Inorganica Chimica Acta, 63 (1982) 183–187

Copper(II) Complexes of Tridentate Schiff Base Ligands

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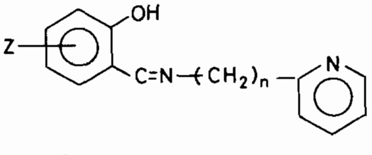
Received April 20, 1982

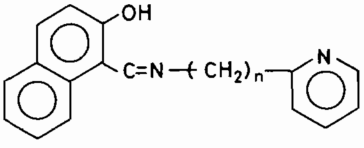
Complexes of emperical formula CuLCl and CuL_2 have been synthesized and characterized wherein L = the Schiff base formed from the condensation of selected salicylaldehydes (Z-SAL) with two polyamines, 2-aminomethylpyridine (AMP) and 2-(2'-aminoethyl–pyridine (AEP). The Cu to L ratio was shown to be dependent on the method of preparation. Magnetic, spectral and elemental analysis data indicate that the environment of Cu(II) is five-coordinate in the solid state. The complexes do not react with DMSO solutions of superoxide.

Introduction

There are numerous accounts in the literature describing the chemistry of copper(II) complexes of Schiff base ligands containing two [1], four [2], five [3–5] and six [6, 7] donor atoms. However, there does not appear to be any reports to our knowledge describing the chemistry of Cu(II) complexes derived from substituted salicylaldehydes (Z-SAL) with 2-aminomethylpyridine (AMP) and 2-(2'-aminoethyl)pyridine (AEP). We report herein the synthesis and characterization of these Cu(II) complexes, Structure I.



n abbreviation
1 Z-SALAMP
2 Z-SALAEP
Z-5-H, 5-NO_2, 5-Cl, 5-CH_3O



n abbreviation
1 NAPAMP
2 NAPAEP

Structure I

The interaction of O_2^{1-} and Cu(II) has been implicated in the enzyme superoxide dismutase [8]. As a result a number of papers have appeared which describe the reaction of superoxide ion with various model Cu(II) complexes [9–11]. In this paper we also describe results obtained when these new Cu(II) complexes interact with O_2^{1-}.

Experimental

Preparation of Cu(Z-SALAMP)Cl and Cu(Z-SALAEP)Cl

To 0.004 mol of either AMP or AEP dissolved in 20 ml 95% ethanol was added 0.004 mol of the appropriately substituted Z-SAL (Z = 5-H, 5-NO_2, 5-Cl, 5-CH_3O) dissolved in 20 ml of 95% ethanol. The yellow solution was stirred for ¼ h followed by dropwise addition of 0.002 mol of $CuCl_2 \cdot 2H_2O$ dissolved in 20 ml of 95% ethanol. Almost immediately upon addition of the Cu a dark green precipitate formed. Stirring was continued for 1 h followed by isolation and washing with 95% ethanol. The complexes were dried overnight at 100 °C in vacuum.

Preparation of Cu(Z-SALAEP)$_2$

To 0.002 mol of the appropriately substituted salicylaldehyde (Z = 5-H, 5-NO_2, 5-CH_3O, NAP)

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0020-1693/82/0000-0000/$02.75

TABLE I. Elemental Analyses and Magnetic Moment Data for Copper Complexes.

Complex	%C		%H		%N		μ_{eff} (BM)
	Calcd.	Found	Calcd.	Found	Calcd.	Found	
Cu(SALAMP)Cl	50.33	50.39	3.56	3.58	9.03	9.07	1.85
Cu(SALAEP)Cl	51.86	52.02	4.03	4.13	8.64	8.69	1.30
Cu(5-NO$_2$SALAMP)Cl	43.95	44.31	2.84	2.99	11.83	11.86	1.82
Cu(5-NO$_2$SALAEP)Cl	45.54	46.06	3.27	3.41	11.38	11.35	1.85
Cu(5-ClSALAMP)Cl	45.30	45.28	2.92	3.01	8.13	8.00	1.85
Cu(5-ClSALAEP)Cl	46.88	46.82	3.36	3.33	7.81	7.91	1.34
Cu(5-CH$_3$OSALAMP)Cl	49.42	49.53	3.84	3.82	8.24	8.25	1.85
Cu(5-CH$_3$OSALAEP)Cl	50.85	50.32	4.27	4.12	7.91	8.31	1.83
Cu(NAPAMP)Cl	57.73	57.93	3.64	3.90	7.78	7.83	1.78
Cu(NAPAEP)Cl	57.75	57.93	4.04	4.13	7.49	7.45	1.85
Cu(NAPAEP)$_2$	70.40	70.52	4.93	5.02	9.12	9.19	2.11
Cu(5-CH$_3$OSALAEP)$_2$	62.76	63.15	5.27	5.32	9.76	9.73	1.88
Cu(5-NO$_2$SALAEP)$_2$·H$_2$O	54.06	53.43	4.21	4.05	13.51	13.48	1.88

in 20 ml of 95% ethanol was added 0.002 mol of AEP. The yellow solution was stirred for ¼ h followed by dropwise addition of 0.002 mol of $CuCl_2 \cdot 2H_2O$ in 95% ethanol. To this dark green solution was added 0.002 mol solid NaOH. Almost immediately a light green precipitate formed. Stirring was continued for 1/3 h followed by isolation and washing with 95% ethanol. The complexes were dried at 100 °C in vacuum overnight.

