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Metal Complexes of Aminoacids and their Derivatives.
Part XIV. Magnetic and Spectroscopic Studies of Complexes of Copper(II) and Nickel(II) with the Schiff Base N-salicylidenearginine

SHUI-TSE CHOW, D. M. JOHNS and C. A. McAULIFFE
Department of Chemistry, University of Manchester, Institute of Science and Technology, Manchester M60 1QD
and
D. J. MACHIN
Department of Chemistry, University of Manchester, Manchester M13 9PL, U.K.

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The preparation is described of complexes of copper(II) and nickel(II) with the Schiff base derived from salicylaldehyde and L-arginine. Infra-red and electronic spectra and magnetic susceptibilities from 300–80K are reported for the complexes $CuLNO_3$, $CuLNO_3 \cdot H_2O$, $CuLCl \cdot 2H_2O$, $NiLNO_3$, and $NiLCl \cdot H_2O$ (L = N-salicylidinearginine). Both of the copper–nitrate complexes are antiferromagnetic ($T_N = 250$ K) and a tetrametic structure is proposed. The chloride appears to be a mixture of the same tetrameric species and a magnetically dilute form which may be dimeric. Both of the nickel complexes obey Curie–Weiss laws with $\theta = 20K$ and $30K$ for the nitrate and chloride. Their low magnetic moments suggest that they may be mixtures of octahedral and square-planar configurations.

Introduction

Transition metal complexes of salicylaldehyde–aminoacid Schiff bases are analogous to those of pyridoxal–aminoacid Schiff bases which are of considerable biological importance in such systems as nonenzymatic catalysed transamination reactions [1–3]. Recently, interest has focused on the activation of the α-CH position of Schiff bases derived from amino acids [4–6] and the synthetic applications of these Schiff base complexes [7, 8].

In view of the fact that the electronic spectra of the metal complexes of salicylaldehyde–aminoacid Schiff bases are similar to those of pyridoxal–aminoacid Schiff bases [9], even though the former form more stable complexes [10, 11], the results drawn from the simpler salicylaldehyde–aminoacid systems may well be applicable to the more complicated pyridoxal–aminoacid systems [12].

Although transition metal complexes of Schiff bases have been extensively investigated [13] those derived from salicyldehyde and aminoacids are relatively less well known [14–22]. With dibasic aminoacids such as ornithine and lysine, chemical and spectrophotometric observations showed [23] that condensation with aromatic aldehyde (1 mol) occurs at the terminal aminogroup, but arginine behaves like a simple monobasic α-aminoacid. Only in one case is a $N^{\alpha,\omega}$-disalicylidene derivative known – a copper(II) complex of a lysine derivative [24].

In this study the nickel(II) and copper(II) complexes of Schiff bases derived from salicylaldehyde and L-arginine have been investigated, in order to elucidate their structures, and also to see if the unusual behaviour of simple complexes of L-arginine [25–27] was extended to their Schiff base analogues.

Experimental

L-Arginine (Koch-Light Ltd.), salicylaldehyde, cupric and nickel(II) salts (all from British Drug Houses Ltd.) were used without further purification.

N-Salicylidenearginine was prepared by refluxing a suspension of L-arginine (0.1 mol) and salicylaldehyde (0.1 mol) in 95% ethanol (100 cm^3) for 2–3 hr after which a bright yellow crystalline precipitate formed. The solid was filtered, washed twice with 95% ethanol and acetone (2 X 25 cm^3) and then dried *in vacuo* over anhydrous calcium chloride.

Metal complexes of N-salicylidenearginine were prepared by the following methods.

A. A mixture of L-arginine (0.002 mol) and salicylaldehyde (0.002 mol) in 95% ethanol (50 cm^3) was reacted with metal salt (0.002 mol). Upon cooling to room temperature the crystalline solid precipitated, was filtered, washed with 95% ethanol and acetone (2 X 25 cm^3 and dried *in vacuo* over anhydrous calcium chloride.

B. To a suspension of N-salicylidenearginine (0.001 mol) in 95% ethanol (50 cm^3) was added the metal salt (0.001 mol) and the mixture refluxed for several hours. Upon cooling to room temperature the microcrystalline solid precipitated. This was

TABLE I. Physical, Analytical, and Spectroscopic Data of the Complexes.

