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Synthetic, Spectroscopic, Magnetic, and X-ray Structural Studies on a Vitamin B_6–Amino Acid Schiff Base Complex, Aqua(5′-phosphopyridoxylidenetyrosinato)copper(II) Tetrahydrate

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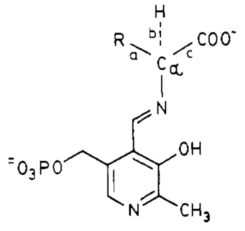
A Schiff base metal complex, $[Cu^{II}(PLP\text{–}DL\text{-tyrosinato})(H_2O)]\cdot 4H_2O$ (PLP = pyridoxal phosphate), with the molecular formula $CuC_{17}O_{13}N_2H_{27}P$ has been prepared and characterized by magnetic, spectral, and X-ray structural studies. The compound crystallizes in the triclinic space group $P\bar{1}$ with $a = 8.616$ (2) Å, $b = 11.843$ (3) Å, $c = 12.177$ (3) Å, $\alpha = 103.40$ (2)°, $\beta = 112.32$ (2)°, $\gamma = 76.50$ (1)°, and $Z = 2$. The structure was solved by the heavy-atom method and refined by least-squares techniques to a final R value of 0.057 for 3132 independent reflections. The coordination geometry around Cu^{II} is distorted square pyramidal with phenolic oxygen, imino nitrogen, and carboxylate oxygen from the Schiff base ligand and water oxygen as basal donor atoms. The axial site is occupied by a phosphate oxygen from a neighboring molecule, thus resulting in a one-dimensional polymer. The structure reveals π–π interaction of the aromatic side chain of the amino acid with the pyridoxal π system. A comparative study is made of this complex with similar Schiff base complexes. The variable-temperature magnetic behavior of this compound shows a weak antiferromagnetic interaction.

Introduction

PLP–amino acid Schiff bases are key intermediates in a variety of metabolic reactions involving amino acids, such as decarboxylation, transamination, racemization, and C–C bond cleavage, which are catalyzed by enzymes that require PLP as a cofactor.[1] These reactions usually proceed by the labilization of one of the three bonds a–c to the amino acid α-carbon atom (see structure Ia). Dunathan[2] has suggested that the bond to be labilized must be oriented perpendicular to the π system of the Schiff base as the result of minimization of the energy of the transition state for bond breaking by allowing maximum σ–π overlap. Further, the enzyme governs reaction specificity by controlling the conformation around the N–C_α bond.[3] In model systems metal ions promote these reactions by maintaining the planarity of the conjugated system in the aldimine or ketimine intermediates and by acting as "superacids", drawing electrons away from the C_α–H bond through binding to the aldimine nitrogen.[4] A number of studies have been undertaken on these systems both in the solid state and in solution with the aim of elucidating the mechanism of the reactions.[5,6]



Ia

Tyrosine plays an important role in living organisms, not only by acting as a building unit in proteins but also by taking part in the biosynthesis of hormones, neurotransmitters, and pigments.[7] Both decarboxylation and transamination are of importance in these processes. Tyrosine transaminase and pyridoxal kinase are some of the enzymes[8] that require both PLP and tyrosine at the active site for their reactivity. A study of the stereochemistry of vitamin B_6–tyrosine Schiff base systems with metal ions, which can mimic enzymatic reactions in model systems, would therefore be of considerable interest from the mechanistic point of view.

In this paper we report for the first time the synthesis, magnetic and spectral studies, and X-ray crystal structure of a copper complex with PLP–tyrosine Schiff base, an intermediate for nonenzymatic transamination reaction, and a comparative study of this complex with similar systems.

Experimental Section

Preparation of the Complex. PLP (1 mmol) was dissolved in warm water, and the solution was cooled to room temperature. This solution was added to an acidified aqueous solution (0.1 N HNO_3) of DL-tyrosine, and the new solution was heated at 65 °C for 20 min. The pH was adjusted to ca. 6 by adding 0.1 N NaOH. To this was added aqueous $Cu(NO_3)_2\cdot 3H_2O$ (1 mmol). The resultant mixture was stirred at 55–60 °C till the tyrosine completely dissolved. After numerous unsuccessful attempts green platelike crystals suitable for X-ray diffraction were finally obtained by evaporation (yield 78.8%). Anal. Calcd for $CuC_{17}O_{13}N_2H_{27}P$: C, 36.33; N, 4.99; H, 4.81. Found: C, 36.99; N, 5.22; H, 4.43.

