

Synthesis and magnetism of 6-nitrobenzimidazolate and imidazolate-bridged copper(II) complexes

Zong-Hui Jiang*, Chao-Li Deng†, Dai-Zheng Liao, Shi-Ping Yan and Geng-Lin Wang

National Laboratory of Elemento-Organic Chemistry, Department of Chemistry, Nankai University, Tianjin, China

Summary

Four new trinuclear copper(II) complexes, [Cu(phen)(NBzIm)](ClO₄) (1), [Cu(bpy)(NBzIm)](ClO₄) (2), [Cu(Me₂-bpy)(NBzIm)](Ac)·1/2H₂O (3) and [Cu(Me₂-bpy)(Im)](ClO₄)·1/2H₂O (4) (phen = 1,10-phenanthroline, bpy = 2,2'-bipyridine, NBzIm = 6-nitrobenzimidazolate ion, Im = imidazolate ion) have been prepared and characterized by variable temperature magnetic susceptibility measurements. A weak antiferromagnetic spin exchange interaction operates between copper(II) ions, exchange integrals evaluated as $J = -23.82 \text{ cm}^{-1}$ for (1) and $J = -21.91 \text{ cm}^{-1}$ for (2).

Introduction

The interaction of imidazole and benzimidazole with transition metal ions is believed to be crucial in determining the activity of many biologically important molecules and metalloproteins⁽¹⁾. Very recently, interest in imidazolate (Im)-bridged transition metal ions has increased due to the involvement of imidazolate ion as a bridging ligand between copper(II) and zinc(II) ions in the enzyme superoxide dismutase (SOD)^(2,3). Cryomagnetic investigation of the copper-substituted enzyme Cu₄-BESOD revealed that an antiferromagnetic spin-exchange interaction operates within each Cu²⁺-Im-Cu²⁺ unit, the exchange integral being evaluated at -26 cm^{-1} ^(2,4).

So far binuclear and tetranuclear copper(II) complexes with imidazolate bridge have been prepared and characterized⁽⁵⁻⁷⁾. However not only are there few complexes with benzimidazolate(BzIm⁻) ion as a bridging ligand⁽⁶⁾ but only a limited number of transition metal complexes contain BzIm⁻ as a ligand⁽¹⁾. No 6-nitrobenzimidazolate-bridged binuclear and trinuclear complexes are known.

In this study we have prepared three new 6-nitrobenzimidazolate-bridged trinuclear copper(II) complexes and an imidazolate-bridged trinuclear copper(II) complex: [Cu(phen)(NBzIm)](ClO₄) (1), [Cu(bpy)(NBzIm)](ClO₄) (2), [Cu(Me₂-bpy)(NBzIm)](Ac)·1/2H₂O (3) and [Cu(Me₂-bpy)(Im)](ClO₄)·1/2H₂O (4). (phen = 1,10-phenanthroline, bpy = 2,2'-bipyridine, Me₂-bpy = 4,4'-bimethylbipyridine NBzIm = 6-nitrobenzimidazolate ion, Im = imidazolate ion). The triangular structure has been characterized on the basis of elemental analyses, i.r., e.p.r. spectra, variable-temperature magnetic susceptibility measurements, and Dreiding model considerations.

Experimental

Materials

Cu(ClO₄)₂·6H₂O, Cu(Ac)₂·H₂O, phen, bpy, Me₂bpy, 6-nitrobenzimidazolate and imidazole (analytical grade) were used as supplied.

Syntheses

The methods used to prepare the complexes are virtually identical and are exemplified by [Cu(phen)(NBzIm)](ClO₄). Cu(OAc)₂·H₂O (200 mg) and phen (198 mg) were dissolved in a 1:1 MeOH-H₂O mixture (10 cm³) which was heated to 60°C. To this was added an aqueous solution (2 cm³) of NaOH (0.5 M) and NaClO₄·H₂O (140 mg) with stirring for 1 h to give a dark green precipitate. 6-Nitrobenzimidazole (163 mg) was then added with stirring and heating for 7 h. The precipitate, which changed to grey-blue, was removed by filtration, thoroughly washed with hot H₂O and dried *in vacuo*.

