

Synthetic, spectral and solution studies on imidazolate-bridged copper(II)–copper(II) and copper(II)–zinc(II) complexes

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Abstract. Synthesis, spectral and solution studies on 2-ethyl imidazolate-bridged (2-EtIm) homo-binuclear copper(II)–copper(II) and hetero-binuclear copper(II)–zinc(II) homologue are described. Magnetic moment values of homo-binuclear complexes indicate that the imidazolate group can mediate antiferromagnetic interactions. Optical spectra of hetero-binuclear complex at varying pH values suggest that the imidazolate-bridged complex is stable over the pH-range 7–15–10.0.

Keywords. 2-Ethylimidazolate-bridged; homo/hetero-binuclear complexes; anti-ferromagnetic interactions.

1. Introduction

The deprotonated form of imidazole can serve as a bridging ligand for transition metal ions^{1–15}. Imidazolate-bridged binuclear metal complexes like bovine superoxide dismutase [Cu(II)–Im–Zn(II)SOD]¹⁶ are of much interest. Of late, synthesis and characterization of several imidazolate-bridged binuclear copper(II) complexes have been reported^{1–17}. All these complexes exhibit antiferromagnetic spin-exchange interactions. A survey of the literature shows that only a few studies on imidazolate-bridged copper(II)-zinc(II) complexes pertaining to the SOD model have been reported^{18–26}. In this paper, we report the synthesis of substituted 2-ethyl imidazolate (2-EtIm) bridged copper(II)–copper(II) and copper(II)-zinc(II) complexes as models for Cu-CuSOD and Cu-ZnSOD respectively.

2. Experimental

2.1 Materials

Diethylenetriamine and 2-ethylimidazole (both from SD Fine Chem) and copper perchlorate hexahydrate (Aldrich) were used as supplied. All other chemicals used were of reagent grade.

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2.2 Synthesis of complexes

2.2a [(Dien)Cu-2-EtIm-Cu(dien)](ClO₄)₃: Methanol–acetonitrile (5:1) solutions of copper(II) perchlorate hexahydrate (0.740 gm, 2 mmol), diethylenetriamine (0.206 gm, 2 mmol) and 2-ethylimidazole (0.082 gm, 1 mmol) were mixed together and well stirred. The pH of the solution was raised to 10.5 by addition of 1 M NaOH solution. On leaving the contents overnight, dark blue crystals were formed, which were filtered, washed with ethanol and dried *in vacuo* at room temperature. Yield ≈ 60%.

2.2b [(Dien)Cu-2-EtIm-Zn(dien)](ClO₄)₃: Methanol–acetonitrile (5:1) solutions of copper(II) perchlorate hexahydrate (0.370 gm to 370 gm, 1 mmol), diethylenetriamine (0.103 gm 1 mmol) and 2-ethylimidazole (0.082 gm, 1 mmol) were mixed together and stirred well (part A). Similarly, methanol–acetonitrile (5:1) solutions of zinc(II) perchlorate hexahydrate (0.372 gm, 1 mmol) and diethylenetriamine (0.103 gm, 1 mmol) were mixed together and stirred well (part B). Again, solutions of part A and part B were mixed together and stirred well. The pH of this resulting solution was raised to around 10.0 pH by adding 1 M NaOH solution and the contents were left overnight. Blue crystals of the desired complex formed were collected, washed with ethanol and dried *in vacuo* at room temperature. Yield ≈ 55%.

2.3 Instrumentation

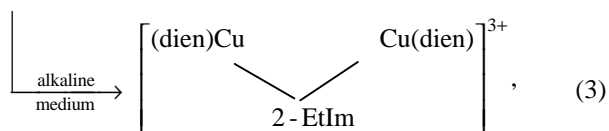
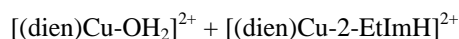
2.3a EPR spectra: X-band EPR spectra were recorded with a Varian E-line century series EPR spectrometer equipped with a dual cavity and operating at X-band with 100 kHz modulation frequency. TCNE ($g = 2.0028$) was used as field marker.

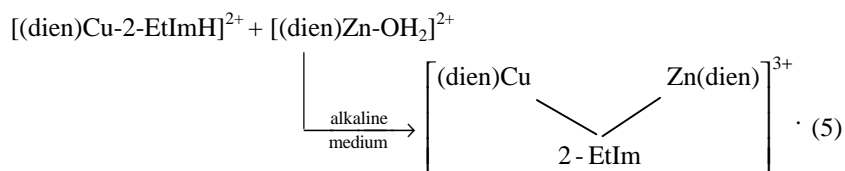
2.3b Optical spectra: Optical spectra were recorded in 100% DMSO and in 50% aqueous DMSO solution on a Shimadzu UV-VIS 160 spectrophotometer.

