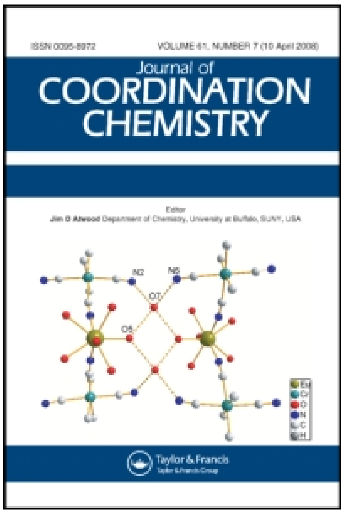

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PENTADENTATE LIGANDS VIII. COPPER(II) COMPLEXES OF SCHIFF BASE LIGANDS

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PENTADENTATE LIGANDS VIII. COPPER(II) COMPLEXES OF SCHIFF BASE LIGANDS

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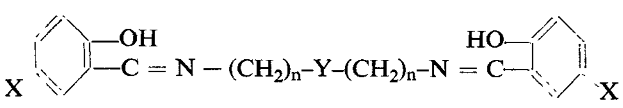
Copper(II) complexes of a related series of potentially pentadentate ligands derived from substituted salicylaldehydes and 2,2′-(aminoethyl)-sulfide, 3,3′-bis(aminopropyl)sulfide, 3,3′-bis(aminopropyl)ether and diethylenetriamine have been prepared. Elemental analysis, mass, infrared and visible spectra and magnetic susceptibility measurements have been employed in order to characterize these new compounds. The materials appear to be monomeric in the solid state exhibiting no abnormal magnetic properties at room temperature. In comparison with the visible spectra of a series of known copper(II) complexes of tetradentate ligands, the structure of these complexes is postulated to be essentially square planar. However, the possibility of weak coordination by the middle donor in some of the pentadentate ligands can not be ruled out.

INTRODUCTION

The chemistry of copper(II) complexes containing polydentate Schiff base ligands has been reviewed on several occasions during the last ten years.[2–4] The lack of pentadentate ligands complexed with copper(II) is noteworthy. Only one example has been reported to date,[5] (i.e. Cu(HSALDPT), *IV*, which is postulated to be a five coordinate trigonal bipyramidal complex with all five donor atoms bonded to the copper (II) ion). We wish to report here the preparation and characterization of some new copper(II) complexes of a series of pentadentate ligands derived from a variety of substituted salicylaldehydes and four polyamines which are as follows: 2,2′-bis(aminoethyl)sulfide (DAES), 3,3′-bis(aminopropyl)sulfide(DAPS), 3,3′-bis(aminopropyl)ether(DAPE) and diethylenetriamine (DIEN)).[6] The spectral and magnetic properties of related but known complexes are also reported and compared with similar data concerning these new materials. Specifically these will include complexes of Schiff base tetradentate ligands derived from salicylaldehyde and different diamines. The ligands with their corresponding abbreviated notation are tabulated below.



	Y	*n*	*Notation*
I	S	2	XSALDAES
II	S	3	XSALDAPS
III	N—H	2	XSALDIEN
IV	N—H	3	XSALDPT
V	O	3	XSALDAPE

EXPERIMENTAL

Materials

DAES was donated by the Dow Chemical Company, Midland, Mich., DAPE was prepared by a previously reported method.[7] DAPS was prepared by a modification of the procedure by Lehmann[8] employing the Gabriel synthesis. DIEN, salicylaldehyde and 3-methoxysalicylaldehyde were obtained from the Aldrich Chemical Company. The latter chemical was recrystallized twice from hot 95% ethanol in the presence of charcoal prior to using it. 5-Bromo-, and 5-methylsalicylaldehyde and XSALDAES were prepared as previously described.[9] All other chemicals and solvents were reagent grade or equivalent. Uncomplexed pentadentate ligands (XSALDAPS and XSALDAPE) were prepared by adding one molecular equivalent of DAPS or DAPE to two molecular equivalents of the appropriate salicyladehyde dissolved in 95% ethanol at room temperature. After stirring for fifteen minutes, the solution was chilled and a yellow low melting precipitate appeared. The product in each case was identified by n.m.r., infrared and elemental analysis. The bis(salicylaldehydo)copper(II) complexes were obtained as green hydrated solids following the method of Holm.[10]

