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Synthesis of Copper(II) and Nickel(II) Complexes of N-(Hydroxyalkylaminoalkyl)salicylamides

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Copper(II) and nickel(II) complexes are prepared of potentially quadridentate ligands (LH_3), N-{2-(2-hydroxyethylamino)ethyl}- (seeH_3), N-{3-(2-hydroxyethylamino)propyl}- (steH_3), and N-{2-(3-hydroxypropylamino)ethyl}-salicylamide (setH_3). The nickel complexes Na[Ni(see)] and Na[Ni(set)]·1/2H_2O are diamagnetic and square-planar, in which the ligands act as a quadridentate one coordinated through secondary amino-N, and deprotonated phenolic-O, alcoholic-O, and amido-N atoms. The three copper complexes Na[CuL]·H_2O (L = see, ste, set) with a normal magnetic moment have a similar square-planar structure. In another type complexes Cu(LH)·H_2O (LH = seeH, setH) an alcohol group is not deprotonated. Two isomers are present in Cu(seeH)·H_2O: one has a normal and the other a subnormal magnetic moment. The difficulty of complex formation of steH_3 may be attributed to an unfavourably fused 6-6-5 membered chelate ring with strain.

Introduction

Transition metal complexes of salicylaldehyde Schiff bases have extensively been studied[1–5], but only a few reports have been published on complexes of salicylamides[6–11] up to the present. The authors have continuous interest in behaviour of an acid amide group toward transition metal ions, especially in complexes coordinated with deprotonated amide-N atoms. In previous papers[6–8], copper(II) complexes of tridentate N-substituted salicylamide derivatives have been studies and the study is now extended to quadridentate derivatives, N-(hydroxyalkylaminoalkyl)salicylamides, 2-HO–C_6H_4–CONH–$(CH_2)_n$–NH–$(CH_2)_m$–OH (generally abbreviated as LH_3), where n = m = 2 (seeH_3); n = 2, m = 3 (setH_3); and n = 3, m = 2 (steH_3). If these three act as a quadridentate ligand, the size of the fused chelate rings formed will be 6-5-5 for seeH_3, 6-5-6 for setH_3, and 6-6-5 for steH_3, while if they are terdentate without coordination of a terminal alcoholic-O atom, the size may be 6-5 for both seeH_3 and setH_3, and 6-6 for steH_3. The ligands are chemically similar to one another, but chelate ring sizes are different and the effect of the difference is expected to be found out in an investigation of their complexes.

Experimental

Syntheses of the Ligands

A mixture of 0.2 mol of methyl salicylate and 0.2 mol of an appropriate aminoalcohol was heated for 3 hours at 130° C. The resulting viscous liquid was used to prepare the following complexes (Table I) without isolation.

Syntheses of the Complexes

Na[Cu(see)]·H_2O

To a solution containing 0.1 mol of copper sulfate and 0.1 mol of the crude ligand in 100 ml of water was added a solution of 0.3 mol of sodium hydroxide dissolved in 50 ml of water. The violet mixture obtained was filtered and evaporated to dryness under reduced pressure at 50° C. The residue was extracted with ethanol and evaporated to dryness. The same procedure was repeated once more. The resulting solid was dissolved in a minimum amount of warm methanol and to the solution was added acetone in one-third a volume of the solution. Reddish violet crystals precipitated were recrystallized from a mixture of acetone and methanol to yield 12.5 g.

The other copper and nickel complexes of this type were prepared in a similar way. The nickel complexes were, however, recrystallized from methanol.

m-Cu(seeH)·H_2O

A warm solution of 3.3 g of Na[Cu(see)]·H_2O in 100 ml of water was adjusted to pH 7.0 by the addition of dilute sulfuric acid and filtered. After the solution had been allowed to stand at room temperature, purplish blue crystals were collected and recrystallized from water to yield 2.5 g.

TABLE I. Colours and Analytical Data for the Complexes.

