_2]^+$ cation displays a pseudotetrahedral arrangement of the two almost planar mbmp ligands around Cu(I) with a mean Cu–N distance of 2.02 (11) Å which is comparable to those found in other $[Cu(\alpha,\alpha'\text{-diimine})_2]^+$ cations (α,α'-diimine = 2,2′-bipyridine (bipy; 2.021 Å),[35] 6,6′-dimethyl-2,2′-bipyridine (dmbipy; 2.034 Å),[23] 1,10-phenanthroline (phen; 2.049 Å),[36] 2,9-dimethyl-1,10-phenanthroline (dmphen; 2.071 Å)[37]). However, the Cu–N distances in $[Cu(mbmp)_2]^+$ are significantly different for the two mbmp ligands. One mbmp ligand is almost symmetrically bound to Cu(I) while the other mbmp is slightly twisted leading to a short Cu–N(benzimidazole) bond (1.91 (1) Å) and a long Cu–N(pyridine) distance (2.11 (1) Å) which precludes the existence of a crystallographic C_2 axis in the cation. The intraligand bite angles (80.4(5)°, 81.5(5)°) are also similar to those found in other $[Cu(\alpha,\alpha'\text{-diimine})_2]^+$ cations.[23,35-37] The four interligand N–Cu–N angles (121.8 (4) < α < 131.8 (4)°) and the dihedral crossing angle between the two mbmp units (87.4°) deviate only

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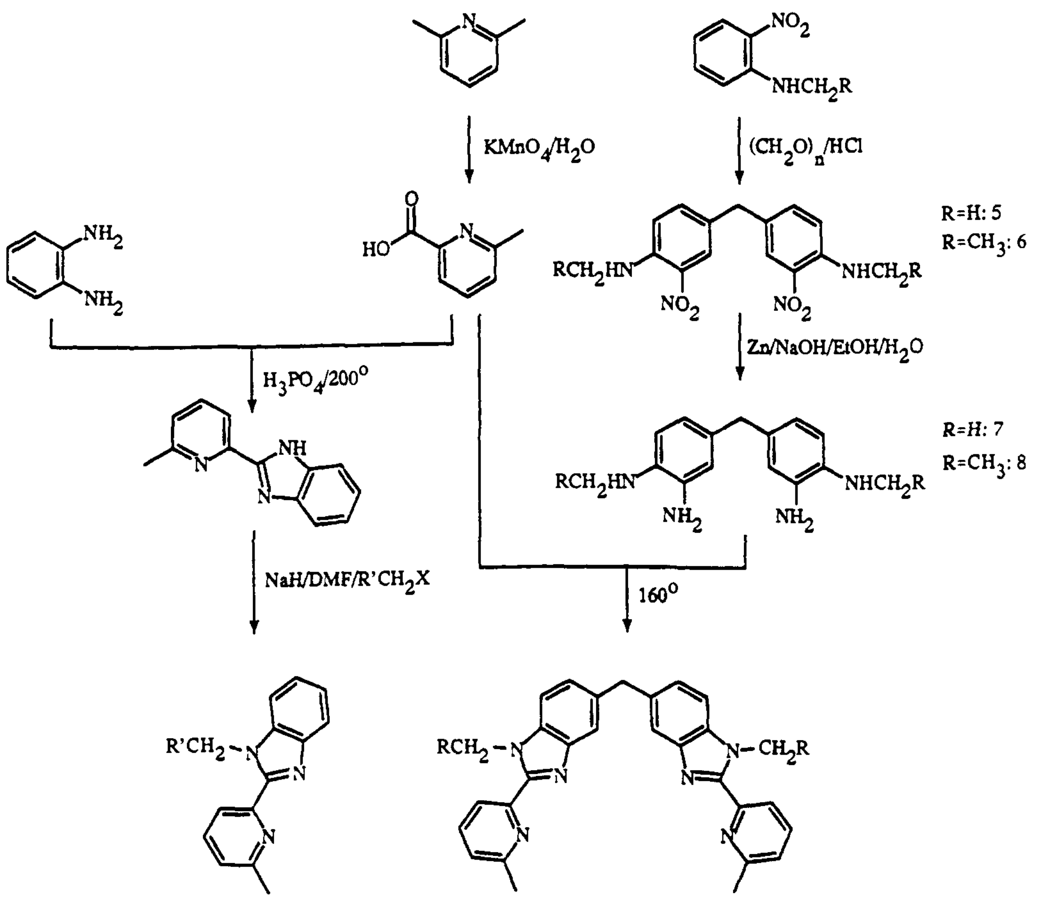
Scheme I



R'=H: mbmp (1)

R'=(MeO)$_2$C$_6$H$_3$: dmbbmp (2)

R=H: bismbmp (3)

R=CH$_3$: bisebmp (4)

Table II. Conductivity Data in DMF at 25 °C[a]

complexes	$\Lambda_m(10^{-3}$M), Ω^{-1} mol^{-1} cm^2	Λ^0_m, Ω^{-1} mol^{-1} cm^2	slope (A), Ω^{-1} mol^{-1} cm^2 L$^{1/2}$ eq$^{-1/2}$	electrolyte
NBu_4ClO_4	98 (3)	133 (2)	1098 (37)	1:1
NBu_4PF_6	95 (3)	128 (2)	999 (25)	1:1
$Cu(ClO_4)_2$	224 (5)	320 (5)	1380 (42)	2:1
$Cu(mbzimpy)(ClO_4)_2$	210 (5)	310 (5)	1505 (74)	2:1
$Cu_2(dmbbzimpy)_2(ClO_4)_2$	164 (5)	250 (10)	1538 (46)	2:1
$Cu_2(bismbmp)_2(ClO_4)_2$	160 (5)	250 (10)	1455 (91)	2:1

[a] $\Lambda_m(10^{-3}$ M), molar conductivity at 10^{-3} M; Λ^0_m, molar conductivity at infinite dilution; A, slope of Onsager law $\Lambda_{eq} = \Lambda^0_{eq} - A\sqrt{C_{eq}}$; mbzimpy = 2,6-bis(1-methylbenzimidazol-2-yl)pyridine; dmbbzimpy = 2,6-bis(1-(3,5-dimethoxybenzyl)benzimidazol-2-yl)pyridine.[13]

slightly from the values of 125.4° and 90° expected for pseudo-D_{2d} symmetry.[38]

As previously observed with $[Cu(tmbp)_2]ClO_4$[39] and $[Ag(tmbp)_2]ClO_4$[40] (tmbp = 4,4',6,6'-tetramethyl-2,2'-bipyridine), the mbmp ligands are packed in layers along two almost orthogonal directions producing slipped stacks of approximately parallel ligand molecules (interplane angle = 7.5 (3)°). The contact distances between the stacked aromatic planes lie in the range 3.34–3.63 Å, suggesting quite strong stacking interactions which may be responsible for the slight inequalities in Cu–N bond lengths. In conclusion, the pseudo-tetrahedral geometry observed for the cation $[Cu(mbmp)_2]^+$ is similar to that found in the well-known $[Cu(\alpha,\alpha'\text{-diimine})_2]^+$ cations and implies that mbmp may be considered as an analogue of the dmbipy ligand giving a similar pseudotetrahedral $[Cu(N_4)]^+$ chromophore.[41]

Structure in Solution. In order to establish the structure of dinuclear $[Cu_2(bismbmp)_2](ClO_4)_2\cdot H_2O$ in solution, we have studied the conductivity, the UV–visible and the ^{1}H NMR spectra, and the cyclic voltammograms in polar aprotic solvents. We have also studied the well-characterized mononuclear $[Cu(mbmp)_2](ClO_4)$ in order to confirm the presence of the same pseudotetrahedral chromophore $[Cu(N_4)]^+$ in the dinuclear complex.