Preparation of Cu(XSALDAES)

The appropriate XSALDAES ligand (0.01 mole) was dissolved in 150 ml of hot *N,N*-dimethylformamide and the solution was brought to reflux. $Cu(C_2H_3O_2)_2 \cdot H_2O$ (2.00 g, 0.01 mole) dissolved in 200 ml of methanol was added dropwise to the refluxing solution. After the addition had been completed, the solution was refluxed for one hour. During this time a green solid formed. The mixture was then cooled, isolated by filtration, washed with ether, and dried overnight *in vacuo* at 100°C.

Preparation of Cu(5–BrSALDAPE)

BrSALDAPE (2.33 g, 0.005 mole) and triethylamine (1.01 g, 0.01 mole) were dissolved in 100 ml of 95% ethanol and the solution was brought to reflux. $Cu(C_2H_3O_2)_2 \cdot H_2O$ (1.00 g, 0.005 mole) was dissolved in 150 ml of ethanol and added dropwise to the refluxing solution. The solution changed color from yellow to green immediately after the addition was started. After addition of $Cu(C_2H_3O_2)_2 \cdot H_2O$ was complete, the solution was refluxed for an hour. During this time a green solid formed. The solution was cooled and the solid isolated by filtration. The solid was dried *in vacuo* as described above.

Preparation of Cu(XSALDAPS)

$Cu(C_2H_3O_2)_2 \cdot H_2O$ (1.00 g, 0.005 mole), triethylamine (1.01 g, 0.01 mole), and triethylorthoformate (1.48 g, 0.01 mole) were dissolved in 100 ml of *n*-butanol and the solution brought to reflux. XSALDAPS (0.005 mole) dissolved in 125 ml of *n*-butanol was added dropwise to the refluxing solution. After the addition was complete, the solution was refluxed for one hour. During this time a small amount of a dark solid formed. The solution was cooled and a dark green crystalline solid was isolated and dried as described.

Preparation of Cu(XSALDIEN)

The appropriately substituted bis(salicylaldehydo) copper(II) dihydrate (0.01 mole) was suspended in absolute ethanol and brought to reflux after which DIEN (0.01 mole) dissolved in a small amount of ethanol was quickly added. The suspended material immediately dissolved yielding a dark green solution which was refluxed for approximately 3 hours. During this time a green precipitate appeared which was filtered and dried as described previously.

Physical Measurements

Infrared spectra were obtained in the region 5000–400 cm^{-1} using a Perkin-Elmer Model 621 spectrophotometer. Solid state I.R. spectra were recorded as KBr pellets and as Nujol or hexachlorobutadiene mulls. Solution visible spectra in the region 5000–35,000 cm^{-1} were taken as $CHCl_3$ and pyridine solutions using matched solution cells on a Cary 14 recording spectrophotometer. Spectra of solid samples were obtained by a diffuse transmittance technique[11] employing Nujol mulls impregnated on Whatman No. 1 filter paper.

Magnetic susceptibility measurements on solid samples were obtained by the Faraday method. Diamagnetic corrections were made employing Pascal's constants.[12]

Mass spectra were obtained on a Hitachi-Perkin-Elmer RMU–7 double focusing mass spectrometer using a solid inlet probe. The solid probe temperature was minimized in order to prevent decomposition of the samples. The source temperature was maintained at approximately the temperature of the solid probe. Analyzer tube and ion source pressures of less than 10^{-6} torr were employed. Where necessary mass to charge ratios were calibrated with perfluorokerosene.

Elemental analyses were performed in this laboratory using a Perkin-Elmer Model 240 C, H & N Analyzer.

