Inorganica Chimica Acta, 27 (1978) 167–171
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Copper(II) Chelates with Isomeric Schiff-base Ligands. Derivatives of 1- and 2-Adamantanamines

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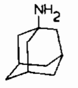
Received July 26, 1977

The syntheses of isomeric copper(II) Schiff base complexes formed by the condensation of 1- and 2-adamantanamines with salicylaldehyde, o*-vanillin and pyrrole-2-carboxaldehyde are described. The electronic structures of the complexes have been probed using electronic absorption and electron paramagnetic resonance (EPR) spectroscopy. The electronic spectra indicate that both the 1- and 2-adamantyl groups lead to distortions from planar geometry with the 1-adamantyl substituted compounds being the most "tetrahedral". The pseudotetrahedral geometries of the 1-adamantyl substituted derivatives are further supported by the comparatively lower isotropic electron spin–nuclear spin hyperfine coupling constants observed in the EPR spectra.*

Introduction

Numerous copper(II) chelates with Schiff base ligands have been prepared and characterized [1–5] but comparatively few studies of chelates with isomeric ligands have been reported. Isomeric N-substituents can profoundly effect the structures of the complexes. Bis(N-n-propylsalicylaldiminato)- and bis(N-isopropylsalicylaldiminato)copper(II) are relevant examples of complexes with isomeric ligands. The N-n-propyl derivative has a planar structure while the N-isopropyl complex is noticeably distorted toward a tetrahedral geometry [6]. The analogous N-n-butyl and N-*tert*-butyl complexes behave similarly [6]. In general, bulky, *i.e.*, other than straight chain, N-substituents, *e.g.* isopropyl, *tert*-butyl and cyclohexyl [7] groups, tend to favor formation of pseudotetrahedral Schiff base complexes. It is thought that a balance of steric factors (repulsive forces) associated with the bulky N-substituents and C–H···O attractive interactions determines the degree of tetrahedral distortion [5].

In view of the above and the relevance of pseudotetrahedral copper(II) complexes to modeling [8–10] the "blue" copper proteins [11] it was deemed worthwhile to examine the spectral and magnetic properties of the copper complexes of the Schiff bases formed by condensing 1-aminoadamantane(I)



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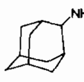

II

and 2-aminoadamantane(II) with salicylaldehyde, 3-methoxysalicylaldehyde (*o*-vanillin) and pyrrole-2-carboxaldehyde. These complexes were also of interest in light of the known antiviral properties of 1-aminoadamantane and medicinal properties of adamantane derivatives [12].

Experimental

The organic ligands employed in this work were synthesized from starting materials purchased from Aldrich Chemical Co., Milwaukee, Wisconsin. Other chemicals were of the best available reagent or spectroscopic grades. Elemental (CHN) analyses were performed by Chemalytics, Inc., Tempe, Arizona and Galbraith Laboratories, Knoxville, Tennessee.

The complexes were prepared by refluxing stoichiometric amounts of the amine hydrochloride, sodium ethoxide and the aldehyde in absolute ethanol for 10 minutes, adding a stoichiometric amount of copper(II) acetate monohydrate, and refluxing the final reaction mixture for an additional 30 minutes. The reaction mixture was then taken to dryness and the complexes extracted with chloroform. The chloroform solutions were filtered and allowed to evaporate to dryness. This latter step was repeated three or four times. The complexes were finally dried over calcium chloride in a desiccator overnight. Analytical results are listed in Table I.

Electronic spectra were obtained with a Cary Model 17 recording spectrophotometer using matched 1.0 cm cells. Mull (transmittance) spectra were obtained by a technique described previously [13]. Electron spin resonance spectra were recorded with a Varian E-3 spectrometer. Quartz sample tubes were employed for powders and chloroform solutions. Spectra were calibrated using diphenylpicryl-

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TABLE I. Analytical Data.

