

Synthesis, structure and properties of ternary copper(II) complexes of ONO donor Schiff base, imidazole, 2,2'-bipyridine and 1,10-phenanthroline

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Abstract

Reaction of copper(II) salt with salicylidene anthanilic acid (SAA), a tridentate ligand and imidazole (ImH), a monodentate ligand or bidentate polypyridyl ligands like 2,2'-bipyridine (bipy) or 1,10-phenanthroline(phen) in MeOH:MeCN (1:1 V/V) yields [Cu(SAA)(ImH)] (**1**), [Cu(SAA)(bipy)]CH₃CN (**2**) and [Cu(SAA)(phen)] (**3**) in ~80% yield. These complexes were characterized by elemental analysis, magnetic susceptibility, X-band e.p.r., electronic spectroscopy and cyclic voltammetry. All the reported complexes show $g_{\parallel} > g_{\perp} > 2.0023$ and G values falling within the range of 2–4 are consistent with a $d_{x^2-y^2}$ ground state in a square planar or square pyramidal geometry. Single crystal X-ray analysis of **1** has revealed the presence of a distorted square planar geometry (N₂O₂) and **2** has revealed the presence of distorted square pyramidal (4 + 1) geometry. In both structures the ONO Schiff base occupies the basal plane. Magnetic susceptibility measurements at room temperature were in the range 1.79 ± 0.01 BM. Superoxide dismutase (SOD) activity of the present complexes were also measured.

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Keywords: Schiff base; Monodentate ligand; Bidentate polypyridyl ligands; X-band e.p.r.; SOD; Cyclic voltammetry

1. Introduction

Transition metal complexes with Schiff base ligands containing the carboxylate group have been of great interest due to their importance as essentially biologically active [1–6], models for metalloproteins [7,8]. Particular attention has been devoted to salicylidene Schiff base derivatives because they can promote chelation and provide extra stability to the metal centers [9]. Copper is an important trace element for plants and animals, and is involved in mixed ligand complex formation in a number of biological processes [10]. Copper complexes containing polypyridine ligands and their derivatives are of great interest since they exhibit numerous biological activities such as antitumor

[11], anti-candida [12], antimicrobial [13] and antimicrobial [14,15] activities, etc. Imidazole is also one of the most biologically important ligands. It behaves like a monodentate ligand at lower pH and at higher pH serves as a bridging ligand. The deprotonated form of imidazole is involved in the active site of bovine erythrocyte superoxide dismutase (BESOD) [16]. It bridges copper(II) and zinc(II) ions. The presence of copper in the active site of Cu₂Zn₂SOD has led many groups to search for stable, non-toxic, low-molecular weight complexes of this metal that have SOD activity (functional models) and could be substituted for SOD in clinical applications with desirable qualities being cell permeability, low cost and non-immunogenicity [17]. Therefore in the continuation of our work [15,18–20] on mixed ligand copper(II) complexes, this time we communicate the synthesis, structure, spectroscopic, magnetic measurement, cyclic voltammetry and superoxide dismutase (SOD) activity of ternary copper(II) complexes

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containing a tridentate Schiff base (SAA) and a monodentate ligand (ImH)/bidentate ligands (bipy, phen). The single crystal X-ray analysis of complex **1** has revealed the presence of a distorted square planar geometry and complex **2** has a distorted square pyramidal geometry.

2. Experimental

2.1. Materials and methods

$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, KOH, 1,10-phenanthroline, 2,2'-bipyridine, imidazole, MeOH, MeCN (S.D. Fine Chemicals) were used as purchased. The Schiff base was synthesized by reacting salicylaldehyde and anthranilic acid in an equimolar ratio at room temperature in methanol. Elemental analyses were performed on an elemental analyzer. FAB mass spectra were recorded on JEOL SX 102/DA 6000 mass spectrometer using xenon (6 kV, 10 mA) as the FAB gas. The magnetic susceptibility data were recorded on a Gouy balance at room temperature using mercury(II) tetrathiocyanato cobaltate(II) ($\chi_{\text{g}} = 16.44 \times 10^{-6}$ cgs unit) as the calibrant. The e.p.r. spectra were recorded at RT and also at LNT (77 K) on a Varian E-line Century Series EPR spectrometer operating at 9.4 GHz with TCNE as a calibrant. The e.p.r. parameters were measured using a reported method [21]. UV–Vis spectra were recorded on a Shimadzu UV–Vis 160 spectrophotometer

