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Complexes of Copper(II) with Schiff Bases Formed from Salicylaldehydes and N-Substituted Ethylenediamines

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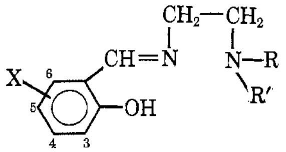
Schiff bases, derived from ring-substituted salicylaldehydes and N-substituted ethylenediamines, form two series of compounds with copper(II), *i.e.*, [X–SALen–N(R)R′]$_2$Cu^{II} (I) and [X–SALen–N(R)R′]CuY (II), where Y = Cl, Br, CH_3COO. The complexes of type I have distorted *trans*-planar configurations, when R = H or CH_3, R′ = C_6H_5, and R = R′ = C_2H_5 or C_6H_5. When R = H or CH_3 and R′ = CH_3, however, they probably have pentacoordinate configurations. In complexes with formula II only one Schiff base, which acts as a tridentate ligand, is linked to the copper(II), while the fourth coordination position is occupied by the halogen or the acetate group. The chloro complexes are also formed by dechlorination of solvents like $CHCl_3$ or CCl_4.

Introduction

Nickel(II) and cobalt(II) complexes with Schiff bases, formed from salicylaldehydes and N-substituted ethylenediamines of the general formula [X–SALen–N(R)R′]



have been described in previous papers.$^{1-3}$ According to the steric requirements and the electronic properties of R, R′, and X, bases of this type behave in a bidentate or tridentate manner. In the bidentate case tetracoordinate complexes are formed (planar with Ni(II) and tetrahedral with Co(II)), while in the tridentate case the complexes are octahedral. In particular cases, pentacoordinate complexes are formed in which one base functions in a bidentate and the other in a tridentate manner.^{2}

Copper(II) complexes of these ligands are reported in this paper. Two types of complexes have been obtained and characterized: one has the general formula [X–SALen–N(R)R′]$_2$Cu^{II} (I), and the other is of the type [X–SALen–N(R)R′]CuY (II), with Y = Cl, Br, CH_3COO. Their structure has been elucidated by recording visible absorption and reflectance spectra and measuring the dipole moments of some characteristic compounds.

Experimental Section

Preparation of the Compounds.—The [X–SALen–N(R)R′]$_2$Cu^{II} (I) complexes, listed in Table I, have been prepared by heating the complexes bis(X-salicylaldehyde)copper(II) (10 mmoles) dissolved together with the appropriate N-substituted ethylenediamines (22 mmoles) in ethanol (*ca.* 50 ml) under reflux, until precipitation took place. In some cases a little water was added to facilitate the precipitation. After cooling the reaction mixture, the precipitate was filtered off and recrystallized from benzene–petroleum ether (bp 40–70°) solution. The compounds of general formula II, (X–SALen–N(R)R′]CuCl, with the exception of R = CH_3 or C_6H_5 and R′ = C_6H_5 derivatives, have been prepared in two ways: (1) Work was performed as above but in chlorine-containing solvents such as $CHCl_3$ or CCl_4 rather than in ethanol. After cooling under reflux for 0.5 hr, the solution was concentrated until precipitation began. In some cases cyclohexane or petroleum ether was added to assist precipitation. After cooling, the precipitate was filtered and recrystallized from methanol or ethanol. The same result is obtained by heating and recrystallizing the corresponding complexes of series I in $CHCl_3$ or CCl_4. (2) The Schiff bases were mixed with an alcoholic solution, containing an equimolecular proportion of $CuCl_2$. Crystals were obtained by evaporation of the solvents, filtered off, and recrystallized as above. All attempts to prepare complexes of this type in which R = CH_3 or C_6H_5 and R′ = C_6H_5 were unsuccessful. The complexes [SALen–N(H)CH_3]CuBr and [SALen–N(H)CH_3]CuCH_3COO were obtained by the second method using $CuBr_2$ and Cu($CH_3COO)_2$, respectively. The analytical data for the most typical of these compounds are summarized in Table I.

Spectrophotometric Measurements.—The absorption spectra were recorded with a Beckman DK2 spectrophotometer. The solvents were purified by the standard procedures used for spectrophotometric measurements. The reflectance spectra were recorded using the standard Beckman reflectance attachment and magnesium oxide as a reference. Concentrations of the solutions were in the range 0.01–0.02 *M*.

Dielectric Polarization Measurements.—The apparatus and the procedures used have been previously described.^{4} The molar refraction for the sodium D line, R_D, of the complexes was calculated by adding the proper values of bond refractions to the measured molar refraction of the bis(N-methylsalicylaldimino)nickel(II) complex.^{5} Values of the orientation polarization, P_o, were calculated by assuming a value of 20% R_D for the atom polarization.