Physical Measurements. The electronic spectra of the compound were recorded with a Hitachi Model U-3400 spectrophotometer. The infrared spectra were obtained by using a Perkin-Elmer 599 spectrometer on a Nujol mull as support in the 4000–600-cm^{-1} spectral range. The ESR spectrum was recorded on a Varian E109 spectrometer. C, H, and N analysis was done by using a Perkin-Elmer 240 elemental analyzer.

Variable-temperature magnetic susceptibility data were obtained by the Faraday method using a Cahn 2000 microbalance and a Lewis-coil magnetometer. The calibrant was $HgCo(NCS)_4$. The susceptibility data were corrected for diamagnetism by using Pascal constants.[12]

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Table I. Summary of Crystallographic Data

mol formula	$CuC_{17}O_{13}N_2H_{27}P$
mol wt	561.54
cryst system	triclinic
space group	$P\bar{1}$
a/Å	8.616 (2)
b/Å	11.843 (3)
c/Å	12.177 (3)
α/deg	103.40 (1)
β/deg	112.00 (2)
γ/deg	75.50 (1)
V/Å^3	1106
Z	2
F(000)	582
ρ(calcd)/g cm^{-3}	1.686
ρ(obsd)/g cm^{-1} ^{a}	1.66
diffractometer	CAD 4
radiation (λ/Å)	graphite-monochromated Mo Kα (0.71073)
temp/°C	21
reflcns measd	$+h,\pm k,\pm l$
scan type	$\omega/2\theta$
θ range/deg	1.0–25.0
no. of measd reflcns	4819
no. of obsd unique reflcns	3132 ($F_o > 3\sigma(F_o)$)
cryst size/mm	0.32 × 0.25 × 0.19
abs coeff/cm^{-1}	11.6
transm coeff	0.96–1.05^b
weightg scheme (w)	$[\sigma^2(F_o) + 0.000F_o^2]^{-1}$
R^c	0.057
R_w^d	0.062

^{a}By flotation in $CHCl_3$ + $CHBr_3$. ^{b}Normalized to an average of unity. $^c R = \sum |F_o - |F_c|| / \sum F_o$. $^d R_w = [\sum w(F_o - |F_c|)^2 / \sum F_o^2]^{1/2}$.

X-ray Data Collection and Processing. Preliminary cell parameters, determined by rotation and Weissenberg photographs, were refined by a least-squares procedure applied to 23 carefully centered reflections on a CAD4 single-crystal diffractometer. Details regarding the data collection and processing are presented in Table I. The data were corrected for Lorentz, polarization, and absorption effects.[13]

X-ray Structure Solution and Refinement. The structure was solved by conventional Patterson and Fourier methods. All the hydrogen atoms, except those belonging to the tyrosine hydroxyl group and lattice waters, were located from difference electron density maps and their positions and isotropic temperature factors refined. Lattice water oxygen atom O(W5) and hydrogen atom H(1) attached to N(1) showed very large shifts both in positional coordinates and temperature factors, and therefore, these parameters were fixed during the refinement. The shifts in parameters in the last cycle was less than 0.1σ for non-hydrogen atoms. Final residuals R and R_w are 0.057 and 0.062, respectively. The final difference electron density map revealed no significant electron density except a few peaks less than 0.8 e Å^{-3} at distances 0.6–0.9 Å from the heavy atom.

Major calculations were performed on a DEC 1090 computer using the SHELX-76 system of programs[14] for Fourier and least-squares calculations and ORTEP-II[15] and PLUTO-78[16] programs for diagrams. Calculations other than those specifically noted were performed with locally written programs. The scattering factors for H, C, N, O, and P were used as available in the SHELX-76 program, and for Cu they were taken from ref 17 (anomalous dispersion corrections applied). The final atomic coordinates are given in Table II.

