Alkoxy and Phenoxy Bridged Dimeric Copper(II) Complexes with Salicylaldimine Ligands

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(Received December 13, 1971)

The tridentate Schiff base *N*-3-hydroxy-*n*-propylsalicylaldimine can be coordinated with copper(II) to form three kinds of dimeric oxy-bridged antiferromagnetic complexes (metal: ligand ratio—1: 1), as well as the normal monomeric complex. In one of the dimeric complexes pairs of copper atoms are bridged by pairs of the deprotonated alcoholic oxygens of the ligands. The others have an extra ligand X (X=-Cl, $-ONO_2$) per copper atom, the metals are bridged by phenolic oxygens, the alcoholic hydroxyls are not deprotonated, but are either coordinated (if X=Cl) to five-coordinated copper atoms in discrete dimer molecules, or participate in intermolecular hydrogen bonding linking individual dimeric molecules in which the copper atoms are four-coordinated. In the presence of pyridine, ammonia, or mild inorganic base, a rearrangement reaction can be induced, resulting in conversion of the phenolic-bridged (five-coordinated copper) dimer into the related alcoholic-bridged (four-coordinated copper) dimer. This behaviour is not followed by *N*-hydroxyethylsalicylaldimine which appears to form only one kind of copper complex [Cu(Lig)X] (X=-Cl, $-ONO_2$); in which the metal atoms are essentially planar and do not take part in strong antiferromagnetic interactions.

Yamada *et al.*[1a)] and Kato *et al.*[1b)] found that 3-hydroxy-*n*-propylsalicylaldimine can be used to form dimeric copper(II) complexes. Two possible structures were recognised for these complexes, I and II, of which I was preferred by the latter authors.[1b)]

Contemporary and subsequent work on salicylaldimines without alcoholic side-chains showed that binuclear and trinuclear complexes can be formed very readily using the ability of phenolic oxygens to become three-coordinated.[2)] Bidentate salicylaldimines were used to form dimers, III(a),[3)] III(b),[4)] and tetradentate salicylaldimines to form bi- and tri-nuclear metal complexes IV[5)] and V.[6)] The structures were assigned on the basis of synthetic, magnetic, ultraviolet-visible and infrared data. In particular a shift of about 20 cm^{-1} in the infrared absorption near 1540 cm^{-1} tentatively assigned to the phenolic C–O stretch,[3,4)] was found to be characteristic of the formation of complexes III—V from monomeric complexes. This infrared shift can be taken as characteristic of bridging *via* the phenolic oxygens of salicylaldimines, and if bridging occurs without involving the phenolic oxygens, as in structure I, no such shift is expected.

Single crystal X-ray studies have since confirmed these structures for two binuclear copper(II) complexes of type III,[7)] and three of type IV,[7,8)] and two mixed metal complexes of type V, one with metal atoms (Cu–Na–Cu) in a flattened isosceles triangular array[9)] and one with the metals (Cu–Mn–Cu) in a straight line.[10)] A complex of type III, but with the substituent R-groups 3-hydroxy-*n*-propyl, has also been subjected to X-ray study, and found to have phenolic oxygen bridged structure, with the alcoholic hydroxyl groups coordinated to the copper atoms VI.[11)]

These results appear to indicate a preference for bridging *via* phenolic oxygens in polynuclear salicylaldimines, even if alocholic oxygens are available in the ligand. However, the nonexistence of alcoholic oxygen bridges does not necessarily follow. It is now of interest to determine whether such bridging occurs, and, if it does, under what conditions. We report here an investigation of dimeric complexes with –R–OH substituted salicylaldimines, where R=$-CH_2-CH_2-$ and $-CH_2-CH_2-CH_2-$.

Regardless of whether alocholic or phenolic oxygen bridging is preferred in complex I (or II), this complex is closely related to complex VI. Complex VI, $[CuC_{10}H_{11}NO_2\cdot HCl]_2$ may be regarded as a hydrochloride addition compound of complex I (or II) $[CuC_{10}H_{11}NO_2]_2$, and it should therefore be possible to find conditions for the conversion of the less stable of the two complexes to the more stable, and perhaps also for the reverse reaction. This aspect is also investigated.