2.3c Magnetic moment: Magnetic susceptibility measurements were carried out with mercury(II)tetrathiocyanato cobaltate (II) ($c_g = 16.44 \times 10^{-6}$ cgs unit) as standard reference.

3. Results and discussion

The 2-ethylimidazolate-bridged (2-EtIm) homo-/hetero-binuclear complexes were prepared by the following sequential routes without isolation of the mononuclear species.





These homo-/hetero-binuclear complexes give satisfactory elemental analyses (table 1).

Table 1. Analytical and physical data for imidazolate-bridged copper(II) complexes.

Complex	Colour	D. temp.* (°C)	Elemental analysis % found (calc.)					μ_{eff} (BM)
			C	H	N	Cu	Zn	
$[(\text{dien})\text{Cu}-2\text{-EtIm}-\text{Cu}(\text{dien})](\text{ClO}_4)_3$	Deep blue	180	21.42 (21.46)	4.48 (4.54)	15.46 (15.41)	17.52 (17.48)	–	1.46
$[(\text{dien})\text{Cu}-2\text{-EtIm}-\text{Zn}(\text{dien})](\text{ClO}_4)_3$	Blue	165	21.39 (21.41)	4.48 (4.53)	15.34 (15.37)	8.70 (8.72)	8.73 (8.70)	1.79

*Decomposition temperature

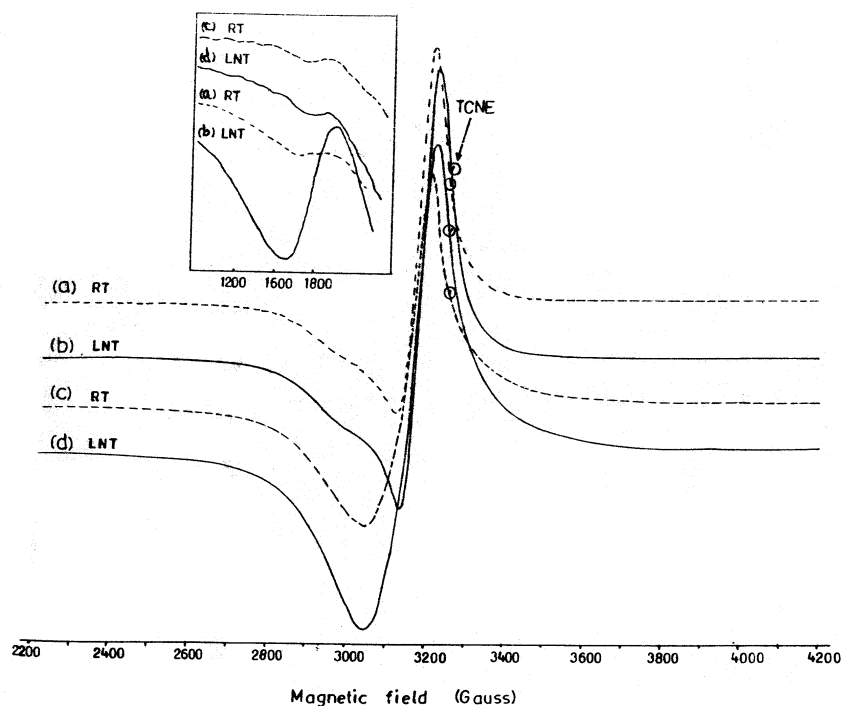


Figure 1. X-band EPR spectra of $[(\text{dien})\text{Cu}-2\text{-EtIm}-\text{Cu}(\text{dien})]^{3+}$ (a) and (b), and $[(\text{dien})\text{Cu}-2\text{-EtIm}-\text{Zn}(\text{dien})]^{3+}$ (c) and (d) in polycrystalline powder recorded at RT and LNT. (Inset, half-field signals.)

3.1 Magnetic properties

Room temperature effective magnetic moment (μ_{eff}) values for both homo-/hetero-binuclear complexes are summarized in table 1 along with their physical data. The low values of magnetic moment (1.46 BM) of homo-binuclear complexes are indicative of antiferromagnetic exchange. As expected, room temperature magnetic moment values of hetero-binuclear complexes differ markedly from that of the homo-binuclear copper(II)–copper(II) complex. The observed room temperature magnetic moments are around 1.79 BM, in agreement with a one-spin ($S = 1/2$) system.

