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Structures and Spectral Properties of Iron(II), Cobalt(II), and Copper(II) Complexes Involving 2-(Dimethylamino)-4(3*H*)-pteridinone

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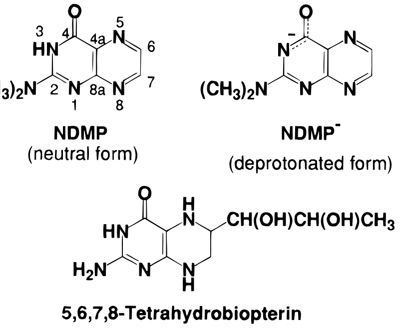
With a view to understanding the pterin cofactor−metal ion interactions, some divalent transition metal complexes containing 2-(dimethylamino)-4(3*H*)-pteridinone (NDMP), $M(NDMP)_2(CH_3OH)_2$ (M = Fe(II) (**1**), Co(II) (**2**), Cu(II) (**3**)) and $Fe(NDMP)_2Cl_2$ (**4**), have been prepared and investigated by magnetic, spectroscopic, and X-ray diffraction methods. Complexes **1**, **2**, and **4** were found to be in a typical high-spin state, and complex **3** was found to be in a $d_{x^2-y^2}$ ground state. Complexes **1**−**3** were structurally determined. $[Fe(NDMP)_2(CH_3OH)_2]\cdot 2CH_3OH$ (**1**) crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 8.54(1)$ Å, $b = 9.353(10)$ Å, $c = 8.45(2)$ Å, $\alpha = 96.5(1)°$, $\beta = 98.3(2)°$, $\gamma = 79.13(9)°$, $V = 653$ Å^3, and $Z = 2$. $[Co(NDMP)_2(CH_3OH)_2]\cdot 2CH_3OH$ (**2**) is isomorphous with **1** with $a = 8.4753(6)$ Å, $b = 9.430(1)$ Å, $c = 8.3695(5)$ Å, $\alpha = 95.885(7)°$, $\beta = 98.412(6)°$, $\gamma = 79.421(8)°$, $V = 648.48$ Å^3, and $Z = 2$. $[Cu(NDMP)_2(CH_3OH)_2]$ (**3**) crystallizes in the monoclinic system, space group $P2_1/a$, with $a = 8.428(1)$ Å, $b = 14.3857(8)$ Å, $c = 8.9570(8)$ Å, $\beta = 95.225(8)°$, $V = 1081.5$ Å^3, and $Z = 4$. The final R and R_w values are 0.042 and 0.033 for **1**, 0.056 and 0.040 for **2**, and 0.040 and 0.018 for **3**, respectively. The geometries around the metal ions are essentially the same, and each metal ion is octahedrally coordinated with 4-carbonyl oxygens and 5-nitrogens of NDMP molecules in the equatorial positions and two methanol molecules in the axial positions. The Fe(II) complexes **1** and **4** exhibited an absorption band centered at 568 nm ($\epsilon = 1900$ M^{-1} cm^{-1}) in DMF and a peak at 674 nm in the reflectance spectrum, respectively, both of which are assigned to a charge transfer. This and other spectroscopic and structural properties have been comparatively discussed.

Introduction

2-Amino-4(3*H*)-pteridinone and its derivatives, which are called “pterins”, are widely distributed in Nature, and pterin cofactors such as folic acid and biopterin play important roles in biological reactions.[1−8] Tetrahydrobiopterin (Chart 1) has been known to be essential for catalytic hydroxylation of aromatic amino acids by iron-containing aromatic amino acid hydroxylases.[4,5] Recently, nitric oxide synthase (NOS), which contains a P450-type heme iron, has been reported to require tetrahydrobiopterin for activity, whose function is unknown.[8] Molybdopterin functions as a cofactor for enzymes such as Mo-containing xanthine oxidase, sulfite oxidase, and DMSO reductase.[9−13] Metal ions at the active site of these enzymes have been inferred to be closely associated with the pterin cofactors in the catalytic reactions, and the very recent structural analyses of aldehyde oxidoreductase,[10] DMSO reductase,[11] formate dehydrogenase,[12] and tungsten-containing aldehyde ferredoxin oxidoreductase[13] established the Mo or W binding through the side-chain dithiolate moiety of molybdopterin.

Chart 1



The pterin-dependent aromatic amino acid hydroxylases such as phenylalanine hydroxylase (PAH) have been thoroughly reviewed recently.[14] They contain a non-heme iron per monomer and introduce a hydroxyl group into the aromatic ring

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of the amino acids by activating dioxygen.[4,5,14,15] In the activation process, the pterin cofactor, biopterin in the tetrahydro form, has been reported to reduce the iron ion at the active site.[16] Reactions of pterins with Cu-containing phenylalanine hydroxylase from *Chromobacterium violaceum* were also investigated by spectroscopic measurements.[17−20] However, Benkovic et al. recently concluded that the active hydroxylating species of the bacterial PAH may not require a redox-active metal.[21−23] The structures and roles of the metal sites of PAH and other hydroxylases and the mechanisms of dioxygen activation and hydroxylation reactions still remain unclear.[24] There are several lines of evidence suggesting the mode of tetrahydropterin−metal center interactions. ESR studies of bacterial PAH−tetrahydropterin systems clearly showed direct binding of tetrahydropterin to the Cu(II) center via the N(5) atom.[19] For mammalian aromatic amino acid hydroxylases, spectroscopic studies of tyrosine hydroxylase suggested that direct pterin coordination to the iron center is rather unlikely and that tetrahydropterin binds within 3−4 Å of the metal ion at the active site.[24] However, exogenous ligands such as catechols are bound to the metal center to inhibit the catalytic reaction.[24]