in quartz cells. A BAS-100 Epsilon electrochemical analyzer was used for cyclic voltammetric experiments in a DMSO solution of the complex containing tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. The three electrode measurement was carried out at 298 K under a nitrogen atmosphere with a platinum working electrode, a platinum wire auxiliary electrode and a silver/silver chloride reference electrode (Ag/AgCl). The SOD activities were evaluated using alkaline DMSO as a source of superoxide radicals (O_2^-) and nitrobluetetrazolium chloride (NBT) as scavenger [18].

2.2. Synthesis of the complexes

2.2.1. Synthesis of $[\text{Cu}(\text{SAA})(\text{ImH})]$ (**1**), $[\text{Cu}(\text{SAA})(\text{bipy})]\text{CH}_3\text{CN}$ (**2**) and $[\text{Cu}(\text{SAA})(\text{phen})]$ (**3**)

All the present complexes were synthesized following the same general procedure. To a MeOH solution (10 ml) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (1.0 mmol, 0.170 g) a solution of the potassium salt of the Schiff base (1 mmol, 0.240 g) was added and the reaction mixture was stirred for 30 min at 25 °C. To the above reaction mixture, a MeOH solution (10 ml) of ImH (1 mmol, 0.078 g) was added and the stirring was continued for 30 min more. The precipitate was separated by filtration and was dissolved in MeOH:MeCN (1:2 V/V) for recrystallization. After 2–3 days of slow evaporation of the reaction mixture, dark green prismatic crystals were

Table 1

Crystal data and structure refinement for complexes $[\text{Cu}(\text{SAA})(\text{ImH})]$ (**1**) and $[\text{Cu}(\text{SAA})(\text{bipy})]\text{CH}_3\text{CN}$ (**2**)

Empirical formula	$\text{C}_{17}\text{H}_{13}\text{CuN}_3\text{O}_3$	$\text{C}_{26}\text{H}_{20}\text{CuN}_4\text{O}_3$
Formula weight	370.84	500.00
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073 Å
Crystal system, space group	orthorhombic, $Pna2_1$	triclinic, $P\bar{1}$
Unit cell dimensions		
a (Å)	9.3805(9)	9.165(3)
b (Å)	11.546(4)	10.0261(19)
c (Å)	14.5258(14)	13.1393(18)
α (°)	90	76.469(14)
β (°)	90	79.100(19)
γ (°)	90	76.13(2)
V (Å ³)	1573.2(6)	1128.2(5)
D_{calc} (Mg/m ³)	1.566	1.472
Z	4	2
Absorption coefficient (mm ⁻¹)	1.409	1.005
$F(000)$	756	514
Crystal size (mm)	0.18 × 0.15 × 0.13	0.35 × 0.30 × 0.30
θ Range for data collection (°)	3.13–32.00	3.00–30.16
Limiting indices	$-13 \leq h \leq 13, -16 \leq k \leq 16, -21 \leq l \leq 21$	$-12 \leq h \leq 12, -14 \leq k \leq 14, -17 \leq l \leq 18$
Reflections collected/unique [R_{int}]	21 681/4649 [0.0245]	15 730/6571 [0.0186]
Completeness to θ	25.00, 99.8%	25.00, 99.5%
Absorption correction	semi-empirical from equivalents	
Maximum and minimum transmission	0.8381 and 0.7856	
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	4649/1/217	6571/0/308
Goodness-of-fit on F^2	0.956	1.045
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0249, wR_2 = 0.0570$	$R_1 = 0.0327, wR_2 = 0.0905$
R indices (all data)	$R_1 = 0.0361, wR_2 = 0.0595$	$R_1 = 0.0537, wR_2 = 0.0945$
Absolute structure parameter	–0.008(8)	
Largest difference in peak and hole (e Å ⁻³)	0.247 and –0.267	0.402 and –0.234

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