2144 *Inorg. Chem.* **1991**, *30*, 2144-2148

Contribution from the Laboratoire de Chimie des Métaux de Transition et de Catalyse (URA 424 du CNRS), 4 Rue Blaise Pascal, 67000 Strasbourg, France, and Laboratoire de Chimie Supramoléculaire (URA 422 du CNRS), 4 Rue Blaise Pascal, 67000 Strasbourg, France

Formation of Dihelicate and Mononuclear Complexes from Ethane-Bridged Dimeric Bipyridine or Phenanthroline Ligands with Copper(I), Cobalt(II), and Iron(II) Cations

Marie-Thérèse Youinou,[†] Raymond Ziessel,[‡] and Jean-Marie Lehn*[,‡]

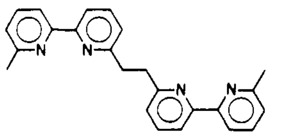
Received October 16, 1990

The dimeric ethane-bridged ligands 1,2-bis(6′-methyl-2,2′-bipyridin-6-yl)ethane (**1**) and 1,2-bis(9-methyl-1,10-phenanthrolin-2-yl)ethane (**2**) form a double-stranded helicate by complexation with copper(I), yielding the dinuclear complexes $[Cu_2(\mathbf{1})_2](ClO_4)_2$ (**1a**) and $[Cu_2(\mathbf{2})_2](ClO_4)_2$ (**2a**). The double-helical structure, in which two ligands are wrapped around two copper(I) cations, has been assigned by ^1H NMR studies and confirmed in the case of the dinuclear complex **1a** by X-ray diffraction. This complex $C_{48}H_{44}O_8Cl_2Cu_2$ crystallizes in the monoclinic space group $P2_1/n$ with four molecules per unit cell of dimensions $a = 19.162$ (7) Å, $b = 11.701$ (6) Å, $c = 20.215$ (7) Å, $\beta = 95.25$ (2)°, and $V = 4513$ Å^3 at −100 °C. The structure was refined to $R = 0.048$ ($R_w = 0.076$) for 3848 reflection data with $I > 3\sigma(I)$. The copper cations, which are arranged in a distorted tetrahedral fashion, are separated by a distance of 5.926 (1) Å. The dinuclear copper complexes with ligands **1** and **2** are oxidized in a single reversible dielectronic wave at potentials somewhat higher than those of the mononuclear analogues. Ligand **2** gives a mononuclear cobalt(II) species of octahedral geometry, which has been fully characterized by X-ray diffraction. This complex $C_{30}H_{22}N_4O_6F_6S_2Co$ crystallizes in the monoclinic space group $P2_1/n$ with four molecules per unit cell of dimensions $a = 11.509$ (2) Å, $b = 14.296$ (3) Å, $c = 19.436$ (3) Å, $\beta = 106.10$ (2)°, and $V = 3072$ Å^3 at room temperature; $R = 0.055$ ($R_w = 0.075$) for 3094 reflections with $I > 3\sigma(I)$. Ligand **3** (1,2-bis(5′-methyl-2,2′-bipyridin-5-yl)ethane) leads to a triply bridged dinuclear iron species.

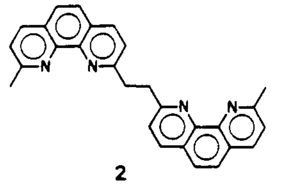
Introduction

Polypyridine ligands display a variety of interesting complexation properties and have been extensively used in the synthesis of photosensitive and electroactive complexes[1] as well as for the catalytic activation of small molecules such as H_2O, CO_2, and CO.[2] Covalently linked bipyridines lead to the preparation (i) of polynuclear complexes that present intramolecular energy-transfer properties[3] and (ii) of a triply bridged dinuclear tris(bipyridine)iron complex displaying significant interaction between the two metal centers.[4]

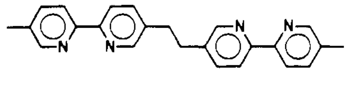
Recently, oligobipyridine ligands containing bipyridine units linked by CH_2OCH_2 bridges have been shown to coordinate copper(I) or silver(I)[5] with formation of double-stranded helicates by a self-assembly process. A CH_2CH_2-bridged bis(bipyridine) ligand **1** has also been shown to form a Cu(I) complex, to which a dihelicate structure was assigned on the basis of NMR spectroscopic data.[6] Previous work on a methyl-substituted quaterpyridine (p-QP) had shown that a dinuclear copper(I) complex was formed, in which two twisted p-QP molecules were wrapped around the two copper(I) cations in a distorded tetrahedral coordination geometry.[7a] This p-QP ligand gave a mononuclear copper(II) complex, whose coordination geometry was a tetragonal pyramid having the four nitrogen atoms as base and an apical water molecule. An interesting monomer–dimer interconversion process, controlled by the oxidation state of the cation, has been demonstrated electrochemically.[7b] We recently found that the reaction of a monocarbanion of methyl-substituted bipyridine or phenanthroline with Br_2 gave dimeric ligands[8] in high yield. We describe here the synthesis and electrochemical and structural studies of copper(I), cobalt(II), and iron(II) complexes of some of these dimeric 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) ligands **1**–**3**, in which the subunits are linked by a CH_2CH_2 bridge. The formation of the dinuclear Cu(I) complex of **1** has been reported earlier.[6]



1



2



3

Experimental Section

Syntheses and Spectroscopic Data. Manipulations were performed under argon by using standard Schlenk techniques. CH_2Cl_2 and CH_3CN were distilled over CaH_2. ^1H and ^{13}C NMR spectra were obtained on a Bruker SY-200 or SY-400 spectrometer in dichloromethane-d_2 or acetonitrile-d_3. ^1H NMR shifts were measured relative to residual protiated solvent: CD_2Cl_2, δ 5.32; CD_3CN, δ 1.93. ^{13}C NMR shifts are relative to the solvent resonance: CD_3CN, δ 117.2. Coupling constants are given in hertz. IR spectra (cm^{-1}) were recorded on a Perkin-Elmer-597 spectrometer in KBr pellets. UV/vis spectra (λ in nm) were measured on a Cary-219 spectrophotometer in acetonitrile, and molar extinction coefficients (ε in M^{-1} cm^{-1}) were obtained from absorbance measurements on at least two different concentrations of complex. Mass spectra were determined by FAB$^+$ using a ZAB-HF VG apparatus in a *m*-nitrobenzyl alcohol (NBA) or thioglycerol (Thio) matrix. Electrochemical measurements were carried out on a classical three-electrode potentiostatic setup described before.[2] Elemental analyses were performed by the Service Central de Microanalyse due CNRS, Strasbourg, France.