Studies on the metal−pteridine complexes with emphasis on their biological aspects have been reported for Mo, Mn, Fe, Co, Ni, and Cu,[25−36] and some complexes were isolated and structurally characterized by the X-ray diffraction method. Because of the potential importance of iron in the enzymatic activity, detailed information on the iron complexes has been awaited. We have been studying the structures and properties of copper(II)−pterin complexes with a view to clarifying the metal-binding ability of the pterin ring and thus the mode of active site metal−pterin interactions. A ternary Cu(II) complex containing pterin-6-carboxylate (PC) and 2,2′-bipyridine (bpy) revealed a unique terdentate coordination of PC with the 5-nitrogen atom (N(5)) in the coordination plane.[28] The N(5) coordination was previously concluded from solution studies[26,37] and established by the structural determinations.[25,27−36] Cu(II) has been found to undergo a redox reaction with 6,7-dimethyl-5,6,7,8-tetrahydropterin to give Cu(I) and the protonated trihydropterin radical.[38]

As an extension of our studies on metal−pterin complexes, we now made a comparative study on the coordination mode of the pterin ring to transition metal ions, Fe(II), Co(II), and Cu(II), by magnetic, spectroscopic, and X-ray diffraction methods by using 2-(dimethylamino)-4(3*H*)-pteridinone (NDMP). We established that the pterin−Fe(II) complex is formed through coordination of the O(4) and N(5) atoms under usual experimental conditions, which may point to a possibility of Fe(II)−pterin interactions in biological systems. To our knowledge this is the first structural characterization of Fe(II)-pterin complexes.

Experimental Section

Materials. Anhydrous $FeCl_2$ and sodium methoxide were purchased from Wako. All other reagents used were purchased from Nacalai Tesque and were of analytical grade or the highest grade available. Dimethylformamide (DMF) was dried by 4A molecular sieves (Wako) and carefully distilled below 30 °C under vacuum. 2-(Dimethylamino)-4(3*H*)-pteridinone (NDMP) was prepared according to the procedure reported by Visontini et al.[39] The purity of NDMP was checked by elemental analysis and the ^{1}H NMR spectrum.

Preparation of Complexes. [Fe(NDMP)$_2$(MeOH)$_2$] (1). To a stirred solution of anhydrous $FeCl_2$ (0.127 g, 1.0 mmol) in MeOH (100 mL) were added NDMP (0.382 g, 2.0 mmol) and sodium methoxide (0.11 g, 2.0 mmol) dissolved in MeOH (100 mL), when a brown solution was obtained. After standing at room temperature for a few days, the solution gave brown platelets, which were filtered off, washed with a small amount of methanol, and dried in the open air. Yield: 0.133 g (26.6%). Anal. Calcd for $C_{18}H_{24}N_{10}O_4Fe$: C, 43.21; H, 4.835; N, 27.99. Found: C, 42.99; H, 4.609; N, 28.26%.

[Co(NDMP)$_2$(MeOH)$_2$] (2). To a stirred solution of Co(acetate)$_2$·4H_2O (0.25 g, 1.25 mmol) in MeOH (100 mL) was added NDMP (0.382 g, 2.0 mmol) dissolved in MeOH (100 mL). The reaction mixture kept in a refrigerator overnight gave orange-brown prismatic crystals, which were filtered off, washed with a small amount of methanol, and dried under vacuum. Yield: 0.425 g (84.5%). Anal. Calcd for $C_{18}H_{24}N_{10}O_4Co$: C, 42.94; H, 4.805; N, 27.82. Found: C, 43.07; H, 4.739; N, 28.29.

[Cu(NDMP)$_2$(MeOH)$_2$] (3). To a stirred solution of Cu(acetate)$_2$·H_2O (0.100 g,0.5 mmol) in hot methanol (30 mL) was added NDMP (0.192 g, 1.0 mmol) dissolved in hot methanol (20 mL). A yellowish-green precipitate formed immediately. Acetic acid (ca. 10 mL) was added to this hot reaction mixture until the precipitate was dissolved. After standing in a refrigerator overnight, it gave yellowish green crystals, which were filtered off, washed with a small amount of methanol, and dried in the open air. Yield: 0.090 g (35.4%). Anal. Calcd for $C_{18}H_{24}N_{10}O_4Cu$: C, 42.56; H, 4.762; N, 27.57. Found: C, 42.67; H, 4.646; N, 27.42.

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Table 1. Crystallographic Data for [Fe(NDMP)$_2$(MeOH)$_2$]·2MeOH (**1**), [Co(NDMP)$_2$(MeOH)$_2$]·2MeOH (**2**), and [Cu(NDMP)$_2$(MeOH)$_2$] (**3**)

	1	**2**	**3**
formula	$Fe_{0.5}C_{10}H_{16}N_5O_3$	$Co_{0.5}C_{10}H_{16}N_5O_3$	$Cu_{0.5}C_9H_{12}N_5O_2$
fw	282.19	283.73	254.00
color	brown	brown	greenish brown
cryst size/mm	0.08 × 0.04 × 0.20	0.10 × 0.10 × 0.17	0.03 × 0.06 × 0.30
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/a$
a/Å	8.54(1)	8.4753(6)	8.428(1)
b/Å	9.353(10)	9.430(1)	14.3857(8)
c/Å	8.45(2)	8.3695(5)	8.9570(8)
α/deg	96.5(1)	95.885(7)	
β/deg	98.3(2)	98.412(6)	95.225(8)
γ/deg	79.13(9)	79.421(8)	
V/Å^3	653	648.48	1081.5
Z	2	2	4
D_c/g cm^{-3}	1.433	1.453	1.560
radiation		Cu Kα (1.541 78 Å)	
μ/cm^{-1}	51.06	56.74	18.59
F(000)/e	296.0	297.0	526.0
scan method	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
2θ max/deg	120.0	120.1	120.1
scan speed/deg min^{-1}	8.0	16.0	4.0
scan range/deg	$1.78 + 0.30 \tan\theta$	$1.57 + 0.30 \tan\theta$	$0.94 + 0.30 \tan\theta$
no. of rflns obsd	1919	1879	1491
no. of rflns used	1348	928	688
R^a	0.042	0.056	0.040
$R_w{}^a$	0.033	0.040	0.018

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(F_o)$.