Physical Measurements

Infrared spectra were obtained as Nujol mulls on a Beckman IR-5A recording spectrophotometer. Electron spin resonance spectra were obtained on a Varian Model 4500 spectrometer. Magnetic susceptibilities were determined using the Faraday method. Elemental analyses were performed by the Microchemical Analysis Laboratory, University of California, Berkeley, Calif.

Materials

AMP, AEP and 5-CH$_3$OSAL were obtained from Aldrich Chemical Co. 2-Hydroxyl-1-naphthaldehyde (NAP), 5-ClSAL and 5-NO$_2$SAL were obtained from Eastman Chemical Co. $CuCl_2 \cdot 2H_2O$ was obtained from Fisher Scientific Co. Potassium superoxide was obtained from Alfa Ventron Inorganics. All other materials were reagent grade or equivalent.

Results and Discussion

During the course of the synthesis of the salicylaldehyde-derived complexes we were able to dictate the Cu to L ratio by employing NaOH. In the absence of base the complexes were isolated as Cu(L)Cl even when the Cu to L ratio in the preparation was 1:2. However, if NaOH were added to the solution wherein the Cu to L ratio was ½, complexes of the general formula CuL$_2$ were isolated where L = 5-NO$_2$-SALAEP, 5-CH$_3$OSALAEP, and NAPAEP. The subject complexes (Table I) range in color from dark green to light yellow. They are soluble in water, dimethylsulfoxide (DMSO) and certain derivatives are soluble in chloroform.

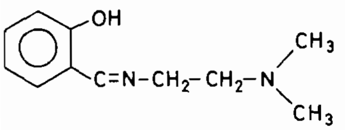
Infrared spectra on the complexes were obtained as Nujol mulls. All of the complexes display an absorption at ~1625 cm^{-1} which is assigned to the coordinated Schiff base linkage [12]. In addition there are well resolved-sharp bands at 1600, 1590, 1470, 1440, 1200, 1155, 1055 and 1025 cm^{-1} all assigned to a coordinated pyridine ring [13]. We were unable to discern any consistent patterns in the pyridine absorption bands when the IRs of the complexes Cu(Z-SALAEP)Cl and Cu(Z-SALAEP)$_2$ were compared. Our aim was to find evidence indicating whether or not both pyridine moieties were coordinated in the Cu(Z-SALAEP)$_2$ cases. In an earlier report on the chemistry of some bis(salicylaldiminato)copper(II) complexes, it was found [1] that Cu(II) bound two SAL moieties and that the Cu(II) geometry was related to the bulkiness of the ligand. By placing a third donor atom on the SAL moiety, N-β-dimethylaminoethylsalicylaldimine (Structure II), Chick and Palenik [14] were able to show by X-ray diffraction studies that indeed two ligands were attached to the Cu(II) but only a five coordinate structure with an O$_2$N$_3$ ligand field was produced. The second tertiary nitrogen was not coordinated to the Cu(II). It follows, therefore, that our complexes, Cu(Z-SALAEP)$_2$, could also be five coordinate with

TABLE II. Electronic Absorption Spectra of Copper Complexes in Various Solvents.

Complex	H_2O	DMSO	$CHCl_3$	Nujol Mull
Cu(SALAMP)Cl	630	610	840sh 645	–
Cu(5-ClSALAMP)Cl	640	840 640	635	640
Cu(5-CH_3OSALAMP)Cl	640	840sh	642	630
Cu(NAPAMP)Cl	600	840sh 640	640	630
Cu(5-NO_2SALAMP)Cl	640	840sh 640	i[a]	640
Cu(SALAEP)Cl	640	650	600sh	860
Cu(5-ClSALAEP)Cl	640	840 650	630	860
Cu(5-CH_3OSALAEP)Cl	630	840sh	840sh 640sh	860sh 630
Cu(NAPAEP)Cl	620	640	i[a]	820
Cu(5-NO_2SALAEP)Cl	i[a]	650	840sh 650	670
Cu(5-CH_3OSALAEP)$_2$	i[a]	840sh	i[a]	730
Cu(NAPAEP)$_2$	i[a]	840 610	840sh 620	670
Cu(5-NO_2SALAEP)$_2$	i[a]	i[a]	i[a]	860 610

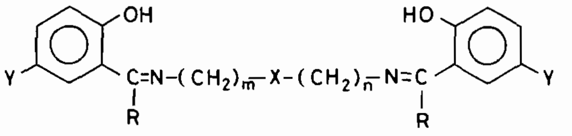
[a] i = insoluble.

an O_2N_3 ligand field. Infrared spectroscopy, however, does not shed light on this question.