1,2-Bis(6′-methyl-2,2′-bipyridin-6-yl)ethane (**1**), 1,2-bis(9-methyl-1,10-phenanthrolin-2-yl)ethane (**2**), and 1,2-bis(5′-methyl-2,2′-bipyridin-5-yl)ethane (**3**) were synthesized and purified as previously described.[8]

Dinuclear Copper(I) Complexes $[Cu_2(1)_2](ClO_4)_2$ (1a) and $[Cu_2(2)_2](ClO_4)_2$ (2a). Addition of $[Cu(CH_3CN)_4](ClO_4)$[9] (1 equiv in

---

[†] Laboratoire de Chimie des Métaux de Transition et de Catalyse.

[‡] Laboratoire de Chimie Supramoléculaire.

(1) Balzani, V.; Bolleta, F.; Gandolfi, M. T.; Maestri, M. *Top. Curr. Chem.* **1978**, *75*, 1. Meyer, T. J. *Acc. Chem. Res.* **1978**, *11*, 94. Sutin, N.; Creutz, C. *Pure Appl. Chem.* **1980**, *52*, 2717. Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159. Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; Von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85.

(2) Ziessel, R.; Hawecker, J.; Lehn, J.-M. *Helv. Chim. Act* **1986**, *69*, 1065. Hawecker, J.; Lehn, J.-M.; Ziessel, R. *Helv. Chim. Acta* **1986**, *69*, 1990. Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1988**, 16 and references therein.

(3) Schmehl, R. H.; Auerbach, R. A.; Wacholtz, W. F.; Elliot, C. M.; Freitag, R. A.; Merkert, J. W. *Inorg. Chem.* **1986**, *25*, 2440.

(4) Serr, B. R.; Andersen, K. A.; Elliott, C. M.; Anderson, O. P. *Inorg. Chem.* **1988**, *27*, 4499.

(5) Lehn, J.-M.; Rigault, A.; Siegel, J.; Harrowfield, J.; Chevrier, B.; Moras, D. *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 2565. Lehn, J.-M.; Rigault, A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1095. Garrett, T. M.; Koert, U.; Lehn, J.-M.; Rigault, A.; Meyer, D.; Fischer, J. *J. Chem. Soc., Chem. Commun.* **1990**, 557.

(6) He, Y.; Lehn, J.-M. *Chem. J. Chin. Univ.* **1990**, *6*, 183.

(7) (a) Lehn, J.-M.; Sauvage, J.-P.; Simon, J.; Ziessel, R.; Piccinni-Leopardi, C.; Germain, G.; Declercq, J.-P.; Van Meerssche, M. *Nouv. J. Chim.* **1983**, *7*, 4133. (b) Gisselbrecht, J.-P.; Gross, M.; Lehn, J.-M.; Sauvage, J.-P.; Ziessel, R.; Piccinni-Leopardi, C.; Arrieta, J.; Germain, G.; Van Meerssche, M. *Nouv. J. Chim.* **1984**, *8*, 661.

(8) Lehn, J.-M.; Ziessel, R. *Helv. Chim. Acta* **1988**, *71*, 1511.

0020-1669/91/1330-2144$02.50/0 © 1991 American Chemical Society

Table I. Crystallographic Data for **1a** and **2b**

chem formula	$[C_{48}H_{44}N_8Cu](ClO_4)_2$	$[C_{30}H_{22}N_4Co](CF_3SO_3)_2$
fw	1058.92	771.58
space group	$P2_1/n$	$P2_1/n$
a, Å	19.162 (7)	11.509 (2)
b, Å	11.701 (6)	14.296 (3)
c, Å	20.215 (7)	19.436 (3)
β, deg	95.25 (2)	106.10 (2)
V, Å^3	4513	3072
Z	4	4
d(calcd), g·cm^{-3}	1.558	1.668
λ, Å	1.5418 (Cu Kα)	0.71073 (Mo Kα)
temp, °C	−100	20
μ, cm^{-1}	27.9	7.7
transm factors (max/min)	1.22/0.84	1.32/0.66
R_F/R_{wF}, %	4.8/7.6	5.5/7.5

CH_3CN) to a suspension of **1** or **2** (1 equiv in CH_3CN) gave a deep orange homogeneous solution. After 2 h of stirring at room temperature the solvent was removed (reduced pressure) and the residue chromatographed on silica (20:1 $CH_2Cl_2/MeOH$), giving respectively $[Cu_2(\mathbf{1})_2](ClO_4)_2$ (**1a**) (90%, $R_f = 0.36$, deep orange microcrystalline compound from CH_3CN/Et_2O) and $[Cu_2(\mathbf{2})_2](ClO_4)_2$ (**2a**) (95%, $R_f = 0.35$, deep red microcrystalline complex from CH_3CN).

1a. ^1H NMR (CD_3CN): δ 8.16 (d, $^3J = 8.0$, 2 H), 8.04 (d, $^3J = 7.9$, 2 H), 8.02 (t, $^3J = 7.8$, 2 H), 7.77 (t, $^3J = 7.9$, 2 H), 7.47 (d, $^3J = 7.6$, 2 H), 7.00 (d, $^3J = 7.7$, 2 H), 2.93 (ABCD m, 4 H, CH_2), 2.01 (s, 6 H, CH_3). ^{13}C NMR (CD_3CN): δ 160.28, 158.57, 152.22, 139.65, 139.38, 126.85, 124.28, 120.73, 120.39, 38.25 (CH_2), 24.72 (CH_3). FAB$^+$ (NBA): m/z 959.1 (15%, $[M - ClO_4]^+$), 860.1 (17%, $[M - 2ClO_4]^+$), 429.0 (100%, $[M/2 - ClO_4]^+$). UV–vis (CH_3CN): 264 (44 400), 301 (57 000), 445 (9400). Anal. Calcd for $C_{48}H_{44}N_8Cl_2O_8Cu_2$: C, 54.44; H, 4.19; N, 10.10. Found: C, 54.36; H, 4.03; N, 9.96.

