Binuclear Complexes of Dimethylsilane and Copper(II) Salicylaldoximates

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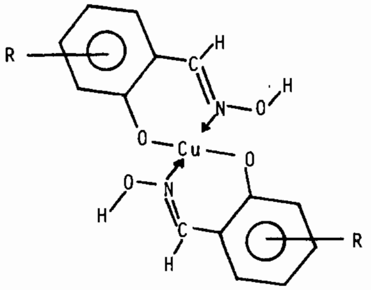
Introduction

In recent years there has been a continuing interest in the synthesis and characterization of binuclear, bimetallic complexes [1–3]. In a previous study by Biradar and Mahale [4], nickel(II) aldoximates and tin(IV) chloride were shown to form 1:1 adducts. In this continuing study bimetallic complexes of copper(II) salicylaldoximate and dimethyl silicon were prepared. The complexes were characterized by elemental analysis, conductance measurements, magnetic measurements, electronic, infrared and electron paramagnetic resonance (epr) spectra.

Experimental

All the chemicals used in this work were of reagent grade. The substituted salicylaldoximines were prepared by dissolving hydroxylamine hydrochloride (0.1 mol) in the minimum amount of water, then adding this solution to a hot ethanolic solution of the substituted salicylaldehyde (0.1 mol). The mixture was then mixed with copper(II) chloride and refluxed for 30 minutes. Upon cooling, crystals corresponding to copper(II) salicylaldoximates were obtained. These were washed repeatedly with alcohol, filtered, then dried over anhydrous calcium chloride. The following copper(II) salicylaldoximates were prepared:



Complex	R
A	H
B	5-CH_3
C	4-CH_3
D	3-CH_3
E	3-Cl

Name	
A	Bis(salicylaldoximato) copper(II)
B	Bis(5-methylsalicylaldoximato) copper(II)
C	Bis(4-methylsalicylaldoximato) copper(II)
D	Bis(3-methylsalicylaldoximato) copper(II)
E	Bis(3-chlorosalicylaldoximato) copper(II)

The binuclear complexes of dimethyl silicon and copper(II) salicylaldoximates were prepared by mixing equimolar amounts of dimethyldichlorosilane and the copper(II) salicylaldoximate in dry benzene. After digesting overnight, a precipitate formed which was then filtered, washed with dry benzene and dried under vacuum over P_2O_5. Table I correlates each copper(II) salicyadoximate (A–E) with its corresponding dimethylsilyl bimetallic analogue (I–V).

TABLE I. Analytical and Physical Data for the Binuclear Complexes[a].

Copper Complex	Binuclear Complex	Empirical Formula of Binuclear Complex	Cu %	N %	Cl %	C %	H %	Molar Cond. (ohm^{-1} cm^2 mol^{-1})
A	I	$(C_{14}H_{12}O_4N_2Cu)(CH_3)_2SiCl_2$	13.65 (13.67)	6.12 (6.03)	15.32 (15.29)	41.28 (41.33)	3.79 (3.88)	25.5
B	II	$(C_{16}H_{16}O_4N_2Cu)(CH_3)_2SiCl_2$	12.70 (12.89	5.66 (5.69)	14.33 (14.42)	43.78 (43.86)	4.40 (4.47)	21.8
C	III	$(C_{16}H_{16}O_4N_2Cu)(CH_3)_2SiCl_2$	12.96 (12.89)	5.37 (5.69)	14.48 (14.42)	43.72 (43.86)	4.52 (4.47)	18.7
D	IV	$(C_{16}H_{16}O_4N_2Cu)(CH_3)_2SiCl_2$	12.68 (12.89)	6.01 (5.69)	14.37 (14.42)	43.99 (43.86)	4.31 (4.47)	17.4
E	V	$(C_{14}H_{10}O_4N_2Cl_2Cu)(CH_3)_2SiCl_2$	11.86 (11.90)	5.30 (5.25)	13.27 (13.31)	36.20 (35.99)	2.87 (3.00)	15.3

[a] Figures in the parentheses are calculated values.

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Elemental analyses were carried out by a procedure described elsewhere [5]. Copper was determined as its pyridine thiocyanate complex. Chlorine was determined as the silver chloride precipitate, while the method of Kjeldahl was used to determine the nitrogen content of the complexes. Carbon and hydrogen were determined using standard analytical techniques.

