Preparation and molecular structure of a cobalt(III) complex with a sexidentate pyridoxal derivative [Co(Htpdh)] (tpdh = 1,3,4,6-tetrakis[4-(2-methyl-3-hydroxy-5-hydroxymethyl)pyridyl]-2,5-diaza-1,5-hexadiene)

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Abstract

The H_2O_2 oxidation of an aqueous solution containing pyridoxal, L-alanine and cobalt(II) nitrate resulted in the formation of a novel cobalt(III) complex with the sexidentate title ligand (tpdh). The crystal structure of this complex was determined by a single crystal X-ray diffraction technique The crystal was monoclinic with space group *C2/c*, $a = 8.690(1)$, $b = 34.894(6)$, $c = 10.895(3)$ Å, $\beta = 104.69(2)°$, $V = 3196(2)$ Å^3, $Z = 4$, and $R = 0.056$ for 5299 independent reflections ($F_o > 3\sigma(F_o)$). In [Co(Htpdh)], the cobalt atom is surrounded octahedrally by two *cis* nitrogen and four oxygen atoms of the sexidentate ligand which contains four pyridyl rings. The entire complex has two asymmetric carbon atoms and both of them takes the *S* configuration for the Λ isomer (*R* for Δ). The structure in acidic solution (*c.* pH 3.4) was discussed on the basis of the absorption and NMR spectral behavior. The formation of the sexidentate tpdh ligand was also discussed.

Introduction

Metal complexes with Schiff bases, which are derived from pyridoxal and α-amino acids, have been investigated for their biochemical interests such as vitamin B_6 [1–9], and for the stereochemical property that the Schiff bases are trapped in the coordination sphere of the metal ions in the inert complexes [2, 5–9]. Most of the Schiff base complexes contain the pyridoxylideneaminoacidate ligands, which have been prepared from pyridoxal, amino acid and divalent first-row transition-metals [1, 5, 6], iron(III) [7] or cobalt(III) [4]. Recently, Long *et al.* have reported an unusual result that the slow air evaporation of an aqueous solution containing pyridoxal, alanine and iron(II) perchlorate causes a Schiff base condensation of pyridoxal and pyridoxamine, which was derived in this reaction, to give the dimeric iron(III) complex [8]. So, we attempted to prepare a Schiff base cobalt(III) complex by the oxidation of an aqueous solution containing pyridoxal, L-alanine and cobalt(II) nitrate. In this reaction, the brown neutral cobalt(III) complex, [Co(Htpdh)], was newly formed. Herein, we report the crystal structure determination of this novel neutral complex. The structure in acidic solution (*c.* pH 3.4) is also discussed on the basis of the absorption and NMR spectra.

Experimental

Materials

All reagents were purchased from the Wako Pure Chemical Ind. Co. Ltd. or Tokyo Chemical Ind. Co. Ltd. in Japan. All chemicals were of reagent grade and were used without further purification.

Preparation of complex

Neutral complex: [Co(Htpdh)]

A solution containing 1.45 g of $Co(NO_3)_2 \cdot 6H_2O$ in 50 cm^3 of ice-cold ethanol was added to a solution containing 2.03 g of pyridoxal·HCl, 0.89 g of L-alanine and 0.21 g of NaOH. To this was carefully added 4 cm^3 of 30% hydrogen peroxide with stirring. The color of the solution changed to brown. This mixture was continuously stirred for 2 h at room temperature. The solution was filtered and passed through a column of QAE-Sephadex A-25 (Cl^- form) eluting with water. No band was adsorbed. The eluate was concentrated to a small volume with a rotary evaporator at 25–30 °C. The solution was poured onto a column of SP-Sephadex C-25 (Na^+ form, 3.5 × 60 cm). When the

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column had been swept with acidic water adjusted with HCl to *c*. pH 3.4, the neutral complex was eluted. The brown eluate was concentrated to a small volume again, and left to stand in a refrigerator for two weeks. The crystals which appeared were collected by filtration, washed with ethanol, and then dried in a vacuum desiccator. The crystals were only soluble in acidic water (*c*. pH 3.4). One of the crystals of a suitable size was used for X-ray crystal analysis. *Anal.* Found: C, 50.51; H, 5.39; N, 10.99. Calc. for $C_{32}H_{33}N_6O_8Co \cdot 4H_2O$: C, 50.55; H, 5.44; N, 11.05%.