RESULTS AND DISCUSSION

Nine new complexes of empirical formula CuL (Table I) have been prepared where L is a linear potentially pentadentate ligand in which the middle donor atom may be a secondary amine, an ether oxygen or a thioether linkage. In addition, the number of methylene carbons joining the middle donor atom and two Schiff base groups is variable being two or three. The complexes are reasonably stable being unaffected by air or moisture and range in color from dark green to an olive colored appearance. All the complexes have reasonably

TABLE I

Analytical data

	Calculated			Found		
	C	*H*	*N*	*C*	*H*	*N*
Cu(HSALDIEN)	57.91	5.09	11.26	57.75	5.12	11.24
Cu(5-BrSALDIEN)	40.53	3.19	7.88	41.05	3.48	7.83
Cu(HSALDAES)	55.38	4.62	7.18	55.24	4.53	7.04
Cu(5-BrSALDAES)	39.27	2.91	5.09	39.53	2.82	5.17
Cu(5-CH$_3$SALDAES)	57.14	5.24	6.66	57.39	5.50	6.46
Cu(3-CH$_3$OSALDAES)	53.33	4.88	6.22	53.32	4.89	5.97
Cu(HSALDAPS)	57.42	5.26	6.70	57.06	5.52	6.75
Cu(5-BrSALDAPS)	41.67	3.47	4.86	42.24	3.92	4.53
Cu(5-BrSALDAPE)	42.86	3.56	5.00	42.64	3.34	5.11

good solubility in most solvents with the exception of the XSALDAES derivatives.

Infrared spectra in the form of Nujol mulls have been measured on several of the ligands and all the complexes, and they are consistent with the proposed molecular structure of the respective ligand (Structures I–V). The observed IR absorption frequencies along with their corresponding inference for several of the complexes are collected in Table II. The spectra of all the compounds have many similar features. One or two bands are observed in the spectrum of each complex in the 1610–1640 cm^{-1} region which can be assigned to the asymmetric and symmetric C=N stretching modes of a coordinated Schiff base. The reduction in stretching frequency upon coordination is not as large as expected because in the free ligands the C=N stretch is abnormally low due to conjugation with the benzene ring. Bands around 1140 cm^{-1}, 700–900 cm^{-1} and 685 cm^{-1} are assigned respectively to the aromatic carbon-oxygen stretch, carbon-hydrogen bend of the appropriately substituted benzene ring and the aromatic carbon-bromine stretch where applicable.[13] Cu(HSALDIEN) shows a weak intensity, sharp band at 3300 cm^{-1} attributable to a N–H stretch; however, Cu(5-BrSALDIEN) exhibits only a very weak broad band *c.* 3200 cm^{-1}. An equally broad band is observed in the free ligand in this region. A judgment regarding whether the secondary amine is or is not coordinated to the copper ion cannot be made based solely on the IR data. Aliphatic secondary amines exhibit a single absorption in the 3350–3310 cm^{-1} region. The XSALDIEN complexes show no absorption at these frequencies although the band at 3300 cm^{-1} borders on this region. This may be interpreted as being diagnostic of a non-coordinated amine. However, the broad band observed at 3200 cm^{-1} for Cu(5-BrSALDIEN) which would not be expected to have a different coordination environment could be suggestive of a coordinated amine. Alternatively, hydrogen-bonding could account for the broadened and lower energy absorption. Cu(HSALDPT) has been reported to exhibit medium sharp band at 3250 cm^{-1} which has been suggestive of a copper-nitrogen

TABLE II

Infrared spectral data and corresponding assignments for selected copper(II) complexes (cm^{-1})

HSALDIEN	HSALDAES	Cu(HSALDIEN)	Cu(HSALDAES)	Cu(5-BrSALDIEN)	Cu(5-BrSALDAES)	Inference
3250	—	3300	—	3200	—	N–H str.
1665	—	1645	—	1650	—	N–H def.
1630, 1635	1630, 1605	1630, 1610	1620	1615	1630, 1615	sym. and asym. C = N str.
1150	1145	1130	1150	1145	830	C–O str.
715	715	715 sh	—	835	650	C–H bend, substituted benzene
—	—	—	—	685	—	C–Br str.

coordination bond.[5] Coordination of the amine to the copper(II) ion is therefore rather dubious. In the analogous nickel (II) case it has been established that the two carbon methylene chain does not provide enough flexibility for the secondary amine to bond to the metal.[6, 14] Considerable Jahn-Teller distortion would be expected to enhance a similar situation in the case of Cu(XSALDIEN). This, of course, precludes coordination of both phenolic oxygens and azomethine groups. In the spectrum of Cu(5-BrSALDAPE), a sharp medium intensity band is observed at 1120 cm^{-1} which is assigned to the C–O–C asymmetric stretching vibrational mode. A comparison of the 1150–1000 cm^{-1} region in the free ligand and in the complex reveals no major shift in any of the band positions. We believe that this observation is indicative of the lack of coordination of the ether oxygen by the copper (II) ion. Coordinated ethers normally have this vibrational mode shifted *c.* 100 cm^{-1} [7] to lower energy.

