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Unusual Cu(III)–Schiff's Base Complexes

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Abstract

A new series of Cu(III) complexes of the type $[Cu(SB)]ClO_4$, where SB is a dibasic tetradentate Schiff's base, were synthesized and characterized by elemental analysis, IR and electronic spectra. The prepared complexes are compared with Cu(II) complexes of the same ligands. The room temperature magnetic susceptibility and the x-band EPR spectra of the two types of complexes showed different behaviour. Cu(II) complexes were non conducting whereas Cu(III) complexes gave a conductance corresponding to 1:1 electrolyte. In fact this is the first report on the Cu(III) complexes with the tetradentate Schiff base ligands.

Introduction

As part of a systematic study of Cu(II)–Schiff's base complexes [1–10], we have prepared and characterized a number of complexes of the unusual Cu(III) oxidation state having the general formula $[Cu(SB)]ClO_4$, where SB represents one of a variety of dibasic tetradentate Schiff's bases. The existence of Cu(III) species has been mentioned before in some complex structures [11, 12].

To get a clear understanding of the structure and characterization of the Cu(III)–SB complexes, some of the corresponding Cu(II)–SB complexes (either for known ligands or novel new ones) were prepared. The data for the Cu(II) complexes are compared with those of Cu(III). An investigation of the effect of varying the Schiff base on the structure and properties of the complexes was also attempted. The investigations were carried out using elemental analysis, IR, electronic and EPR spectra as well as room temperature magnetic moment measurements.

Experimental

Physical Measurements

A Perkin-Elmer Model 598 spectrophotometer was used to obtain the infrared spectra of the solid samples as Nujol mulls. Electronic spectra were recorded on a Cary 14 spectrophotometer. Magnetic susceptibility was measured by the Gouy method using $Hg[Co(CNS)_4]$ as the standard. Diamagnetic corrections were calculated from the relevant Pascal constants. Electron paramagnetic resonance (EPR) spectra were recorded on a Varian E-9 x-band spectrometer equipped with the E101 microwave bridge. The magnetic field was calibrated with a 2,2-diphenyl-1-picryl hydrazyl sample purchased from Aldrich.

Preparation of $[Cu(SB)]\cdot H_2O$ Complexes

These complexes were prepared using a modification of the method of Miller and Oliver [13] and the procedures are the same as described previously [14].

Preparation of $[Cu(SB)]ClO_4$ Complexes

These complexes were prepared by dissolving 0.1 M NaOH in 10 cm^3 of distilled water and mixing with (0.05 M) of the Schiff's base in 200 cm^3 of ethanol. The mixture was stirred causing the ligand to dissolve and then 0.05 M solution of Cu(II) perchlorate, dissolved in 100 cm^3 of ethanol, was added. On stirring the reaction mixture in air for about ten days, the green solid which initially precipitated was converted to a reddish brown solution. The same result was achieved by treating the reaction mixture with 3 equivalents of H_2O_2 and stirring for 24 hours when the green solid was converted to the clear red brown solution. The solution was filtered off and the filtrate was reduced in volume to 25 ml. The addition of ether to the red solution led to the precipitation of a reddish brown solid. The solid was subjected to recrystallization from ethanol/ether and then filtered off, washed with ether and dried *in vacuo*.

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TABLE I. Analytical Data for $[Cu(SB)]\cdot H_2O$ and $[Cu(SB)(H_2O)_2]ClO_4$ Complexes.

