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Binuclear Copper(I) Complexes Derived from Xylyl Binucleating Ligands and Their Carbonyl and Imidazole Adducts

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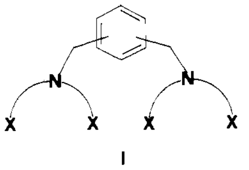
The binuclear copper(I) complexes of the ligands, *N,N,N′,N′*-tetrakis[2-(4-Z-benzylidenimino)ethyl]-α,α'-diamino-*m*-xylene, MXBA (Z = H) and MXPNB (Z = NO_2), have been obtained as diperchlorate salts. The complexes are unreactive toward dioxygen in the solid state and in solution provided that dry solvents are used. Binding by the donor groups of the ligands to the copper(I) centers has been investigated by IR and NMR spectroscopy. It has been concluded that in solution two imine and one tertiary amine nitrogen donors are coordinated to each metal ion, with additional binding by a solvent molecule. In the solid state the imine groups are coordinated, while binding by the tertiary amine groups cannot be established. These binuclear complexes form dicarbonyl and diimidazole adducts that are stable to oxidation but display somewhat weak binding of copper(I) to the added ligand. Electronic, and in the case of the diimidazole adducts, perhaps also steric effects account for this apparently low affinity of copper(I) for the added ligands.

Introduction

Binuclear copper complexes containing metal centers in close proximity are the subject of recent extensive investigation since these structural units are thought to be involved in a variety of important biochemical processes, especially oxygen transport[1] and oxygen activation by oxidase[2] and monooxygenase enzymes.[3,4] A number of binuclear copper(II)[5-9] and copper(I)[9-11] complexes have therefore been reported and studied as models of metal–metal interactions and redox catalysis. The metal centers of these complexes are often incorporated into the cavity of macrocyclic polydentate ligands, though a special interest has recently focused on the synthesis and reactivity of binuclear copper(I) and copper(II) complexes of a series of binucleating ligands derived from α,α'-diamino-*o*-, -*m*-, or -*p*-xylene (I).[12-15] These xylyl residues can be easily conju-



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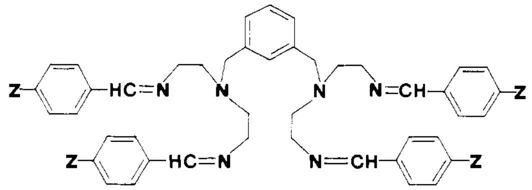

Z = H , NO_2

II

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gated with flexible alkyl chains carrying a variety of nitrogen, sulfur, or oxygen donor atoms (X), thereby enabling a control of structure and reactivity of the metal centers upon systematic change of the donor sets. Binuclear complexes of "wishbone" ligands of type I have provided copper(I)[13a] and cobalt(II)[16] systems which react reversibly with dioxygen and copper systems with oxidase[15a] and monooxygenase[14b] activity. In this paper we report the binuclear copper(I) complexes of *N*,*N*,-*N'*,*N'*-tetrakis[2-(4-Z-benzylidenamino)ethyl]-α,α'-diamino-*m*-xylene (II), MXBA (Z = H) and MXPNB (Z = NO_2). These copper(I) complexes with nitrogen donor atoms are unreactive toward dioxygen and form stable carbon monoxide and imidazole adducts.

Experimental Section

All reagents and solvents were reagent grade. Acetonitrile and DMF were distilled from calcium hydride; the other solvents, acetonitrile-d_3 and acetone-d_6, were dried and stored over molecular sieves (3 Å). Tetrakis(acetonitrile)copper(I) perchlorate was prepared according to a literature method.[17] Diphthaloyldiethylenetriamine was obtained as described by Martell et al.[12] The synthesis of the copper(I) complexes was performed under an atmosphere of purified, dried nitrogen with use of Schlenk glassware. Although these complexes are stable toward oxidation by dry oxygen, they are somewhat moisture sensitive and were therefore stored under an inert atmosphere. Elemental analyses were from the microanalytical laboratory of the University of Milan and the Mikroanalytisches Labor Pascher, Bonn, West Germany. Proton NMR spectra were obtained with a Bruker WP-80 spectrometer operating at 80 MHz and using a pulsed Fourier transform technique. Infrared spectra were recorded on a Nicolet MX-1E FT-IR instrument.

α,α'-Bis(diphthaloyldiethylenetriamino)-*m*-xylene. Diphthaloyldiethylenetriamine (33.0 g, 90 mmol), α,α'-dibromo-*m*-xylene (8.9 g, 34 mmol), and dry sodium carbonate (7.8 g, 74 mmol) were refluxed in anhydrous DMF (350 mL) for 40 h. The solution was filtered hot and cooled to room temperature with stirring. Precipitation of the product began to occur upon cooling and was completed by the addition of cold water (~30 mL). The crude product was collected by filtration, washed with boiling ethanol, filtered hot, and dried under vacuum (yield 35%). Anal. Calcd for $C_{48}H_{40}N_6O_8$: C, 69.49; H, 4.86; N, 10.13. Found: C, 69.10; H, 4.76; N, 9.74. IR (KBr): 3080 w, 2960 w, 2820 w, 1790 s, 1730 vs, 1630 m, 1410 s, 1340 m, 1200 m, 1120 m, 1090 s, 1020 m, 870 m, 790 w, 715 s cm^{-1}.