Fe(NDMP)$_2$Cl$_2$ (4). FeCl$_2$ (0.128 g, 1.0 mmol) was added to a methanol solution (50 mL) of NDMP (0.382 g, 2.0 mmol), and the blue reaction mixture was allowed to stand at room temperature for a few days to give a blue precipitate, which was filtered off, washed with a small amount of methanol, and dried in the open air. Yield: 0.180 g (35.4%). Anal. Calcd for $C_{16}H_{18}N_{10}O_2Cl_2Fe$: C, 37.74; H, 3.563; N, 27.51. Found: C, 37.91; H, 3.931; N, 28.41.

Measurements. Electronic absorption spectra were taken on a Shimadzu UV-3101PC spectrophotometer at room temperature. Reflectance spectra were obtained at room temperature by using a JASCO UVIDEC-660 spectrophotometer. X-band ESR spectra of frozen solutions were recorded at 77 K by using a JEOL RE-1X ESR spectrometer. All samples for reflectance spectra were diluted with MgO, and those for electronic absorption and ESR spectral measurements were prepared in DMF. The samples of neutral and deprotonated NDMP for UV absorption spectral measurements were prepared in H$_2$O. The concentrations were 0.3 mM (1 M = 1 mol dm^{-3}), except as noted below. More concentrated sample solutions (3 mM) were used for near-infrared absorption spectral measurement of **2** and visible absorption and ESR spectral measurements of **3**. Infrared (IR) absorption spectra were recorded in KBr disks on a Perkin-Elmer Model 1600 FT-IR spectrophotometer. Elemental analyses were performed on a Leco CHN-900 analyzer. Magnetic susceptibilities were measured at room temperature by the Evans method,[40] and the diamagnetic contributions from the ligands were corrected by using Pascal's constants.

X-ray Structure Determinations of Complexes 1−3. The single crystals of complexes **1**−**3** suitable for X-ray analyses were obtained from methanol solutions. Complexes **1** and **2** were isolated as crystals with two molecules of crystalline methanol. Crystal data and experimental details for the complexes are summarized in Table 1. Diffraction data were collected with a Rigaku AFC-5R four-circle automated diffractometer at 295 K. The reflection intensities were monitored by three standard reflections for every 150 measurements, and the decays of intensities for these crystals were not significant. Reflection data were corrected for Lorentz and polarization effects. Absorption corrections were empirically applied to all the crystals. For the determination and refinements of these structures, independent reflections with $|F_o| \geq 3\sigma(|F_o|)$ were used.

The structures were solved by the heavy-atom method and refined anisotropically for non-hydrogen atoms by full-matrix least-squares calculations. All refinements were continued until all shifts were smaller than one-third of the standard deviations of the parameters involved. Atomic scattering factors and anomalous dispersion terms were taken from literature.[41] All hydrogen atoms for the three structures were included as isotropic in the structure factor calculations at the final stage of refinement; some of their positions were located on the calculated positions. The final R and R_w values were 0.042 and 0.033 for **1**, 0.056 and 0.040 for **2**, and 0.040 and 0.018 for **3**, respectively. The weighting scheme $w = 1/\sigma^2(F_o)$ was employed for all crystals. The final difference Fourier map did not show any significant features except the ghost peaks close to metal atoms. The calculations were performed on an SGI IRIS Indigo 4D/RPC computer by using the program system teXsan.[42] The final atomic parameters for non-hydrogen atoms are listed in Tables 2, 3, and 4 for **1**, **2**, and **3**, respectively.

EHMO Calculations for NDMP. EHMO calculations for the neutral and deprotonated NDMP molecules were performed on an Epson model PC-286V personal computer, by using the program coded by Kitaura,[43] where the atomic orbital parameters reported by Hoffmann et al.[44,45] were used.

Results and Discussion

Preparations and Magnetic Properties of Complexes 1−4. Several transition metal−pterin complexes have been synthesized and studied by the crystallographic method, which showed that pterins coordinate to metal ions through O(4) and N(5) atoms with deprotonation from the N(3)H−C(4)O amide bond. From the reaction mixture of Cu(II), bpy, and folate in water we isolated the first pterin-containing Cu(II) complex, [Cu(bpy)(PC)(H$_2$O)], and determined the crystal structure, where PC coordinates to Cu(II) as a terdentate ligand through the N(5) atom at an equatorial position with the carbonyl and carboxylate