In DMF, $[Cu_2(bismbmp)_2](ClO_4)_2\cdot H_2O$ behaves as a strong electrolyte obeying the Onsager law[42] $\Lambda_{eq} = \Lambda^\circ_{eq} - A\sqrt{C_{eq}}$, and giving a slope A = 1455 (91) [Ω^{-1} eq$^{-3/2}$ cm^2 L$^{1/2}$]). Comparison with well-defined 1:1 electrolytes (NBu_4ClO_4, NBu_4PF_6) and 2:1 electrolytes ($Cu(ClO_4)_2$, $Cu(mbzimpy)(ClO_4)_2$,[16] $[Cu_2(dmbbzimpy)_2](ClO_4)_2$[13]) in the same conditions (Table II) clearly shows that $[Cu_2(bismbmp)_2](ClO_4)_2\cdot H_2O$ behaves as a typical

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Table III. Electronic Spectral Data for the Ligands and Complexes with Co(III) in Acetonitrile and for Complexes with Cu(I) in Propylene Carbonate at 20 °C

compound	$\pi_2 \rightarrow \pi^*$	$\pi_1 \rightarrow \pi^*$	others
mbmp (**1**)	42190 (11700)[a]	32360 (22000)	
bismbmp (**3**)	43100 (33350)	31550 (46800)	
dmbipy	40980 (8540)	34600 (15300)	
$[Cu(\mathbf{1})_2]ClO_4$ (9)	*b*	31750 (40300)	22580 (3700)[c]
$[Cu_2(\mathbf{3})_2](ClO_4)_2$ (**11**)	*b*	31150 (79950)	22620 (6500)[c]
$[Cu(dmbipy)_2]ClO_4$	*b*	33440 (28400)	21980 (6200)[c]
$[Co(\mathbf{1})_3](ClO_4)_2$ (**13**)	42190 (34800)	32050 (52100)	18250 (23)[d] sh 19080 (24) 20200 (26) sh
$[Co_2(\mathbf{3})_3](ClO_4)_4$ (**14**)	42290 (83950)	30870 (111930)	18600 (67)[d] sh 19230 (79) sh 19960 (93)

[a] Energies are given for the maximum of the band envelope in cm^{-1} and molar absorption coefficient (ϵ) in parentheses in $M^{-1}\ cm^{-1}$; sh = shoulder. [b] Solvent absorption masks this transition. [c] Cu(I)–π^* MLCT. [d] LF transitions.

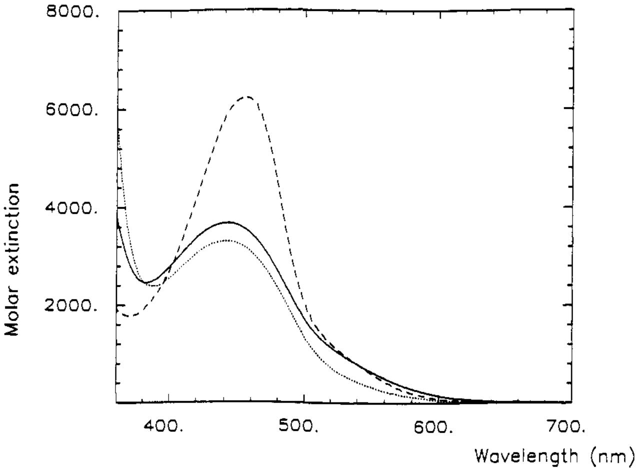

Figure 3. Electronic spectra of the complexes $[Cu(mbmp)_2]^+$ (—), $[Cu(dmbipy)_2]^+$ (---), and $[Cu_2(bismbmp)_2]^{2+}$ (···) in propylene carbonate (molar extinction coefficients are given per copper atom).

2:1 electrolyte in polar aprotic solvents which implies the existence of the dinuclear cation $[Cu_2(bismbmp)_2]^{2+}$ in solution.[13]

The UV spectra of the colorless free ligands mbmp (**1**) and bismbmp (**3**) in acetonitrile display two intense absorptions around 32 000 cm^{-1} (ϵ = 22 000 and 46 000 $M^{-1}\ cm^{-1}$, respectively) and 42 500 cm^{-1} (ϵ = 12 000 and 34 000 $M^{-1}\ cm^{-1}$) attributed to $\pi_1 \rightarrow \pi^*$ and $\pi_2 \rightarrow \pi^*$ by comparison with 2,2'-bipyridine (bipy) and 6,6'-dimethyl-2,2'-bipyridine (dmbipy)[43,44] (Table III). Upon complexation to Cu(I), these two transitions do not change significantly, but a new absorption, responsible for the red color, appears near 22 200 cm^{-1} (ϵ = 3500–4000 $M^{-1}\ cm^{-1}$ per copper(I)) for $[Cu(mbmp)_2](ClO_4)$ and $[Cu_2(bismbmp)_2](ClO_4)_2{\cdot}H_2O$ and may be assigned to MLCT (Cu(I) → π^*) transitions, typical of pseudotetrahedral $[Cu(\alpha,\alpha'\text{-diimine})_2]^+$ chromophores.[5,44] Comparison with the well-known MLCT (Cu(I) → π^*) transitions of pseudotetrahedral $[Cu(dmbipy)_2]^+$[44] (Table III, Figure 3) unambigously confirms the same type of chromophore for the three complexes demonstrating similar pseudotetrahedral coordination of each Cu(I) in $[Cu(mbmp)_2]^+$ and the dinuclear complex $[Cu_2(bismbmp)_2]^{2+}$ in solution.

The ^{1}H-NMR spectra of the two bidentate ligands mbmp (**1**) and dmbbmp (**2**) show pseudo-first-order spectra for the pyridine protons H_1–H_3 and a complicated ABCD spin system for the benzimidazole protons H_4–H_7 with one proton giving a multiplet around 7.8 ppm and the three other protons a multiplet between 7.3–7.4 ppm. For the two bis(bidentate) ligands bismbmp (**3**) and bisebmp (**4**), we observe two equivalent benzimidazole–pyridine moieties showing ^{1}H-NMR characteristics similar to those described for **1** and **2**. However, the disappearance of the H_5 proton, due to the presence of the methylene bridge in **3** and **4**, greatly simplifies the spectra, leading to an easily interpretable pseudo-first-order AMX spin system for the benzimidazole protons. The very different coupling constants $J^3(H_6\text{–}H_7)$ = 8 Hz and $J^4(H_4\text{–}H_6)$ = 1.5 Hz allow the unambigous attribution of the low-field signal (7.68 ppm in **3**) to H_4 which strongly suggests that the isolated downfield multiplet observed for ligand **1** (7.8 ppm) corresponds also to H_4. These results were confirmed by NOE experiments on the tridentate ligands 1,3-bis(*N*-alkylbenzimidazol-2-yl)benzene[13] where H_4 always corresponds to the lowest-field signal of the H_4–H_7 spin system.[45]

Upon complexation to Cu(I), the pyridine protons of the ligands still display pseudo-first-order spectra, but at lower field for the protons H_1 and H_2 (0.33–0.45 ppm for H_2) which is typical for N-coordination of the pyridine ring.[8,13,46] H_3 shows only small shifts upon complexation as a result of the conformational change between *trans*- and *cis*-[α,α'-diimine] when the ligands **1**–**4** are coordinated to Cu(I).[47] As previously described for 2,6-bis(*N*-alkylbenzimidazol-2-yl)pyridine,[8,13] the ^{1}H-NMR signals of the benzimidazole protons H_4–H_7 of ligands **1** and **2** are only slightly modified in the complexes to give pseudo-first-order spectra with two triplets (H_5, H_6) and two doublets (H_4, H_7) in the range 7.3–7.8 ppm (Table IV). A similar trend is observed for the H_6 and H_7 protons in the dinuclear complexes $[Cu_2(bismbmp)_2]^{2+}$ and $[Cu_2(bisebmp)_2]^{2+}$, but the ^{1}H-NMR signal of the isolated H_4 proton is significantly shielded (0.5–0.7 ppm; Figure 4), which contrasts strongly with the weak shielding (0.2 ppm) observed for the mononuclear complexes. These results and the careful examination of molecular models indicate that H_4 lies in the shielding region of the second benzimidazole ring of the same ligand. This strongly suggests a twist of the ligand compatible with a double-helical structure for the dinuclear complexes in which bismbmp and bisebmp act as bis(bidentate) ligands twisted about the Cu–Cu axis. Each copper will then have a pseudotetrahedral coordination in agreement with the observed electronic spectrum.