Positive charged complex: $[Co(H_2tpdh)]^+$

The adsorbed band on the top of the column of SP-Sephadex C-25 was eluted with a 0.075 mol dm^{-3} aqueous solution of NaCl, which was adjusted with HCl to *c*. pH 3.4. Two bands, a small amount of brown band (A-1) and a large amount of brown band (A-2), were eluted in this order. The eluate A-1 disappeared during the elution. The eluate A-2 showed an absorption spectrum identical with that of the neutral complex dissolved in acidic water (*c*. pH 3.4). The eluate A-2 was fractionated into twenty parts. It was found from the absorption and CD spectral measurements that the earlier and later fractions showed an enantiomeric CD spectral pattern. This means that the complex is optically active and was partially resolved in the column chromatographic treatments, depending on the interaction between the optically active matrix of the column and the optical isomers. The $\Delta\epsilon$ values of the earliest fraction containing the $(+)^{CD}_{550}$ isomer were evaluated on the basis of the absorption spectrum of the neutral complex dissolved in acidic water (*c* pH 3.4).

X-ray data collection for the neutral complex

Unit cell parameters and intensity data for a single dark brown crystal (*c*. $0.15 \times 0.20 \times 0.25$ mm) were measured on an Enraf Nonius CAD4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å, 50 kV and 26 mA). Unit-cell parameters were determined by least-squares refinement from 25 reflections with $20 < 2\theta < 25°$. Crystal data: $[Co(C_{32}H_{32}N_6O_8)] \cdot 3H_2O$, $M_r = 741.63$, monoclinic, $C2/c$ (No. 15), $a = 8.690(1)$, $b = 34.894(6)$, $c = 10.895(3)$ Å, $\beta = 104.69(2)°$, $V = 3196(2)$ Å^3, $Z = 4$, $D_x = 1.54$ g cm^{-3}, $\mu = 6.0$ cm^{-1}, $F(000) = 1548$, room temperature.

The intensity data were collected by the ω-2θ scan mode in the $2 < 2\theta < 56°$ range with scan width $(0.8 + 0.35 \tan \theta)°$ and scan rate varied from 1 to 5° min^{-1} (on ω). The intensities were corrected for Lorentz and polarization effects, but not for absorption. A total of 5299 reflections with $F_o > 3\sigma(F_o)$ of the independent 6998 reflections for the measured 8184 reflections was considered as 'observed' and used for structure determination.

Determination of crystal structure

The cobalt, two nitrogen, and four oxygen atom positions were determined by direct methods [10]. The other non-hydrogen and hydrogen atom positions were determined from the successive difference Fourier maps. The O(22) and O(23) atoms exhibited positional disorder and were constrained to the occupancy factors of 0.6 (O(22)) and 0.4 (O(23)), respectively, because they converged to nearly 0.6:0.4. The hydrogen atom (H(N11)) attached to the N(11) atom was also constrained to the occupancy factor of 0.5, because it converged to nearly 0.5. The structure was refined by full-matrix least-squares on *F* using anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms. The hydrogen atoms for H_2O and CH_3 were fixed by thermal constraints ($B = 5.0$ Å^2). The final residual values were $R = 0.056$ and $R_w = 0.061$, $w = 4F_o^2/\sigma^2(F_o)^2$, $S = 1.42$. The largest parameter shift was 0.01 times e.s.d. and $|\Delta\rho|_{max}$ in the final difference Fourier map was 0.51 e Å^{-3}. All calculations were performed on a Vax computer using Molen [10]. The final atomic parameters are listed in Table 1.