1,3-Bis[(bis(2-aminoethyl)amino)methyl]benzene Hexahydrochloride. α,α'-Bis(diphthaloyldiethylenetriamino)-*m*-xylene (8.7 g, 10.5 mmol) and aqueous hydrochloric acid (1:2; 250 mL) were refluxed overnight. The solution was cooled to room temperature, evaporated to a small volume under vacuum, and cooled in a refrigerator for several hours. The solid present was filtered off, and the filtrate was evaporated to dryness under vacuum. The solid residue was refluxed in absolute ethanol, filtered hot, and dried under vacuum (yield 70%). Anal. Calcd for $C_{16}H_{32}N_6{\cdot}6HCl{\cdot}2H_2O$: C, 34.12; H, 7.52; N, 14.92. Found: C, 34.12; H, 7.13; N, 15.06. The proton NMR spectrum of the product in D_2O shows three singlet peaks at δ 3.58, 4.45, and 7.65 in the ratio of 4:1:1.

***N*,*N*,*N'*,*N'*-Tetrakis[2-(4-nitrobenzylideneamino)ethyl]-α,α'-diamino-*m*-xylene (MXPNB).** 1,3-Bis[(bis(2-aminoethyl)amino)-methyl]benzene was freed from the hexahydrochloride salt (1.20 g, 2.13 mmol) by treatment with absolute ethanol (20 mL), methanolic 1N sodium hydroxide (12.78 mmol), and chloroform (100 mL) with stirring. The precipitate of sodium chloride was filtered off, and the solution was evaporated to dryness under vacuum to give a light yellow oil. This was dissolved in absolute ethanol (40 mL), and *p*-nitrobenzaldehyde (1.93 g, 12.78 mmol) was added with stirring. The mixture was refluxed for 1 h and then cooled to room temperature. The precipitate of the Schiff base was collected by filtration, washed with ethanol, and dried under vacuum (yield 88%). Anal. Calcd for $C_{44}H_{44}N_{10}O_8$: C, 62.85; H, 5.27; N, 16.66. Found: C, 62.55; H, 5.25; N, 16.46. IR (Mujol mull): 1647 m, 1601 m, 1516 s, 1343 s, 1312 w, 1292 w, 1215 w, 1102 w, 1071 w, 1019 w, 938 w, 850 m, 747 m, 688 m cm^{-1}. ^1H NMR (CD_3CN/Me_4Si):[18] δ2.79 (t, J = 6.1 Hz, 8 H, α-CH_2), 3.56 (s, 4 H, γ-CH_2), 3.68 (t, 8 H, β-CH_2), 7.1–7.4 (m, 4 H, xyl CH), 7.6–8.4 (m, 16H, Ph CH), 8.25 (s, 4 H, N=CH).

[Cu_2(MXPNB)][ClO_4]$_2$. To a degassed solution of MXPNB (1.57 g, 1.87 mmol) in dichloromethane (30 mL) was added solid tetrakis(acetonitrile)copper(I) perchlorate (1.25 g, 3.8 mmol) with stirring. The mixture was refluxed for 0.5 h and then cooled to room temperature. The orange precipitate was filtered, washed with degassed dichloromethane, and dried under vacuum (yield 65%). Anal. Calcd for $C_{44}H_{44}N_{10}Cu_2Cl_2O_{16}$: C, 45.29; H, 3.80; N, 12.00. Found: C, 44.98; H, 3.92; N, 12.30. IR (Nujol mull): 1632 m, 1600 m, 1519 s, 1345 s, 1297 m, 1225 w, 1095 vs (broad), 980 sh, 974 sh, 971 w, 945 w, 900 w, 892 w, 885 w, 867 m, 845 m, 833 m, 746 s, 697 m, 623 s cm^{-1}. ^1H NMR (CD_3CN/Me_4Si): δ 2.91 (~t, $J \approx 5$ Hz, 8 H, α-CH_2), 3.80 (~t, 8 H, β-CH_2), 4.22 (s, 4 H, γ-CH_2), 7.4–7.6 (m, 4 H, xyl CH), 8.07 (~s, 16 H, Ph CH), 8.52 (s, 4 H, N=CH).

[Cu_2(MXBA)][ClO_4]$_2$. A solution of 1.3-bis[(bis(2-aminoethyl)-amino)methyl]benzene (2.15 mmol, freed from the hexahydrochloride salt as described above) and benzaldehyde (0.90 g, 8.60 mmol) in absolute ethanol (30 mL) was refluxed for several hours under nitrogen. After the mixture cooled, solid tetrakis (acetonitrile)copper(I) perchlorate (1.44 g, 4.40 mmol) was added to the solution with stirring. The mixture was refluxed under nitrogen for approximately 3 h and then cooled to room temperature. The yellow precipitate was filtered, washed with degassed absolute ethanol, and dried under vacuum (yield 70%). Anal. Calcd for $C_{44}H_{48}N_6Cu_2Cl_2O_8$: C, 53.55; H, 4.90; N, 8.52. Found: C, 53.17; H, 4.86; N, 8.80. IR (Nujol mull): 1632 s, 1596 w, 1575 m, 1341 w, 1299 w, 1221 w, 1098 vs (broad), 1025 w, 970 m, 958 m, 888 m, 815 m, 760 s, 720 w, 693 s, 623 s cm^{-1}. ^1H NMR (CD_3CN/Me_4Si): δ 2.94 (~t, $J \approx 5$ Hz, 8 H, α-CH_2), 3.84 (~t, 8 H, β-CH_2), 4.27 (s, 4 H, γ-CH_2), 7.4–8.3 (m, 24 H, xyl CH + Ph CH), 8.51 (s, 4 H, N=CH).