To establish definitively the helical nature of $[Cu_2(bismbmp)_2](ClO_4)_2{\cdot}H_2O$ and $[Cu_2(bisebmp)_2]^{2+}$ in solution, we have studied the intramolecular diastereotopic effect on the ^{1}H-NMR spectra[13,48] and, to this end, have designed the ligands dmbbmp (**2**) and bisebmp (**4**) which possess a RCH_2 probe covalently bound to the backbone of the ligand.[13] Although the mononuclear complex $[Cu(dmbbmp)_2]^+$ is chiral (C_2 symmetry), we were unable to observe diastereotopic effects for the H_8,H_9 protons which remain enantiotopic even at −50 °C in $CDCl_3$ at 200 MHz, strongly suggesting a rapid interconversion between the two enantiomers on the NMR time scale. Similar behavior was observed for the dinuclear $[Cu_2(bisebmp)_2]^{2+}$ at room temperature, which was also attributed to rapid interconversion between the helical enantiomers. However, on lowering the temperature the quartet observed for protons H_8,H_9 (A_2X_3 spin system) is transformed into a complicated multiplet (ABX_3 spin system) resulting from the non-equivalence on the NMR time scale of H_8 and H_9 below 0 °C in DMF-d_7 (Figure 5). The possibility that this might arise from hindered rotation of ethyl residues in $[Cu_2(bisebmp)_2]^{2+}$ may be ruled out since such an effect would also have been observed in the mononuclear complex $[Cu(dmbbmp)_2]^+$ in which the CH_2 group is part of a bulkier, substituted benzyl moiety. The chiral nature of the cation $[Cu_2(bisebmp)_2]^{2+}$ in solution is thus confirmed. Finally, the ^{1}H-NMR signals of the methyl groups bound to the pyridine rings are

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Table IV. ^{1}H NMR Shifts (with respect to TMS) for Ligands and Complexes in Aprotic Solvents

compound	solvent	H_1	H_2	H_3	H_4	H_5	H_6	H_7	CH_3[b]
mbmp, **1**	$CDCl_3$	7.19	7.72	8.16		7.3–7.9 (m)[a]			2.63
dmbbmp, **2**	$CDCl_3$	7.18	7.50	8.20		7.3–7.9 (m)[a]			2.55
bismbmp, **3**	$CDCl_3$	7.16	7.69	8.14	7.68		7.19	7.30	2.61
bisembmp, **4**	$CDCl_3$	7.10	7.63	8.12	7.63		7.14	7.27	2.55
$[Cu(mbmp)_2]^+$	CD_3NO_2	7.55	8.14	8.35	7.76	7.29	7.4–7.6 (m)[a]		2.23
$[Cu(dmbbmp)_2]^+$	$CDCl_3$	7.88	7.90	7.85	7.52	7.35	7.40	7.52	2.17
$[Cu_2(bismbmp)_2]^+$	CD_3NO_2	7.46	8.02	8.13	7.17		7.3–7.4 (m)[a]		2.09
$[Cu_2(bismbmp)_2]^{2+}$	DMSO-d_6	7.48	8.06	8.28	6.93		7.36	7.79	1.86
$[Cu_2(bisebmp)_2]^{2+}$	DMSO-d_6	7.48	8.04	8.12	7.08		7.38	7.80	1.91
$[Cu_2(bisebmp)_2]^{2+}$	DMF-d_7	7.60	8.17	8.31	7.12		7.48	7.87	2.02
$[Co_2(bismbmp)_3]^{4+}$	CD_3CN	47.6	15.1	62.2	−43.5		33.1	3.6	−58.1
$[Co_2(bisebmp)_3]^{4+}$	CD_3CN	48.6	14.3	62.5	−45.8		33.3	4.0	−56.1

[a] m, multiplet. [b] Methyl groups bound to the pyridine rings.

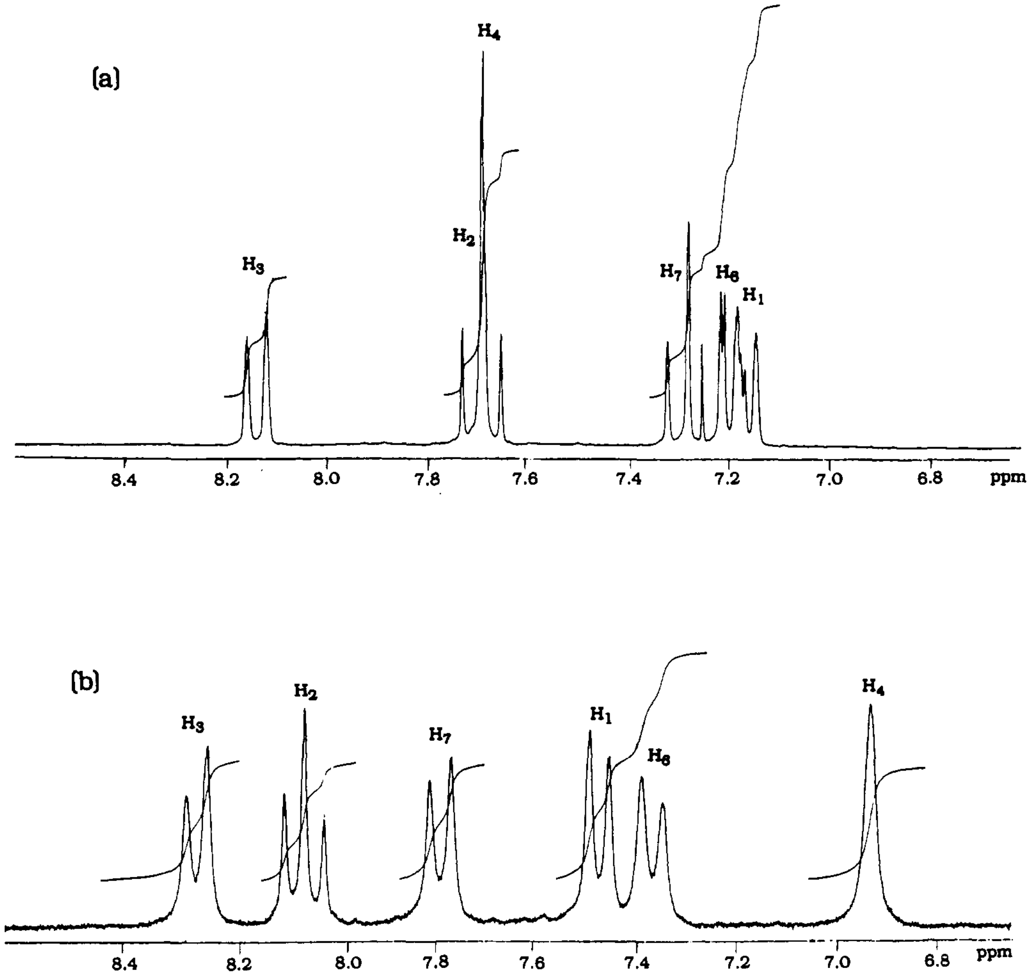

Figure 4. 200-MHz ^{1}H-NMR spectrum of (a) bismbmp in $CDCl_3$ and (b) $[Cu_2(bismbmp)_2]^{2+}$ in DMSO-d_6.

systematically shifted toward higher field in the mononuclear pseudo-tetrahedral complexes $[Cu(mbmp)_2](ClO_4)$, $[Cu(dmbbmp)_2]^+$, and $[Cu(dmbipy)_2]^+$ (0.35, 0.40 and 0.38 ppm respectively) as a result of the ligand geometry which puts the methyl groups of one ligand in the shielding region of the other. The dinuclear double helical complexes parallel this behavior, displaying highfield shifts in the range 0.5–0.8 ppm which imply a similar pseudo-tetrahedral arrangement around each Cu(I).