Mass spectral measurements have been attempted on all the complexes with varying results. The spectra were taken at as low a source and inlet temperature as possible. In practically all cases the samples underwent decomposition during the measurement. Specifically Cu(5-BrSALDIEN), Cu(5-BrSALDAES), Cu(HSALDAES), Cu(HSALDAPS) and Cu(5-BrSALDAPS) decomposed on the probe prior to vaporization; therefore, no high mass fragment ions were observed. Relatively weak parent ion clusters were detected for Cu(3-CH_3-OSALDAES) and Cu(5-CH_3SALDAES). Only Cu(5-BrSALDAPE) exhibited a very intense parent ion cluster. The spectra of none of the complexes revealed fragment ions of m/e greater than the mono-nuclear formulation. This suggests that in the gas phase little or no inter-molecular interaction exists. It is surprising that most of these materials fail to give a mass spectrum in light of the fact that the analogous nickel (II) and cobalt (II) complexes give rise to highly interpretable spectra.[9, 14, 15] A very low vapor pressure coupled with decomposition at the melting point may account for these observations.

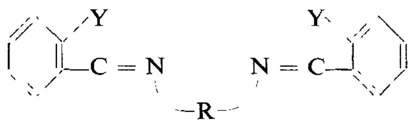
Magnetic susceptibility measurements have been performed on the subject compounds as well as a number of previously reported complexes in the solid state at room temperature, Table III. (Abbreviated notation for these ligands are listed below.) The calculated magnetic moments reveal only a small orbital contribution to the predicted spin only value. In contrast to the nickel (II) case which may be square planar or five-coordinate the spin state is not dependent on whether the middle donor group coordinates to the copper (II). Consequently magnetic measurements yield essentially no information regarding structure. The notable lack of any anomalous moments might suggest the absence of antiferromagnetic behavior. Although judging from previous data collected for Cu(SALEN) (*VI*), magnetic measurements at room temperature are not expected to reveal appreciable intermolecular interaction in the solid phase. Cu(SALEN) has a dimeric structure in the solid state although its magnetic moment is normal[16] at room temperature. Our measured Cu(SALOPHEN) moment is in contrast to a previously reported measurement[17] of 1.56 B.M. We find this complex to yield a normal magnetic moment at room temperature.

TABLE III

Magnetic moments measured at room temperature in the solid state

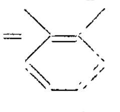
Compound	μeff (B.M.)
Cu(HSALDIEN)	1.83
Cu(5-BrSALDIEN)	1.65
Cu(HSALDAES)	1.82
Cu(5-BrSALDAES)	1.69
Cu(5-CH_3SALDAES)	1.78
Cu(3-CH_3OSALDAES)	1.79
Cu(HSALDAPS)	1.75
Cu(5-BrSALDAPS)	1.81
Cu((5-BrSAL)DAPE)	1.81
Cu(SALDPT)[a]	1.93
CuSALEN	1.78
Cu((5-NO_2S)ALEN)	1.77
Cu(SALTM)	1.81
Cu(SALOPH)EN	1.78
CuOABEN	1.72
Cu(OABNH)$_2$	1.73

[a] L. Sacconi and I. Bertini, *J. Amer. Chem. Soc.* **88**, 5180 (1966).