2a. ^1H NMR (CD_3CN): δ 8.60 (d, $^3J = 8.3$, 2H, H–C4), 8.11 (d, $^3J = 8.9$, 2 H, H–C5), 7.85 (d, $^3J = 8.9$, 2 H, H–C6), 7.80 (d, $^3J = 8.3$, 2 H, H–C3), 7.59 (d, $^3J = 8.3$, 2 H, H–C7), 6.78 (d, $^3J = 8.3$ Hz, 2 H, H–C8), 2.90 (ABCD m, 4 H, CH_2), 2.34 (s, 6 H, CH_3). Proton relaxation time T_1 (s): 1.98 (H–C4), 1.71 (H–C5), 1.61 (H–C6), 1.60 (H–C3), 1.76 (H–C7), 1.57 (H–C8). ^{13}C NMR (CD_3CN): δ 161.80, 159.72, 142.46, 142.03, 137.19, 136.40, 127.22, 126.97, 126.00, 125.51, 122.14, 37.54 (CH_2), 24.82 (CH_3). FAB$^+$ (NBA): m/z 1055.1 (33%, $[M - ClO_4]^+$), 954.1 (23%, $[M - 2ClO_4]^+$), 477.0 (100%, $[M/2 - ClO_4]^+$). UV-vis (CH_3CN): 204 (108 100), 227 (124 700), 275 (95 200), 443 (11 500). Anal. Calcd for $C_{56}H_{44}N_8Cl_2O_8Cu_2$: C, 63.69; H, 3.84; N, 9.70. Found: C, 63.52; H, 3.68; N 9.59.

Mononuclear Cobalt(II) Complex $[Co(\mathbf{2})](CF_3SO_3)_2$ (2b). Addition of $[Co(DMSO)_6](CF_3SO_3)_2$[10] (1 equiv in CH_3CN) to a solution of **2** (1 equiv in CH_2Cl_2) gave a light brown solution. After 10 h, addition of Et_2O caused the crystallization of the air- and water-sensitive $[Co(\mathbf{2})](CF_3SO_3)_2$ complex (89%, light brown crystals from $CH_3CN/CH_2Cl_2/Et_2O$. UV–vis (CH_3CN): 208 (54 000), 228 (65 500), 271 (47 500). FAB$^+$ (NBA): m/z 622.1 (100%, $[M - CF_3SO_3]^+$), 473.1 (100%, $[M - 2CF_3SO_3]^+$). Anal. Calcd for $C_{30}H_{22}N_4O_6F_6S_2Co$: C, 46.70; H, 2.87; N, 7.26. Found: C, 46.56; H, 2.78; N, 7.24.

Dinuclear Iron(II) Complex $[Fe_2(\mathbf{3})_3](ClO_4)_4$ (3a). Addition of $FeSO_4 \cdot 7H_2O$ (1.5 equiv in H_2O) to a suspension of **3** (1 equiv in EtOH) gave a deep red homogeneous solution. After 1 h of heating at 80° C the solvent was removed (reduced pressure) and the residue dissolved in a minimum amount of water. Precipitation occurred after addition of a few drops of a $LiClO_4$-saturated water solution, and the deep red complex was recovered by filtration, washed with cold H_2O and Et_2O, and dried under high vacuum, giving the $[Fe_2(\mathbf{3})_3](ClO_4)_4 \cdot 3H_2O$ complex **3a** (98%, deep red microcrystals obtained by slow diffusion of Et_2O in an acetone/water solution). UV–vis (CH_3CN): 257 (64 800), 308 (113 000), 357 (11 700), 515 (16 400). FAB$^+$ (Thio): m/z 1509.1 (65%, $[M - ClO_4]^+$, 1410.1 (37%, $[M - 2ClO_4]^+$). Anal. Calcd for $C_{72}H_{72}N_{12}Cl_4O_{19}Fe_2$: C, 52.00; H, 4.36; N, 10.10. Found: C, 51.86; H, 4.31; N, 10.02.

Table II. Electronic, Charge-Transfer Absorption Spectra and Redox Potentials of Complexes with Ligands **1–3** and Their dmbpy, dmphen, p-QP, and bpy Analogues[a]

complex	λ_{max}, nm (ϵ, M^{-1} cm^{-1})[b]	$E_{1/2}$, V[c] (ΔE, mV)[d]	no. of electrons[e] exchanged
$[Cu_2(\mathbf{1})_2](ClO_4)_2$	445 (9400)	+0.88 (70)	2
		−1.68 (irrev)	
$[Cu(dmbpy)_2](CF_3SO_3)$	454 (6700)	+0.72 (60)	1
		−1.73 (irrev)	
$[Cu_2(p\text{-}QP)_2](ClO_4)_2$	454 (12 700)	+0.53 (70)	1
		+0.72 (70)	1
$[Cu_2(\mathbf{2})_2](ClO_4)_2$	443 (11 500)	+0.85 (70)	2
		−1.55 (irrev)	
$[Cu(dmphen)_2]$-(CF_3COO)	455 (7300)	+0.67 (60)	1
		−1.89 (irrev)	
$[Co(\mathbf{2})](CF_3SO_3)_2$		−0.67 (60)	1
		−1.24 (60)	1
		−1.68 (60)	1
$[Co(bpy)_3](ClO_4)_2$		+0.32 (60)	1
		−0.95 (70)	1
		−1.55 (60)	2
$[Fe_2(\mathbf{3})_3](ClO_4)_4$	515 (16 400)	+0.88 (80)	2
$[Fe(bpy)_3](ClO_4)_2$	520 (8050)	+0.79 (70)	1

[a] dmbpy = 6,6′-dimethyl-2,2′-bipyridine, dmphen = 2,9-dimethyl-1,10-phenanthroline, p-QP = 5,5′,3″,5‴-tetramethyl-2,2′:6′,2″:6″,2‴-quaterpyridine, and bpy = 2,2′-bipyridine. [b] Measured in CH_3CN. [c] Obtained from cyclic voltammetry studies on platinum (2 mm^2) or glassy carbon (3.5 mm^2) in dry acetonitrile solvent containing 0.1 M TBAP as supporting electrolyte. Solutions were ca. 1×10^{-3} M in complex, and measurements were made at room temperature under Ar at 0.2 V s^{-1} scan rate, with reference to ferrocene (+0.39 V) as internal standard but are quoted relative to the saturated calomel electrode (SCE) reference electrode. [d] Separation between anodic and cathodic peak potentials, ΔE_p, for ferrocene under the same conditions was 70 mV. No compensation was made for internal cell resistance. [e] Obtained by coulometry studies on a platinum wire by using the same conditions as in *c*.