Experimental

The parent monomeric complexes were prepared in the standard way[12)] by warming the copper(II) complex of the salicylaldehyde or 5-chlorosalicylaldehyde with the appro-

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Table 1. Microanalytical data

Complex	Empirical formula	Calcd (%)			Found (%)		
		C	H	N	C	H	N
[Cu(EtOH·ClSal)NO$_3$]	CuClC$_9$H$_9$N$_2$O$_5$	33.4	2.8	8.6	33.5	2.9	8.2
[Cu(EtOH·ClSal)Cl]	CuCl$_2$C$_9$H$_9$NO$_5$	36.3	3.0	4.7	36.1	3.0	4.5
[Cu(EtOH·Sal)NO$_3$]	CuC$_9$H$_{10}$N$_2$O$_5$	37.3	3.5	9.7	37.0	3.5	9.5
[Cu(EtOH·Sal)Cl]	CuClC$_9$H$_{10}$NO$_5$	41.1	4.0	5.3	41.0	4.3	5.2
[Cu(3-PrOH·Sal)NO$_3$]$_2$	Cu$_2$C$_{20}$H$_{24}$N$_4$O$_{10}$	39.5	4.0	9.2	39.5	4.0	9.2
[Cu(3-PrOH·Sal)Cl]$_2$	Cu$_2$C$_{20}$H$_{24}$N$_2$O$_4$Cl$_2$	43.3	4.4	5.1	43.4	4.5	5.0
[Cu(3-PrO·Sal)]$_2$	Cu$_2$C$_{20}$H$_{22}$N$_2$O$_4$	49.9	4.6		50.0	4.6	

priate amine, and recrystallising from chloroform–ethanol. Cu(PrOH·Sal)$_2$ formed as an oil, and a solid was obtained only after standing.

The copper chloride or nitrate adducts were prepared by the standard method for complexes of type III,[3,4] *viz.* by the reaction of the appropriate copper(II) salicylaldimine complex with copper(II) chloride or copper(II) nitrate in methanol.

For brevity, we denote 3-hydroxy-*n*-propylsalicylaldimine and 2-hydroxyethyl-5-chlorosalicylaldimine as 3-PrOH·Sal and EtOH·ClSal respectively. Deprotonation of the alcoholic hydroxyl group is indicated by omission of "H" from the abbreviation.

Analytical data are listed in Table 1.

Infrared Spectra. IR spectra were determined on nujol and hexachlorobutadiene mulls of the compounds. Both a Unicam SP200 and a Perkin-Elmer 221 spectrophotometer were used to obtain the spectra. The spectrum of a polystyrene film was recorded on the same chart as a reference to allow accurate measurements of the bands.

Electronic Spectra. Electronic spectra were determined on the solid compounds using a Unicam SP200 spectrophotometer.

Electron Spin Resonance Measurements. ESR measurements were made on a Varian V4502-15 ESR spectrometer at the Physics and Engineering Laboratory of the D.S.I.R., Wellington. We are grateful to Mr. M. Collins for access to this apparatus.

Magnetic Susceptibility Measurements.[14] Magnetic susceptibility measurements were made as previously described,[3,5] in the range 100—400°K on a cryostat-controlled Gouy balance apparatus. The agreement of the observed magnetic susceptibility values, per gram atom of copper, χ_M (corrected for diamagnetism using Pascal's constants[13] with the Bleaney-Bowers Eq. (1) was tested where appropriate, and the value of the singlet-triplet separation, $-2J$, and of the Landé splitting factor, g, obtained from the best fit.[2-5,14]

$$\chi_M = \frac{Ng^2\beta^2}{3kT}\left(1+\frac{1}{3}e^{-2J/kT}\right)^{-1} + N\alpha \qquad (1)$$

Here the symbols have their usual meanings. $N\alpha$ was assumed to have the value 6×10^{-5} c.g.s.e.m.u.[2-5,14,15] Where Eq. (1) was not satisfied, the data was compared with Eq. (2) for trinuclear complexes,[16] as well as models for infinite lattice interactions

$$\chi_M = \frac{Ng^2\beta^2}{12kT}\cdot(e^{-A+B}+e^{-A-B}+10e^{A})/$$
$$(e^{-A+B}+e^{-A-B}+2e^{A}) + N\alpha \qquad (2)$$

where $A=(J_{12}+J_{23}+J_{13})/kT$, $B=(J_{12}{}^2+J_{23}{}^2+J_{13}{}^2-J_{12}J_{23}-J_{12}J_{13}-J_{23}J_{13})^{1/2}/kT$ and the J_{ij} are the exchange integrals between the three pairs of copper atoms.