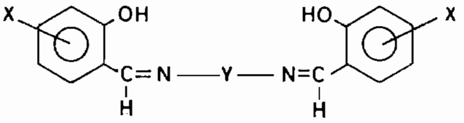
Complex	Colour	Microanalysis Results					μ_{eff}[b]	ω[c]
		% C[a]	% H[a]	% N[a]	% Cl[a]	% Cu[a]		
$[Cu(naphtm)]\cdot H_2O$	green	64.45(64.20)	5.58(5.30)	6.02(5.90)		13.64(13.40)	1.60	10
$[Cu(salen)(H_2O)_2]ClO_4$	red-brown	41.29(41.40)	3.87(4.10)	6.02(6.30)	7.63(7.50)	13.66(13.40)	3.12	125
$[Cu(saltm)(H_2O)_2]ClO_4$	red-brown	42.58(42.40)	4.17(4.30)	5.85(6.10)	7.41(7.30)	13.26(12.90)	3.08	118
$[Cu(salben)(H_2O)_2]ClO_4$	red-brown	52.97(52.80)	3.74(4.00)	4.75(4.50)	6.03(5.80)	10.78(10.40)	2.89	128
$[Cu(naphen)(H_2O)_2]ClO_4$	red-brown	50.62(50.80)	4.57(4.30)	4.92(4.70)	6.24(6.00)	11.16(10.80)	2.95	126
$[Cu(naphtm)(H_2O)_2]ClO_4$	red-brown	51.45(51.30)	4.80(4.50)	4.80(4.60)	6.09(5.80)	10.89(10.60)	2.90	129
$[Cu(naphben)(H_2O)_2]ClO_4$	red-brown	58.87(58.60)	4.33(4.10)	4.04(4.00)	5.12(4.80)	9.16(8.70)	2.85	130

[a] % Calculated (% Found). [b] μ_{eff}/M BM. [c] ohm^{-1} cm^2 mol^{-1}; 10^{-3} M solution in acetone.

Trials to grow single crystals from the prepared solid complexes were not successful.

All the prepared complexes were then subjected to elemental microanalysis and the results are listed in Table I.

The ligands used in the present investigation have the following formula:



in which X and Y are as follows:

	X	Y
salen	H	$-(CH_2)_2-$
naphen	C_6H_4	$-(CH_2)_2-$
salben	H	$-(C_6H_4-C_6H_4)-$
naphben	C_6H_4	$-(C_6H_4-C_6H_4)-$
saltm	H	$-(CH_2)_3-$
naphtm	C_6H_4	$-(CH_2)_3-$

Results and Discussion

The green Cu(II) and red Cu(III) Schiff's base complexes under investigation exhibit marked differences from each other due to the changed nature of the complexes. While the former type would be neutral molecules, the latter one is expected to display ionic properties. Cu(II)–Schiff's base complexes are slightly soluble in ethanol, chloroform and acetone whereas Cu(III)–Schiff's base complexes are highly soluble in ethanol, chloroform, acetone and DMF and have limited solubility in benzene, toluene and carbon tetrachloride.

The Cu(II)–Schiff's base complexes formed have one water molecule associated as water of crystallization, while the Cu(III)–Schiff's base complexes have two water molecules coordinated to the central metal atom. This conclusion is reached from the results of thermogravimetric analysis of Cu(II) and Cu(III) complexes which show the dehydration of water molecules from the complexes under investigation at 60–80 °C and 130–140 °C, respectively. The low dehydration temperature of water of the Cu(II) complexes reveals that water molecules would be essentially interstitial in the crystal lattice rather than coordinated to the metal atoms. The water molecules in the Cu(III) complexes are much more strongly held due to coordination with the metal atom.

The infrared group frequencies of diagnostic importance are collected in Table II. In general all infrared spectra of the solid complexes have the same general features. The observed shift of the C=N stretching frequency (1625 cm^{-1} to 1610 cm^{-1}) to

TABLE II. IR, Electronic Spectral and EPR g Values Data for Cu(SB)·H_2O and [Cu(SB)$(H_2O)_2$]ClO_4.

Complex	IR Frequencies (cm^{-1})					Electronic Spectra	EPR g_{eff} values	
	ν_{OH}	$\nu_{C=N}$	$\nu_{Cl\rightarrow O}$	ν_{M-O}	ν_{M-N}	λ_{max} (nm)	$g_{\parallel}$	$g_{\perp}$
[Cu(salen)]·H_2O	3400	1620		485	385	725, 425		2.1234
[Cu(naphen)]·H_2O	3410	1625		480	380	720, 425		2.1789
[Cu(naphtm)]·H_2O	3415	1615		480	380	720, 420		2.1135
[Cu(naphben)]·H_2O	3420	1615		475	380	725, 420		2.1056
[Cu(salen)$(H_2O)_2$]ClO_4	3380	1615	1085	475	375	520, 350	2.2967	2.1005
[Cu(saltm)$(H_2O)_2$]ClO_4	3380	1610	1090	475	375	515, 345	2.2875	2.0921
[Cu(salben)$(H_2O)_2$]ClO_4	3360	1610	1090	470	380	510, 380	2.2794	2.0862
[Cu(naphen)$(H_2O)_2$]ClO_4	3370	1610	1100	460	375	515, 345	2.2956	2.0967
[Cu(naphtm)$(H_2O)_2$]ClO_4	3370	1610	1095	465	380	505, 345	2.2276	2.0835
[Cu(naphben)$(H_2O)_2$]ClO_4	3350	1610	1080	460	375	500, 350	2.1785	2.0611

