

Synthesis, Crystal Structure, and Solution Properties of a Hexacopper(II) Complex with Bridging Hydroxides, Pyrazolates, and Nitrates

Ken Sakai,*[†] Yasutaka Yamada,[†] Taro Tsubomura,[†] Masayuki Yabuki,[‡] and Motowo Yamaguchi[‡]

Department of Industrial Chemistry, Faculty of Engineering, Seikei University, Kichijoji-Kitamachi, Musashino, Tokyo 180, Japan, and Department of Industrial Chemistry, Faculty of Engineering, Tokyo Metropolitan University, Minami-osawa, Hachioji, Tokyo 192-03, Japan

Received February 15, 1995

Introduction

In our recent efforts to obtain bifunctional molecules containing more than two metal ions, we have been paying special attention to the pyrazolate-bridged compounds that have been extensively studied so far with use of Pt^{II},¹ Ru^{II},² Cu^{II},³ Ir^{III},⁴ and other ions.⁵ In the present study, a new pyrazolate-bridged hexacopper(II) complex made up of two trimer units has been isolated and characterized. Spectrophotometric and electric conductivity measurements have also been carried out to understand the stability of the hexacopper(II) core in solution.

Experimental Section

Chemicals and Measurements. Pyrazole (Tokyo Kasei) and Cu(NO₃)₂·3H₂O (Kokusen) were used as received. An IR spectrum was acquired on a JEOL JIR-3500 spectrometer. UV–visible spectra were acquired on a JASCO V-520 spectrophotometer. Electric conductivity measurements were performed with a TOA CM-20S instrument. A FAB mass spectrum was obtained on a JEOL JMS-LX1000 spectrometer using *m*-nitrobenzyl alcohol as a matrix.

[Cu(pzH)₄(NO₃)₂] (1) (pzH = Pyrazole). This compound was previously reported by Reedijk et al.⁶ but was prepared by our method. A solution of Cu(NO₃)₂·3H₂O (15 mmol) and pzH (60 mmol) in H₂O (100 mL) was stirred at 70 °C for 2 h. Filtration while the solution was hot and standing at room temperature overnight afforded the product as violet needles, which were collected and air-dried (yield: 55%). Anal. Calcd for Cu₆O₁₄N₁₀C₁₂H₁₆: C, 31.34; H, 3.51; N, 30.46. Found: C, 31.45; H, 3.86; N, 30.62.

[Cu₃(μ₃-OH)(μ-pz)₃(μ₄-NO₃)(pzH)₃]₂(μ-NO₃)₂ (2) (pz = Pyrazolate). Cu(NO₃)₂·3H₂O (10 mmol) and **1** (5 mmol) were dissolved in water (50 mL) followed by adjustment of pH to 6 with 1 M NaOH.

[†] Seikei University.

[‡] Tokyo Metropolitan University.