Magnetic moments (in Bohr Magnetons) were calculated using the relation

$$\mu_{\text{eff}} = \sqrt{8.0(\chi_M - N\alpha)T}$$

In the absence of magnetic exchange interactions, g may be estimated from the relation $\mu_{\text{eff}}=g\sqrt{S(S+1)}$.

X-Ray Powder Diffraction Patterns. X-Ray diffraction paterns were recorded using a powder diffractometer with a Phillips Wide Range Goniometer PW1050/25.

Density Measurements. Densities were measured at 20°C by suspending crystals in solutions of equal density. The suspending solutions comprised acetone–carbon tetrachloride–bromoform mixtures and their densities were measured with a set of hydrometers calibrated to 0.0005 g cm^{-3}. The observed crystal densities are considered accurate and reproducible to ±0.005 g cm^{-3}.

Results and Discussion

Magnetic Properties. Kato *et al.*[1] prepared complexes I (or II) [Cu(3-PrO·Sal)]$_2$ with four different ring substituents X, but found the properties to be so similar within the series that the complex with X=H can be taken as a representative compound when making comparisons with compounds belonging to different groups. In fact, variation of the ring substituent X in [Cu(3-PrO·Sal)]$_2$ has rather less effect on the properties than similar variation of X in complexes of type III[2,5-7] or IV.[2-6,17] This suggests that [Cu(3-PrO·Sal)]$_2$ may belong to a different category than III and IV, in agreement with the postulate for structure I for the complex.[1b]

Table 2 lists the magnetic properties of the various complexes with 3-PrOH·Sal, EtOH·Sal, and EtOH·ClSal. The complexes with 3-PrOH·Sal behave as binuclear antiferromagnets and Fig. 1 compares the experimental data with those calculated from Eq. (1). The values of J and g required to fit the data are listed in Table 3. The data indicate a much stronger interaction in [Cu(3-PrO·Sal)]$_2$ than in any of the others, again suggesting that complexes of the types [Cu·

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TABLE 2. MAGNETIC DATA FOR DIMERIC COPPER(II) COMPLEXES

Temperature T in K; χ_M in c.g.s.e.m.u.; μ_{eff} in B.M.

[Cu(3-PrOH·Sal)NO$_3$]$_2$												
T	114.0	143.0	175.0	204.5	233.0	308.5	345.5					
$10^6\chi_M$	290	456	602	668	732	755	735					
μ_{eff}	0.47	0.58	0.87	1.01	1.11	1.31	1.36					
[Cu(3-PrOH·Sal)Cl]$_2$												
T	138.0	166.5	191.5	227.0	264.0	286.0	306.5	348.5	387.5			
$10^6\chi_M$	144	211	239	340	420	465	492	522	530			
μ_{eff}	0.30	0.46	0.53	0.72	0.87	0.96	1.03	1.13	1.20			
[Cu(3-PrO·Sal)]$_2$[a]												
T	288	303										
$10^6\chi_M$	91	101										
μ_{eff}	0.27	0.31										
[Cu(EtOH·ClSal)NO$_3$]												
T	79.0	102.0	116.5	127.5	147.5	168.0	193.0	212.5	234.0	260.8	283.5	345.5
$10^6\chi_M$	2549	2277	1955	1806	1670	1534	1398	1299	1261	1175	1113	977
μ_{eff}	1.25	1.34	1.32	1.33	1.37	1.40	1.43	1.45	1.49	1.52	1.54	1.59
[Cu(EtOH·ClSal)Cl]												
T	77.0	114.0	136.0	181.0	214.0	247.0	272.5	302.0	348.0	381.5		
$10^6\chi_M$	4963	3437	2931	2280	1901	1600	1434	1288	1162	1065		
μ_{eff}	1.74	1.77	1.78	1.81	1.80	1.77	1.76	1.76	1.79	1.80		
[Cu(EtOH·Sal)NO$_3$]												
T	86.0	103.0	123.5	141.5	164.5	184.0	201.1	219.5	296.0	320.5		
$10^6\chi_M$	4101	3642	2961	2665	2354	2132	1927	1829	1459	1402		
μ_{eff}	1.66	1.71	1.69	1.71	1.73	1.74	1.73	1.76	1.82	1.85		
[Cu(EtOH·Sal)Cl]												
T	118.3	150.2	191.2	246.6	309.4							
$10^6\chi_M$	3380	2602	2119	1630	1338							
μ_{eff}	1.79	1.77	1.80	1.79	1.82							

