change, and $[Ni(2,9\text{-dmp})Cl_2]_2$ and $[Ni(2,2'\text{-biq})Cl_2]_2$ show[32,33] antiferromagnetic exchange, but not one of the $FeLCl_2$ compounds with five-coordinate Fe(II) sites displays the magnetic exchange expected for strongly coupled paramagnetic metal ions.

Strong ferromagnetic exchange has been detected in the red $Fe(bpy)Cl_2$ isomer and in similar, polymeric, pseudooctahedral complexes such as $Fe(phen)Cl_2$, $Mn(bpy)Cl_2$, and α-$Co(bpy)Cl_2$.[34] X-ray crystallographic analysis of a single crystal of α-$Co(bpy)Cl_2$ has revealed[35] that the molecular structure of this compound is a stepped, zigzag, chain in which each Co(II) center is linked to the next by twin chloro bridges (this structure can be generated from Figure 4 if the Fe centers are changed to Co centers and the terminal chlorine atoms are made into bridging atoms). The far-infrared spectra of $Fe(phen)Cl_2$, $Mn(bpy)Cl_2$, the red $Fe(bpy)Cl_2$ isomer, and α-$Co(bpy)Cl_2$[1,2,23,26] indicate that these compounds are isomorphous to each other. The strong ferromagnetic exchange observed in these four compounds suggests that they have very similar molecular structures. The twin chloro bridges produce a chain with bond lengths and bond angles that are favorable to strong magnetic exchange.

We believe that the red, pseudooctahedral isomer of $Fe(bpy)Cl_2$ is kinetically favored and that the orange isomer, the isomer with five-coordinate Fe(II), is thermodynamically favored. The red form can be obtained by the Broomhead–Dwyer synthesis: a hot, acidic, aqueous solution of $FeCl_2$ is decanted onto a thin layer of finely ground 2,2′-bipyridine, and the reaction mixture is stirred, heated, and concentrated until the red isomer precipitates.[1,36] During some of our recent attempts to prepare the red form in solution, we discovered that if the reaction mixture is stirred and heated too long, the color changes from red to orange. The Mössbauer spectrum of the product isolated from any one of these excesses reveals that both isomers are present in a ratio of approximately one part red to three parts orange. This observation is consistent with our synthesis of the orange form in solution: if a 2,2′-bipyridine/absolute ethanol solution is gradually added with heating and stirring to a freshly prepared $FeCl_2$/ethanol solution (bpy/Fe molar ratio 1/10) and the reaction mixture is heated and stirred further, then just the orange isomer precipitates (see Experimental Section). Furthermore, while careful vacuum thermolysis (10 μm Hg for 10 h) of $[Fe(bpy)_3]Cl_2$ in the solid state at moderate temperatures (145 °C) produces only the red form of $Fe(bpy)Cl_2$, prolonged (>20 h) vacuum thermolysis at higher temperatures (>150 °C) yields an approximately 1/1 mixture of the two isomers.[1]

Conclusions

The spectra and the magnetic behavior recorded for the orange $Fe(bpy)Cl_2$ isomer and related $FeLCl_2$ compounds (L = 5,5′-Me_2-, 4,4′-Me_2-, and 4,4′-Ph_2bpy) are most consistent with our proposed molecular structure: a chain of single chloro bridges and five-coordinate, high-spin Fe(II) sites. The differences between the two isomers of $Fe(bpy)Cl_2$ indicate that a rich variety of molecular structures and chemical and physical properties is to be found among $FeLX_2$ compounds where L = endo bidentate ligand and X = halogen or pseudohalogen.

Acknowledgment. We are very grateful for the financial support of the U.S. National Science Foundation, Division of Materials Research, Solid State Chemistry Program Grants 8016441 and 8313710. We thank Drs. Edward H. Witten and Karoly Lázár for executing magnetic susceptibility and Mössbauer spectroscopy measurements of $Fe(4,4'\text{-}Ph_2bpy)Cl_2$, and we thank Brian Rappoli for devising a reliable preparation of this complex.

Registry No. $Fe(bpy)Cl_2$, 32425-36-8; $Fe(4,4'\text{-}Me_2bpy)Cl_2$, 102630-78-4; $Fe(4,4'\text{-}Ph_2bpy)Cl_2$, 102630-79-5.

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New Route to Bimetallic Imidazolate-Bridged Complexes. 1. Synthesis and Solid-State Properties of a Homodinuclear (Copper–Copper) Complex and Its Heterodinuclear (Copper–Nickel) Homologue. Structure of the Heterodinuclear Complex

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Received October 28, 1985

The synthesis and magnetic properties of the (μ-imidazolato)bis(7-amino-4-methyl-5-aza-3-hepten-2-onato(1−))dicopper(II) perchlorate complex and its heterodinuclear (copper–nickel) homologue are described. The structure of the heterodinuclear complex is reported. It crystallizes in the triclinic space group C_i^1-$P\bar{1}$ with two formula weights in a cell having the dimensions $a = 11.227$ (2) Å, $b = 13.218$ (2) Å, $c = 8.271$ (1) Å, $\alpha = 103.34$ (1)°, $\beta = 100.27$ (1)°, and $\gamma = 76.87$ (1)°. $\Delta M_S = 2$ transitions are observed in EPR spectra related to solid samples of both complexes. Their disappearance upon dilution suggests that dipolar interactions between the individual dinuclear units are operative in the solid. Static susceptibility measurements point to an intramolecular exchange interaction ($2J = -43.0$ cm^{-1}) between the two copper(II) ions of the dicopper complex.