[Cu_2(MXPNB)(CO)$_2$][ClO_4]$_2$. A solution of [Cu_2(MXPNB)]-[ClO_4]$_2$ (~100 mg) in absolute methanol or dichloromethane (20 mL) was treated with CO (1 atm), yielding a yellow solution with a light brown precipitate. This was collected by filtration and dried under vacuum. Anal. Calcd for $C_{46}H_{44}Cu_2N_{10}Cl_2O_{18}$: C, 45.18; H, 3.63; N, 11.46; Cu, 10.4; Cl, 5.80. Found: C, 45.56; H, 3.86; N, 11.42; Cu, 10.4; Cl, 5.95. IR (Nujol mull): 2104 s, 2089 s, 1645 w, 1633 m, 1599 m, 1519 s, 1345 s, 1222 w, 1086 vs (broad), 987 w, 975 w, 968 w, 955 w, 919 w, 906 w, 898 w, 889 w, 868 w, 858 w, 846 w, 833 m, 748 m, 734 w, 701 w, 689 w, 623 m cm^{-1}. The resulting filtrate gave upon evaporation to dryness a residue with an IR spectrum identical with that of [Cu_2(MXPNB)(CO)$_2$][ClO_4]$_2$.

[Cu_2(MXBA)(CO)$_2$][ClO_4]$_2$. A solution of [Cu_2(MXBA)][ClO_4]$_2$ (~100 mg) in dry dichloromethane (20 mL) was treated with CO (1 atm), yielding a pale green solution. This was evaporated to dryness with a stream of CO, giving a light green residue. Anal. Calcd for $C_{46}H_{48}N_6Cu_2Cl_2O_{10}$: C, 52.97; H, 4.64; N, 8.06; Cu, 12.2; Cl, 6.80. Found: C, 52.53; H, 4.62; N, 8.24; Cu, 12.2; Cl, 6.96. IR (Nujol mull): 2084 s, 1637 s, 1599 m, 1578 m, 1343 m, 1298 w, 1226 w, 1095 vs (broad), 1028 w, 979 w, 961 m, 904 w, 890 w, 817 w, 757 s, 734 m, 691 s, 622 s cm^{-1}. ^1H NMR (CD_3COCD_3/Me_4Si): δ 3.05, 3.33 (broad, 8 H, α-CH_2), 4.04 (broad, 8 H, β-CH_2), 4.49 (s, 4 H, γ-CH_2), 7.3–8.3 (m, 24 H, xyl CH + Ph CH), 8.84 (s, 4 H, N=CH).

[Cu_2(MXPNB)(Im)$_2$][ClO_4]$_2$. A mixture of [Cu_2(MXPNB)][ClO_4]$_2$ (600 mg, ~0.5 mmol), imidazole (Im, 170 mg, 2.5 mmol), and absolute methanol (20 mL) was refluxed for about 1 h. After the mixture was cooled and was stirred for several hours at room temperature, the orange precipitate was collected by filtration, washed with absolute methanol, and dried under vacuum. Anal. Calcd for $C_{50}H_{52}N_{14}Cu_2Cl_2O_{16}$: C, 46.08; H, 4.02; N, 15.05; Cu, 9.7; Cl, 5.44. Found: C, 46.39; H, 4.23; N, 14.79; Cu, 9.2; Cl, 5.16. IR (Nujol mull): 3328 m, 1629 m, 1623 sh, 1597 s, 1519 vs, 1342 vs, 1295 w, 1256 w, 1223 w, 1095 vs (broad), 984 w, 972 w, 964 w, 951 w, 940 w, 919 w, 906 w, 898 w, 869 w, 857 w, 849 m, 835 s, 749 s, 690 m, 660 m, 622 s cm^{-1}. ^1H NMR (CD_3COCD_3/Me_4Si): δ 3.14 (broad, 8 H, α-CH_2), 4.10 (broad, 12 H, β-CH_2 + γ-CH_2), 7.3–7.6 (m, 4 H, xyl CH), 7.9–8.5 (m, 22 H, Ph CH + Im CH), 8.77 (s, 4 H, N=CH).

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(18) The labeling scheme for the proton resonances is given in Figure 1.

$[Cu_2(MXBA)(Im)_2][ClO_4]_2$. A mixture of $[Cu_2(MXBA)][ClO_4]_2$ (250 mg, ~0.25 mmol), imidazole (85 mg, 1.25 mmol), and absolute methanol (20 mL) was refluxed for a few minutes and then cooled. A yellow precipitate was obtained upon adding dropwise to the solution a small amount of dry diethyl ether. The product was filtered, washed with methanol/ether, and dried under vacuum. Anal. Calcd for $C_{50}H_{56}N_{10}Cu_2Cl_2O_8$: C, 53.47; H, 5.02; N, 12.48; Cu, 11.3; Cl, 6.31. Found: C, 53.05; H, 5.13; N, 12.82; Cu, 11.5; Cl, 6.64. IR (Nujol mull): 3302 m, 1631 s, 1598 w, 1577 m, 1537 m, 1340 w, 1327 w, 1316 w, 1296 w, 1258 w, 1224 w, 1095 vs (broad), 1026 m, 984 w, 957 m, 904 w, 883 m, 841 w, 816 m, 757 s, 725 w, 692 s, 660 m, 652 w, 622 s cm^{-1}. ^1H NMR (CD_3COCD_3/Me_4Si): δ 3.07 (broad, 8 H, α-CH_2), 4.06 (broad, 12 H, β-CH_2 + γ-CH_2), 7.2–8.4 (m, 30 H, xyl CH + Ph CH + Im CH), 8.65 (s, 4 H, N=CH).