Results

Table II. Fractional Atomic Coordinates [for Copper (×10^5) and for the Rest (×10^4)] and Equivalent Isotropic Temperature Factors (×10^4) with Their ESD's in Parentheses^a

atom	x	y	z	U(iso), Å^2
Cu	20138 (6)	6506 (4)	47985 (4)	187 (2)
O(W1)	3972 (4)	591 (3)	6278 (2)	443 (13)
N(1)	−1842 (5)	4726 (3)	5375 (3)	371 (16)
C(1)	−395 (6)	3987 (4)	5734 (4)	324 (17)
C(2)	−194 (5)	2841 (4)	5106 (3)	294 (16)
C(3)	−1580 (5)	2505 (3)	4102 (3)	274 (15)
C(4)	−3116 (5)	3313 (4)	3754 (4)	298 (16)
C(5)	−3194 (5)	4409 (4)	4387 (4)	383 (19)
C(6)	974 (6)	4408 (4)	6856 (4)	460 (20)
C(7)	−4649 (6)	3013 (4)	2725 (4)	366 (18)
O(1)	1248 (4)	2172 (3)	5528 (3)	371 (12)
O(2)	−5253 (3)	2040 (2)	2865 (2)	333 (11)
P	−6366 (1)	2242 (1)	3710 (1)	288 (4)
O(3)	−5226 (4)	2738 (3)	4990 (2)	364 (12)
O(4)	−7865 (4)	3174 (2)	3334 (3)	390 (12)
O(5)	−6666 (3)	1037 (2)	3663 (2)	324 (11)
C(8)	−1512 (5)	1335 (4)	3389 (3)	304 (16)
N(2)	−163 (4)	553 (3)	3546 (3)	293 (13)
C(9)	−213 (5)	−543 (4)	2712 (3)	327 (16)
C(10)	1289 (6)	−1456 (4)	3305 (3)	329 (17)
C(11)	86 (6)	−368 (5)	1585 (4)	450 (20)
O(6)	2462 (4)	−1063 (2)	4243 (2)	354 (12)
O(7)	1331 (5)	−2484 (3)	2835 (3)	482 (14)
C(12)	−1348 (7)	420 (5)	829 (4)	455 (21)
C(13)	−1274 (7)	1578 (5)	929 (4)	567 (24)
C(14)	−2579 (8)	2299 (6)	151 (5)	668 (27)
C(15)	−3926 (8)	1722 (7)	−730 (5)	721 (30)
C(16)	−4033 (8)	593 (6)	−819 (5)	692 (31)
C(17)	−2750 (7)	−28 (6)	−33 (5)	571 (23)
O(8)	−5182 (6)	2417 (5)	−1575 (4)	966 (23)

^{a}The thermal parameter is of the form $U_{eq}(\mathrm{iso}) = {}^1/_3 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

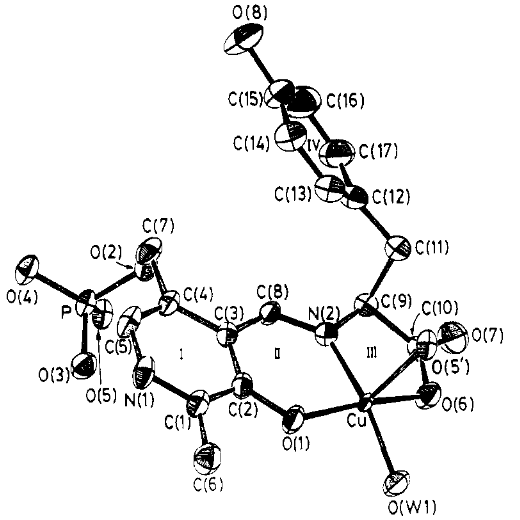

Figure 1. ORTEP drawing of the molecule, showing the atom numbering and thermal motion ellipsoids (50% probability level) for non-hydrogen atoms.

Spectral Studies. The electronic spectrum in aqueous solution, which shows an absorption maximum at 678 nm, is comparable with those reported for some of the square-pyramidal Cu(II) complexes.[18] This is in agreement with the EPR results.

