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Transition Metal Complexes of Vitamin B_6-Related Compounds. 2. Synthesis and Properties of several Iron(III) Complexes of Pyridoxylideneglycine and 5′-Phosphopyridoxylideneglycine

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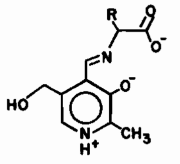
Iron(III) complexes of pyridoxylideneglycine and 5′-phosphopyridoxylideneglycine have been prepared and their electronic and structural properties investigated. The compounds are the essentially monomeric five-coordinate complexes, Fe(PLgly)(H_2O)X, where PLgly is the pyridoxylideneglycine Schiff-base dianion and X is Cl, Br, or OAc and Fe(PLPgly)(H_2O)(OAc), where PLPgly is 5′-phosphopyridoxylideneglycine. Infrared spectra indicate that PLgly and PLPgly are coordinated to iron(III) through their azomethine nitrogen, phenolic oxygen, and carboxylic oxygen donor atoms. These spectra also indicate the presence of coordinated water. The complexes are predominantly high-spin with magnetic moments which decrease from ca. *5.8 μ_B at room temperature to* ca. *5.40 μ_B at 120 K. This behavior is explained in terms of weak intermolecular antiferromagnetic coupling. Mössbauer effect spectral parameters for these compounds are consistent with five-coordinate iron(III) but do not eliminate the possibility of weak bonding at the sixth coordination site. The chemical isomer shifts are in the range of 0.40–0.50 mm/s (relative to natural α-iron foil) and the quadrupole interactions are* ca. *0.70 mm/s. The magnetically perturbed Mössbauer spectrum of Fe(PLgly)(H_2O)Cl obtained at 6 Tesla and 4.2 K indicates a large asymmetry parameter and an internal hyperfine field which is the same as the applied field. These compounds exhibit several intense charge-transfer and intraligand absorption bands and, as a result, only a single d–d band is observed at* ca. *11000 cm^{-1}.*

Introduction

Recently we reported [1] the synthesis and characterization of a number of pyridoxylideneamino acid complexes with divalent first-row transition metal ions. We isolated several iron(II) complexes which were formulated as Fe($HPLaa$)$_2$, where HPLaa is the pyridoxylideneamino acid Schiff-base ligand, (1). Subsequently we have prepared iron(III) chelates of pyridoxylideneglycine, (PLgly, 2), and 5′-phosphopyridoxylideneglycine, (PLPgly, 3). Although Christensen reported [2] the preparation of analogous bis complexes, Fe(PLgly)(HPLgly), we find that the properties of the compounds discussed herein are best formulated as the mono complexes, Fe(PLgly)(H_2O)X, where X is Cl, Br, or OAc, and as Fe(PLPgly)(H_2O)(OAc).



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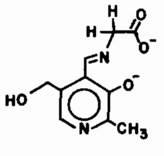

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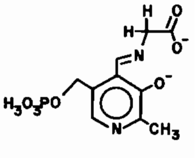

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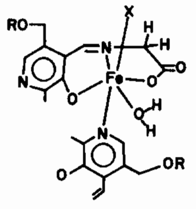

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Experimental

Materials

Pyridoxal hydrochloride, pyridoxal-5′-phosphate, and glycine were purchased from Sigma Chemical Co. Iron salts were purchased from Ventron Corp. These materials were used without further purification.

Fe(PLPgly)(H_2O)(OAc)

Acetoaquo-N-5′-phosphopyridoxylideneglycinato-iron(III) was prepared by dissolving stoichiometric amounts of pyridoxal-5′-phosphate, glycine, and Fe-

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TABLE I. Magnetic Susceptibility Results.