Results and Discussion

Series I: [X–SALen–N(R)R′]$_2$Cu^{II}.—The compounds in which R = CH_3 or C_6H_5 and R′ = C_6H_5 give reflectance spectra, with a single absorption band at *ca.* 15,000 cm^{-1}, which are similar to those of the distorted *trans*-planar bis(N-methylsalicylaldiminato)-copper(II) complexes.^{4} The corresponding ligands also act in a bidentate manner with Ni(II)^1 and Co(II),^{3}

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(1) L. Sacconi, P. Nannelli, and U. Campigli, *Inorg. Chem.*, **4**, 818 (1965).

(2) L. Sacconi, P. Nannelli, N. Nardi, and U. Campigli, *ibid.*, **4**, 943 (1965).

(3) L. Sacconi, M. Ciampolini, and G. P. Speroni, *ibid.*, **4**, 1116 (1965).

(4) L. Sacconi, M. Ciampolini, F. Maggio, and F. P. Cavasino, *J. Inorg. Nucl. Chem.*, **19**, 73 (1961).

(5) L. Sacconi, P. Paoletti, and G. Del Re, *J. Am. Chem. Soc.*, **79**, 4062 (1957).

TABLE I

SUMMARY OF PHYSICAL AND ANALYTICAL DATA FOR SOME [X–SALen–N(R)R']$_2$Cu^{II} AND [X–SALen–N(R)R']CuY COMPLEXES

		Calcd %			Found %		
	Mp, °C	Cu	N	Y	Cu	N	Y
[5-Cl–SALen–N(H)CH$_3$]$_2$Cu	111–115	13.05	11.49		12.98	11.25	
[SALen–N(CH$_3$)$_2$]$_2$Cu	156–157	14.25	12.56		14.34	12.82	
[5-Cl–SALen–N(C$_2$H$_5$)$_2$]$_2$Cu	83–84	11.13	9.82		11.01	9.86	
[SALen–N(H)C$_6$H$_5$]$_2$Cu	181–182	11.73	10.33		11.46	10.47	
[SALen–N(CH$_3$)C$_6$H$_5$]$_2$Cu	134–135	11.15	9.83		11.02	9.81	
[SALen–N(C$_6$H$_5$)$_2$]$_2$Cu	208–210	9.17	8.07		9.34	7.99	
[SALen–N(H)CH$_3$]CuCl	249–252	23.02	10.13	12.86	23.10	10.03	12.81
[SALen–N(CH$_3$)$_2$]CuCl	165–168	21.90	9.66	12.24	22.32	9.60	12.17
[SALen–N(C$_2$H$_5$)$_2$]CuCl	186–188	19.99	8.80	11.08	20.10	8.69	10.94
[SALen–N(H)C$_6$H$_5$]CuCl	236–239	18.79	8.28	10.40	18.88	8.41	10.50
[SALen–N(H)CH$_3$]CuBr	224–226	19.20	8.75	25.01	19.09	8.84	25.01
[SALen–N(H)CH$_3$]Cu(CH$_3$COO)[a]	215–218	21.18	9.34		21.00	9.36	

[a] Carbon and hydrogen analysis: Calcd: C, 48.10; H, 5.34. Found: C, 48.83; H, 5.58.

as the β nitrogen has a very small donor power because of the electronic and steric properties of the phenyl group. The dipole moment in benzene solution is 2.20 D. (see Table II) for both of the copper complexes.

TABLE II

DIELECTRIC POLARIZATION DATA FOR SOME [SALen–N(R)R']$_2$Cu^{II} COMPLEXES IN BENZENE AT 25°

R	R'	$P_{2\infty}$, cc	R_D, cc	P_o, cc	μ, D.
CH$_3$	CH$_3$	343	128	189	3.03
CH$_3$	C$_6$H$_5$	300	165	102	2.23
C$_6$H$_5$	C$_6$H$_5$	346	204	100	2.20

This value is high with respect to the values of 1.20 D. for the analogous Ni(II) complexes[1] and of *ca.* 1.70 D. for the bis(N-*n*-alkylsalicylaldiminato)copper(II)[6] complexes. For the latter compounds it has been suggested[4] that the molecules of the complexes undergo a deformation in solution. The X-ray structure has recently shown that in the solid state the bis(N-ethylsalicylaldiminato)copper(II) complex has a structure which is intermediate between *trans* planar and tetrahedral.[7] The dipole moment of 2.20 D. probably only indicates a greater distortion from the *trans*-planar configuration. The relatively high intensity of the absorption band at *ca.* 16,500 cm^{-1} for these two complexes (ϵ 120 and 150 in CHCl$_3$) can be interpreted as due to this distortion.[8] The absorption spectra of [SALen–N(H)C$_6$H$_5$]$_2$Cu^{II} and [5-Cl–SALen–N(C$_2$H$_5$)$_2$]$_2$Cu^{II} are also indicative of a *trans*-planar configuration. It is interesting to note that the ligand 5-Cl–SALen–N(C$_2$H$_5$)$_2$ gives rise to pentacoordinate structures with Ni(II)[2] and Co(II)[3] because the steric hindrance, due to the two ethyl groups linked to the β nitrogen, opposes six-coordination.