Measurements

The electronic absorption spectra of the complex were recorded on a JASCO UVIDEC-610C spectrophotometer. The CD spectra were recorded on a JASCO J-20 spectropolarimeter. All measurements were carried out in aqueous solutions at room temperature. The 100 MHz ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-FX-100 or a JNM-FX-90Q NMR spectrometer at prove temperature. The 500 MHz NMR spectra were recorded with a BRUKER-AM-500 NMR spectrometer under the same conditions as the 100 MHz ^1H NMR ones. Sodium 4,4-dimethyl-4-silapentane-1-sulfonate was used as an internal reference.

Results and discussion

Description of structure for the neutral complex

The entire molecular structure for the neutral complex, [Co(Htpdh)], and its numbering scheme are illustrated in Fig. 1. Bond distances and angles are listed in Table 2. The central cobalt atom is located at (0, *y* $\frac{3}{4}$) and the individual bond distances and angles are associated in pairs by the two-fold axis bisecting the N–Co–N(#) and O(11)–Co–O(11#) angles*. The coordination geometry around the cobalt atom is approximately octahedral, surrounded by the two nitrogen and four oxygen atoms. Namely, the ligand has four

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*The atoms with the symbol # denote the same atoms which are associated by a C_2 symmetry

TABLE 1. Final atomic coordinates and equivalent isotropic thermal parameters (B_{eq} (Å^2)) for non-H atoms and isotropic thermal parameters (B (Å^2)) for H atoms

Atom	x	y	z	B_{eq}[a] or B
Co	0.0	0.35246(1)	0.75	1.591(7)
N	0.1401(2)	0.39072(6)	0.7317(2)	1.65(4)
O(11)	0.1452(2)	0.31353(5)	0.7298(2)	2.22(3)
O(12)	0.3191(3)	0.41556(6)	0.4449(2)	3.11(4)
N(11)	0.4341(3)	0.28789(7)	0.5676(2)	2.80(5)
C(11)	0.3299(3)	0.28518(8)	0.6369(3)	2.32(5)
C(12)	0.2524(3)	0.31867(7)	0.6668(2)	1.99(5)
C(13)	0.3019(3)	0.35409(8)	0.6289(2)	1.97(4)
C(14)	0.4093(3)	0.35552(8)	0.5511(2)	2.28(5)
C(15)	0.4719(3)	0.32167(9)	0.5222(3)	2.72(5)
C(16)	0.2964(4)	0.24712(8)	0.6853(3)	3.01(6)
C(17)	0.2514(3)	0.38938(7)	0.6760(2)	1.88(4)
C(18)	0.4531(3)	0.39302(9)	0.5000(3)	2.75(5)
O(21)	0.0910(2)	0.35354(5)	0.9262(2)	2.14(3)
O(22)	0.2399(6)	0.52073(9)	1.0420(3)	3.81(9)
O(23)	0.3259(9)	0.5016(2)	0.9233(7)	6.0(2)
N(21)	0.2267(3)	0.41565(7)	1.1897(2)	2.87(5)
C(21)	0.1803(3)	0.38490(8)	1.1188(2)	2.36(5)
C(22)	0.1304(3)	0.38645(7)	0.9842(2)	1.87(4)
C(23)	0.1321(3)	0.42266(7)	0.9258(2)	1.76(4)
C(24)	0.1800(3)	0.45459(7)	1.0032(2)	2.21(5)
C(25)	0.2257(4)	0.44981(8)	1.1321(3)	2.87(6)
C(26)	0.1839(5)	0.34723(9)	1.1846(3)	3.67(7)
C(27)	0.0905(3)	0.42621(6)	0.7815(2)	1.68(4)
C(28)	0.1874(4)	0.49403(8)	0.9475(3)	2.87(6)
O(1w)	0.6073(4)	0.23465(8)	0.4792(3)	6.84(8)
O(2w)	0.0	0.0339(1)	0.25	6.4(1)
H(O12)	0.293(3)	0.4134(8)	0.360(3)	2.4(6)
H(O1w1)	0.597(4)	0.251(1)	0.407(3)	5.0
H(O1w2)	0.574(4)	0.219(1)	0.440(3)	5.0
H(O2w)	0.051(5)	0.024(1)	0.317(3)	5.0
H(C15)	0.543(4)	0.3209(9)	0.468(3)	2.9(7)
H(C161)	0.334(4)	0.246(1)	0.775(3)	5.0
H(C162)	0.351(4)	0.225(1)	0.650(3)	5.0
H(C163)	0.193(4)	0.241(1)	0.659(3)	5.0
H(C17)	0.300(4)	0.4126(9)	0.667(3)	2.9(7)
H(C181)	0.511(4)	0.3870(9)	0.435(3)	3.3(7)
H(C182)	0.524(4)	0.4087(9)	0.568(3)	3.6(8)
H(C25)	0.253(4)	0.4702(9)	1.182(3)	2.9(7)
H(C261)	0.200(4)	0.349(1)	1.266(3)	5.0
H(C262)	0.081(4)	0.332(1)	1.148(3)	5.0
H(C263)	0.250(4)	0.328(1)	1.154(3)	5.0
H(C27)	0.144(3)	0.4496(8)	0.757(3)	2.0(6)
H(C28)	0.093(4)	0.5018(9)	0.882(3)	3.1(7)
H(N11)	0.465(7)	0.265(2)	0.539(5)	2(1)

