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Correlations between Magnetism and Structure in Dinuclear CuIIFeIII Complexes with Integer Spin EPR Signals

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($\mathbf{2}^{2\ominus}$, Table 1). The more twisted the helicene is, the more the paratropicity of the 4nπ system is quenched.[4]

In order to study this phenomenon, we concentrated on the proton chemical shifts at positions 9 and 10 of the substituted phenanthrenes. The same trend is observed for the protons of the other positions. The 9,10 positions have the largest charge density, as deduced from NMR spectra and ωβ-HMO calculations for a doubly charged phenanthrene ($\mathbf{1}^{2\ominus}$). Without exception, the more twisted the phenanthrene moiety is, the less the spectrum is shifted towards higher field (Table 1). For example, in the spectrum of phenanthrene dianion ($\mathbf{1}^{2\ominus}/2Li^{\oplus}$) the resonances of protons at positions 9,10 are shifted to $\delta = -1.14$, whereas the resonances of the same protons in 2,4,5,7-tetramethylphenanthrene dianion ($\mathbf{3}^{2\ominus}/2Li^{\oplus}$) are shifted to $\delta = +1.65$. Thus, a dramatic chemical shift difference of 2.79 ppm results from the different paratropicities of $\mathbf{1}^{2\ominus}$ and $\mathbf{3}^{2\ominus}$. In the spectrum of 2,4-di-*tert*-butyl-5,7-dimethylphenanthrene dianion ($\mathbf{4}^{2\ominus}/2Li^{\oplus}$) those proton resonances appear at $\delta = 2.49$ and 2.28. In all cases studied the same charge distribution pattern has been observed. Changing the countercation, solvent, and temperature did not affect the observed trend of line shape and chemical shift differences.

The paratropicity of 4nπ "antiaromatic" systems and the line shapes of their ^1H NMR signals thus correlate with the degree of twisting. Since antiaromaticity (as well as aromaticity) requires an efficient delocalization, we believe that twisting of the system quenches its antiaromatic properties. Therefore, the paratropic shift and the NMR line shapes can be applied as probes for so-called "antiaromaticity".

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CAS Registry numbers:
1, 85-01-8; **1**, dianion, 67382-15-4; **1**, 2 Li$^{\oplus}$, 54667-02-6; **2**, 3674-69-9; **2**, dianion, 128054-52-4; **2**, 2 Na$^{\oplus}$, 128054-56-8; **2**, 2 Li$^{\oplus}$, 128054-60-4; **3**, 7396-38-5; **3**, dianion, 128054-53-5; **3**, 2 Na$^{\oplus}$, 128054-58-0; **3**, 2 Li$^{\oplus}$, 128083-45-4; **4**, 128054-51-3; **4**, dianion, 128054-54-6; **4**, 2 Na$^{\oplus}$, 128083-43-2; **4**, 2 Li$^{\oplus}$, 128054-62-6.

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[6] D NMR studies of the dianions are under way. The ΔG values of neutral systems are known [2]. The ΔG value of 1,4,8-trimethyl-5-isopropylphenanthrene dianion has a lower limit of 65 kJ mol^{-1}.

[7] MNDO calculations were performed on a CDC Syber 180/855 running under NOS 2.7.1 and NOS/VE 1.4.1. Program: M. J. S. Dewar, W. Thiel, *Molecular Theory Program, Version 2.5*. Hydrogen bonding and lithium parameters included by A. Golblum, Hebrew University of Jerusalem, 1986.

[8] a) The MMX calculations were performed on an Olivetti M 240 computer with a math coprocessor 18087 applying the PC Model MMX calculations Serena Software, USA. b) X-ray studies: R. Cosmo, T. W. Hambley, S. Sternhell, *J. Org. Chem. 52* 3119 (1987).

[9] The NMR spectra were recorded with a Bruker WP-200 SY pulsed-FT spectrometer operating at 200.133 MHz for ^1H NMR, equipped with a ^2H lock system and an Aspect-2000 computer (32 K).