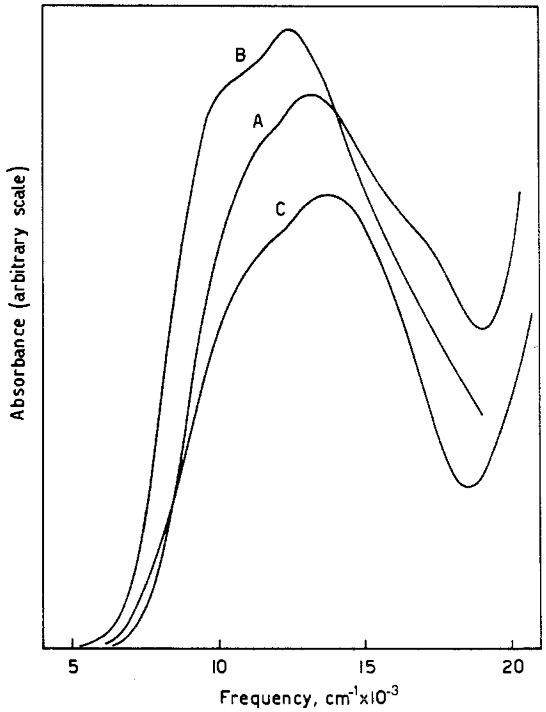

Figure 1.—Diffuse reflectance spectra of (A) [SALen–N(CH$_3$)$_2$]$_2$Cu^{II}, (B) bis(salicylidene-γ-iminopropyl)aminecopper(II), (C) bis(N-methylsalicylaldiminato)copper(II).

The reflectance spectra of [5-Cl–SALen–N(H)CH$_3$]$_2$Cu^{II} and [SALen–N(CH$_3$)$_2$]$_2$Cu^{II} are different from those of the preceding compounds. The absorption maximum is displaced to lower energies from *ca.* 16,500 to 13,300 cm^{-1}. These spectra show strong similarities (Figure 1) to the spectrum of the bis(N-methylsalicylaldiminato)copper(II) which exhibits a trigonal-bipyramidal configuration[9] when it is guest in the lattice of the zinc analog and to the spectrum of the bis(salicylidene-γ-iminopropyl)aminecopper(II) complex which has a distorted trigonal-bipyramidal configuration.[10] The infrared spectrum of the –N(H)CH$_3$ complex shows two bands in the region of N–H stretching frequencies: one weak and sharp at 3300 cm^{-1} and the other medium and broad at 3125 cm^{-1}. The frequency of the first band and its features are characteristic of the N–H stretching of a secondary amine completely free of further bonds. The large shift of the second band cannot be explained by assuming only a Cu–NH coordination bond.

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(6) L. Sacconi, M. Ciampolini, F. Maggio, and G. Del Re, *J. Am. Chem. Soc.*, **82**, 815 (1960).

(7) C. Panattoni, private communication.

(8) R. L. Belford and T. S. Piper, *Mol. Phys.*, **5**, 251 (1962).

(9) L. Sacconi, M. Ciampolini, and G. P. Speroni, *J. Am. Chem. Soc.*, **87**, 3102 (1965).

(10) L. Sacconi and I. Bertini, *ibid.*, in press.

Furthermore, the shape of this band is indicative of a hydrogen bond. The difference between the two N–H groups present in the molecule might be explained by the fact that only one β nitrogen is linked to the copper atom so that the complex has a pentacoordinate structure of the type of $[5\text{-Cl-SALen-N}(C_2H_5)_2]_2\text{-}Ni^{II}$.[11] In this case, the hydrogen bond would be intramolecular and involve the oxygen of the other coordinated salicylaldimine group. The acceptance of a pentacoordinate structure could also account for the shift of the absorption band in the reflectance spectrum to a lower frequency. It is known for instance that adding ammonia to a $Cu(NH_3)_4{}^{2+}$ solution to form $Cu(NH_3)_5{}^{2+}$ causes a lowering of the frequency of the absorption maximum.[12] The possibility of an octahedral structure of the type of the analogous Ni(II) and Co(II) complexes seems less probable. In fact the octahedral coordination could not give a reasonable explanation of the splitting of the N–H stretching bands of the $N(H)CH_3$ compound. The absorption spectra of both the $N(H)CH_3$ and $N(CH_3)_2$ complexes in benzene solution indicate the existence of an equilibrium between the *trans*-planar and probably pentacoordinate forms, the proportion in the planar form being very high at room temperature. The rather high value of 3.03 D. at 20° for the dipole moment of $[\text{SALen-N}(CH_3)_2]_2Cu^{II}$ in benzene solution supports this hypothesis.

