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Synthesis and Characterization of Copper Complexes with Schiff Bases Derived from 2-Thiophenealdehyde and Alkylamines

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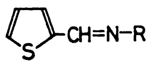
Synopsis. Copper(I) and copper(II) complexes with Schiff bases derived from 2-thiophenealdehyde and alkylamines were prepared. Probable structures of these complexes are discussed mainly on the basis of electronic and infrared spectra and magnetism.

In a recent work,[1] the present authors have synthesized a number of cobalt(II), nickel(II), and copper(II) complexes with 2-thiophenealdehyde oxime and have concluded that the oxime is bound as a unidentate ligand through the nitrogen atom to the metal ions in these complexes, the sulfur atom not being involved in the bonding with the metal ion. As an extension to the previous study, the present paper describes synthesis and characterization of copper(I) and copper(II) complexes with Schiff bases (abbreviated as tal-R, I) obtained from 2-thiophenealdehyde and alkylamines. A single copper(II) complex of this series was reported in the literature.[2]



I

Experimental

Materials. N-(2-Thenylidene)alkylamines were prepared by methods similar to that described previously for the methyl-derivative.[2]

Copper(I) Complexes. Complexes of the type Cu(tal–R)X ($R=CH_3$, X=Cl, Br; $R=n\text{-}C_3H_7$, X=I; $R=i\text{-}C_3H_7$, X=Cl, Br, I) were obtained as yellow crystals by the following two methods A and B.

Method A (for $R=CH_3$, i-C_3H_7; X=Cl, Br). A mixture of $CuX_2\cdot 2H_2O$ (0.01 mol) and 2,2-dimethoxypropane (25—30 ml) in ethanol (30 ml) was stirred at about 35 °C for 2 h. The solution was evaporated at about 40 °C nearly to dryness, and the residue was dissolved in ethanol (100 ml). To the resulting solution was added a Schiff base (0.02 mol) and heated at 70 °C for 2 h. A yellow precipitate was filtered and recrystallized from chloroform to yield pure crystals of the compound.

Method B (for $R=CH_3$, X=Cl, Br; R=i-C_3H_7, X=Cl, Br, I; R=n-C_3H_7, X=I). A mixture of CuX (0.01 mol) and a Schiff base (0.02 mol) in ethanol (100 ml) was heated at 50—60 °C for 1 h ($R=CH_3$, X=Cl, Br) or at 70—80 °C for 5—7 h ($R=CH_3$, X=I; $R=i\text{-}C_3H_7$, X=Cl, Br, I; $R=n\text{-}C_3H_7$, X=I). A yellow precipitate was filtered and recrystallized from chloroform or ethanol.

$Cu(tal\text{-}CH_3)_2I$ was obtained by the method B.

The copper(I) complexes obtained are gradually decomposed in the atmosphere.

Copper(II) Complexes. Complexes of the type $Cu(tal\text{-}R)_2X_2$, ($R=CH_3$, X=Cl, Br; $R=C_2H_5$, X=Cl) were synthesized by heating a mixture of anhydrous CuX_2 (0.01 mol) and a Schiff base (0.02 mol) in ethanol (100 ml) at 60—70 °C for 2 h. A crystalline precipitate was washed with hot ethanol several times.