- (1) (a) Minghetti, G.; Banditelli, G.; Bonati, F. *J. Chem. Soc., Dalton Trans.* **1979**, 1851. (b) Bandini, A. L.; Banditelli, G.; Minghetti, G.; Bonati, F. *Can. J. Chem.* **1979**, *57*, 3237.
- (2) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J.; Peedin, J. *Inorg. Chem.* **1979**, *18*, 3369.
- (3) (a) ten Hoedt, R. W. M.; Hulsbergen, F. B.; Verschoor, G. C.; Reedijk, J. *Inorg. Chem.* **1982**, *21*, 2369. (b) Hulsbergen, F. B.; ten Hoedt, R. W. M.; Verschoor, G. C.; Reedijk, J. *J. Chem. Soc., Dalton Trans.* **1983**, 539.
- (4) (a) Beveridge, K. A.; Bushnell, G. W.; Dixon, K. R.; Eadie, D. T.; Stobart, S. R. *J. Am. Chem. Soc.* **1982**, *104*, 920. (b) Coleman, A. W. (T.); Eadie, D. T.; Stobart, S. R. *J. Am. Chem. Soc.* **1982**, *104*, 922. (c) Beveridge, K. A.; Bushnell, G. W.; Stobart, S. R.; Atwood, J. L.; Zaworotko, M. J. *Organometallics* **1983**, *2*, 1447. (d) Nussbaum, S.; Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem.* **1985**, *63*, 692. (e) Lichtenberger, D. L.; Copenhaver, A. S.; Gray, H. B.; Marshall, J. L.; Hopkins, M. D. *Inorg. Chem.* **1988**, *27*, 4488.
- (5) (a) Trofimenko, S. *Inorg. Chem.* **1971**, *10*, 1372. (b) Trofimenko, S. *Chem. Rev.* **1972**, *72*, 497. (c) Fieslmann, B. F.; Stucky, G. D. *Inorg. Chem.* **1978**, *17*, 2074. (d) Lopetz, G.; Ruiz, J.; Garcia, G.; Vicente, C.; Casabo, J.; Molins, E.; Miravittles, C. *Inorg. Chem.* **1991**, *30*, 2605.
- (6) Reedijk, J.; Windhorst, J. C. A.; van Ham, N. H. M.; Groeneveld, W. L. *Recl. Trav. Chim. Pays-Bas* **1971**, *90*, 234.

Table 1. Crystallographic Data for **1** and **2**

	1	2
formula	Cu ₆ O ₁₄ N ₁₀ C ₁₂ H ₁₆	Cu ₆ O ₁₄ N ₂₈ C ₃₆ H ₄₄
fw	459.87	1474.20
space group	C2/c (No. 15)	P4 ₂ /m (No. 113)
<i>a</i> , Å	13.725(1)	17.650(3)
<i>b</i> , Å	9.939(2)	17.650(3)
<i>c</i> , Å	14.733(1)	9.241(2)
β, deg	112.023(5)	90
<i>V</i> , Å ³ ; <i>Z</i>	1863.2(4); 4	2878.8(9); 2
ρ _{calcd} , g/cm ³ ; μ, cm ⁻¹	1.639; 12.28	1.701; 22.60
<i>R</i> ^a ; <i>R</i> _w ^b	0.039; 0.031	0.066; 0.055

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}, \quad w = 1/\sigma^2(F_o).$$

The solution was then stirred at 80 °C for 3 h followed by filtration while hot for removal of insoluble materials. Standing at room temperature overnight afforded the product as dark blue prisms, which were collected and air-dried (yield: 45%). Anal. Calcd for Cu₆O₁₄N₂₈C₃₆H₄₄: C, 29.33; H, 3.01; N, 26.60. Found: C, 28.74; H, 3.21; N, 26.19. IR (KBr): 3261 (s, br), 1626 (w), 1383 (vs, br), 1182 (m), 1167 (w), 1128 (m), 1067 (s), 756 (s), 623 (m), 606 (m), 455 (w, br), 357 (s).

X-ray Crystallography. Crystals were mounted on glass fibers. Diffraction data at 23 °C were measured on a Rigaku AFC-5S diffractometer using graphite-monochromated Mo Kα (0.710 69 Å) radiation and the ω–2θ scan technique (8 deg/min). Crystal data are listed in Table 1. All data sets were corrected for Lorentz and polarization effects and for absorption (Ψ scan method for **1** and DIFABS⁷ for **2**). Metal atom positions were determined by the direct method SAPI91,⁸ and the remaining atoms were located using both the DIRDIF⁹ program and difference Fourier synthesis. All non-hydrogen atoms were refined anisotropically by full-matrix least squares. All hydrogen atoms, located in their idealized positions (C–H = 0.95 Å and N–H = O–H = 0.87 Å), were included in the final refinements and were not refined. All the calculations were performed on the teXsan¹⁰ software. Final positional parameters of **1** and **2** are given in Table 2.