lower energy in the Schiff base complexes compared to the free ligand, reveals that the C=N group would contribute in coordination with the copper atoms via the nitrogen lone pair. The ν_{OH} (3420–3400 cm^{-1}), δ_{OH} (860–840 cm^{-1}) and ν_{C-OH} (1210–1190 cm^{-1}) bands for the ligands are not observed in the spectra of the chelates indicating the displacement of the two OH protons through the metal ion on complex formation. These changes in the IR spectra of the ligand on bonding to the metal ions occur through a covalent linkage with the oxygen atom of the phenolic group and a coordinate bond with the azomethine nitrogen lone pair. This behaviour indicates that the SB reacted with the metal ion as a dianionic tetradentate ligand. The spectra of the complexes show prominent broad absorption at 625 and 575 cm^{-1} due to chelate ring deformation [13]. The far infrared indicates that M–O and M–N absorption would occur at 460–485 cm^{-1} and 385–375 cm^{-1}, respectively. These bands are observed as new absorption peaks of the complexes that are not present originally in the spectra of free ligands. The main difference between the IR spectra of Cu(II) and Cu(III) complexes is the appearance of a broad intense band located at 1100–1090 cm^{-1} for the latter complexes which can be assigned to non-coordinated ClO_4^{-1} ($\nu_{Cl\rightarrow O}$).

The solution conductance values for the solid complexes [Cu(SB)]ClO_4 in acetone, Table I, indicate the non-coordinated nature of ClO_4^{-1} and are in agreement with the data obtained by previous author [15] for 1:1 electrolytes, whereas those of [Cu(SB)] are too low to account for any ionic character. These results confirm those of the IR spectra.

The electronic reflectance spectra of the Cu(II)–Schiff's base complexes show a group of identical asymmetric broad bands with λ_{max} at 720–725 nm, Fig. 1. The general shape and position of such bands are closely similar to those previously measured in the case of the [Cu$(O_2PCl_2)_2$] compound, where Cu(II) was assumed to be in a square planar coordination [16, 17]. Therefore, it could be safely concluded that Cu(II)–Schiff's base complexes might be present in the same geometrical coordination. Accordingly, the absorption band may be assigned to the transition

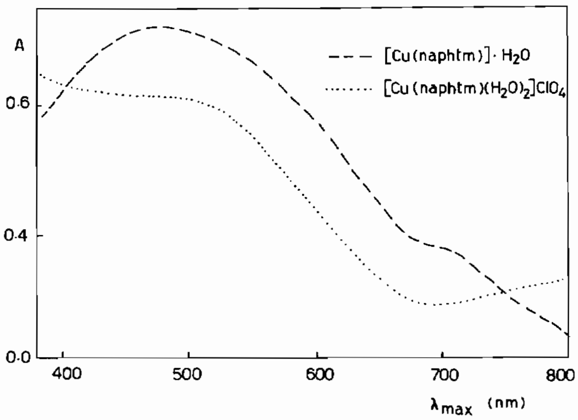


Fig. 1. Electronic reflectance spectra of Cu(II) (– – –) and Cu(III) (······) Schiff base complexes.

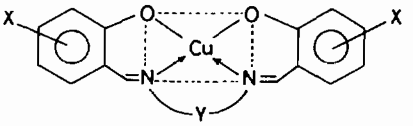
$$^2B_{1g}(^2E_g) \longrightarrow {}^2E_g(^2T_{2g})$$

within the energy level diagram of Cu(II) by considering a highly distorted arrangement (tetragonal elongation → square planar) due to the strong splitting of the Jahn-Teller unstable octahedral ground state term ^2E_g. However, it was suggested that such a highly split ^2E_g ground state and consequently an overlapping with the splitting term $^2T_{2g}$ are characteristic of square planar coordination [18].