[a] $B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j$

pyridyl rings and coordinates to the cobalt(III) ion as a *cis*-$(N)_2(O)_4$-type sexidentate ligand, as well as the ethylenediaminetetraacetate (edta) one [11a]. The neutral complex molecule has two kinds of chiralities, Δ and Λ, due to the skew pair of the chelate rings and *R* or *S* due to the asymmetric carbon atoms, C(27). The crystal is racemate (space group *C*2/*c*), and both of the asymmetric carbon atoms take an *S* configuration for the Δ isomer as shown in Fig. 1.

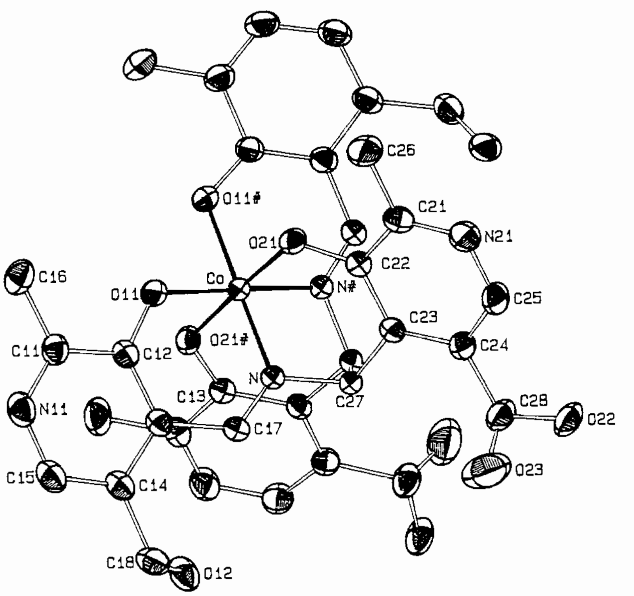

Fig. 1. ORTEP drawing of [Co(Htpdh)] (50% probability thermal ellipsoids) with the atom-numbering scheme. H atoms are omitted for clarity

The Co–O(21) distance (1.882(2) Å) of the in-plane is apparently longer than those (1.904(2) Å for Co–O(11)) of the out-of-plane (Table 2). A similar trend was observed for the corresponding distances of $[Co(edta)]^-$ [11a], although the situation around the nitrogen and oxygen donor atoms is different. The Co–N distance (1.851(2) Å) is apparently shorter than the corresponding distances of $[Co(edta)]^-$ (1.921(8) and 1.929(8) Å) [11a]. This suggests the influence of the electron-donating of the imine nitrogen atom. The N–C(17) distance is 1.266(4) Å, indicating the double bond character. Similar values for the N–C distance were also observed for metal complexes with pyridoxal derivatives [5, 8]. In contrast to the N–C(17) distance, the N–C(27) distance is 1.460(3) Å. This apparently indicates the single bond character.