TABLE 1. ANALYTICAL DATA OF COPPER(I) AND COPPER(II) COMPLEXES WITH N-(2-THENYLIDENE)ALKYLAMINES

Compound	Found, (Calcd) %			Mp °C	μ
	C	H	N		
$Cu(tal\text{-}CH_3)Cl$	31.96 (32.14	3.33 3.15	6.08 6.25)	200—202	dia
$Cu(tal\text{-}CH_3)Br$	27.05 (26.90	2.96 2.64	5.38 5.23)	195—196	dia
$Cu(tal\text{-}CH_3)_2I$	32.52 (32.69	3.46 3.20	6.25 6.36)	125—126	dia
$Cu(tal\text{-}n\text{-}C_3H_7)I$	27.68 (27.96	3.42 3.23	4.16 4.08)	133—134	dia
$Cu(tal\text{-}i\text{-}C_3H_7)Cl$	37.87 (38.09	4.59 4.40	5.54 5.55)	141—142	dia
$Cu(tal\text{-}i\text{-}C_3H_7)Br$	32.20 (32.38	3.87 3.74	4.86 4.72)	193—194	dia
$Cu(tal\text{-}i\text{-}C_3H_7)I$	27.80 (27.96	3.38 3.23	4.23 4.08)	170—171	dia
$Cu(tal\text{-}CH_3)_2Cl_2$	37.44 (37.45	3.67 3.67	7.27 7.28)	187—188	1.98
$Cu(tal\text{-}CH_3)_2Br_2$	30.68 (30.42	3.18 2.98	5.85 5.91)	153—154	1.95
$Cu(tal\text{-}C_2H_5)_2Cl_2$	40.52 (40.23	4.39 4.45	6.79 6.85)	147—148	1.96

μ: BM at room temperature.

The copper(II) compounds obtained, which are brown-yellow ($R=CH_3$, X=Cl, Br) or grey-olive ($R=C_2H_5$, X=Cl), are soluble in pyridine but almost insoluble in other common organic solvents.

Analytical data of the complexes are shown in Table 1.

Measurements. Electronic absorption spectra of the complexes in Nujol were recorded on a Shimadzu MPS-50L spectrophotometer. Infrared spectra were measured as Nujol mulls on Hitachi EPI-S2, EPI-L, and FIS-3 infrared spectrophotometers.

Magnetic measurements at room temperature were carried out by the Gouy method using $CoHg(SCN)_4$ as a calibrant.

Results and Discussion

Copper(I) Complexes. The following two types of copper(I) complexes were isolated in the present work: (1) Cu(tal-R)X and (2) $Cu(tal\text{-}CH_3)_2I$. Some of the copper(I) complexes were obtained from copper(II) salts when the reactants containing 2,2-dimethoxypropane were refluxed (method B). Otherwise, copper(II) complexes were isolated instead of the copper(I) complexes. It is probable that 2,2-dimethoxypropane undergoes decomposition during the reactions to yield some reducing species in the solution.

These copper(I) complexes are diamagnetic and show

TABLE 2. MAIN INFRARED BANDS(cm^{-1}) OF COPPER(I) COMPLEXES WITH *N*-(2-THENYLIDENE)ALKYLAMINES

Compound	ν(C=N)	$\nu(Cu\text{-}X_{br})$
Cu(tal-CH_3)Cl	1615	200
Cu(tal-CH_3)Br	1610	152
Cu(tal-CH_3)$_2$I	1605	135
Cu(tal-*i*-C_3H_7)Cl	1610	194
Cu(tal-*i*-C_3H_7)Br	1605	158
Cu(tal-*i*-C_3H_7)I	1605	130
Cu(tal-*n*-C_3H_7)I	1620	135

no d-d bands in the visible region. As seen in Table 2, ν(C=N) frequencies of the copper(I) complexes shift toward lower frequencies as compared with those (1640—1650 cm^{-1}) of the free ligands, suggesting that the ligands may be coordinated through the nitrogen atom to the copper(I) ion. Inspection of Table 2 also indicates that the halide ions function as bridging ligands, since the copper(I) complexes exhibit $\nu(Cu\text{-}X_{br})$ frequencies in the region expected for the bridging Cu–X, and no infrared bands occur in the region (around 250 cm^{-1}) expected for the Cu–S frequencies.³⁾ All these results combined seem to show that in the copper(I) complexes the ligands tal-R are coordinated as unidentate ligands through the nitrogen atom, the halide ion acting as a bridging ligand. Binuclear, cyclic trinuclear, cubane or other multinuclear structures may be proposed for these copper(I) complexes.

A similar argument as to the infrared spectra applies to Cu(tal–CH_3)$_2$I (Table 2). Thus the ligand tal-CH_3 is coordinated as a unidentate ligand through the nitrogen atom, the iodide ion acting as a bridging ligand. The compound Cu(tal–CH_3)$_2$I may probably have a structure similar to that of Cu(tal–R)X, except that an additional ligand tal–CH_3 is placed on each copper(I) ion in Cu(tal–R)X.