Compound[a]	Color	Calculated			Found		
		%C	%H	%N	%C	%H	%N
Cu(1-ad-sal)$_2$	Black	71.36	7.05	4.90	71.62	7.20	4.80
Cu(2-ad-sal)$_2$	Khaki	71.36	7.05	4.90	71.74	7.35	4.77
Cu(1-ad-van)$_2$	Black	68.39	7.01	4.43	68.74	7.34	4.40
Cu(2-ad-van)$_2$	Brown	68.39	7.01	4.43	67.94	7.27	3.78
Cu(1-ad-pyr)$_2$	Black	69.54	7.39	10.81	69.24	7.14	9.83
Cu(2-ad-pyr)$_2$	Dark Brown	69.54	7.39	10.81	69.34	7.70	10.88

[a] In the abbreviations for the ligands 1-ad and 2-ad indicates 1- and 2-adamantanamine, respectively. Sal, van and pyr indicate the salicylaldehyde, *o*-vanillin and pyrrole-2-carboxaldehyde, respectively, employed in the syntheses of the Schiff-base ligands.

TABLE II. Electronic Spectral Data (Dichloromethane Solutions).

Compound[a]	ν (kK)[b]
Cu(1-ad-sal)$_2$	13.5(208), 20.40(1247)
Cu(2-ad-sal)$_2$	15.7(204), 21.20(1010)sh
Cu(I-ad-van)$_2$	13.00(245)sh 19.10(1274)
Cu(2-ad-van)$_2$	15.50(230)sh 20.40(820)sh
Cu(1-ad-pyr)$_2$	15.75(1400)sh 21.95(3510)sh
Cu(2-ad-pyr)$_2$	14.50(195)sh 18.2(330)

[a] Abbreviations for the complexes are given in a footnote to Table I.

[b] 1 kK = 1000 cm^{-1}. Molar absorptivities (M^{-1} cm^{-1}) in parentheses. Shoulders are indicated by sh.

hydrazyl (DPPH, g = 2.0036) as a field marker. A sample of polycrystalline DPPH taped to a tube containing oxobis(2,4-pentanedionato)vanadium(IV) in benzene served as a double standard for checking field strength, frequency and sweep rate settings [14].

Results and Discussion

Electron Spectra

Table II summarizes the electronic spectra of the copper(II) Schiff base complexes in dichloromethane solution and representative spectra are shown in Figures 1 and 2. The spectra of the corresponding ad-van and ad-sal (see footnote to Table I for abbreviations) complexes are rather similar. In both sets of complexes the 1-adamantane derivatives have a shoulder or band some 2 kK lower in energy than the corresponding 2-adamantane derivatives. We attribute the bands or shoulders at ~ 13 and ~ 15 kK in the ad-sal and ad-van complexes to the manifold of "d–d" transitions [7]. In view of previous analyses of the electronic spectra of Cu(II) Schiff base complexes [7, 15–17], we conclude that the 1-adamantyl

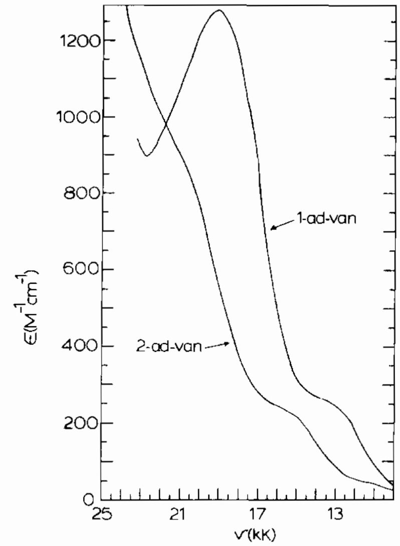

Figure 1. Electronic spectra of Cu(1-ad-van)$_2$ and Cu(2-ad-van)$_2$ in dichloromethane.

