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Mononuclear Copper(II) Hydroxo Complex: Structural Effect of a 3-Position of Tris(pyrazolyl)borates

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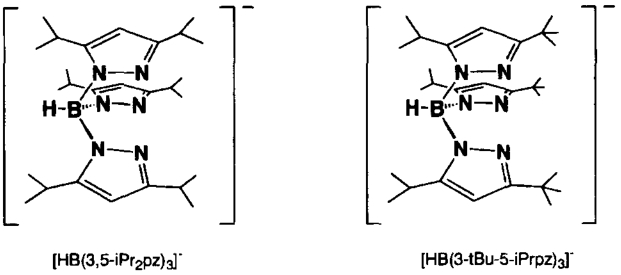
New mononuclear nitratocopper(II) complexes ([Cu(NO$_3$){HB(3,5-*i*Pr$_2$pz)$_3$}] (**1**)[1] and [Cu(NO$_3$){HB(3-*t*Bu-5-*i*Prpz)$_3$}] (**3**)) and a novel mononuclear hydroxocopper(II) complex ([Cu(OH){HB(3-*t*Bu-5-*i*Prpz)$_3$}] (**4**)) have been prepared. These complexes were characterized by X-ray analysis and IR, UV-vis, and EPR spectroscopies. Except for the dinuclear complex ([{Cu[HB(3,5-*i*Pr$_2$pz)$_3$]}$_2$(μ-OH)$_2$] (**2**)), the complexes are mononuclear structures having square-pyramidal (**1**), trigonal-pyramidal (**3**), and distorted tetrahedral (**4**) geometry. In comparison with these structures and their physicochemical properties, the structural effects on the alkyl substitutions at the close 3-position in hydrotris(pyrazolyl)borates play an important role in modifying the coordination environment about a copper(II) center and their physicochemical properties.

Poly(pyrazolyl)borates are among the most widely used ligands in inorganic, organometallic, and bioinorganic chemistries.[2—5] In many varieties of poly(pyrazolyl)borates, hydrotris(pyrazolyl)borate has attracted the most interest, because of its close analogy to the ubiquitous cyclopentadienyl system.[2] In fact, many complexes with the hydrotris(pyrazolyl)borate ligands are now known for most of the metals in the periodic table.

We have used the hydrotris(pyrazolyl)borate ligands for both structural and functional models for metalloproteins including copper, iron, and manganese ions.[4] In the use of [HB(3,5-*i*Pr$_2$pz)$_3$]$^-$,[1,6] mononuclear or dinuclear complexes are formed (Scheme 1). However, by using a more-hindered [HB(3-*t*Bu-5-*i*Prpz)$_3$]$^-$,[1,7] only a mononuclear complex is formed. These subtle geometric changes clearly result from differences in the steric properties of [HB(3,5-*i*Pr$_2$pz)$_3$]$^-$ and [HB(3-*t*Bu-5-*i*Prpz)$_3$]$^-$, where the larger tertiary butyl substituents effectively prevent dimerization. For example, by using [HB(3,5-*i*Pr$_2$pz)$_3$]$^-$, the dinuclear μ-η^2 : η^2-peroxocopper(II) complex ([{Cu[HB(3,5-*i*Pr$_2$pz)$_3$]}$_2$(μ-η^2 : η^2-O$_2$)]) is obtained.[6] On the other hand, in the case of [HB(3-*t*Bu-5-*i*Prpz)$_3$]$^-$, only the mononuclear side-on superoxocopper(II) complex, ([Cu(O$_2$){HB(3-*t*Bu-5-*i*Prpz)$_3$}]) is formed.[8] However, it is well known that copper(II) dioxygen complexes are thermally unstable. Therefore, there are some difficulties to discuss these structural and spectroscopic data in detail. In the present study, other small minus-one molecules, such as nitrate ion and hydroxide ion, were employed for detailed observations of structural effects on hydrotris(pyrazolyl)borate ligands.



[HB(3,5-iPr$_2$pz)$_3$]$^-$ [HB(3-tBu-5-iPrpz)$_3$]$^-$

Scheme 1.

This paper concerns the results from our recent investigations of the structural effects on the 3-position of hydrotris(pyrazolyl)borate ligands. We report herein on the syntheses and X-ray structural determinations of nitratocopper(II) complexes [Cu(NO$_3$){HB(3,5-*i*Pr$_2$pz)$_3$}] (**1**) and [Cu(NO$_3$){HB(3-*t*Bu-5-*i*Prpz)$_3$}] (**3**) and a novel mononuclear hydroxocopper(II) complex [Cu(OH){HB(3-*t*Bu-5-*i*Prpz)$_3$}] (**4**); **4** is the first example of a four-coordinate terminal hydroxocopper(II) complex. These complexes were characterized by IR, UV-vis, and EPR spectroscopies. The results indicate that the 3-position of hydrotris(pyrazolyl)borates plays an important role in modifying the coordination environment about a metal center.