The two pyridyl rings, whose least-square planes A [C(11)–C(12)–C(13)–C(14)–C(15)–N(11)] and B [C(21)–C(22)–C(23)–C(24)–C(25)–N(21)] are calculated, are almost planar. The angle between the planes A and A(#) is 10.3(3)° and that between the planes B and B(#) is 17.60(7)°*. These indicate that the planes A and A(#) or the planes B and B(#) are almost parallel to each other. The angle between the planes A and B is 119.43(9)°. As a result, the C(26) atom is close to pyridyl ring A, while the C(16) atom is not close to any pyridyl ring. Therefore, this suggests that

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*Planes A and A(#) or B and B(#) for the pyridyl rings are associated in pairs by a C_2 symmetry.

TABLE 2. Bond distances (Å) and angles (°)

Distances			
Co–N	1.851(2)	C(14)–C(18)	1.508(4)
Co–O(11)	1.904(2)	O(21)–C(22)	1.314(3)
Co–O(21)	1.882(2)	O(22)–C(28)	1.378(4)
N–C(17)	1.266(4)	O(23)–C(28)	1.323(9)
N–C(27)	1.460(3)	N(21)–C(21)	1.324(4)
O(11)–C(12)	1.302(4)	N(21)–C(25)	1.346(4)
O(12)–C(18)	1.407(3)	C(21)–C(22)	1.420(3)
N(11)–C(11)	1.321(4)	C(21)–C(26)	1.494(4)
N(11)–C(15)	1.351(4)	C(22)–C(23)	1.417(3)
C(11)–C(12)	1.427(4)	C(23)–C(24)	1.396(3)
C(11)–C(16)	1.485(4)	C(23)–C(27)	1.526(3)
C(12)–C(13)	1.405(4)	C(24)–C(25)	1.369(4)
C(13)–C(14)	1.412(4)	C(24)–C(28)	1.512(4)
C(13)–C(17)	1.444(4)	C(27)–C(27#)	1.549(3)
C(14)–C(15)	1.370(4)		
Angles			
N–Co–O(11)	91.65(8)	N–C(17)–C(13)	122.7(2)
N–Co–O(21)	88.73(8)	O(12)–C(18)–C(14)	112.6(2)
O(11)–Co–O(21)	90.73(8)	Co–O(21)–C(22)	120.0(2)
N–Co–O(11#)	179.27(9)	C(21)–N(21)–C(25)	118.7(2)
O(21)–Co–O(21#)	177.71(8)	N(21)–C(21)–C(22)	122.7(2)
Co–N–C(17)	128.9(2)	N(21)–C(21)–C(26)	117.8(2)
Co–N–C(27)	107.9(2)	C(22)–C(21)–C(26)	119.5(2)
C(17)–N–C(27)	122.9(2)	O(21)–C(22)–C(21)	116.0(2)
Co–O(11)–C(12)	123.1(2)	O(21)–C(22)–C(23)	126.5(2)
C(11)–N(11)–C(15)	122.5(3)	C(21)–C(22)–C(23)	117.5(2)
N(11)–C(11)–C(12)	120.2(2)	C(22)–C(23)–C(24)	118.4(2)
N(11)–C(11)–C(16)	119.4(3)	C(22)–C(23)–C(27)	120.6(2)
C(12)–C(11)–C(16)	120.3(3)	C(24)–C(23)–C(27)	121.0(2)
O(11)–C(12)–C(11)	116.7(2)	C(23)–C(24)–C(25)	119.2(2)
O(11)–C(12)–C(13)	126.1(2)	C(23)–C(24)–C(28)	121.4(2)
C(11)–C(12)–C(13)	117.1(3)	C(25)–C(24)–C(28)	119.4(2)
C(12)–C(13)–C(14)	120.4(2)	N(21)–C(25)–C(24)	123.5(2)
C(12)–C(13)–C(17)	120.2(2)	N–C(27)–C(23)	107.4(2)
C(14)–C(13)–C(17)	119.3(2)	N–C(27)–C(27#)	101.4(2)
C(13)–C(14)–C(15)	118.0(3)	C(23)–C(27)–C(27#)	103.8(2)
C(13)–C(14)–C(18)	121.3(3)	O(22)–C(28)–C(24)	110.8(2)
C(15)–C(14)–C(18)	120.8(3)	O(23)–C(28)–C(24)	113.4(4)
N(11)–C(15)–C(14)	121.4(3)		