Results and Discussion

Selected interatomic distances and angles for **1** and **2** are summarized in Table 3. Complex **1** possesses an elongated tetragonal octahedral stereochemistry (see Table 3), which is similar to that of [Cu(imidazole)₄(OH₂)₂]²⁺.¹¹ On the other hand, **2** turned out to be a hexacopper(II) complex made up of two trimer units, and two crystallographic mirrors pass through the center of the molecule (Figure 1). The intertrimer linkage is supported by two bridging nitrate ions. The rest of the nitrate ions are weakly bound to the three Cu atoms of a trimer unit in a μ₄-mode. Thus, in the crystal, **2** is a neutral molecule having C_{2v} symmetry. The trinuclear [Cu₃(μ₃-OH)(μ-pz)₃]²⁺ core involved in **2** was previously identified in the X-ray study of an infinite chain complex [Cu₃(μ₃-OH)(μ-pz)₃(NO₃)(pzH)₂](NO₃)·H₂O (**3**).^{3b} All the terminal sites in **2** are occupied with monodentate pyrazoles, whereas **3** involves a terminally ligated nitrate ion. Nevertheless, the Cu^{II} stereochemistry in **2** is less symmetrical; all the Cu^{II} ions have a distorted square pyramidal geometry in **3** with an axial ligation of μ₃-nitrate, while **2**

(7) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(8) Fan, H. F. *Structure Analysis Programs with Intelligent Control*; Rigaku Corporation: Tokyo, Japan, 1991.

(9) Parthasarathi, V.; Beurskens, P. T.; Slot, H. J. B. *Acta Crystallogr.* **1983**, *A39*, 860.

(10) *Single Crystal Analysis Software. Version 1.6f*; Molecular Structure Corporation: 3200 Research Forest Drive, The Woodlands, TX 77381, 1994.

(11) Vreugdenhil, W.; Birker, P. J. M. W. L.; ten Hoedt, R. W. M.; Verschoor, G. C.; Reedijk, J. *J. Chem. Soc., Dalton Trans.* **1984**, 429.

Table 2. Atomic Coordinates and Equivalent Isotropic Temperature Factors for **1** and **2**

atom	x	y	z	B_{eq}^a
Complex 1				
Cu(1)	3/4	1/4	1/2	2.88(1)
O(1)	0.5060(2)	0.5414(4)	0.3742(2)	9.2(1)
O(2)	0.6275(2)	0.4319(2)	0.4838(2)	5.04(7)
O(3)	0.6532(3)	0.6315(3)	0.4530(2)	7.7(1)
N(1)	0.7482(2)	0.2259(2)	0.6347(2)	3.04(6)
N(2)	0.6772(2)	0.2871(2)	0.6632(2)	3.70(6)
N(3)	0.6265(2)	0.1266(2)	0.4439(2)	3.05(6)
N(4)	0.6342(2)	-0.0074(3)	0.4418(2)	3.82(7)
N(5)	0.5912(3)	0.5342(3)	0.4355(2)	4.10(8)
C(1)	0.6919(3)	0.2580(4)	0.7562(2)	4.40(8)
C(2)	0.7753(3)	0.1734(4)	0.7897(2)	4.42(9)
C(3)	0.8080(2)	0.1559(3)	0.7122(2)	3.84(8)
C(4)	0.5398(3)	-0.0650(4)	0.3941(3)	4.4(1)
C(5)	0.4693(3)	0.0371(4)	0.3651(3)	4.5(1)
C(6)	0.5255(2)	0.1536(3)	0.3966(2)	3.75(8)
Complex 2				
Cu(1)	0.4337(1)	0.2024(1)	0.5458(3)	3.69(6)
Cu(2)	0.3142(1)	0.1858	0.8123(4)	3.85(4)
O(1)	0.3707(7)	0.1293	0.662(2)	3.2(2)
O(2)	0.297(1)	0.275(1)	0.581(2)	10.4(7)
O(3)	0.237(1)	0.2631	0.387(3)	18.3(8)
O(4)	0.639(1)	0.1390	0.416(3)	7.8(4)
O(5)	0.558(1)	0.140(1)	0.594(2)	13.3(8)
N(1)	0.4086(8)	0.1465(8)	0.372(2)	4.2(4)
N(2)	0.480(1)	0.2882(9)	0.435(2)	4.9(5)
N(3)	0.5535(9)	0.297(1)	0.402(2)	4.8(5)
N(4)	0.4555(8)	0.2538(8)	0.727(2)	3.5(4)
N(5)	0.4045(9)	0.2509(8)	0.835(2)	4.4(4)
N(6)	0.248(1)	0.2518	0.923(2)	5.6(4)
N(7)	0.202(1)	0.2976	0.862(3)	6.1(4)
N(8)	0.252(1)	0.2477	0.495(3)	8.1(5)
N(9)	0.612(1)	0.1119	0.532(2)	4.0(3)
C(1)	0.405(1)	0.0945	0.147(3)	6.2(5)
C(2)	0.439(1)	0.147(1)	0.232(2)	6.1(7)
C(3)	0.563(1)	0.357(2)	0.322(3)	7.2(8)
C(4)	0.496(2)	0.391(1)	0.295(3)	7.1(8)
C(5)	0.446(1)	0.345(1)	0.366(3)	5.6(7)
C(6)	0.511(1)	0.295(1)	0.777(2)	5.0(6)
C(7)	0.498(1)	0.322(1)	0.898(3)	6.5(7)
C(8)	0.430(1)	0.292(1)	0.945(2)	5.4(6)
C(9)	0.162(1)	0.3383	0.957(4)	6.2(5)
C(10)	0.185(2)	0.3151	1.095(4)	7.5(6)
C(11)	0.238(1)	0.2617	1.053(6)	7.6(8)