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Table 2. Positional Parameters and Equivalent Isotropic Temperature Factors for the Non-Hydrogen Atoms of $[Fe(NDMP)_2(MeOH)_2]\cdot 2MeOH$ (**1**)

atom	*x*	*y*	*z*	$B_{eq}{}^{b}$
Fe	0	0	0	3.34(3)
N(1)	−0.0873(4)	0.2338(3)	0.5805(3)	3.44(9)
C(2)	0.0387(5)	0.2884(4)	0.5488(5)	3.5(1)
N(2)	0.1063(4)	0.3775(4)	0.6641(4)	4.1(1)
N(3)	0.1062(4)	0.2676(3)	0.4082(4)	3.47(9)
C(4)	0.0436(5)	0.1804(4)	0.2907(5)	3.2(1)
O(4)	0.1005(3)	0.1549(3)	0.1548(3)	3.87(7)
C(4a)	−0.0915(4)	0.1167(4)	0.3125(4)	2.8(1)
N(5)	−0.1510(4)	0.0271(3)	0.1930(3)	3.16(8)
C(6)	−0.2757(5)	−0.0294(5)	0.2183(5)	3.6(1)
C(7)	−0.3365(6)q	0.0019(5)	0.3655(5)	4.4(1)
N(8)	−0.2808(4)	0.0895(4)	0.4851(4)	4.0(1)
C(8a)	−0.1524(5)	0.1469(4)	0.4601(4)	3.0(1)
C(m1)	0.2499(9)	0.432(1)	0.645(1)	5.9(2)
C(m2)	0.038(1)	0.4229(8)	0.8151(7)	5.5(2)
C(m)	−0.326(1)	0.208(1)	−0.120(1)	7.7(2)
O(m)	−0.1606(3)	0.1672(3)	−0.1268(3)	4.18(8)
C(M)[a]	0.430(1)	0.352(1)	0.219(2)	9.1(3)
O(M)[a]	0.3724(5)	0.2514(6)	0.1139(5)	10.8(2)

[a] M refers to the methanol of crystallization. [b] $B_{eq} = 8\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U12aa^*bb^* \cos \gamma + 2U_{13}aa^*cc^* \cos \beta + 2U_{23}bb^*cc^* \cos a)/3$.

Table 3. Positional Parameters and Equivalent Isotropic Temperature Factors for the Non-Hydrogen Atoms of $[Co(NDMP)_2(MeOH)_2]\cdot 2MeOH$ (**2**)

atom	*x*	*y*	*z*	$B_{eq}{}^{b}$
Co	1	0	1	3.18(5)
N(1)	0.9111(8)	0.2311(7)	1.5800(7)	3.3(2)
C(2)	1.039(1)	0.2856(9)	1.545(1)	3.8(3)
N(2)	1.105(1)	0.3752(7)	1.6631(8)	4.3(2)
N(3)	1.1069(8)	0.2650(7)	1.4045(7)	3.7(2)
C(4)	1.045(1)	0.1805(8)	1.2867(8)	2.9(2)
O(4)	1.1032(6)	0.1643(5)	1.1514(5)	3.7(1)
C(4a)	0.909(1)	0.1146(8)	1.3097(8)	2.7(2)
N(5)	0.8504(8)	0.0257(6)	1.1875(6)	2.9(2)
C(6)	0.725(1)	−0.031(1)	1.216(1)	3.6(3)
C(7)	0.660(1)	−0.001(1)	1.360(1)	4.3(3)
N(8)	0.7160(9)	0.0842(8)	1.4830(7)	4.3(2)
C(8a)	0.845(1)	0.1444(8)	1.4577(9)	3.2(2)
C(m1)	1.249(1)	0.435(1)	1.643(1)	6.3(4)
C(m2)	1.036(2)	0.420(2)	1.814(1)	5.5(4)
C(m)	0.681(1)	0.211(2)	0.883(1)	8.3(4)
O(m)	0.8451(7)	0.1627(5)	0.8722(5)	3.9(2)
C(M)a	0.425(1)	0.356(1)	0.222(1)	9.2(4)
O(M)a	0.378(1)	0.251(1)	0.1146(8)	11.3(3)

[a] M refers to the methanol of crystallization. [b] $B_{eq} = 8\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos \gamma + 2U_{13}aa^*cc^* \cos \beta + 2U_{23}bb^*cc^* \cos \alpha)/3$.

Table 4. Positional Parameters and Equivalent Isotropic Temperature Factors for the Non-Hydrogen Atoms of $[Cu(NDMP)_2(MeOH)_2]$ (**3**)

atom	*x*	*y*	*z*	$B_{eq}{}^{b}$
Cu	$^1/_2$	0	$^1/_2$	3.16(4)
N(1)	1.0218(7)	−0.0139(4)	0.2575(6)	3.0(2)
C(2)	0.960(1)	0.0700(5)	0.2165(8)	2.9(2)
N(2)	1.0509(8)	0.1223(4)	0.1320(7)	3.5(2)
N(3)	0.8196(8)	0.1086(4)	0.2456(7)	3.3(2)
C(4)	0.727(1)	0.0598(5)	0.3276(8)	2.8(2)
O(4)	0.5912(6)	0.0878(3)	0.3625(6)	3.2(1)
C(4a)	0.784(1)	−0.0308(4)	0.3827(8)	2.4(2)
N(5)	0.6906(7)	−0.0789(4)	0.4692(6)	2.4(2)
C(6)	0.741(1)	−0.1608(5)	0.516(1)	3.2(2)
C(7)	0.833(1)	−0.1963(5)	0.472(1)	4.0(3)
N(8)	0.9767(7)	−0.1508(4)	0.3871(7)	3.7(2)
C(8a)	0.926(1)	−0.0643(5)	0.3408(8)	2.9(2)
C(m1)	1.007(2)	0.2176(9)	0.089(2)	5.9(4)
C(m2)	1.198(2)	0.0897(7)	0.082(1)	5.1(4)
C(m)	0.392(2)	−0.126(1)	0.181(2)	7.7(4)
O(m)	0.3444(9)	−0.0792(4)	0.3036(7)	4.6(2)

[a] M refers to the methanol of crystallization. [b] $B_{eq} = 8\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos \gamma + 2U_{13}aa^*cc^* \cos \beta + 2U_{23}bb^*cc^* \cos \alpha)/3$.