Divalent metal complexes of Schiff bases derived from PL and α-amino acids usually have two characteristic absorption bands in the UV region; the longer λ band at ca. 390 nm has been called the π_1 band, and the shorter one at ca. 270 nm, the π_2 band.[19,20] These bands are assigned as a $\pi \rightarrow \pi^*$ transition of the extended conjugated system formed by the pyridine ring, phenolic oxygen,

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Table III. Bond Lengths (Å) and Angles (deg) Involving Non-Hydrogen Atoms with Their ESD's in Parentheses

Cu–O(W1)	1.955 (3)	P–O(3)	1.562 (3)
Cu–O(1)	1.901 (3)	P–O(4)	1.490 (3)
Cu–O(5′)	2.265 (3)	P–O(5)	1.494 (3)
Cu–N(2)	1.933 (4)	C(8)–N(2)	1.288 (6)
Cu–O(6)	1.980 (3)	N(2)–C(9)	1.449 (5)
N(1)–C(1)	1.331 (6)	C(9)–C(10)	1.540 (6)
N(1)–C(5)	1.375 (6)	C(9)–C(11)	1.553 (6)
C(1)–C(2)	1.402 (6)	C(10)–O(6)	1.285 (5)
C(1)–C(6)	1.502 (7)	C(10)–O(7)	1.219 (5)
C(2)–C(3)	1.407 (6)	C(11)–C(12)	1.501 (7)
C(2)–O(1)	1.299 (6)	C(12)–C(13)	1.363 (8)
C(3)–C(4)	1.423 (6)	C(12)–C(17)	1.390 (8)
C(3)–C(8)	1.456 (6)	C(13)–C(14)	1.422 (9)
C(4)–C(5)	1.348 (6)	C(14)–C(15)	1.436 (9)
C(4)–C(7)	1.488 (6)	C(15)–C(16)	1.338 (11)
C(7)–O(2)	1.437 (6)	C(15)–O(8)	1.431 (8)
O(2)–P	1.598 (3)	C(16)–C(17)	1.354 (9)
O(W1)–Cu–O(1)	86.5 (1)	O(2)–P–O(4)	109.8 (2)
O(W1)–Cu–O(5′)	97.1 (1)	O(2)–P–O(5)	103.9 (2)
O(W1)–Cu–N(2)	166.0 (1)	O(3)–P–O(4)	106.8 (2)
O(W1)–Cu–O(6)	93.4 (1)	O(3)–P–O(5)	111.3 (2)
O(1)–Cu–O(5′)	103.2 (1)	O(4)–P–O(5)	118.5 (2)
O(1)–Cu–N(2)	93.0 (1)	C(3)–C(8)–N(2)	123.9 (4)
O(1)–Cu–O(6)	164.9 (1)	Cu–N(2)–C(8)	127.5 (3)
O(5′)–Cu–N(2)	96.6 (1)	Cu–N(2)–C(9)	113.7 (3)
O(5′)–Cu–O(6)	91.8 (1)	N(2)–C(9)–C(10)	108.3 (4)
N(2)–Cu–O(6)	83.5 (1)	N(2)–C(9)–C(11)	109.3 (4)
C(1)–N(1)–C(5)	122.2 (4)	C(10)–C(9)–C(11)	106.2 (4)
N(1)–C(1)–C(2)	120.5 (4)	C(9)–C(10)–O(6)	116.9 (4)
N(1)–C(1)–C(6)	117.8 (4)	C(9)–C(10)–O(7)	118.7 (4)
C(2)–C(1)–C(6)	121.6 (4)	O(6)–C(10)–O(7)	124.3 (4)
C(1)–C(2)–C(3)	117.6 (4)	C(9)–C(11)–C(12)	113.5 (4)
C(3)–C(2)–O(1)	125.8 (4)	Cu–O(6)–C(10)	114.7 (3)
C(2)–C(3)–C(4)	120.3 (4)	C(11)–C(12)–C(13)	120.9 (5)
C(2)–C(3)–C(8)	122.2 (4)	C(11)–C(12)–C(17)	120.7 (5)
C(3)–C(4)–C(5)	118.6 (4)	C(13)–C(12)–C(17)	118.3 (5)
C(3)–C(4)–C(7)	123.4 (4)	C(12)–C(13)–C(14)	120.7 (5)
C(3)–C(4)–C(5)	118.6 (4)	C(13)–C(14)–C(15)	115.7 (6)
C(3)–C(4)–C(7)	123.4 (4)	C(14)–C(15)–C(16)	124.2 (6)
C(5)–C(4)–C(7)	118.0 (4)	C(14)–C(15)–O(8)	116.2 (6)
N(1)–C(5)–C(4)	120.7 (4)	C(16)–C(15)–O(8)	119.6 (6)
C(4)–C(7)–O(2)	112.0 (4)	C(15)–C(16)–C(17)	116.3 (6)
Cu–O(1)–C(2)	126.9 (3)	C(12)–C(17)–C(16)	124.8 (6)