Introduction

Binding of imidazole-type molecules to metal complexes is a subject of considerable interest because of the frequent occurrence of imidazole derivatives in biologically important metal complexes. One of the most extensively studied members of this group is the Cu–Zn superoxide dismutase,[1] which has been shown by X-ray crystallography to have an imidazolate bridge between the two metals. Consequently a number of model compounds have been prepared. They involve pairs of either identical or dissimilar metals bridged by a deprotonated imidazole-type molecule.[2-15]

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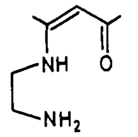

Figure 1. The AEH ligand.

Our interest in this area is focused on proposing a method to build easily M–Im–M′ units (M and M′ are being metal ions and Im standing for imidazolate ion) with the possibility of varying the metal centers M and M′ and the environment of one of them. The synthetic strategy relies on the terdentate Schiff base 7-amino-4-methyl-5-aza-3-hepten-2-one (abbreviated as AEH in the following and represented in Figure 1), which results from the condensation of one molecule of acetylacetone with one molecule of diamine. This ligand has recently been used to obtain various types of complexes in which the metal (copper or nickel) is hexa- or pentacoordinated.[16–18] Recently, we succeeded in preparing the less-common four-coordinated complexes $[(AE)M^{II}py]^+$ (M^{II} = Cu^{II}, Ni^{II}; py = C_5H_5N), which suggest a possible route to dinuclear species.[19] Replacing the monodentate ligand pyridine by the potentially bidendate one, imidazole, would allow for coordination of a second metal through the outer nitrogen of the deprotonated imidazole. This has been actually realized in the case of homo- and heterodinuclear (copper, nickel) complexes. The present paper is devoted to the copper-containing species $[(AE)CuImNi(AE)]^+$ (**1**) and $[(AE)CuImCu(AE)]^+$ (**2**). Data concerning the dinickel complex and the related mononuclear complexes will be published elsewhere.

Experimental Section

Compound Preparation. (Imidazole)(7-amino-4-methyl-5-aza-3-hepten-2-onato(1−))copper(II) Perchlorate ([(AE)CuImH]ClO$_4$). To a 7 × 10^{-3} M solution of AEH in ethanol were first triethylamine (2 mL), then imidazole (0.5 g), and, a few minutes later, the equivalent amount of copper perchlorate hexahydrate (2.6 g) dissolved in ethanol. Upon being stirred, the blue solution gave a plum-colored precipitate, which was filtered, washed successively with ethanol and ether, and then dried. The yield was 73%. Anal. Calcd for $C_{10}H_{17}ClCuN_4O_5$: C, 32.26; H, 4.57; Cl, 9.52; Cu, 17.07; N, 15.05. Found: C, 32.37; H, 4.43; Cl, 9.16; Cu, 16.83; N, 14.89.

(Pyridine)(7-amino-4-methyl-5-aza-3-hepten-2-onato(1−))nickel(II) Perchlorate ([(AE)Ni(py)]ClO$_4$). This compound has been prepared as described earlier.[19]

Table I. Crystal Data and Experimental Details of the X-ray Diffraction Studies

(a) Crystal Parameters[a] at 20 °C

formula	$(C_{17}H_{29}N_6O_2CuNi)(ClO_4)$	V, Å^3	1152.8 (5)
mol wt	570.7	cryst syst	triclinic
a, Å	11.227 (2)	space group	C_i^1-$P\bar{1}$
b, Å	13.218 (2)	Z	2
c, Å	8.271 (1)	ρ(calcd), g/cm^3	1.644
α, deg	103.34 (1)	ρ(obsd),[b] g/cm^3	1.65
β, deg	100.27 (1)	F(000)	590
γ, deg	76.87 (1)		

(b) Measurement of Intensity Data[c]

instrument	Enraft-Nonius CAD4 diffractometer
radiation	Mo Kα (λ = 0.71073 Å) graphite monochromatized
cryst dimens, mm	0.450 × 0.150 × 0.063
detector window	
height, mm	4
width, mm	4
takeoff angle, deg	4.0
scan mode	θ–2θ
scan range, deg	1.20 + 0.35 (tan θ)
max 2θ, deg	54
stds	
intensity[d]	3 reflcns every 7200 s
orientation	3 reflcns every 200 data reflcns
no. of reflcns collcd	5029

(c) Treatment of Intensity Data[e]

reducn to F_o^2 and $\sigma(F_o)^2$	cor for bkgd, attenuators, and Lorentz–polarization in the usual manner
μ, cm^{-1}	19.1
transmission coeff[f]	
T_{max}	1.00
T_{min}	0.86
no. of obsd unique data $\lvert F_o\rvert \geq 6\sigma(F_o)$, n	2576
no. of variables, m	289
R[g]	0.033
R_w[h]	0.036
weighting scheme	unit weights
S[i]	1.13

[a] From the least-squares fitting of the setting angles of 25 reflections. [b] Flotation. [c] Process described in: Mosset, A.; Bonnet, J.-J.; Galy, J. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *B33*, 2639–2644. [d] Showed only random, statistical fluctuations. [e] All calculations were performed on a VAX-11/730 DEC computer with use of SDP and SHELX-76 packages. [f] Intensity data were corrected for empirical absorption corrections: North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gem. Crystallogr.* **1968**, *A24*, 351–359. [g] $R = \sum||F_o| - |F_c|/\sum|F_o|$. [h] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. [i] Error in an observation of unit weight, $S = [\sum w(|F_o| - |F_c|)^2/(n - m)]^{1/2}$.

