

A THIOLATO-BRIDGED OCTANUCLEAR COPPER(I,II) MIXED-VALENCE COMPLEX WITH N,N,S-TRIDENTATE LIGAND[§]

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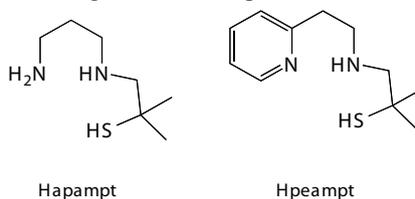
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Abstract: Thiolato-bridged complex $[\text{Cu}^{\text{I}}\text{Cu}^{\text{II}}_4(\text{peampt})_4\text{Cl}_8]\cdot 2\text{H}_2\text{O}$ (Hpeampt = 1-(2-pyridylethyl)amino methylpropane-2-thiol) has been synthesized and characterized by the elemental analysis, IR and UV-vis spectroscopies and magnetic susceptibility measurement. The X-ray crystal structure analysis of this complex shows a localized mixed-valence octanuclear cage structure made up of four trigonal-bipyramidal $\text{Cu}^{\text{II}}\text{N}_2\text{SCl}_2$, two trigonal $\text{Cu}^{\text{I}}\text{S}_2\text{Cl}$, and two tetrahedral $\text{Cu}^{\text{I}}\text{S}_2\text{Cl}_2$ coordination sites. Temperature dependence of magnetic susceptibility (4.5—300 K) shows that a fairly strong antiferromagnetic interaction is operating between the four Cu^{II} ions.

Keywords: thiolato-bridged complexes; mixed-valence complexes; copper complexes; octanuclear complexes.

INTRODUCTION

Thiolato-bridged metal complexes with organic thiolic ligands have attracted much attention during the several decades because of their utilities as model complexes in relation to ubiquitous metal-cysteine centers of biologically important metal enzymes [1-3]. For example, thiolato-bridged copper species have been focused from a view of model compounds for nitrous oxide reductase and cytochrome c oxidase and these sites are interesting mixed-valent copper cluster with the spin-delocalized state [2]. However, isolation of thiolato-bridged metal complexes was generally hampered by the presence of undefined and undesired byproducts caused by electron-rich thiolato sulfur having a great affinity for various metal ions. Formation of discrete thiolato-bridged metal complexes could be expected to be feasible by the use of tridentate chelate ligands which have N,N,S-donor set by virtue of the chelating effect. Thus, we synthesized thiolic ligands such as 2-[(2-aminoethyl)amino]ethanethiol (Haeat), 2-[(3-aminopropyl)amino]ethanethiol (Hapaet), 2-[(2-pyridylmethyl)amino]ethanethiol (Hpmaet), and 2-[[2-(2-pyridyl)ethyl]amino]ethanethiol (Hpeaet) and initiated a systematic study on thiolato-bridged metal complexes with these chelate ligands.



Scheme 1. N,N,S-tridentate thiolic ligands.

We isolated dinuclear nickel(II) complexes [4] and unique tetranuclear palladium(II) complexes [5] by reactions with nickel(II) and palladium(II) salts, respectively. In the case of zinc(II), linear and cyclic trinuclear and chain polynuclear complexes were obtained by these ligands [6]. Linear trinuclear structure consisting of octahedral-tetrahedral-octahedral coordination environments seems to be most favorable pattern in our systems and we isolated such species for the cases of Zn^{II} , Cd^{II} , Mn^{II} , Fe^{II} , Co^{II} , and Ni^{II} [7-11]. We explored a facile synthetic method of trinuclear heterometal complexes by using one-pot reaction of Hapaet [11]. After getting these experiences, we tried to make copper systems of our thiolic ligands and obtained a polymeric compound of apaet⁻ which could not be crystallized [12]. By the use of a similar NNS-chelating ligand containing methyl groups at the β -position, 1-[(3-aminopropyl)amino]-2-methylpropane-2-thiol (Hapampt), we could successfully isolate a hexanuclear mixed-valence complex with unique $\text{Cu}^{\text{I}}_3\text{Cu}^{\text{II}}_3$ cluster in copper systems [12,13]. This may be ascribed to the presence of the methyl groups of the thiolic ligand to stabilize the mixed-valence state. We can expect formation of different type of copper complexes, if we introduce pyridyl group to this promising methyl-group-attached thiolic ligand, because it is known that pyridyl group is softer than the amino group. In this study, we synthesized a new thiolic ligand, 1-[(2-pyridylethyl)amino]methylpropane-2-thiol (Hpeampt) and examined the reactions with copper(II) ion in the hope of attaining to make mixed-valence species.

