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Self-Assembly and Interconversion of Tetranuclear Copper(II) Complexes

Katharina Isele,[†] Patrick Franz,[‡] Christina Ambrus,[‡] Gérald Bernardinelli,[§] Silvio Decurtins,[‡] and Alan F. Williams*,[†]

Department of Inorganic, Analytical and Applied Chemistry, University of Geneva, 30 quai Ernest Ansermet, CH 1211 Geneva 4, Switzerland, Department of Chemistry and Biochemistry, Universität Bern, Freiestrasse 3, 3009 Bern, Switzerland, and X-ray Crystallography Laboratory, University of Geneva, 24 quai Ernest Ansermet, CH 1211 Geneva 4, Switzerland

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The ligand 1,2-bis(benzimidazol-2-yl)-1,2-ethanediol (H_2bzimed, **1**) and its N-methylated analogue (H_2mbzimed**, 2**) form a variety of polynuclear complexes with copper(II), all of which contain a planar Cu_2O_2 lozenge as a central element and in which the bridging oxygen belongs to an alkoxo group of the ligand. Syntheses are reported for dinuclear $[Cu_2(Hmbzimed)_2](ClO_4)_2\cdot 1.5H_2O$, $Cu_2\mathbf{2}_2$, and the tetranuclear species $[Cu_4(Hbzimed)_4(ClO_4)_2](NO_3)_2\cdot 4H_2O$, $Cu_4\mathbf{1}_4$, $[Cu_4(Hmbzimed)_2(mbzimed)Cl_2](ClO_4)_2\cdot 2H_2O\cdot C_2H_5OH$, $Cu_4\mathbf{2}_3$, and *rac*-$[Cu_4(H_2bzimed)_4(bzimed)(ClO_4)_2](ClO_4)_4\cdot 1.5H_2O\cdot 3.5C_2H_5OH$, $Cu_4\mathbf{1}_5$. Crystal structures are reported for the tetranuclear species. $Cu_4\mathbf{1}_4$ shows a cubane structure, $Cu_4\mathbf{2}_3$ a stepped cubane structure, and *rac*-$Cu_4\mathbf{1}_5$ a novel structure in which one doubly deprotonated ligand lies between the two Cu_2O_2 units. Magnetic susceptibility measurements indicate that all complexes show antiferromagnetic coupling in the solid state. Studies in solution (ESI-MS, CD, NMR) show that $Cu_2\mathbf{2}_2$ and $Cu_4\mathbf{2}_3$ persist in solution but that $Cu_4\mathbf{1}_4$ dissociates partially and *rac*-$Cu_4\mathbf{1}_5$ completely. The six coordination modes of the ligands are discussed together with the effect of the N-methylation on the ligand conformation.

It has been remarked that the attention of coordination chemists is increasingly directed to polynuclear systems.[1] Complexes containing two or more metal ions allow the interaction of different metal centers offering new patterns in reactivity (as evidenced by the many multinuclear complexes in biology),[2] the transfer of energy between centers,[3,4] and magnetic exchange.[5] Polynuclear systems are ideal candidates for the synthesis of single-molecule magnets.[6] Despite the interest in the properties of such systems, synthetic methods have yet to reach the level of efficiency attained with mononuclear complexes. Indeed the term "serendipity" is frequently used in connection with the syntheses, although the many successes obtained by certain laboratories[7−11] would seem to support Pasteur's contention that "Fortune favors the prepared mind". Nonetheless, it is often difficult if not impossible to answer the question why one polynuclear complex is obtained rather than another. In this work, we present a system where the same metal and two very similar ligands form a variety of polynuclear complexes, show how they can interconvert, and discuss the factors favoring the formation of a given complex.

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* Author to whom correspondence should be addressed. E-mail: Alan.Williams@chiam.unige.ch.

[†] Department of Inorganic, Analytical and Applied Chemistry, University of Geneva.

[‡] Department of Chemistry and Biochemistry, University of Bern.

[§] Laboratory for X-ray Crystallography, University of Geneva.

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Chart 1. Di- and Tetranuclear Copper(II) Species

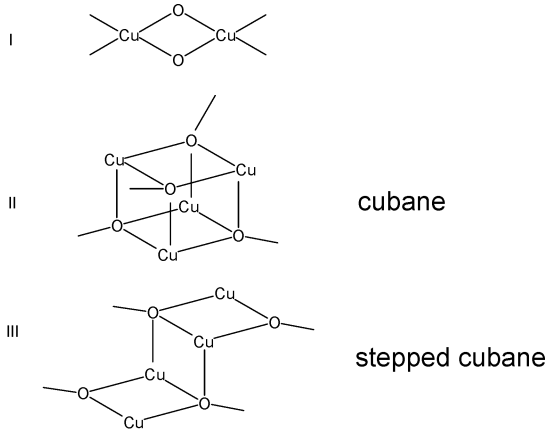
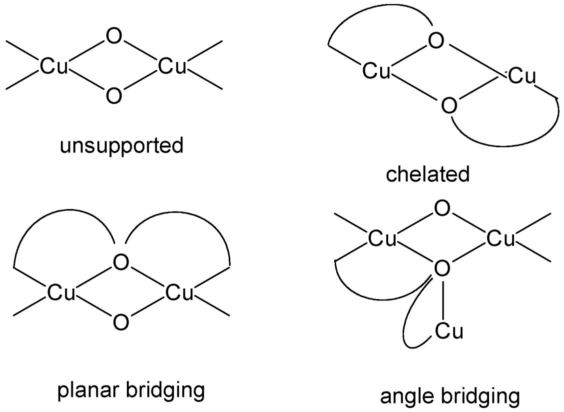


Chart 2. Structural Classification of Ligand Types



Copper(II) complexes have been particularly popular since the ion is paramagnetic and polynuclear clusters are easily accessible. Copper(II) forms many dinuclear complexes in which it shows a basically square planar coordination with two bridging ligands, very frequently hydroxide or alkoxide groups, linking the two metals (Chart 1, **I**). Copper(II) readily accepts a fifth ligand above the plane, and this offers a means of association of two dimeric units to give either the so-called cubane unit (Chart 1, **II**) or the stepped cubane (Chart 1, **III**).

Control over the formation of one or other of these species may be attained by introducing constraints into the ligands. The bridging hydroxide or alkoxide may be free (unsupported in Chart 2), part of a chelate ring involving one of the terminal ligands (chelated in Chart 2), or part of a ligand which supplies terminal ligands to more than one copper (bridging in Chart 2). We may distinguish between planar bridging, in which all four metal−oxygen bonds are coplanar, and angle bridging, where the planes defined by two pairs of metal−oxygen bonds are inclined to each other.

There is abundant structural data on such complexes. The first report of a type II cubane structure (Chart 1) featured a chelated bridging alkoxide based on ethanolamine,[12] and the same authors showed a few years later that if the five-membered chelate ring was increased to a six-membered one, then a dimeric structure (type **I** in Chart 1) was observed.[13,14] The tendency to form a cubane structure with a five-membered chelate ring is generally observed,[15] and there are many structures where an ethanolamine unit acts as the chelate ring.[12,14,16,17] Unsupported cubanes are known,[18−21] and there are two examples of angle-bridged cubanes.[22,23] The first report of a stepped cubane actually preceded the first cubane[24] and showed a chelating phenolate group. Stepped cubanes are less common than cubanes, but a number of structures have been reported and include unsupported complexes with bidentate diimine ligands such as bipy[25−28] and diketonates which act as terminal ligands[21] as well as chelating the bridging oxygen.[29] An interesting example of a highly structured ligand was observed with a tris(imidazole)-derivatized calix[6]arene ligand[30] $[Cu_4(L)_2(\mu\text{-}OH)_4Cl_2]^{2+}$. In this case two imidazoles of one ligand bound to one copper of a $Cu_2(\mu\text{-}OH)_2$ dimer and the third imidazole bound to a copper of the second dimer, the two dimers being arranged in the stepped cubane structure. Two chlorides complete the coordination sphere of the copper. Planar bridging ligands have been observed to give stepped cubanes[29] and dimers[31] but not cubanes. There is thus a relative abundance of structural data in the solid state for these compounds, although it does not allow one to draw many general conclusions about the factors favoring one structure over another. There are very little data concerning the solution behavior and in particular as to whether the structures observed in the solid actually persist in solution.

Our interest in this type of complex arises from our studies on ligands H_2bzimed, **1**, and H_2mbzimed, **2** (Chart 3). These chiral ligands are readily synthesized from tartaric acid and may act as facially coordinating tridentate ligands, forming

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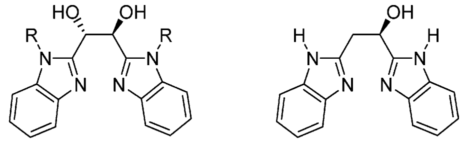
Chart 3. Ligands Discussed in This Work



R = H : **1,** H_2bzimed
R = CH_3 : **2,** H_2mbzimed

3

bis-ligand complexes with octahedral metal ions.[32] In the course of this work we noticed that copper(II) also formed complexes with a 1:1 metal ligand ratio as had been reported previously for the related ligand **3** (Chart 3), which forms a cubane with copper(II) in which the ligand adopts an angle-bridging mode.[23] In this article we report on the synthesis and structures of four complexes of ligands **1** and **2** with copper(II). We study to what extent these structures are maintained in solution and may be interconverted. The magnetic data are reported briefly.

Experimental Section

Safety Note. Although no problems were experienced in handling perchlorate compounds, these salts when combined with organic ligands are potentially explosive and should be manipulated with care and used only in small quantities.

Starting Materials. Ligands **1** and **2** were prepared as described previously.[32] Other compounds were purchased commercially and used as supplied unless specified otherwise.