Results and Discussion

The synthesis of 1,3-bis[(bis(2-aminoethyl)amino)methyl]benzene was carried out with use of a modification of the method employed by Martell et al.[12] for the synthesis of the 1,4-isomer. The tetrakis(Schiff base) derivative MXPNB could be easily obtained by condensation of the hexaamine with *p*-nitrobenzaldehyde, while the corresponding ligand derived from benzaldehyde, MXBA, was not isolated because the reaction between 1,3-bis[(bis(2-aminoethyl)amino)methyl]benzene and excess benzaldehyde is extremely slow. The binuclear copper(I) complex $[Cu_2(MXBA)][ClO_4]_2$, however, could be obtained in satisfactory yield by template synthesis. Any attempt to isolate the binuclear copper(II) complexes of either MXPNB or MXBA in reasonable purity was unsuccessful due to their extreme instability toward hydrolysis even in the solid state. Contact with atmospheric moisture produced an instantaneous change in the appearance of the solid copper(II) complexes, while the IR spectra of these materials showed the presence of significant amine $\nu(NH_2)$ bands at 3340 and 3290 cm^{-1} and of a carbonyl $\nu(C{=}O)$ band near 1700 cm^{-1}. The imine hydrolysis reaction is known to occur on complex formation for several Schiff base ligands and is probably related to some strain between adjacent chelate rings.[19] The copper(I) complexes of MXPNB and MXBA are much more stable to hydrolysis than their copper(II) analogues and can be conveniently handled also in solution, provided dried solvents are used.

$[Cu_2(MXBA)][ClO_4]_2$ and $[Cu_2(MXPNB)][ClO_4]_2$. It is generally difficult to obtain structural information from the spectra of complexes containing metal ions, such as Cu^+, which are diamagnetic and have poor optical spectral properties. By careful inspection of their IR and NMR spectra, however, it is often possible to obtain some direct indication of the groups involved in metal binding. In the binuclear copper(I) complexes of MXPNB and MXBA the ligand can potentially bind each copper(I) in a tridentate fashion, while additional coordination positions may be available for solvent or other ligand molecules. The solid-state IR spectra of $[Cu_2(MXBA)][ClO_4]_2$ and $[Cu_2(MXPNB)][ClO_4]_2$ exhibit a single imine stretching band at 1632 cm^{-1}. This is significantly shifted to lower frequency relative to the position in free MXPNB (1647 cm^{-1}) and indicates that the imine groups are coordinated to the metal centers.[19d,20] By contrast, the IR bands associated with the aromatic nitro groups of MXPNB (at 1516 and 1343 cm^{-1}) are little affected by complexation, and the broad and unsplit bands near 1100 cm^{-1} are typical for noncoordinated perchlorate ions.[21] The IR spectra of $[Cu_2(MXBA)][ClO_4]_2$ and $[Cu_2(MXPNB)][ClO_4]_2$ recorded in various solvents show that the imine groups remain coordinated to the metal ions in solution. Although the position of the $\nu(C{=}N)$ stretch shows some solvent dependence (e.g. for $[Cu_2(MXBA)][ClO_4]_2$ this occurs at 1634 cm^{-1} in acetonitrile and at 1638 cm^{-1} in dichloromethane), it is noteworthy that a single band is observed in each case. The tertiary amine nitrogen donors are also potential metal binding sites, though coordination by these groups cannot be inferred with confidence from the IR spectra.

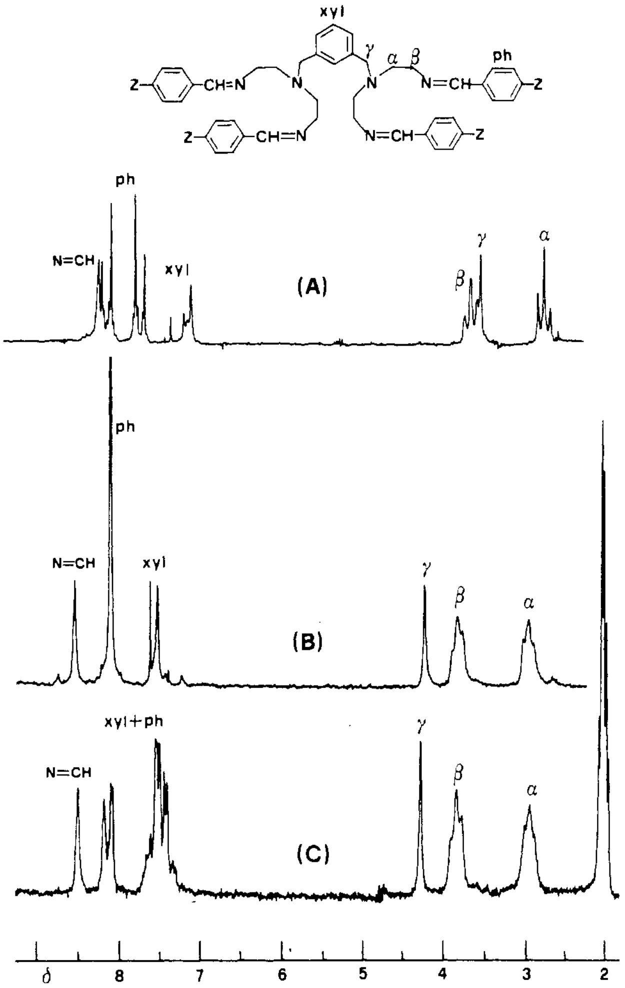

Figure 1. Proton NMR spectra in CD_3CN solution of (A) the MXPNB ligand, (B) $[Cu_2(MXPNB)][ClO_4]_2$, and (C) $[Cu_2(MXBA)][ClO_4]_2$.