$B_{\text{eq}} = \frac{8}{3}\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos \gamma + 2U_{13}aa^*cc^* \cos \beta + 2U_{23}bb^*cc^* \cos \alpha)$.

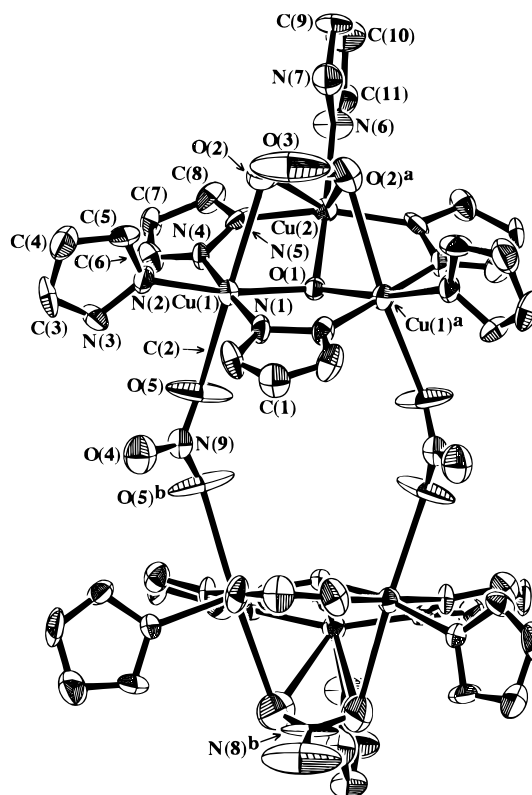
involves two elongated octahedral geometries (Cu(1) and Cu(1)^a) and a regular bicapped square pyramidal geometry¹² (Cu(2)). The μ_3 -hydroxide atom (O(1)) is displaced out of the Cu₃ plane by 0.605 Å, which compares with 0.478 Å in **3**.^{3b} Several interhexamer hydrogen-bonding interactions are also found in the crystal (see Table 3).