Synthesis of Tetrakis(*SS*-1,2-bis(benzimidazol-2-yl)-1,2-ethanediolato)tetracopper Diperchlorate Nitrate, [Cu_4(Hbzimed)$_4$-(ClO_4)$_2$](NO_3)$_2$·$3H_2O$, $Cu_4$1$_4$. A mixture of $Cu(ClO_4)_2\cdot 6H_2O$ (0.0742 g, 0.2 mmol), $Cu(NO_3)_2\cdot 3H_2O$ (0.0484 g, 0.2 mmol), and *SS*-H_2bzimed (0.1177 g, 0.4 mmol) was dissolved in 1 mL of ethanol and 1 mL of water. Slow evaporation led within 1 week to blue prismatic crystals. Those were washed by water and vacuum-dried at 40 °C. Yield: 0.0870 g (49%). Solubility: soluble in DMSO, methanol, and ethanol; less soluble in acetonitrile and acetone; not soluble in water and chloroform. Anal. Calcd for $C_{64}H_{52}N_{16}O_8\cdot 4Cu\cdot 2NO_3\cdot 2ClO_4\cdot 3H_2O$: C, 42.68; H, 3.24; N, 13.97. Found: C, 42.73; H, 3.38; N, 14.06. IR (KBr disk; cm^{-1}): 3279 (br, s), 1618 (m), 1596 (m) 1459 (s), 1381 (s), 1335 (s), 1280 (s), 1229 (m), 1086 (s), 996 (m), 919 (w), 883 (w), 815 (m), 741 (s), 669 (m), 620 (s), 595 (m), 537 (m), 474 (m), 425 (m), 317 (m), 304 (m), 282 (m). UV/vis ($T = 22$ °C/$c = 0.0\ 833$ M/methanol) [λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1})]: fresh solution, 642 (73); 3 h, 687 (64). CD ($T = 22$ °C/$c = 0.00833$ M/methanol) [λ_{max}/nm ($\Delta\epsilon$/dm^3 mol^{-1} cm^{-1})]: fresh solution, 588 (0.3442), 697 (0.2735); 3 h, sh 588 (0.0687), 671 (0.1457). Visible reflectivity spectrum in MgO (λ_{min}/nm): 650. ESI-MS (DMSO) [*m*/*z* (%)]: 552.3 (100), [Cu_2(Hbzimed)$_2$(DMSO)$_5$]$^{2+}$; 513.2 (98), [Cu_2(Hbzimed)$_2$-(DMSO)$_4$]$^{2+}$; 474.2 (57), [Cu_2(Hbzimed)$_2$(DMSO)$_3$]$^{2+}$; 591.3 (28), [Cu_2(Hbzimed)$_2$(DMSO)$_6$]$^{2+}$; 435.2 (26), [Cu_2(Hbzimed)$_2$-(DMSO)$_2$]$^{2+}$; 791.2 (18), [Cu_2(Hbzimed)(bzimed)(DMSO)]$^{+}$/[Cu_4-(Hbzimed)$_2$(bzimed)$_2$(DMSO)$_2$]$^{2+}$; 869.2 (18), [Cu_2(Hbzimed)-(bzimed)(DMSO)$_2$]$^{+}$; 396.2 (12), [Cu_2(Hbzimed)$_2$(DMSO)]$^{2+}$; 357.1 (6), [Cu_2(Hbzimed)$_2$]$^{2+}$. ESI-MS (methanol) [*m*/*z* (%)]: 357.1 (100), [Cu_2(Hbzimed)$_2$]$^{2+}$; 565.1 (42), [Cu_4(bzimed)$_3$]$^{2+}$; 713.2 (19), [Cu_2-(Hbzimed)(bzimed)]$^{+}$/[Cu_4(Hbzimed)$_2$(bzimed)$_2$]$^{2+}$; 813.0 (11), [Cu_2-(Hbzimed)$_2$(ClO_4)]$^{+}$/[Cu_4(Hbzimed)$_4$(ClO_4)$_2$]$^{2+}$. ^{1}H NMR (CD_3OD, $T = 22$ °C) (δ/ppm): 10.07 (s, br, 1H_{arom}, tentative), 8.16 (s, 1H_{arom}), 7.50 (s, 2H_{arom}), 7.29 (s, 1H_{arom}), 6.27 (s, 1H_{arom}), 5.65 (s, 1H_{arom}), 4.51 (s, br, 1CH, tentative), 4.09 (s, br, 1CH, tentative). ^{1}H NMR (DMSO-d_6, $T = 22$ °C) (δ/ppm): 15.35 (s, br, 1 NH), 15.07 (s, br, 1 NH), 10.11 (s, br, 1H_{arom}, tentative), 8.46 (s, 1 H_{arom}), 8.03 (s, 1 OH), 7.92 (s, 1 H_{arom}), 7.45 (s, 1 H_{arom}), 7.24 (s, 1 H_{arom}), 6.14 (s, 1 H_{arom}), 5.40 (s, 1 H_{arom}), 4.04 (s, br, 2CH, tentative).

Synthesis of Tris(*RR*-1,2-bis(1-methylbenzimidazol-2-yl)-1,2-ethanediolato)dichlorotetracopper Diperchlorate, [Cu_4-(Hmbzimed)$_2$(mbzimed)Cl_2](ClO_4)$_2$·$2H_2O$·C_2H_5OH, $Cu_4$2$_3$. A mixture of $Cu(ClO_4)_2\cdot 6H_2O$ (0.0741 g, 0.2 mmol), $CuCl_2\cdot 2H_2O$ (0.0347 g, 0.2 mmol), and *RR*-H_2mbzimed (0.0966 g, 0.3 mmol) was dissolved in 4 mL of acetonitrile. Some drops of water were added until the color of the solution turned from olive green to grass green. Diffusion of ethanol into the solution via the gas phase led within 7 days to green prismatic crystals. The solution was filtered, and the crystals were washed by ethanol and vacuum-dried. Yield: 0.0871 g (56%). Solubility: insoluble in most organic solvents and water; soluble in DMSO. Anal. Calcd for $C_{54}H_{50}N_{12}O_4\cdot 4Cu\cdot 2ClO_4\cdot 2Cl$: C, 44.58; H, 3.46; N, 11.51. Found: C, 44.97; H, 3.86; N, 11.61. IR (KBr disk; cm^{-1}): 3400 (br,w), 3058 (br, w), 2925 (br, w), 1614 (m), 1485 (s), 1455 (s), 1420 (w), 1297 (m), 1095 (br, s), 1010 (m), 896 (m), 834 (w), 806 (w), 790 (w), 743 (s), 623 (m), 601 (w), 528 (w), 504 (w). UV/vis ($T = 22$ °C/$c = 0.0027$ M/DMSO) [λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1})]: 704 (57). CD ($T = 22$ °C/$c = 0.0027$ M/DMSO) [λ_{max}/nm ($\Delta\epsilon$/dm^3 mol^{-1} cm^{-1})]: 701 (−0.286), 604 (0.127). Visible reflectivity spectrum in MgO (λ_{min}/nm): 705. ESI-MS (DMSO) [*m*/*z* (%)]: 385.1 (100), [Cu_2(Hmbzimed)$_2$]$^{2+}$; 424.1 (44), [Cu_2(Hmbzimed)$_2$(DMSO)]$^{2+}$; 644.2 (42), [Cu_4(Hmbzimed)$_2$(mbzimed)(Cl)$_2$]$^{2+}$; 323.1 (42), [H_3mbzimed]$^{+}$; 463.1 (18), [Cu_2(Hmbzimed)$_2$(DMSO)$_2$]$^{2+}$; 683.1 (14), [Cu_4(Hmbzimed)$_2$(mbzimed)(Cl)$_2$(DMSO)]$^{2+}$; 1322.9 (5), [Cu_4(Hmbzimed)(mbzimed)$_2$(Cl)$_2$(H_2O)$_2$]$^{+}$; 1396.8 (5), [Cu_4-(Hmbzimed)$_2$(mbzimed)(Cl)$_2$(ClO_4)]$^{+}$; 722.2 (4), [Cu_4(Hmbzimed)$_2$-(mbzimed)(Cl)$_2$(DMSO)$_2$]$^{2+}$. ^{1}H NMR (DMSO-d_6, $T = 23$ °C) (δ/ppm): 28.10 (s, br, 1H_{arom}, tentative), 15.38 (s, br, 1H_{arom}, tentative), 13.80 (s, br, 1H_{arom}, tentative), 13.27 (s, 1H_{arom}), 12.93 (s, br, 2H_{arom}), 9.53 (s, br, 1 OH, tentative), 9.26 (s, br, 1CH, tentative), 7.19 (s, 1H_{arom}), 6.92 (m, br, 2H_{arom}), 6.83 (s, 1H_{arom}), 5.99 (s, H_{arom}), 5.80 (s, 1H_{arom}), 4.72 (s, br, CH, tentative), 3.83 (s, CH_3), 3.58 (3H s, CH_3), 1.99 (s, CH_3).

Synthesis of Pentakis(*rac*-1,2-bis(benzimidazol-2-yl)-1,2-ethanediolato)diperchloratotetracopper Tetraperchlorate, [Cu_4-(H_2bzimed)$_4$(bzimed)(ClO_4)$_2$](ClO_4)$_4$·$1.5H_2O$·$3.5C_2H_5OH$, $Cu_4$1$_5$. A mixture of $Cu(ClO_4)_2\cdot 6H_2O$ (0.1482 g, 0.4 mmol), *SS*-H_2bzimed (0.0589 g, 0.2 mmol), and *RR*- H_2bzimed (0.0589 g, 0.2 mmol) was dissolved in 3 mL of ethanol. Slow evaporation led within 3 weeks to blue prismatic crystals. The crystals were washed with water and vacuum-dried. Yield: 0.1499 g (59.7%). Solubility: soluble in DMSO, methanol, and acetonitrile; less soluble in ethanol; not soluble in water and chloroform. Anal. Calcd for $C_{80}H_{68}N_{20}O_{10}Cu_4\cdot 6ClO_4\cdot 1.5EtOH\cdot 6.5H_2O$: C, 39.84; H, 3.51; N, 11.22. Found: C, 39.75; H, 3.73; N, 11.21. IR (KBr disk; cm^{-1}): 3288 (br, s), 2018 (w), 1624 (m), 1597 (m), 1530 (m), 1455 (s), 1379 (m), 1321 (m), 1282 (m), 1227 (m), 1100 (br, s), 945 (s), 922 (m), 853 (w), 806 (w), 787 (w), 742 (s), 6624 (s), 518 (w). UV/vis ($T = 22$ °C/$c = 0.0106$ M/) [λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1})]: ethanol/water 711 (51), DMSO 732 (56), acetonitrile 710 (72), methanol 722 (63). Visible reflectivity spectrum in MgO (λ_{min}/nm): 704.

