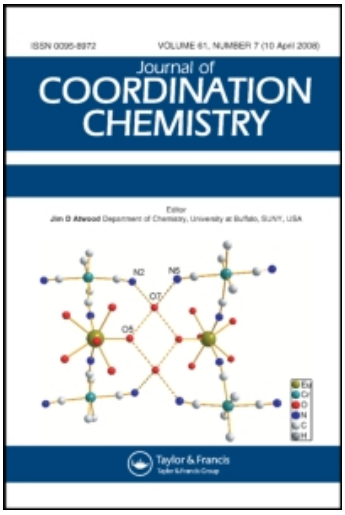

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SYNTHESIS AND CHARACTERIZATION OF TWO ISOMERS OF THE MONONUCLEAR COPPER COMPLEXES OF *N*, *N*′-BIS-(3-CARBOXYSALICYLIDENE)-ETHYLENEDIAMINE

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SYNTHESIS AND CHARACTERIZATION OF TWO ISOMERS OF THE MONONUCLEAR COPPER COMPLEXES OF *N,N'*-BIS-(3-CARBOXYSALICYLIDENE)-ETHYLENEDIAMINE

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Two isomers of the mononuclear copper(II) complex, $CuH_2fsaen \cdot H_2O$, were prepared by reacting *N, N'*-bis(3-carboxysalicylidene)ethylenediamine (H_4fsaen) with $Cu(CH_3COO)_2 \cdot H_2O$ in methanol. The complexes were characterized by elemental analyses, IR, electronic spectra, TG and X-ray photoelectron spectroscopy (XPS). In the green complex, the copper(II) ion occupies the outer compartment ($-O_2O_2$), reducing the fluroscence intensity compared to that of the ligand, while in the violet complex, the copper(II) ion lies in the inner compartment ($-N_2O_2$), making the fluroscence intensity completely quenched.

Keywords: Compartmental ligand; mononuclear; copper(II); isomers

INTRODUCTION

The reaction of α,ω-diamines with a terminal keto-function of a β-diketone, ketophenol or ketocarboxylic acid leads to the formation of a Schiff base having adjacent, dissimilar coordination compartments.[1] One of the compartments would resemble a Schiff base and is designated $-N_2O_2$; the other

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may be compared with a diketone, ketophenol or ketocarboxylic acid and is designated $-O_2O_2$. In metal complex ion rection with such a compartmental ligand, the metal is presented with a choice of coordination sites.

The relatively easy preparation, stability and versitility of Schiff bases make them very useful tools to study metal–metal interaction, metal ion recognition, encapsulation, transport and separation, and the like.[2,3] *N*,*N*′-bis(3-carboxysalicylidene)ethylenediamine (H_4fsaen) is derived from 3-formysalicylic acid and ethylenediamine. For this ligand, the inner coordination site has $-N_2O_2$, while the outer site has $-O_2O_2$ coordinating atoms. Since there is a considerable difference in the ligand field strength between inner and outer sites, mononuclear complexes in which metals are coordinated in different compartments would have quite different spectroscopic properties. It was reported that all mononuclear complexes derived from H_4fsaen only contain the transition metal in the inner $-N_2O_2$ compartment.[4] In this paper, we report the synthesis of two isomers of copper(II) mononuclear complexes of H_4fsaen. Their structures were characterized by elemental analyses, IR, electronic spectra, TG and X-ray photoelectron spectra (XPS). The influence of the different coordinating sites was investigated.

EXPERIMENTAL

3-Formylsalicylic acid was prepared by a literature method.[5] H_4fsaen and CuH_2fsaen (violet) were synthesized according to the method reported.[6] Elemental analyses were determined with a Perkin-Elmer 240C instrument; infrared spectra were recorded on a Magna IR-750 (KBr disc); electronic spectra were recorded on Shimadzu recording spectrophotometer (UV-240); TG-DTA measurement was obtained with a Shimadzu DTA-50 differential thermal analyzer in a nitrogen environment at a heating rate of $10°C\,min^{-1}$; fluorescence spectra were recorded on Hitachi 850 fluorescence spectrophotometer; XPS measurements were carried out using a VG ESCALAB MK-II X-ray photoelectron spectrometer.

CuH_2fsaen · H_2O (green)

H_4fsaen (0.7120 g, 2 mmol) dissolved in methanol ($400\,cm^3$) was added dropwise to a methanol solution ($120\,cm^3$) of $Cu(CH_3COO)_2 \cdot H_2O$ (0.4000 g, 2 mmol) at room temperature, then a methanol solution ($10\,cm^3$) containing $LiOH \cdot H_2O$ (0.1680 g, 4 mmol) was added. After a few minutes,

a green precipitate appeared and this was stirred for 3 h, filtered, washed with methanol and dried under vacuum. *Anal.* Found (%) C, 50.27; H 3.72; N, 6.42. Calc. for $C_{18}H_{16}O_7Cu$: C, 49.60; H, 3.67; N, 6.43.