[10] Sample preparation: Lithium or sodium wire was introduced in the upper part of an extended NMR tube containing the polycyclic compound (5–10 mg) dissolved in 0.7 mL of [D$_8$] THF (Aldrich). The frozen solution was degassed and sealed under vacuum. The solution was then brought into contact with the metal by turning the tube upside down.

Correlations between Magnetism and Structure in Dinuclear Cu^{II}Fe^{III} Complexes with Integer Spin EPR Signals **

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Carlos Juarez-Garcia, Eckard Münck,
and *Lawrence Que, Jr.**

The relationship between structure and magnetism in coupled dinuclear transition metal complexes has attracted great interest among inorganic and bioinorganic chemists, due to the unique physical properties of these complexes[1] as well as their relevance to biological systems.[1, 2] The magnetism of these systems depends on the electronic configurations of the individual metal centers, which, in turn, determine their fundamental spectroscopic properties. Recently, we have developed a systematic method for synthesizing heterobimetallic complexes of the dinucleating ligand 2,6-bis(bis-2-pyridylmethylamino)methyl)-4-methylphenol (Hbpmp),[3] affording a series of M^{II}Fe^{III} compounds.[4, 5] Herein, we report the structures of two Cu^{II}Fe^{III} complexes[6] of bpmp$^{\ominus}$ which exhibit integer spin EPR signals that correspond to their markedly different magnetochemistry.[7]

$[Cu^{II}Fe^{III}(bpmp)(O_2CC_2H_5)_2](PF_6)_2$ **1a**

$[Cu^{II}Fe^{III}(bpmp)(O_2CCH_3)(OCH_3)](BPh_4)_2 \cdot 0.22\ CH_3CO_2H$ **2a**

X-ray structure analyses of **1a**[8, 9] and **2a**[9, 10] revealed the following features:

In **1a** the cation consists of a discrete, dinuclear Cu^{II}Fe^{III} complex (Fig. 1, top), in which the two metals are bridged by the phenolate oxygen atom of the bpmp$^{\ominus}$ ligand and by two propionate groups. The $Fe^{III}\cdots Cu^{II}$ distance is 3.401(4) Å, consistent with those of similar triply bridged dinuclear cores.[4] The bpmp$^{\ominus}$ ligand and the propionate groups provide a six-coordinate, roughly octahedral ligand array about each of the metal atoms in **1a**, but the coordination environment about the Cu^{II} atom shows the effects of Jahn-Teller elongation along the N2–Cu–O3 axis.

In **2a** (Fig. 1, bottom), one of the bridging carboxylate groups of **1a** is replaced by a terminal methoxide ligand that is coordinated only to the roughly octahedral Fe^{III} atom, leaving the Cu^{II} atom five-coordinate. One Cu-ligand bond (Cu–O1 = 2.176(4) Å) is elongated considerably relative to the other four in **2a**; this pattern suggests that the bridging phenolate oxygen atom, O1, is best regarded as the apical ligand atom of a square pyramidal coordination array about Cu^{II}. The Fe–O1 bond is also elongated due to the influence of the methoxide ligand, as the strong Fe–OCH_3 interaction affords a short (1.849(4) Å) Fe–O bond and decreases the affinity of the Fe for the phenolate bridge. The lengthening of both M–O1 bonds in **2a**, relative to those in **1a**, is the primary factor in the elongation of the $Fe\cdots Cu$ distance by 0.24 Å, to 3.641(1) Å.