The following dissociation reactions of the tetramer in DMSO and methanol have been confirmed by ESI-MS and ^{1}H NMR

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spectroscopy. Dissociation in DMSO**:** $2[\mathrm{Cu_4(H_2bzimed)_4(bzimed)}]^{6+} \rightarrow 3[\mathrm{Cu_2(Hbzimed)_2}]^{2+} + 2[\mathrm{Cu(H_2bzimed)_2}]^{2+} + 2\mathrm{H}^{+}$. ESI-MS (DMSO) [*m*/*z* (%)]: 474.3 (100), $[\mathrm{Cu_2(Hbzimed)_2(DMSO)_3}]^{2+}$; 435.3 (83), $[\mathrm{Cu_2(Hbzimed)_2(DMSO)_2}]^{2+}$; 442.8 (74), $[\mathrm{Cu(H_2bzimed)_2(DMSO)_3}]^{2+}$; 481.8 (53), $[\mathrm{Cu(H_2bzimed)_2(DMSO)_4}]^{2+}$; 513.3 (4), $[\mathrm{Cu_2(Hbzimed)_2(DMSO)_4}]^{2+}$; 403.8 (38), $[\mathrm{Cu(H_2bzimed)_2(DMSO)_2}]^{2+}$; 396 (29), $[\mathrm{Cu_2(Hbzimed)_2(DMSO)}]^{2+}$; 357.3 (14), $[\mathrm{Cu_2(Hbzimed)_2}]^{2+}$; 365 (13), $[\mathrm{Cu(H_2bzimed)_2(DMSO)}]^{2+}$. ^{1}H NMR of $[\mathrm{Cu_2(Hbzimed)_2}]^{2+}$ ($\mathrm{Cu_2}\mathbf{1}_2$) (DMSO, $T = 22$ °C) (δ/ppm): 33.35 (s, br, 1 NH), 27.11 (s, br, 1 NH), 18.88 (s, 1H$_{\mathrm{arom}}$), 17.54 (s, 1H$_{\mathrm{arom}}$), 13.00 (s, br, 1OH), 12.27 (s, br, 1H$_{\mathrm{arom}}$, tentative), 9.13 (s, br, 1H$_{\mathrm{arom}}$, tentative), 6.99 (s, 1H$_{\mathrm{arom}}$), 6.89 (s, 1H$_{\mathrm{arom}}$), 6.57 (s, 1H$_{\mathrm{arom}}$), 6.45 (s, br, 1H$_{\mathrm{arom}}$). Dissociation in methanol in two steps: **(**1**)** $[\mathrm{Cu_4(H_2bzimed)_4(bzimed)}]^{6+} \rightarrow 2[\mathrm{Cu_2(Hbzimed)_2}]^{2+} + 1[\mathrm{H_4bzimed}]^{2+}$; (2) $2[\mathrm{Cu_2(Hbzimed)_2}]^{2+} \Leftrightarrow$ *rac*-$[\mathrm{Cu_4(Hbzimed)_4}]^{4+}$ ($\mathrm{Cu_4}\mathbf{1}_4'$). ESI-MS (methanol/DMSO impurity) [*m*/*z* (%)]: 357.2 (100), $[\mathrm{Cu_2(Hbzimed)_2}]^{2+}$; 396.3 (64), $[\mathrm{Cu_2(Hbzimed)_2(DMSO)}]^{2+}$; 295.3 (53), $[\mathrm{H_3bzimed}]^{+}$; 435.2 (40), $[\mathrm{Cu_2(Hbzimed)_2(DMSO)_2}]^{2+}$; 813.1 (17), $[\mathrm{Cu_2(Hbzimed)_2(ClO_4)}]^{+}$; 711.2 (10), $[\mathrm{Cu_2(Hbzimed)(bzimed)}]^{+}$; 650.3 (10), $[\mathrm{Cu(H_2bzimed)(Hbzimed)}]^{+}$. ^{1}H NMR of $[\mathrm{Cu_2(Hbzimed)_2}]^{2+}$ ($\mathrm{Cu_2}\mathbf{1}_2$) (methanol, $T = 22$ °C) (δ/ppm): 19.34 (s, 1H$_{\mathrm{arom}}$), 18.19 (s, 1H$_{\mathrm{arom}}$), 12.57 (s, br, 1H$_{\mathrm{arom}}$, tentative), 9.72 (s, br, 1H$_{\mathrm{arom}}$, tentative), 6.96 (m, 2H$_{\mathrm{arom}}$), 6.59 (s, 1H$_{\mathrm{arom}}$), 6.44 (s, 1H$_{\mathrm{arom}}$). ^{1}H NMR of $[\mathrm{H_4bzimed}]^{2+}$ (methanol, $T = 22$ °C) (δ/ppm): 7.70 (m, 4H$_{\mathrm{arom}}$), 7.55 (m, 4H$_{\mathrm{arom}}$), 5.75 (s, 2 CH). ^{1}H NMR of *rac*-$[\mathrm{Cu_4(Hbzimed)_4}]^{4+}$ ($\mathrm{Cu_4}\mathbf{1}_4'$) (methanol, $T = 22$ °C) (δ/ppm): 9.79 (1H$_{\mathrm{arom}}$, br, superposition of two broad signals of species $\mathrm{Cu_4}\mathbf{1}_4'$ and $\mathrm{Cu_2}\mathbf{1}_2$), 7.99 (1H$_{\mathrm{arom}}$, s), 12.57 (1H$_{\mathrm{arom}}$, tentative, br), 9.72 (1H$_{\mathrm{arom}}$, tentative, br), 6.96 (2H$_{\mathrm{arom}}$, m), 6.59 (1H$_{\mathrm{arom}}$, s), 6.44 (1H$_{\mathrm{arom}}$, s).

Synthesis of Bis(*SS*-1,2-bis(1-methylbenzimidazol-2-yl)-1,2-ethanediolato)dicopper Diperchlorate, $[\mathbf{Cu_2(Hmbzimed)_2}](\mathbf{ClO_4})_2\cdot$1.5H$_2O, Cu_2$2$_2$. A mixture of $\mathrm{Cu(ClO_4)_2\cdot6H_2O}$ (0.1098 g, 0.3 mmol) and *SS*-H$_2$mbzimed (0.0967 g, 0.3 mmol) was dissolved in 15 mL of hot ethanol. A turquoise precipitate was formed. The suspension was maintained at 60 °C overnight. The cooled solution was filtered and the crystalline turquoise powder dried in a vacuum. Yield: 0.111 g (75%). Solubility: soluble in DMSO and acetonitrile; less soluble in methanol and ethanol; not soluble in water and chloroform. Anal. Calcd for $\mathrm{C_{36}H_{34}N_8O_4\cdot2Cu\cdot2ClO_4\cdot1.5H_2O}$: C, 43.43; H, 3.75; N, 11.25. Found: C, 43.48; H, 3.99; N, 11.20. IR (KBr disk; cm^{-1}): 3423 (br, m), 3063 (w), 2956 (w), 2360 (w), 1616 (m), 1485 (s), 1457 (s), 1423 (m), 1324 (m), 1299 (m), 1275 (w), 1247 (w), 1091 (s, br), 1010 (w), 933 (w), 901 (m), 804 (w), 791 (w), 741 (s), 683 (w), 623 (s), 595 (w), 554 (w), 530 (w), 500 (w), 413 (m, br), 356 (w). UV/vis ($T = 22$ °C/$c = 0.0151$ M) [$\lambda_{\max}$/nm (ϵ/dm^3 mol^{-1} cm^{-1})]: DMSO 738 (62), acetonitrile 692 (59), methanol 712 (55). CD ($T = 22$ °C/$c = 0.0151$ M) [$\lambda_{\max}$/nm ($\Delta\epsilon$/dm^3 mol^{-1} cm^{-1})]: DMSO 584 (−0.0451), 684 (0.0624), acetonitrile 544 (−0.0382), 659 (0.1476), methanol 566 (−0.0560), 672 (0.1030). Visible reflectivity spectrum in MgO ($\lambda_{\min}$/nm): 689. ESI-MS (DMSO) [*m*/*z* (%)]: 424.1 (100), $[\mathrm{Cu_2(Hmbzimed)_2(DMSO)}]^{2+}$; 463.1 (70), $[\mathrm{Cu_2(Hmbzimed)_2(DMSO)_2}]^{2+}$; 385.2 (38), $[\mathrm{Cu_2(Hmbzimed)_2}]^{2+}$; 868.8 (12), $[\mathrm{Cu_2(Hmbzimed)_2(ClO_4)}]^{+}$; 946.8 (5), $[\mathrm{Cu_2(Hmbzimed)_2(ClO_4)(DMSO)}]^{+}$; 502.2 (4), $[\mathrm{Cu_2(Hmbzimed)_2(DMSO)_3}]^{2+}$. ESI-MS (acetonitrile) [*m*/*z* (%)]: 385.2 (100), $[\mathrm{Cu_2(Hmbzimed)_2}]^{2+}$; 426.2 (14), $[\mathrm{Cu(Hmbzimed)(CH_3CN)}]^{+}$; 869.1 (6), $[\mathrm{Cu_2(Hmbzimed)_2(ClO_4)}]^{+}$. ESI-MS (methanol) [*m*/*z* (%)]: 385.2 (100), $[\mathrm{Cu_2(Hmbzimed)_2}]^{2+}$; 869.1 (9), $[\mathrm{Cu_2(Hmbzimed)_2(ClO_4)}]^{+}$. ^{1}H NMR (DMSO, $T = 26$ °C) (δ/ppm): 20.36 (s, 1H$_{\mathrm{arom}}$), 19.20 (s, 1H$_{\mathrm{arom}}$), 14.05 (s, br, 1H$_{\mathrm{arom}}$, tentative), 13.17 (s, br, OH), 9.90 (s, br, 1H$_{\mathrm{arom}}$, tentative), 6.87 (s, 1H$_{\mathrm{arom}}$), 6.80 (s, 1H$_{\mathrm{arom}}$), 6.57 (s, 1H$_{\mathrm{arom}}$), 6.49 (s, 1H$_{\mathrm{arom}}$), 5.11 (s, br, 1 or 2 CH, tentative), 3.00 (s, CH$_3$), 1.35 (s, CH$_3$). ^{1}H NMR (acetonitrile, $T = 20$ °C) (δ/ppm): 23.04 (s, 1H$_{\mathrm{arom}}$), 21.98 (s, 1H$_{\mathrm{arom}}$), 14.59 (s, br, 1H$_{\mathrm{arom}}$, tentative), 13.00 (s, br, OH), 11.45 (s, br, 1H$_{\mathrm{arom}}$, tentative), 6.94 (s, 1H$_{\mathrm{arom}}$), 6.79 (s, 1H$_{\mathrm{arom}}$), 6.61 (s, 1H$_{\mathrm{arom}}$), 6.38 (s, 1H$_{\mathrm{arom}}$), 2.61 (s, CH$_3$, the methyl peak covers the CH signal), 0.69 (s, CH$_3$). ^{1}H NMR (methanol, $T = 22$ °C) (δ/ppm): 21.06 (s, 1H$_{\mathrm{arom}}$), 20.01 (s, 1H$_{\mathrm{arom}}$), 13.49 (s, br, 1H$_{\mathrm{arom}}$, tentative), 10.54 (s, br, 1H$_{\mathrm{arom}}$, tentative), 6.93 (s, 1H$_{\mathrm{arom}}$), 6.80 (s, 1H$_{\mathrm{arom}}$), 6.55 (s, 1H$_{\mathrm{arom}}$), 6.45 (s, 1H$_{\mathrm{arom}}$), 4.31 (s, br, 1 or 2 CH, tentative), 2.88 (s, CH$_3$), 1.04 (s, CH$_3$).