[Cu(Me₂bpy)(Im)](ClO₄)·1/2H₂O was obtained in the same way, except that Me₂-bpy (184 mg) and Im (118 mg) was used instead of phen and NBzIm, respectively.

Measurements

C, H, N analyses (see Table 1) were obtained with a Perkin-Elmer analyser Model 240. Metal contents were determined by EDTA titration. I.r. spectra were measured on a Shimadzu i.r. spectrometer Model 408 using KBr pellets and reflectance spectra were recorded on a Hitachi Model 340 spectrophotometer. Variable temperature magnetic susceptibilities were measured on a vibrating sample magnetometer Model CF-1. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms, and the magnetic moments were calculated using the equation: $\mu_{\text{eff}} = 2.828(XT)^{1/2}$, where X = susceptibility; T = temperature. E.p.r. spectra of powder samples were recorded with a JES-FEIXG e.p.r. apparatus using an X band.

Results and discussion

The i.r. and electronic spectra and magnetic and elemental analyses indicate that copper(II) acetate reacts with phen (or bpy, Me₂bpy) and NBzIm (or Im) to yield the complexes [CuL(NBzIm)]X (L = phen, bpy, Me₂bpy; X = ClO₄⁻, Ac⁻) and [Cu(Me₂bpy)(Im)ClO₄]·1/2H₂O when the appropriate amount of base and NaClO₄ is added. (Added base keeps the 6-nitrobenzimidazolate or imidazolate in the deprotonated form in solution). Deprotonation of 6-nitrobenzimidazole or imidazole nitrogen in these complexes was apparent because no N—H stretching mode in the 3200–3500 cm⁻¹ region was observed. The characteristic absorption of the uncoordinated perchlorate group appears at 1100 cm⁻¹ for (1), (2) and (4) complexes. The acetoxyl group vibration at 1580 and 1415 cm⁻¹ were present in complex (3). The difference (165 cm⁻¹) between two frequencies indicates that Ac⁻ group is uncoordinated⁽⁸⁾. Reflectance spectra of the complexes show a d-d band at ~17000 cm⁻¹. Judging from the fact that the d-d frequency of [Cu(Me₂-bpy)(Im)](ClO₄)·1/2H₂O (17360 cm⁻¹) is nearly the same as that (17500 cm⁻¹) of [Cu(TMEDA)(imH₂)](ClO₄)₂ (TMEDA = N,N',N',N'-tetramethylethylenediamine) which

* Author to whom all correspondence should be directed.

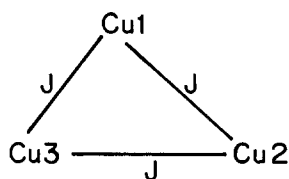
† Current address: Department of Chemistry, Zhengzhou Light Industry College, Zhengzhou, Henan, China.

Table 1. Elemental analyses of complexes.

Complex	Found (Calcd.)%			
	C	H	N	Cu
(1)	45.7(45.2)	2.2(2.4)	13.7(13.9)	12.7(12.6)
(2)	42.1(42.4)	2.4(2.5)	14.3(14.5)	13.0(13.2)
(3)	52.8(52.8)	4.1(4.2)	14.6(14.7)	13.6(13.4)
(4)	42.3(42.5)	3.7(4.0)	13.2(13.2)	14.9(15.0)

Table 2. Magnetic parameters of complexes.