Complex	Prep.	M. Pt. °C	Analyses[a]			Infra-red Spectra (cm^{-1})					Electronic Spectra (cm^{-1})
			%C	%H	%N	ν(NH)	ν(C=N)	$\nu(COO^-_{asym})$	$\nu(COO^-_{sym})$	NO_3^-	
Cu(Sal–ArgH)NO_3	A	212	38.5(38.6)	4.5(4.2)	17.1(17.3)	3348s, sp; 3285m, sh	1667s, sp	1634s, br	1380s, br	823m, sp	15,250
Cu(Sal–ArgH)NO_3·H_2O	B	208	36.9(37.1)	4.4(4.5)	16.7(16.6)	3330s, sp; 3280m, sh	1666s, sp	1634s, br	1386s, br	823m, sp	15,250
Cu(Sal–ArgH)Cl·$2H_2O$	A, B	164	37.9(37.8)	5.1(5.1)	13.8(13.5)	3325s, sp; 3250m, sh	1653s, sp	1620s, sp	1402s, sp		14,900
Ni(Sal–ArgH)NO_3	C	230	39.7(39.4)	4.3(4.2)	17.5(17.6)	3340s, sp; 3270m, sh	1675s, sp	1645s, br	1385m, br	824m, sp	10,900; 17,600
Ni(Sal–ArgH)CL·H_2O	C	220	40.2(40.0)	5.2(5.1)	15.3(15.6)	3330s, sp; 3250w, sh	1670s, sp	1640s, br	1392m, sp		10,800; 17,500
Sal–ArgH_2		196	55.1(56.1)	6.6(6.5)	20.0(20.2)	3368s; 3310w, sh	1658s, sp	1630s, br	1403m, sp		

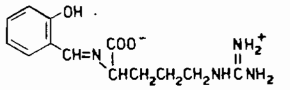
[a] Found (Calculated).

filtered, washed with 95% ethanol and acetone (2 X 25 cm^3) and dried *in vacuo* over anhydrous calcium chloride.

C. L-Arginine (0.002 mol) was dissolved in water (10 cm^3) and treated with salicylaldehyde (0.002 mol) in 95% ethanol (40 cm^3). The resulting pale yellow solution was heated to 50 °C and then treated with the metal salt (0.002 mol). The precipitate was filtered, washed with 95% ethanol and acetone (2 X 25 cm^3) and dried *in vacuo* over anhydrous calcium chloride. Physical measurements were obtained as previously described [28].

Results and Discussion

Regardless of the molar ratio of salicylaldehyde to L-arginine a 1:1 Schiff base was obtained from all preparations. In order to determine which of the amine groups of arginine is involved in the condensation with the aldehyde the infrared spectra of salicylaldehyde, arginine, and the condensation product were compared and assigned (Table). From the infrared assignments of known Schiff bases such as N^α-benzylidenearginine [29] and of those prepared by Brooks and Morman [30] it can be reasonably suggested that condensation takes place at the α-amino group to produce N-salicylidenearginine (I)



(I)

Copper(II) Complexes

The electronic reflectance spectra of the copper(II)–N-salicylidenearginine complexes (Table) are consistent with spin-doublet species reported for copper(II)–Schiff base complexes obtained from amino acids [5, 18, 31]. The consistent absorption maxima *ca.* 15,000 cm^{-1} strongly suggest a common Cu(II) chromophore composed of the NO_2 donor atoms from the Schiff base and two or three additional ligands [20, 21, 32, 33]. However, the infrared spectra of the nitrate compounds (Table) are not indicative of a coordinated nitrato ligand [34].

The magnetic susceptibility data as a function of temperature for the copper(II) complexes are shown in Figures 1–3, and two types of magnetic behaviour is observed. In the case of the nitrate compounds the plots of magnetic susceptibility *versus* temperature (Fig. 1) are characteristic of antiferromagnetic interaction [35]. This may suggest a binuclear structure as envisaged for acetylacetonemono(*o*-hydroxyanil)-copper(II) [36]. But more recently Hatfield and Inman [37] have postulated a tetrametallic structure to explain such behaviour, and Carlisle and co-workers [19] have used this model, (II),

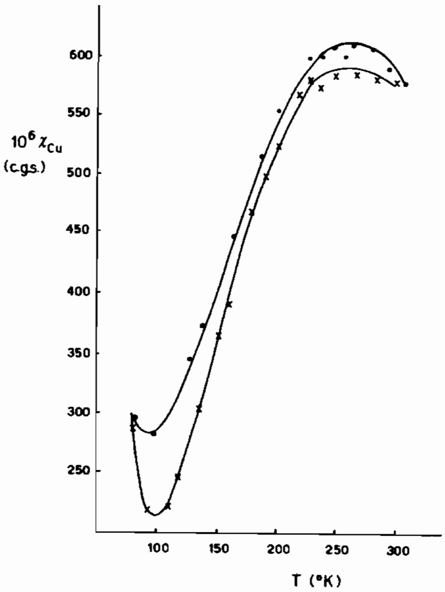
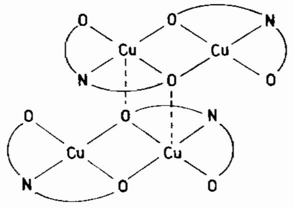


Figure 1. Magnetic susceptibilities (in c.g.s units) *vs.* temperature for (A), [Cu(Sal–ArgH)]NO_3 and (B), [Cu-(Sal–ArgH)]-$NO_3 \cdot H_2O$.