(μ-Imidazolato)bis(7-amino-4-methyl-5-aza-3-hepten-2-onato(1−))copper(II)nickel(II) Perchlorate ([(AE)CuImNi(AE)]ClO$_4$). To a 1 × 10^{-3} M solution of [(AE)CuImH]ClO$_4$ in methanol was added another solution containing 1 × 10^{-3} M of [(AE)NiPy]ClO$_4$. Then 0.2 mL of a 5.4 M NaOMe solution was added upon stirring, giving readily a red precipitate of the desired compound, which was filtered, washed successively with methanol and ether, and dried under vacuum. The yield was 70%. Anal. Calcd for $C_{17}H_{29}ClCuN_6NiO_6$: C, 35.80; H, 5.09; Cl, 6.22; Cu, 11.14; N, 14.74; Ni, 10.17. Found: C, 35.04; H, 5.01; Cl, 6.12; Cu, 10.80; N, 14.25; Ni, 10.23.

Slow recrystallization from a CH_3CN solution gave crystals suitable for an X-ray diffraction study. The crystal used for data collection was shown by energy dispersive analysis by X-ray methods to contain copper and nickel.

(μ-Imidazolato)bis(7-amino-4-methyl-5-aza-3-hepten-2-onato(1−))dicopper Perchlorate ([(AE)CuImCu(AE)]ClO$_4$). This compound was prepared by using the procedure described above, with [(AE)CuImH]ClO$_4$ (0.37 g) and [(AE)CuBr]$_2$ (0.28 g) as starting materials.[17] The product was isolated as a violet powder with a yield of 70%. Anal. Calcd for $C_{17}H_{29}ClCu_2N_6O_6$: C, 35.45; H, 5.04; Cl, 6.17; Cu, 22.07; N, 14.60. Found: C, 35.30; H, 4.92; Cl, 6.30; Cu, 21.66; N, 14.34.

In spite of many attempts, no crystal suitable for X-ray structure determination has yet been obtained.

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Table II. Fractional Atomic Coordinates with Esd's in Parentheses

atom	*x*/*a*	*y*/*b*	*z*/*c*
Cu	0.40291 (6)	0.58222 (5)	0.14103 (8)
Ni	0.74370 (6)	0.26582 (5)	0.49695 (8)
O(1)	0.4867 (3)	0.6938 (3)	0.1681 (5)
O(2)	0.8914 (3)	0.3141 (3)	0.5506 (5)
N(1)	0.2562 (4)	0.6525 (3)	0.0248 (5)
N(2)	0.3162 (4	0.4627 (4)	0.0917 (7)
N(3)	0.5445 (3)	0.5127 (3)	0.2765 (5)
N(4)	0.6716 (4)	0.3946 (3)	0.4140 (5)
N(5)	0.8111 (4)	0.1371 (3)	0.5715 (6)
N(6)	0.5896 (4)	0.2141 (4)	0.4547 (6)
C(1)	0.4442 (6)	0.7829 (4)	0.1170 (7)
C(2)	0.3315 (6)	0.8083 (4)	0.0291 (7)
C(3)	0.2405 (5)	0.7434 (4)	−0.0181 (7)
C(4)	0.5307 (6)	0.8597 (5)	0.1695 (8)
C(5)	0.1212 (6)	0.7855 (5)	−0.1205 (8)
C(6)	0.1603 (5)	0.5882 (4)	−0.0337 (7)
C(7)	0.1831 (5)	0.5061 (4)	0.0707 (7)
C(8)	0.6375 (4)	0.5603 (4)	0.3760 (6)
C(9)	0.7145 (5)	0.4874 (4)	0.4576 (7)
C(10)	0.5693 (5)	0.4153 (4)	0.3057 (7)
C(11)	0.9915 (5)	0.2716 (5)	0.6330 (7)
C(12)	1.0074 (5)	0.1806 (5)	0.6916 (7)
C(13)	0.9195 (6)	0.1158 (5)	0.6625 (8)
C(14)	1.0944 (5)	0.3295 (5)	0.6580 (8)
C(15)	0.9540 (7)	0.0163 (5)	0.7350 (9)
C(16)	0.7251 (6)	0.0625 (4)	0.5394 (8)
C(17)	0.6204 (6)	0.0985 (5)	0.4134 (8)
Cl	0.26760 (15)	0.20413 (14)	0.21371 (22)
O(3)	0.3695 (4)	0.2451 (4)	0.1904 (6)
O(4)	0.1651 (5)	0.2886 (6)	0.2216 (9)
O(5)	0.2473 (6)	0.1180 (5)	0.0875 (8)
O(6)	0.2946 (6)	0.1725 (5)	0.3708 (7)

Caution. The compounds reported here were isolated as perchlorate salts. We have worked with these compounds in a number of organic solvents without incident and, as solids, they seem to be reasonably stable to shock and heat. In spite of these observations, the unpredictable behavior of perchlorate salts[20] necessitates extreme caution in their handling.

Physical Measurements. Microanalyses were performed by the Service Central de Microanalyse du CNRS, Lyon, France. Electronic spectra were obtained with a Cary 14 spectrometer. Magnetic susceptibility data were collected on powdered samples of the compounds with use of a Faraday-type magnetometer using mercury tetrakis(thiocyanato)cobaltate (susceptibility at 20 °C 16.44×10^{-6} cm^3 mol^{-1}) as susceptibility standard. Data were corrected for diamagnetism of the ligands and anions (estimated from Pascal constants[21] to be -238×10^{-6} cm^3 mol^{-1} for both complexes) and for temperature-independent paramagnetism. This term was estimated to be 110×10^{-6} cm^3 mol^{-1} in the case of **1** (vide infra) and fixed to 120×10^{-6} cm^3 mol^{-1} in the case of **2**. EPR spectra were recorded at X-band frequency (9.4–9.5 GHz) with a Bruker 200 TT spectrometer.

Collection and Reduction of X-ray Data. The crystal used for the structure determination was a red needle with the approximate dimensions reported in Table I. Details of the data collection and reduction are also given in Table I.