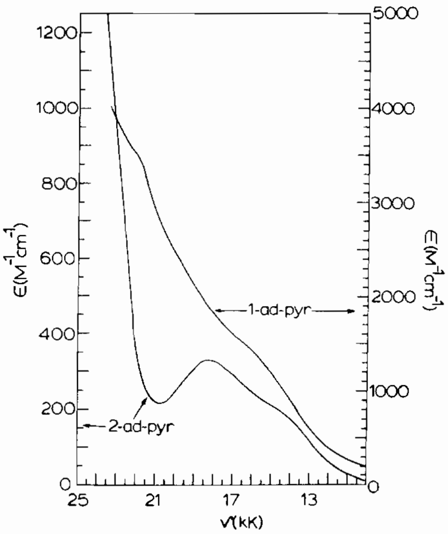

Figure 2. Electronic spectra of Cu(1-ad-pyr)$_2$ and Cu(2-ad-pyr)$_2$ in dichloromethane.

derivatives are more tetrahedral than the 2-adamantyl compounds which are also distorted away from a square planar toward a tetrahedral type geometry. It is well-established that the more tetrahedral the geometry of Cu(II) complexes, the lower the band maximum of the manifold of "d–d" electronic excitations. For pseudotetrahedral tetrachlorocuprates(II) a quantitative relationship relating electronic spectra and geometry has been established [18]. The tetrahedral nature of the complexes is also evident in the intensities of the "d–d" bands. Belford and Yeranos [17] demonstrated that centric Cu(II) Schiff base complexes exhibit molar absorptivities, ϵ, of less than 50 M^{-1} cm^{-1} whereas acentric complexes have higher transition moments, *i.e.*, $\epsilon > 50\ M^{-1}$ cm^{-1}. The spectra of 1-ad-sal and 1-ad-van complexes compare rather closely with the spectrum of "tetrahedral" [6] bis(N-t-butylsalicylaldiminato)copper(II) in chloroform (ν = 13.40 kK, ϵ = 180) [16]. The bands in the region 19–22 kK can presumably be assigned to $\pi^* \rightarrow$ d or ligand $\pi \rightarrow \pi^*$ transitions [15].

The spectra of the pyrrole-2-carboxaldehyde derivatives (Figure 2) differ somewhat from those of the ad-sal and ad-van complexes although the conclusion that the 1-adamantyl derivative is more tetrahedral than the 2-adamantyl derivative seems warranted. The lower symmetry of the 1-ad-pyr complex is also evident in the markedly higher molar absorptivity. The intensities of the spectra of Cu(1-ad-pyr)$_2$ and Cu(2-ad-pyr)$_2$ exceed that of Cu(N-t-butyl-pyr)$_2$ [19] which has an established [7] pseudotetrahedral geometry.

Electron Paramagnetic Resonance Spectra

Typical EPR spectra are shown in Figures 3–5 and the data are summarized in Table III. The lower than axial symmetry of Cu(1-ad-sal)$_2$ and Cu(1-ad-van)$_2$ is evidenced in the EPR spectra of the pure compounds which show three well-resolved g-values (*e.g.*, Figure 3). The other compounds yielded spectra typical of tetragonal type geometries. All of the complexes have rather similar spectra in frozen dichloromethane (77 °K) solutions. In no instance was nitrogen superhyperfine splitting resolved even under high gain and expanded scale settings.

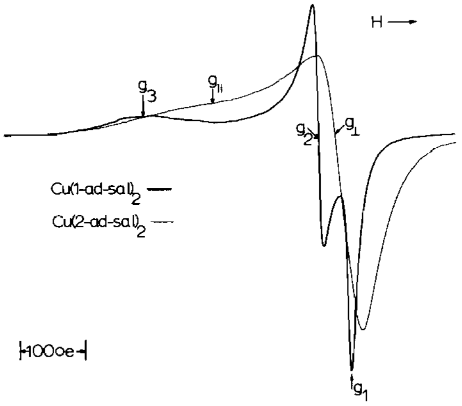

Figure 3. Electron paramagnetic resonance spectra of polycrystalline Cu(1-ad-sal)$_2$ and Cu(2-ad-sal)$_2$. Room temperature.