The mononuclear complex $[Cu(mbmp)_2]^+$ is oxidized by cyclic voltammetry in a single quasireversible monoelectronic wave at $E_{1/2} = +0.52$ V vs SCE in MeCN ($E^a - E^c = 140$ mV). This value is somewhat lower than that for $[Cu(dmbipy)_2]^+$ ($E_{1/2} = +0.72$ V vs SCE) and $[Cu(dmphen)_2]^+$ ($E_{1/2} = +0.67$ V vs SCE),[49] but it probably reflects a greater steric constraint by the two methyl groups in dmbipy or dmphen compared to that of the single methyl substituent in mbmp. The dinuclear complex $[Cu_2(bismbmp)_2]^{2+}$ is oxidized in a single quasireversible wave ($E^a - E^c = 260$ mV) at $E_{1/2} = +0.30$ V vs SCE in MeCN, a lower value than those observed by Lehn for his dinuclear double-helical $[Cu_2L_2]^{2+}$ complexes where L is an oligobipyridyl or an oligophenanthroline ligand ($E_{1/2} = +0.88$ and $+0.85$ V vs SCE).[6] It is interesting to note that the $E_{1/2}$ value for the dinuclear complex is approximately 220 mV less positive than that observed for the mononuclear analogue which might be due to a greater deviation from pseudo-tetrahedral geometry in the dinuclear complex.[35]

Having established the existence of the dinuclear double-helical complex $[Cu_2(bismbmp)_2]^{2+}$ in solution, it is of interest to know if this complex is the only species produced by the self-assembly reaction. Spectrophotometric titration of ligand bismbmp with $[Cu(CH_3CN)_4]^+$ in acetonitrile (Cu:ligand ratio in the range 0.2–2.8) shows a roughly linear rise in extinction coefficient due

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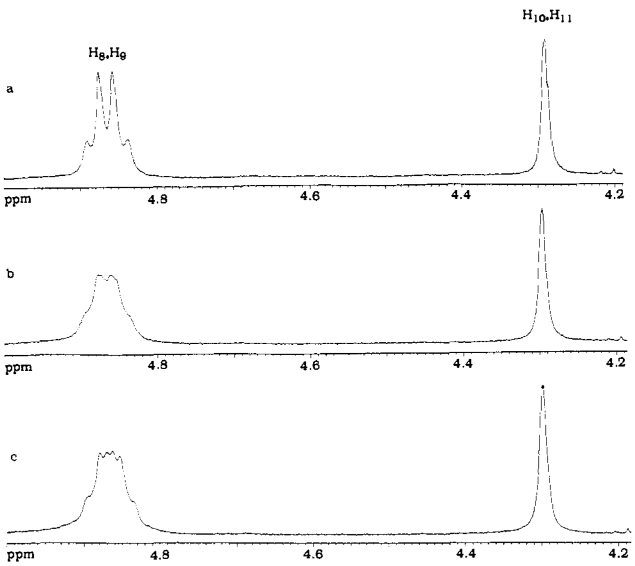

Figure 5. 400-MHz ^{1}H-NMR spectra of the diastereotopic protons H_8 and H_9 in $[Cu_2(bisebmp)_2]^{2+}$ in DMF-d_7 at 283 (a), 273 (b), and 263 K (c).

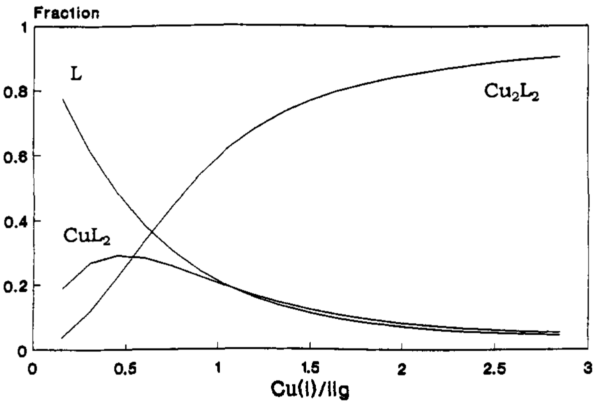

Figure 6. Distribution of the species from the spectrophotometric titration of bismbmp (3) with $[Cu(CH_3CN)_4]^+$ in CH_3CN.

to the MLCT transition up to a Cu:ligand ratio of 1, followed by a slow leveling out. This could be satisfactorily fitted with equilibria 1 and 2 involving the expected helical cation $[Cu_2(bismbmp)_2]^{2+}$ and a mononuclear complex $[Cu(bismbmp)_2]^+$ which is present in significant amounts for Cu:ligand ratios in the range 0.3–0.7 (Figure 6).

$$2\,\text{bismbmp} + Cu^+ \leftrightarrow [Cu(bismbmp)_2]^+ \qquad \log(\beta_1) = 8.3\ (5) \quad (1)$$

$$2\,\text{bismbmp} + 2\,Cu^+ \leftrightarrow [Cu_2(bismbmp)_2]^{2+} \qquad \log(\beta_2) = 13.0\ (3) \quad (2)$$

An attempt to fit the data with a 1:1 complex only gave a very poor fit; a 2:2 complex gave a much better fit which showed however a significant deviation around the Cu:ligand ratio of 0.5, suggesting a significant presence of a 1:2 complex. Incorporation of a 1:2 complex into the model gave a root-mean-square value for the difference between calculated and observed absorbance of 0.003 absorbance units. Although the least-squares estimates of the errors in the stability constants are probably too small (the similarity of the calculated spectra for the two complexes gives very strong correlation between the values), the fit is very sensitive to the stoichiometry of the complexes used in the model, and we therefore have confidence in the identification of the species present.

^{1}H-NMR spectra at different Cu:ligand ratios in CD_3NO_2 confirm the coexistence of the double-helical cation $[Cu_2(bismbmp)_2]^{2+}$ with an asymmetrical species displaying 12 different aromatic signals of equal intensity which we tentatively assign to $[Cu(bismbmp)_2]^+$ (Figure 7).

3. Complexes with Cobalt(II). The Co(II) complexes are prepared by mixing ligands mbmp, bismbmp, and bisebmp with stoichiometric amounts of $Co(H_2O)_6(ClO_4)_2$ in dichloromethane/acetonitrile. The perchlorate salts of the cobalt(II) complexes with mbmp can easily be crystallized in good yield by slow diffusion of ether into the solution to give beige crystals whose elemental analysis corresponds to $Co(mbmp)_3(ClO_4)_2{\cdot}CH_3CN$ probably as a mixture of pseudooctahedral *mer* and *fac* stereoisomers. Slow evaporation at 60 °C of an acetonitrile solution containing the Co(II) complex of bismbmp leads to salmon colored crystals whose elemental analysis is compatible with the formulation $[Co_2(bismbmp)_3](ClO_4)_4{\cdot}3H_2O$. The FAB-MS spectrum of this compound shows peaks centered at m/z = 1791.3, 1333.1, and 1074.3 whose isotopic distributions correspond respectively to the species $[Co_2(bismbmp)_3(ClO_4)_3]^+$, $[Co_2(bismbmp)_2(ClO_4)_3]^+$, and $[Co(bismbmp)_2(ClO_4)]^+$ and confirm the dinuclear nature of the complex. The IR spectra of complexes $Co(mbmp)_3(ClO_4)_2{\cdot}CH_3CN$ and $[Co_2(bismbmp)_3](ClO_4)_4{\cdot}3H_2O$ show the characteristic splitting of the ligand vibration (C═C, C═N stretching) into two components (1605, 1570 cm^{-1}) upon complexation to Co(II) as previously observed with copper(I). The ClO_4^- anions all show the two expected symmetrical vibrations (1095, 625 cm^{-1}) typical of ionic perchlorates.[34] The X-ray crystal structure of the related compound $[Co_2(bismbmp)_3](ClO_4)_4{\cdot}2.5CH_3CN$ unambigously shows the dinuclear triple-helical structure of the cation $[Co_2(bismbmp)_3]^{4+}$ [14] (Figure 8). The cation has approximate D_3 symmetry with the three bis(bidentate) ligand molecules wrapped around the Co–Co axis in such a way as to give each cobalt(II) cation a distorted octahedral coordination.