Structure Solution and Refinement. A Patterson map revealed the positions of the two metallic atoms. They were introduced as Cu and Ni atoms, respectively, although they could not be discriminated at that time. Subsequent Fourier maps and a least-squares refinement process revealed the positions of all non-hydrogen atoms, which were refined anisotropically. The hydrogen atoms were located from a difference electron density map. They were introduced in calculations in constrained geometry (C–H = N–H = 0.97 Å) with an isotropic temperature factor $U = 0.065$ Å^2 kept fixed.

The atomic scattering factors used were those proposed by Cromer and Waber[22] with anomalous dispersion effects.[23] Scattering factors for the hydrogen atoms were taken from Stewart et al.[24]

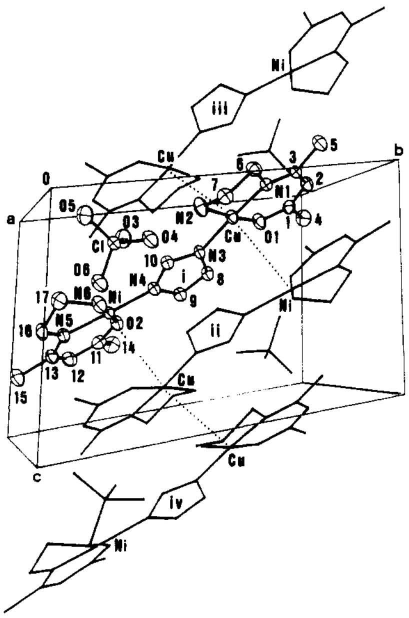

Figure 2. Molecular packing in the structure of [(AE)CuImNi(AE)]ClO$_4$ with numbering scheme. Symmetry codes: (i) *x*, *y*, *z*; (ii) 1 − *x*, 1 − *y*, 1 − *z*; (iii) 1 − *x*, 1 − *y*, −*z*; (iv) *x*, *y*, 1 + *z*.

Full-matrix least-squares refinement was carried on by exchanging Cu and Ni. There was no difference on *R* factors. Thermal parameters converged to the same values. Maximal residuals on Fourier difference maps have the same values in both cases, 0.34 e/Å^3 at 1.06 Å from Cu, 0.45 e/Å^3 at 0.88 Å from Ni. Careful examination of interatomic distances and comparison with related complexes[25] led to the assignment of Cu and Ni atoms (vide infra).

Final refinement converged to $R = 0.033$ and $R_w = 0.036$. An analysis of variance showed no unusual trends. The parameter shifts range from 0.001σ to 0.1σ, mean value 0.03σ. The final fractional atomic coordinates are listed in Table II.

Results and Discussion

Preparation. The reaction of pentane-2,4-dione (acetylacetone) with 1,2-diaminoethane (ethylenediamine) generally yields the quadridentate Schiff base *N*,*N*′-ethylenebis(acetylacetone imine). However if the reaction is carried out with a 1:1 ratio of reagents in chloroform and under dilute conditions, single condensation occurs to yield the terdentate ligand 7-amino-4-methyl-5-aza-3-hepten-2-one (abbreviated AEH).[16] In spite of a moderate thermal stability, AEH may be isolated with a fair degree of purity by vacuum distillation and used subsequently to complex metal ions. The mononuclear species [(AE)MB]$^+$ (M being either Ni^{2+} or Cu^{2+} and B either pyridine (py) or imidazole (ImH)) are readily obtained by adding the ligands AEH and B to a methanolic solution of the metal salt.

The interest of these mononuclear complexes mainly originates in their use to prepare heterodinuclear species. For instance the reaction of [(AE)CuImH]$^+$ with [(AE)Ni(py)]$^+$ in the presence of NaOCH$_3$ leads to the expected [(AE)CuImNi(AE)]$^+$. Similarly the dicopper complex is obtained from the reaction of [(AE)CuImH]$^+$ with [(AE)CuBr]$_2$. It may be noted that the reaction of [(AE)NiImH]$^+$ with [(AE)Cu(py)]$^+$ yields a mixture of the heterodinuclear complex **1** (80%) and the related dinickel complex (20%).

Description of the Structure of [(AE)CuImNi(AE)]ClO$_4$. The structure consists of dinuclear cations and perchlorate anions but does not include any solvent molecule.

The unit cell packing view is given in Figure 2. The relevant distances and angles are listed in Table III. As previously noted in the Experimental Section, in the refining of the structure there

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Table III. Interatomic Distances (Å) and Angles (deg)[a] for $[(CuAE)Im(NiAE)]ClO_4$