The spectra of [Cu(SB)]ClO_4 are completely different from those of Cu(II)–Schiff's base complexes, λ_{max} = 500–520 and 350–345 nm. The shape and position of such bands, Fig. 1, are closely similar to the d^8 ion of octahedral arrangement, *i.e.* Ni(II) complexes where the ion is involved in an octahedral coordination [19]. Therefore, it is reasonable to conclude that Cu(III)–Schiff's base complexes might be present in the same geometrical coordination as octahedral Ni(II) complexes. Thus the electronic spectra of Cu(II) complexes display bands having the general characteristics of divalent copper ions (d^9), those of Cu(III) complexes exhibit the bands comparable to the spectra of divalent nickel ions (d^8).

The bulk magnetic susceptibility measurements for [Cu(SB)] and [Cu(SB)]ClO_4 are in general lower than the spin only value for d^9 and d^8 complexes respectively, Table II. This lowering of the expected moment may be due to antiferromagnetic interaction between adjacent metal atoms that may lead to the formation of some dimeric species in the solid state [20]. It appears from the data depicted in Table II that the Schiff's base with bulkier substituents tends to favour the formation of a dimer in the solid state.

Divalent copper complexes are particulary suitable to an EPR study. The x- band EPR spectrum of [Cu(naphtm)] at 300 K, Fig. 2, shows an intensive broad signal with no obvious copper hyperfine structure; the $g_{eff} = g_\perp$ values are depicted in Table II; for the Cu(II)–Schiff's base complexes under investigation, the line broadening observed in Fig. 2 and the pattern of the g values for the [Cu(SB)] complexes indicate a square planar geometry around the Cu(II) ion. On the basis of the results, the Cu(II)–Schiff's base complexes have the following structure:



The EPR spectra of powdered Cu(III)–Schiff's base complexes at room temperature 300 K and liquid nitrogen temperature 93 K exhibit a four-line isotropic signal ($g_{\parallel}$ = 2.29–2.17, $g_\perp$ = 2.10–2.06).

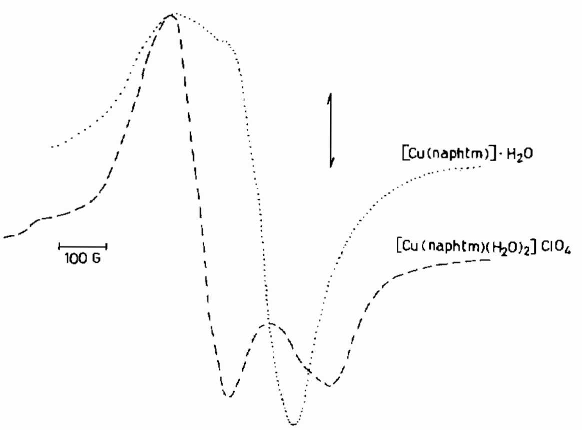
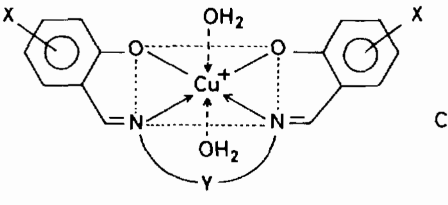


Fig. 2. X-Band EPR spectra of Cu(II) (······) and Cu(III) (– – –) Schiff base complexes at 93 °K.

The amplification and expansion show the hyperfine splitting of the band. The source of the hyperfine splitting is possibly due to the dissimilar bonds coordinated to the metal atom. As the spectrum shows no appreciable line broadening, Fig. 2, it is possible that water molecules would occupy axial positions suggesting that the Cu(III)–Schiff's base complexes would have the following spatial distribution:



The g_{eff} values have a positive contribution from the value of the free-electron, g = 2.0023, which may be due to an increase in covalent nature between ligand and metal ion [21].

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