X-ray Experimental Section

Suitable orange crystals of **1a** and light brown crystals of **2b** were obtained by slow diffusion of Et_2O into a CH_3CN solution (copper) or 1:1 CH_3CN/CH_2Cl_2 solution (cobalt) of the complex at room temperature. For **1a**, data were collected on a Philips PW1100/16 diffractometer equipped with a low-temperature device using nickel-filtered Cu Kα radiation (λ = 1.5418 Å); in the case of **2b**, data were collected on an Enraf-Nonius CAD-4F instrument at room temperature, with use of graphite-monochromatized Mo Kα radiation (λ = 0.7107 Å). The crystal data and data collection parameters are summarized in Table I. No significant changes were observed for three standard reflections monitored every 1 h during the data collection period. The Enraf-Nonius SDP package[11] was used on a Microvax II computer for all computations, except that a local data reduction program was employed. The initial step-scan data were converted to intensities by the Lehmann–Larson method[12] and then corrected for Lorentz, polarization, and absorption factors with the latter being computed by the empirical method of Wacker and Stuart.[13]

Both structures were solved by using the heavy-atom method. The remaining non-hydrogen atoms were located on subsequent difference Fourier maps. Hydrogen atoms were introduced at computed coordinates (C–H = 0.95 Å) with isotropic temperature factors $B(H) = 1 + B_{eqv}(C)$ Å^2. In the case of **1a**, one of the ClO_4^- anions is distorted over two positions for three oxygen atoms, for which a half-occupancy has been arbitrarily given. Full least-squares refinements converged to the *R* factors shown in Table I. Final difference maps revealed no significant maxima.

Results and Discussion

When ligands **1** or **2** were treated with $[Cu(CH_3CN)_4]ClO_4$, a 2:2 ligand/metal complex **1a** (m/z 959.1, $[M = ClO_4]^+$) or **2a** (m/z 1055.1, $[M - ClO_4]^+$) was isolated in high yield. The electronic absorptions of the two complexes (Table II) are in good agreement with those expected for Cu^{I}bpy or -phen complexes on the basis of the properties displayed by the mononuclear $[Cu^I(6,6'\text{-}Me_2bpy)_2]^+$[14] or $[Cu^I(2,9\text{-}Me_2\ phen)_2]^+$[15] complexes

---

(9) Hathaway, B. J.; Holah, D. G.; Postlethwaite, J. D. *J. Chem. Soc.* **1961**, 3215.

(10) $[Co(DMSO)_6](CF_3SO_3)_2$ was synthesized by a modified procedure given by: Currier, W.F.; Weber, J. H. *Inorg. Chem.* **1967**, *6*, 1539.

(11) Frentz, B. A. In *Computing in Crystallography*; Schenk, H., Olthof-Hazekamp, R., van Koningaveld, H., Bassi, C. G., Eds.; Delft University Press: Delft, The Netherlands, 1978; p 64.

(12) Lehmann, M. S.; Lansen, F. K. *Acta Crystallogr.* **1974**, *A30*, 580.

(13) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

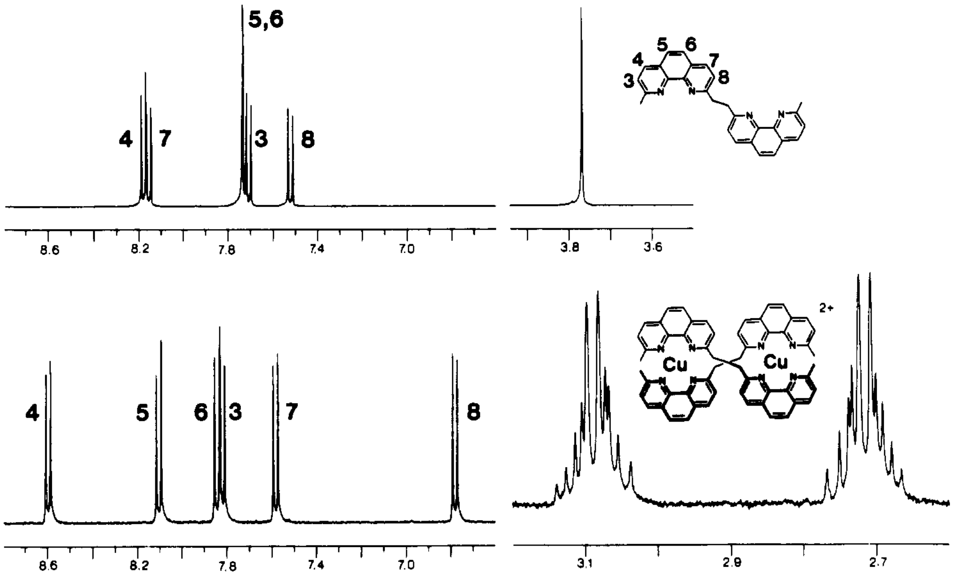


Figure 1. 200-MHz NMR spectra of ligand **2** (CD_2Cl_2) and of $[Cu_2(\mathbf{2})_2]^{2+}$ (**2a**) (CD_3CN). The signal of the CH_2 protons of the complex (ABCD patterns) is shown amplified by a factor of ca. 5; the CH_3 and solvent signals are not shown.

and by the dinuclear Cu(I) complex of p-QP.[7a]