Compound	χ_M^c, cgsu	T, K	χ_M', cgsu	μ_{eff}, μ_B
Fe(PLgly)(H_2O)(OAc)	–180	294.5	14800	5.91
MWt., 355.11		248.5	17300	5.87
		208.0	19990	5.77
		161.0	24450	5.61
		133.0	28910	5.55
		122.5	30590	5.47
Fe(PLPgly)(H_2O)(OAc)	–160	295.0	14400	5.83
MWt., 436.12		266.5	15740	5.79
		233.0	17630	5.73
		194.0	20560	5.65
		166.0	23450	5.58
		132.0	28400	5.48
		111.0	32700	5.39
Fe(PLgly)(H_2O)Cl	–155	297.5	13940	5.76
MWt., 331.52		271.5	15060	5.72
		232.0	17220	5.65
		171.5	22210	5.52
		129.0	28370	5.41
Fe(PLgly)(H_2O)Br	–165	298.5	14080	5.80
MWt,, 375.26		248.0	16490	5.72
		192.0	20400	5.60
		140.0	26720	5.47
		117.5	30860	5.39

$(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in a neutral aqueous acetate buffer solution and heating to 75 °C for 15 min. Upon cooling the resulting brown precipitate was washed with cold methanol and dried at room temperature over P_2O_5. *Anal:* Calcd for $FeC_{12}H_{16}N_2O_{10}P$: Fe, 12.81; C, 33.05; H, 3.70; N, 6.42. Found: Fe, 12.72; C, 32.86; H, 4.00; N, 6.40.

Fe(PLgly)(H₂O)(OAc)

Acetoaquo-N-pyridoxylideneglycinatoiron(III) was prepared in the same manner as the PLPgly analog except that $FeSO_4 \cdot 7H_2O$ was used. The dark red crystalline product was washed with methanol and dried at room temperature over P_2O_5. *Anal.* Calcd for $FeC_{12}H_{15}N_2O_7$: Fe, 15.73; C, 40.59; H, 4.26; N, 7.89; aldehyde, 31.0; amine, 20.3. Found: Fe, 15.79; C, 40.64; H, 4.27; N, 7.73; aldehyde, 32.8; amine, 21.0.

Fe(PLgly)(H₂O)Cl

Aquochloro-N-pyridoxylideneglycinatoiron(III) was prepared by adding stoichiometric amounts of pyridoxal free base, glycine, and iron(III) chloride to water. The resulting solution was heated to 50 °C and stirred for ten hours. Upon cooling, the dark red precipitate which formed was washed with cold water, methanol, and dried at room temperature over P_2O_5. *Anal.* Calcd for $FeC_{10}H_{12}N_2O_5Cl$: Fe, 16.85; C, 36.23; H, 3.62; N, 8.45; Cl, 10.71; aldehyde, 59.57; amine, 21.7. Found: Fe, 16.52; C, 36.54; H, 3.60; N, 8.40; Cl, 11.0; aldehyde, 60.2; amine, 21.0.

Fe(PLgly)(H₂O)Br

Aquobromo-N-pyridoxylideneglycinatoiron(III) was prepared in the same manner as the chloride complex except that iron(III) bromide was used. The dark red precipitate was washed with methanol, and dried at room temperature over P_2O_5. *Anal.* Calcd for $FeC_{10}H_{12}N_2O_5Br$: Fe, 14.86; C, 31.95; H, 3.20; N, 7.45; Br, 21.26; aldehyde, 52.6; amine, 19.1. Found: Fe, 15.44; C, 32.03; H, 3.46; N, 7.56; Br, 21.0; aldehyde, 50.9; amine, 19.0.

