Proc. Indian Acad. Sci. (*Chem. Sci.*), Vol. 113, No. 1, February 2001, pp 21–27

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

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MS received 14 August; revised 24 October 2000

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 *p*H values suggest that the imidazolate-bridged complex is stable over the *p*H-range 7·15–10·0.

Keywords. 2-Ethylimidazolate-bridged; homo/hetero-binuclear complexes; antiferromagnetic 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)](ClO$_4$)$_3$:* 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 *p*H 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)](ClO$_4$)$_3$:* 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 *p*H of this resulting solution was raised to around 10·0 *p*H 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)tetrathiocynato cobaltate (II) ($c_g = 16{\cdot}44 \times 10^{-6}$ 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.

$$Cu^{2+} + \text{dien} \rightarrow [(\text{dien})\text{Cu-OH}_2]^{2+}, \quad (1)$$

$$[(\text{dien})\text{Cu-OH}_2]^{2+} + \text{2-EtImH} \rightarrow [(\text{dien})\text{Cu-2-EtImH}]^{2+}, \quad (2)$$

$$[(\text{dien})\text{Cu-OH}_2]^{2+} + [(\text{dien})\text{Cu-2-EtImH}]^{2+} \xrightarrow[\text{medium}]{\text{alkaline}} \left[(\text{dien})\text{Cu}\begin{array}{c}\diagdown\\ \text{2-EtIm}\\ \diagup\end{array}\text{Cu(dien)}\right]^{3+}, \quad (3)$$

$$Zn^{2+} + \text{dien} \rightarrow [(\text{dien})Zn\text{-}OH_2]^{2+}, \quad (4)$$

$$[(\text{dien})Cu\text{-}2\text{-}EtImH]^{2+} + [(\text{dien})Zn\text{-}OH_2]^{2+} \xrightarrow[\text{medium}]{\text{alkaline}} \left[\begin{array}{c}(\text{dien})Cu \qquad\qquad Zn(\text{dien}) \\ \diagdown \quad \diagup \\ 2\text{-}EtIm\end{array}\right]^{3+} \cdot \quad (5)$$

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.) C	H	N	Cu	Zn	μ_{eff} (BM)
$[(\text{dien})Cu\text{-}2\text{-}EtIm\text{-}Cu(\text{dien})](ClO_4)_3$	Deep blue	180	21·42 (21·46)	4·48 (4·54)	15·46 (15·41)	17·52 (17·48)	–	1·46
$[(\text{dien})Cu\text{-}2\text{-}EtIm\text{-}Zn(\text{dien})](ClO_4)_3$	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

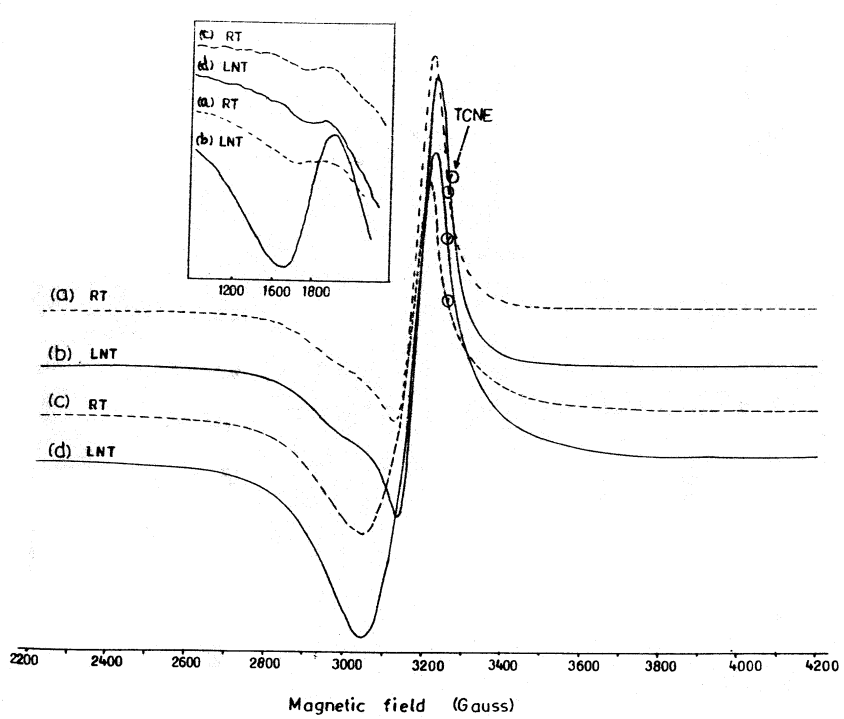

Figure 1. X-band EPR spectra of $[(\text{dien})Cu\text{-}2\text{-}EtIm\text{-}Cu(\text{dien})]^{3+}$ (**a**) and (**b**), and $[(\text{dien})Cu\text{-}2\text{-}EtIm\text{-}Zn(\text{dien})]^{3+}$ (**c**) and (**d**) in polycrystalline powder recorded at RT and LNT. (Inset, half-field signals.)