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RESULTS AND DISCUSSION

In the case of the reaction of Hapampt ligand with copper(II) ion, a mixed-valent species, $[\text{Cu}^{\text{I}}_3\text{Cu}^{\text{II}}_3(\text{apampt})_3\text{Cl}_6]\cdot 2\text{H}_2\text{O}$ (**1**), was formed. The X-ray crystal structure analysis shows a hexanuclear cage structure, where each apampt⁻ ligand is bonded to one copper(II) ion to form two adjacent chelates with six- and five-membered rings and each thiolato-sulfur is further bound to one copper(I) ion [12].

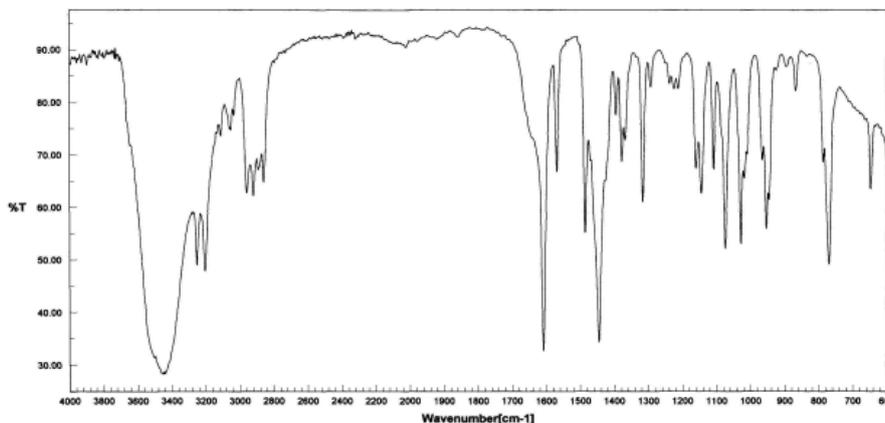


Fig. 1. Infrared spectra of $[\text{Cu}^{\text{I}}_4\text{Cu}^{\text{II}}_4(\text{peampt})_4\text{Cl}_8]\cdot 2\text{H}_2\text{O}$ (**2**).

The localized mixed-valence structure was also supported by the electronic spectra and the magnetic susceptibility data. From the structural similarity, it can be considered that the peampt⁻ ligand is capable of forming two adjacent six- and five-membered chelate rings like the apampt⁻ ligand. Therefore it was expected to obtain similar mixed-valent complexes to the hexanuclear cluster **1**, although we can expect something different feature for product from reaction of the present thiolic ligand with copper(II) ion. Reaction of Hpeampt with copper(II) chloride dihydrate in methanol resulted in deprotonation of the thiolic ligand and gave black crystals of thiolato complex (**2**).

Table 1

Crystallographic data for $[\text{Cu}^{\text{I}}_4\text{Cu}^{\text{II}}_4(\text{peampt})_4\text{Cl}_8]\cdot 2\text{H}_2\text{O}$ (**2**)

	$[\text{Cu}^{\text{I}}_4\text{Cu}^{\text{II}}_4(\text{peampt})_4\text{Cl}_8]\cdot 2\text{H}_2\text{O}$ (2).
Empirical formula	$\text{C}_{44}\text{H}_{72}\text{Cl}_8\text{Cu}_8\text{N}_8\text{O}_2\text{S}_4$
Formula weight	1665.35
Temperature / K	293
Crystal dimensions /mm	$0.1 \times 0.1 \times 0.05$
Crystal system	monoclinic
Space group	$P2_1/c$ (No. 12)
$a / \text{\AA}$	12.829(11)
$b / \text{\AA}$	24.24(2)
$c / \text{\AA}$	12.494(11)
$\alpha / ^\circ$	90
$\beta / ^\circ$	116.952(17)
$\gamma / ^\circ$	90
$V / \text{\AA}^3$	3464(5)
Z	2
$d_{\text{calcd.}} / \text{gcm}^{-3}$	1.597
μ / mm^{-1}	2.873
Diffractometer	Bruker SMART APEX CCD
No. of reflection	11909
No. of observation	3633
Refl./Parameter ratio	10.7
$R1, wR2 [I > 2\sigma(I)]^{[a]}$	0.1291, 0.3039
Goodness-of-fit on F^2	1.282

In the infrared spectrum of **2**, the absorption bands due to the peampt⁻ ligand appear as a set of absorption bands in a similar frequency region to that of the free thiol with lacking the $\nu(\text{SH})$ band as shown in Fig. 1. The presence of H_2O is suggested from the broad band around 3449 cm^{-1} attributable to the $\nu(\text{OH})$ band of the crystal water molecules.