Coordination Sphere			
Cu–O(1)	1.874 (4)	Ni–O(2)	1.855 (4)
Cu–N(1)	1.911 (4)	Ni–N(5)	1.892 (5)
Cu–N(2)	1.967(5)	Ni–N(6)	1.948 (5)
Cu–N(3)	1.950 (4)	Ni–N(4)	1.934 (4)
O(1)–Cu–N(1)	93.9 (2)	O(2)–Ni–N(5)	94.0 (2)
O(1)–Cu–N(2)	175.0 (2)	O(2)–Ni–N(6)	176.5 (2)
O(1)–Cu–N(3)	87.8 (2)	O(2)–Ni–N(4)	87.5 (2)
N(1)–Cu–N(2)	84.4 (2)	N(5)–Ni–N(6)	84.0 (2)
N(1)–Cu–N(3)	174.9 (2)	N(5)–Ni–N(4)	178.0 (2)
N(2)–Cu–N(3)	94.3 (2)	N(6)–Ni–N(4)	94.5 (2)
Ligand Geometry			
O(1)–C(1)	1.302 (7)	O(2)–C(11)	1.288 (6)
C(1)–C(2)	1.355 (8)	C(11)–C(12)	1.362 (10)
C(1)–C(4)	1.502 (9)	C(11)–C(14)	1.485 (9)
C(2)–C(3)	1.426 (9)	C(12)–C(13)	1.404 (10)
C(3)–N(1)	1.296 (7)	C(13)–N(5)	1.320 (7)
C(3)–C(5)	1.515 (8)	C(13)–C(15)	1.513 (10)
N(1)–C(6)	1.469 (7)	N(5)–C(16)	1.482 (8)
C(6)–C(7)	1.488 (9)	C(16)–C(17)	1.493 (8)
C(7)–N(2)	1.468 (6)	C(17)–N(6)	1.461 (7)
Cu–O(1)–C(1)	126.7 (4)	Ni–O(2)–C(11)	126.6 (4)
O(1)–C(1)–C(2)	124.7 (6)	O(2)–C(11)–C(12)	125.1 (6)
O(1)–C(1)–C(4)	113.8 (5)	O(2)–C(11)–C(14)	114.1 (6)
C(2)–C(1)–C(4)	121.5 (5)	C(12)–C(11)–C(14)	120.8 (5)
C(1)–C(2)–C(3)	125.5 (6)	C(11)–C(12)–C(13)	125.0 (5)
C(2)–C(3)–N(1)	122.6 (5)	C(12)–C(13)–N(5)	122.5 (6)
C(2)–C(3)–C(5)	117.2 (5)	C(12)–C(13)–C(15)	117.7 (5)
N(1)–C(3)–C(5)	120.1 (5)	N(5)–C(13)–C(15)	119.8 (6)
Cu–N(1)–C(3)	126.4 (4)	Ni–N(5)–C(13)	125.4 (4)
Cu–N(1)–C(6)	113.7 (3)	Ni–N(5)–C(16)	114.5 (3)
C(3)–N(1)–C(6)	119.6 (4)	C(13)–N(5)–C(16)	119.6 (5)
N(1)–C(6)–C(7)	108.2 (4)	N(5)–C(16)–C(17)	107.3 (5)
C(6)–C(7)–N(2)	107.9 (5)	C(16)–C(17)–N(6)	107.9 (5)
Cu–N(2)–C(7)	107.8 (3)	Ni–N(6)–C(17)	107.4 (4)
Imidazolate Geometry			
N(3)–C(8)	1.384 (6)	N(4)–C(10)	1.341 (6)
C(8)–C(9)	1.358 (7)	C(10)–N(3)	1.323 (7)
C(9)–N(4)	1.367 (7)		
C(10)–N(3)–C(8)	104.6 (4)	Cu–N(3)–C(8)	125.9 (3)
N(3)–C(8)–C(9)	108.0 (5)	Cu–N(3)–C(10)	129.3 (3)
C(8)–C(9)–N(4)	109.2 (4)	Ni–N(4)–C(9)	126.5 (3)
C(9)–N(4)–C(10)	104.2 (4)	Ni–N4)–C(10)	129.2 (4)
N(4)–C(10)–N(3)	114.0 (5)		
Perchlorate Geometry			
Cl–O(3)	1.430 (6)	Cl–O(5)	1.387 (6)
Cl–O(4)	1.410 (6)	Cl–O(6)	1.417 (7)
O(3)–Cl–O(4)	107.0 (4)	O(4)–Cl–O(5)	112.9 (4)
O(3)–Cl–O(5)	111.1 (4)	O(4)–Cl–O(6)	107.8 (4)
O(3)–Cl–O(6)	108.4 (3)	O(5)–Cl–O(6)	109.5 (4)

was some question as to which positions the copper and nickel atoms were located on, respectively. Comparison with related complexes[25] shows that the M–N and, to a lesser extent, the M–O bonds are shorter when M = Ni than when M = Cu and suggests the assignment as made in Figure 2. This is further supported by arguments deduced from the spectroscopic properties of the complex (vide infra).

Each metal atom displays a square-planar coordination by two nitrogen atoms and one oxygen atom of the AE ligand and a nitrogen atom from the deprotonated imidazole. The least-squares-planes fit shows tetrahedral distortions, the larger deviations being associated with the copper moiety.[26]

The bridging imidazolate ring is planar with the largest deviation from the mean plane being 0.004 (6) Å. The copper atom is 0.1050 (7) Å out of this plane while the nickel atom only deviates by 0.0281 (7) Å from the plane on the same side. Thus the dinuclear cation looks "boat"-shaped.

Table IV. Hydrogen Bonds and Intermolecular Contacts[a]

N(2)...O(3)	3.071 (7)	N(6)...O(3)	3.014 (6)
N(2)...O(1)^{iii}	3.370 (6)	N(6)...O(1)^{ii}	3.268 (6)
H(1(N2))...O(3)	2.335 (7)	H(1(N6))...O(3)	2.136 (6)
N(2)–H(1(N2))... O(3)	132.1 (5)	N(6)–H(1(N6))...O(3)	149.7 (6)
H(2(N2))...O(1)^{iii}	2.519 (6)	H(2(N6))...O(1)^{ii}	2.337 (6)
N(2)–H(2(N2))... O(1)^{iii}	146.4 (4)	N(6)–H(2(N6))...O(1)^{ii}	160.5 (5)
Cu...Cu^{iii}	3.499 (1)	Cu...Ni^{ii}	3.632 (1)
Cu...Ni	5.932 (1)	Cu...Ni^{iii}	5.906 (1)
O(1)–Cu...Cu^{iii}	91.8 (1)	O(1)–Cu–Ni^{ii}	86.6 (1)
N(1)–Cu...Cu^{iii}	110.9 (1)	N(1)–Cu–Ni^{ii}	81.7 (1)
N(2)–Cu...Cu^{iii}	84.5 (1)	N(2)–Cu–Ni^{ii}	97.8 (2)
N(3)–Cu...Cu^{iii}	73.8 (1)	N(3)–Cu–Ni^{ii}	93.6 (1)
Cu^{iii}–Cu–Ni^{ii}	167.35 (3)		
O(2)–Ni–Cu^{ii}	98.5 (1)	N(5)–Ni–Cu^{ii}	99.8 (1)
N(4)–Ni–Cu^{ii}	81.3 (1)	N(6)–Ni–Cu^{ii}	79.0 (1)

[a] Symmetry codes: (no superscript) x, y, z; (ii) $1 - x, 1 - y, 1 - z$; (iii) $1 - x, 1 - y, -z$. Distances in Å, angles in deg.