Copper(II) Complexes. Copper(II) complexes of the type Cu(tal–R)$_2X_2$ were obtained in the present work. One of them, Cu(tal–CH_3)$_2Cl_2$, was reported previously.²⁾ A *trans*-planar configuration was predicted for this complex chiefly from formal analogy of this complex to bis[*N*-(2-pyrrolidene)methylaminato]copper(II). The compound of the same composition obtained in the present work is not soluble enough for the conductivity measurement in nitrobenzne.

The copper(II) complexes Cu(tal–R)$_2X_2$ are paramagnetic with moments corresponding to one spin-free electron (Table 1). They exhibit ν(C=N) bands at 1620—1625 cm^{-1}, which are significantly lower than those of the free ligands (1640—1650 cm^{-1}), showing that the ligands tal-R are coordinated through the nitrogen atom to the copper(II) ion.

The electronic absorption spectrum of Cu(tal–CH_3)$_2Br_2$ is very similar to that of Cu(tal–C_2H_5)$_2Cl_2$, while the spectrum of Cu(tal–CH_3)$_2Cl_2$ differs from those of the other two complexes (Fig. 1). It is interesting to note that the spectra of Cu(tal–CH_3)$_2Br_2$ and Cu(tal–C_2H_5)$_2Cl_2$ are similar to those of Cu(tox)$_2Cl_2$ and Cu(py)$_2Cl_2$, which were previously concluded to have a multinuclear structure with six-coordinated copper(II) ions and bridging chloride ions.¹⁾⁴⁾ The notations tox and py represent 2-thiophenealdehyde oxime and pyridine, respectively. The maxima of their main d-d bands (14.6 and 14.7×10³ cm^{-1}) are close to those of Cu(tox)$_2Cl_2$ and Cu(py)$_2Cl_2$ (14.3 and 14.5×10³ cm^{-1}). It is, therefore, very likely that these two copper(II) complexes, may also have a structure similar to that of Cu(tox)$_2Cl_2$ and Cu(py)$_2Cl_2$.

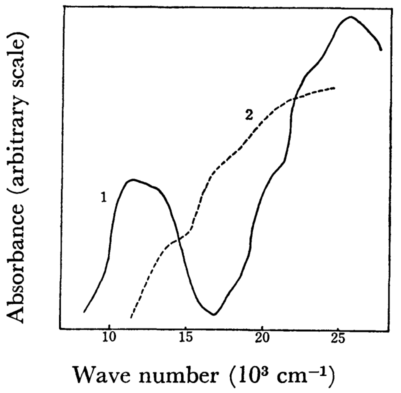


Fig. 1. Electronic absorption spectrum of copper(II) complexes in Nujol: 1, Cu(tal-CH_3)$_2Cl_2$; 2, Cu(tal-CH_3)$_2Br_2$.

The sulfur atom of the ligand is not bound with copper(II) ion in Cu(tal–CH_3)$_2Br_2$ and Cu(tal–C_2H_5)$_2$-Cl_2, since they show no charge transfer band characteristic of copper(II) complexes with sulfur-coordinating ligands. It has recently been reported that such copper(II) complexes show a characteristic band of considerably high intensity at about 23—31×10³ cm^{-1}.⁵⁾ The very low frequency of the d-d band maximum for Cu(tal-CH_3)$_2Cl_2$ requires considerable distortion of the structure and seems to be consistent with a distorted tetrahedral or a trigonal bipyramidal structure.⁶⁾⁷⁾ A very intense charge transfer band, which is characteristic of the copper(II) complexes with sulfur-coordinating ligand, occurs at 25.7×10³ cm^{-1} in the spectrum of Cu(tal–CH_3)$_2Cl_2$, suggesting that the sulfur atom as well as the nitrogen atom of the ligand tal–CH_3 is also bound with the copper(II) ion. A possibility of coordination of the chloride to copper ion or of a multinuclear structure may not be excluded.

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