and imine nitrogen. The lack of the conjugated imine linkage, on the other hand, would cause a shift of these absorption bands to a shorter λ. In the present complex the π_1 band appears as a broad peak in the range 389–381 nm and the π_2 band appears at 271 nm as a weak band, confirming the formation of the Schiff base metal complex.

The IR spectrum of the polycrystalline solid sample with peaks at 1655, 1340, and 1510 cm^{-1} is in good agreement with the literature values reported for similar complexes[21,22] and supports the UV results.

X-ray Structure. The molecular structure and the atom-labeling scheme are shown in Figure 1.

In the structure Cu^{II} has a distorted square-pyramidal geometry. The tetradentate Schiff base exists as a divalent anion with phenolate and carboxylate groups deprotonated and pyridine nitrogen and phosphate group protonated. The copper ion is coordinated by the Schiff base through the phenolate oxygen O(1), carboxylate oxygen O(6), and imino nitrogen N(2), and the fourth basal donor is a water molecule O(W1). The coordination distances are 1.901 (3), 1.980 (3), 1.993 (4), and 1.955 (3) Å, respectively. The axial position is occupied by the phosphate oxygen O(5′) from a neighboring molecule at a longer distance of 2.265 (3) Å, thus resulting in a one-dimensional polymer. The cis bond angles in the basal plane range from 83.5 (1) to 93.4 (1)°, the smallest being that of the five-membered chelate ring. These values are in the range expected for this type of complexes. The four basal atoms show small tetrahedral deviations [−0.008 (2) to +0.011 (4) Å] from the least-squares plane through these atoms (supplementary material Table S-6). The two chelate rings II and III make dihedral angles of 8.10 and 4.87°, respectively, with the basal plane. The Cu(II) ion deviates by 0.2457 (5) Å from this plane. The dihedral angle between the rings I and II is 3.53°.

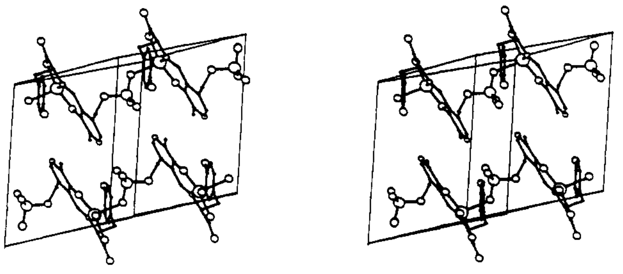
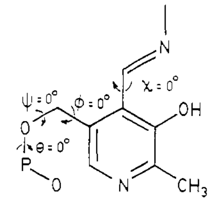


Figure 2. Stereoplot of the molecular packing (down *b*). Centrosymmetrically related molecules have been omitted for clarity.

The heterocyclic ring (I) and benzene ring (IV) are planar, the largest deviations from the best planes being 0.012 (5) and 0.014 (6) Å, respectively. On the other hand, the chelate rings are much less planar. The largest deviations in the case of five-membered and six-membered chelate rings are 0.111 (4) and 0.060 (3) Å, respectively. Torsional angles and asymmetry parameters[23] (supplementary material Table S-7) indicate half-chair confirmations for both the rings.

The bond lengths and bond angles (Table III) in the ligand, except a few that will be discussed later, are in the range observed for similar complexes.[5,6] The value of bond angle C(1)–N(1)–C(5) = 122.2 (4) Å[24] and the location of hydrogen at N(1) indicate that the pyridine nitrogen is protonated. The phosphate group, as a whole, bears a negative charge with O(3) being protonated and the double bond being delocalized along the two short bonds P–O(4) and P–O(5).