3.2 EPR studies

EPR spectra of polycrystalline powder of both homo-/hetero-binuclear complexes at liquid nitrogen temperature (LNT) as well as room temperature (RT) are shown in figure 1. Basic spectral characteristics at both temperatures are the same with slightly better

Table 2. EPR and optical parameters (100% DMSO) for imidazolate-bridged copper(II) complexes.

Complex	g_{iso}	g_{\parallel}	g_{\perp}	$A_{\parallel}(\text{G})$	$I_{\text{max}}(\text{nm})$
$[(\text{dien})\text{Cu}-2\text{-EtIm}-\text{Cu}(\text{dien})](\text{ClO}_4)_3$	2.057	2.20	2.06	185	606
$[(\text{dien})\text{Cu}-2\text{-EtIm}-\text{Zn}(\text{dien})](\text{ClO}_4)_3$	2.049	2.20	2.05	182	612

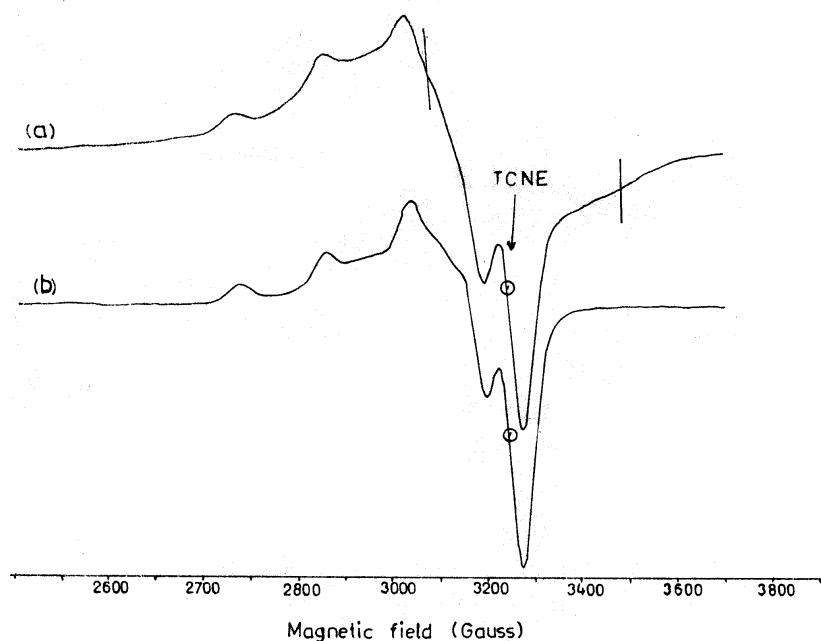


Figure 2. X-band EPR spectra of $[(\text{dien})\text{Cu}-2\text{-EtIm}-\text{Cu}(\text{dien})]^{3+}$ and $[(\text{dien})\text{Cu}-2\text{-EtIm}-\text{Zn}(\text{dien})]^{3+}$ in frozen 50% aqueous DMSO solution at 77 K.

resolution at LNT. Confirming the magnetic measurements, the spectra of homo-binuclear complex show the spectral features of an antiferromagnetically coupled binuclear species: (i) The $\Delta M_s = \pm$ 'half-field' signals is observed at ~ 1600 G, (ii) $\Delta M_s = \pm 1$ region shows two broad signals at -2940 G and 3200 G (RT) and is characteristic of isotropic spectral feature. The calculated value of g_{iso} is 2.06 . The spectra of hetero-binuclear complex are characteristic of $S = 1$.

EPR spectra of the homo/hetero-binuclear complexes in frozen 100% DMSO solution at LNT are shown in figure 2. The EPR parameters calculated from their respective spectra are given in table 2. The $\Delta M_s = \pm 1$ regions of EPR spectra of homo-binuclear complex show two broad signals at -3070 and 3500 G. The parallel and perpendicular components of separations d_{\parallel} and d_{\perp} is derived from the following expressions:

$$d_{\parallel} = 2|D|/g_{\parallel} \quad \text{and} \quad d_{\perp} = |D|/g_{\perp}, \quad (6)$$

where D is the zero-field splitting parameter. The two broad signals at 3070 and 3500 G were thus assigned to the split g_{\perp} signal, allowing the calculation of zero-field splitting parameter (D). Analysis of the spectrum gave the following values: $|D| = 0.04 \text{ cm}^{-1}$, $g_{\parallel} = 2.20$ and $g_{\perp} = 2.06$. The value of D is consistent with those of other binuclear complexes¹⁷. The spectrum of hetero-binuclear complex exhibits the usual line-shape for mononuclear copper(II) complexes with $g_{\parallel} > g_{\perp} > 2.03$, indicating axial symmetry. The calculated values are $g_{\parallel} = 2.195$, $g_{\perp} = 2.05$, $A_{\parallel} = 168$ G and $g_{\parallel}/A_{\parallel} = 130$ G, indicating square pyramidal geometry with dx^2-y^2 ground state. The spectrum is similar to the earlier reported binuclear copper(II)–zinc(II) complexes^{23–27}.