the substituent on pyridyl ring B, such as the methyl groups, interacts with pyridyl ring A. These relations will also be retained in acidic solution (*vide infra*). The H(N11) atom, which is attached to the N(11) atom, has an occupancy factor of 0.5. This means that the nitrogen atom (N(11) or N(11#)) of either pyridyl ring A or A(#) is protonated to form [Co(Htpdh)], but the nitrogen atom (N(21) or N(21#)) of ring B or B(#) is not.

Characterization

The absorption and CD spectra of the positive charged complex in acidic water (*c*. pH 3.4) are shown in Fig. 2. The absorption spectrum of this complex is identical with that of the neutral complex, [Co(Htpdh)], dissolved in acidic water. Further, the two complexes in acidic solution exhibit ^{1}H and ^{13}C NMR spectra identical with each other (Fig. 3). These indicate that the positive charged complex is [Co(H$_2$tpdh)]$^+$, in which the protonations occur on the nitrogen atom in the pyridyl rings. In the absorption spectrum of energy lower than 19×10^3 cm^{-1}, the positive charged complex exhibits two shoulders with weak intensities, which are assignable as d–d transitions (Fig. 2) The intense absorption bands in the region of 19–45×10^3 cm^{-1} are assigned as charge transfer and intraligand transitions, as in the case of the first-row transition metal complexes with the pyridoxal derivative Schiff base ligands [8]. In the d–d transition band region, the $(+)^{\text{CD}}_{550}$ isomer exhibits a negative (15.68×10^3 cm^{-1}; -0.55 mol^{-1} dm^3 cm^{-1}) and a positive (18.08×10^3 cm^{-1}; $+1.31$ mol^{-1} dm^3 cm^{-1}) CD band from lower energy (Fig. 2), suggesting that the $(+)^{\text{CD}}_{550}$ isomer takes the Δ configuration.

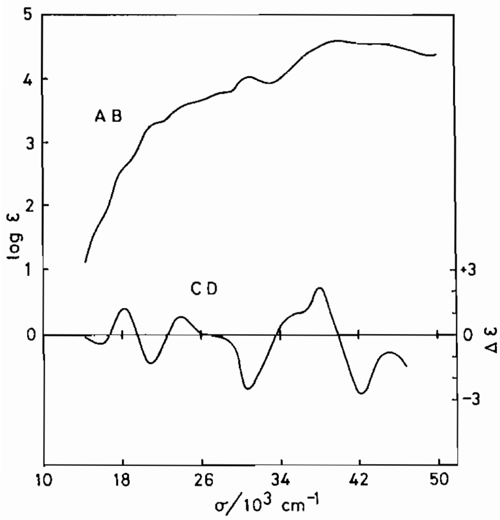

Fig 2. Absorption and CD spectra of $(+)^{CD}_{550}$-$[Co(H_2tpdh)]^+$.