Experimental

Materials. Dichloromethane and acetonitrile were carefully purified by refluxing/distilling under an argon atmosphere over P$_2$O$_5$ and CaH$_2$, respectively.[9] Acetone and heptane were of commercially spectroscopic grade. Other reagents and solvents were commercially available and used without further purification. The preparation and handling of all the complexes were performed under an argon atmosphere using standard Schlenk techniques.

Physical Measurements. Electronic spectra at room temperature were measured on a JASCO V-570 spectrophotometer. IR spectra were recorded in a solid KBr disk on a JASCO FT/IR-550 or 5300 spectrometer. EPR spectra were recorded on a Bruker EMX-T ESR spectrometer as a frozen solution at 140 K in quartz tubes (diameter 5 mm). Mass spectra were performed on a Hitachi M-80 spectrometer by a field-desorption method. Elemental analyses were performed by an analytical facility at the Research Laboratory of Resource Utilization, Tokyo Institute of Technology.

Preparations. **[Cu(NO$_3$){HB(3,5-*i*Pr$_2$pz)$_3$}] (1).** To a solution of Cu(NO$_3$)$_2$·3H$_2$O (0.271 g, 1.12 mmol) in acetone (35 cm^3) was added K[HB(3,5-*i*Pr$_2$pz)$_3$] (0.565 g, 1.12 mmol) dissolved in dichloromethane (60 cm^3). The color of the solution gradually turned to green, and a small amount of white solid was precipitated. After stirring for 1 h, the solvent was removed under vacuum. The residue was extracted with dichloromethane and part of the organic solution was separated by filtration. The organic solvent was evaporated under reduced pressure to give a green solid. Recrystallization from dichloromethane/acetonitrile at −30 °C gave a green powder (0.563 g, 85%). Single crystals of **1** suitable for X-ray diffraction were obtained by slow recrystallization from a toluene solution. UV-vis (CH$_2$Cl$_2$, λ_{max}/nm (ε/cm^{-1} mol^{-1} dm^3)) 293 (1850), 773 (130). FT-IR (KBr) 2966 (C–H), 2930 (C–H), 2868 (C–H), 2560 (B–H), 1544, 1474, 1382, 1304, 1244, 1174, 1135, 1056, 1015, 822, 791, 764, 718 cm^{-1}. EPR (140 K, CH$_2$Cl$_2$) $g_{//}$ 2.31, $A_{//}$ 146 G, $g_{\perp}$ 2.08. Found: C, 55.11; H, 8.13; N, 16.45%. Calcd for C$_{27}$H$_{46}$N$_7$BCuO$_3$: C, 54.86; H, 7.85; N, 16.59%. FD-MS 590 (M$^+$).

[{Cu[HB(3,5-*i*Pr$_2$pz)$_3$]}$_2$(μ-OH)$_2$] (2). This complex was prepared from **1** with a modified method described in the literature[6] (yield 68%).

[Cu(NO$_3$){HB(3-*t*Bu-5-*i*Prpz)$_3$}] (3). To a solution of Cu(NO$_3$)$_2$·3H$_2$O (0.243 g, 1.01 mmol) in acetone (20 cm^3) was added K[HB(3-*t*Bu-5-*i*Prpz)$_3$] (0.500 g, 0.915 mmol) dissolved in dichloromethane (60 cm^3). The color of the solution gradually turned to yellow, and a small amount of white solid was precipitated. After stirring for 1 h, the solvent was removed under vacuum. The residue was extracted with dichloromethane and part of the organic solution was separated by filtration. The organic solvent was evaporated under reduced pressure to give a green solid. Recrystallization from dichloromethane/acetonitrile at −30 °C gave a yellow powder (0.402 g, 70%). Single crystals of **3** suitable for X-ray diffraction were obtained by slow recrystallization from toluene/dichloromethane solution. UV-vis (CH$_2$Cl$_2$, λ_{max}/nm (ε/cm^{-1} mol^{-1} dm^3)) 297 (2250), 797 (170). FT-IR (KBr) 2969 (C–H), 2936 (C–H), 2870

Table 1. Summary of Crystallographic Data of [Cu(NO$_3$){HB(3,5-*i*Pr$_2$pz)$_3$}] (**1**), [Cu(NO$_3$){HB(3-*t*Bu-5-*i*Prpz)$_3$}] (**3**) and [Cu(OH){HB(3-*t*Bu-5-*i*Prpz)$_3$}] (**4**)