RESULTS AND DISCUSSION

Spectroscopic Characterization of the Two Isomers

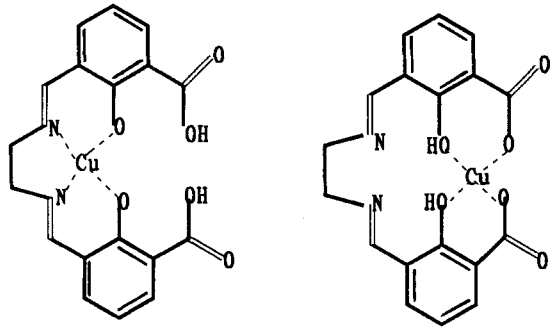
Infrared (IR) data for the two isomer complexes and the ligand are given in Table I. In the violet complex, the C=O stretching vibration appears at 1705 cm^{-1} and the azomethine vibration at 1642 cm^{-1}. In the ligand H_4L, these occur at 1700 and 1652 cm^{-1}, respectively. This fact clearly indicates that the copper(II) ion is bonded to the inner $-N_2O_2$ coordination site. In the green complex, the C=O stretching vibration appears at 1532 cm^{-1}, about 170 cm^{-1} lower than that of the ligand; the azomethine group vibration occurs at 1630 cm^{-1}, 22 cm^{-1} lower than that of the ligand and the C=C stretching vibration is at 1590 cm^{-1}, with a red shift of about 10 cm^{-1}, compared with the ligand. All these facts suggest that in the green complex, the copper(II) ion occupies the outer $-O_2O_2$ site. From reflectance data for the complexes, it was apparent that the coordination field strength of the violet complex was stronger than that of the green one. This can be easily explained in terms of differing coordination sites (absorption maxima). Reflectance data for the two complexes are also shown in Table I. For the violet complex, an intense band at 550 nm is attributed to the copper(II) ion bound in the stronger N_2O_2 coordination field; in the green complex, the band at 735 nm is assigned to the outer copper(II) ion in the weaker O_2O_2 coordination field.[7]

The TG curve of $CuH_2fsaen \cdot H_2O$ in the temperature range 30–600°C shows a weight loss at about 85°C (3.62%), indicating the loss of one H_2O molecule (calculated 4.13%); the result indicates that the H_2O molecule is not coordinated to copper(II). The complex decomposes from 311°C and at 552°C, only CuO is left. Total weight loss is 80.85% (calculated 81.75%).

TABLE I Spectroscopic data for the isomers

Compound	*IR* (cm^{-1})			*Reflectance* (nm)
	$\nu_{C=O}$	$\nu_{C=N}$	$\nu_{C=C}$	ν(max)
H_4fsaen (yellow)	1700	1652	1600	—
CuH_2fsaen (violet)	1705	1642	1600	550
$CuH_2fsaen \cdot H_2O$ (green)	1532	1630	1590	735

In the XPS spectra, for the green complex, the N_{1S} spectrum is very similar to that of the ligand; both have a single peak at about 401.6 eV. In the N_{1S} spectrum of the violet complex, a single peak appears at 400.7 eV. This is consistent the violet complex having nitrogen coordinated to the copper(II) ion. In the green complex, with copper(II) in the outer $-O_2O_2$ compartment, there is little effect on the N_{1S} spectrum as compared with the ligand. The excitation wavelength for fluorescence spectra was fixed in the region of the ligand absorption ($\lambda_{ex} = 360$ nm). It was observed that for the emission spectrum of the ligand, the fluorescence ($L^* - L$) was strong. In the green complex, fluorescence intensity decreased drastically and the emission wavelength displayed some red shift; in the purple complex, fluorescence intensity was quenched completely. Coordination of copper(II) with C=N perturbs the ligand electronic system and decreasing conjugation causes much weaker luminescence.[8]



(a) (b)

(a) CuH_2fsaen(violet), (b) CuH_2fsaen · H_2O (green).

In conclusion, two mononuclear copper(II) complex isomers derived from *N,N'*-bis(3-carboxysalicylidene)ethylenediamine have been prepared as shown above. In the green complex, the H_2O molecule is not coordinated to copper(II). XPS spectra indicate different ligand field strengths for the inner and outer coordination spheres. Differences in structure result in different luminescence properties.

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