The bonds between the copper atom and the donor sites O(1), N(1), and N(2) of the AE ligand are shorter than in previously reported complexes where the metal has a square-pyramidal environment.[17,18,27] The Cu–N(imidazolate) distance of 1.950 (4) Å is within the range of values normally found for this bond.[10c,12b,15a]

The acetylacetone ring around the copper atom is planar with no atom deviating from the least-squares plane by more than 0.03 Å, the metal being included in this plane.[26] More important deviations, up to 0.1 Å, characterize the acetylacetone ring around the nickel atom. Both five-membered rings defined by the metal centers and ethylenediamine are nonplanar and have a gauche conformation as usually observed.

Contact distances less than 3.5 Å are listed in Table IV. Contacts between perchlorate oxygen O(3) and N(2) on the one hand and N(6) on the other hand are noteworthy. The N···O distances of 3.071 (7) and 3.014 (6) Å, respectively, could represent hydrogen bonds with associated H···O distances of 2.335 (7) and 2.136 (6) Å. This may be related to the boat shape of the dinuclear cation.

As illustrated in Figure 2, four dinuclear units pile up to form discrete Ni···Cu···Cu···Ni chains with a relatively short Cu···Cu distance of 3.499 1) Å, the shortest intermolecular Cu···Ni and Ni···Ni distances being 3.632 (1) and 7.269 (1) Å, respectively. It may be noted that reversing the location of the copper and nickel ions with respect to the attributions used in Figure 2 would cause an important lengthening of the intermolecular Cu···Cu distance (7.269 Å), which is seemingly inconsistent with the EPR data.

Spectroscopic and Magnetic Properties. The electronic spectrum of the heterodinuclear complex (**1**) (solid sample, Nujol mull) shows two broad absorptions with maxima at 450 and 560 nm, which may be attributed to d–d transitions of the nickel and copper ions, respectively. In the case of the dicopper complex (**2**), a single absorption is observed at 570 nm. These positions agree with a nearly planar geometry around the metal ions in both complexes.

Unexpectedly, undiluted solid samples of **1** and **2** give very similar EPR spectra (X-band, 100 K) comprising two features of very different intensities. In both cases, a $\Delta M = 1$ signal appears as a single broad absorption at $g = 2.083$ (**1**) or 2.078 (**2**). A much weaker signal is observed at $g = 4.30$ (**1** and **2**) and is recognized as a $\Delta M = 2$ transition. Since this feature appears unchanged in the homodinuclear and heterodinuclear complexes, one may conclude that magnetic interactions between the individual dinuclear units are operative in solid samples of **1** and **2**. The broadening of the $\Delta M = 1$ transition and the absence of hyperfine structure suggest that these interactions would be mainly

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(26) Supplementary material.

(27) Costes, J. P.; Dahan, F.; Laurent, J. P., in press.

Table V. Structural Parameters of Four Imidazolate-Bridged Copper(II) Complexes[a]

	r^b	ϕ^c	α^d	θ^e	$-2J^f$	ref
$[Cu_2(TMDT)_2(Im)(ClO_4)_2]^+$	1.944	160.2	90	143.2	51.6	4
	1.966	161.9	91.8			
$[Cu_2L(Im)]^{3+}$	1.919	158.9	68.8	145.5	42.0	12b
	1.984	166.3	79.1			
$[Cu_2(Gly\text{-}GlyO)_2(Im)]^-$	1.928	157.5	5.8	135.0	38.0	10c
	1.940	157.2	10.4			
$[(CuAE)_2(Im)]^+$	(1.950)	(162.3)	(11.8)	(114.6)	43.0	*g*

[a] Ligand abbreviations: Im, imidazolate; TMDT, 1,1,7,7-tetramethyldiethylenetriamine; L, 30-membered macrocycle prepared from 2,6-diacetylpyridine and 3,6-dioxaoctane-1,8-diamine; Gly-GlyO, glycylglycinate(2-); AE, see text. [b] Cu-N(Im) distance in Å. [c] Angle (deg) between Cu-N and N-N(Im) vectors. [d] Angle (deg) between copper coordination plane and the imidazole plane. [e] Angle (deg) between the two Cu-N(Im) vectors. [f] Singlet-triplet separation in cm^{-1}. [g] This work, see text.

dipolar in character. This view would be in line with a relatively short intramolecular Cu⋯Cu distance. From the value of the resonant field of the $\Delta M = 2$ transition, i.e. 1565 G (X-band), a zero-field splitting of ca. 0.05 cm^{-1} may be evaluated. It would correspond to a Cu⋯Cu distance of ca. 3.6 Å in the point-dipole approximation. This is consistent with the structural assignment made in Figure 2, which leads to a Cu⋯Cu distance of 3.499 (1) Å for the heterodinuclear complex (**1**). The occurrence of intermolecular interactions is further substantiated by the disappearance of the "half-field" signal upon dilution of **1** and **2** in their diamagnetic homologue $[(AE)NiImNi(AE)]^+$. In this instance, an axial spectrum with $g_\perp = 2.078$, $g_\parallel = 2.180$ and $|A_\parallel| = 204 \times 10^{-4}$ cm^{-1} is observed for **1** while **2** yields a single derivative at $g = 2.083$. Very similar patterns are observed for frozen-solution ($(CH_3)_2CO$ and CH_2Cl_2, 100 K) spectra. As expected, the data related to dilute samples of **1** are consistent with an isolated square-planar copper(II) ion. It is noteworthy that the spectra of **2**, even those related to dilute samples, do not show the features that are considered characteristic of the imidazolate-bridged dicopper complexes,[14] including the four-copper form of bovine erythrocyte superoxide dismutase Cu_2Cu_2SOD,[28] i.e. a $\Delta M = 2$ transition at half-field and, in the $\Delta M = 1$ area, a broad absorption with a well-resolved feature at high field (*g* ca. 1.9). These features have been recently interpreted[29] in terms of triplet spectra with very anisotropic zero-field splitting. Furthermore, this analysis indicates that exchange between one ion in its ground state and the other ion in an excited state affords a dominant contribution to this zero-field splitting. This is seemingly not the case for complex **2** since the observation of a single signal with a width of 125 G is hardly compatible with a large zero-field splitting.