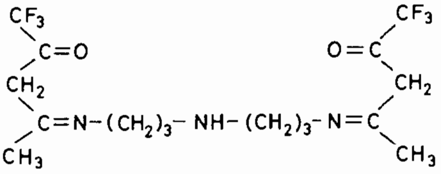
Structure II

Electronic spectra of Cu(II) complexes with multidentate ligands are not, in general, good indicators of geometry. Tong and Brewer have stated that absorption bands between 900–800 nm are characteristic of six-coordinate Cu(II) [15]. Hathaway, *et al.* [16, 17] have suggested that an absorption band in the region 550–670 nm is indicative of a five coordinate-square pyramid (SPY), whereas, an absorption band between 800–850 nm is characteristic of a five-coordinate trigonal bipyramid (TBP). The complex Cu(cbpS) (Structure III) has been shown by X-ray crystallography [18] to have a distorted SPY structure and to exhibit an absorption band at 680 nm [19, 20]. The solid state visible spectrum of Cu(SALDIEN) (Structure III) has been reported [21] to contain absorption bands at 730 and 630 nm. Later, McKenzie and Selvey [22] showed by X-ray crystallography that Cu(SALDIEN) contained a Cu(II) ion in a distorted TBY arrangement. Likewise Freyberg *et al.* have reported the crystal structure of the complex [Cu(2,3-mmbpN)] • $2H_2O$ (Structure III) to be TBY with an absorption band at 833 nm in the solid state [23]. The complex Cu(SALDPT) (Structure III) which is believed to be five coordinate [21] absorbs at 813 nm again indicating TBY geometry. The complex Cu(tfacDPT) (Structure IV) shows an absorption at 805 nm which was assigned a distorted SPY structure [5] even though previous critera would suggest TBY. More recently, Bereman and Shields [24] have stated that absorption between 833–769 nm is indicative of SPY structures; whereas, absorptions between 1000–909 nm are due to a TBP geometry. The apparent conclusion from this brief review is that the literature is not overly specific with regard to the geometry of five coordinate species. It does, however, offer an opportunity to distinguish six, five and four coordinate Cu(II) complexes from each other.



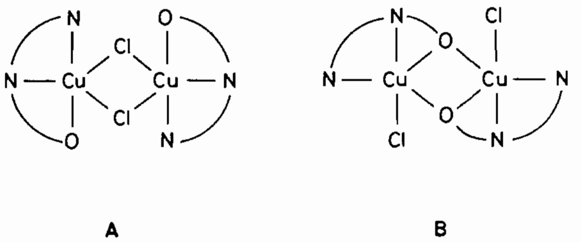
cbps; X = S, Y = Cl, R = C_6H_5, m = n = 3
SALDIEN; X = NH, Y = H, R = H, m = n = 2
SALDPT; X = NH, Y = H, R = H, m = n-3
mmbpN; X = NH, Y = CH_3, R = p-$CH_3C_6H_4$, m = 2, n = 3
SALDAPE; X = O, Y = H, R = H, m = n = 3

Structure III



Structure IV

Cu(Z-SALAMP)Cl and Cu(Z-SALAEP)Cl all fit the criteria for five coordination by exhibiting absorption bands between 860 and 630 nm, Table II. It should be pointed out that this requires that there be bridging Cl$^-$ ions or phenolic oxygen to form the fifth donor atom, Structure VA or VB. From the solid stae data, it would seem that the Cu(Z-SALAMP)Cl complexes are more closely related in their spectral characteristics to that of Cu(cbps) (680 nm) which has previously been shown to be a distorted SPY structure. Whereas, Cu(Z-SALAEP)Cl complexes are more closely related to Cu(SALDPT) (810 nm) which has been assigned a TBY geometry. When the complexes, Cu(Z-SALAEP)Cl, are dissolved in H_2O, DMSO or $CHCl_3$ changes in the visible spectrum are observed. The low energy band located around 840 nm does *not* appear in any of the solution spectra. This result could be interpreted as a change from TBY geometry in the solid state to SPY in solution. In all cases it seems that no six coordinate complexes are prepared when dissolved in donor solvents.