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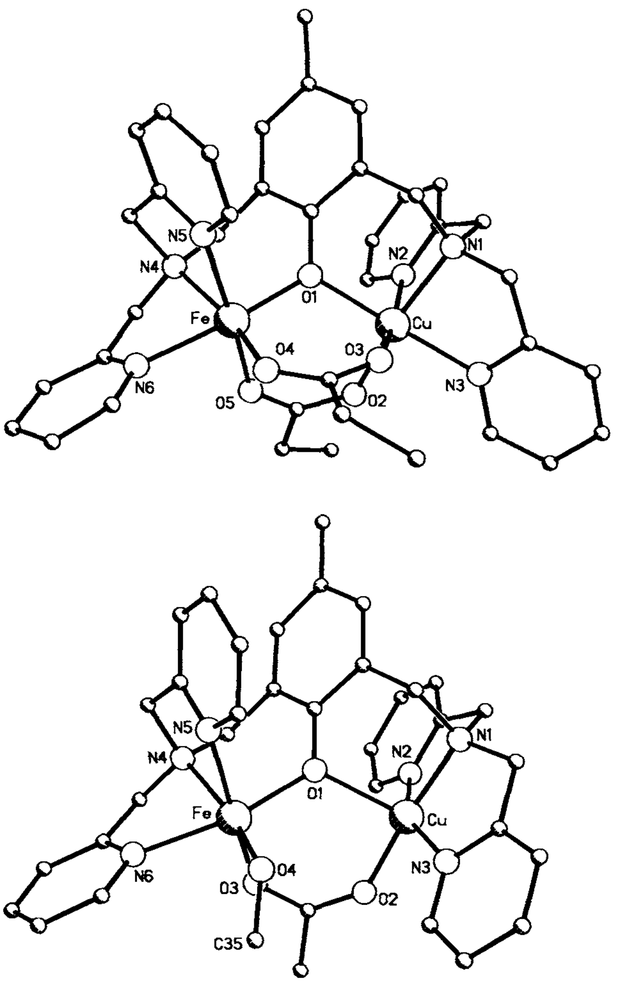

Fig. 1. Top: Structure of the dinuclear complex cation of **1a** in the crystal. Atoms are represented as spheres of arbitrary radii. Selected distances [Å] and angles [°]: Fe···Cu 3.401(4), Fe-O1 1.93(1), Fe-O4 1.90(2), Fe-O5 2.11(1), Fe-N4 2.15(1), Fe-N5 2.15(2), Fe-N6 2.12(2), Cu-O1 2.01(1), Cu-O2 1.94(1), Cu-O3 2.31(2), Cu-N1 2.09(1), Cu-N2 2.19(1), Cu-N3 2.03(1), <Fe-O1-Cu 119.3(5). Bottom: Structure of the dinuclear complex cation of **2a** in the crystal. Atoms are represented as spheres of arbitrary radii. Selected distances [Å] and angles [°]: Fe···Cu 3.641(1), Fe-O1 1.975(4), Fe-O3 2.016(4), Fe-O4 1.849(4), Fe-N4 2.255(5), Fe-N5 2.132(4), Fe-N6 2.175(5), Cu-O1 2.176(4), Cu-O2 1.945(4), Cu-N1 2.034(5), Cu-N2 2.006(4), Cu-N3 1.975(5), <Fe-O1-Cu 122.5(2).

The spectroscopic properties of the two complexes correlate well with their crystal structures. The Mössbauer parameters of **1b** ($\delta = 0.46$ mm/s; $\Delta E_Q = 0.42$ mm/s) are similar to those of other triply bridged complexes in this series.[4] In contrast, **2b** ($\delta = 0.49$ mm/s; $\Delta E_Q = 1.27$ mm/s) has the larger ΔE_Q value, most likely due to the presence of the short Fe–OMe bond. Magnetic susceptibility studies[11] indicate that the dinuclear center in **1b** is antiferromagnetically coupled ($J = 50$ cm^{-1} for $\mathcal{H} = J S_1 \cdot S_2$, $S_1 = 5/2$, $S_2 = 1/2$), while the center in **2b** is weakly ferromagnetically coupled ($J = -3$ cm^{-1}) (Fig. 2). This difference in coupling