Magnetic susceptibility data were collected for solid samples of **1** and **2** in the range 5-270 K. In the case of complex **1**, the data corrected for diamagnetism and TIP are well fitted to the Curie-Weiss law $\chi_M^{cor} = C/(T - \Theta)$ where $C = 0.38$ deg cm^3 mol^{-1} and $\Theta = -0.4 \pm 0.2$ K. Extrapolation of the data to infinite temperature yields a χ_{TIP} value of ca. 110×10^{-6} cm^3 mol^{-1}. The effective magnetic moment and *g* values of 1.82 μ_B and 2.08, respectively, are typical of copper(II). The nonzero value of Θ may indicate that a very weak intermolecular interaction is operative.

A plot of χ_A vs. T for complex **2** is represented in Figure 3. The susceptibility passes through a maximum at ca. 40 K and then decreases. This behavior is typical of an antiferromagnetically coupled system. The absence of a Curie tail in the low-temperature region indicates that the sample is free of paramagnetic (mononuclear) impurities. Therefore, the χ_A values may be fitted to the Bleaney-Bower expression for isotropic exchange in a copper(II) dimer without including a paramagnetic correction. The resulting values of *g* and $2J$ are 2.12 and -43.0 cm^{-1}, respectively. In Figure 3, the best-fitted curve is represented by a solid line, and it can be seen that the fit to the experimental data is good for the whole range of temperatures. As previously noted, the analysis of the magnetic data of complex **1** points to a possible antiferromagnetic interaction between the individual dinuclear units. In the case of **2**, this additional interaction may be taken into consideration by substituting the term $(T - \Theta)^{-1}$ for the terms T^{-1} in the Bleaney-Bower equation. The fit is slightly improved for a Θ value of -0.3 K,[30] which is almost identical with that obtained for complex **1**. Returning to complex **2**, we can conclude that the intermolecular contribution to the exchange process is practically insignificant with respect to the intramolecular contribution. As an aside, examination of the magnetic properties of **1** and **2** confirms that the former complex is not simply a mixture of the two related homodinuclear species but a genuine heterodinuclear complex.

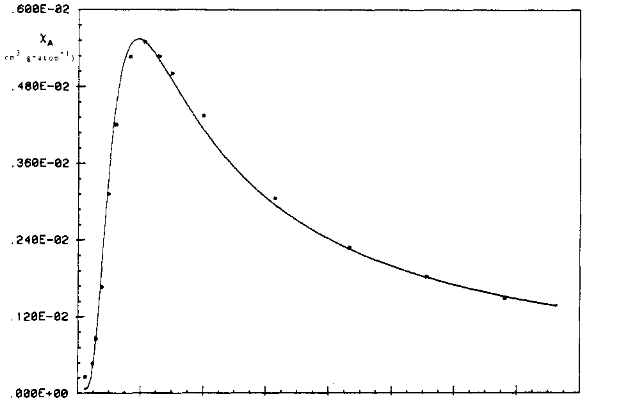

Figure 3. Susceptibility (asterisks) vs. temperature for **2**. The solid line shows the least-squares fit to the data using the parameters described in the text.

Several studies have already been reported in which structural data have been used to find correlations between structure and magnetic coupling in imidazolate-bridged dicopper(II) complexes. Three of these complexes are of special interest for the present study since they exhibit J values very similar to those of $[(AE)CuImCu(AE)]^+$ (Table V). Furthermore, in the four complexes, the imidazolate ion connects the two copper atoms through in-plane sites of two square-planar units. Unfortunately, the structural parameters of complex **2** have not been determined due to the lack of suitable crystals. Tentatively, they may be approximated by assuming that they do not appreciably differ from those of the [(AE)CuIm] moiety in complex **1**. The resulting values are quoted in Table V. They support the conclusion of a recent paper[32] devoted to the analysis of exchange interaction mediated by an imidazolate bridge. According to this analysis, the extent of antiferromagnetic coupling would be mainly affected by the angle (ϕ) between Cu-N(Im) and N-N(Im) vectors but it would have some dependence on the angle (α) between the

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(30) This procedure allows a rapid evaluation of the intermolecular interactions in complexes **1** and **2**. However, it is not strictly correct theoretically in the case of **2** where intramolecular interactions are also operative. In this case, the molecular field approximation[31] seems a better procedure. When applied to complex **2**, it yields an intermolecular exchange constant $|J'|$ of less than ca. 0.5 cm^{-1}.

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copper coordination plane and the imidazole plane. This dependence results from interactions between the bridging imidazolate and the terminal ligand (AE in complex **2**). From Table V, it appears that the smooth variation of $|2J|$ essentially reflects the small differences between corresponding ϕ values. The dependence of $|2J|$ on the angle α is more difficult to detect since a rather large variation of this parameter does not significantly affect the singlet–triplet separation. More examples of closely related complexes are needed to clarify this point.