a) Calc. from data in Ref. 1

TABLE 3. VALUES OF $-2J$ AND g FOR THE COMPLEXES

	Susceptibility[a]		ESR		
	$-2J$	g	$g_{//}$ ($\pm$0.01)	$g_\perp$ ($\pm$0.004)	$\langle g \rangle$
[Cu(EtOH·ClSal)NO$_3$]	(b)	(b)			
[Cu(EtOH·ClSal)Cl]	<10	2.06	2.28	2.018	2.11$\pm$0.01
[Cu(EtOH·Sal)NO$_3$]	<30	(b)			
[Cu(EtOH·Sal)Cl]	<10	2.06			
[Cu(3-PrOH·Sal)NO$_3$]$_2$	320	2.08	2.29	2.037	2.12$\pm$0.01
[Cu(3-PrOH·Sal)Cl]$_2$	470	2.09	2.31	2.048	2.14$\pm$0.01
[Cu(3-PrO·Sal)]$_2$	1020[c]	2.10	—	—	2.05$\pm$0.03[d]

a) Accuracy of J is expected to be better than 3%; accuracy of g should be about 4% when estimated from Eq. (1).
b) Not evaluated (see text).
c) Accuracy is expected to be low due to very low paramagnetism.
d) Accuracy low owing to very small population of the triplet state, which results in very poor signal to noise ratio.

LigH]$_2$ and [Cu·Lig·X]$_2$ fall into two separate categories where LigH=3-PrOH·Sal.

The relative accuracy of experimental points on the χ *vs.* T curves is much greater than their absolute accuracy, and therefore the accuracy of J values obtained by comparison with Eq. (1) is expected to be high while the accuracy of the g values is expected to be low. ESR measurements were made at room temperature and at 77 K to obtain accurate g values. The values of g were estimated from the ESR spectra in the normal way.[18] (Table 3).

The magnetic properties of the complexes [Cu-(EtOH·ClSal)X] differ markedly from their 3-PrOH·Sal analogues. When X=Cl, the complex shows no significant interactions and when X=ONO$_2$, antiferromagnetic interactions are observed, but the magnetic properties are more consistent with Eq. (2) than Eq. (1). However, we do not consider the data to be sufficiently characteristic to make a positive assignment of structure, at this stage. Measurements down to liquid helium temperatures are desirable, and X-ray

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Table 4. Electronic spectra (18000—8000 cm^{-1} region), selected infrared bands, melting points (°C), and densities (g·cm^{-1})

	λ	1540[a] region	3000 region	-ONO$_2$ region	Mp	Density
[Cu(EtOH·Sal)NO$_3$]	15000	1550(7)	3300	1286 1022 810	dec	1.79
[Cu(EtOH·Sal)Cl]	14300	1548(5)	3200	—	187	1.73
[Cu(EtOH·ClSal)NO$_3$]	15300	1544(8)	3350	1490sh 1289s 1019m 800m	dec	1.82
[Cu(EtOH·ClSal)Cl]	14200	1535(−1)	3150	—	189	1.79
[Cu(3-PrOH·Sal)NO$_3$]$_2$	14800	1558(18)	2880	1277s 1026s 814m	dec	1.76
[Cu(3-PrOH·Sal)Cl]$_2$	13400sh 11400s	1562(22)	3380	—	166	1.70
[Cu(3-PrO·Sal)]$_2$	17600	1578(−2)	—	—	280	1.67

s=strong; m=medium; sh=shoulder.

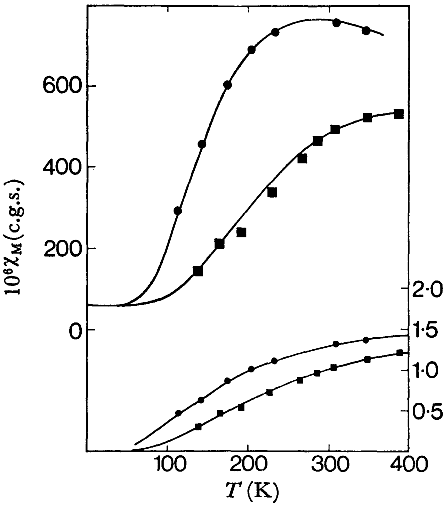

Fig. 1. Experimental and calculated (Eq. (1)) magnetic properties for [Cu(PrOH·Sal)NO$_3$]$_2$ and [Cu(PrOH·Sal)-Cl]$_2$.

crystallographic studies will be undertaken to clarify the situation.