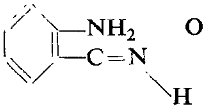


VI Y=OH R=—CH_2—CH_2— SALEN

VII Y=OH R=—CH_2—CH_2—CH_2— SALTM

VIII Y=OH R=  SALO-PHEN

IX Y=NH_2 R=—CH_2—CH_2— OABEN



OABNH

The assignment of gross stereochemical features to copper (II) complexes from spectral data is made exceedingly difficult because of the broadness of the major absorption maxima arising from as many as three closely spaced electronic transitions, Jahn Teller distortion, spin-orbit coupling,[18] solvent coordination and inter-complex interaction. The linear pentadentate ligands employed here afford ample opportunity for numerous structural and electronic modifications such as (1) five-coordina-

TABLE IV

Visible spectra of copper complexes (cm^{-1})

Compound[a]	Medium	Absorption Maxima[c]
Cu(HSALDIEN)	Nujol	13,700 sh; 15,800; 27,000
	CHCl$_3$	17,390 (370); 26,800 (1100)
	Pyridine	16,400 (72); 26,500 (200)
Cu(5–BrSALDIEN)	Nujol	17,700; 27,200
	CHCl$_3$	18,000 (234); 25,800 (6600)
	Pyridine	15,870 (213); 25,500 (5,960)
Cu(HSALDAES)	Nujol	15,900; 25,800
	Pyridine	15,900 (50); 27,800 (1100); 31,750 (5390)
Cu(5–BrSALDAES)	Nujol	15,200; 25,600
	Pyridine	17,900 (82); 26,500 (1260)
Cu(5–CH$_3$SALDAES)	Nujol	15,300 sh; 16,600 sh; 25,800
	Pyridine	16,700 sh (40); 26,800 (297)
Cu(3–CH$_3$OSALDAES)	Nujol	12,500 sh, 18,700 sh; 26,700
	CHCl$_3$	16,300 (162); 26,400 (7380)
Cu(HSALDAPS)	Nujol	16,260; 22,900 sh; 27,100
	CHCl$_3$	14,500 (184); 26,800 (9360)
	Pyridine	15,400 (143); 27,000 (11,400)
Cu(5–BrSALDAPS)	Nujol	16,100; 22,200; 25,700
	CHCl$_3$	14,100 (283); 25,800 (9550)
	Pyridine	15,600 (81); 26,500 (8,650)
Cu(5–BrSALDAPE)	Nujol	13,840 sh; 18,000; 22,700; 26,700
	CHCl$_3$	15,000 (132); 26,400 (10,100)
	Pyridine	15,800 (125); 26,700 (10,100)
Cu(HSALDPT)	Nujol	10,000 sh; 12,200; 15,500 sh; 26,800
	CHCl$_3$	10,340 (200); 12,300 (251); 27,600 (10,400)
	Pyridine	8,760 (77); 12,200 (182); 29,200 (11,300)
Cu(SALEN)	Nujol	17,500; 27,000
	CHCl$_3$	17,700 (433); 27,100 (11,700)
	Pyridine	16,700 (302); 26,900 (11,600)
Cu(5–NO$_2$SALEN)	Nujol	18,900
	Pyridine	16,300 (350); 26,200 (12,000)
Cu(SALTM)	Nujol	17,200; 19,300; 25,640
	CHCl$_3$	16,800 (260); 27,000 (10,800)
	Pyridine	16,300 (160); 23,800 (14,600)
Cu(SALOPHEN)	Nujol	17,700; 22,000
	CHCl$_3$	18,100 (410); 23,400 (22,400); 25,400 (1690); 32,280 (28,500)
	Pyridine	16,600 (253); 30,500 (21,800)
Cu(OABEN)	Nujol	12,500 sh; 14,900; 18,700 sh; 22,100 sh; 23,500
	CHCl$_3$	16,300 sh (480); 19,100 sh (1700); 26,500 (5240)
	Pyridine	14,700 (64); 23,900 (12,100)
Cu(OABNH)$_2$	Nujol	15,000; 22,200; 23,500
	CHCl$_3$	15,500 sh (320); 20,400 (1125); 26,700 (7500)
	Pyridine	17,600 sh (240); 32,400 (11,000)

[a] Cu(NO$_2$SALEN), Cu(HSALDAES), Cu(5–BrSALDAES), and Cu(5–CH$_3$SALDAES) did not exhibit sufficient solubility in CHCl$_3$ and Cu(CH$_3$OSALDAES)[3] in pyridine to obtain a visible spectra.

[b] Onset of strong absorption begins *c.* 25,000 cm^{-1}. Slits of the spectrophotometer open completely before the peak is maximized.