(II)

to explain the anomalous magnetic behaviour of N-salicylidene–L-valinatocopper(II).

The plot of magnetic susceptibility *versus* temperature of Cu(Sal–ArgH)Cl$\cdot 2H_2O$ (Fig. 2) is highly unusual and shows that this complex does not obey a Curie–Weiss law, nor is it characteristic of either ferromagnetism or antiferromagnetism. Kobayashi and co-workers [38] explained a similar χ *vs.* T curve for 2,5-dihydroxy-*p*-benzoquinonatocopper(II) as a sum of an antiferromagnetic and a Curie–Weiss component. Similar procedures were adopted by Inone and co-workers [39] and Ison and Kokot [40] to explain like unusual behaviour in copper(II) complexes. We thus suggest that the observed magnetic susceptibility of Cu(Sal–ArgH)Cl$\cdot 2H_2O$ may be the sum of a Curie–Weiss law component and an antiferromagnetic component as shown schematically in Fig. 3. The fact that the maximum near 250 °K of the proposed antiferromagnetic component coincides with that of Cu(Sal–ArgH)NO_3 and Cu(Sal–ArgH)$NO_3 \cdot H_2O$ is evidence of the merit of the proposed scheme. We thus tentatively suggest the presence of two structural types in this complex.

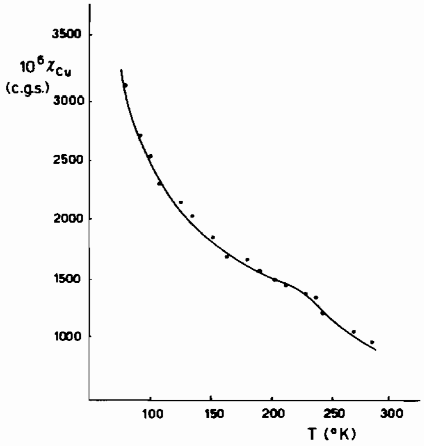


Figure 2. Magnetic susceptibilities (in c.g.s. units) *vs.* temperature for [Cu(Sal–ArgH)]Cl$\cdot 2H_2O$.

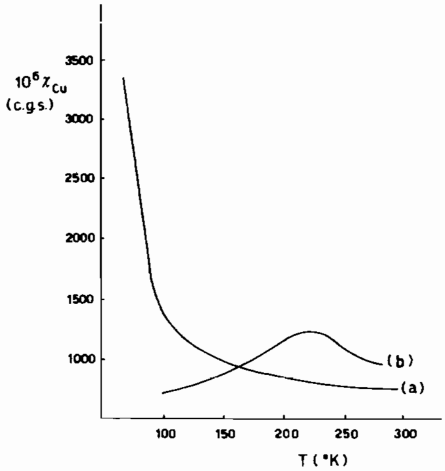
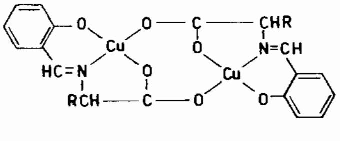
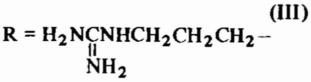


Figure 3. Illustration of contributions from (a) paramagnetic and (b) antiferromagnetic species which will give rise to the curve of Figure 2.

Kishita and Kubo [41] have proposed a binuclear structure for the copper(II) complex of 4-nitrosalicylidene–anthranilic acid (which has a magnetic moment greater than the spin-only value) in which a bidentate bridging carboxylate group is involved. It is significant that the asymmetric carboxylate stretching frequency in Cu(Sal–ArgH)Cl$\cdot 2H_2O$ is distinctly lower than in the nitrato complexes (Table), and this is in accord with data which suggests a bridging bidentate carboxylate group [26, 42]. Thus a structure such as (III) would explain the Curie–Weiss component.