Complex	Colour	Analysis, found (calcd.)				
		M %	C %	H %	N %	H_2O %
$Na[Cu(see)] \cdot H_2O$	Reddish violet	19.27	40.46	4.76	8.60	5.30
		(19.50)	(40.55)	(4.64)	(8.61)	(5.53)
$Na[Ni(see)]$	Yellowish orange	19.37			8.82	
		(19.38)			(9.26)	
d-$Cu(seeH) \cdot H_2O$	Bluish green	20.98	43.39	5.17	9.22	5.87
		(20.92)	(43.49)	(5.31)	(9.22)	(5.93)
m–$Cu(seeH) \cdot H_2O$	Purplish blue	20.92			9.28	[a]
		(20.92)			(9.22)	
$Na[Cu(ste)] \cdot H_2O$	Violet	18.64			8.42	5.00
		(18.70)			(8.25)	(5.30)
$Na[Cu(set)] \cdot H_2O$	Bluish violet	18.52			8.03	5.01
		(18.70)			(8.25)	(5.30)
$Na[Ni(set)] \cdot 1/2H_2O$	Brick-red	17.92			8.65	2.59
		(18.01)			(8.60)	(2.72)
$Cu(setH) \cdot H_2O$	Greenish blue	19.97	45.43	5.85	8.88	5.66
		(19.99)	(45.35)	(5.71)	(8.81)	(5.67)

[a] Could not be dehydrated.

d-Cu(seeH) $\cdot$ *H_2O*

The neutralized aqueous solution prepared above was evaporated to dryness and residual solid was extracted with methanol. The solution was filtered and concentrated to a small volume to precipitate bluish green crystals. The product was recrystallized from methanol to give 1.6 g.

Cu(setH) $\cdot$ *H_2O*

A solution of 3.0 g of $Na[Cu(set)] \cdot H_2O$ in 100 ml of water was adjusted to pH 7.0 with dilute sulfuric acid. After removal of the solvent under reduced pressure, the residue was extracted with 50 ml of warm methanol and to the filtered solution was added 50 ml of water while hot. The solution was allowed to stand at room temperature to form a crystalline precipitate. The product was recrystallized from a mixture of water and methanol (1 : 1) to afford 2.4 g of the greenish blue complex.

Measurements

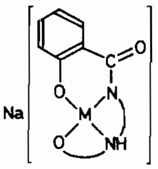
Infrared spectra were obtained with a Hitachi 215 infrared spectrophotometer by using Nujol and hexachlorobutadiene mulls. Electronic spectra of solutions were recorded on a Hitachi 124 spectrophotometer and diffuse reflectance spectra on a Hitachi 323 spectrophotometer with a diffuse reflectance attachment. Magnetic susceptibilities were measured by the Gouy method at room temperature.

Results and Discussion

Copper(II) formed two different type complexes, $Cu(LH) \cdot H_2O$ and $Na[CuL] \cdot H_2O$, depending upon synthetic conditions, especially upon the pH, while nickel(II) gave only the latter type at a high pH range (Table I). In the pH range in which copper(II) yielded the former uncharged complexes, nickel(II) precipitated only its hydroxide. This may be due to a lower affinity of nickel(II) toward these salicylamides. The ligand $steH_3$ is exceptional in that it precipitated copper hydroxide without formation of a complex of composition $Cu(LH) \cdot H_2O$ in that pH range and further that no nickel(II) complex was obtained for $steH_3$. This may be due to a different size of a fused chelate ring.

Nickel(II) Complexes

The two nickel(II) complexes $Na[Ni(see)]$ and $Na[Ni(set)] \cdot 1/2H_2O$ are diamagnetic showing their square-planar structures (Table II). The ligand field spectra are also characteristic of a square-planar nickel (II) complex[5], and the absorption maximum is at a different frequency and shifts to a lower frequency in the order of L: see(6-5-5)>set(6-5-6). This may be caused by the difference in a size of a fused chelate ring. The infrared spectra of these are very similar to those of the corresponding copper complexes which will be discussed in the next section. These nickel complexes are, therefore, assumed to have the structure shown in Formula I:



I

TABLE II. Magnetic Moments and Electronic Spectra of the Complexes.