From theoretical and solution studies Tamanyan et al.[26] showed that the conformations of PLP imine compounds can be specified by χ, Φ, ψ, and θ values (see structure Ib). The preferred values



Ib

for χ are close to 0°. There are four permitted combinations of Φ and ψ values corresponding to χ = 0°. Here θ is kept constant at 60° because of the symmetry of the phosphate group. In the present complex the values obtained (χ = 5.9°, Φ = 121.1°, ψ = 280.1°) correspond to one of the stable conformations (IVa) deduced for the Schiff base.[26] This brings the phosphate oxygen O(5) of one molecule within the coordinating distance of the copper atom of a translationally related molecule and explains the one-dimensional polymeric nature of this compound.

In the structure, centrosymmetrically related chains of molecules run in zigzag fashion parallel to the *a* axis (Figure 2). The shortest distance between two coppers in the chain is 8.616 Å. The benzene ring makes a dihedral angle of 31.28° with the basal plane. The molecules are held together in the lattice through H-bonds and van der Waals interactions. The pyridine nitrogen, phosphate oxygens, O(4) and O(5), carboxylate oxygens, tyrosine

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Table IV. Selected Bond Lengths (Å) and Angles (deg) in Copper Schiff Base Complexes[35]

no.	compd	C(1)–C(6)	C(3)–C(8)	C(8)–N(2)	N(2)–C(9)	C(9)–C(11)	C(8)–N(2)–C(9)–H(9)	C(9)–H(9)	Cu–N(2)	ref
1	[Cu(PLP–glycinato)(H_2O)]·$3H_2O$	1.49 (2)	1.47 (1)	1.27 (1)	1.47 (1)		62.0	1.07	1.935 (9)	5
							−55.1	1.09		
2	[Cu(PL–DL-valinato)]	1.45 (2)	1.40 (2)	1.34 (2)	1.46 (2)	1.50 (2)	35.7	1.08	1.95 (1)	36
3	[Cu(PL–*O*-phospho-DL-threoninato)(H_2O)]·H_2O	1.479 (6)	1.447 (5)	1.288 (6)	1.464 (4)	1.545 (7)	33.4	0.95 (4)	1.939 (3)	37
4	[Cu(PLP-DL-tyrosinato)(H_2O)]·$4H_2O$	1.502 (7)	1.456 (6)	1.288 (6)	1.449 (5)	1.553 (6)	39.2	1.11 (5)	1.933 (4)	present work

hydroxyl group, and coordinated and lattice waters take part in hydrogen-bond formation. The possible H-bonds and short contacts up to 3.50 Å are given in Tables S-8 and S-9 (supplementary material), respectively.

Magnetic Studies. Magnetic interactions of Cu(II) ions have been the subject of extensive investigations in binuclear and polymeric systems.[27] Schiff base metal complexes have been a source of one-dimensional systems with unusual magnetic and electrical properties.[28] The one-dimensional character of the present complex and the long-range electron transfer, which has been observed in biological systems,[29] prompted us to carry out a variable-temperature (12.6–298.6 K) magnetic susceptibility study. The χ vs T plot showed very weak antiferromagnetic interaction. This prompted us to analyze the system in more detail.

It is well-known that the exchange between Cu(II) ions in chains may be described by the $S = {}^1/_2$ Heisenberg Hamiltonian[30,31]

$$H = -2J\sum[S_z^iS_z^{i+1} + \alpha(S_x^iS_x^{i+1} + S_y^iS_y^{i+1})]$$

where $\alpha = 1$. There are no exact or closed-form solutions for the Heisenberg model for an $S = {}^1/_2$ one-dimensional system.[12,30] However, Hatfield and co-workers[31] have noted that the shape of the reduced magnetic susceptibility curve as obtained by Bonner[30] is similar to that of a serpentine curve and have consequently fitted the susceptibility with a quadratic/cubic function. The following expression for the magnetic susceptibility of linear chains of $S = {}^1/_2$ ions has been derived by them:

$$\chi_{\text{chain}} = \frac{Ng^2\beta^2}{kT}\,\frac{0.25 + 0.14995x + 0.30094x^2}{1.0 + 1.9862x + 0.68854x^2 + 6.0626x^3} \qquad (1)$$

$$x = |J|/kT$$

To estimate the exchange coupling between the chains, the expression for susceptibility can be modified by the addition of a mean-field correction to account for interchain interaction:

$$\chi_{\text{m}} = \chi_{\text{chain}}/(1 - 2ZJ'\chi_{\text{chain}}/Ng^2\beta^2) \qquad (2)$$