The perfect equivalence of the imine groups in $[Cu_2(MXBA][ClO_4]_2$ and $[Cu_2(MXPNB)][ClO_4]_2$ is clearly evident also in their proton NMR spectra (Figure 1). In a comparison of the NMR spectra of MXPNB and $[Cu_2(MXPNB)][ClO_4]_2$ in CD_3CN solution it can be noted that the resonances due to the methylene protons (α, β, and γ) and to the azomethine protons undergo appreciable downfield shifts upon complexation (Figure 1). Similar downfield shifts have been observed in several cases for the protons on carbons attached to the donor atoms upon binding to copper(I)[10c,19d,22] and have been explained in terms of the influence of the positively charged metal ion.[22a,b] Particularly large is the shift undergone by the xylyl methylene protons. This seems to

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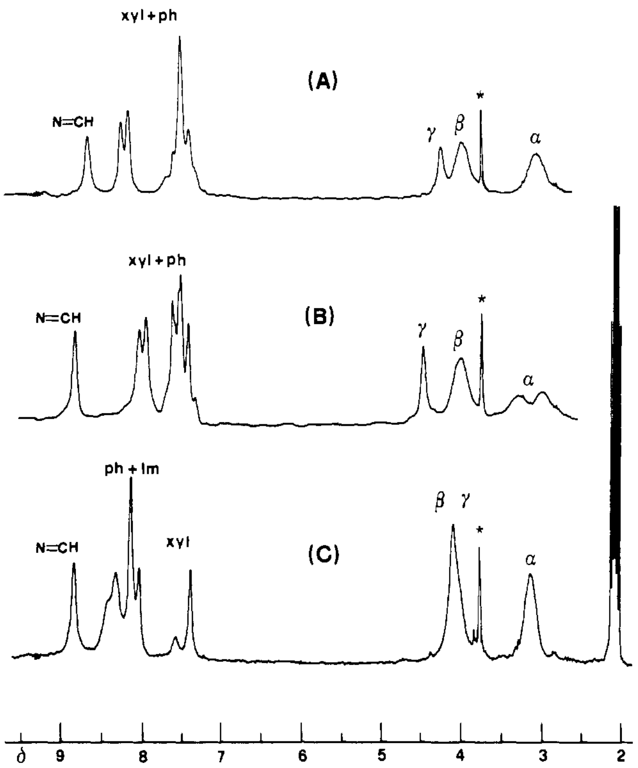
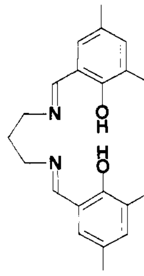


Figure 2. Proton NMR spectra in CD_3COCD_3 solution of (A) $[Cu_2(MXBA)][ClO_4]_2$, (B) $[Cu_2(MXBA)(CO)_2][ClO_4]_2$, and (C) $[Cu_2(MXPNB)(Im)_2][ClO_4]_2$. The signal marked with an asterisk is a small impurity contained in the solvent.

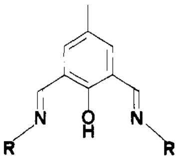
provide convincing evidence for binding of the rather "hard" tertiary amine nitrogen atoms to the copper(I) centers in solution. Also noteworthy are the change of pattern for the para-disubstituted phenyl nuclei of MXPNB, from AA′XX′ to AA′BB′, upon coordination of the imine groups and the near-identity of the various proton group signals of $[Cu_2(MXPNB)]^{2+}$, which is consistent with symmetry between the two functional parts of the molecule. Except for the signals of the aromatic protons, the NMR spectrum of $[Cu_2(MXBA)][ClO_4]_2$ in CD_3CN is very similar to that of $[Cu_2(MXPNB)][ClO_4]_2$, suggesting that the copper(I) ions of these complexes have a similar coordination environment.

The addition of KBr to solutions of either $[Cu_2(MXBA)]^{2+}$ or $[Cu_2(MXPNB)]^{2+}$ in CD_3CN results in significant upfield shifts of the azomethine protons (to near δ 8.35) as a consequence of ready coordination by the added anion, while all the other signals are almost completely unaffected. The availability of coordination positions in solution is confirmed by the solvent dependence of the IR spectra mentioned above and also by some solvent dependence of the NMR spectra of the complexes. The NMR spectra recorded in CD_3COCD_3 (Figure 2)[23] or CD_2Cl_2 solution show, in fact, that the near-perfect identity of the α or β methylene protons observed in CD_3CN is partially lost. Since the donor groups of the ligands are still apparently coordinated to the coppers,[23] we ascribe these minor changes to some conformational change undergone by the diethylenetriamine residues of the ligands to accommodate somewhat bulkier solvent molecules within the metal coordination sphere. According to the above results it seems reasonable to assume that in solution each copper(I) center of $[Cu_2(MXBA)]^{2+}$ and $[Cu_2(MXPNB)]^{2+}$ exhibits the expected pseudotetrahedral geometry with two imine and a tertiary amine nitrogen ligand originating from the same diethylenetriamine residue and additional binding by a solvent molecule.