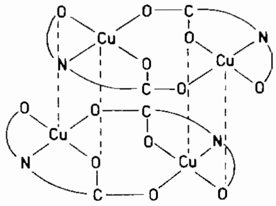


(III)



$R = H_2N\underset{\underset{NH_2}{\|}}{C}NHCH_2CH_2CH_2-$

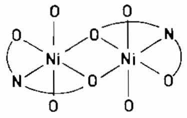
And to account for the antiferromagnetic component structure (III) may be combined with Hatfield and Inman's tetrametallic model. Thus, a structure similar to (IV) seems to be a suitable fit


(IV)

for Cu(Sal–ArgH)Cl·$2H_2O$, in which superexchange interaction occurs between the pairs of copper atoms Cu(1)–Cu(3) and Cu(2)–Cu(4) and results in the observed antiferromagnetism. Since the superexchange interaction is expected to be weak due to the distance between the two binuclear layers, the experimental results (Fig. 2) are in agreement with this as they indicata a predominantly Curie–Weiss component.

Nickel(II) Complexes

The electronic reflectance spectra of Ni(Sal–ArgH)NO_3 and Ni(Sal–ArgH)Cl·H_2O (Table) are typical of a pseudoctahedral configuration [43], and as they are almost identical this suggests that the anions are not coordinated. Moreover, the infrared spectrum of the nitrate derivative indicates ionic nitrate, and no ν(Ni–Cl) band is seen in the chloride. Thus, a dimeric octahedral structure, (V), of the type suggested by Theriot and co-workers [21] for nickel(II) complexes of N-salicylideneaminoacids may be thought applicable. However, the low magnetic moments of


(V)

these complexes suggest that this is not a simple system. The plots of reciprocal susceptibility *vs.* temperature (Fig. 4) obey Curie–Weiss laws rather rigorously and the calculated Weiss constants, θ, are surprisingly large ($\theta = -20$ °K for nitrate; $\theta = 30$ °K for chloride). The susceptibility is independent of field strength indicating an absence of ferromagnetism.

Anomalous magnetic behaviour of nickel(II) complexes in the solid state may result from either spin–spin equilibria [44, 45] or configurational equilibria [46, 47]. The fact that the Curie–Weiss law is obeyed would seem to preclude any possibility of a spin–spin equilibrium, as this would entail an increase of susceptibility with temperature. Although we have no direct evidence for the coexistence of more than one configuration, a configurational equilibrium is indirectly suggested by the observed low magnetic moments. By assuming an equilibrium between paramagnetic octahedral (a value of 3.2 B.M. is the average of magnetic moments of nickel(II) complexes of N-salicylidene aminoacids [21]) and diamagnetic square planar configurations it can be calculated that the ratio of octahedral:planar types is approximately 3:2 for both nitrate and chloride. We thus suggest that these complexes are mixtures of the octahedral configuration (V), in which the octahedral sites are completed by bridging carbonyl oxygens or water molecules (in the case of the chloride),

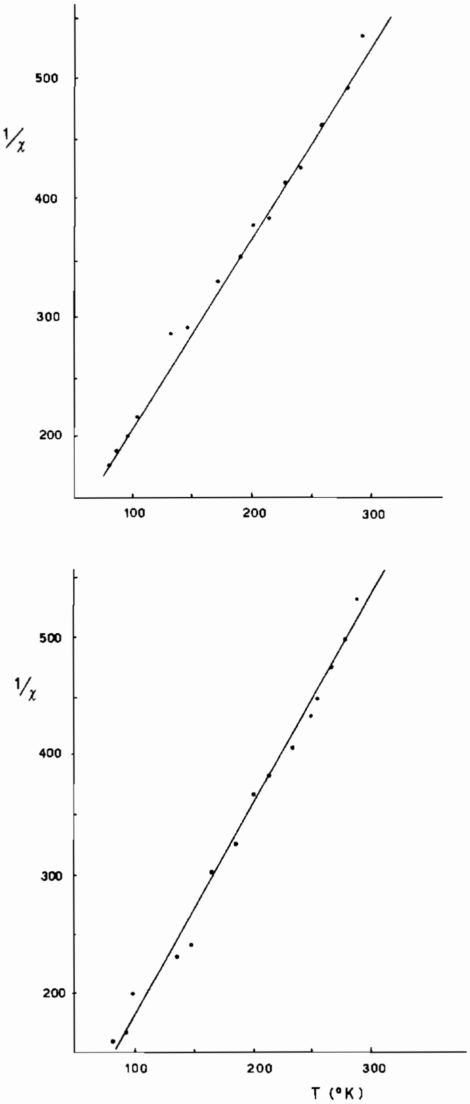
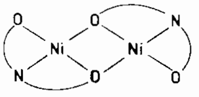


Figure 4. Inverse magnetic susceptibilities (in c.g.s. units) *vs.* temperature for (A), [Ni(Sal–ArgH)]Cl·H_2O and (B), [Ni(Sal–ArgH)]NO_3.


(VI)

and the planar configuration (VI).

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