Analytical Methods and Physical Measurements

Iron was determined by using either dichromate titrimetry or 1,10-phenanthroline compleximetry. Halides were determined gravimetrically as silver halide. Total aldehyde and amine content was determined as previously reported [1] and the results are accurate to one and two percent, respectively. Carbon, hydrogen, and nitrogen analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

Infrared and electronic spectra were recorded on a Perkin Elmer 180 and a Cary 14 spectrophotometer. Solid-state infrared spectra were measured in a

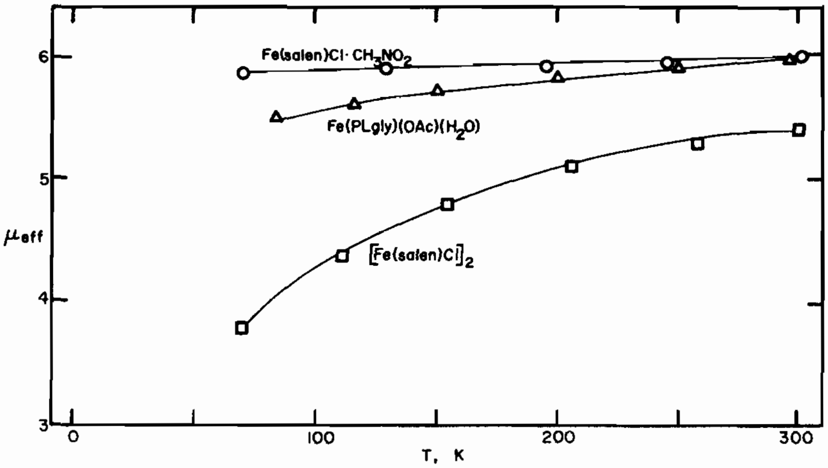

Fig. 1. A comparison of the magnetic moments as a function of temperature for Fe(salen)Cl•CH_3NO_2, Fe(PLgly)(H_2O)(OAc), and $[Fe(salen)Cl]_2$.

KBr matrix and electronic spectra were measured in fluorocarbon mulls. Magnetic susceptibilities were measured on polycrystalline samples by using a standard Gouy balance calibrated with $HgCo(NCS)_4$. Corrections for ligand diamagnetism were calculated from a table of Pascal's constants [3]. The magnetic susceptibility values were measured at five different field strengths and were found to be independent of the applied field.

The Mössbauer effect spectra were obtained either on an Austin Science Associates or a Harwell constant acceleration spectrometer. Both spectrometers utilized a room-temperature rhodium or copper-matrix source and were calibrated with natural α-iron foil. The liquid helium spectra were obtained in cryostats in which the sample was placed directly in the liquid helium. The magnetically perturbed spectrum was obtained with a British Oxygen Corp. superconducting magnet and cryostat which produced a transverse field. The applied magnetic field was calibrated by measuring the change in the iron foil internal hyperfine field produced by the magnet. The Mössbauer spectra were evaluated by using least-squares minimization programs and the University of Missouri IBM 370/168 computer facilities. The magneticially perturbed spectrum was evaluated by using the computer program developed by Lang and Dale [4]. The Mössbauer effect parameters reported herein have error limits of *ca.* ±0.02 mm/s.

Results and Discussion

The compounds under study are stable complexes which show no signs of decomposition over a period of several years. They are slightly soluble in water but insoluble in all common organic solvents. Although the compounds do not give a sharp decomposition point, the onset of decomposition is approximately 140 °C.

Magnetic Susceptibility Results

The magnetic susceptibility and moment for each of the compounds under study are listed in Table I. For each compound there is a small but significant decrease in μ_{eff} between room temperature and *ca.* 120 K. Because this behavior may indicate the presence of antiferromagnetic exchange we have fit the magnetic moments to an $S_1 = S_2 = 5/2$ dimeric iron(III) exchange coupling model. The best fits were obtained with values of g between 2.0 and 2.1 and with J between −2.0 and −3.3 cm^{-1}, values which seem quite reasonable for weak antiferromagnetic exchange. The experimental and calculated results for Fe(PLgly)(H_2O)(OAc) are presented in Fig. 1 where they are compared with similar results for $[Fe(salen)Cl]_2$ and Fe(salen)Cl•CH_3NO_2. Salen is the N,N′-ethylenebis(salicylideneiminate) dianionic ligand.