The dinuclear copper complexes $[Cu_2(\mathbf{1})_2]^{2+}$ and $[Cu_2(\mathbf{2})_2]^{2+}$ are oxidized by cyclic voltammetry, in a single reversible dielectronic wave, at $E_{1/2} = +0.88$ V and $E_{1/2} = +0.85$ V vs SCE in CH_3CN, respectively. These values are somewhat higher than those of the analogous mononuclear copper complexes $[Cu(dmbpy)_2]^+$ ($E_{1/2} = +0.72$ V) and $[Cu(dmphen)_2]^+$ ($E_{1/2} = +0.67$ V)[16] or of the dinuclear p-QP species $[Cu_2(p\text{-}QP)_2]^{2+}$ in which two different monoelectronic oxidation steps have been observed at $E_{1/2} = +0.53$ V and $E_{1/2} = +0.72$ V vs SCE[7b] (Table II). It is of interest to note that these dimeric bpy and phen ligands strongly stabilize the copper(I) versus copper(II) complexes, mostly due to a steric effect of the methyl and methylene substituents α to the chelating nitrogens, which inhibit pentahedral or octahedral geometries favorable to copper(II). Consequently the monovalent complexes are stabilized and the donor atoms are roughly arranged in a tetrahedral geometry.[17] The proton NMR spectra of the ligands **1** and **2** are markedly different from those of their Cu(I) complexes. The signals of the phenanthroline protons are shifted on complexation and are well separated (Figure 1). Peak attributions have been assigned by nuclear Overhauser enhancement (NOE) experiments. The proton ortho (8) to the methylene link shifts upfield by more than 0.7 ppm, while the proton ortho (3) to the methyl group shifts downfield by only 0.1 ppm; these observations clearly indicate that proton 8 lies in the shielding region of the phenanthroline subunits of the second ligand, whereas proton 3 is only slightly influenced. By analogy, the same behavior has been observed for complex **1a** in which proton H–C15 lies in the shielding region of the bipyridine subunits of the second ligand, while proton H–C22 is not perturbed (Figure 2). Also, significant changes occur for the CH_2CH_2 signals; these protons, which appear as a singlet in the free ligand, shift upfield by more than 0.8 ppm and display an ABCD pattern in the complex. Clearly, the CH_2 protons have become nonequivalent in the complex due to the loss of the corresponding plane of symmetry. Furthermore, their strong upfield shift suggests that they now probably lie in the shielding region of the phenanthroline subunits. On the basis of earlier observation,[5] these data indicate that a chiral double-helical structure can be assigned to complex **2a**. Such an arrangement has been taken as basis for the synthesis of a molecular trefoil knot.[18] The same observations have been made for complex **1a**, and the formation of a double-helical structure has been confirmed by a crystal structure determination.

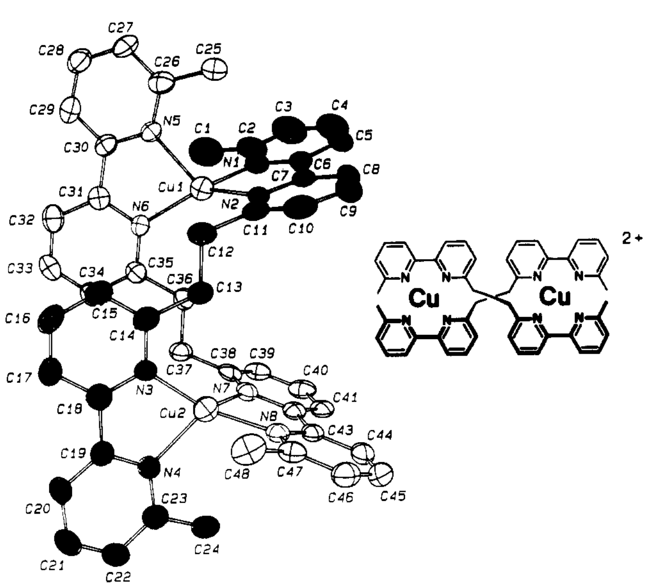


Figure 2. ORTEP representation of the structure of $[Cu_2(\mathbf{1})_2]^{2+}$ (**1a**) with thermal ellipsoids drawn at the 50% probability level.

Structure of Bis(1,2-bis(6′-methyl-2,2′-bipyridin-6-yl)ethane)dicopper(I) Diperchlorate (1a). X-ray diffraction analysis of **1a** was performed in order to determine the geometry about Cu(I) and to confirm its double-helical nature, inferred earlier on the basis of NMR data.[6] The structure obtained is depicted in Figure 2. Selected bond lengths and bond angles are listed in Table III. In the structure of **1a**, the Cu1–Cu2 distance is 5.926 (1) Å, and each Cu(I) possesses a distorted tetrahedral geometry; the N–Cu–N cis bond angles (average value of 81.4°) combined with the N–Cu–N trans bond angles (from 109.4 (1) to 136.5 (1)° for Cu1 and from 116.9 (1) to 132.0 (2)° for Cu2) clearly demonstrate the deformation from the ideal tetrahedron. As expected, the copper–nitrogen bond lengths are similar for the two copper sites and close to values detected in the $[Cu(dmbpy)_2]^+$ complex.[19] However, the Cu–N bonds to one of the bpy units at each end of the complex differ significantly, one being longer (2.057, 2.076

---

(14) Hall, J. R.; Litzow, M. R.; Plowman, R. A. *Anal. Chem.* **1963**, *35*, 2124.

(15) Blaskie, M. W.; McMillin, D. R. *Inorg. Chem.* **1980**, *19*, 3519.

(16) Federlin, P.; Kern, J.-M.; Rastegar, A.; Dietrich-Buchecker, C.; Marnot, P. A.; Sauvage, J.-P. *New J. Chem.* **1990**, *14*, 9.

(17) James, B. R; Williams, R. J. P. *J. Chem. Soc.* **1961**, 2007.

(18) Dietrich-Buchecker, C.; Sauvage, J.-P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 189.

(19) Burke, P. J.; McMillin, D. R.; Robinson, W. R. *Inorg. Chem.* **1980**, *19*, 1211.