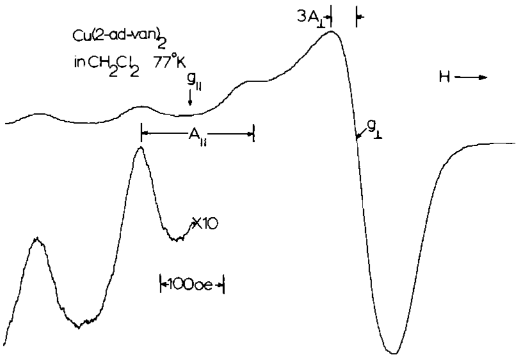

Figure 4. Frozen solution electron paramagnetic resonance spectrum of Cu(2-ad-van)$_2$.

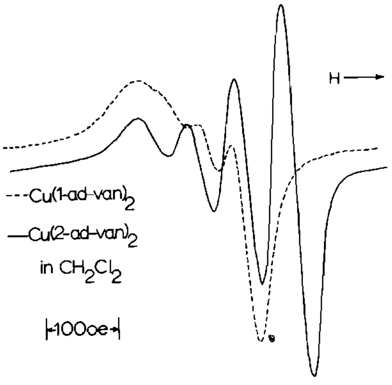

Figure 5. Room temperature solution electron paramagnetic resonance spectra of Cu(1-ad-van)$_2$ and Cu(2-ad-van)$_2$.

Extensive studies of planar CuN$_2$O$_2$ chromophore Schiff base complexes [7, 20–24] have established that $g_\parallel$ and $A_\parallel$ values of 2.10–2.23 and 165–205 X 10^{-4} cm^{-1}, respectively, are to be expected. The data in Table III show that the 2-ad-sal and 2-ad-van complexes yield EPR spectra with spin-Hamiltonian parameters within the range expected for roughly planar CuN$_2$O$_2$ chromophores whereas the 1-adamantyl complexes are more tetrahedral than the 2-adamantyl derivatives. Similarly, data for CuN$_4$ chromophore Schiff base complexes [25–27] are indicative of a more planar geometry for Cu(2-ad-pyr)$_2$ than Cu(1-ad-pyr)$_2$. Unfortunately, the frozen solution EPR spectra of the pyrole-2-carboxaldehyde compounds are not as well resolved and the anisotropic spectra are not as definitive in providing geometry assignments.

The isotropic EPR spectra of dichloromethane solutions (Table III, Figure 5) show that the isotropic ^{63,65}Cu nuclear hyperfine coupling constants are

TABLE III. Electron Paramagnetic Resonance Data.