Complex	μ_{eff} B.M.	Electronic Spectrum (in 10^3 cm^{-1}) Diffuse Reflectance	Absorption (logε)[a]
$Na[Cu(see)] \cdot H_2O$	1.81	18.0	17.7(2.17) 27.0sh[b]
$Na[Ni(see)]$	Dia.[c]	13.5sh 18.3sh 21.9	18.2sh 21.4(2.38)
d-$Cu(seeH) \cdot H_2O$	1.69	16.6 25.5sh	16.9(2.08) 25.9(2.35)
m-$Cu(seeH) \cdot H_2O$	1.84	16.9 26.5sh	16.7(2.12)[d] 26.3sh
$Na[Cu(ste)] \cdot H_2O$	1.79	15.5sh 18.5br	16.0sh 18.3br(1.98) 25.7sh
$Na[Cu(set)] \cdot H_2O$	1.81	17.5	17.5(2.15) 26.0sh
$Na[Ni(set)] \cdot 1/2H_2O$	Dia.	17.5sh 20.8	18.0sh 20.9(2.20)
$Cu(setH) \cdot H_2O$	1.83	16.1 26.0sh	17.3(2.03) 25.8(2.42)

[a] In methanol. [b] sh = shoulder, br = broad. [c] Dia. = diamagnetic. [d] In water.

Copper(II) Complexes

Na[CuL]·H$_2$O

Only this type complexes are available for all the three ligands. The infrared spectra of the complexes exhibited ν(N–H) between 3200–3250 cm^{-1} due to a coordinated secondary amino group[12], and no band assignable to ν(O–H) (alcoholic and phenolic) and ν(N–H) (amide group) was observed suggesting deprotonation of these groups. Two strong bands at *ca.* 1270 and 1110 cm^{-1} are tentatively assigned to ν(C–O) (phenolic) and ν(C–O) (alcoholic), respectively[13]. The value of the latter is at a higher frequency than that observed for $Cu(LH) \cdot H_2O$ (which will be discussed below). This indicates probably coordination of an alcoholic-O atom with deprotonation (Formula I). Other bands are difficult to assign owing to the complicated spectral pattern.

The magnetic moments of these are normal and the electronic spectra in the solid exhibited a maximum in the d–d region which shifts in the order of L: ste(6-6-5) > see(6-5-5) > set(6-5-6) (Table II). It is interesting that the shape of the spectrum of $Na[Cu(ste)] \cdot H_2O$ is appreciably different from those of the remaining two in that the former has an additional shoulder at *ca.* 15.5 × 10^3 cm^{-1} and it is much broader. This is true for the absorption spectra in methanol (Fig. 1). The different spectral pattern is considered to be due to the distortion of a ligand field which is caused by strain of a fused chelate ring[14], since an acid amide group strongly prefers a rigid planar structure, so that such a strain exists for a fused 6-6-5 membered chelate ring. The origin of the fact that no nickel(II) complex could be obtained with $steH_3$ may be primarily attributed to the strain.

Cu(LH)·H$_2$O

It is interesting that two isomers of $Cu(seeH) \cdot H_2O$ have been obtained depending only upon solvent of recrystallization and they are mutually interconvertible. A bluish green isomer with a subnormal magnetic moment formed from methanol and a purplish blue isomer with a normal magnetic moment from water (Tables I and II). The former is hereafter denoted as *d*-Cu(seeH)·H$_2$O and the latter as *m*-Cu(seeH)·H$_2$O. The water of crystallization of the *m*-isomer could not be dehydrated without decomposition, while that of the *d*-isomer was dehydrated easily.

Both the absorption and diffuse reflectance spectra of the *d*-isomer show a pronounced absorption in the near ultraviolet region (Figure 2). A similar band is sometimes considered to be indicative of Cu–Cu inter-

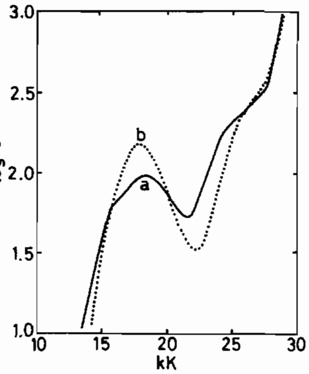


Figure 1. Absorption spectra of a: $Na[Cu(ste)] \cdot H_2O$ and b: $Na[Cu(see)] \cdot H_2O$ in methanol.