$[Cu^{II}Fe^{III}(BPMP)(O_2CCH_3)_2](BPh_4)_2$ **1b**

$[Cu^{II}Fe^{III}(BPMP)(O_2CC_2H_5)(OCH_3)](BPh_4)_2$ **2b**

interaction can be rationalized by inspection of the magnetic orbitals in the two complexes, assuming that the phenolate provides the principal coupling pathway.[1, 6c] For **1a**, the Jahn-Teller distortion on the Cu^{II} atom directs the magnetic

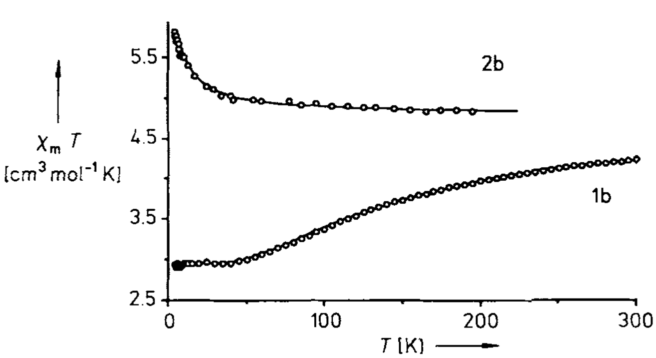

Fig. 2. Experimental (∘∘∘) and theoretical (——) temperature dependence of $\chi_m T$ for **1b** and **2b**. Fitting parameters: **1b**, $J = 50$ cm^{-1}, $D_{Fe} = 0.5$ cm^{-1}, $E/D = 0.23$, $g_x = g_y = g_z = 2.0$, $D_{Cu} = 0$, $g_x = g_y = 2.08$, $g_z = 2.35$; **2b**, $J = -3$ cm^{-1}, $D_{Fe} = 0.8$ cm^{-1}, $E/D = 0.23$, $g_x = g_y = g_z = 2.0$, $D_{Cu} = 0$, $g_x = g_y = 2.12$, $g_z = 2.40$.

orbital along the axis of the phenolate bond and allows it to interact antiferromagnetically with the Fe^{III} magnetic orbitals. The elongation axis for the Cu^{II} atom in **2a**, however, is along the phenolate bridge; this places the magnetic orbital in the plane perpendicular to the phenolate bond and renders it orthogonal to the magnetic orbitals of the Fe^{III} atom, engendering the ferromagnetic interaction.

Interestingly, complex **1b** gives rise to a low field EPR signal at $g = 8$, while complex **2b** exhibits signals at $g = 12$ and $g = 8$ (Fig. 3). The intensity of the low field resonances

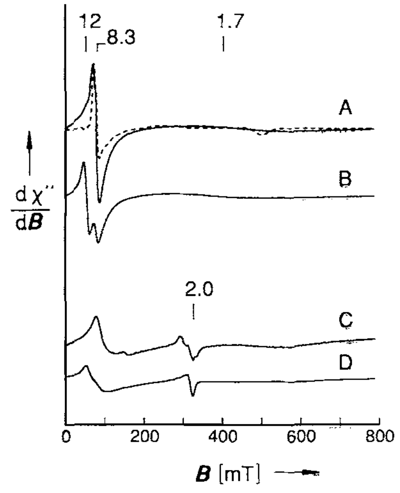

Fig. 3. EPR spectra of **1b** and **2b** in CH_3CN (4 mM) at 3 K. A) **1b**, $\boldsymbol{B}_1 \parallel \boldsymbol{B}$; B) **2b**, $\boldsymbol{B}_1 \parallel \boldsymbol{B}$; C) **1b**, $\boldsymbol{B}_1 \perp \boldsymbol{B}$; D) **2b**, $\boldsymbol{B}_1 \perp \boldsymbol{B}$. The dashed spectrum in A is a polycrystalline sample of **1b**. The signal at $g = 2.0$ is a preparation-dependent species, presumably a Cu^{II} impurity. An extremely broad signal at $g \approx 1.7$ has significant area under the absorption spectrum, but its origin is yet unclear. Instrumental parameters: 9.1 GHz at 0.02 mW, all below microwave saturation; modulation 100 kHz at 0.1 mT$_{pp}$; d$\boldsymbol{B}$/dT, 3.3 mT s^{-1}. The frozen solution spectra are all properly normalized.