Table 1. X-ray Crystallographic Data for $[\mathrm{Cu_4(Hbzimed)_4(ClO_4)_2}](\mathrm{NO_3})_2\cdot4\mathrm{H_2O}$ ($\mathrm{Cu_4}\mathbf{1}_4$), $[\mathrm{Cu_4(Hmbzimed)_2(mbzimed)Cl_2}](\mathrm{ClO_4})_2\cdot2\mathrm{H_2O}\cdot\mathrm{C_2H_5OH}$ ($\mathrm{Cu_4}\mathbf{2}_3$), and *rac*-$[\mathrm{Cu_4(H_2bzimed)_4(bzimed)(ClO_4)_2}](\mathrm{ClO_4})_4\cdot1.5\mathrm{H_2O}\cdot3.5\mathrm{C_2H_5OH}$ (*rac*-$\mathrm{Cu_4}\mathbf{1}_5$)

	$\mathrm{Cu_4}\mathbf{1}_4$	$\mathrm{Cu_4}\mathbf{2}_3$	*rac*-$\mathrm{Cu_4}\mathbf{1}_5$
formula	$\mathrm{C_{64}H_{60}N_{18}Cu_4Cl_2O_{26}}$	$\mathrm{C_{56}H_{60}N_{12}Cu_4Cl_4O_{17}}$	$\mathrm{C_{87}H_{92}N_{20}Cu_4Cl_6O_{39}}$
fw	1822.5	1569.2	2508.9
cryst system	orthorhombic	orthorhombic	triclinic
space group	$P2_12_12_1$	$P2_12_12_1$	$P\bar{1}$
a (Å)	16.8565(6)	15.4291(10)	17.2589(12)
b (Å)	17.3548(9)	16.9541(8)	18.3400(11)
c (Å)	24.6059(11)	25.2232(9)	20.7116(12)
α (deg)	90	90	110.350(7)
β (deg)	90	90	101.109(7)
γ (deg)	90	90	111.292(7)
V (Å^3)	7198.2(6)	6598.0(6)	5331.7(9)
Z	4	4	2
T (K)	200	200	200
μ (mm^{-1})	1.34	1.51	1.03
D_{calcd} (g cm^{-3})	1.682	1.580	1.564
data measd	91 133	83 120	46 988
unique data (R_{int})	14 056 (0.079)	12 315 (0.063)	19 558 (0.069)
obsd data	6810	7449	8587
R,[a] wR[b]	0.032, 0.032	0.043, 0.048	0.059, 0.058
weights, *p*[c]	0.000 3	0.000 3	0.000 15
S	1.24(1)	1.98(2)	1.77(1)
Flack param[50]	−0.01(1)	−0.01(2)	

[a] $R = \Sigma|F_o - F_c|/\Sigma F_o$. [b] $wR = [\Sigma[\omega(F_o^2 - F_c^2)^2]/\Sigma[\omega(F_o^2)^2]]^{1/2}$. [c] $\omega = 1/[\sigma^2(F_o) + p(F_o)^2]$.

Magnetic Measurements. Magnetic susceptibility data were collected with a Quantum Design SQUID magnetometer (XL5S) operating in the temperature range 300−2 K with a field of 1000 G. The data were corrected for sample holder contribution (saran foil) and for the diamagnetic contribution estimated using Pascal's constants.[5]

Physical and Spectroscopic Measurements. Proton NMR spectra were recorded on a Varian Gemini instrument at 300 MHz. Infrared spectra were recorded as KBr disks on a Perkin-Elmer Spectrum One spectrometer. UV/vis spectra were recorded with a Perkin-Elmer Lambda 900 UV/vis/NIR machine; reflectivity spectra used the same instrument equipped with a 60 mm integration sphere. The white standard was PTFE. Samples were prepared in a 1 mm cell after mixing the compound with roughly nine times the amount of MgO. CD spectra were recorded on a Jasco J-715 spectrometer.

X-ray Crystallographic Data Collection and Refinement of Structures. All structures were measured at 200 K using a Stoe IPDS diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). They were solved by direct methods, and refinements and other calculations were carried out with the XTAL system[33] and the ORTEP program.[34] Crystallographic data for the three structures are summarized in Table 1. The crystallographic

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(33) Hall, S. R.; Flack, H. D.; Stewart, J. M. *XTAL 3.2 User's Manual*; Universities of Western Australia, Geneva, and Maryland, 1992.

(34) Johnson, C. K. *ORTEP II Report ORNL-5138*; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

data have been deposited with the Cambridge Crystallographic Data Centre (12 Union Road, Cambridge CB2 1EZ, U.K.; fax (+44) 1223-336-033 or deposit@ccdc.cam.ac.uk) and may be obtained free of charge from www.ccdc.cam.ac.uk/conts/retieving.html. The reference numbers are 260575−260577.

Structure of Tetrakis(*SS*-1,2-bis(benzimidazol-2-yl)-1,2-ethanediolato)tetracopper Diperchlorate Nitrate, $[\mathrm{Cu_4(Hbzimed)_4(ClO_4)_2](NO_3)_2 \cdot 4H_2O}$, $\mathrm{Cu_4}\mathbf{1}_4$. The structure was solved with SHELXS-97.[35] One of the nitrate anions was disordered and was modeled as two ions sharing a common nitrogen with relative populations of 70 and 30%. The hydrogens of hydroxo groups and water molecules were not observed.

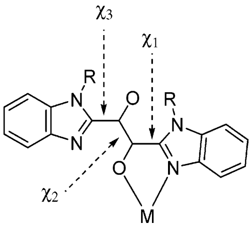
Structure of Tris(*RR*-1,2-bis(1-methylbenzimidazol-2-yl)-1,2-ethanediolato)dichlorotetracopper Diperchlorate, $[\mathrm{Cu_4(Hmbzimed)_2(mbzimed)Cl_2](ClO_4)_2 \cdot 2H_2O \cdot C_2H_5OH}$, $\mathrm{Cu_4}\mathbf{2}_3$. The structure was solved with MULTAN-87.[36] Only one of the hydrogens of the hydroxo groups was observed and was refined with a fixed displacement parameter, before being fixed in the final stage of refinement. The ethanol molecule was disordered as were the two water sites O2w and O3w, refined isotropically and with population parameters of 0.75 and 0.25, respectively.

Structure of Pentakis(*rac*-1,2-bis(benzimidazol-2-yl)-1,2-ethanediolato)diperchloratotetracopper Tetraperchlorate, *rac*-$[\mathrm{Cu_4(H_2bzimed)_4(bzimed)(ClO_4)_2](ClO_4)_4 \cdot 1.5H_2O \cdot 3.5C_2H_5OH}$, $\mathrm{Cu_4}\mathbf{1}_5$. The structure was solved with SHELXS-97.[35] The atoms of the complex and the two perchlorate ions bonded to copper were well resolved, but the other anions and the solvent molecules were more or less disordered and were refined with restraints on bond lengths and angles.

Results

Synthesis of Complexes. Reaction of equimolar amounts of copper(II) perchlorate and ligand $\mathrm{H_2bzimed}$ in aqueous ethanol gave blue crystals of $[\mathrm{Cu_4(Hbzimed)_4}]^{4+}$ which could be crystallized as a mixed nitrate and perchlorate salt by slow evaporation of the solution. The complex was characterized by X-ray crystallography, elemental analysis, electrospray mass spectrometry (ESI-MS), and ^{1}H NMR spectroscopy. If ligand $\mathrm{H_2mbzimed}$ was used instead of $\mathrm{H_2bzimed}$, the product was the turquoise dinuclear species $[\mathrm{Cu_2(Hmbzimed)_2}]^{2+}$. Unfortunately, crystals of X-ray quality could not be obtained for this compound, but ESI-MS and NMR measurements discussed below clearly establish the complex to be binuclear. If chloride is present, the course of the reaction is changed: a mixture of $[\mathrm{Cu_2(Hmbzimed)_2}]^{2+}$ and green $[\mathrm{Cu_4(Hmbzimed)_2(mbzimed)Cl_2}]^{2+}$ crystallized. The yield of $[\mathrm{Cu_4(Hmbzimed)_2(mbzimed)Cl_2](ClO_4)_2}$ could be optimized by using stoichiometric amounts of $\mathrm{H_2mbzimed}$, $\mathrm{CuCl_2}$, and $\mathrm{Cu(ClO_4)_2}$. The crystal structure of this compound is described below. In a final experiment, a racemic mixture of *RR*-$\mathrm{H_2bzimed}$ and *SS*-$\mathrm{H_2bzimed}$ was reacted with copper(II) perchlorate in ethanol. Slow evaporation led to blue prismatic crystals characterized by X-ray crystallography as $[\mathrm{Cu_4}(\mathit{rac}\text{-}\mathbf{1})_5](\mathrm{ClO_4})_6$.