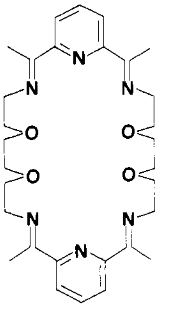
Perhaps the most striking feature exhibited by $[Cu_2(MXBA)][ClO_4]_2$ and $[Cu_2(MXPNB)][ClO_4]_2$ is their stability to oxidation. Solutions of both complexes in dry solvents are completely stable upon exposure to dioxygen. In undried, protic solvents, however, the complexes slowly decompose upon exposure to air, producing green solutions, because the products of imine hydrolysis are apparently less stable. In general, the reactivity of $[Cu_2(MXPNB)]^{2+}$ in these oxidations is much lower than that of $[Cu_2(MXBA)]^{2+}$, indicating that the presence of strong electron-withdrawing nitro groups in the ligand produces further stabiliztion of the cuprous state. In a comparison of the reactivity of $[Cu_2(MXBA)]^{2+}$ and $[Cu_2(MXPNB)]^{2+}$ toward dioxygen with that exhibited by the other binuclear copper(I) complexes derived from I, it can be noted that the aromatic imine groups apparently stabilize the copper(I) ions more than pyridine,[14b] imidazole,[15b] or even thioether[13] residues. Other binuclear copper(I) complexes of Schiff bases, with the ligands III,[9c] IV,[10a,11a] or V,[9e,f] are unstable to oxidation. The rather rigid, planar geometry enforced by the ligands is probably responsible for the relative instability of these complexes. The flexible diethylenetriamine residues of II can adopt a wide range of different conformations; however, inspection of molecular models indicates that the arrangement providing three nitrogen donors in roughly a trigonal plane is rich with steric strain. Therefore, conceivable structures for the copper centers of $[Cu_2(MXBA)]^{2+}$ and $[Cu_2(MXPNB)]^{2+}$ in the solid state cannot include a planar, three-coordinate CuN_3 core with imine groups originating from the same diethylenetriamine residue. Several other structures are possible, according to whether or not the tertiary amine ligands are involved in coordination to copper(I) (examples for both cases exist in the recent literature[10c,11b]) and taking into account that copper(I) often exhibits some preference (predicted[24] and documented[10c,25-27]) for structural



III



IV



V

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[23] The proton NMR data in CD_3COCD_3/Me_4Si are as follows: MXPNB: δ 2.88 (t, J = 6.3 Hz, 8 H, α-CH_2), 3.66 (s, 4 H, γ-CH_2), 3.78 (t, 8 H, β-CH_2), 7.1–7.4 (m, 4 H, xyl CH), 7.7–8.3 (m, 16 H, Ph CH), 8.39 (s, 4 H, N=CH). $[Cu_2(MXPNB)][ClO_4]_2$: δ 3.20 (broad, 8 H, α-CH_2), 4.11 (broad, 8 H, β-CH_2), 4.40 (s, 4 H, γ-CH_2), 7.3–7.7 (m, 4 H, xyl CH), 7.9–8.5 (m, 16 H, Ph CH), 8.84 (s, 4 H, N=CH). $[Cu_2(MXBA)][ClO_4]_2$: δ 3.11 (broad, 8 H, α-CH_2), 4.04 (broad, 8 H, β-CH_2), 4.28 (s, 4 H, γ-CH_2), 7.3–8.3 (m, 24 H, xyl CH + Ph CH), 8.68 (s, 4 H, N=CH). Imidazole: δ 7.12 (s, 2 H, 4-H + 5-H), 7.76 (s, 1 H, 2-H), ~12 (very broad, 1 H, NH).

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arrangements that favor a direct Cu–Cu interaction.

Carbonyl and Imidazole Adducts. Carbonyl adducts of $[Cu_2(MXBA)][ClO_4]_2$ and $[Cu_2(MXPNB)][ClO_4]_2$ can be easily formed upon exposure of methanol or dichloromethane solutions of these complexes to an atmosphere of carbon monoxide. The $[Cu_2(MXPNB)(CO)_2][ClO_4]_2$ adduct precipitates readily from these solutions, though a solid $[Cu_2(MXBA)(CO)_2][ClO_4]_2$ adduct can be isolated only by evaporation of the carbonylated solution in a stream of carbon monoxide, while evaporation under vacuum leads to the partial to complete loss of CO by the complex. The solid-state IR spectrum of $[Cu_2(MXBA)(CO)_2][ClO_4]_2$ displays a single carbonyl stretching band at 2084 cm^{-1}, while that of $[Cu_2(MXPNB)(CO)_2][ClO_4]_2$ exhibits a strong, sharp pair of CO bands at 2089 and 2104 cm^{-1}. These CO stretching frequencies are rather high compared to those usually found in copper carbonyl complexes[10b,11a,b,13a,26-30] and indicate that CO is weakly bound to copper(I) in $[Cu_2(MXBA)(CO)_2]^{2+}$ and $[Cu_2(MXPNB)(CO)_2]^{2+}$. In fact, while these adducts are unreactive toward dioxygen, their dissolution in acetonitrile results in the immediate and complete evolution of carbon monoxide. The presence of several conjugated imine groups in the ligands and the overall cationic character of the complexes probably reduce the extent of π-back-bonding from the coppers into the π^* ortibals of the CO ligands. This seems confirmed by the observation that the CO bands of $[Cu_2(MXPNB)(CO)_2]^{2+}$, where the ligand contains strong electron-withdrawing nitro groups, occur at higher frequency than those of $[Cu_2(MXBA)(CO)_2]^{2+}$.