is approximately four times stronger when the microwave magnetic field $\boldsymbol{B}_1$ is parallel to the static field $\boldsymbol{B}$ (parallel mode). The signal positions and enhanced parallel field intensities are indicative of transitions between levels of an integer-spin system.[12] The spectrum of polycrystalline **1b** (Fig. 3 A, dashed) is similar to that of the dilute, frozen solution spectrum. This indicates that intermolecular magnetic interactions are small for the polycrystalline material and do not significantly affect the determination of J. The temperature dependence of the resonance at $g = 8$ for the complex

1b (Fig. 3A) indicates that it results from a ground-state doublet. A temperature study of complex **2b** indicates that the signals at $g = 12$ and $g = 8$ (Fig. 3B) are from ground and excited doublets, respectively. The line positions and temperature data suggest the following: for complex **1b**, the $g = 8$ resonance is from the ground state with $S = 2$ (antiferromagnetic coupling). For complex **2b**, the $g = 12$ signal is from the lowest doublet of the ground state with $S = 3$ (ferromagnetic coupling) and the $g = 8$ signal is from an excited doublet of either the $S = 2$ or $S = 3$ manifolds. The relative signs of the exchange couplings are in agreement with the magnetization results. The observation of integer spin signals from **1b** and **2b** and their correspondence to the magnetostructural data provide us with a set of complexes for further studies of integer spin systems and their spectroscopic manifestations.

Experimental

1a: A methanolic solution of Hbpmp (20 mL, 3.8 mM) was treated sequentially with 1 equiv. of $Fe(NO_3)_3$, 1 equiv. of $Cu(NO_3)_2$, and 2 equiv. of $NaO_2CC_2H_5$ to produce a purplish brown solution. After addition of 1 equiv. of NH_4PF_6, the solution was allowed to evaporate slowly to yield the crystals used for the X-ray diffraction study.

1b: A methanolic solution of Hbpmp (20 mL, 3.8 mM) was treated sequentially with 1 equiv. of $FeCl_3$, 1 equiv. $CuCl_2$, and 4 equiv. of $NaBPh_4$, resulting in a green solid (75% yield) formulated as $[Cu^{II}Fe^{III}bpmpCl_2](BPh_4)_2$. Treatment of an acetone solution of the green complex with 2.2 equiv. of AgO_2CCH_3 afforded a purplish brown solution, which was filtered to remove the AgCl solid. Vapor phase diffusion of ethyl acetate into the acetone solution furnished crystals of **1b** (50% yield). UV/VIS (CH_3COCH_3): $\lambda_{sh} = 500$ nm.

2b: A methanolic solution of Hbpmp (20 mL, 3.8 mM) was treated sequentially with 1 equiv. of $Fe(NO_3)_3$, 1 equiv. of $Cu(NO_3)_2$, and 4 equiv. of $NaO_2CC_2H_5$ to produce a red/brown solution. Metathesis with $NaBPh_4$ yielded a brown solid, which was recrystallized from acetone/methanol to yield crystals with the composition **2b** $\cdot C_2H_5CO_2H$ (75% yield). UV/VIS(CH_3COCH_3): $\lambda_{sh} = 485$ nm.

2a: This complex was synthesized according to the procedure for **2b** with the exception that NaO_2CCH_3 was used in place of $NaO_2CC_2H_5$.