Chart 4. Torsion Angles Used To Characterize the Conformation of Ligands



It is worth noting that although the copper−ligand ratio affected the yield of the reaction, it did not determine the product. Thus, a 1:1 copper:ligand ratio gave $\mathrm{Cu_2L_2}$, $\mathrm{Cu_4L_3}$, $\mathrm{Cu_4L_4}$, or $\mathrm{Cu_4L_5}$, the nature of the species formed depending on the nature of the ligand, the presence of chloride, and the enantiopurity of the sample.

Structural Studies. The ligands $\mathrm{H_2bzimed}$ and $\mathrm{H_2mbzimed}$ are flexible and may adopt several conformations characterized by the torsion angles in Chart 4.

χ_1 is defined as the torsion angle N(R)−C−C−O for the five-membered chelate, χ_2 as the O−C−C−O torsion, and χ_3 as O−C−C−N(R) for the six-membered chelate (O−C−C−C−N) when present. χ_2 in previous structures generally has a value[32] close to 180° corresponding to a trans-conformation for the oxygens, with the benzimidazole functions gauche. Intuitively one would not expect χ_1 and χ_3, which depend on rotation about a carbon−benzimidazole bond, to be particularly well defined. We have carried out calculations in another context[37] showing that the rotation barrier is small for R = H but increases significantly if R = Me, the methyl group exerting significant repulsive effect. Of course the formation of a chelate cycle will have a significant effect on χ_1 and χ_3, and in complexes where $\mathrm{H_2bzimed}$ and $\mathrm{H_2mbzimed}$ act as tridentate facially coordinating ligands[32] typical values for χ_1 and χ_3 are around 150 and 60°, respectively.

Structure of $[\mathrm{Cu_4(Hbzimed)_4(ClO_4)_2](NO_3)_2 \cdot 4H_2O}$. This compound adopts a cubane structure (**II** in Chart 1) with deprotonated alcohol functions acting as triply bridging ligands as observed by van Albada et al. for the copper(II) complex of ligand **3**.[23] The ligand Hbzimed acts as an angle bridging ligand (Chart 2), and the complex (Figure 1) has approximate D_2 symmetry.

The copper coordination sphere may be described as 4 + 2, with four ligands roughly in a plane (two benzimidazoles from different ligands and two bridging alkoxo functions) and bound tightly (bond distances in the range 1.92−2.00 Å) and two further ligands (a bridging alkoxo function and the oxygen of a perchlorate) above and below the plane at distances between 2.50 and 2.82 Å. The ideal cubane structure is distorted in two ways: It is elongated along one dimension so that the $\mathrm{Cu_4O_4}$ cube may be regarded as two $\mathrm{Cu_2O_2}$ squares weakly associated. Cu−O distances within the squares average 1.95 Å, those between the squares average 2.71 Å. This was described as type I distortion by Mergehenn and Haase.[38] The second distortion consists of a

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(35) Sheldrick, G. M. University of Göttingen: Göttingen, Germany, 1997.

(36) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, D.; Declercq, J. P.; Woolfson, M. M. Universities of York and Louvaine-La-Neuve: York, U.K., Louvaine-La-Neuve, Belgium, 1987.

(37) Matthews, C. J.; Bernardinelli, G.; Morgantini, P.-Y.; Lavergnat, F.; Williams, A. F. Unpublished observations.

(38) Mergehenn, R.; Haase, W. *Acta Crystallogr.* **1977**, *B33*, 1877−1882.

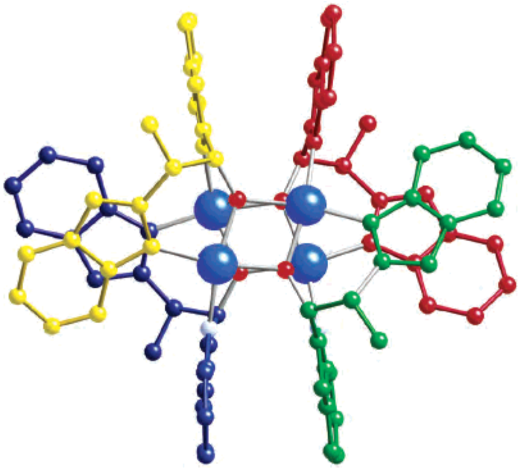

Figure 1. View of the complex $[Cu_4(Hbzimed)_4]^{4+}$ along one of the pseudo-2-fold axes.

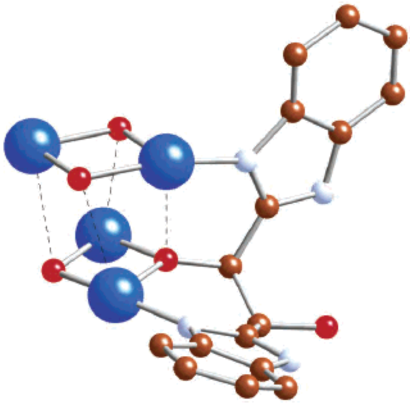

Figure 2. Cu_4O_4 unit of the complex $[Cu_4(Hbzimed)_4]^{4+}$ showing the twisting of the Cu_2O_2 lozenges and the angle bridging mode adopted by ligand H_2bzimed.

slight rotation of one Cu_2O_2 square with respect to the other about the axis passing through the center of each square. The distortion, together with a representation of the angle bridging mode, is shown in Figure 2. Figure 3 gives a stereoview of the complex and shows the coordination of the perchlorates.

The long Cu−O bonds are part of five-membered chelate cycles. Two perchlorate anions are bound above and below the cubane and placed on the axis of elongation; each donates two oxygens to complete the 4 + 2 coordination of the copper atoms. The eight benzimidazole functions form four roughly parallel pairs with interplane distances in the range 3.3−3.4 Å. Although this might suggest some stacking interaction, the overlap of the planes is quite small. The conformation of all four ligands is identical, with a trans conformation of the alcohol functions (average value of χ_2: 172°) and average values of 155 and 20° for χ_1 and χ_3. The NH functions show hydrogen bonding to nitrate and lattice water molecules.

Structure of $[Cu_4(Hmbzimed)_2(mbzimed)Cl_2](ClO_4)_2 \cdot 2H_2O \cdot C_2H_5OH$. In this structure the ligands all adopt a conformation in which the benzimidazoles are trans and the alcohol oxygens are gauche, with χ_2 values between 57 and 73°. The four copper ions are roughly coplanar and form a parallelogram. Below the plane of the coppers, ligand **b** with both alcohol functions deprotonated binds to all four coppers via two nitrogens and two alkoxide functions (Figure 4). We designate this mode of coordination as μ_4-syn. Above the plane of the coppers two singly deprotonated ligands (**a**, **c**) act as planar bridging ligands (Chart 2), each one to two of the copper ions. The complex has approximate C_2 symmetry, the 2-fold axis passing through the quadruply bridging, fully deprotonated, ligand and perpendicular to the plane of the coppers. The two planar bridging ligands **a** and **c** are thus related by this axis and show an intramolecular stacking interaction with the imidazole function of one ligand lying over the phenyl group of the other.

The copper ions have essentially square planar coordination and may be regarded as forming two Cu_2O_2 lozenges (Figure 5). Two coppers have N_2O_2 coordination and two have N_2OCl coordination, the chloride ions completing the coordination of the copper. The copper ions of one Cu_2O_2 lozenge interact weakly with a perchlorate ion acting as a bridging ligand (as seen for $[Cu_4(Hbzimed)_4(ClO_4)_2](NO_3)_2 \cdot 4H_2O$ above) with Cu−O distances of 2.599(8) and 2.531(8) Å, and one of the other pair interacts with a water molecule (Cl−O distance 2.46(1) Å) which forms an intramolecular hydrogen bond to an alcohol function. The Cu_2O_2 lozenges are parallel to the pseudo-2-fold axis and are slipped with respect to each other in an arrangement topologically identical with the stepped cubane (Chart 1), but the Cu−O distances between lozenges are very long (>2.7 Å).

Structure of *rac*-$[Cu_4(H_2bzimed)_4(bzimed)(ClO_4)_2](ClO_4)_4 \cdot 1.5H_2O \cdot 3.5C_2H_5OH$. This compound was the only racemate studied. It shows three different ligand binding modes. Ligand **a** adopts a conformation with the alcohol functions trans and the benzimidazole groups mutually gauche. It is doubly deprotonated and bridges all four copper ions, two bound on one side and two on the other (Figure 6), and the conformation may be described as μ_4-anti. The copper ions again form Cu_2O_2 lozenges, linked by ligand **a** acting as a chelating bridge to each lozenge (Chart 2). The ligands **b** and **c**, of opposite chirality with respect to **a**, are bound to the other sides of the lozenges and adopt a planar bridging mode seen for $[Cu_4(Hmbzimed)_2(mbzimed)Cl_2](ClO_4)_2 \cdot 2H_2O \cdot C_2H_5OH$. The benzimidazoles are trans, and the oxygens gauche (χ_2 close to 60°). Finally, ligands **d** and **e**, of chirality identical with that of **b** and **c**, bind via one benzimidazole function to complete the square planar coordination of the copper, and the vicinal alcohol function is also bound weakly (bond distances 2.349(8) and 2.489(8) Å) to the same copper. The bond lengths are similar to those observed in the two previous structures. Ligands **d** and **e** adopt a trans conformation for the oxygens (χ_2: 175(1) and 178(1)°). There is a slight ambiguity over the protonation state of the ligands: the complex as a whole has a charge 6+, as established by the number of perchlorate anions. We have assumed that the bridging alkoxo functions are all deprotonated since we have not observed any cases in which they are protonated, and the sum of bond angles at the oxygen atoms lies in the range 355−360°, indicating little

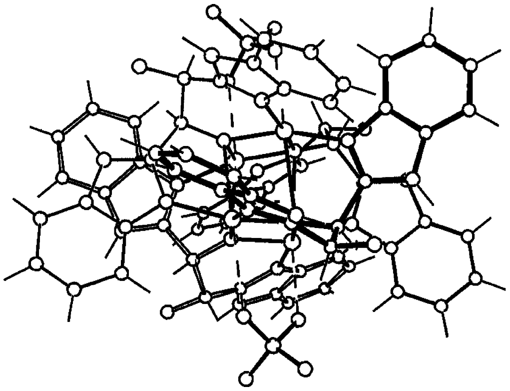

Figure 3. Stereoview of $[Cu_4(Hbzimed)_4](ClO_4)_2{}^{2+}$.