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) for Complexes **1a** and **2b**

1a		**2b**	
	Bond Lengths		
Cu1–N1	2.026 (4)	Co–O1	2.215 (4)
Cu1–N2	2.036 (4)	Co–O4	2.215 (3)
Cu1–N5	2.057 (4)	Co–N1	2.146 (4)
Cu1–N6	2.005 (5)	Co–N2	2.127 (4)
Cu2–N3	2.012 (3)	Co–N3	2.108 (4)
Cu2–N4	2.076 (4)	Co–N4	2.144 (4)
Cu2–N7	2.046 (4)	S1–O1	1.446 (4)
Cu2–N8	2.027 (4)	S1–O2	1.414 (4)
		S1–O3	1.439 (4)
		S2–O4	1.456 (3)
		S2–O5	1.425 (4)
		S2–O6	1.426 (4)
	Bond Angles		
N1–Cu1–N2	81.1 (2)	O1–Co–O4	172.5 (1)
N1–Cu1–N5	109.4 (1)	O1–Co–N1	81.4 (1)
N1–Cu1–N6	132.2 (2)	O1–Co–N2	98.8 (2)
N2–Cu1–N5	116.5 (1)	O1–Co–N3	76.2 (1)
N2–Cu1–N6	136.5 (1)	O1–Co–N4	102.5 (1)
N5–Cu1–N6	81.9 (1)	O4–Co–N1	103.1 (1)
N3–Cu2–N4	81.6 (1)	O4–Co–N2	76.5 (1)
N3–Cu2–N7	131.8 (1)	O4–Co–N3	99.5 (1)
N3–Cu2–N8	132.0 (2)	O4–Co–N4	82.5 (1)
N4–Cu2–N7	117.6 (1)	N1–Co–N2	78.3 (2)
N4–Cu2–N8	116.9 (1)	N1–Co–N3	157.4 (2)
N7–Cu2–N8	81.0 (2)	N1–Co–N4	103.8 (1)
		N2–Co–N3	107.3 (2)
		N2–Co–N4	158.7 (1)
		N3–Co–N4	79.1 (2)

Å) and the other two shorter (2.005, 2.012 Å) than the average of the other four bonds. This may be due to strain induced by the CH_2CH_2 bridge, which, if somewhat too short, could indeed decrease one Cu–N distance and lengthen the other one.

Each pyridine group is planar with a maximum deviation of 0.02 Å. The two bipyridine fragments in each ligand **1** are different in terms of planarity, one being almost planar as reflected by their dihedral angle (average value of 5° for the bipyridines containing N1 and N2 or N7 and N8). On the other hand, when N3 and N4 or N5 and N6 are involved, the bipyridine subunits are twisted about the ring junction with an average angle of 17°. This accounts for the lack of a C_2 symmetry axis in the molecule. The dihedral angle of 35.4 (1)° between the two almost planar bipyridine units at each copper center corresponds to a distortion of the whole molecule. As a result, the two terminal pyridine planes (with N5 and N4) belonging to the nonplanar bipyridines are bent, as demonstrated by their dihedral angle value of 38.3 (2)°.

The structural features of the ligands about the copper centers are such that each ligand is arranged in a helical manner by complexation with copper(I). This is supported by the values of the dihedral angles between the mean planes of the two bipyridines belonging to the same ligands (94.17 (6)° between planes containing N2, N1 and N3, N4; 84.27 (6)° between planes containing N5, N6 and N7, N8). The dimeric nature of **1a** allows the formation of a double helicate, as previously observed with analogous oligobipyridine ligands containing bpy units linked by CH_2OCH_2 bridges.[5]

When ligand **2** was treated with $[Co(DMSO)_6]^{2+}$, a 1:1 ligand/metal complex **2b** (*m/z* 622.1, $[M - OTf]^+$) was isolated almost quantitatively. It had a light brown color characteristic of an octahedral coordination geometry around the metal. The IR spectrum of complex **2b** (KBr pellet) showed the presence of two S–O stretching vibrations (ν_{S-O} 1285 and 1250 cm^{-1}). Splitting of the ν_{S-O}(asym) band has been reported previously[20] for copper and cobalt complexes where coordination of the triflate anion to the metal was proposed. Such splitting arises in our case from a weak coordination of the anion as an unidentate ligand, whose structure has been further confirmed by X-ray analysis (vide infra). The mononuclear cobalt complex $[Co(\mathbf{2})](CF_3SO_3)_2$ was reduced on a platinum rotating disk electrode in a reversible monoelectronic wave at $E_{1/2}$ = –0.67 V (cobalt(II/I)) as well as in two additional reversible monoelectronic waves at –1.24 and –1.68 V (ligand-based reduction). Complex **2b** was easier to reduce than the corresponding $[Co(bpy)_3]^{2+}$ ($E_{1/2}$ = –0.95 V)[21] (Table II) or $[Co(terpy)_2]^{2+}$ ($E_{1/2}$ = –0.77 V)[22] species by 280 and 100 mV, respectively. The dimeric ligand **2** seems not to strongly stabilize the cobalt(II) cation, as a quinquepyridine ligand does.[23] Further studies of the reactivity of this complex toward water or oxygen clearly confirmed it.[24] Cyclic voltammetric measurements showed the absence of any oxidation response (up to 2.3 V with tetrabutylammonium hexafluorophosphate as supporting electrolyte or up to 1.5 V with pyridine as solvent). This surprising observation might be explained by a very slow process at the electrode surface.[25]

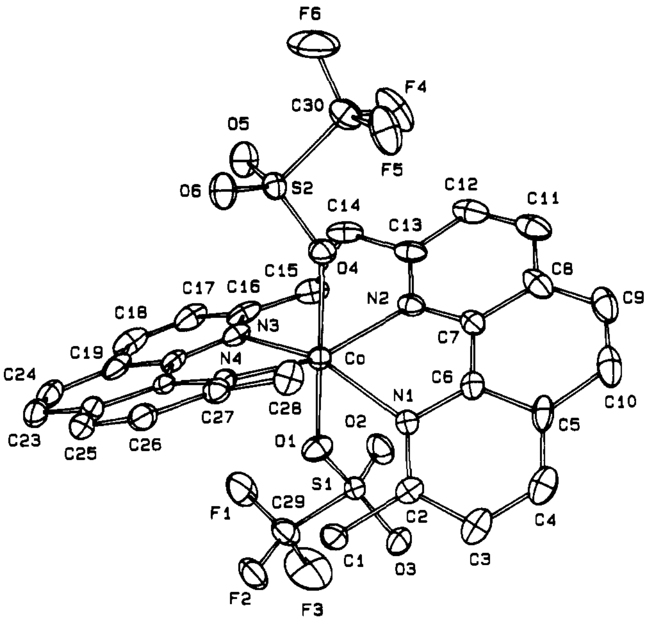


Figure 3. ORTEP representation of the structure of $[Co(\mathbf{2})](CF_3SO_3)_2$ (**2b**) with thermal ellipsoids drawn at the 50% probability level.