In this expression χ_{chain} is the susceptibility of an isolated Heisenberg chain, J' is the exchange parameter, and Z is the number of nearest neighbors. A plot of susceptibility vs temperature is given in Figure 3. The solid line is the least-squares fit to eq 2. In the fitting procedure J and J' were allowed to vary freely. The EPR g value of 2.07 was used. The best-fit values for the parameters obtained were $J = 5.6$ K and $ZJ' = 10.9$ K, with a maximum in the susceptibility at 7.1 K.

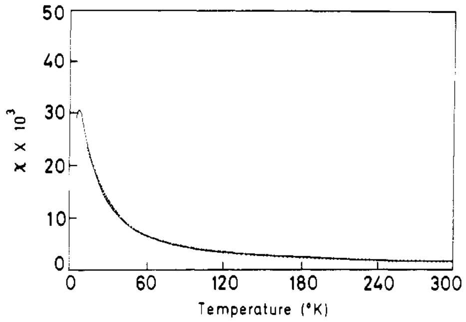

Figure 3. Magnetic susceptibility versus temperature plot for the complex. The solid line is the best fit for the Heisenberg linear-chain $S = {}^1/_2$ model to the data.

The room-temperature EPR spectrum of the polycrystalline sample ($g_\perp = 2.03$ and $g_\parallel = 2.07$) is in agreement with the square-pyramidal coordination observed for copper(II).[18]

Discussion

Complexes of the type under discussion are considered to be catalytic intermediates in the nonenzymatic transamination reactions. It has been reported from NMR studies[32] that, in vitamin B_6 catalyzed reactions, amino acids with aromatic side chains show higher reactivity compared to that of the nonaromatic amino acids. This was attributed to the intramolecular π–π interaction between the pyridoxal π system and the aromatic ring of the amino acid. An examination of the packing diagram (Figure 2) of the present structure shows that in this complex also a part of the pyridoxal π system lie almost above the aromatic ring with the following short contacts (Å): C(8)–C(12) = 3.099, C(8)–C(13) = 3.159, N(2)–C(12) = 3.052, N(2)–C(13) = 3.392.

Since this is the first report[33] on a vitamin B_6–amino acid Schiff base involving an aromatic amino acid, it is instructive to make a comparison with other related structures involving nonaromatic amino acids (Table IV). The table shows that while the estimated standard deviations in bond lengths are considerably large for the structures of compounds **1** and **2**, structure **3** is more accurately determined. Nevertheless, a perusal of the table shows that the N(2)–C(9) bond is the shortest in the present complex, indicating that the nitrogen carries more electrons than usual. This type of partial double-bond character for this bond has been related to the reactivity in transamination processes.[38] There is also a hint of the lengthening of the C(9)–H(9) bond, as compared to

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that in complex 3. The weakening of this bond explains the unexpected racemization[39] that resulted during persistent efforts to prepare the Schiff base complex with the biologically more relevant L-tyrosine.[40] In addition to N(2)–C(9), C(3)–C(8) also shows partial double-bond character. The pyridine ring shows two short bonds of 1.354 (9) and 1.338 (11) Å in agreement with a quinoid structure as in the case of a salicylaldehyde–glycine complex.[41] The C(1)–C(6) bond length is almost normal.[42]

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Supplementary Material Available: Tables S-1–S-9, listing complete positional and thermal parameters, including those of the hydrogen atoms, bond distances and angles involving hydrogen atoms, least-squares planes, selected torsion angles and asymmetry parameters, possible H bonds, and intermolecular short contacts (15 pages); a table of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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(39) Details of this work will be published elsewhere.