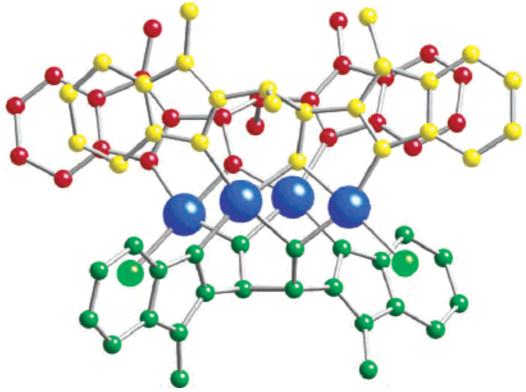

Figure 4. Structure of the cation $[Cu_4(Hmbzimed)_2(mbzimed)Cl_2]^{2+}$. The pseudo-2-fold axis relating the yellow (**a**) and the red (**c**) ligand is vertical, and the terminal chloride ligands are behind (left) and in front (right) of the doubly deprotonated ligand (**b** in green).

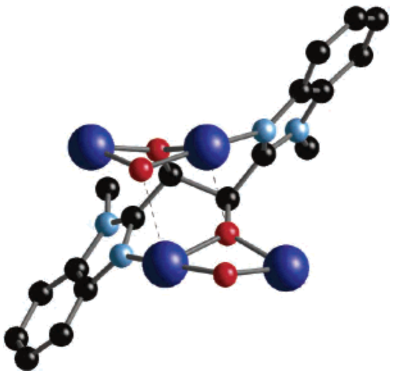

Figure 5. Partial structure of $[Cu_4(Hmbzimed)_2(mbzimed)Cl_2]^{2+}$, showing the two Cu_2O_2 lozenges linked by the doubly deprotonated ligand **b**.

pyramidal character. This requires the noncoordinated benzimidazole functions to be protonated and that the cation should formally be written as $[Cu_4(bzimed)(Hbzimed)_2(H_3bzimed)_2]^{6+}$.

The copper ions all show weak interactions with a fifth ligand: in two cases this is the vicinal alcohol function of the monodentate benzimidazole ligands **d** and **e** (Cu−O distances 2.349(8) and 2.489(8) Å) and in the others a weak interaction with perchlorate anions (distances 2.59(1) and 2.67(1) Å). Finally, the uncoordinated (and presumably protonated) benzimidazoles of ligands **d** and **e** are almost parallel to the benzimidazoles of ligands **b** and **c**, and although the overlap is small, the distances around 3.4 Å are consistent with a stacking interaction. The complex as a whole has approximate C_2 symmetry, the 2-fold axis bisecting ligand **a**. The uncoordinated alcohols and the benzimidazole NH groups are involved in hydrogen bonding to water, ethanol, and perchlorate.

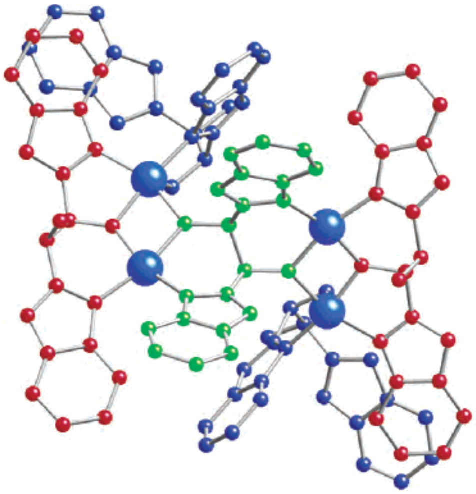

Figure 6. Structure of the complex $[Cu_4(bzimed)(Hbzimed)_4]^{6+}$. The green ligand (**a**) has a chirality opposite that of the red ligands (**b** and **c**) and the blue ligands (**d** and **e**).

Solid-State Properties. The infrared spectra for the complexes for which structural data are available agree with the X-ray structures, notably by the splitting of the perchlorate band in complexes where coordinated perchlorate was observed. The diffuse reflectance spectra of the d−d bands were recorded since these offer an interesting comparison with solution data. The band minima were the following: for $[Cu_4(Hbzimed)_4(ClO_4)_2](NO_3)_2 \cdot 4H_2O$, 650 nm; for $[Cu_2(Hmbzimed)_2](ClO_4)_2 \cdot 1.5H_2O$, 689 nm; for $[Cu_4(Hmbzimed)_2(mbzimed)Cl_2](ClO_4)_2 \cdot 2H_2O \cdot C_2H_5OH$, 705 nm; for $[Cu_4(H_2bzimed)_4(bzimed)(ClO_4)_2](ClO_4)_4 \cdot 1.5H_2O \cdot 3.5C_2H_5OH$, 704 nm.

The magnetic properties of this type of complex have been studied in great detail over the years,[39,40] and a magneto−structural correlation based on the Cu−O−Cu bridging angle α has been established (eq 1).[41]

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$$-2J = 82.1\alpha - 7857\ \text{cm}^{-1} \qquad (1)$$

The complexes for which we have structures all show Cu−O−Cu angles greater than 99° and on the basis of this correlation would be expected to show antiferromagnetic coupling in the Cu_2O_2 units with J values more negative than $-100\ \text{cm}^{-1}$. The magnetic data qualitatively confirm this. The compound $[Cu_4(H_2bzimed)_4(bzimed)(ClO_4)_2](ClO_4)_6\cdot 1.5H_2O\cdot 3.5C_2H_5OH$ is essentially diamagnetic. It possesses two structurally very similar Cu_2O_2 units with an average angle of 104.5°, and with application of the magneto−structural correlation, this corresponds to a J value of $-359\ \text{cm}^{-1}$. Also $[Cu_4(Hbzimed)_4(ClO_4)_2](NO_3)_2\cdot 4H_2O$ is essentially diamagnetic. For both Cu_2O_2 units together the average Cu−O−Cu angle is 103.6° corresponding to a J value of $-322\ \text{cm}^{-1}$. The magnetic data for $[Cu_4(Hmbzimed)_2(mbzimed)Cl_2](ClO_4)_2\cdot 2H_2O\cdot C_2H_5OH$ (Figure 7) show χT values well below the expected spin-only values. At 300 K the χT value is 0.12 emu K mol^{-1} in comparison to the spin-only value which lies typically in the range 0.36−0.45 emu K mol^{-1}. Only the complex $[Cu_2(Hmbzimed)_2](ClO_4)_2\cdot 1.5H_2O$, which we postulate from solution data to be a dinuclear species, shows a χT value at 300 K of 0.368 emu K mol^{-1} which approaches the spin-only value for two uncoupled $S = 1/2$ systems (Figure 7). However, the magnetic moment decreases steadily as the temperature falls, and we were unable to fit the data satisfactorily with a simple dimer model.[42]

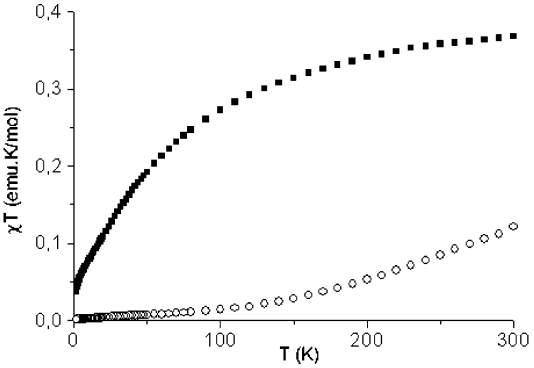

Figure 7. Observed values of χT for $[Cu_4(Hmbzimed)_2(mbzimed)Cl_2](ClO_4)_2\cdot 2H_2O\cdot C_2H_5OH$ (○) and $[Cu_2(Hmbzimed)_2](ClO_4)_2\cdot 1.5H_2O$ (■).

Structure in Solution. To study the structure in solution as well as the interconversion of the four structures we have used a combination of UV/vis, circular dichroism (CD), electrospray mass spectrometry (ESI-MS), and ^1H NMR spectroscopy. Copper(II) complexes generally have rather long relaxation times and are thus suitable for study by EPR spectroscopy but not by NMR. However, the incorporation of the paramagnetic ion in a di- or polynuclear structure results in new, efficient electronic relaxation mechanisms,[43] and NMR spectroscopy of copper(II) complexes is possible. There are now several cases where polynuclear copper(II) complexes have been found to give useful NMR spectra.[42,44−47] We will discuss initially the characterization and then the interconversion reactions observed.