Spectra. The electronic spectra of the complexes, listed in Table 3, indicate a four-coordinated environment[5,19] about copper, for all the complexes except [Cu(3-PrOH·Sal)Cl]$_2$, VI, which is known to be five-coordinated, with a trigonal bipyramid configuration. The spectrum of complex VI is similar to those[20] of known[21] distorted bipyramidal complexes such as [Cu(tren)NCS]SCN and [Cu(bipy)$_2$I]I. The most noteworthy feature of the spectra is the difference between the complexes [Cu(3-PrOH·Sal)X]$_2$ (X=Cl, NO$_3$). It appears that when X is changed from Cl to NO$_3$, the structure changes from VI to a four-coordinate arrangement. This behaviour is not paralleled by the analogous complexes with EtOH·ClSal.

The spectra of the four-coordinated complexes suggest a copper environment that is closer to planar than tetrahedral. The shift of 500 cm^{-1} from [Cu(EtOH·ClSal)NO$_3$] to [Cu(3-PrOH·Sal)NO$_3$]$_2$ suggests a slightly greater distortion from planarity in the latter complex,[6,19] since the ligand field strengths of EtOH·ClSal and 3-PrOH·Sal should be fairly close in magnitude. The other differences between the absorption maxima of the four-coordinate complexes are expected to arise from differences in ligand field strengths (X=Cl, NO$_3$, or no ligand) as well as the differences in the relative distortions from planarity.

Infrared Spectra. The formation of a phenolic oxygen bridge between two metal atoms is considered to result in a shift (~20 cm^{-1}) to higher energies of the salicylaldimine phenolic C–O stretching frequency near 1540 cm^{-1}. This is therefore a most important band for structural assignments and is listed for each complex in Table 4. The expected shift is observed in all the complexes with 3-PrOH·Sal except [Cu(3-PrO·Sal)]$_2$, indicating absence of phenolic oxygen bridging, and hence structure I for this complex, but structures of types III and VI for the other complexes. Of the complexes with EtOH·Sal and EtOH·ClSal, only [Cu(EtOH·ClSal)NO$_3$] exhibits a small shift in this region, indicating weak phenolic oxygen bridges for this complex and no significant phenolic bridging for the other complexes.

The infrared absorptions due to the nitrato group in [Cu(EtOH·ClSal)NO$_3$]$_2$ and [Cu(3-PrOH·Sal)-NO$_3$]$_2$ confirm that the nitrate is coordinated rather than ionic, but add no new information, since infrared spectra cannot distinguish between mono- and bidentate nitrate coordination.[22] It is therefore necessary to invoke the structural assignment from visible spectra

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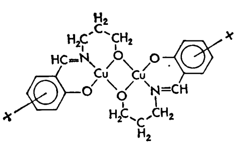
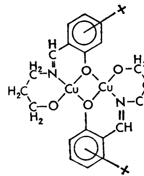
to determine monodentate nitrato coordination. Such coordination appears to be necessary in order to make up the required coordination number in each case. (In the special case where the alcoholic oxygens are involved in hydrogen bonding they are unlikely to be available for coordination to copper). These nitrato complexes are similar to the nitrato complexes of type III with Cl replaced by monodentate ONO_2.[4] In all these complexes, infrared absorptions at 790—813, 1005—1022, 1280—1286, 1488—1495 cm^{-1}, typical of coordinated nitrate,[22,23] were observed only in the nitrato complexes, but not in the analogous chloro derivatives (III or VI), nor in the parent monomeric Schiff base complexes.[4]



(I)



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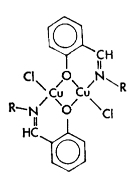

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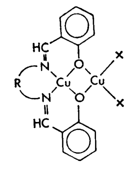

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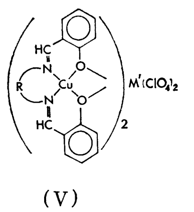