Conductivities were measured in dimethylformamide (DMF) using an Elico-CM-82 conductivity bridge with a cell having a cell constant of 0.829 cm^{-1}. All conductivity measurements were performed at room temperature using 10^{-3} *M* solutions of complex.

Effective magnetic moments (μ_{eff}) were measured using a Gouy balance at room temperature. All measured susceptibilities were corrected for the diamagnetic contribution of each atom [6, 7].

The infrared spectra were obtained using a Carl-Zeiss UR-10 infrared spectrometer. Samples were prepared as KBr pellets. UV-visible spectra were obtained on a Perkin-Elmer, 492-5000 spectrophotometer.

Ellectron paramagnetic resonance (epr) spectra were obtained on a Varian S60-C instrument. The field strength was set at 3300 gauss with a modulation frequency of 9.489 GHz. 1,1-diphenyl-2-picrylhydrazyl (DPPH) was used as an internal standard ($g = 2.0036$).

Results and Discussion

Analytical Data

All the complexes (I–V) are colored, amorphous and insoluble in common organic solvents. The complexes were soluble in dimethylformamide (DMF) and dimethylsulfoxide (DMSO). The elemental analyses (see Table I) agree well with 1:1 (dimethylsilyl:copper(II) salicylaldoximate) stoichiometry. The molar conductivities are in the range 15–25 ohm^{-1} cm^2 mol^{-1} indicating nonelectrolytic behavior.

Magnetic Properties

The magnetic moments of simple copper(II) complexes (those lacking Cu–Cu interactions) are generally in the range 1.75–2.20 B.M. regardless of stereochemistry, and therefore it is difficult to determine the stereochemistry based on magnetic properties alone [8]. In a study by Ray and Sen [9] the tetracoordinated complexes of copper(II) were shown to exist in two groups: one group having an effective magnetic moment in the range 1.72 to 1.82 B.M., and the second having an effective magnetic moment in the range 1.90 to 2.20 B.M. The authors suggested a planar dsp^2 structure for the first group and a tetrahedral sp^3 or planar sp^2d configuration for the second. X-ray crystallographic data indicate that bis(salicylaldoximato) copper(II) [10] and the substituted bis(5-chlorosalicylaldoximato) copper(II) [11] are *trans*-planar in the solid state. If a bulky alkyl group (isopropyl or t-butyl) is substituted for the hydroxy group bonded to the azomethine nitrogen, then distorted tetrahedral structures occur [12]. The magnetic moments of salicylaldimine planar compounds are in the range 1.83–1.86 B.M. whereas four-coordinate pseudotetrahedral complexes exhibit magnetic moments in the range 1.89–1.92 B.M. [13, 14]. Based on the available X-ray crystallographic data and magnetic moments of bis(salicylaldimato) copper(II) complexes, all the bimetallic complexes (I–IV) are square planar (see Table II). Complex V has an effective magnetic moment (μ_{eff}) of 1.93 B.M.; however, the complex is formulated to be isostructural with the other four complexes (I–IV). The magnetic moment of the bis(3-chlorosalicylaldoximato) copper(II) complex is higher than the others because of the contribution of the C–Cl bond moment [15].

TABLE II. Electronic and Magnetic Data for the Binuclear Complexes.

Binuclear Complex	(μ_{eff}) B.M.	Electronic Transitions	
		$^2B_{1g} \longrightarrow {}^2A_{1g}$	$^2B_{1g} \longrightarrow {}^2E_g$
I	1.79	560	360
II	1.83	555	360
III	1.81	555	360
IV	1.87	550	362
V	1.93	560	360

Electronic Spectra

All the binuclear complexes (I–V) exhibit two low intensity bonds at 555 ± 5 nm (18,200 cm^{-1}) and 360 nm (27,400 cm^{-1}); these are assigned to the $^2B_{1g} \longrightarrow {}^2A_{1g}$ and $^2B_{1g} \longrightarrow {}^2E_g$ transitions for square planar copper(II) complexes [16, 17]. The spectra of the complexes (I–V) are comparable with the known spectra of square planar Schiff-base copper(II) complexes [13–19]. Since the spectra of the binuclear complexes do not show much deviation from those of the square planar copper complexes, the copper(II) has retained its configuration even after complexation with dimethyldichlorosilane.

Infrared Spectra

Important IR frequencies and their assignments are tabulated and available upon request from Dr. T. M. Aminabhavi.