[c] Numbers in parentheses are molar extinction coefficients.

tion in which the middle donor atom is strongly or weakly bonded to give either a trigonal or *cis/trans* square pyramidal type structure,[19] (2) square planar or tetrahedral coordination in which the middle donor is dangling; (3) five coordination achieved by the bridging of pairs of copper (II) ions by a common phenolic oxygen[20] or (4) a four coordinate planar structure distorted towards a tetrahedron (or equivalently a flattened tetrahedral structure). No bands are observed in the solid state spectra below 10,000 cm^{-1}. Therefore, a tetrahedral structure may be ruled out.[18] Although, it is entirely possible for distortion to occur such that a buckled square planar configuration could give rise to absorption between 10,000 and 16,000 cm^{-1}. None of the complexes studied appear to be truly five-coordinate except Cu(SALDPT) whose spectra and structure have been previously reported.[5] All the complexes exhibit one major band accompanied by one or more shoulders on either the high or low energy side in the 15,000–18,000 cm^{-1} region indicative of square planar geometry about the copper. However, the extent and effect of distortion from a normal square plane on the copper (II) spectra is not known with certainty. Copper complexes where the geometry is anticipated and known in some cases to be square planar (i.e. Cu(SALEN), *VI*, Cu(SALTM), *VII*, Cu(5-NO$_2$SALEN), Cu(SALOPHEN), *VIII*, and Cu(OABEN), *IX*) reinforce this argument. Low energy shoulders observed for Cu(3-CH$_3$OSALDAES), Cu(HSALDIEN), Cu(5-BrSALDAPE) and Cu(OABEN) may possibly be interpreted as a weak perturbation at a fifth coordination site. Finally a major band is observed between 25,000–30,000 cm^{-1} assignable to an internal ligand transition.

In CHCl$_3$ where associative effects should be minimal none of the complexes appear to be five-coordinate except Cu(SALDPT). An octahedral complex obtained by some kind of intermolecular association, however, cannot completely be overlooked. Some workers report that it is impossible to correlate the absorption maxima of a *d–d* band with the formation of addition compounds.[21] Waters et. al., on the other hand, have suggested that the appearance of a band at lower energy (ca. 14,000 cm^{-1}) in CHCl$_3$ is consistent with an increase in coordination number resulting from solvation.[22] Applying this premise it would appear that only Cu(3-CH$_3$OSALDAES), Cu(XSALDAPS) and Cu(5-BrSALDAPE) are significantly solvated in CHCl$_3$. The expected bathochromic shifts in the visible region caused by formation of a five or six coordinate structure in pyridine are not realized in all cases. Comparing the Nujol, CHCl$_3$, and pyridine spectra reveals no systematic variation in band shifts. It is probable that four, five and six coordination is occurring in solution accompanied by changes in the conformation of the ligand which may result in considerable buckling of the ligating atoms around the copper. Clearly, the correlation between the structure and band position for copper (II) is not a straightforward one.

The assumption that the middle donor in these pentadentate ligands is without effect on the copper ion is subject to some discussion. A weakened in-plane ligand field is predicted for these complexes as compared with Cu(SALEN) and Cu(SALTM) if the middle donor is not coordinated to copper. Holm[10] has predicted that as the number of non donor atoms joining azomethine linkages increases the in-plane field should decrease. A comparison of the CHCl$_3$ solution spectra reveals the following points. The five atom chain in Cu(XSALDIEN) causes a negligible shift in band maxima when compared to Cu(SALEN) and Cu(SALTM) which possess a two and three atom chain. It might be assumed, therefore, that in XSALDIEN the secondary nitrogen is interacting albeit feebly with the metal. Clearly, making the ligand more flexible-compare SALDPT-enhances the secondary amine-copper interaction. The five atom chain in Cu(3-CH$_3$OSALDAES), however, results in a considerable shift to the red. A much larger shift is seen for the seven-atom-containing chain in Cu(XSALDAPS) and Cu(XSALDAPE). It is tempting to speculate that the thioether and oxygen ether linkages are non donors to copper (II) in these complexes. Certainly the known poor coordinating ability of these two groups justifies such speculation. Caution should be exercised here in that all of these complexes may not be structurally similar. For example, the corresponding cobalt (II) complexes have been found to be square planar with SALEN, distorted trigonal bipyramidal with SALDPT and tetrahedral with XSALDAES.[15]

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