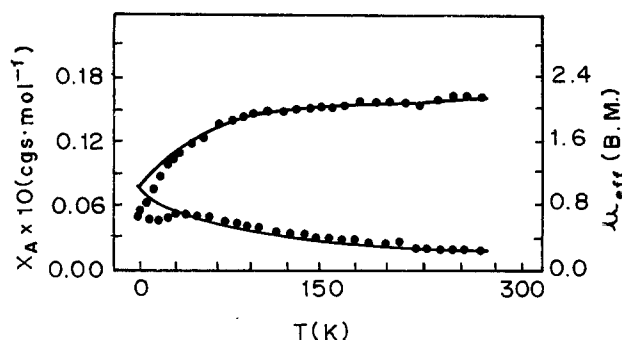
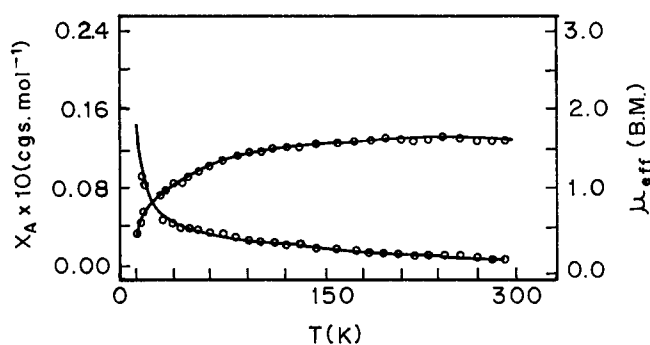
Complex	$-J$ (cm^{-1})	g	θ	μ (B.M.)
(1)	23.82	2.04	-5.62	1.68
(2)	21.91	2.01	-5.24	1.59
(3)				1.79
(4)				1.82

**Figure 1.**

possesses a nearly coplanar $[\text{CuN}_4]$ chromophore⁽⁹⁾, all the complexes are assumed to have a planar configuration with four nitrogen donor atoms. This suggests that the complexes contain bridging 6-nitrobenzimidazole or imidazolate groups.

Magnetic moments of the complexes (1) and (2) at room temperature (Table 2) are considerably lower than the spin-only value (1.73 BM), which suggests operation of an antiferromagnetic spin-exchange interaction in the complexes. This result also implies that polynuclear complexes are bridged by 6-nitrobenzimidazole group. In order to obtain further information on the structure of the complexes, variable-temperature (4.2–300 K) magnetic susceptibility data were collected for (1) and (2) and the magnetic analysis was carried out using the susceptibility equation based on the Heisenberg spin-exchange operator for triangular-trinuclear copper(II) system shown in Figure 1. ($\hat{H} = -2J(\hat{S}_1\hat{S}_2 + \hat{S}_1\hat{S}_3 + \hat{S}_2\hat{S}_3)$, $S_1 = S_2 = S_3 = 1/2$)⁽⁹⁾. $X_A = Ng^2\beta^2[12k(T - \theta)]^{-1}[5 + \exp(-3J/KT)][1 + \exp(-3J/KT)]^{-1} + N\alpha$. X_A denotes the susceptibility per atom, $N\alpha$ the temperature independent paramagnetism ($120 \times 10^{-6} \text{ cgs} \cdot \text{mol}^{-1}$). Other symbols have their usual meaning.

As shown in Figures 2 and 3, good least-squares fits for the experimental data were attained with Equation 1. The agreement factor [$F = \sum_i (X_i^{\text{obs}} - \sum_i^{\text{calc}})^2 (X_i^{\text{obs}})^{-1}$] is $\sim 5 \times 10^{-4}$ and implies that the complexes contain a triangular trinuclear copper(II) system. The magnetic parameters are given in Table 2. These results ($J < 0$) indicate that the complexes undergo an antiferromagnetic spin-exchange interaction, but the exchange integrals are smaller than for $[\text{Cu}(\text{phen})(\text{Im})]\text{ClO}_4$ ($J = -37 \text{ cm}^{-1}$) and $[\text{Cu}(\text{bpy})(\text{Im})]\text{ClO}_4$ ($J = -44 \text{ cm}^{-1}$)⁽⁹⁾. The only difference between $[\text{CuL}(\text{NBzIm})]\text{ClO}_4$ and $[\text{CuL}(\text{Im})]$ -

**Figure 2.** X_A versus T plots for $[\text{Cu}(\text{phen})(\text{NBzIm})](\text{ClO}_4)$. The curve is drawn based on Equation 1 with the magnetic parameters given in the text.**Figure 3.** X_A versus T plots for $[\text{Cu}(\text{bpy})(\text{NBzIm})](\text{ClO}_4)$. The curve is drawn based on Equation 1 with the magnetic parameters given in the text.