Structure V

As stated previously we were able to synthesize and characterize a set of complexes formulated as Cu(Z-SALAEP)$_2$. The solid state spectra of these materials suggest that they are also five coordinate species. The complexes are not soluble in H_2O in contrast to the behavior of Cu(Z-SALAMP)Cl and Cu(Z-SALAEP)Cl. Two derivatives, Cu(5-CH$_3$OSALAEP)$_2$ andCu(NAPAEP)$_2$, are soluble in DMSO and $CHCl_3$, but the complexes do not show any significant change in their UV–VIS spectra when compared to the solid state spectra indicating no change in Cu(II) geometry. From these additional visible spectral data it seems that these complexes are indeed very much like the five coordinate complex described earlier by Chick and Palenik [14].

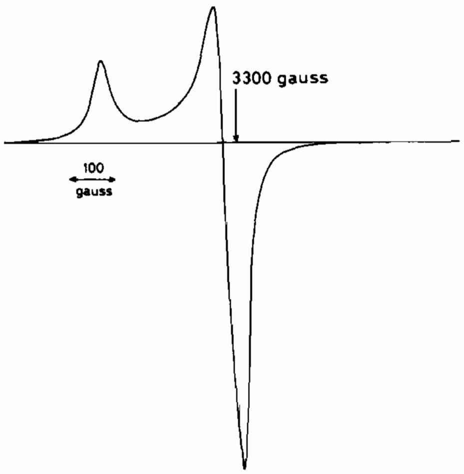


Fig. 1. Powder ESR Spectrum of Cu(5-NO$_2$SALAEP)Cl.

In addition to electronic spectra, electron spin resonance spectra (ESR) were obtained on the complexes in the solid state (powders) at room temperature. The powder ESR spectra of Cu(II) complexes have been shown to be related to the ligand field geometry about the Cu(II) ion [25]. Distinct spectral characteristics are obtained for six, five and four coordinate Cu(II) ions. Employing these ESR spectral characteristics as an indicator of structure, the majority of the complexes reported herein display spectra consistent with a five-coordinate Cu(II) environment, Fig. 1. The exceptions are a) Cu(NAPAEP)Cl and Cu(NAPAMP)Cl which both display spectra described as being 'uninformative' indicating only the presence of exchange coupling, and b) Cu(5-ClSALAMP)Cl whose powder spectrum is consistent with a six coordinate Cu(II) environment. This is in contrast to the visible spectral data which supports a five coordinate Cu(II) environment for Cu(5-ClSALAMP)Cl.

To this point, two physical probes have indicated that the complexes described herein are best characterized as containing 5-coordinate Cu(II) necessitating that dimeric bridging structures be invoked. It is known that when individual Cu(II) ions in a complex are not well separated from each other, spin–spin interactions can occur. These interactions are antiferromagnetic in nature and usually result in a lowering of the magnetic moment from the predicted value. The magnetic susceptibility data in Table I indicate that there is no antiferromagnetic character in the majority of the complexes. Cu(SALAEP)Cl, in contrast, apparently possesses some antiferromagnetic characteristics. It is surprising that these complexes which are postulated to be dimeric in nature do not possess more antiferromagnetic tendencies than they do. Instead magnetic moment values fall within those known for other Cu(II) monomeric systems. It should be mentioned that normal magnetic susceptibility has been seen with a Cu(II) complex, $[Cu(SALDIEN)]_2$, known to contain dimeric type structures with two Cu(II) centers contained within the structure [21, 22].

The first step in the proposed mechanism of action of the Cu–Zn superoxide dismutase enzyme is the reduction of Cu(II) with O_2^{1-} to yield Cu(I) and O_2 [9]. Consequently, we examined the reaction of O_2^{1-} with these Cu(II) complexes and found, unfortunately, that none of the complexes were observed to react with O_2^{1-}. No change in visible spectrum occurred. Also no change in the solution ESR was observed. We also examined the reactions of O_2^{1-} with $Cu(SAL)_2 \cdot 2H_2O$ [3], Cu(SALEN) [27] and Cu(SALDAPE) [21] (Structure III) dissolved in DMSO. No reaction was observed in these cases as well. These results coupled with those found by Valentine and coworkers [9, 10] suggest that the ligand field plays a predominate role in controlling the reactivity patterns of Cu(II) with O_2^{1-}. The geometry of the Cu complex apparently does not provide the overriding factor because Cu(SALEN) is square planar like $Cu(phen)_2X_2$ [10] which reacts with O_2^{1-}; yet, the former fails to react with O_2^{1-}. Five coordination apparently is also not crucial in O_2^{1-} reactivity insofar as 'SAL-type' complexes are concern. The causative factor therefore must be the reduction potential of the Cu(II) which is dictated by the square planar N_4 ligand field in bis(1,10-phenanthroline), phen.

Acknowledgement

We wish to thank Mr. Fred Frederick for making magnetic susceptibility measurements.

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