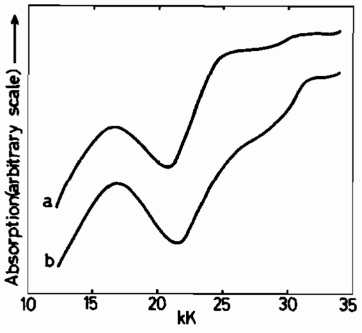
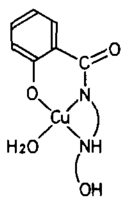


Figure 2. Diffuse reflectance spectra of a: *d*-Cu(seeH)·H$_2$O and b: *m*-Cu(seeH)·H$_2$O.

action through a oxygen atom of sp^2 hybridization.[15] Through the oxygen atom antiferromagnetic interaction can occur and a magnetic moment results in a subnormal value.[16]

The bands ν(N–H) of the *m*- and *d*-isomers were observed at 3277 and 3225 cm^{-1}, respectively, as a sharp peak. Since the back ground between 1800–3600 cm^{-1} are very broad, other bands are difficult to assign. The *m*-isomer showed ν(C–O) (alcoholic) at 1050 cm^{-1} in the region typical for a free primary alcohol[17], whereas the *d*-isomer exhibited it at 1014 cm^{-1} suggesting its coordination to copper[18] or formation of hydrogen bonding. For the *d*-isomer ν(C–O) (phenolic) was observed at 1232 cm^{-1} and that of the *m*-isomer at 1261 cm^{-1}, the position of which is close to that (1267 cm^{-1}) of Na[Cu(see)]·H_2O in which the phenolic-O atom is terminal (Formula I). The lower frequency ν(C–O) of the *d*-isomer may indicate that the oxygen atom serves as a bridging atom between two copper ions. These facts suggest that the *d*-Cu(seeH)·H_2O is dimeric and the *m*-isomer monomeric, and the proposed structures are illustrated below, where apical coordination of an alcoholic-O atom might be occur (Formulae II and III).



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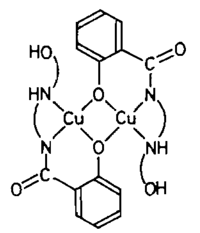

III

No isomerism was observed for Cu(setH)·H_2O and this complex was dehydrated easily. The infrared spectrum exhibited ν(C–O) (alcoholic) at 1060 and ν(C–O) (phenolic) at 1236 cm^{-1}, and the position of the latter implies that the oxygen atom acts as a bridging center between copper ions. The two bands observed at 1663 and 3425 cm^{-1} for Cu(setH)·H_2O, which disappeared upon dehydration, may be assigned to an H_2O group[19] and a strong band at 3130 cm^{-1} may be ν(N–H) or/and ν(O–H).

The magnetic moment of Cu(setH)·H_2O is normal and the diffuse reflectance spectrum similar to that of *m*-Cu(seeH)·H_2O, implying that there is no Cu–Cu interaction. The absorption spectrum in H_2O is nearly identical to that of *m*-Cu(seeH)·H_2O, while that in methanol is very similar to that of *d*-Cu(seeH)·H_2O. The structures of the two in the same solvent may be similar. The spectral change of Cu(setH)·H_2O upon dissolution in methanol may suggest a change of hybridization of the bridging phenolic-O atom from sp^3 (in the solid) to sp^2 (in methanol). It has been shown that if the oxygen atom bridging between copper ions is in an sp^3 hybridization, there is roughly no appreciable interaction which reduces a room temperature magnetic moment and produces a marked absorption in the near ultraviolet region[16,20]. Thus the structure in the solid state may be a dimeric one bridged by an sp^3 oxygen atom (Formula III), but it should be confirmed by a X-ray analysis.

No successful isolation of the corresponding complex of $steH_3$ may be due to instability of the strained 6-6 membered chelate ring with an amide group as was mentioned above. Attempts to prepare complexes of composition $Cu_3L_2{}^2$ were unsuccessful so far.

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