$[Cu_2(SS\text{-}Hmbzimed)_2](ClO_4)_2\cdot 1.5H_2O$. ESI-MS measurements in acetonitrile, methanol, and DMSO showed a clean spectrum with peaks corresponding to $[Cu_2(SS\text{-}Hmbzimed)_2]^{2+}$ and $[Cu_2(SS\text{-}Hmbzimed)_2](ClO_4)^+$. In acetonitrile, weaker peaks showed that adducts with one or two solvent molecules were also formed. There was no sign of species of higher nuclearity. The UV/vis spectrum in acetonitrile showed a broad band at 692 nm (very close to the value of 689 nm observed in the solid state) which was red shifted to 712 and 738 nm in methanol and DMSO, respectively. Measurements at different concentrations showed no shift or change in extinction coefficient, arguing against a dimer−tetramer equilibrium. The CD spectrum was quite different from those of other species (see below) and showed three bands in acetonitrile, a negative peak at 544 nm, a positive band at 659 nm, and a rise to a third, positive band around 850 nm (the upper wavelength limit of the instrument). Spectra in methanol and DMSO were similar but slightly red-shifted. The ^1H NMR spectrum (Figure 8a) shows peaks spread out over a range of 24 ppm. The spectrum is essentially the same in acetonitrile, methanol, or DMSO, the only significant difference being the disappearance of a broad peak around 13 ppm in methanol, attributed to the exchangeable, noncoordinated alcohol OH, and a broad peak around 5 ppm observed in methanol and DMSO but missing in acetonitrile. Variable-temperature measurements established that this peak lies under the methyl signal seen at 2.61 ppm in acetonitrile. The methyl signals may readily be assigned by their greater intensity. The aromatic protons may be partially identified by a COSY spectrum which shows cross-peaks between the two sharp signals around 22 ppm and the four signals around 7 ppm. The remaining two aromatic protons are attributed to the broad signals at 11 and 15 ppm. The protons not so far accounted for are the two protons of the C*H*OH functions. One, assumed to be associated with the noncoordinated alcohol function, is attributed to the peak around 2.6 ppm, which is covered in acetonitrile by a methyl signal. The final proton, attributed to a bridging alkoxide CHO^-, could not be observed, but since it would be expected to be only about 3.5 Å from the two copper centers, this is perhaps not surprising. A possible structure for the complex is shown in Chart 5.

This structure is consistent with the two halves of the ligand being inequivalent, but the two ligands equivalent and the binding mode of the ligand is similar to the planar bridging mode of two of the three ligands in $[Cu_4(Hmbzimed)_2(mbzimed)Cl_2]^{2+}$. The complex as drawn has a 2-fold axis perpendicular to the Cu_2O_2 plane, but we could equally imagine a structure in which the 2-fold axis passes through the two copper atoms, which would then be inequivalent. The available data do not allow us to distinguish between the two, although we prefer the structure in which the two

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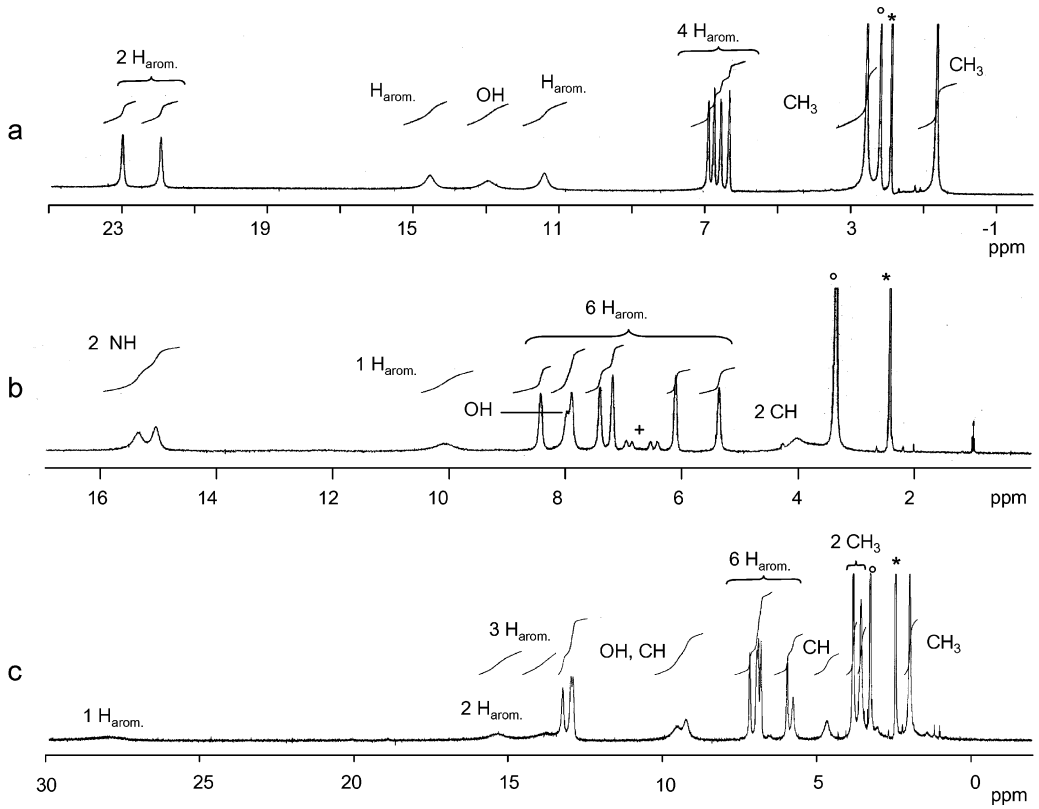
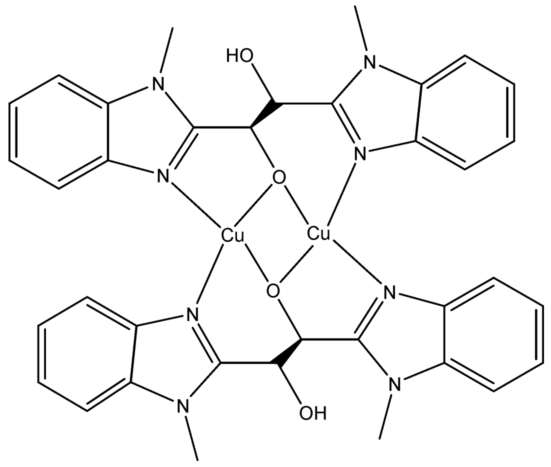


Figure 8. ^{1}H NMR spectrum of (a) $[Cu_2(SS\text{-}Hmbzimed)_2](ClO_4)_2\cdot 1.5H_2O$ in CD_3CN, (b) $[Cu_4(SS\text{-}Hbzimed)_4(ClO_4)_2](NO_3)_2\cdot 4H_2O$ in DMSO-d_6, and (c) $[Cu_4(RR\text{-}Hmbzimed)_2(RR\text{-}mbzimed)Cl_2](ClO_4)_2\cdot 2H_2O\cdot C_2H_5OH$ in DMSO-d_6. Key: (*) solvent peak; (°) water peak; (+) signals of the dimeric dissociation product.

Chart 5. Proposed Structure for $[Cu_2(SS\text{-}Hmbzimed)_2]^{2+}$



coppers are equivalent. The effect of changing the temperature is quite small: in the range −40 to +40 °C the maximum peak shift was less than 2 ppm toward the diamagnetic region of the spectrum. In principle the temperature dependence of the shifts may be used to derive exchange coupling parameters J [42] but the accuracy of such values is quite low given the limited temperature range and the small changes in chemical shift. This problem was also found for the tetranuclear species discussed below where the chemical shift changes were even smaller and where the presence of several J values and the observation of partial dissociation vitiates any attempt to extract J values.

$[Cu_4(SS\text{-}Hbzimed)_4(ClO_4)_2](NO_3)_2\cdot 4H_2O$. ESI-MS in methanol solution showed $[Cu_2(Hbzimed)_2]^{2+}$ as the strongest peak, but peaks were also observed for $[Cu_4(bzimed)_3]^{2+}$ and a peak centered at m/z 713 could be identified as a mixture of $[Cu_2(Hbzimed)(bzimed)]^+$ and $[Cu_4(Hbzimed)_2(bzimed)_2]^{2+}$ from the isotopic pattern. In DMSO solution, only the dimer was observed. UV/vis and CD spectroscopy confirmed the dissociation of $[Cu_4(Hbzimed)_4]^{4+}$. In methanol the UV/vis spectrum of a freshly prepared solution showed a broad band with a maximum at 642 nm, comparable with the diffuse reflectance spectrum of the solid (λ_{max} = 650 nm), but when the sample was left standing, the band broadened and moved to longer wavelengths, with a maximum at 687 nm observed at the equilibrium after 3 h. The CD spectrum of the fresh solution showed two positive bands at 588 and 697 nm, but when the sample was left standing, new positive bands appeared at 672 and 850 nm, very similar to those observed for $[Cu_2(SS\text{-}Hmbzimed)_2]^{2+}$. The CD spectrum suggested strongly that an equilibrium between dinuclear and tetranuclear species was established. In DMSO the dissociation of the tetramer was faster and apparently complete.

^{1}H NMR confirmed the conclusions of the other studies. A fresh solution in methanol showed a broad signal around 4 ppm, six sharp signals in the range 5−9 ppm which were shown by a COSY spectrum to be aromatic protons, and a broad signal at 10 ppm which we believe to be an aromatic proton. In DMSO, three further signals associated with the two NH functions and an OH function were observed (Figure 8b). Assuming the peak at 4 ppm to be an aliphatic proton, there are two protons missing (one aromatic and one aliphatic), but these are presumably too close to the para-

Table 2. Observed Conformations for Ligands **1** and **2** in the Solid State[a]

mode no.	coordn	χ_1 (deg)	χ_2 (deg)	χ_3 (deg)	ref
1	nonbridging, tridentate	148	173	51	32
2	μ_3, angle bridging	155	172	20	$[Cu_4(Hbzimed)_4]^{4+}$
3	μ_4, anti	0	175	3	$[Cu_4(bzimed)(H_2bzimed)_4]^{6+}$
4	μ_2, planar bridging	172	66	107	$[Cu_4(bzimed)(H_2bzimed)_4]^{6+}$, $[Cu_4(mbzimed)(Hmbzimed)_2Cl_2]^{2+}$
5	μ_4, syn	140	57	130	$[Cu_4(mbzimed)(Hmbzimed)_2Cl_2]^{2+}$
6	monodentate	174	60	110	$[Cu_4(bzimed)(H_2mbzimed)_4]^{6+}$

[a] For definition of the torsion angles χ, see Chart 4.

magnetic copper centers. When the sample was left standing, a new spectrum appeared which was very similar to $[Cu_2(SS\text{-}Hmbzimed)_2]^{2+}$, as may readily be seen by the two signals around 18 ppm, and this is assigned to $[Cu_2(SS\text{-}Hbzimed)_2]^{2+}$. In methanol roughly 30% of the tetramer dissociates in agreement with the CD results, but in DMSO, essentially complete conversion was observed, although there were traces of another product which was not identified.