It is interesting to note that the pair of CO bands in the IR spectrum of $[Cu_2(MXPNB)(CO)_2][ClO_4]_2$ is accompanied by a pair of imine $\nu(C{=}N)$ bands, at 1645 (w) and 1633 (m) cm^{-1}, and by further splittings of the bands of $[Cu_2(MXPNB)][ClO_4]_2$ in the 1000–650-cm^{-1} region. This suggests that the copper(I) centers of $[Cu_2(MXPNB)(CO)_2][ClO_4]_2$ may have unequal environments, and it is tempting to relate the more stable copper carbonyl (2089 cm^{-1}) to the center where displacement of a coordinated imine group ($\nu(C{=}N)$ at 1645 cm^{-1}) has apparently occurred. Unfortunately, the almost negligible solubility of this compound in solvents like acetone or dichloromethane prevents an examination of its behavior in solution. For $[Cu_2(MXBA)(CO)_2][ClO_4]_2$, the single CO band observed in its IR spectrum corresponds to a single $\nu(C{=}N)$ band typical for coordinated imine bonds and to the presence of a single azomethine proton signal in its NMR spectrum recorded in CD_3COCD_3 solution. As shown in Figure 2, a single set of resonances is also observed for the β- and γ-CH_2 groups, while two broad and equally intense signals of α-CH_2 groups are present. Since binding by the tertiary amine nitrogen atoms to the coppers is indicated by the (low field) position of the β- and γ-CH_2 signals and is apparently required to provide stability to the copper–carbonyl bond,[29] the nonequivalence of the α-CH_2 protons must be determined by the presence of the CO ligands and, possibly, of solvent molecules in the copper coordination spheres. The CO stretching band of $[Cu_2(MXBA)(CO)_2][ClO_4]_2$ in acetone solution occurs at 2091 cm^{-1}, but it is difficult to state whether the shift of this band relative to the position observed in the solid-state IR spectrum is due to additional coordination by solvent or simply to a slight difference in the symmetry of the metal coordination sets.[31]

Reaction of $[Cu_2(MXBA)][ClO_4]_2$ or $[Cu_2(MXPNB)][ClO_4]_2$ with excesss imidazole yields the diimidazole adducts of these complexes, $[Cu_2(MXBA)(Im)_2][ClO_4]_2$ and $[Cu_2(MXPNB)(Im)_2][ClO_4]_2$. The IR spectra of these adducts show that coordination of imidazole to copper(I) occurs without displacement of the imine groups of the ligands. Infrared bands typical for imidazole residues appear near 3300 (ν(NH)), 1530 (ν(ring),[32] this band is buried under the intense absorption of aromatic nitro groups in the spectrum of $[Cu_2(MXPNB)(Im)_2][ClO_4]_2$), and 660 cm^{-1} (γ(ring)[32]). The proton NMR spectra of the diimidazole adducts recorded in CD_3COCD_3 show a rather complex pattern of signals in the aromatic region. It is difficult to locate the imidazole protons in these spectra since, as shown by the NMR spectrum of $[Cu_2(MXPNB)(Im)_2][ClO_4]_2$ in Figure 2, it is quite possible that also the pattern of phenyl proton signals in the spectra of the adducts has changed with respect to that of their precursors. The NMR spectra of the imidazole adducts show, however, other interesting features. Thus, while binding of copper(I) to the imine groups is apparently maintained in solution, the signals of the γ-CH_2 protons of $[Cu_2(MXBA)(Im)_2]^{2+}$ and $[Cu_2(MXPNB)(Im)_2]^{2+}$ are superimposed on those of the β-CH_2 groups and show significant upfield shifts relative to the positions observed for the γ-CH_2 resonances of $[Cu_2(MXBA)]^{2+}$ and $[Cu_2(MXPNB)]^{2+}$ (Figure 2).[23] Although we cannot simply conclude that the tertiary amine groups are unbound in the adducts, since the signals of the α-CH_2 and γ-CH_2 groups of $[Cu_2(MXBA)(Im)_2]^{2+}$ and $[Cu_2(MXPNB)(Im)_2]^{2+}$ are still found at lower fields than those of the corresponding signals of MXPNB,[23] it is probably not incidental that the α-CH_2 signals of the imidazole adducts occur at slightly higher field than those of their precursors, while the positions of the β-CH_2 signals are essentially unaffected by adduct formation. Since the bulky polydentate MXBA and MXPNB ligands are expected to prevent a rapid interchange of bonded and nonbonded tertiary amine nitrogen donors on the NMR time scale, the above results can be explained by considering that binding of imidazole to the copper centers weakens the "unfavorable" copper(I)–amine interaction. This is not unexpected in view of the good σ-donor and π-acceptor capability of imidazole as a ligand,[33] but it is worthwhile to emphasize that this contrasts with the behavior of $[Cu_2(MXPNB)(CO)_2]^{2+}$, where binding of CO (a π-acid) occurs at the expense of a coordinate imine group. Imidazole itself is not tightly bound to copper(I) in the adducts, since dissolution of either $[Cu_2(MXBA)(Im)_2][ClO_4]_2$ or $[Cu_2(MXPNB)(Im)_2][ClO_4]_2$ in acetonitrile results in the slow deposition of imidazole and restores the solvated $[Cu_2$-

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(31) The elemental analysis of $[Cu_2(MXBA)(CO)_2][ClO_4]_2$ would not be inconsistent with the presence of a single CO molecule. However, the perfect identity of imine groups exhibited by the IR and NMR spectra of the compound would imply a bridging rather than terminal CO. This possibility is discarded because the CO stretching frequency expected for bridging CO is much lower than those observed here.[21,27]

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$(MXBA)][ClO_4]_2$ and $[Cu_2(MXPNB)][ClO_4]_2$ complexes, respectively. Steric factors may also be important in these displacement reactions, since accommodation of imidazole rings within the copper coordination spheres may cause excessive crowding with the various phenyl residues of the ligands.

In conclusion, the present investigation shows that by proper choice of the residues to be conjugated with the xylyl frame I it is possible to obtain stable binuclear copper(I) complexes with nitrogen donor ligands. The metal centers of these systems can come in close proximity by proper conformational arrangement of the flexible xylyl side chains,[13b,14b,d] though in the absence of structural determinations, only magnetic studies on the copper(II) analogues can give an estimate of the metal–metal interaction. Binding of the various functional groups of the ligand to copper(I) can, however, be conveniently deduced by careful examination of their IR and NMR spectra. Besides the donor groups of the ligands, the binuclear copper(I) complexes described here have other coordination sites available. These can be filled by solvent molecules or binding to external ligands such as carbon monoxide or imidazole. This is an important requisite in model studies based on binuclear copper(I) systems such as those derived from I, where small differences in structure or donor set can produce significant changes in reactivity.