In conclusion, this work illustrates the use of the [(AE)CuImH]$^+$ unit to obtain homo- and heterodinuclear complexes. Works are in progress to extend the scope of these possibilities to other pairs of metal centers with identical [(AE)MImM'(AE)]$^{n+}$ or different [(AE)MImM'L]$^{n+}$ environments (L being a polydentate ligand different from AEH). The latter type of complexes may be valuable to probe the dependence of the exchange coupling on ligand–ligand interactions.[32]

Acknowledgment. We thank Dr. A. Mari for his contribution to the magnetic measurements.

Registry No. [(AE)CuImNi(AE)]ClO$_4$, 102575-61-1; [(AE)CuImCu(AE)]ClO$_4$, 102575-63-3; [(AE)CuImH]ClO$_4$, 102575-65-5; [(AE)NiPy]ClO$_4$, 97398-11-3; [(AE)CuBr]$_2$, 102629-50-5.

Supplementary Material Available: Listings of anisotropic thermal parameters, hydrogen parameters, and least-squares-planes equations (4 pages). Ordering information is given on any current masthead page.

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Coordination Mode of Tris(2-pyridyl)carbinol to Cobalt(III): Crystal Structure of Li[Co{(2-py)$_3$COH}$_2$](S$_2$O$_6$)$_2$·10H$_2$O

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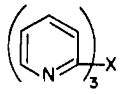
The bis[tris(2-pyridyl)carbinol]cobalt(III) complex was isolated as either of two linkage isomers, dependent on conditions of synthesis. A symmetrical form has all donor atoms being py N (i.e. ((py)$_3$COH-*N*,*N'*,*N''*)$_2$), while the unsymmetrical form has one deprotonated ligand which is coordinated through two py N atoms and the alkoxy O (i.e. ((py)$_3$COH-*N*,*N'*,*N''*)-((py)$_3$CO$^-$-*N*,*N'*,*O*)). The X-ray crystal structure of the symmetrical form as Li[Co{(2-py)$_3$COH}$_2$](S$_2$O$_6$)$_2$·10H$_2$O is reported: the complex of formula $C_{32}H_{46}N_6O_{24}S_4LiCo$ is monoclinic, space group $C2/c$, β = 109.88 (2)°, with cell dimensions a = 19.177 (6) Å, b = 10.533 (2) Å, c = 23.390 (7) Å, and Z = 4. The cation has the six pyridine N atoms coordinated to the metal center in almost perfect octahedral geometry (Co(III)–N bond distances range between 1.931 (3) and 1.944 (3) Å). Electrochemical studies of this symmetric linkage isomer reveal similarities to the [Co(bpy)$_3$]$^{n+}$ species, with both the Co(III)/Co(II) and Co(II)/Co(I) redox couples apparent on the cyclic voltammetric time scale.

Introduction

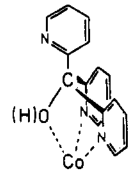
There have been a number of recent reports of the coordination of tripodal ligands in which the three ligating atoms belong to π-acceptor groups, such as N-heterocyclic ring systems. Boggess et al.[3-5] have synthesized first-row transition-metal complexes of the ligands



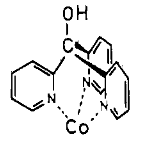
X = CH, COH, P, P=O, As, N

and have studied the spectral and electrochemical properties of these species. Canty et al.[6-8] have used a wide range of ligands of the types XY$_3$ (where the bridgehead atom X = CH or COH, and Y = 2-pyridyl, 1-pyrazolyl or *N*-methylimidazol-2-yl) to impose unusual coordination geometries on metal centers such as Hg(II) and Au(III).

We have been engaged on a study of the group VIII (groups 8–10[29]) complexes of these ligands, particularly with Ru[9] and Rh.[10] Within this group, reports of the coordination mode of tris(2-pyridyl)carbinol in the bis(ligand)cobalt(III) complex are conflicting. Boggess and Boberg[4] and White and Faller[11] have identified the complex to contain one deprotonated and one nondeprotonated ligand: the deprotonated ligand was considered to have an N,N',O-coordination mode (i.e. two pyridine nitrogen atoms and the deprotonated hydroxyl oxygen atom being the ligating atoms, **1**). The reports differ however as to the nature of the coordination mode of the nondeprotonated ligand, viz. N,N',O[4] or N,N',N'' (**2**).[11] We also synthesized this bis(tridentate) complex as part of our studies and observed a form of the complex whose ^{13}C NMR spectrum was inconsistent with either of the two previous assignments. We report here an X-ray crystal structure of the complex Li[Co{(2-py)$_3$COH}$_2$](S$_2$O$_6$)$_2$·10H$_2$O in which both ligands show N,N',N''-coordination.



(py)$_3$CO(H)-*N*,*N'*,*O*
1



(py)$_3$COH-*N*,*N'*,*N''*
2

Experimental Section

Physical Measurements. Electronic spectra were recorded with a Cary 219 spectrophotometer, and NMR spectra were obtained in CD$_3$CN or D$_2$O solutions by using a Bruker AM-300 NMR spectrometer, with *p*-dioxane (δ = 66.5) as an internal standard.

All electrochemical measurements were made in acetonitrile/0.1 M tetraethylammonium perchlorate (TEAP) solution vs. an Ag/AgCl (3 M NaCl) reference electrode by using a Bioanalytical Systems Inc. (BAS) CV-27 voltammograph.

Elemental microanalyses were carried out by the Canadian Microanalytical Service, Vancouver, Canada.

Syntheses. Tris(2-pyridyl)carbinol, (2-py)$_3$COH, was prepared from bis(2-pyridyl)ketone and 2-lithiopyridine as detailed previously[11,12] in 48%

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