3.3 Solution studies of hetero-binuclear complex

pH -dependence stability of an aqueous solution of hetero-binuclear complex was also studied by optical spectrophotometry. Visible spectra recorded as a function of pH clearly show that the complex is stable over the pH -range 7.15 – 10.0 (figure 3). The pH of the solution in the range 2.00 to 11.50 pH unit was adjusted using HClO_4 and NaOH solutions. Attempts were made to study the species formed due to breaking of imidazolate-bridge. In 50% aqueous DMSO solution at pH 7.15 , the spectrum (figure 3)

Table 3. I_{\max} (nm) at variable pH values and EPR data (at pH 7.15) for $[(\text{dien})\text{Cu}-2\text{-EtIm-Zn}(\text{dien})](\text{ClO}_4)_3$ in 50% aqueous DMSO solution.

pH	I_{\max} (nm)	g_{\parallel}	g_{\perp}	A_{\parallel} (G)
2.00	760	–	–	–
3.00	626	–	–	–
4.50	620	–	–	–
6.00	616	–	–	–
7.15	613	2.21	2.05	185
8.50	613	–	–	–
10.00	613	–	–	–
11.50	607	–	–	–

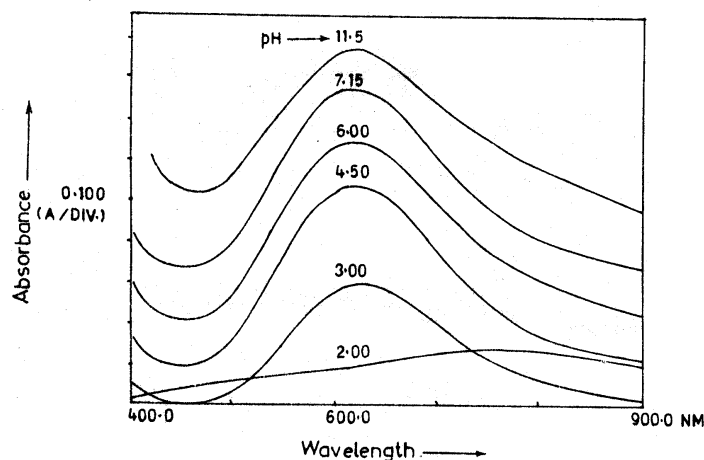
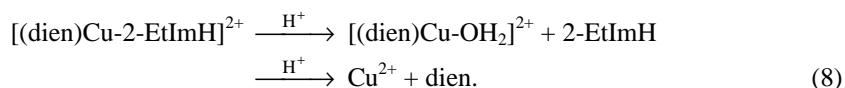
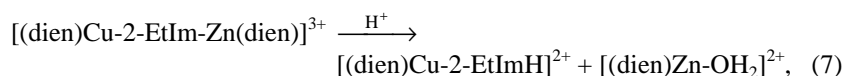


Figure 3. pH-dependent optical spectra of $[(\text{dien})\text{Cu}-2\text{-EtIm}-\text{Zn}(\text{dien})]^{3+}$ complex in 50% aqueous DMSO solution at room temperature.

shows a $d-d$ band at I_{max} 613 nm which remains unchanged up to pH 10.0. As the pH is decreased from 7.15 to 2.0, we observe a broad band at 760 nm characteristic of the Cu^{2+} ion in 50% aqueous DMSO. Below the physiological pH < 7.15, bridge breaking takes place according to the following reaction.



Above pH 10.0, the I_{max} value is 607 nm which is indicative of the bridge homo-binuclear species $[(\text{dien})\text{Cu}-2\text{-EtIm}-\text{Cu}(\text{dien})]^{3+}$. The I_{max} value is also observed at 606 nm in 100% DMSO and supports the formation of bridged homo-binuclear copper complexes.

4. Conclusion

The synthesized hetero-imidazolate bridged (2-EtIm) complex shows its stability over the pH-range 7.15–10.0. The homo-binuclear imidazolate-bridged complex demonstrates a model for antiferromagnetic exchange interactions. All results indicate that these imidazolate-bridged complexes act as good models for superoxide dismutase.

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