Unfortunately, all of the crystals were twinned and we failed to obtain a satisfactory quality of crystallographic data for this complex, despite of many attempt to get good quality of single-crystals, and therefore a more detailed analysis of the structure of **2** could not be performed. However, we can find that the preliminary X-ray crystal structure reveals an octanuclear structure with formulation of $[\text{Cu}^{\text{I}}_4\text{Cu}^{\text{II}}_4(\text{peampt})_4\text{Cl}_8]\cdot 2\text{H}_2\text{O}$ that is distinctly different from **1**. The elemental analysis and the IR data also support this formulation. Crystal data and details concerning data collection are given in Tab. 1. An ORTEP drawing of **2** with atom-labeling scheme is shown in Fig. 2.

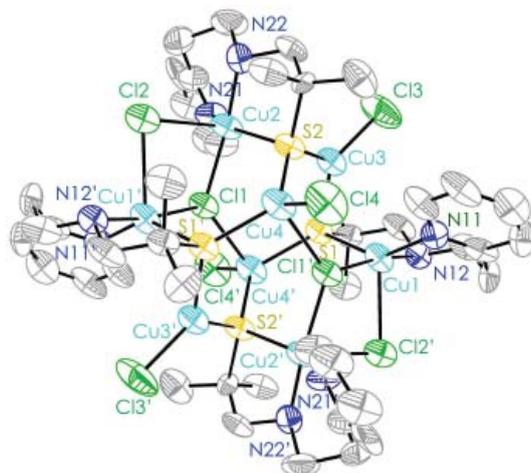


Fig. 2. ORTEP drawing of the structure of $[\text{Cu}^{\text{I}}_4\text{Cu}^{\text{II}}_4(\text{peampt})_4\text{Cl}_8]\cdot 2\text{H}_2\text{O}$ (**2**) showing the 50% probability thermal ellipsoids and atom labeling scheme. Water molecules are omitted for clarity.

Selected bond distances and angles are listed in Table 2. The octanuclear molecule has a crystallographically inversion center. The Cu1 (Cu1') atom is coordinated to the pyridyl-nitrogen N11 (N11'), amino-nitrogen N12 (N12'), and thiolato-sulfur S1 (S1') atoms of peampt in a *meridional* form, forming two adjacent six- and five-membered chelate rings. The Cu2 (Cu2') atom is also coordinated to the pyridyl N21 (N21'), amino N22 (N22'), and thiolato S2 (S2') of the thiolic ligand in a similar mode.

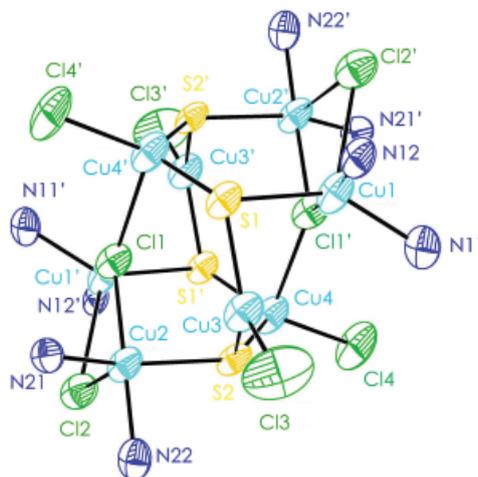


Fig. 3. Core structure of of $[\text{Cu}^{\text{I}}_4\text{Cu}^{\text{II}}_4(\text{peampt})_4\text{Cl}_8]\cdot 2\text{H}_2\text{O}$ (**2**).

The Cu3 (Cu3') atom is coordinated to the thiolato S1 and S2 (S1' and S2') atoms to connect the Cu1(peampt) and Cu2(peampt) (the Cu1'(peampt)' and Cu2'(peampt)') moieties. Similarly, the Cu4 (Cu4') atom is coordinated to the thiolato S2 and S1 (S2' and S1) atoms to connect the Cu2(peampt) and Cu1'(peampt)' (the Cu2'(peampt)' and Cu1(peampt)) moieties. The octanuclear core is shown in Fig. 3.