A single-crystal X-ray study [6] has shown that Fe(salen)Cl•CH_3NO_2 is composed of discrete five-coordinate Fe(salen)Cl monomers whereas $[Fe(salen)Cl]_2$ is composed of six-coordinate dimers formed by bridging phenolic oxygen atoms [7]. The magnetic data [8] for Fe(salen)Cl•CH_3NO_2 indicate that it is a normal paramagnetic compound with no exchange coupling. Alternately, the magnetic moment of $[Fe(salen)Cl]_2$ indicates [9] the presence of antiferromagnetic exchange with a g value of 2.00 and an exchange coupling constant of −7.5 cm^{-1}. The major pathway for exchange in this compound most likely involves superexchange through the bridging oxygen atoms. Because of the small negative values of J obtained for the PLgly and PLPgly complexes reported herein we propose that the iron(III) ions are relatively-well isolated from one

TABLE II. Mössbauer Effect Spectral Parameters.[a]

Compound	T, K	ΔE_Q	δ	Γ_1^b	Γ_2^b	A^c	%ε
Fe(PLPgly)(H_2O)(OAc)	RT	0.74	0.38	0.52	0.54	1.12	–
	78	0.79	0.42	0.54	0.56	1.10	–
Fe(PLgly)(H_2O)(OAc)	RT	0.75	0.42	0.80	0.71	1.09	0.4
	78	0.74	0.51	0.56	0.56	1.02	1.5
	4.2	0.73	0.53	0.29	0.30	1.00	7
Fe(PLgly)(H_2O)Cl	RT	0.69	0.42	0.79	0.79	1.18	0.3
	78	0.70	0.51	0.53	0.53	0.98	2
	4.2	0.70	0.53	0.29	0.32	0.88	9
Fe(PLgly)(H_2O)Br	RT	0.70	0.39	0.76	0.79	0.84	0.06
	78	0.70	0.50	0.88	0.83	0.99	0.7
	4.2	0.66	0.53	0.27	0.29	1.00	6

[a] All data in mm/sec relative to natural α-iron foil. [b] Full-width at half-maximum intensity. [c] Area ratio of low velocity line to high velocity line.

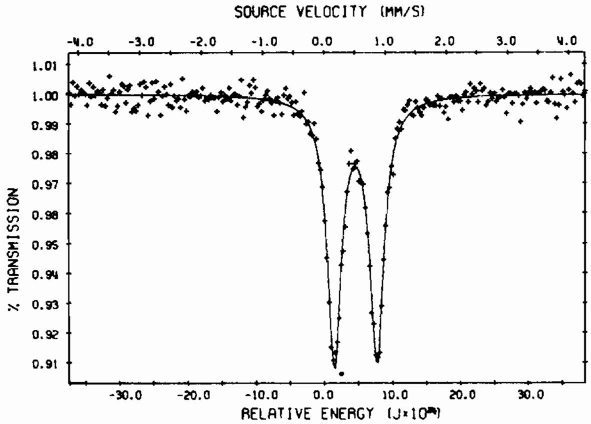

Fig. 2. The Mössbauer effect spectrum of Fe(PLgly)(H_2O)-Cl obtained at 4.2 K.

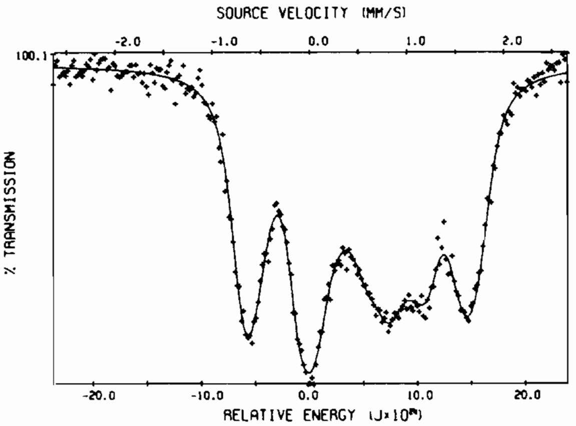

Fig. 3. The Mössbauer effect spectrum of Fe(PLgly)(H_2O)-Cl obtained at 4.2 K in a 6 Tesla transverse applied field.