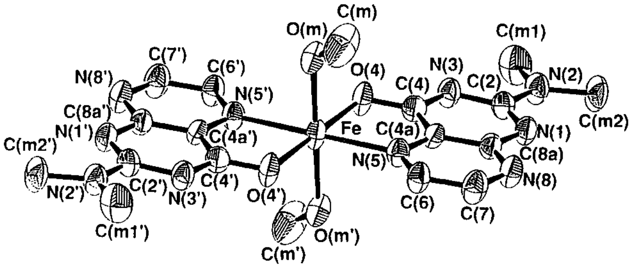

Figure 1. Molecular structure of $[Fe(NDMP)_2(MeOH)_2]\cdot 2MeOH$ (**1**) showing the atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

oxygen atoms at the axial positions. The Cu(II)−PC bonding is stabilized by two axial coordinations. Burgmayer et al. reported the synthesis of several metal complexes in organic solvents and determined the structures of Co(II) and Cu(II) complexes by X-ray analyses.[27,29] Because of the low solublities of most pterins in various solvents, it is difficult to synthesize and study metal−pterin complexes. To overcome the difficulties, we used a 2-(*N*,*N*-dimethyl)-substituted pterin, NDMP, whose solublity in organic solvents such as methanol enabled us to isolate crystals of a series of metal−pterin complexes.

The magnetic susceptibilities of the complexes in the solid state were measured at room temperature, and ESR spectra at 77 K were recorded for the DMF solutions. Complexes **1** and **4** showed $\mu_{eff} = 5.14$ and 5.73 μ_B, respectively, but their ESR spectra were silent as has often been observed for Fe(II) complexes. Complex **2** exhibited $\mu_{eff} = 4.93$ μ_B and a broad ESR signal typical of a high-spin Co(II) complex at $g = \sim 4$. The results indicate that **1**, **2**, and **4** are in a divalent high-spin state. The ESR spectrum of **3** in DMF gave an axially symmetric signal in a $d_{x^2-y^2}$ ground state ($g_\perp = 2.06$, $g_{||} = 2.26$, and $|A_{||}| = 17.7$ mT), indicating that **3** has an axially elongated octahedral geometry with Jahn−Teller distortion.

Crystal and Molecular Structures of $[Fe(NDMP)_2(CH_3OH)_2]\cdot 2CH_3OH$ (1), $[Co(NDMP)_2(CH_3OH)_2]\cdot 2CH_3OH$ (2), and $[Cu(NDMP)_2(CH_3OH)_2]$ (3). Crystals **1** and **2** are isomorphous, and each contains in the unit cell two molecules of $[M(NDMP)_2(CH_3OH)_2]$ and four molecules of methanol, which are hydrogen-bonded to the O(4) atoms of the deprotonated NDMP ($NDMP^-$) rings with O−O distances of 2.73 and 2.72 Å. The coordinated methanols in **1**, **2**, and **3** form hydrogen bonds with the N(1) atoms of the $NDMP^-$ rings of neighboring complex molecules, the N−O distances being 2.80, 2.75, and 2.87 Å, respectively. The crystal structure of **1** established here is the first example of iron complexes containing pterins. The molecular structures of **1**, **2**, and **3** are shown in Figures 1, 2, and 3, respectively, and the bond lengths and angles are listed in Table 5. We see from these results that **1**−**3** have essentially the same coordination structures, although there are some subtle differences in their bond parameters. Each metal ion is in a six-coordinate octahedral geometry with two NDMP molecules at the equatorial positions and two methanol molecules at the axial positions. The elemental analysis indicates that **4** also has an octahedral structure similar to that of **1** with two chloride ions in place of methanol molecules in the axial positions. Consequently, it is concluded that the

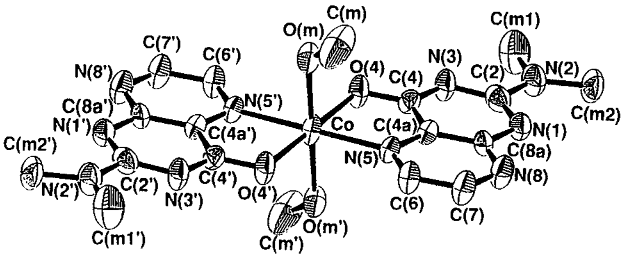

Figure 2. Molecular structure of [Co(NDMP)$_2$(MeOH)$_2$]·2MeOH (**2**) showing the atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

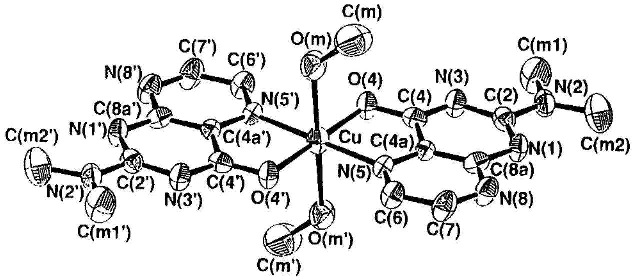

Figure 3. Molecular structure of [Cu(NDMP)$_2$(MeOH)$_2$] (**3**) showing the atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

Table 5. Selected Bond Distances (Å) and Angles (deg) for [Fe(NDMP)$_2$(MeOH)$_2$]·2MeOH (**1**), [Co(NDMP)$_2$(MeOH)$_2$]·2MeOH (**2**), and [Cu(NDMP)$_2$(MeOH)$_2$] (**3**)