$[Cu_4(RR\text{-}Hmbzimed)_2(RR\text{-}mbzimed)Cl_2](ClO_4)_2\cdot 2H_2O\cdot C_2H_5OH$. This compound was soluble only in DMSO. The ESI-MS spectrum showed its strongest peak at *m*/*z* 1322.9 corresponding to $\{[Cu_4(RR\text{-}Hmbzimed)_2(RR\text{-}mbzimed)Cl_2](OH)(OH_2)\}^+$. Other peaks were observed corresponding to $[Cu_4(RR\text{-}Hmbzimed)_2(RR\text{-}mbzimed)Cl_2]^{2+}$ and $\{[Cu_4(RR\text{-}Hmbzimed)_2(RR\text{-}mbzimed)Cl_2](ClO_4)\}^+$. Satellite peaks corresponding to DMSO adducts were also observed. These data suggest that the complex is stable in solution, although a peak corresponding to $[Cu_2(SS\text{-}Hmbzimed)_2]^{2+}$ was also observed. The UV/vis spectrum with a maximum at 704 nm agreed with the diffuse reflectance spectrum of the solid, and the CD spectrum showed a positive band at 604 nm and a negative band at 701 nm. Over a period of several days, signals due to the dimer gradually appear representing 25% of the spectral intensity after 12 days.

The ^1H NMR spectrum was concentrated in the range 0−15 ppm, although two broad features were observed around 15 and 29 ppm (Figure 8c). COSY spectra could be recorded and, as above, allowed the identification of aromatic protons. In this case three triplets of aromatic protons could be observed: this is in agreement with the crystal structure, where one ligand lies on a 2-fold axis, which relates the other two ligands. Three methyl resonances of equal intensity were observed, again in agreement with the solid-state structure. Integration of the spectrum indicated 24 protons compared to 25 expected from the crystal structure.

***rac*-$[Cu_4(bzimed)(H_2bzimed)_4](ClO_4)_6\cdot 1.5H_2O\cdot 3.5C_2H_5OH$.** This compound dissociates completely in solution in methanol or DMSO. ESI-MS in methanol showed the formation of $[Cu_2(Hbzimed)_2]^{2+}$ and protonated ligand, while in DMSO we observed $[Cu_2(Hbzimed)_2]^{2+}$ and the mononuclear species $[Cu(H_2bzimed)_2]^{2+}$. The UV/vis spectra in DMSO, methanol, and acetonitrile were consistent with this, showing maxima close to those observed for $[Cu_2(Hmbzimed)_2]^{2+}$. The ^1H NMR spectrum corresponds to that assigned to $[Cu_2(SS\text{-}Hbzimed)_2]^{2+}$ above and is very similar to that of $[Cu_2(SS\text{-}Hmbzimed)_2]^{2+}$. Since we used a racemic mixture of ligands, this suggests that there is a self-sorting process leading to homochiral products and that the heterochiral products are not formed. After standing for 24 h, the sample in methanol showed a slightly different spectrum, with the appearance of new peaks which could be assigned to $[Cu_4(Hbzimed)_4]^{4+}$. This confirms that the dimer−tetramer conversion is indeed an equilibrium.

Interconversion Experiments. The characterization experiments in solution having established the dimer−tetramer equilibrium, we carried out two further experiments on the formation and interconversion of complexes. The first concerned the formation of $[Cu_2(Hmbzimed)_2]^{2+}$: addition of an equimolar amount of ligand $SS\text{-}H_2mbzimed$ to copper(II) perchlorate solution induced a weak CD signal in the region of the copper d−d transition which was similar to that reported for $[Cu(SS\text{-}H_2mbzimed)_2]^{2+}$.[32] On addition of 1 equiv of triethylamine, however, the CD spectrum of $[Cu_2(SS\text{-}Hmbzimed)_2]^{2+}$ was obtained quantitatively. The second experiment concerned the chlorocomplex $[Cu_4(RR\text{-}Hmbzimed)_2(RR\text{-}mbzimed)Cl_2]^{2+}$. Since the chloride appeared to be quite strongly bound, as shown by the ESI-MS data, it seemed possible that it could be playing a structural role. We investigated the effect of adding $CuCl_2\cdot 2H_2O$ to a solution of $[Cu_2(Hmbzimed)_2]^{2+}$ in DMSO with stoichiometric ratio 1:2. The ^1H NMR spectrum showed the appearance of new peaks which corresponded to the spectrum of $[Cu_4(RR\text{-}Hmbzimed)_2(RR\text{-}mbzimed)Cl_2]^{2+}$ reported earlier. The two peaks around 13 ppm were particularly good indicators of the reaction. The conversion was not complete even after 2 h, and we believe that the reaction 2 attains a position of equilibrium. This is confirmed by the partial dissociation of the tetramer in DMSO within several days mentioned above. Thus, this experiment does establish that the formation of $[Cu_4(SS\text{-}Hmbzimed)_2(SS\text{-}mbzimed)Cl_2]^{2+}$ is driven by chloride and that the interconversion is possible.

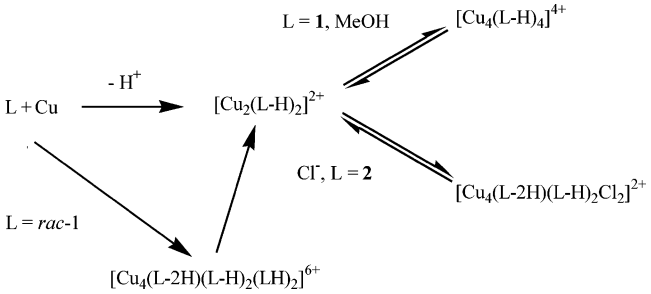
$$2[Cu_2(SS\text{-}Hmbzimed)_2]^{2+} + CuCl_2\cdot 2H_2O \leftrightarrow [Cu_4(SS\text{-}Hmbzimed)_2(SS\text{-}mbzimed)Cl_2]^{2+} + Cu^{2+} + SS\text{-}H_2mbzimed \quad (2)$$

Discussion

The structures presented here, taken with those published previously,[32] show the ligands $H_2bzimed$ and $H_2mbzimed$ to possess a considerable variety of coordination modes. Table 2 gives a summary of the conformations observed as characterized by the values of the torsion angles χ_{1-3}. The values given are averages over noncrystallographic symmetry where present and typically vary by a few degrees between structures.

The conformations may be classed according to the value of χ_2 as trans or gauche for the O−C−C−O torsion angle.

Scheme 1. Interconversion of Complexes Observed in This Work



Methylation at the nitrogen of the benzimidazole has no effect for modes nos. 1, 4, and 5 and is unlikely to affect the trivial case of no. 6. However, we have seen that H_2mbzimed does not form the cubane structure observed for $[Cu_4(Hbzimed)_4]^{4+}$, and examination of Table 2 suggests that this may be a result of the value of χ_3 close to zero for this conformation (no. 2), which would bring the methyl group very close to the noncoordinated alcohol function. Similarly we might expect that mode no. 3 would be unfavorable for a methylated ligand, and this is supported by examination of the structure of $[Cu_4(bzimed)(H_2bzimed)_4]^{6+}$. The methylation of the ligand is thus a means of exerting some control over the conformation of the ligand and thereby over the nature of the polynuclear species formed.

The results of the solution studies are summarized in Scheme 1. The complex isolated from the racemate, $[Cu_4(bzimed)(Hbzimed)_2(H_3bzimed)_2]^{6+}$, is unstable in solution, and we presume that its formation arises from its lower solubility or greater ease of crystallization than the complex $[Cu_2(L\text{-}H)_2]^{2+}$, which we were never able to crystallize. NMR spectroscopy showed no difference in solution between racemic mixtures of ligands and enantiopure ligands and allowed us to exclude the formation of heterochiral species, thus indicating a certain selectivity. The difficulty of crystallizing $[Cu_2(L\text{-}H)_2]^{2+}$ is presumably responsible for the formation of $[Cu_4(L\text{-}H)_4]^{2+}$ in the solid state for ligand H_2bzimed, where steric hindrance to the adoption of the μ_3 angle bridging mode (no. 2) is absent. The cubane species is in equilibrium with the dinuclear species in solution.

In the presence of chloride, the tetranuclear species $[Cu_4(mbzimed)(Hbzimed)_2Cl_2]^{2+}$ is formed and is, rather surprisingly, much more stable in solution than $[Cu_4(Hbzimed)_4]^{2+}$. We suspect this greater stability to arise from two effects: the greater negative charge on the ligands reduces the overall charge on the complex, thus reducing the Coulombic pressure toward dissociation; the observation of an intramolecular stacking between the two μ_2, planar bridging ligands. The arrangement in which the imidazole fragment lies over the phenyl fragment has been shown to be favorable in the solid state,[48] and intramolecular stacking has been shown previously to stabilize the formation of higher nuclear species.[49]

In conclusion, the two ligands H_2bzimed and H_2mbzimed form a variety of polynuclear complexes with copper(II) and show a variety of coordination modes. Selection of one mode over another may be achieved by control of the ligand conformation: methylation at the exterior of the ligand offers one way of influencing this, as shown by the differences between the two ligands. We are currently studying the effect of chelate ring size on the conformation of similar ligands. The results in solution show that the solid-state structures are not necessarily retained in solution and that interconversion occurs. From an experimental point of view, the power of NMR spectroscopy for the study of polynuclear copper(II) complexes is confirmed, and the CD spectra show significant changes in these complexes, even when the d−d bands of copper(II) do not.

Acknowledgment. We thank the Swiss National Science Foundation for their support of this work.

Supporting Information Available: Tables of bond lengths and angles for the three structures (Tables S1−S3), figures showing atom numbering and ellipsoids for the crystal structures, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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