Compound	Lattice	g-Values[a]	A-Values ($\times 10^4$ cm^{-1})[b]
Cu(1-ad-sal)$_2$	Pure powder	$g_\perp = 2.051$	Not resolved
		$g_2 = 2.085$;	
		$g_3 = 2.261$	
		$\langle g \rangle = 2.132$	
	CH_2Cl_2, RT	$g_0 = 2.144$	$A_0 = 43.8$
	CH_2Cl_2, 77°K	$g_\perp = 2.089$	$A_\perp = 22.4$
		$g_\parallel = 2.262$	$A_\parallel = 145.2$
		$\langle g \rangle = 2.147$	$\langle A \rangle = 63.3$
Cu(2-ad-sal)$_2$	Pure powder	$g_\perp = 2.064$	Not resolved
		$g_\parallel = 2.189$	
		$\langle g \rangle = 2.106$	
	CH_2Cl_2, RT	$g_0 = 2.108$	$A_0 = 63.1$
	CH_2Cl_2, 77°K	$g_\perp = 2.068$	$A_\perp = 10.9$
		$g_\parallel = 2.233$	$A_\parallel = 176$
		$\langle g \rangle = 2.123$	$\langle A \rangle = 65.9$
Cu(1-ad-van)$_2$	Pure powder	$g_1 = 2.044$	Not resolved
		$g_2 = 2.088$	
		$g_3 = 2.237$	
		$\langle g \rangle = 2.123$	
	CH_2Cl_2, RT	$g_0 = 2.144$	$A_0 = 48.5$
	CH_2Cl_2, 77°K	$g_\perp = 2.083$	$A_\perp = 19.3$
		$g_\parallel = 2.317$	$A_\parallel = 139$
		$\langle g \rangle = 2.161$	$\langle A \rangle = 59.2$
Cu(2-ad-van)$_2$	Pure powder	$g_\perp = 2.065$	Not resolved
		$g_\parallel = 2.183$	
		$\langle g \rangle = 2.104$	
	CH_2Cl_2, RT	$g_0 = 2.116$	$A_0 = 64.1$
	CH_2Cl_2, 77°K	$g_\perp = 2.057$	$A_\perp = 13.5$
		$g_\parallel = 2.230$	$A_\parallel = 163$
		$\langle g \rangle = 2.115$	$\langle A \rangle = 63.3$
Cu(1-ad-pyr)$_2$	Pure powder	$g_\perp = 2.087$	Not resolved
		$g_\parallel = 2.257$	
		$\langle g \rangle = 2.144$	
	CH_2Cl_2, RT	$g_0 = 2.117$	$A_0 = 62.5$
	CH_2Cl_2, 77°K	$g_\perp = 2.089$	
		$g_\parallel = 2.234$	$A_\parallel = \sim 111$
		$\langle g \rangle = 2.137$	
Cu(2-ad-pyr)$_2$	Pure powder	$g_\perp = 2.087$	Not resolved
		$g_\parallel = 2.046$	
		$\langle g \rangle = 2.060$	
	CH_2Cl_2, RT	$g_0 = 2.113$	$A_0 = 63.2$
	CH_2Cl_2, 77°K	$g_\perp = 2.079$	Not resolved
		$g_\parallel = 2.218$	
		$\langle g \rangle = 2.125$	

[a] $\langle g \rangle = 1/3(g_1 + g_2 + g_3)$ or $1/3(2g_\perp + g_\parallel)$. g_0 = isotropic g-value. All g values ± 0.005. [b] $\langle A \rangle = 1/3(2A_\perp + A_\parallel)$. All A values $\pm 0.8 \times 10^{-4}$ cm^{-1}.

larger for the 2-adamantyl substituted chelates than for the 1-adamantyl derivatives. A number of studies [7–10, 23, 28–31] have demonstrated that the more tetrahedral the complex, the smaller the nuclear hyperfine coupling constant. The origin of the small nuclear hyperfine coupling constants has been largely attributed to 4p orbital mixing into the ground state [32–35]. The present complexes can be expected to be distorted in such a way as to have no, *i.e.*, C_1, symmetry. This means that the ground state will be a mixture of all of the metal d, s, and p orbitals. The nuclear hyperfine coupling constants of centrosymmetric Cu(II) compounds, which arise from core polarization, have a negative sign. The admixture of 4s character into the ground state in noncentrosymmetric complexes provides a positive contribution [36] to the hyperfine splitting thus reducing the observed hyperfine coupling constant. Yokoi [29] has commented on this problem and the difficulties in sorting out the various contributions to the observed hyperfine coupling constants. Nonaka *et al.* [23] have also noted that among the various factors contributing to the failure to observed ^{14}N-superhyperfine splitting is the distortion from square planar geometry.

Inspection of (Benjamin–Maruzen) molecular models of the compounds shows that the 2-adamantyl derivatives are very similar to bis(N-isopropylsalicylaldiminato)copper(II) [6] ($A_0 = 61.4 \times 10^{-4}$ cm^{-1} in chloroform [7]) whereas the 1-adamantyl compounds should have significant repulsive interactions between the 1-adamantyl group and the aromatic portion of the chelate derived from the parent aldehyde. This indicates that the 1-adamantyl group behaves sterically much like a t-butyl moiety (bis-(N-t-butylsalicylaldiminato)copper(II) [6], $A_0 = 41.6 \times 10^{-4}$ cm^{-1} in chloroform [7]).

In summary, ESR and electronic spectral studies of Cu(II) Schiff base complexes derived from 1- and 2-adamantanamines have noncentric geometries and have properties related to corresponding isopropyl and t-butyl compounds.

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