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[8] **1a** was obtained mainly as highly efflorescent crystals which diffracted poorly. Among these crystals were a few thin, stable, plate-like crystals that belonged to the orthorhombic system, space group *Pnma* or $Pna2_1$, $Z = 4$, with $a = 20.849(6)$ Å, $b = 17.411(4)$ Å, $c = 12.587(3)$ Å, and $V = 4569$ Å^3 at 143 K. The structure was solved in $Pna2_1$ by using direct methods on 2530 unique reflections, 3371 measured. Refinement (anisotropic thermal parameters on non-hydrogen atoms, H atoms in idealized positions, 294 least squares parameters) converged at $R = 0.094$, $R_w = 0.124$, and GOF = 1.34.

[9] Details of crystallographic experiments: Nicolet R3m diffractometer, $Mo_{K\alpha}$ radiation ($\lambda = 0.7107$ Å), $\theta/2\theta$ scans, $4° < 2\theta < 45°$, $I > 1.25\sigma(I)$. Further details of the crystal structure analyses are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB21EW (UK), on quoting the complete journal citation.

[10] **2a** was obtained as red/green dichroic crystals in the triclinic system, space group $P\bar{1}$, $Z = 2$, with $a = 13.135(3)$ Å, $b = 13.503(3)$ Å, $c = 20.940(5)$ Å, $\alpha = 93.62(2)°$, $\beta = 93.81(2)°$, $\gamma = 92.76(2)°$, $V = 3693$ Å^3 (at 146 K). The structure was solved by using direct methods on 8886 unique reflections, 13899 measured. Refinement (anisotropic thermal parameters on non-hydrogen atoms, H atoms in idealized positions, 909 least squares parameters) converged at $R = 0.086$, $R_w = 0.082$, and GOF = 1.34 after placement of a fractional (occupancy factor = 0.22) molecule of acetic acid in the structural model.

[11] Magnetization data were collected on microcrystalline powders using a Quantum Design SQUID susceptometer over the temperature range from 1.9 to 300 K for **1b** and 1.9 to 200 K for **2b**, both at 0.31 T. We thank Dr. *E. P. Day* for his valuable help.

[12] Similar low field signals have been observed in other coupled FeCu systems [6e, 7b, 13].

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Torand Synthesis by Trimerization—New Receptors for Guanidinium[**]

By *Thomas W. Bell*[*] and *Jia Liu*

Toroidal complexing agents having exceptionally rigid, yet accessible cavities, may be composed entirely of smaller rings fused to form the perimeter of a macrocycle.[1, 2] The first examples of such hosts, termed "torands", are **1**[2] and the parent dodecahydrohexaazakekulene.[1] Preorganization of six pyridine dipoles by the hexagonal framework of **1** leads to exceptionally stable complexes of alkali metal cations.[2] Extension of this architecture to a molecular cleft[3] afforded "hexagonal lattice receptor" **2**,[4] which tightly binds a neutral organic molecule (urea), despite the inherently weaker interactions between neutral hosts and guests. Here we describe effective syntheses of a larger torand (**3**) and its nonmacrocyclic analogue (**4**), as well as the formation of 1:1 complexes between both new hosts and guanidinium chloride.

The 1,8-naphthyridine units of both new receptors were synthesized via Friedlander condensation of heteroaromatic *o*-aminoaldehydes with annelated cyclohexanones (Scheme 1). The common intermediate in the syntheses of **1**–**4** is benzylideneketone **5**, which was prepared in five steps from cyclohexanone and pentanal by previously described methods[2, 5] (23% overall yield). Condensation of **5** with 4-aminopyrimidine-5-carboxaldehyde gave **6**, which underwent acidic hydrolysis to aminoaldehyde **7**, isolated as its HCl salt. Condensation of **7** with **5**, followed by ozonolysis afforded diketone **2**, as previously reported.[4] This urea receptor was then converted into novel guanidinium receptor **4** in one step by alkaline condensation with 2-aminonicotinaldehyde.

A key to our new torand synthesis is the discovery that the *o*-aminoaldehyde functionality of **7** survives ozonolytic cleavage of the benzylidene group. Crude ketoaminoalde-

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