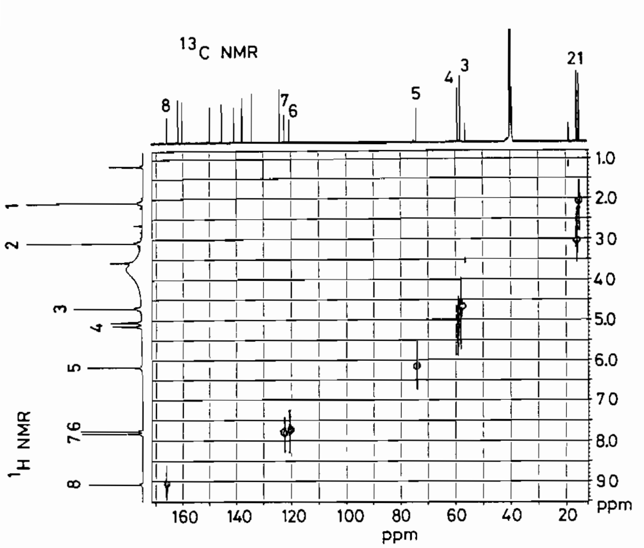

Fig. 3 Two-dimensional NMR spectra of $[Co(H_2tpdh)]^+$

¹H and ¹³C NMR spectra

The two two-dimensional NMR spectrum of $[Co(H_2tpdh)]^+$ is shown in Fig. 3. In the ^1H NMR spectra, each of the resonance lines due to the Schiff base protons in d-DMSO shifts slightly to lower magnetic field than in the acidic D_2O solution. This reflects the difference of the proton dissociation constant in the d-DMSO and D_2O solvents. In the C–H correlation spectroscopy (COSY), this complex exhibits eight sets of resonance lines in the ^1H NMR spectrum and sixteen lines in the ^{13}C NMR spectrum (Fig. 3), which correspond to the resonance lines due to a half group in the sexidentate ligand. From the correlation peaks, it is obvious that the protons 1–8 are coupling with the carbon atoms 1–8, respectively (Fig. 3)*. Judging from the INEPT (insensitive nuclei enhanced by polarization transfer) method for the ^{13}C NMR spectrum, the carbon atoms 1(C) and 2(C) are due to the methyl group, 3(C) and 4(C) due to the methylene group, 5(C) due to the methine group, 6(C) and 7(C) due to the aromatic carbon attached to the hydrogen atom, and 8(C) due to the –CH=N– group. Ten ^{13}C NMR resonance lines in the region 120–162 ppm (including 6(C) and 7(C)) are assigned to the ten carbon atoms in the pyridyl ring (Fig. 3). Therefore, two resonance lines at 2.12 (1(H)) and 3.10 (2(H) ppm are due to the methyl protons, two sets of resonance lines at 4.71 (3(H)) and 5.07 (4(H)) ppm are due to the methylene protons of the $-CH_2OH$ group, one resonance line at 6.11 ppm (5(H)) is due to the methine proton, two resonance lines at 7.80 (6(H)) and 7.86 (7(H)) ppm are due to the aromatic protons in the pyridyl ring, and one resonance line at 8.78 (8(H)) ppm is due to the proton of the Schiff base, –CH=N– (Fig. 3). In the ^1H NMR spectral behavior, it is noted that the resonance line at 3.10 ppm due to the methyl protons in the pyridoxal moieties appears at a significantly lower magnetic field than that at 2.12 ppm due to the other methyl protons (Fig. 3). This difference in the methyl groups reflects the anisotropic influence, that is, the methyl group attached to pyridyl ring A is placed over pyridyl ring B, while the methyl group attached to pyridyl ring B is not placed over any pyridyl ring, as is found in the crystal structure of [Co(Htpdh)] (Fig. 1). Further, the ^1H and ^{13}C NMR spectral behavior imply that the complex in the acidic solution has a C_2 symmetry. Taking the absorption, CD and NMR spectral behavior, and the X-ray crystal analysis into consideration, therefore, it is concluded that the molecular structure in the crystalline state is retained in acidic solution**, although the protonations occur symmetrically on the two nitrogen atoms in pyridyl rings A and A(#).