ClO_4 is that there is an added carbon skeleton on the C(4) and C(5) atoms of the imidazole in the former. The $\text{Cu}-\text{N}-\text{C}(2)$ bond angle would probably decrease in the 6-nitrobenzimidazolate as a result of the $\text{Cu}(\text{phen})^{2+}$ [or $\text{Cu}(\text{bpy})^{2+}$] moiety moving away from the added carbon skeleton on the C(4) and C(5) atoms of the imidazole. The decreased $\text{Cu}-\text{N}-\text{C}(2)$ angle expected in $[\text{CuL}(\text{NBzIm})]\text{ClO}_4$ could lead to a weaker interaction⁽⁶⁾. It is important to understand this variation in exchange parameter. The magnitude of J in the complexes under discussion is close to that in the 4- Cu^{2+} SOD protein ($J = -26 \text{ cm}^{-1}$). This type of the structure of the present complexes may be a better model of 4- Cu^{2+} SOD protein.

E.p.r. spectra

The powder e.p.r. spectra of the complexes at room temperature are shown in Figure 4. For trinuclear copper(II) complexes, the antiferromagnetic interaction between the metal centres exhibits three molecular spins $S_T = 1/2, 1/2$ and $3/2$, in which a $S = 1/2$ state is the ground state according to the magnetic date (see Table 2). Trinuclear molecular (ground state $S = 1/2$) and trinuclear molecular (ground state $S = 1/2$) couple to yield a spin singlet ($S = 0$) and a spin triplet ($S = 1$)⁽¹⁰⁾ due to antiferromagnetic interaction between the molecules. As shown in Figure 4, three complexes show a dissymmetric shape in their upper and lower peaks at $\sim 3200 \times 10^{-4} \text{ T}$ corresponding to the allowed transitions of $\Delta M_s = \pm 1$, which indicates a very weakly anisotropic triplet state⁽¹¹⁾. Thus, using g_3 and g_4 of Mn-reference in Figure 4, the spectrum parameters can

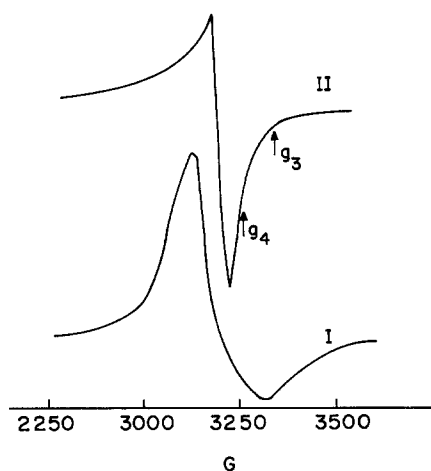
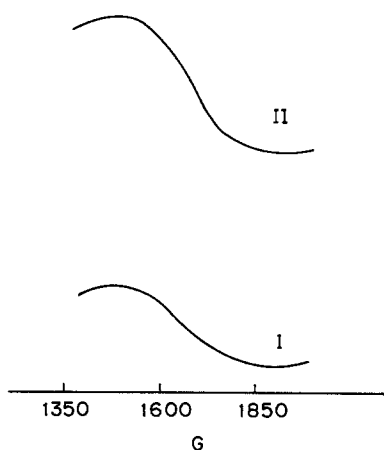


Figure 4. Powder X-band e.p.r. spectra of the complexes: I, (1); II, (2).

be deduced: $g_{\parallel} = 1.99$, $g_{\perp} = 2.19$ (1); $g_{\parallel} = 2.09$, $g_{\perp} = 2.05$ (2). Moreover, a very weak signal ($g \approx 4$) at half field ($\sim 1600 \times 10^{-4}$ T) can be assigned to the $\Delta M_s = \pm 2$ forbidden transition, which is roughly 10^{-3} times the $\Delta M_s = 1$ transition. The appearance of the half-field signals confirms the existence of a magnetic interaction between trinuclear units for these complexes.

Further investigation on this and similar systems is required in order to explain that $g_{\perp} > g_{\parallel}$ for (1) (phen) but $g_{\parallel} > g_{\perp}$ for (2) (bpy).

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