An intense band around 1640 cm^{-1} observed in the copper salicylaldoximate complexes (A–E) is ascribed to the O–H deformation vibration of the oxime moiety. The band is shifted to 1650 cm^{-1} on formation of the binuclear complexes (I–V) thus indicating the formation of a Si–O linkage [4]. Bands at 1600 cm^{-1} due to ν(C=N) and 1320 cm^{-1} due to ν(C–O) do not shift suggesting that the stereochemistry and coordination around the copper(II) has not changed. The strong absorption bands in the range, 1225–1185 cm^{-1}, and in the range 920–910 cm^{-1} are assigned to ν(N–O) [20, 21]. One of the bands at 915 cm^{-1} in the spectra of copper salicylaldoximates splits when the complexes react with dimethyldichlorosilane and the band appears as a split peak centered at 980 cm^{-1} in the spectra of the binuclear complexes. The evidence corroborates the fact that the oxygen of the oxime moiety bands to the silicon of dimethyldichlorosilane. This bonding is further confirmed by the presence of a band at 1030 cm^{-1} assigned to ν(Si–O). The bands observed at 540 cm^{-1} and 470 cm^{-1} in the bis complexes are assigned to ν(Cu–N) and ν(Cu–O) repesctively. The bands do not shift on formation of the binuclear complexes. Finally, a strong band at 620 cm^{-1} is assigned to ν(Si–Cl) [22].

Electron Paramagnetic Resonance Spectra

The g-values (spectroscopic splitting constants) of complexes I–V, as calculated from the epr spectra, are in the range 2.261–2.266. Comparing the average g value (2.26) with values obtained from bis(salicylaldoximato) copper(II) ($g_0 = 2.11$, $g = 2.06$, $g_{11} = 2.22$) [23] and bis(salicylaldimato) copper(II) ($g_x = 2.04$, $g_y = 2.05$, $g_z = 2.20$) [24], indicates that the binuclear complex g-value may increase on coordination with dimethyldichlorosilane. The differing g-values may also be due to the temperature variation between the experimental procedures. Figure 1 gives the epr spectrum of bis(5-methylsalicylaldoximato) copper(II)·[Si(CH$_3$)$_2$Cl$_2$].

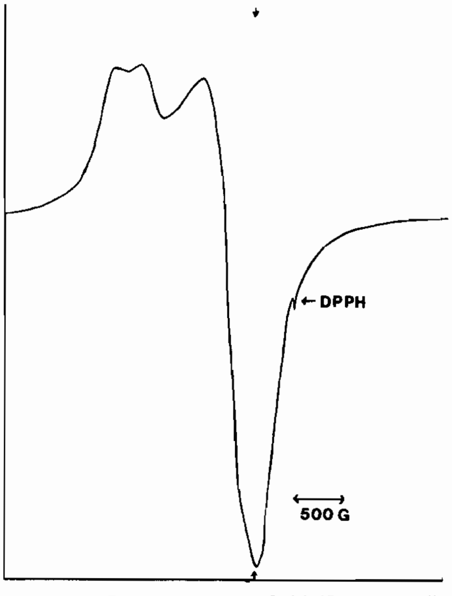
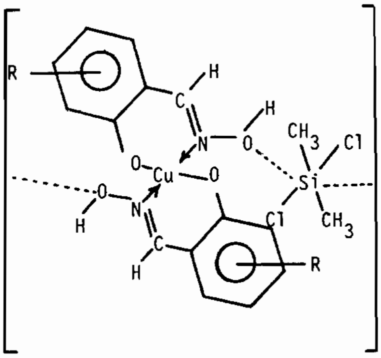


Fig. 1. EPR spectrum of bis(5-methylsalicylaldoximato) copper(II)·[Si(CH$_3$)$_2$Cl$_2$]. Field set at 3300 G. Frequency 9.489 GH$_2$. DPPH is the internal standard.

Conclusions

A few binuclear complexes have been synthesized and characterized by elemental analysis, conductivity measurements, magnetic and spectral data. The analytical data suggest that the complexes have a 1:1 (dimethylsilyl:copper(II) salicylaldoximate) stoichiometry. A silicon–oxygen bond is formed between the oxygen of the oxime moiety of the salicylaldoximine and the silicon of the dimethylsilyl moiety. The binuclear complexes are non electrolytes. On the basis of the available magnetic and spectroscopic data, the following structure is proposed:



Bis(R-salicylaldoximato) copper(II)·[Si(CH$_3$)$_2$·Cl$_2$]
where R = H, 5-CH$_3$, 4-CH$_3$, 3-CH$_3$, 3-Cl

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