On the other hand, we have examined the behavior of **2** in aqueous media, as described below. Figure 2a shows an electronic absorption spectrum of **2** in water. It was confirmed that the spectrum is stable in air at room temperature for more than a day and is sensitive to pH. (The absorption intensity at 291 nm decreases on addition of HNO₃.) Moreover, the spectrum ($\lambda > 250$ nm) exhibits no change upon addition of a large excess of pyrazole, and therefore the [pzH]-dependence, which has been often observed for the Cu^{II}-pyrazole compounds,^{3b,13} can be ruled out in the present case. This implies that the LMCT band observed for Cu(pzH)₄²⁺ ($\pi(\text{pyrazole}) \rightarrow$

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for **1** and **2**

Complex 1			
Cu(1)–O(2)	2.420(2)	Cu(1)–N(1)	2.008(2)
Cu(1)–N(3)	2.002(2)		
O(2)–Cu(1)–N(1)	85.45(9)	O(2)–Cu(1)–N(1) ^b	94.55(9)
O(2)–Cu(1)–N(3)	88.14(9)	O(2)–Cu(1)–N(3) ^b	91.86(9)
N(1)–Cu(1)–N(3)	90.73(9)	N(1)–Cu(1)–N(3) ^b	89.27(9)
Complex 2			
Cu(1)–Cu(2)	3.256(4)	Cu(1)–Cu(1) ^a	3.396(4)
Cu(1)–O(1)	2.01(1)	Cu(1)–N(1)	1.94(2)
Cu(1)–N(2)	2.00(2)	Cu(1)–N(4)	1.94(1)
Cu(1)–O(5)	2.50(1)	Cu(1)–O(2)	2.76(2)
Cu(2)–O(1)	1.98(2)	Cu(2)–O(2)	2.67(2)
Cu(2)–N(5)	1.98(2)	Cu(2)–N(6)	1.94(3)
O(2)–N(3) ^c	3.03(2) ^f	O(4)–N(3) ^d	3.18(2) ^f
O(4)–N(7) ^e	3.02(4) ^f		
O(1)–Cu(1)–O(2)	75.6(6)	O(1)–Cu(1)–O(5)	96.1(7)
O(1)–Cu(1)–N(1)	89.4(6)	O(1)–Cu(1)–N(2)	169.4(7)
O(1)–Cu(1)–N(4)	87.1(6)	O(2)–Cu(1)–O(5)	162.9(6)
O(2)–Cu(1)–N(1)	97.8(6)	O(2)–Cu(1)–N(2)	93.9(6)
O(2)–Cu(1)–N(4)	81.6(6)	O(5)–Cu(1)–N(1)	97.0(6)
O(5)–Cu(1)–N(2)	93.8(7)	O(5)–Cu(1)–N(4)	83.1(6)
N(1)–Cu(1)–N(2)	93.2(6)	N(1)–Cu(1)–N(4)	176.5(6)
N(2)–Cu(1)–N(4)	90.3(7)	O(1)–Cu(2)–O(2)	78.1(6)
O(1)–Cu(2)–O(2)	78.1(6)	O(1)–Cu(2)–N(5)	87.7(5)
O(1)–Cu(2)–N(6)	167.2(8)	O(2)–Cu(2)–O(2) ^a	39.1(7)
O(2)–Cu(2)–N(5)	80.5(6)	O(2)–Cu(2)–N(5) ^a	119.4(6)
O(2)–Cu(2)–N(6)	89.8(8)	N(5)–Cu(2)–N(5) ^a	158.1(9)
N(5)–Cu(2)–N(6)	94.6(5)	Cu(1)–O(1)–Cu(1) ^a	115.1(9)
Cu(1)–O(1)–Cu(2)	109.2(6)	Cu(1)–O(2)–Cu(2)	73.6(5)

^{a–e} Symmetry operations for the *a–e* labeled atoms are as follows: (a) $1/2 - Y, 1/2 - X, Z$; (b) $3/2 - X, 1/2 - Y, 1 - Z$; (c) $-1/2 + Y, -1/2 + X, Z$; (d) $-1 + X, Y, Z$; (e) $-1/2 + X, 1/2 - Y, 1 - Z$. ^f Hydrogen bond distances.

**Figure 1.** ORTEP view of **2** (50% thermal ellipsoids). Symmetry operations: (a) $1/2 - Y, 1/2 - X, Z$ and (b) $1/2 + Y, -1/2 + X, Z$.