As with Cu(I), the complex of the lipophilic ligand bisebmp was prepared in situ by mixing stoichiometric amounts of $Co(H_2O)_6(ClO_4)_2$ and bisebmp in acetonitrile.

A titration of the ligand bismbmp in acetonitrile with $Co(H_2O)_6(ClO_4)_2$ (Co:ligand ratio in the range 0.2–2.5) showed a sharp end point near a Co:ligand ratio of 0.7. The data could be satisfactorily fitted with the single equilibrium 3 involving the cation $[Co_2(bismbmp)_3]^{4+}$.

$$3\,\text{bismbmp} + 2\,Co^{2+} \leftrightarrow [Co_2(bismbmp)_3]^{4+} \qquad \log(\beta_3) = 21.4\ (6) \quad (3)$$

For the Co:ligand ratio in the range 0.2–2.5, there was no evidence for the formation of any other complex. This strongly suggests the presence of a cooperative self-assembling process as recently found by Lehn and his collaborators for their metallohelicates.[5] It remains, however, essential to show that the triple-helical structure is maintained in solution and is not merely an artefact of the crystallization process, and we have therefore studied $[Co_2(bismbmp)_3](ClO_4)_4{\cdot}3H_2O$ and the analogous compound with bisebmp in solution.

As previously observed with the copper(I) complexes, the two intense $\pi_{1,2} \rightarrow \pi^*$ transitions centered on the ligands do not change significantly upon complexation to Co(II), but a weak structured band appears in the visible region around 19000 cm^{-1} (ϵ = 20–100 M^{-1}·cm^{-1}) for $Co(mbmp)_3(ClO_4)_2{\cdot}CH_3CN$ and $[Co_2(bismbmp)_3](ClO_4)_4{\cdot}3H_2O$ (Table III). This feature is characteristic of d–d transitions for Co(II) high spin in a pseudooctahedral environment[50] and may be compared with the d–d transitions observed for $[Co(bipy)_3]^{2+}$ (22 000 cm^{-1})[51] and $[Co(pyridine)_6]^{2+}$ (20 400 cm^{-1}).[52] Assuming O_h microsymmetry, the main transition may be assigned to $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ and the multiplet structure arises from the admixture of spin-forbidden transitions derived from ^{2}G and ^{2}H states.[50] These results strongly suggest that pseudooctahedral $[Co^{II}N_6]^{2+}$ high-spin chromophores exist in both mononuclear $[Co(mbmp)_3]^{2+}$ and dinuclear $[Co_2(bismbmp)_3]^{4+}$.

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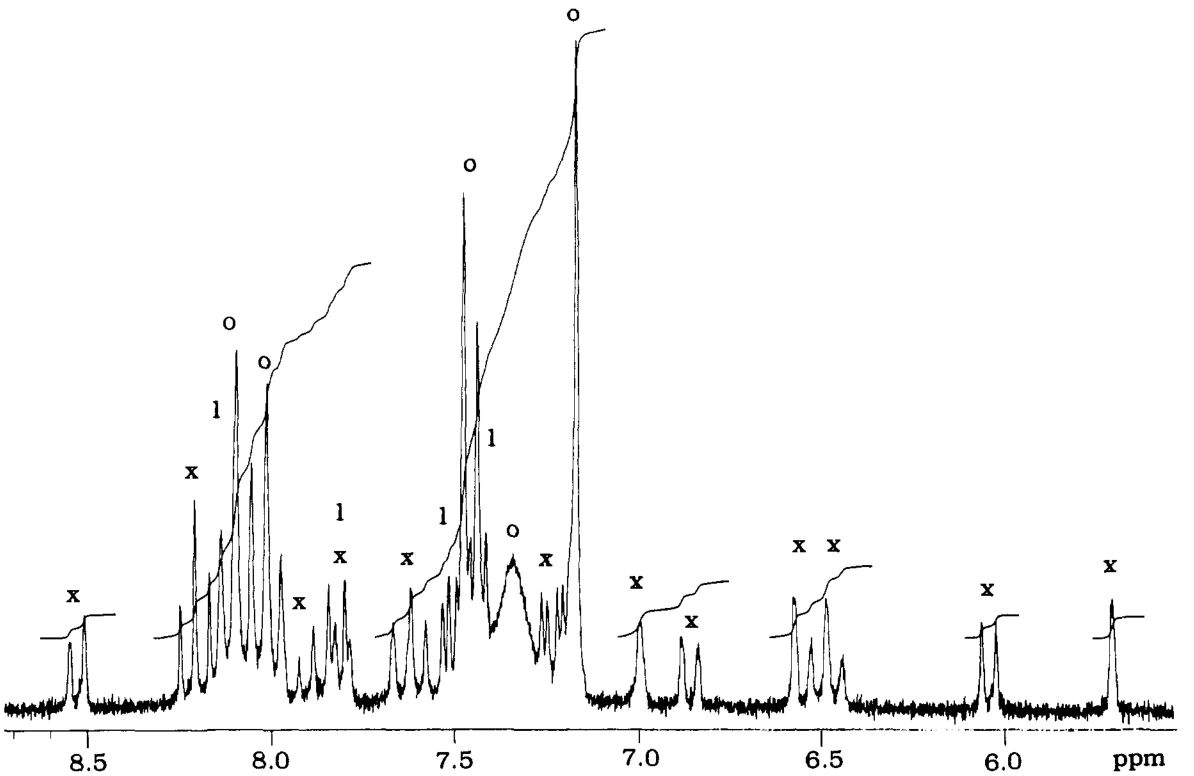

Figure 7. 200-MHz ^1H NMR spectrum for the Cu(I):bismbmp ratio of 0.8 obtained during titration of bismbmp (3) with $[Cu(CH_3CN)_4]^+$ in CD_3NO_2: (o) $[Cu_2(bismbmp)_2]^{2+}$; (x) $[Cu(bismbmp)_2]^{2+}$; (l) bismbmp.

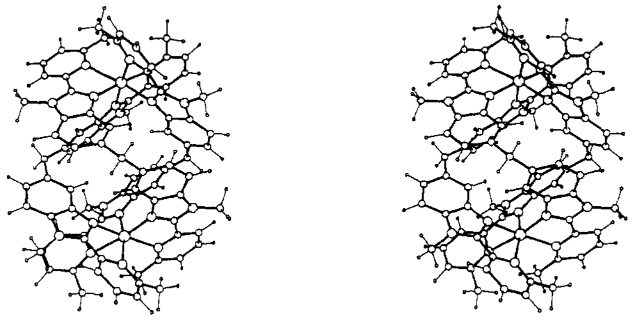

Figure 8. ORTEP[28] stereoview of the triple-helical complex $[Co_2(bismbmp)_3]^{4+}$.