Structure of (1,2-Bis(9-methyl-1,10-phenanthrolin-2-yl)ethane)cobalt(II) Bis(trifluoromethanesulfonate) (2b). Single-crystal X-ray diffraction analysis of **2b** confirmed the ligand:cobalt ratio of 1:1 with a distorted octahedral coordination geometry (Figure 3). Selected bond lengths and bond angles are listed in Table III. The cobalt environment consists of four nitrogen atoms of the pyridine rings, while two CF_3SO_3 anions are located at 2.215 (4) Å. The average Co–N bond length of 2.13 Å is close to that of the Co–N bonds in $[Co(tetrapy)](ClO_4)_2$[26] but shorter than those of the $[Co(quinquepyridine)Cl_2]$ complex.[23] The cobalt cation lies in the plane formed by the four nitrogen donor set at a distance of 0.012 (1) Å, as previously observed in the $[Co(tetrapy)(H_2O)_2](NO_3)_2$ species.[27] The three rings belonging to one phenanthroline of the ligand show some flexibility[28] detected by the deviation from planarity; the dihedral angles between the

---

(20) Arduini, A. L.; Garnet, M.; Thompson, R. C.; Wong, T. C. T. *Can. J. Chem.* **1975**, *53*, 3812. Dedert, P. L.; Thompson, J. S.; Ibers, J. A.; Marks, T. J. *Inorg. Chem.* **1982**, *21*, 969.

(21) Margel, S.; Smith, W.; Anson, F. C. *J. Electrochem. Soc.* **1978**, *125*, 241.

(22) Guadalupe, A. R.; Usifer, D. A.; Potts, K. T.; Hurrell, H. C.; Mogstad, A.-E.; Abruna, H. D. *J. Am. Chem. Soc.* **1988**, *110*, 3462.

(23) Gheysen, K. A.; Potts, K. T. Hurell, H. C.; Abruna, H. D. *Inorg. Chem.* **1990**, *29*, 1589.

(24) Ziessel, R.; Lehn, J.-M.; Youinou, M.-T. Unpublished results.

(25) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; p 86.

(26) Henke, W.; Kremer, S. *Inorg. Chim. Acta* **1982**, *65*, L115.

(27) Von Henke, W.; Kremer, S.; Reinen, D. *Z. Anorg. Allg. Chem.* **1982**, *491*, 124.

(28) Youinou, M.-T.; Ziessel, R. *J. Organomet. Chem.* **1989**, *363*, 197.

pyridine rings of one phenanthroline subunit are respectively 8 (1)° with N3 and N4 involved and 10.54 (8)° with N1 and N2. The preference of cobalt for an octahedral geometry is such that the constraint imposed by the CH_2CH_2 bridges leads to a distortion of the phenanthroline subunit. This may also be the reason for the lack of double-helix formation.

When ligand **3** was treated with iron(II) salts, a 3:2 ligand/metal complex **3a** (m/z 1509.1, $[M - ClO_4]^+$) with a deep red color characteristic of a "$Fe(bpy)_3$" species (Table II), was quantitatively isolated. The structure of complex **3a** might be close to that recently described for an analogous triply bridged dinuclear iron species consisting of three bridging 1,2-bis(4′-methyl-2,2′-bipyridin-4-yl)ethane ligands linking the two Fe(II) centers.[4] The dinuclear iron complex $[Fe_2(3)_3](ClO_4)_4$ was oxidized by cyclic voltammetry in a single reversible dielectronic wave at $E_{1/2}$ = +0.88 V, which compares well with its $[Fe(bpy)_3[(ClO_4)_2$ analogue value of $E_{1/2}$ = +0.70 V.[29]

Conclusion

The present results show that ligands containing two bipyridine or two phenanthroline groups linked by a CH_2CH_2 bridge are able to form a double-stranded helicate by complexation with copper(I). In the case of cobalt(II), the strong tendency to form an octahedral geometry prevents the formation of such a helix.

The double-helical structure of the dinuclear copper complexes was assigned by NMR spectroscopy for **1a** and **2a** and confirmed by the X-ray structure analysis for **1a**. Twisting forces the proton α to the ethane bridge to be in the shielding region of the bipyridine or phenanthroline subunit of the second ligand, a feature characteristic of the existence of a double helix in a given compound.

Finally, the dinuclear copper and iron complexes are oxidized in a single reversible dielectronic wave; this seems to indicate that each redox center is almost electronically independent. Related conjugated ligands might give access to coupled redox centers (see also ref 6).

Acknowledgment. We thank Patrick Maltèse for determining the NOE-DIFF NMR spectra and the CNRS for financial support.