The octanuclear copper core is made up of four trigonal-bipyramidal $\text{Cu}^{\text{II}}\text{N}_2\text{SCl}_2$, two trigonal $\text{Cu}^{\text{I}}\text{S}_2\text{Cl}$, and two tetrahedral $\text{Cu}^{\text{I}}\text{S}_2\text{Cl}_2$ moieties and has adjacent six-membered rings $[-\text{Cu}-\text{S}-\text{Cu}-\text{S}-\text{Cu}-\text{Cl}-]$ containing three of the trigonal-bipyramidal (Cu1, Cu2, Cu1', and Cu2'), trigonal (Cu3 and Cu3'), and tetrahedral (Cu4 and Cu4') copper atoms. Charge consideration requires a formal $\text{Cu}^{\text{I}}_4\text{Cu}^{\text{II}}_4$ description of this core and thus we can assign the Cu1 and Cu2 (Cu1' and Cu2') atoms to copper(II) oxidation state and the Cu3 and Cu4 (Cu3' and Cu4') atoms to copper(I) oxidation state, respectively. The $\text{Cu}^{\text{I}}-\text{Cu}^{\text{II}}$ separations, the Cu1'-Cu2 and Cu1-Cu2 distances, are 3.703(3) and 5.708(3)

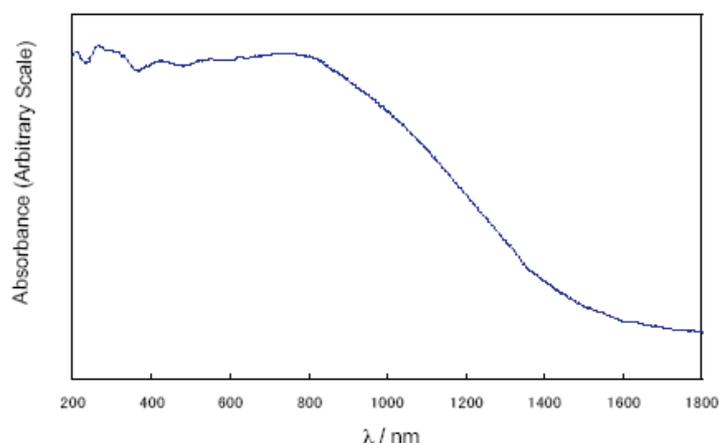
Å, respectively, forming a rectangular array of the four copper(II) ions in the octanuclear core. The Cu^I-Cu^I (Cu³-Cu⁴) distance is 4.016(3) Å. As for the Cu^I-Cu^{II} separations, the Cu²-Cu³, Cu²-Cu⁴, Cu¹-Cu⁴, and Cu¹'-Cu⁴ distances are 3.184(3), 3.968(3), 4.485(3), and 3.961(3) Å, respectively. It is to be noted that the Cu^I-S bond distances [2.273(6)–2.296(6) Å] are comparable to the Cu^{II}-S bond lengths [2.296(6), 2.298(6) Å]. Such a small difference is also found in **1** and both the Cu^I-S and Cu^{II}-S distances are comparable to the values found in thiolato-bridged mixed-valent Cu^ICu^{II} complexes [12-14].

The diffuse reflectance spectra of **2** (Fig. 4) contains broad features at 266, 330sh, 425, 554, 628, 736 nm.

Table 2

Selected bond distances (Å) and angles (°), with esds in parentheses for [Cu^I₄Cu^{II}₄(peampt)₄Cl₈]·2H₂O