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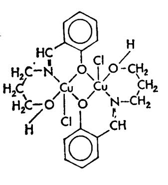

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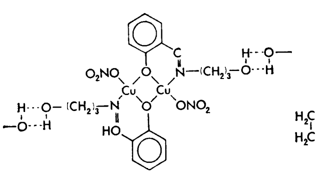
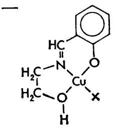


(VII)



(VIII)

The O–H stretching region, 2800—3500 cm^{-1}, was examined to determine the bonding of the OH group (Table 4). As expected, $[Cu(3\text{-}PrO\cdot Sal)]_2$ has no bands in this region. Complex VI, which has the OH group coordinated to the metal, has a high energy band in this region. Similar bands occur in all but one of the remaining complexes, suggesting similar coordination of the OH groups. The significant exception is $[Cu(3\text{-}PrOH\cdot Sal)NO_3]_2$ which has a lower energy band, in keeping with a structure involving hydrogen bonding to the hydroxyalkyl group. This postulate is supported by the observation of extensive intermolecular hydrogen bonding in the X-ray study of $[Cu(EtOH\cdot Sal)_2]$[24] while the analogous complex $[Cu(EtOH\cdot ClSal)]_2$ has its OH band at 3100 cm^{-1}. Thus the most likely structure for the complex $[Cu(3\text{-}PrOH\cdot Sal)NO_3]_2$ is VII. The infrared evidence is not conclusive for the complexes involving EtOH·Sal and EtOH·ClSal since some of the bands are weak and broad, but when the other evidence is taken into account, the most likely structure for these complexes is VIII. Cross-linking *via* intermolecular Cu–O or hydrogen bonds, or both, between individual molecules of type VIII seems probable, especially in the complex $[Cu(EtOH\cdot ClSal)NO_3]$ and to a lesser extent $[Cu(EtOH\cdot Sal)NO_3]$. The former complex should perhaps be formulated as $[Cu(EtOH\cdot ClSal)NO_3]_n$ but, as discussed above, n may not be reliably evaluated at this stage. Fortunately, these complexes readily form large (green) crystals, so that single crystal X-ray studies should be accessible.

Rearrangement Reactions. To test the possibility of the interconversion reaction (3),

$$[Cu(3\text{-}PrO\cdot Sal)]_2 + HX \rightleftharpoons [Cu(3\text{-}PrOH\cdot Sal)X]_2 \quad (3)$$

complex I, $[Cu(3\text{-}PrO\cdot Sal)]_2$ was treated with HCl in methanol, and deep brown crystals which separated from the mixture were shown to be identical with complex VI $[Cu(3\text{-}PrOH\cdot Sal)Cl]_2$, having identical infrared spectra and X-ray diffraction patterns, and the same melting points, densities and optical spectra. The reverse conversion was effected by boiling VI in the base pyridine. Dark red crystals which separated on cooling were shown by the same techniques to be identical with I. In each case the reaction appeared to be complete in a few minutes. The procedure was repeated with the nitrato analogue, VII, and a period of days was required for a smaller yield of the product. This slower reaction is not surprising in view of the different structures VI and VII proposed for the chloro and nitrato complexes: the former could undergo internal rearrangement more readily than the latter. The mechanism of these reactions is under further investigation.

It has not been found possible to prepare the complex analagous to I using EtO·Sal in place of 3-PrO·Sal.[1,25] It appears that dimeric analogues to VI using EtOH·Sal in place of 3-PrOH·Sal are not readily formed either.

Conclusion

The main structures I, VI, and VII, occur in copper(II) complexes with *N*-3-hydroxy-*n*-propylsalicylaldimine, and direct chemical interconversion between them is possible. When the hydroxypropyl group is shortened to hydroxyethyl, only one structure, VIII, seems likely, with some degree of molecular aggregation.

$$CuL_2 + CuX_2 \longrightarrow 2[CuLX]$$

In the 3-PrOH·Sal complexes, if the alcoholic oxygen is not deprotonated, bridging occurs easily *via* the phenolic oxygens to form binuclear complexes. The alcoholic oxygen may be coordinated as in VI, but need not be, and may participate in intermolecular hydrogen bonding (VII) instead. When the alcoholic oxygen is deprotonated and coordinated, bridging *via* this oxygen (I) is preferred.

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