$d_{x^2-y^2}$, $\lambda_{\text{max}} = 301$ nm, $\epsilon = 740$ M⁻¹ cm⁻¹)¹³ would be blue-shifted in **2**; the $d_{x^2-y^2}$ orbitals in **2** would level off at a higher energy compared to that of Cu(pzH)₄²⁺ due to the stronger donor characters of μ -pz and μ_3 -OH compared to that of pzH.

(12) Hathaway, B. J. In *Comprehensive Coordination Chemistry: Copper*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, U.K., 1987; Vol. 5, p 710.

(13) Bernarducci, E.; Schwindinger, W. F.; Hughey, J. L., IV; Krogh-Jespersen, K.; Schugar, H. J. *J. Am. Chem. Soc.* **1981**, *103*, 1686.

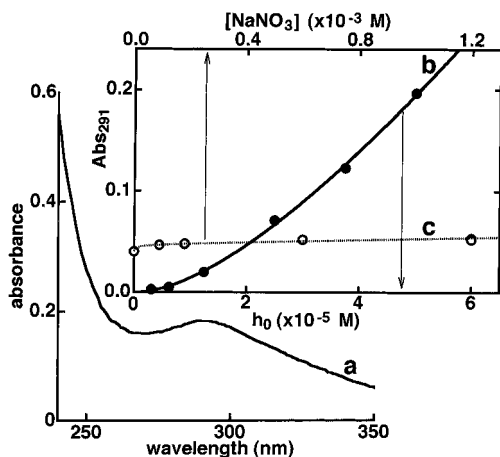


Figure 2. (a) Absorption spectrum of **2** in water (5×10^{-5} M) at room temperature in air. (b) Abs_{291} vs $[\mathbf{2}] (=h_0)$. (c) Abs_{291} vs $[\text{NaNO}_3]$ at $h_0 = 1.8 \times 10^{-5}$ M.

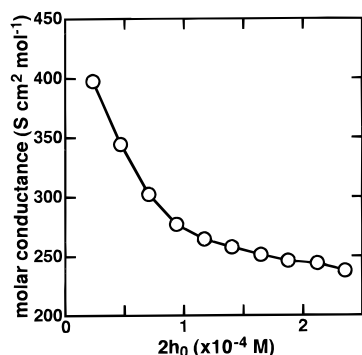
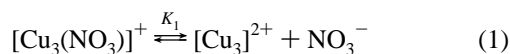


Figure 3. Molar conductance of **2** as a function of the total trimer concentration ($2h_0$).

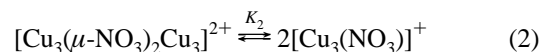
Interestingly, the absorbance at 291 nm (Abs_{291}) as a function of the dissolved hexamer concentration (h_0) shows a meaningful deviation from Beer's law (plots in Figure 2b). In this experiment, all the sample solutions have a constant pH value (6.84) and the maximum wavelength does not show any shift. The former fact indicates that neither a proton dissociation nor a protonation equilibrium is involved in this system. On the other hand, the molar conductance has been measured for the similar samples (Figure 3), revealing that there is an equilibrium accompanying a dissociation of an anion from the cationic complex. The simplest model for this will be given by eq 1, for the molar conductance value at higher complex concentration ($\sim 200\text{--}250$) reflects a 1:1 electrolyte on the basis of the trimer ($[\text{Cu}_3(\text{NO}_3)]^+ \cdot \text{NO}_3^-$; hereafter Cu_3 denotes $[\text{Cu}_3(\mu_3\text{-OH})(\mu\text{-pz})_3(\text{pzH})_3]^{2+}$). Only with this equilibrium in consideration, the K_1



value for eq 1 is expected to be around 10^{-4} M, which can be roughly judged by comparing the data in Figure 3 with the