another and that exchange is occurring through an extended ligand bridge. Although the pyridine nitrogen and hydroxymethyl oxygen atoms are not strongly bonded to the iron(III) ion (see below), they may be weakly coordinated in these complexes. This situation has been confirmed in a single crystal structural study of Cu(PLval) [10]. The PLPgly complex has magnetic properties which are very similar to that of the corresponding PLgly complex. This suggests that the 5′-hydroxymethyl oxygen is not serving as the bridging group.

Mössbauer Effect Spectral Data

The Mössbauer effect spectral parameters for the complexes under study are presented in Table II. The 4.2 K Mössbauer effect spectrum of Fe(PLgly)(H_2O)Cl is illustrated in Fig. 2. Essentially identical 4.2 K spectra were obtained for the remaining compounds. The higher temperature spectra were very similar but exhibited less resolution of the two quadrupole split lines. The Mössbauer effect parameters are typical of those expected for a five or six coordinate high-spin iron(III) complex. The isomer shifts are essentially identical to those observed [9] in $[Fe(salen)Cl]_2$ which has basically a FeN_2O_2Cl coordination geometry with weak coordination in the sixth position. They are also very similar to those observed in a variety of related Schiff-base complexes [11–13]. The quadrupole interaction is relatively small as might be expected for five-coordinate high-spin iron(III) complexes in which there is only a lattice contribution to the electric field gradient tensor. Once again the observed values are rather typical of those observed in other five coordinate iron(III) complexes [9, 11–13]. These complexes do not exhibit the large asymmetry in area and

TABLE III. Electronic Spectral Data and Assignments.

Compound	ν_{max}, cm^{-1}	Assignment
$Fe(PLPgly)(H_2O)(OAc)$	11000(sh)	*d–d*
	23700, 30100(sh), 33000(sh)	charge transfer
$Fe(PLgly)(H_2O)(OAc)$	11000(sh)	*d–d*
	23700, 30000, 33100	charge transfer
$Fe(PLgly)(H_2O)Cl$	10750	*d–d*
	23500, 30000(sh), 33000	charge transfer
$Fe(PLgly)(H_2O)Br$	10500	*d–d*
	23500, 29500(sh), 33000	charge transfer

intensity of the two quadrupole split lines as is often found in complexes of this type [9, 12–14]. There is however a large increase in the linewidth and decrease in percent effect with increasing temperature. These changes are probably associated with the low Debye temperature and low coordination number in these complexes.

The magnetically perturbed Mössbauer effect spectrum of $Fe(PLgly)(H_2O)Cl$ obtained at 4.2 K in a 6 Tesla applied magnetic field is presented in Fig. 3. The spectrum exhibits the expected five poorly resolved lines [14]. The poor resolution of the lines is due, no doubt, in part to the small zero-field quadrupole interaction. In order to evaluate the magnitude of the internal hyperfine field and η, the asymmetry parameter [14], we have used the method of Lang and Dale [4] to model the magnetically perturbed Mössbauer spectrum. The resulting best fit is shown as the solid line in Fig. 3 and corresponds to an isomer shift of 0.52 mm/s, a quadrupole interaction of 0.70 mm/s, an asymmetry parameter of 0.63 and an observed internal hyperfine field of 60.1 kOe. It should be noted that the internal hyperfine field is equivalent to the applied field to within experimental error. We do not observe the small induced negative hyperfine field as was found [13] in $[Fe(salen)Cl]\cdot\frac{1}{2}CH_3NO_2$. There is no augmentation or reduction of the applied field by an induced internal hyperfine field. This is the behavior expected of a high-spin iron(III) complex with only very weak intermolecular magnetic coupling. The large value of the asymmetry parameter seems reasonable for a five-coordinate complex.