The very short electronic relaxation times of pseudooctahedral Co(II) high-spin complexes (10^{-11}–10^{-12} s) allow the observation of rather sharp NMR signals.[53] However, contact and dipolar relaxation mechanisms arising from the coupling of electronic and nuclear magnetic moments broaden the ^1H–NMR signals often leading to the disappearance of ^1H–^1H coupling patterns.[53] The ^1H–NMR spectrum of $[Co_2(bismbmp)_3](ClO_4)_4{\cdot}3H_2O$ shows eight singlets each with an integral of 1 and 2 singlets with an integral of 3 spread over more than 100 ppm (Figure 9). These features correspond to three equivalent bismbmp ligands coordinated to the two high-spin Co(II), implying a C_3 symmetry axis, and the enantiotopic protons of the methylene bridges imply three C_2 axes perpendicular to the C_3 axis reflecting a high symmetry (D_3 or D_{3h}) for the cation $[Co_2(bismbmp)_3]^{4+}$ in solution. The attribution of the pyridine protons H_1–H_3 and benzimidazole protons H_6–H_7 was performed by a two-dimensional homonuclear COSY-correlation spectrum (Table IV). The remaining signals corresponding to H_4 and H_{10},H_{11} were assigned using a ^{13}C-NMR DEPT pulse sequence to locate the secondary carbon of the methylene bridge (32.77 ppm) followed by a two-dimensional heteronuclear ^{13}C–^1H correlation spectrum. Finally, the methyl signals were differentiated by using the analogous complex $[Co_2(bisebmp)_3]^{4+}$ which gives a very similar ^1H–NMR spectrum except for the disappearance of the +18.7-ppm signal which can be consequently attributed to the *N*-methyl groups in $[Co_2(bismbmp)_3]^{4+}$. The ethyl residues in $[Co_2(bisebmp)_3]^{4+}$ display one singlet for the terminal CH_3 substituent at 9.2 ppm and two singlets at 17.1 and 22.8 ppm corresponding to the diastereotopic protons H_8,H_9 which confirm the chiral nature of the complex[13,47] (Figure 10), compatible only with a triple-helical cation $[Co_2(bisebmp)_3]^{4+}$ of D_3 symmetry. These features indicate that the triple-helical structure found in the solid state[14] is maintained in solution and that the two enantiomeric helical conformations do not interconvert at room temperature on the NMR time scale.[54] Further ^1H-NMR measurements in the presence of an excess of ligand show that ligand exchange is also slow on the NMR time scale at room temperature.

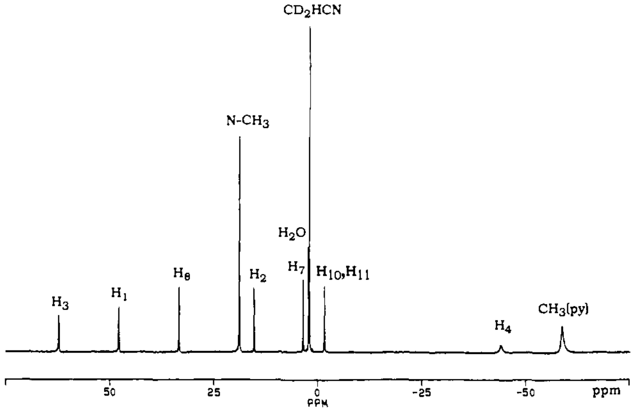

Figure 9. 200-MHz ^1H-NMR spectrum of $[Co_2(bismbmp)_3]^{4+}$ in CD_3CN.

The mononuclear complex $Co(mbmp)_3(ClO_4)_2$ is reduced on a platinum disk electrode with a quasireversible monoelectronic wave at $E_{1/2}$ = –0.96 V vs SCE in MeCN (Co(II)/Co(I); E^a –

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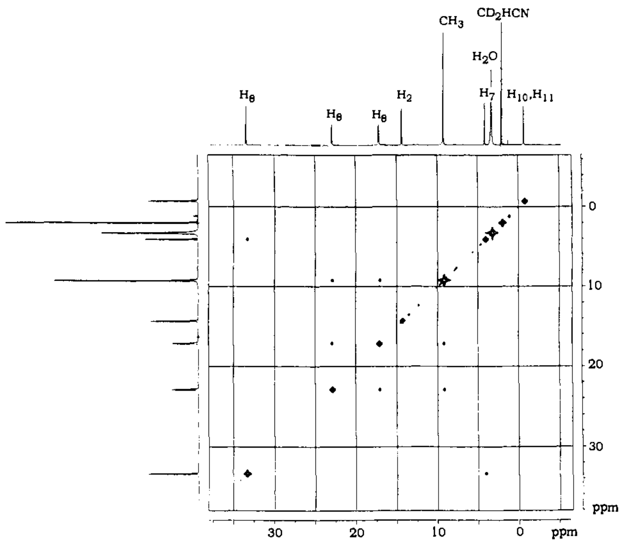

Figure 10. 400-MHz two-dimensional homonuclear COSY ^{1}H-NMR correlation spectrum of $[Co_2(bisebmp)_3]^{4+}$ in CD_3CN showing the diastereotopic protons H_8 and H_9.

E^c = 130 mV) as well as an irreversible wave at −1.28 V and a quasireversible wave at −1.36 V ($E^a - E^c$ = 140 mV) which are attributed to ligand-based reductions.[6,55] It is only slightly more difficult to reduce than $[Co(bipy)_3]^{2+}$ ($E_{1/2}$ = −0.95 V)[55] or $[Co(terpy)_2]^{2+}$ ($E_{1/2}$ = −0.77 V)[56] which suggests that mbmp is a π-acceptor similar to bipy which confirms the similar energies observed for the MLCT transitions in $[Cu(dmbipy)_2]^+$ and $[Cu(mbmp)_2]^+$. The most surprising feature in the voltammograms is the absence of a well-defined oxidation process, and we observe only a small irreversible wave around +0.8 V which differs strongly from the reversible oxidation waves obtained for $[Co(bipy)_3]^{2+}$ ($E_{1/2}$ = +0.32 V)[55] or $[Co(terpy)_2]^{2+}$ ($E_{1/2}$ = +0.27 V).[56] Similar behavior has already been reported by Lehn[6] with a mononuclear pseudooctahedral Co(II) complex which was attributed to a very slow process at the electrode surface.[32] Cyclic voltammograms of the dinuclear triple-helical complex $[Co_2(bismbmp)_3](ClO_4)_4$ parallel those found for the mononuclear complex with one quasireversible wave at $E_{1/2}$ = −1.05 V vs SCE in MeCN (Co(II)/Co(I); $E^a - E^c$ = 140 mV) as well as one irreversible wave at −1.29 V and a quasireversible wave at −1.43 V ($E^a - E^c$ = 120 mV) assigned to ligand-based reductions.[6,55] We do not observe a well-defined oxidation process for the dinuclear complex apart from a small wave around +0.77 V. However, controlled potential coulometric experiments (E = +1.2 V) show that 1.0 ± 0.1 electron per mole of complex is exchanged which might suggest the formation of a mixed oxidation state (Co(II),Co(III)) complex as proposed by Constable[57] for a dinuclear double-helical complex $[Co_2(quinquepyridyl)_2(OAc)]^{3+}$ where small irreversible waves between +0.32 and +0.74 V were assigned to oxidation of the complex. Similarly to quinquepyridyl, the ligands mbmp and bismbmp seem to stabilize the Co(II) cation,[57,58] but it is surprising that the metal-centered Co(II)/Co(I) process is more negative for the dinuclear complex than for the mononuclear analogue ($\Delta E_{1/2}$ = 90 mV). This observation indicates that the electrostatic interactions[12] are more than compensated by another phenomenon which we tentatively attribute to the deviation from pseudooctahedral geometry around Co(II) due to steric constraints of the methyl groups bound to the pyridine nucleus in the triple-helical complex.[14]

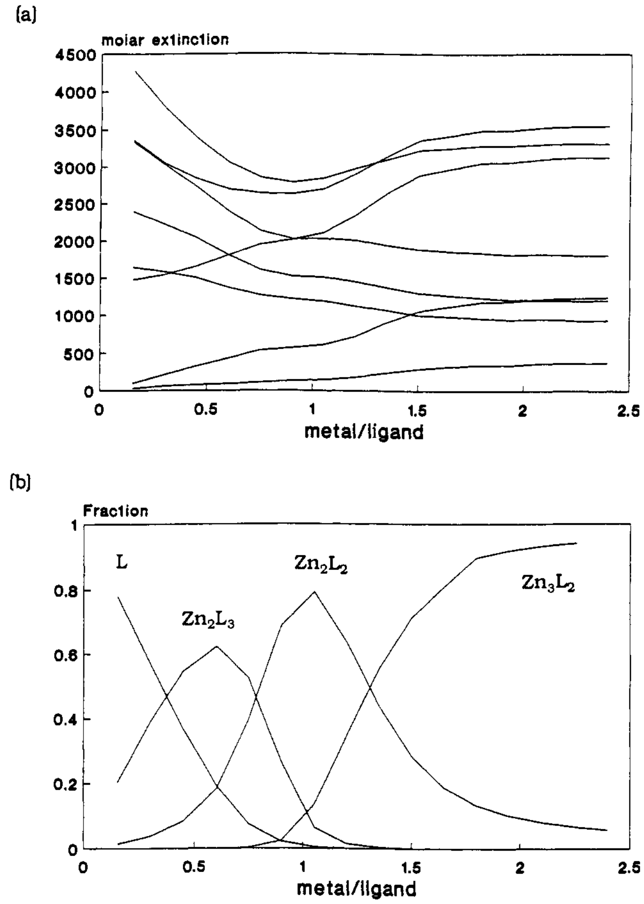

Figure 11. (a) Variation of observed molar extinction coefficients and (b) corresponding calculated speciation of ligand for the spectrophotometric titration of bismbmp (3) with Zn^{2+} in CH_3CN.