2			
Cu(1)–N(12)	2.008(18)	Cu(1)–N(11)	2.082(19)
Cu(1)–S(1)	2.296(6)	Cu(2)–N(22)	1.993(19)
Cu(2)–N(21)	2.031(17)	Cu(2)–S(2)	2.298(6)
Cu(3)–S(1)	2.273(6)	Cu(3)–S(2)	2.279(7)
Cu(4)–Cl(4)	2.268(7)	Cu(4)–S(1)'	2.292(6)
Cu(4)–S(2)	2.296(6)	Cu(4)–Cl(1)	2.683(7)
Cu(1)–Cl(1)'	2.338(6)	Cu(1)–Cl(2)'	2.740(7)
Cu(2)–Cl(1)	2.351(6)	Cu(2)–Cl(2)	2.767(8)
Cu(3)–Cl(3)	2.225(7)		
N(12)–Cu(1)–N(11)	93.6(8)	N(12)–Cu(1)–S(1)	88.5(5)
N(11)–Cu(1)–S(1)	142.0(6)	N(12)–Cu(1)–Cl(1)'	171.1(5)
N(11)–Cu(1)–Cl(1)'	91.5(6)	S(1)–Cu(1)–Cl(1)'	92.0(2)
N(12)–Cu(1)–Cl(2)'	87.3(5)	N(11)–Cu(1)–Cl(2)'	110.5(6)
S(1)–Cu(1)–Cl(2)'	107.6(2)	Cl(1)'–Cu(1)–Cl(2)'	84.2(2)
N(22)–Cu(2)–N(21)	94.5(8)	N(22)–Cu(2)–S(2)	87.2(5)
N(21)–Cu(2)–S(2)	143.8(6)	N(22)–Cu(2)–Cl(1)	169.6(5)
N(21)–Cu(2)–Cl(1)	92.4(6)	S(2)–Cu(2)–Cl(1)	91.9(2)
N(22)–Cu(2)–Cl(2)	87.1(5)	N(21)–Cu(2)–Cl(2)	108.9(6)
S(2)–Cu(2)–Cl(2)	107.3(2)	Cl(1)–Cu(2)–Cl(2)	83.3(2)
Cl(3)–Cu(3)–S(1)	122.7(3)	Cl(3)–Cu(3)–S(2)	121.3(3)
S(1)–Cu(3)–S(2)	116.0(2)	Cl(4)–Cu(4)–S(1)'	119.8(3)
Cl(4)–Cu(4)–S(2)	121.0(3)	S(1)–Cu(4)–S(2)	115.8(2)
Cl(4)–Cu(4)–Cl(1)'	100.4(3)	S(1)'–Cu(4)–Cl(1)'	93.9(2)
S(2)–Cu(4)–Cl(1)'	93.7(2)	Cu(3)–S(1)–Cu(4)'	125.0(3)
Cu(3)–S(1)–Cu(1)	84.9(2)	Cu(4)'–S(1)–Cu(1)	119.4(2)
Cu(3)–S(2)–Cu(4)	122.8(3)	Cu(3)–S(2)–Cu(2)	88.2(2)
Cu(4)–S(2)–Cu(2)	119.5(3)	Cu(1)–Cl(1)'–Cu(2)'	104.3(2)
Cu(1)–Cl(1)'–Cu(4)	126.4(2)	Cu(2)–Cl(1)–Cu(4)	125.9(2)
Cu(1)'–Cl(2)–Cu(2)	84.5(2)		

Fig. 4. Diffuse reflectance spectra of [Cu^I₄Cu^{II}₄(peampt)₄Cl₈]·2H₂O (**2**).

The former two absorption bands in the UV region can be attributed to chloro-to-Cu^{II} and thiolato-to-Cu^{II} charge transfer transitions, respectively [13]. The absorption bands in the visible region can be assigned to the d-d transitions of the Cu^IN₂SCl₂ chromophores. The mixed-valence state of **2** may be considered to be fully localized because of no observation of the IT band in the near IR region.

The magnetic moment of **2** is 2.98 μ_B at 300 K per [Cu^I₄Cu^{II}₄(peampt)₄Cl₈]₂H₂O unit, which is lower than the spin-only value of 3.46 μ_B . Temperature dependence of the magnetic susceptibilities and moments are shown in Fig. 5.

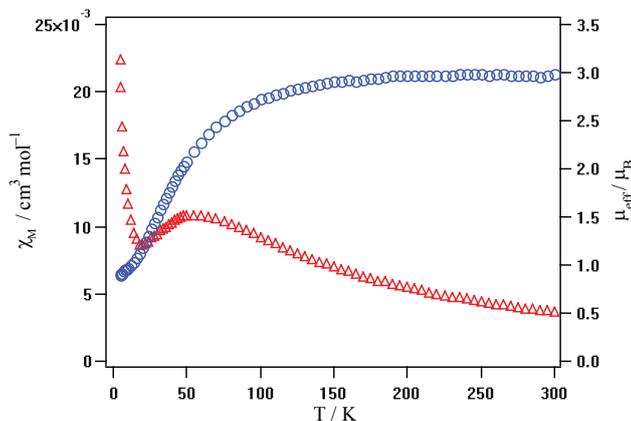


Fig. 5. Temperature dependence of magnetic susceptibilities and moments of [Cu^I₄Cu^{II}₄(peampt)₄Cl₈]₂H₂O (**2**).