Electronic Spectral Results

The complexes reported on herein are dark red, as is common for iron(III) compounds of unsaturated Schiff-base ligands. This color is usually ascribed to the presence of one or more low-lying charge-transfer absorption bands. Because of these very intense bands one does not usually observe d–d transitions in the visible spectra of such compounds. This unfortunate situation is found in the case of the PLgly and PLPgly iron(III) complexes, data for which are given in Table III. Positions and intensities of these bands are only slightly sensitive to the anion. We do however observe a low-intensity band in the near infrared region, at approximately 11000 cm^{-1}, which may be assigned to a ligand-field transition. A similar absorption is found in the electronic spectrum of other five-coordinate iron(III) complexes with a similar donor atom set [8]. Although the proper assignment for this absorption is uncertain, it appears to be a common feature of five-coordinate iron(III) complexes.

Infrared Spectral Data

Because the free ligands are too unstable for solid-state infrared studies it is not possible to assign absorptions on the basis of shifts in band positions upon complexation. Our experience with similar ligands has, however, indicated that the position of several infrared bands is indicative of the mode of coordination [1]. These absorptions include the azomethine C=N stretch, ν_{CN}, the phenolic carbon–oxygen stretch, ν_{CO}, and the asymmetric carboxyl stretch, ν_{COO}. These assignments, among other, are presented in Table IV. The azomethine stretch is commonly observed in the range 1600–1650 cm^{-1} for both N-salicylideneamino acid and N-pyridoxylideneamino acid complexes [16]. We assign a strong band at 1605 cm^{-1} to the ν_{CN} for the PLPgly and PLgly iron(III) complexes. The position of this band is insensitive to the nature of X (see Table IV). The asymmetric carboxyl stretching absorption is found near 1570 cm^{-1} and gradually increases in energy in the order OAc < Cl < Br. The ν_{CO} absorption band near 1510 cm^{-1} is essentially unchanged in this series of compounds. An important feature in the infrared spectra of these complexes is the presence of a strong broad band near 610 cm^{-1} which we have assigned to coordinated water [17]. This band shifts to 520 cm^{-1} in the spectrum of the complex prepared in D_2O. We do not however observe the absorption near 400 cm^{-1} which is characteristic of ν_{M-OH_2}, the metal to water oxygen stretching frequency. Indeed, the presence of a large number of ligand absorptions

TABLE IV. Infrared Spectral Data in Wavenumbers and Assignments.

Compound	ν_{CN}	ν_{COO}	ν_{CO}	ρ_{w,H_2O}
Fe(PLPgly)(H_2O)(OAc)	1606	1572	1510	610
Fe(PLgly)(H_2O)(OAc)	1605	1570	1508	610
Fe(PLgly)(H_2O)Cl	1603	1586	1515	608
Fe(PLgly)(H_2O)Br	1606	1590(sh)	1520	612

in the 600–160 cm^{-1} range precludes the assignment of metal–ligand absorption bands.

Conclusions

The physical properties of the iron(III) complexes of PLPgly and PLgly reported on herein are consistent with a five-coordinate iron(III) monomer with weak intermolecular bonding to an adjacent pyridine nitrogen of pyridoxal (4). This is the first example of a monomeric crystalline trivalent metal-ion complex with an N-pyridoxylideneamino acid. Although the corresponding bis complexes of N-pyridoxylideneglycine [2] and the analogous iron(III) complex of N-salicylideneglycine, $[Fe(H_2O)_6][Fe(salgly)_2]_2 \cdot 2H_2O$ [18], have been reported, the mono complexes have thus far been thought to exist only in solution [19]. The implications of the structure of these mono complexes and their relationship to the reactivity of vitamin B_6 models are at present unknown, Further study of the reactivity of these compounds should illuminate several salient features of vitamin B_6 catalysis.

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