	1	**2**	**3**	euglenapterin[a]
M−O(4)	2.064(4)	2.062(4)	1.969(5)	
M−N(5)	2.187(3)	2.126(5)	2.006(5)	
M−O(m)	2.151(4)	2.099(5)	2.386(6)	
C(m)−O(m)	1.398(7)	1.39(1)	1.38(1)	
N(1)−C(2)	1.347(5)	1.36(1)	1.352(8)	1.314(9)
N(1)−C(8a)	1.351(5)	1.363(8)	1.355(8)	1.373(9)
C(2)−N(2)	1.346(5)	1.36(1)	1.354(8)	1.341(9)
C(2)−N(3)	1.374(4)	1.363(8)	1.353(8)	1.391(9)
N(2)−C(m1)	1.449(7)	1.47(1)	1.46(1)	1.46(1)
N(2)−C(m2)	1.466(6)	1.46(1)	1.43(1)	1.47(1)
N(3)−C(4)	1.328(5)	1.312(8)	1.322(8)	1.394(9)
C(4)−O(4)	1.291(4)	1.283(7)	1.278(8)	1.221(8)
C(4)−C(4a)	1.438(5)	1.45(1)	1.460(8)	1.46(1)
C(4a)−N(5)	1.341(5)	1.351(8)	1.343(8)	1.346(9)
C(4a)−C(8a)	1.400(5)	1.404(8)	1.381(9)	1.416(9)
N(5)−C(6)	1.329(5)	1.330(9)	1.309(8)	1.33(1)
C(6)−C(7)	1.397(5)	1.382(9)	1.39(1)	1.405(9)
C(7)−N(8)	1.318(5)	1.321(9)	1.319(8)	1.318(9)
N(8)−C(8a)	1.361(5)	1.374(9)	1.366(8)	1.35(1)
C(M)−O(M)	1.330(9)	1.341(9)		
O(4)−M−N(5)	79.6(2)	80.8(2)	85.1(2)	
O(4)−M−O(m)	91.4(2)	89.5(2)	93.7(2)	
N(5)−M−O(m)	91.9(2)	92.2(2)	91.3(2)	

[a] Reference 49.

NDMP molecules in **1**−**3** are deprotonated and those in **4** are in the neutral form.

The Fe−N(5) bond (2.187(3) Å) in **1** is longer than the bonds reported for the Fe(II) complexes with chelating pyridine ligands (Fe−N = 1.958−2.182 Å),[46] whereas the Fe−O(4) bond (2.064(4) Å) lies on the shorter side of the usual range observed for similar σ-bonded oxygen ligand complexes (2.043−2.135 Å).[46] The Fe−O(CH$_3$OH) bond length (2.151(4) Å) agrees well with the values reported for the high-spin Fe(II) complexes with CH$_3$OH molecules (2.110,[47] 2.205 Å[48]). For **2** the Co−N(5) bond (2.126(5) Å) is on the shorter side of the range reported hitherto for Co−N(chelating pyridine ligands) (2.126−2.156 Å),[46] and the Co−O(4) bond (2.062(6) Å) is also on the shorter side of the observed range (2.059−2.123 Å).[46] The Co−O(CH$_3$OH) bond (2.101(6) Å) is in the usual range (2.076−2.108 Å).[46] The geometry around the Cu(II) ion in **3** exhibited Jahn−Teller distortion with elongated Cu(II)−methanol bonds (2.386(6) Å) well within the reported range (2.290−2.474 Å).[46] The Cu−N(5) bond (2.006(5) Å) is rather short for Cu(II) complexes with chelating pyridine ligands (1.990−2.053 Å),[46] while the Cu−O(4) bond (1.969(5) Å) is rather long for Cu(II) complexes (1.950−1.973 Å).[46] Taking the reported ranges of M−N and M−O bond lengths into account, we may infer that the relative affinity of the metal ions for the pterin ring is in the order Cu ≈ Co > Fe for the N atom and Fe ≈ Co > Cu for the O atom.

The pterin nucleus in the NDMP complexes exhibited significant changes in bond lengths upon coordination to the metal ions, which may be compared with those in neutral euglenapterin, a natural 2-(*N*,*N*-dimethyl) derivative of pterin, reported previously.[49] In all the complexes the N(1)−C(2) and C(4)−O(4) bonds are longer than those for euglenapterin (=1.314(9) and 1.221(8) Å, respectively), while the C(2)−N(3) and N(3)−C(4) bonds are significantly shorter than those for the same pterin (1.391(9) and 1.394(9) Å, respectively). The shorter N(3)−C(4) and longer C(4)−O(4) bonds are attributed to the localization of a negative charge on the O(4) atom by deprotonation from the N(3)−C(4) moiety upon coordination to the metal ions, and this supports that two molecules of MeOH and not MeO$^-$ ions are coordinated. The C(4)−O(4) bond length tends to increase in the order **3** (1.278 (8)) < **2** (1.283(7)) < **1** (1.291(4) Å), which is in agreement with the affinity of M for O, i.e., the higher the affinity, the longer the C−O bond. On the other hand, **4** was not obtained as single crystals. We reported previously that the Cu(II) complex of the 6,7-dimethyl derivative of NDMP (DMDMP), [Cu(DMDMP)$_2$(NO$_3$)$_2$], has a molecular structure similar to that shown in Figure 3 except that the apical positions are occupied by NO$_3$ ions.[33] This suggests that **4** has the same structure having Cl$^-$ ions in place of the NO$_3$ ions.