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}	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$(G)	l_{max} (nm)
[(dien)Cu-2-EtIm-Cu(dien)]$(ClO_4)_3$	2·057	2·20	2·06	185	606
[(dien)Cu-2-EtIm-Zn(dien)]$(ClO_4)_3$	2·049	2·20	2·05	182	612

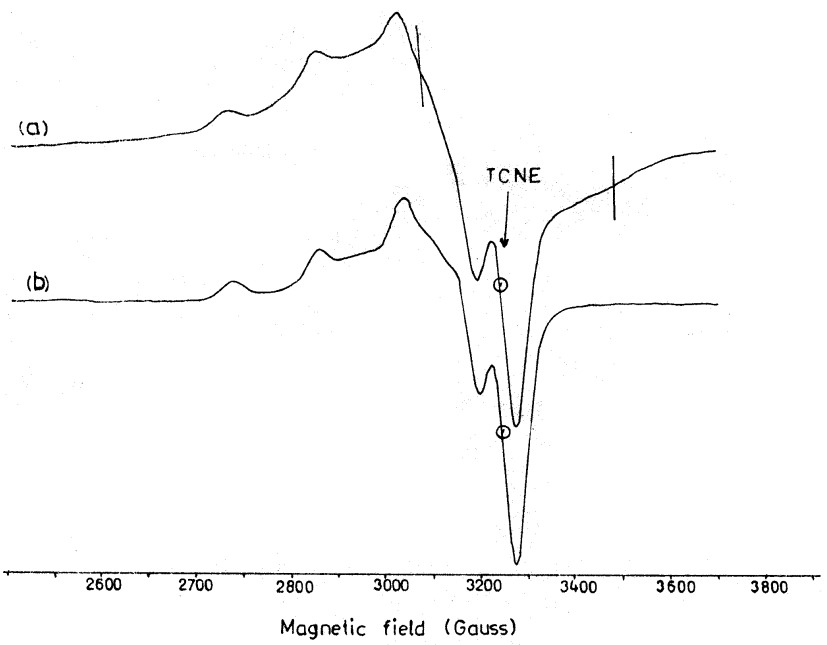

Figure 2. X-band EPR spectra of [(dien)Cu-2-EtIm-Cu(dien)]$^{3+}$ and [(dien)Cu-2-EtIm-Zn(dien)]$^{3+}$ in frozen 50% aqueous DMSO solution at 77 K.

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:

$$d_\parallel = 2|D|/g_\parallel \qquad \text{and} \qquad d_\perp = |D|/g_\perp, \tag{6}$$

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: $|D| = 0{\cdot}04$ cm^{-1}, $g_\parallel = 2{\cdot}20$ and $g_\perp = 2{\cdot}06$. The value of D is consistent with those of other binuclear complexes [17]. The spectrum of hetero-binuclear complex exhibits the usual line-shape for mononuclear copper(II) complexes with $g_\parallel > g_\perp > 2{\cdot}03$, indicating axial symmetry. The calculated values are $g_\parallel = 2{\cdot}195$, $g_\perp = 2{\cdot}05$, $A_\parallel = 168$ 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*

*p*H-dependence stability of an aqueous solution of hetero-binuclear complex was also studied by optical spectrophotometry. Visible spectra recorded as a function of *p*H clearly show that the complex is stable over the *p*H-range 7·15–10·0 (figure 3). The *p*H of the solution in the range 2·00 to 11·50 *p*H 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 *p*H 7·15, the spectrum (figure 3)

Table 3. l_{max} (nm) at variable *p*H values and EPR data (at *p*H 7·15) for [(dien)Cu-2-EtIm-Zn(dien)]$(ClO_4)_3$ in 50% aqueous DMSO solution.

*p*H	l_{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	–	–	–

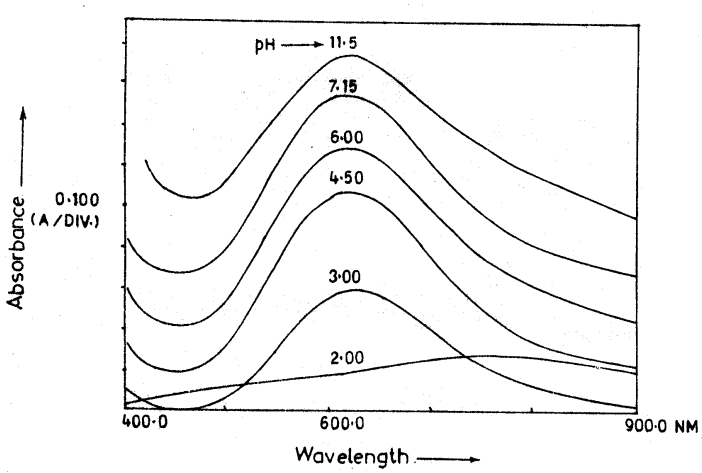

Figure 3. *p*H-dependent optical spectra of $[(dien)Cu\text{-}2\text{-}EtIm\text{-}Zn(dien)]^{3+}$ complex in 50% aqueous DMSO solution at room temperature.

shows a *d–d* band at l_{max} 613 nm which remains unchanged up to *p*H 10·0. As the *p*H 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 *p*H < 7·15, bridge breaking takes place according to the following reaction.

$$[(dien)Cu\text{-}2\text{-}EtIm\text{-}Zn(dien)]^{3+} \xrightarrow{H^+} [(dien)Cu\text{-}2\text{-}EtImH]^{2+} + [(dien)Zn\text{-}OH_2]^{2+}, \quad (7)$$

$$[(dien)Cu\text{-}2\text{-}EtImH]^{2+} \xrightarrow{H^+} [(dien)Cu\text{-}OH_2]^{2+} + 2\text{-}EtImH$$
$$\xrightarrow{H^+} Cu^{2+} + dien. \quad (8)$$

Above *p*H 10·0, the I_{max} value is 607 nm which is indicative of the bridge homo-binuclear species $[(dien)Cu\text{-}2\text{-}EtIm\text{-}Cu\text{-}(dien)]^{3+}$. The l_{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 *p*H-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.

Acknowledgement

EPR spectral facilities provided by the Regional Sophisticated Instrumentation Centre, Indian Institute Technology, Bombay is gratefully acknowledged. One of the authors (SK) thanks the Council of Scientific & Industrial Research, New Delhi for an associateship.

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