Formation of sexidentate ligand

In the present work, it was found that the reaction of pyridoxal, L-alanine and cobalt (II) nitrate followed by H_2O_2 oxidation gave the cobalt(III) complex with the sexidentate ligand tpdh. Since the divalent and trivalent metal ions have been known to catalyze the transamination reaction through the formation of an intermediate Schiff base complex [9], it is likely that pyridoxamine (II) and pyruvic acid are initially formed by the reaction of pyridoxal (I) with L-alanine under the presence of the divalent or trivalent cobalt ion (Scheme 1). The resulting pyridoxamine will undergo

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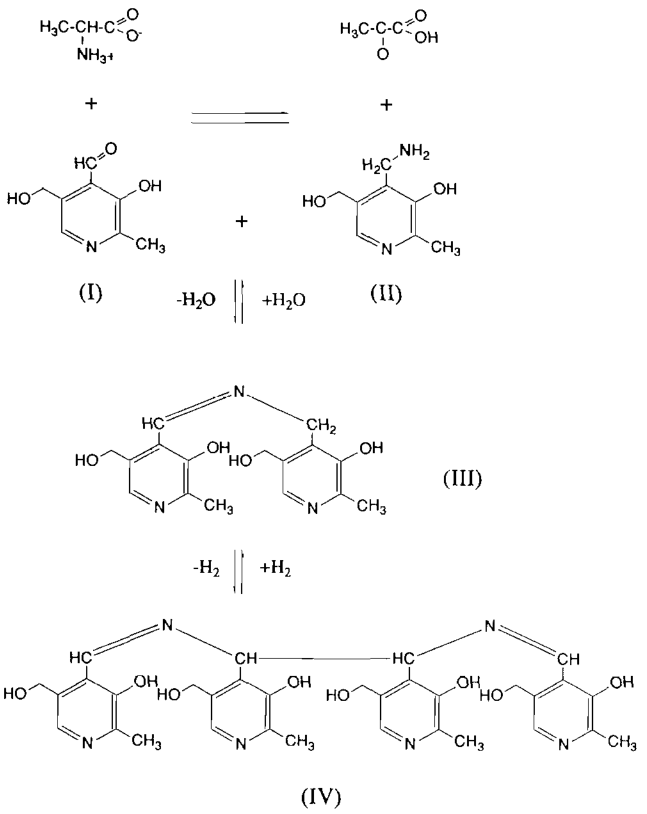
*1(H), 2(H), . . , 1(C), 2(C), . correspond to the numbers of the ^1H NMR and ^{13}C NMR resonance lines in Fig. 3, respectively

**The numbers of the ^{13}C NMR resonance lines in Fig. 3 are associated as follows with the numbering scheme in Fig. 1. 1(C), C(16); 2(C), C(26), 3(C) or 4(C), C(18) or C(28), 5(C), C(27), 6(C) or 7(C), C(15) or C(25); and 8(C), C(17)



Scheme 1.

a condensation with pyridoxal to produce the Schiff base (III in Scheme 1), as in the case of the dimeric Fe(III) complex which has been produced by the slow air evaporation of an aqueous solution containing pyridoxal, alanine and iron(II) perchlorate [8]. Finally, the removal of the hydrogen atom from the Schiff base (III) may occur in the presence of hydrogen peroxide. Then, the sexidentate ligand (IV in Scheme 1), which coordinates to the Co(III) ion, seems to be formed by the oxidative coupling of the Schiff base (III). The cobalt ion will play an important role, not only catalytically but sterically, in the formation of the sexidentate ligand in the present reaction, because the two asymmetric carbon atoms in the ligand have the same absolute configuration in the complex cation.

Supplementary material

Observed and calculated structure factors, and anisotropic thermal parameters are available from Dr K. Okamoto on request.

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