Registry No. **1**, 120096-05-1; **1a**, 132298-91-0; **2**, 120096-06-2; **2a**, 132298-93-2; **2b**, 132298-94-3; **3a**, 132343-37-4; $[Cu_2(\mathbf{1})_2]^{3+}$, 132298-96-5; $[Cu_2(\mathbf{2})_2]^{3+}$, 132298-97-6; $[Co(\mathbf{2})](CF_3SO_3)_2^-$, 132298-98-7; $[Co(\mathbf{2})](CF_3SO_3)_2^{2-}$, 132343-38-5; $[Co(\mathbf{2})](CF_3SO_3)_2^{3-}$, 132298-99-8; $[Fe_2(\mathbf{3})_3]^{5+}$, 132299-00-4; $[Cu(CH_3CN)_4](ClO_4)$, 14057-91-1; $[Co(DMSO)_6](CF_3SO_3)_2$, 132298-95-4; $[Cu(dmbpy)_2]^{2+}$, 90316-91-9; $[Cu_2(p\text{-}QP)_2]^{3+}$, 97093-39-5; $[Cu_2(p\text{-}QP)_2]^{4+}$, 132299-01-5; $[Cu(dmphen)_2]^{2+}$, 14875-91-3; $[Co(bpy)_3]^{3+}$, 19052-39-2; $[Co(bpy)_3]^+$, 47780-35-8; $[Co(bpy)_3]$, 29931-78-0; $[Fe(bpy)_3]^{3+}$, 18661-69-3; $[Cu(dmbpy)_2](CF_3SO_3)$, 116184-54-4; $[Cu_2(p\text{-}QP)_2](ClO_4)_2$, 88178-45-4; $[Cu(dmphen)_2](CF_3COO)$, 132299-02-6; $[Co(bpy)_3](ClO_4)_2$, 21349-81-5; $[Fe(bpy)_3](ClO_4)_2$, 15388-48-4.

Supplementary Material Available: Tables of positional parameters and isotropic thermal parameters, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom parameters (21 pages); tables of observed and calculated structure factors (28 pages). Ordering information is given on any current masthead page.

---

(29) Brandt, W. W.; Dwyer, F. P.; Gyarfas, E. C. *Chem. Rev.* **1954**, *54*, 959.

Contribution from the Lehrstuhl für Anorganische Chemie I, Ruhr-Universität, D-4630 Bochum, FRG,
Institut für Physikalische Chemie, Technische Hochschule, D-6100 Darmstadt, FRG, Institut für Physik,
Medizinische Universität, D-2400 Lübeck, FRG, and Anorganisch-Chemisches Institut der Universität, D-6900 Heidelberg, FRG

Syntheses, Redox Behavior, and Magnetic and Spectroscopic Properties of $Cu^{II}Cu^{II}Cu^{II}$, $Cu^{II}Ni^{II}Cu^{II}$, and $Cu^{II}Pd^{II}Cu^{II}$ Species. Crystal Structure of $[L_2Cu_2Cu(dmg)_2Br]ClO_4{\cdot}CH_3OH$ (L = 1,4,7-Trimethyl-1,4,7-triazacyclononane; dmg = Dimethylglyoximato(2−))

Phalguni Chaudhuri,[*,†] Manuela Winter,[†] Beatriz P. C. Della Vêdova,[†] Eckhard Bill,[‡] Alfred Trautwein,[‡]
Stefan Gehring,[§] Peter Fleischhauer,[§] Bernhard Nuber,[‖] and Johannes Weiss[‖]

Received July 18, 1990

A series of homo- and heterotrinuclear complexes $Cu^{II}Cu^{II}Cu^{II}$, $Cu^{II}Ni^{II}Cu^{II}$, and $Cu^{II}Pd^{II}Cu^{II}$ containing the dimethylglyoximato dianion as bridging ligands and either 1,4,7-trimethyl-1,4,7-triazacyclononane or *N,N,N′,N′*-tetramethylethylenediamine as capping ligands have been synthesized and characterized on the basis of IR, electronic, and EPR spectroscopy and variable-temperature (4-290 K) magnetic susceptibility measurements. The crystal and molecular structure of the compound $[L_2Cu_2(dmg)_2CuBr]ClO_4{\cdot}CH_3OH$ has been established by X-ray diffraction. It crystallizes in orthorhombic system, space group *Pnam* with lattice constants a = 14.006 (7) Å, b = 15.972 (8) Å, c = 19.27 (1) Å, and Z = 4. The structure consists of $Cu^{II}Cu^{II}Cu^{II}$ trinuclear cations, uncoordinated perchlorate anions, and a methanol molecule of crystallization. Each copper ion is in a square-pyramidal environment. The $Cu(dmg)_2^{2-}$ dianion functions as a bridge between two terminal copper ions through its deprotonated oximate oxygen and represents the central copper atom in the trinuclear unit. The central copper atom is coordinated also to a bromide ion. The terminal copper ions achieve a CuN_3O_2 chromophore structure by coordinating to three nitrogen atoms of the cyclic amine and the deprotonated oxygen atoms of dimethylglyoxime dianion. A strong antiferromagnetic interaction (J = −448 cm^{-1}) between adjacent Cu(II) ions has been found for the aforementioned compound, showing that dimethylglyoxime is a good mediator for spin-exchange interactions. A moderately strong antiferromagnetic interaction ($2J$ = −72 cm^{-1}) has been observed for a $Cu^{II}Pd^{II}Cu^{II}$ system, with a diamagnetic square-planar Pd(II) as the central ion, although the Cu···Cu separation is expected to be ca. 7.6 Å. The powder EPR spectra indicate square-pyramidal geometry for the copper with a $(d_{x^2-y^2})^1$ ground state in the homotrinuclear complexes. EPR spectra of heterotrinuclear complexes are quasi-isotropic. The cyclic voltammograms of the $Cu^{II}Cu^{II}Cu^{II}$ complexes revealed, besides other features, a quasi-reversible one-electron oxidation corresponding to the reversible formation of the mixed-valence species $Cu^{II}Cu^{III}Cu^{II}$.

Introduction

Current research work concerning the structural and magnetic properties of polynuclear transition-metal compounds is aimed at understanding the structural and chemical features governing electronic exchange coupling through multiatom bridging ligands.[1-3] This problem has important implications for topics such

---

[†] Ruhr-Universität Bochum.

[‡] Medizinische Universität Lübeck.

[§] Technische Hochschule Darmstadt.

[‖] Universität Heidelberg.

(1) Hendrickson, D. N. In *Magneto-Structural Correlations in Exchange Coupled Systems*; Willett, R. D., Gatteschi, D., Kahn, O., Eds.; NATO ASI Series C; Mathematical and Physical Science; Reidel: Dordrecht, The Netherlands, 1985; p 523.

0020-1669/91/1330-2148$02.50/0 © 1991 American Chemical Society