4. Complexes of Bismbmp with Zinc(II). A titration of bismbmp with $Zn(H_2O)_6(ClO_4)_2$ shows a complicated variation of the UV–visible spectrum for Zn:bismbmp ratios in the range 0.2–2.5 (Figure 11). However, the spectrophotometric data can be satisfactorily fitted with equilibria 4–6.

$$3\,\text{bismbmp} + 2\,Zn^{2+} \leftrightarrow [Zn_2(\text{bismbmp})_3]^{4+} \qquad \log(\beta_4) = 24.2\ (1.6) \quad (4)$$

$$2\,\text{bismbmp} + 2\,Zn^{2+} \leftrightarrow [Zn_2(\text{bismbmp})_2]^{4+} \qquad \log(\beta_5) = 19.4\ (1.4) \quad (5)$$

$$2\,\text{bismbmp} + 3\,Zn^{2+} \leftrightarrow [Zn_3(\text{bismbmp})_2]^{6+} \qquad \log(\beta_6) = 24.3\ (1.3) \quad (6)$$

The first two complexes $[Zn_2(bismbmp)_3]^{4+}$ and $[Zn_2(bismbmp)_2]^{4+}$ display the same stoichiometries as those found for the fully characterized triple-helical complex $[Co_2(bismbmp)_3]^{4+}$ and the double-helical complex $[Cu_2(bismbmp)_2]^{2+}$ and are thus tentatively assigned respectively to triple-helical and double-helical complexes with Zn(II). These results are not surprising if we consider that Zn(II) is known to accommodate either pseudotetrahedral or pseudo-octahedral geometry[59] and that a dinuclear double-helical complex $[Zn_2L_2]$ has been previously reported.[60] The complex $[Zn_3(bismbmp)_2]^{6+}$ has no precedent, but its existence is required for the fitting of the spectrophotometric data with a Zn:bismbmp ratio greater than 1.2. A plausible structure for this complex would have a tetrahedral Zn^{2+} bridging two $[Zn(bismbp)]^{2+}$ units in which each zinc is complexed by one-half of the ligand only; this structure would result from the

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opening up of the double-helical complex.

Discussion

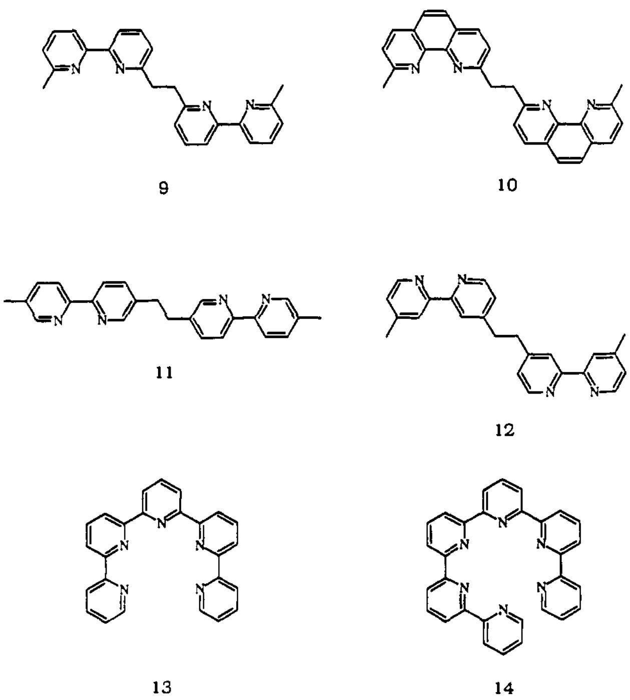
The results show that bismbmp is an efficient dinucleating ligand which forms a variety of dinuclear complexes. The coordination stereochemistry observed with the mononuclear ligand mbmp for Cu(I) and Co(II) is maintained in the dinuclear complexes, and this coordination stereochemistry controls the formation of the dinuclear complex, leading to a double-helical (bis-tetrahedral) complex with copper(I), and a triple-helical (bis-octahedral) complex with cobalt(II). For copper(I) the formation of the double-helical complex does not appear to be cooperative, since mononuclear $[Cu(bismbmp)_2]^+$ is observed by ^{1}H-NMR spectroscopy in nitromethane and is also inferred from the spectroscopic titration. The rapid exchange observed in the ^{1}H-NMR spectrum of $[Cu_2(bisebmp)_2]^{2+}$ at room temperature may arise from a rapid mononuclear ↔ dinuclear equilibrium.

For cobalt(II), however, the triple-helical complex is the only species observed in solution, either by electronic spectroscopy or by NMR. This suggests a cooperative formation of the dinuclear complex, the complexation of the first cobalt creating a favorable coordination environment for the second. Since the d^7 cobalt(II) ion is among those ions for which the transition octahedral → tetrahedral coordination involves the smallest loss of ligand field stabilization energy,[61] the double-helical complex $[Co_2(bismbmp)_2]^{4+}$ might be expected to be formed at high Co:ligand ratios, but there is no spectroscopic evidence for its formation. The structure[14] of $[Co_2(bismbmp)_3]^{4+}$ shows no stacking interactions, implying that the self-assembly is directed by the metal–ligand stereochemistry rather than interligand interactions as proposed for other polynuclear systems.[5,11,62] Molecular models suggest that stacking interactions are also absent in the dinuclear copper complex $[Cu_2(bismbmp)_2]^{2+}$.

The reaction of ligand bismbmp with zinc(II) produces a complicated mixture of complexes depending on the Zn:ligand ratio, but where the spectroscopic titration suggests the successive formation of a triple-helical complex $[Zn_2(bismbmp)_3]^{4+}$ and a double-helical complex $[Zn_2(bismbmp)_2]^{4+}$. The stability constant for the formation of $[Zn_2(bismbmp)_3]^{4+}$ (log β) = 24.2 (1.6)) is close to log (β) = 21.4 (6) found for $[Co_2(bismbmp)_3]^{4+}$ as expected from the Irving–Williams series.[63] The log (β) = 19.4 (1.4) observed for $[Zn_2(bismbmp)_2]^{4+}$ is significantly greater than that found for the double-helical $[Cu_2(bismbmp)_2]^{2+}$ (log (β) = 13.0 (3)), presumably due to the higher positive charge of Zn^{2+}. The observation of a double-helical complex for zinc but not for cobalt(II) may be attributed to the lack of stereochemical preference for the spherical d^{10} zinc(II) ion[60,61] as opposed to the ligand field induced preference for octahedral coordination for Co(II), and is further evidence for the role of the metal ion in directing the self-assembly reaction.