concentration dependence of the relative abundance of $[\text{Cu}_3]^{2+}$ calculated for various K_1 values. Moreover, a least-squares fit of the data in Figure 2b on the basis of eq 1 satisfactorily affords $\epsilon_{\text{Cu}_3\text{NO}_3} = (4.5 \pm 1.4) \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$, $\epsilon_{\text{Cu}_3} = 29 \pm 420 \text{ M}^{-1} \text{ cm}^{-1}$, and $K_1 = (2.0 \pm 1.8) \times 10^{-4}$ M, where $\epsilon_{\text{Cu}_3\text{NO}_3}$ and ϵ_{Cu_3} are molar absorptivities of $[\text{Cu}_3(\text{NO}_3)]^+$ and $[\text{Cu}_3]^{2+}$, respectively. If this is the right model, addition of nitrate to a solution of **2** must promote a dramatic increase in Abs_{291} , since $\epsilon_{\text{Cu}_3\text{NO}_3} \gg \epsilon_{\text{Cu}_3}$ is fulfilled and the relative abundance of $[\text{Cu}_3]^{2+}$ is calculated to be ca. 75% at $[\mathbf{2}] = 1.8 \times 10^{-5}$ M. However, as shown in Figure 2c, only a small change is observed in Abs_{291} over $[\text{NaNO}_3] = 0\text{--}9 \times 10^{-5}$ M, and Abs_{291} at higher $[\text{NaNO}_3]$ merely follows a linear line with the slope being consistent with the molar absorptivity of NO_3^- ($\epsilon_{291} = 6.1 \text{ M}^{-1} \text{ cm}^{-1}$). From these analyses, it is concluded that eq 1 is not a major component in causing the bend in Figure 2b.

The FAB mass spectrum of **2** displayed parent peaks centered at 1279 m/z ($[\mathbf{2}(\text{-pzH})(\text{HNO}_3)_2(\text{H}_2)]^+$), indicating that the hexanuclear core is present, at least, in *m*-nitrobenzyl alcohol. This result implies that the hexanuclear core is rather stable, and we therefore consider eq 2 as another possible candidate accounting for the bend in Figure 2b. A fitting experiment has been performed by omitting eq 1, which satisfactorily affords $\epsilon_{\text{Cu}_3\text{NO}_3} = 12 \pm 420 \text{ M}^{-1} \text{ cm}^{-1}$, $\epsilon_h = (1.1 \pm 0.37) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ and $K_2 = (2.5 \pm 2.3) \times 10^{-4}$ M, where ϵ_h is a molar absorptivity of the hexamer. Since the equilibrium shift in eq



2 will not cause the large change in molar conductance observed in Figure 3, eq 1 should not be abandoned completely. Therefore, it is more reasonable for us to consider both eqs 1 and 2 simultaneously. The concentration dependence of the relative abundances of the three species in eqs 1 and 2 have been calculated for several sets of K_1 and K_2 , which revealed that the data in Figures 2 and 3 can be well understood with eqs 1 and 2 by assuming $\epsilon_{\text{Cu}_3\text{NO}_3} = \epsilon_{\text{Cu}_3} = \sim 0 \text{ M}^{-1} \text{ cm}^{-1}$, $\epsilon_h = \text{ca. } 11\,000 \text{ M}^{-1} \text{ cm}^{-1}$, $K_1 = \text{ca. } 10^{-5}\text{--}10^{-4}$ M, and $K_2 = \text{ca. } 2.5 \times 10^{-4}$ M. These values imply that the band at 291 nm is mainly derived from the hexamer, and its relative abundance is about 50% at $h_0 = 10^{-4}$ M. Although we could not obtain further evidence supporting these concepts, this model, at present, appears to be the most plausible one accounting for all the phenomena observed so far.

Acknowledgment. The present work is financially supported by Grants-in-Aid for Scientific Research (No. 04854061 and 05854065) from the Ministry of Education, Science and Culture of Japan.

Supporting Information Available: Tables of detailed crystallographic data, hydrogen atom parameters, U_{ij} parameters, and bond distances and angles, an ORTEP drawing of **1**, and a FAB mass spectrum of **2** (6 pages). Ordering information is given on any current masthead page.

IC950181J