(40) To our knowledge, the only Schiff base metal complex having an L-amino acid to be crystallographically characterized is Zn^{II}(PL–L-valine).[6a] A comparison of this structure with the corresponding Ni^{II}-(PL–DL-valine) complex showed that the Schiff base moiety has a similar geometry in both complexes.

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Photoaquation of *cis*-Bis(azine)tetraammineruthenium(II) Complexes, *cis*-$Ru(NH_3)_4(L)(L')^{n+}$ [1]

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Near-UV–visible range photolysis of *cis*-$Ru^{II}(NH_3)_4(L)_2$ (L = pyridine (py), 4-picoline (4-pic), isonicotinamide (isn), or 4-acetylpyridine (4-acpy)) and *cis*-$Ru^{II}(NH_3)_4(isn)(L)$ (L = py, 4-pic, pyrazine, or 4-acpy) leads to isn, L, and ammonia aquation. The complexes were irradiated at 313, 365, 405, 436, 480, and 519 nm, in acidic (pH 3.5–4.0) aqueous solution and with $\sim 10^{-3}$ M Ru complex concentration. The cis complexes have ligand field (LF) and metal-to-ligand charge-transfer (MLCT) states as the lowest energy excited states. The relative yields of the photoreactions of the cis complexes show patterns consistent with the excited-state "tuning" model proposed to explain photochemical properties of the pentaammine analogues, $Ru^{II}(NH_3)_5(L)$, which undergo photosubstitution when LF is the lowest energy excited state, as is also the case for the trans complexes. For each cis complex, a fixed ratio of released ligands is observed at all irradiation wavelengths studied, this being a strong evidence that the observed photoreactions occur from one single LF excited state, or an ensemble of equilibrated LF excited states of the same electronic configuration. Ligands are more easily labilized along the axis with the weaker π-acceptor ability. For a particular axis, the ligand with lower π-acceptor ability is more easily labilized.

Introduction

The photosubstitution reactions of d^6 transition-metal ion species that have metal-to-ligand charge-transfer (MLCT) and ligand field (LF) states as the lowest energy excited states (LEES) have been rationalized in terms of the excited-state "tuning" model.[3,4] According to this model, the relatively photosubstitution "reactive" complexes have a LF state as the LEES, and those that are relatively "unreactive" have a MLCT state as the LEES. This model was initially proposed to explain the photosubstitution chemistry of pentaammineruthenium(II) complexes $(NH_3)_5Ru(L)^{n+}$ (where L is an aromatic nitrogen ligand) but has been extended to photoreactions of other systems.[5] Although the MLCT states of $Ru(bpy\text{-}X)_y{}^{2+}$, $Ru(bpy)_x(py\text{-}X)_y{}^{2+}$, and related bipyridine complexes are generally the LEES, the "tuning" model, which can also consider the effect of substituents on the relative energies of their long-lived but relatively unreactive MLCT states and of the substitution labile LF states, can explain much of the photosubstitution chemistry of these species.[6]

Ammineruthenium(II) complexes of unsaturated aromatic nitrogen heterocycles have LF and MLCT as LEES of comparable energies. The energy of the MLCT states in these complexes is highly dependent on the substituents on the coordinated heterocycle on the solvent, while the LF energy has been assumed to be much less sensitive.[3,7] Variation of either of these parameters will determine the nature of the LEES (LF or MLCT) and, thus, "tune" the photoreactivity.[3,4]

The $Ru^{II}(NH_3)_5(L)^{n+}$ (L = pyridine-like ligands) complexes show only one MLCT absorption band (in the visible region),[3a,8] while the *trans*-$Ru^{II}(NH_3)_4(L)(L')^{n+}$ ions display two MLCT bands, with the lower energy one (MLCT-1) being the more intense.[6,9] The absorbance of the higher energy MLCT band (MLCT-2) of *trans*-$Ru^{II}(NH_3)_4(L)(L')^{n+}$ is enhanced when $L \neq L'$.[6,9] Earlier work from these laboratories has shown that in the case of these trans complexes there appeared to be no special character assignable to the photochemistry resulting when the higher energy band (MLCT-2) is irradiated[7]—that is, the product distributions were the same as seen at longer wavelength excitation. Although the higher energy excitations did in some cases show high quantum yield values, these data are clearly consistent with explanations based on the "tuning" model.

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