Interestingly, all the crystal structures exhibit intermolecular aromatic ring stacking between the coordinated pterin rings, the average spacings being 3.47, 3.46, and 3.60 Å in **1**, **2**, and **3**, respectively. Similar stacking interactions have been revealed in the crystal structures of [Co(ethp)$_2$(H$_2$O)$_2$]·2DMF (ethp = 2-(ethylthio)-4-hydroxypteridine)[27] and [Cu(bpy)(PC)(H$_2$O)].[28]

Infrared Absorption Spectra. The IR spectra of **1**−**4** are very similar to each other, suggesting the structural similarity of the complexes. The bands assignable to the C=C, C=N, and C=O stretching vibrations listed in Table 6 shifted to a lower frequency region than that for uncoordinated neutral NDMP upon deprotonation and/or complexation, which is comparable with the changes due to the sodium salt formation of 4-hydroxypteridine.[50] The band at 1692 cm^{-1} due to the C(4)=O(4) stretching vibration of metal-free NDMP shifted to a lower frequency region by complex formation, the shift being in the order **1** (99 cm^{-1}) > **2** (97 cm^{-1}) > **3** (89 cm^{-1}) > **4** (76 cm^{-1}). The C=O stretching vibration for **4** (1616 cm^{-1}) observed at the highest frequency among the four complexes supports that NDMP in **4** is not deprotonated. Therefore, the single-bond character of the carbonyl group is in the order **1** >

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Table 6. Electronic Absorption, Reflectance, and Infrared Absorption Spectral Data for NDMP, $[Fe(NDMP)_2(MeOH)_2]\cdot 2MeOH$ (**1**), $[Co(NDMP)_2(MeOH)_2]\cdot 2MeOH$ (**2**), $[Cu(NDMP)_2(MeOH)_2]$ (**3**), and $Fe(NDMP)_2Cl_2$ (**4**)

sample	λ_{max} (ϵ)/nm (M^{-1} cm^{-1}) in soln[a]					λ_{max}/nm in the solid state[c]			$\nu_{C=O}$, $\nu_{C=N}$, $\nu_{C=C}$/cm^{-1} [d]
NDMP	221 (15500)	283 (17200)	348 (5430)	~370 (4400)		282	386		1692 vs, 1613 vs, 1552 sh, 1535 vs, 1462 vs, 1397 sh, 1378 vs, 1338 m, 1314 s
$NDMP^-$	226 (12900)	270 (22800)		379 (7670)					
1		282 (46800)		398 (11500)	568 (1900)	285	402	578	1593 vs, 1566 vs, 1530 vs, 1485 s, 1414 sh, 1393 s, 1352 s
2		285 (44800)		401 (10560)	1130 (4)	292	402		1595 vs, 1568 vs, 1529 vs, 1490 s, 1422 s, 1394, s, 1352 s
3		287 (55600)	327 (7460)	410 (11860)	676 (70)	290	434	662	1659 sh, 1603 vs, 1565 vs, 1534 vs, 1481 vs, 1446 sh, 1393 vs, 1357 vs, 1335 sh
4			*b*				350	674	1616 vs, 1584 vs, 1544 vs, 1509 m, 1464 s, 1392 sh, 1373 vs

[a] Absorption spectra in solution were measured in the following solvents: NDMP, H_2O (pH 4.9); $NDMP^-$, H_2O (pH 10.2); **1**, **2**, and **3**, DMF. [b] $Fe(NDMP)_2Cl_2$ is unstable in DMF. [c] Reflectance spectra were measured in MgO. [d] IR spectra were measured in KBr disks (vs = very strong, s = strong, sh = shoulder).

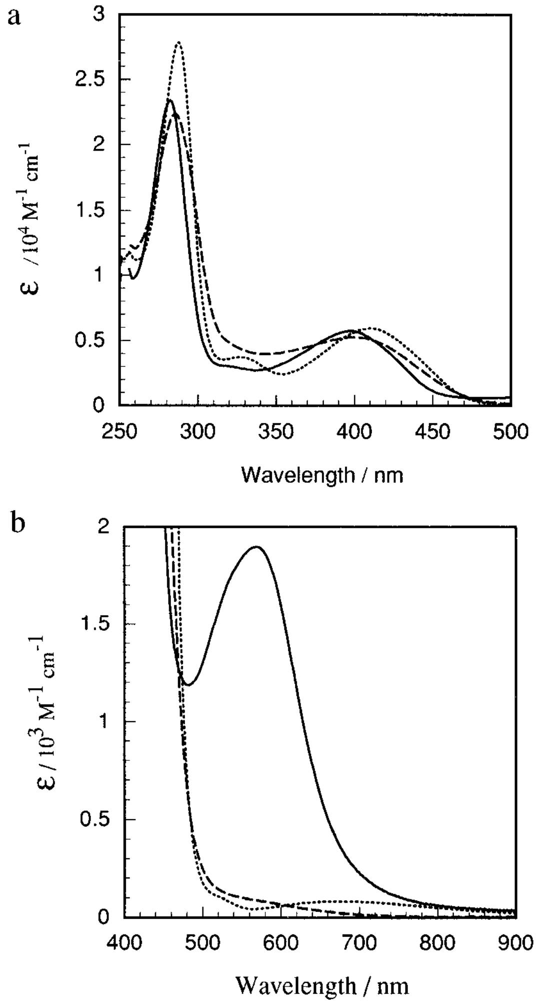

Figure 4. (a) UV and (b) visible absorption spectra for **1**−**3** in DMF. Curves: (—) complex **1**; (− − −) complex **2**; (···) complex **3**.