Series II: [SALen-N(R)R′]CuY (Y = Cl, Br, CH_3COO).—All of the ligands of the complexes studied here, except those with R = CH_3 or C_6H_5 and R′ = C_6H_5, tend to behave as tridentate. This is because the electron-releasing effect of the groups R, R′ confers an increased donor strength to the β nitrogen. The donor capacity of the β nitrogen increases depending on the substituents R, R′ in the following order:[1,2] $N(H)C_6H_5$, $N(C_2H_5)_2$, $N(CH_3)_2$, $N(H)CH_3$. The tendency of these ligands to function as tridentate, together with the tendency of Cu(II) to give square-planar complexes, ensures that, if the preparation of the complexes of series I is conducted in the presence of Cl^- ions, tetracoordinate planar complexes of the general formula [SALen-N(R)R′]CuCl are formed. In these complexes the copper atom is coordinated to only one Schiff base, which behaves tridentately, and the fourth coordination position is occupied by the halogen. These compounds are obtained by allowing $CuCl_2$ to react with the respective Schiff base in alcohol. Moreover, even in the absence of Cl^- ions, the same products are obtained by mixing the appropriate amines with the bis(salicylaldehydate)copper(II) complex in chlorine-containing solvents such as $CHCl_3$ or CCl_4.

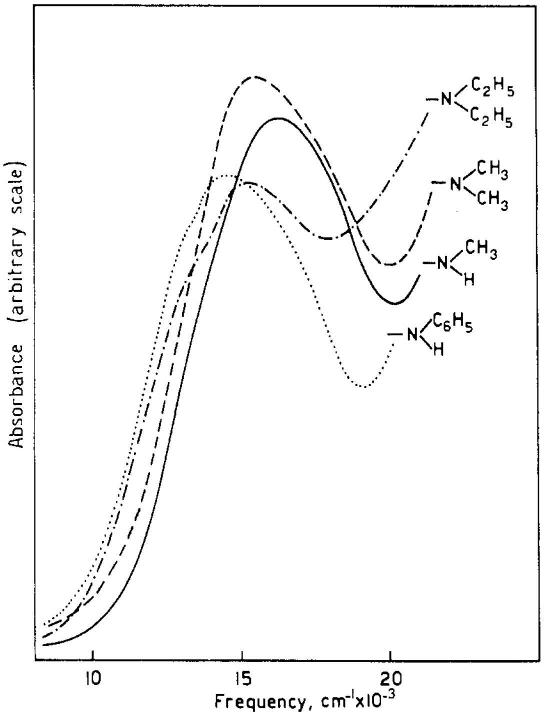

Figure 2.—Diffuse reflectance spectra of some [SALen-N(R)R′]-CuCl complexes.

Finally, if complexes of series I are dissolved in $CHCl_3$ or CCl_4 and are heated at reflux for a short time, the chlorine-containing products of formula II are again obtained. The formation of the complexes therefore involves dehalogenation of the solvents. Attempts to prepare complexes of series II with ligands which behave as bidentates were unsuccessful. By reaction of $CuBr_2$ or $Cu(CH_3COO)_2$ with Schiff bases, compounds in which the fourth coordination position is occupied by a bromine or acetate ion are obtained. The reflectance spectra of the chloro complexes indicate that they are square-planar. It should be noted (Figure 2) that the absorption band is displaced toward lower energies with the increasing substitution on the β nitrogen, as a function of the nature of the R and R′ substituents according to the order given above. This order for the spectrochemical series is in accordance with that found by Meek[13] for octahedral complexes of Ni(II) with N-alkyl-substituted ethylenediamines. It is also in accordance with the series of the donor strength of the amine toward the acceptor with respect to bis(benzoylhydrazone)nickel(II).[14]

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(11) L. Sacconi, P. L. Orioli, and M. Di Vaira, *J. Am. Chem. Soc.*, **87**, 2059 (1965).

(12) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press Inc., New York, N. Y., 1952, p 125.

(13) S. F. Pavkovic and D. W. Meek, *Inorg. Chem.*, **4**, 20 (1965).

(14) L. Sacconi, G. Lombardo, and P. Paoletti, *J. Chem. Soc.*, 848 (1958).