The magnetic moment is decreased with lowering the temperature. Thus, we can expect an antiferromagnetic interaction is operating between the four copper(II) ions. Although some attempts of fitting the magnetic data by using the van Vleck equation based on the Heisenberg model $H = -2[J_1(S_1 \cdot S_2 + S_3 \cdot S_4) + J_2(S_1 \cdot S_4 + S_2 \cdot S_3)]$ considering the location of the four copper(II) ions [15], where J_1 and J_2 correspond to the magnetic interactions between the Cu1' and Cu2' (Cu1 and Cu2') and the Cu1 and Cu2 (Cu1' and Cu2'') ions, respectively, were made, reasonable magnetic parameters were not obtained because of the serious influence of the paramagnetic impurity at low temperature.

CONCLUSIONS

N,N,S-donor tridentate thiol, 1-[(2-pyridylethyl)amino]methylpropane-2-thiol (Hpeampt), was synthesized and proved to be worked to prepare a thiolato-bridged mixed valent complex. Analytical data, IR and UV-vis spectroscopic data, and magnetic susceptibility data as well as X-ray crystal structure support a localized mixed-valent Cu^ICu^{II} state of the thiolato-bridged complex with peampt. The formation of the octanuclear cluster may be achieved by the protection from oxidation reaction and solvent attack through the steric hindrance of the β -methyl groups of the present thiolic ligand.

EXPERIMENTAL

Synthesis: Syntheses of thiolic ligand and metal complex were carried out by using standard Schlenk techniques under argon. The thiolic ligand Hpeampt was synthesized as follows. A toluene solution (70 mL) of isobutylene sulfide (11.8 g, 0.13 mol) was added dropwise to a toluene solution (50 mL) containing 2-(2-aminoethyl)pyridine. The solution was refluxed for 24 h. Then, the solvent was removed by distillation and the product was fractionally distilled at reduced pressure. Bp. 138-140°C/5 mmHg.

[Cu^I₄Cu^{II}₄(peampt)₄Cl₈]₂H₂O (**2**). To a solution of Hpeampt (42 mg, 0.2 mmol) in methanol (5 mL) was added a solution (5 mL) of copper(II) chloride dihydrate (17 mg, 0.1 mmol) in methanol (5 mL). The reaction mixture was stirred at 80°C for 10 min. The resulting dark brown solution was allowed to stand several days at room temperature. The black plates deposited were collected by filtration. Found: C, 32.15; H, 4.39; N, 6.33%. Calcd for C₄₄H₇₂Cl₈Cu₈N₈O₂S₄, C, 31.73; H, 4.36; N, 6.73%. IR (KBr, cm⁻¹): $\nu_{as}(\text{OH})$ 3449, $\nu_s(\text{NH})$ 3254, 3205, $\nu(\text{CH}_3)$ 2960, $\nu(\text{CH}_2)$ 2860. Diffuse reflectance spectra ($\lambda_{\text{max}}/\text{nm}$): 266, 330, 425sh, 554, 628, 736. Magnetic moment (μ_{eff}/μ_B (T/K)): 2.98 (300).

Measurements: Elemental analyses for carbon, hydrogen, and nitrogen were done using a Thermo-Finnigan FLASH EA1112 analyzer. Infrared spectra were measured with a JASCO MFT-2000 FT-IR Spectrometer in the 4000—600 cm⁻¹ region. Electronic spectra were measured with a Shimadzu UV-vis-NIR Recording Spectrophotometer (Model UV-3100). Variable-temperature magnetic susceptibilities were measured with a Quantum Design MPMS-5S SQUID susceptometer operating at a magnetic field of 0.5 T over a range of 4.5—300 K. The susceptibilities were corrected for the diamagnetism of the constituent atoms using Pascal's constants. The effective magnetic moments were calculated from the equation $\mu_{\text{eff}} = 2.828\sqrt{\chi_M T}$, where χ_M is the molar magnetic susceptibility.

X-Ray Crystallography: A preliminary examination was made and data were collected on a Bruker CCD X-ray diffractometer (SMART APEX) using graphite-monochromated Mo- $K\alpha$ radiation at 20 ± 2 °C. The structure was solved by direct methods and refined by full-matrix least-squares. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were inserted at their calculated positions and fixed at their positions. All of the calculations were carried out on a Pentium III Windows NT computer utilizing the SHELXTL software package. CCDC 632152 (2) contains supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB12 1EZ, UK; fax: (internet.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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