Only a few published papers have discussed the effect of varying the metal ion upon self-assembly reactions. Lehn and his collaborators[6] used the oligobipyridine **9** and the oligophenanthroline **10** which possess two bidentate α,α'-diimine donor groups similar to bismbmp, but connected by a flexible ethylene bridge (Chart I). Upon complexation to Cu(I), ligands **9** and **10** form the dinuclear helicates[5] $[Cu_2(\mathbf{9})_2]^{2+}$ and $[Cu_2(\mathbf{10})_2]^{2+}$, but complexation of **10** to cobalt(II) leads to the mononuclear pseudooctahedral complex $[Co(\mathbf{10})(CF_3SO_3)_2]$ where **10** acts as a tetradentate ligand occupying the four equatorial sites. The rigidity of phenanthroline groups constrains the dihedral angles between the pyridine rings to values much smaller than the values observed between pyridine and benzimidazole rings in the crystal structure of $[Co_2(bismbmp)_3]^{4+}$[14] (16.1–30.5°). When ligand **11** was treated with Fe(II), a complex $[Fe_2(\mathbf{11})_3]^{4+}$ containing two pseudooctahedral $[Fe(bipy)_3]$ chromophores was isolated.[6] No structure was reported for this compound, but a triple-helical structure is unlikely given the nonhelical structure of the similar compound $[Fe_2(\mathbf{12})_3]^{4+}$.[12]

Chart I



Constable and his collaborators have used the highly symmetrical polypyridines quinquepy (**13**) and sexipy (**14**) to prepare double-helical complexes with different metal ions.[9-11,57,64,65] Quinquepy may act as a pentadentate ligand in the mononuclear seven-coordinate $[Co(\mathbf{13})Cl_2]$[57] or as a bidentate–terdentate ligand toward two metal ions leading to double-helical structures. Thus, the reaction of **13** with Ni(II),[64] Cu(II),[11] or Co(II)[57] cations gives double-helical complexes $[M_2(\mathbf{13})_2(OAc)]^{3+}$ where one metal ion is complexed by two terpyridyl residues in a pseudooctahedral arrangement and the second metal ion is four-coordinated by the two remaining bipyridyl residues, the coordination sphere being completed by either a monodentate or a bidentate acetate group. The same type of geometry is found in the mixed valence complex $[Cu^{II}Cu^{I}(\mathbf{13})_2]^{3+}$, but in this case copper(I) occupies the pseudotetrahedral site formed by the two bipyridyl residues and no supplementary acetate group is coordinated.[11] In $[Pd_2(\mathbf{13})_2]^{4+}$, each Pd(II) is irregularly pentacoordinated by one terpyridyl and one bipyridyl residue of each strand displaying a head-to-tail arrangement.[65] For all these double-helical structures, Constable observed strong stabilizing stacking interactions between the aromatic groups of the two strands, suggesting that the double-helical arrangement of the ligands forming the strands serves as a mold for the entering metal ions which may then be stabilized by minor deformations of the backbone according to their stereochemical requirements. Similar results were obtained with the ligand sexipy (**14**) which acts as a bis(terdentate) ligand with pseudooctahedral Cd(II), Mn(II), Fe(II), or Cu(II) but as a tris(bidentate) ligand with Cu(I) and Ag(I).[10]

It is instructive to compare the structural features of the different ligands discussed above with bismbmp. The ligands **9–12** offer two bidentate binding sites joined by a flexible $-CH_2-CH_2-$ bridge which offers three torsional degrees of freedom. Although these ligands form dinuclear complexes, they are sufficiently flexible also to act as mononuclear ligands as shown by the isolation of $[Co(\mathbf{10})(CF_2SO_3)_2]$. The polypyridines used by Constable have only the inter-ring torsion angles as degrees of freedom,

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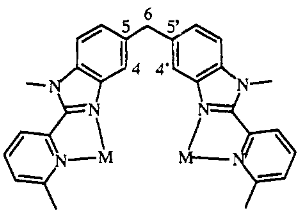
Chart II



but suffer, in comparison with **9–12** and bismbmp, from an ambiguity in their denticity; thus sexipyridyl can act as a bis(tridentate) ligand or as a tris(bidentate) ligand. It is indeed this variety of possible binding modes, coupled with their tendency to stabilize helical complexes via stacking interactions, that gives these ligands such a rich and varied chemistry.

The ligand bismbmp has two bidentate binding sites for metal cations, and the flexibility is limited to two benzimidazole–CH_2 torsion angles. However, examination of molecular models shows that steric repulsion between the hydrogen atoms in the 4-position of the benzimidazole rings should strongly destabilize a planar structure. Calculations using the Brugel molecular modeling program[66] and structural data from the X-ray crystal structure[14] of $[Co_2(bismbmp)_3]^{4+}$ show that the distance between the two H_4 hydrogen atoms is less than two van der Waals radii (2.4 Å)[67] if the torsion angle $\alpha(C_{4'}–C_{5'}–C_6–C_5)$ is less than 60° (if the torsion angle $\alpha(C_4–C_5–C_6–C_{5'})$ is held at 0°, Chart II). This constraint effectively prevents the ligand from adopting a planar structure and acting as a mononuclear tetradentate ligand and makes it an ideal ligand for the formation of dinuclear complexes. The methyl group in position 6 of the pyridine greatly increases the solubility of the ligand, and exercises some control on the stereochemistry of complexes by destabilizing a square-planar coordination as with 6,6′-dimethyl-2,2′-bipyridine; the crystal structure of $[Co_2(bismbmp)_3]^{4+}$ shows however that there is some repulsion between the methyl groups in the cobalt complex.[14]

Conclusions

The synthesis of the ligand bismbmp and its derivatives offers a ligand which combines two well-defined bidentate binding sites with a spacer group which constrains the ligand to adopt a conformation in which it can act as a bis(bidentate) ligand rather than a mononuclear tetradentate ligand. It is therefore ideally suited for the formation of dinuclear metal complexes via self-assembly reactions. The precise nature of the complex formed depends on the stereochemical preferences of the metal ion: copper(I) with a preference for tetrahedral coordination gives a double-helical structure, while cobalt(II), which favors octahedral coordination, gives a triple-helical complex in which three bismbmp ligands form the strands. While double-helical complexes are well established,[5-11] triple-helical complexes are much more rare. A very recent example used the assembly of three bidentate bipyridyl units around divalent metal ions to generate a triple-helical polypeptide[68] while a dinuclear triple-helical complex has been reported for a polydentate tripodal ligand,[69] but in neither case has a crystal structure been determined. The triple-helical complex $[Co_2(bismbmp)_3]^{4+}$ shows remarkable stability, both thermodynamic, with virtually quantitative formation of the complex in solutions at 10^{-4} M concentration, and kinetic, as shown by the resolution of the diastereotopic protons of the bisebmp complex. This stability is important in the perspective of assembly of still more complicated structures using polynuclear complexes as building blocks. The symmetry of the NMR spectra implies that the triple helix has high symmetry (D_3) in solution.

The results presented here are further examples of the ease with which rather symmetric molecules of some elegance may be formed by self-assembly around two or more metal ions. The comparison with previously published work allows us to identify some of the points which are essential if these self-assembly reactions are to give predictable products. Firstly, the ligand should possess separate and well-defined metal binding sites, either mono-, bi-, or terdentate, with good affinity for the metal used. As we have shown in this paper, the matching between the ligand binding sites and the stereochemical preferences of the metal ion will then control the structure adopted, as shown by the difference between copper(I) and cobalt(II) complexes of bismbmp, and the complexes of the polypyridine ligands of Constable. Finally, we must note the essential role of the spacer group in separating the different metal binding sites, and in disposing them in such a way as to favor formation of multinuclear complexes. The spacer group should possess enough flexibility to allow the ligand to bind strongly to the metal, but it should be rigid enough to limit the number of possible conformations. The importance of the spacer group is not unique to supramolecular coordination chemistry, but is also to be found in the chemistry of the nucleic acids, and Eschenmoser[70] has recently shown how the exchange of hexoses for pentoses in oligonucleotides leads to dramatic changes in their structure chemistry.

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Supplementary Material Available: A full table of bond distances and angles (Table SI) (4 pages); full details of the X-ray structure determination of $[Cu(mbmp)_2]ClO_4$ in the format of the Standard Crystallographic File Structure[71] (Table SII) (21 pages). Ordering information is given on any current masthead page.

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