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Registry No. II (Z = NO_2), 86260-99-3; $[Cu_2(MXPNB)][ClO_4]_2$, 86261-01-0; $[Cu_2(MXBA)][ClO_4]_2$, 86261-03-2; $[Cu_2(MXPNB)(CO)_2][ClO_4]_2$, 86261-05-4; $[Cu_2(MXBA)(CO)_2][ClO_4]_2$, 86261-07-6; $[Cu_2(MXPNB)(Im)_2][ClO_4]_2$, 86261-09-8; $[Cu_2(MXBA)(Im)_2][ClO_4]_2$, 86261-11-2; α,α'-bis(diphthaloyldiethylenetriamino)-*m*-xylene, 86260-97-1; 1,3-bis[(bis(2-aminoethyl)amino)methyl]benzene hexahydrochloride, 86260-98-2; diphthaloyldiethylenetriamine, 63563-83-7; α,α'-dibromo-*m*-xylene, 626-15-3; *p*-nitrobenzaldehyde, 555-16-8; benzaldehyde, 100-52-7; tetrakis(acetonitrile)copper(I) perchlorate, 14057-91-1.

Notes

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Fluxional Behavior of a Pseudo-Jahn–Teller Complex: X-ray Crystal Structure of $[Cu(bpy)_2(ONO)][NO_3]$ at 165 and 296 K

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William Fitzgerald,[1c] Suresh Tyagi,[1c] and Brian J. Hathaway[1c]

Received August 18, 1982

The first crystal structure of a [Cu(bpy or phen)$_2$(OXO)]Y complex (bpy = 2,2′-bipyridyl, phen = 1,10-phenanthroline and OXO^- = a bidentate ligand) to be reported was that of $[Cu(bpy)_2(ONO)][NO_3]$.[2] The stereochemistry of the $[Cu(bpy)_2(ONO)]^+$ cation was classified as cis-distorted octahedral, with one nitrogen atom from each bpy ligand axial and the other two nitrogen atoms and both nitrito oxygen atoms equatorial. However, a recent analysis[3] of the crystal structures and temperature dependence of the ESR spectra of a series of $[Cu(phen)_2(CH_3CO_2)][Y]$ "cation-distortion isomers" (Y = $BF_4 \cdot 2H_2O$, $ClO_4 \cdot 2H_2O$, ClO_4, and BF_4) suggests that the molecules are fluxional and that the purported cis-distorted octahedral geometry is not a genuine *static* stereochemistry of Cu(II) complexes in general.[4,5] The apparent fluxionality of these pseudo-Jahn–Teller (PJT) complexes was explained in terms of a potential energy surface involving two thermally accessible minima; the crystallographically observed geometries are thus statistical means weighted according to the relative thermal populations of the two minima.[5] To help establish whether indeed the cis-octahedral CuN_4O_2 chromophore is fluxional, we have determined the structure of $[Cu(bpy)_2(ONO)][NO_3]$ at low temperature (165 K) and have repeated the determination at room temperature. Pertinent crystallographic results, a brief exposition of the distortional behavior in terms of a PJT formalism, and a simple derivation relating the energy difference between conformers to the observed distortions from C_2 symmetry are presented.

Experimental Section

The synthesis of $[Cu(bpy)_2(ONO)][NO_3]$ (**1**) has been previously reported.[6] A single crystal of **1**, a parallelepiped with dimensions 0.23 × 0.17 × 0.14 mm, was selected for X-ray diffraction study and was mounted approximately along its longest dimension. An Enraf-Nonius CAD4 diffractometer using graphite-monochromatized Mo Kα radiation and equipped with an ultrastable refrigeration-type concentric stream low-temperature device was used for preliminary experiments and for the measurement of diffraction intensities at both temperatures. Cell constants and data acquisition procedures are summarized in Table I. The formulas used to derive the intensity and its standard deviation were $I_{raw} = (K/\mathrm{NPI})(C - 2B)$ and $\sigma(I_o) = [(\sigma(I_{raw}))^2 + (pI_{raw})^2]^{1/2}(Lp)^{-1}$, where $\sigma(I_{raw}) = (K/\mathrm{NPI})(C + 4B)^{1/2}$, K = (20.1166)(attenuator constant), NPI = scan speed parameter, C = total integrated count, B = total background count, p = a factor used to downweight intense reflections (0.05), and Lp = Lorentz–polarization factor.[7] The raw intensity data were corrected for Lorentz–polarization effects ($I_o = I_{raw}/Lp$) but not for absorption (μ(Mo Kα) = 11.3 cm^{-1}). The weights of the 2921 (165 K) and 2142 (296 K) observations ($I_o > 2\sigma(I_o)$) used in the least-squares refinements were equal to $[\sigma(F_o)]^{-2}$. Scattering factors for the atoms were taken from ref 8a and corrected for anomalous dispersion.[8b]

Positional coordinates from the original room-temperature determination,[2] which was based on visually estimated intensity data, were used as starting coordinates. Several cycles of full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms led to the final error indices:[9] $R = 0.046$, $R_w = 0.076$, esd =

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(1) (a) Texas A&M University. (b) Present address: Chemistry Department, University of Puerto Rico, Rio Piedras, Puerto Rico 00931. (c) University College, Cork.

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