2 > **3** > **4**, so that the oxygen binds with the metal ion most strongly in **1** with the order of binding as **1** > **2** > **3** > **4**, which is consistent with the M−O(4) and C(4)=O(4) bond lengths obtained from the X-ray crystal structure analyses.

Electronic Absorption Spectra. The electronic absorption spectra in the UV and visible regions (Figure 4, panels a and b, respectively) and reflectance spectra were measured in order to examine the electronic structural changes due to complex formation of NDMP.

The absorption spectra of **1**−**3** (Table 6) were obtained in DMF, which dissolved them well. The precipitate of **4** was sparingly soluble in MeOH and most other solvents and, once dissolved, seemed unstable because the color of the solution faded rapidly. Their reflectance spectra in the solid state gave nearly the same patterns as those in solution, indicating that their solid state structures are maintained also in solution (Table 6). The metal complexes with NDMP demonstrated visible spectra that are characteristic of the respective metal ions. The brown complex **1** exhibited an intense absorption band centered at 568 nm ($\epsilon = 1900$), whose intensity suggests that it is a charge transfer band. It was reported that absorption bands of metal−8-hydroxyquinoline complexes are likely to be due to MLCT and not LMCT, since the quinoline ring allows more delocalization than the benzene ring of phenol.[51] The negative charge of $NDMP^-$ was found to be delocalized in the pteridine ring by the present EHMO calculations, and the transition band at 568 nm is inferred to be an MLCT band. The corresponding band was observed in the reflectance spectrum of the blue complex **4** at an energy lower (674 nm) than that of **1** (578 nm). The band at 674 nm of **4** may be assigned to MLCT between Fe(II) and neutral NDMP, and the difference in the maximum wavelengths is explained as due to the elevation of the energy level of d_π orbitals by the axially coordinated Cl^- ions. Complex **2** showed a weak band at 1130 nm ($\epsilon = 4$) typical of a d−d transition in a high-spin Co(II) complex, and **3** gave a d−d peak at 676 nm ($\epsilon = 70$). It was also reported for metal(II)−picolinic acid *N*-oxide complexes that MLCT energies decrease in the order Cr(III) ≫ Cu(II) > Mn(II) > Ni(II) > Co(II) > Fe(II).[52] The MLCT band was not observed in the spectra of **2** and **3**, because the band was shifted to a higher energy region and obscured by the first $\pi-\pi^*$ band of $NDMP^-$. Such an observation was also made for the ethp complexes.[27,29]

The absorption spectra of NDMP showed significant shifts due to coordination to the metal ions (Table 6). Judging from the absorption maxima, the intense bands detected for NDMP at ~370, 283, and 221 nm and the overlapping peak at 348 nm were tentatively assigned to the first, second, and third $\pi-\pi^*$ transitions and the $n-\pi^*$ transition, respectively, on the basis of the assignments reported for pteridine derivatives.[53] The mentioned $\pi-\pi^*$ transition bands in an aqueous solution (pH 4.89) shifted to 379, 270, and 226 nm at pH 10.2, respectively, by deprotonation. The first and second $\pi-\pi^*$ bands of $NDMP^-$ exhibited bathochromic shifts to 398−410 and 282−287 nm, respectively, upon complex formation in DMF, although these

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could also be due to the solvent effect. The bathochromic effect was in the order **1** < **2** < **3**, which may reflect the perturbation of the pterin π and π^* orbitals by the d_π orbitals. The shoulder observed at 327 nm only in **3** may be assigned to the n−π^* band mainly arising from the lone-pair electrons on N(8),[53,54] whose energy level appears to have been affected by N(5) coordination.

Conclusion

In order to examine possible pterin cofactor−metal ion interaction modes, we performed structural and spectroscopic investigations of the Fe(II), Co(II), and Cu(II) complexes of NDMP and discussed the relationship between the electronic and molecular structures of the complexes. The complexes showed very similar pterin−metal bonding modes and similar coordination structures. On the basis of the molecular structures and IR spectra, the strength of the interaction between the metal ions and NDMP$^-$ has been concluded to be in the order **1** > **2** > **3** > **4** for the M−O(4) bond and **3** > **2** > **1** for the M−N(5) bond. The drastic color change observed upon complex formation of Fe(II) with deprotonated NDMP$^-$ (**1**) (brown) and that with neutral NDMP and Cl$^-$ ions (**4**) (blue) revealed unique charge transfer bands at 568 and 674 nm, respectively. We reported previously that Cu(II) reacts with 6,7-dimethyl-5,6,7,8-tetrahydropterin to give the protonated trihydropterin radical,[38] and a recent study by Viscontini's group[35] revealed that the trihydropterin radical is formed by the reaction of the Fe(III) complex of acetylacetone with 5,6,7,8-tetrahydropterin. These findings provide information of the metal complex formation by the pterin derivatives and the changes accompanying the direct coordination of the pterin ring and may suggest possible metal−pterin interactions in biological systems.

Acknowledgment. We are grateful to Professor Sadao Matsuura, Fujita Health University College, for the synthesis of NDMP and other pterins. The lengths of high−spin iron(II)−O(MeOH) bonds were surveyed by using Ver. 5.06 of the Cambridge Structural Database (CSD). This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 04225102) from the Ministry of Education, Science, Sports, and Culture of Japan, for which we express our thanks.

Supporting Information Available: Tables of atomic coordinates and anisotropic thermal parameters for non-hydrogen atoms, fractional coordinates and isotropic thermal parameters for hydrogen atoms, and bond angles and torsion angles for complexes **1**−**3** (15 pages). Ordering information is given on any current masthead page.

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