Complex	**1**	**3**	**4**·2(CH$_2$Cl$_2$)
Color	Green	Yellow	Yellow
Formula	C$_{27}$H$_{56}$N$_7$BCuO$_3$	C$_{30}$H$_{52}$N$_7$BCuO$_3$	C$_{32}$H$_{57}$N$_6$BOCl$_4$Cu
F.W.	591.06	633.14	758.01
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/a$ (#14)	$P2_1/m$ (#11)	$P\bar{1}$ (#2)
a/Å	16.613(3)	9.568(6)	17.648(12)
b/Å	19.114(4)	17.622(4)	19.548(13)
c/Å	10.460(3)	10.602(6)	9.827(4)
α/°			92.93(6)
β/°	106.37(2)	107.13(4)	100.62(6)
γ/°			140.63(3)
V/Å^3	3187(2)	1708(1)	2009(4)
Z	4	2	2
D_{calc}/g cm^{-3}	1.23	1.23	1.25
Crystal size/mm	0.35×0.30×0.20	0.30×0.30×0.20	0.50×0.50×0.20
Radiation	Graphite-monochromatized Mo $K\alpha$ (0.71069 Å)		
μ(Mo $K\alpha$)/cm^{-1}	7.23	6.79	8.41
F 000	1260	678	802
Scan mode	ω–2θ	ω–2θ	ω–2θ
Scan width/deg	1.30 + 0.14tan θ	1.26 + 0.14tan θ	1.30 + 0.14tan θ
Scan speed/deg min^{-1}	6.0	12.0	6.0
Temp/°C	24	24	−90
2θ range/deg	3—50	3—50	5—48
Octant measured	±h, +k, +l	+h, +k, ±l	±h, ±k, +l
Reflections collected	6149	3318	6727
Unique reflections	5814	3127	6309
No. of observations	3801 ($I > 3\sigma(I)$)	2567 ($I > 3\sigma(I)$)	4876 ($I > 3\sigma(I)$)
No. of variables	352	211	406
Reflect./Para ratio	10.8	12.2	12.0
$R^{a)}$/%	4.98	3.60	5.46
$R_w^{a)}$/%	5.94	4.44	6.33
Good. of fit ind.	2.22	1.93	2.56
Max/min peak/e Å^{-3}	0.72 / −0.60	0.51 / −0.48	0.95 / −0.67

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

(C–H), 2585 (B–H), 1535, 1466, 1364, 1265, 1181, 1067, 1051, 1020, 802, 793, 758, 640 cm^{-1}. EPR (140 K, CH_2Cl_2): g_1 2.30, g_2 2.16, g_3 2.01, A_3 99 G. Found: C, 56.61; H, 8.52; N, 15.51%. Calcd for $C_{30}H_{52}N_7BCuO_3$: C, 56.91; H, 8.28; N, 15.49%. FD-MS 632 (M$^+$).

[Cu(OH){HB(3-*t*Bu-5-*i*Prpz)$_3$}] (4). To a solution of **3** (0.400 g, 0.63 mmol) in dichloromethane (60 cm^3) was added dropwise 5 cm^3 of a 0.2 mol dm^{-3} aqueous NaOH solution. The color of the yellow dichloromethane phase gradually turned to greenish yellow. After stirring for 30 min, the dichloromethane phase was separated and evacuated to dryness under vacuum. Recrystallization of the resultant solid from dichloromethane/heptane gave a yellow powder (0.243 g, 66%). Single crystals of **4** suitable for X-ray diffraction were obtained by slow recrystallization from dichloromethane/*t*BuOH solution. UV-vis (CH_2Cl_2, λ_{max}/nm (ε/cm^{-1} mol^{-1} dm^3)) 312 (1560), 373 (1690), 830 (80). FT-IR (KBr) 3667 (O–H), 2964 (C–H), 2930 (C–H), 2869 (C–H), 2543 (B–H), 1534, 1466, 1425, 1363, 1300, 1240, 1182, 1127, 1062, 1051, 1020, 892, 792, 752, 713, 643, 589 cm^{-1} (Cu–O). EPR (140 K, CH_2Cl_2) $g_{//}$ 2.00, $A_{//}$ 152 G, $g_\perp$ 2.24. Found: C, 60.58; H, 9.04; N, 14.40%. Calcd for $C_{30}H_{53}N_6BCuO$: C, 61.27; H, 9.08; N, 14.29%. FD-MS 587 (M$^+$).

X-Ray Crystal Structure Determinations. The diffraction data for **1**, **3**, and **4** were measured on a Rigaku AFC 5S (**1** and **4**) or AFC 5R (**3**) automated four-circle diffractometer with graphite-monochromated Mo $K\alpha$ (λ = 0.71069 Å) radiation. The data were collected at 24±1 °C using the ω–2θ scan to a maximum 2θ value of 50.0° (**1** and **3**) and −90±1 °C using the ω–2θ scan to a maximum 2θ value of 48.0° (**4**). Because of a rapid loss of the crystallinity of **4** at room temperature, the mounting and sealing of the crystal in a glass capillary by apiezon grease were performed at low temperature. Other crystals were mounted on a glass fiber by epoxy glue. The unit-cell parameters of each crystal were obtained from a least-squares refinement based on 20 ($24 < 2\theta < 26°$) (**1**), 20 ($19 < 2\theta < 21°$) (**3**), and 25 ($24 < 2\theta < 26°$) (**4**) reflections. The intensities of three representative reflections monitored every 100 reflections (**1** and **4**) or every 150 reflections (**3**) did not show any decay in each experiment. Therefore, no decay correction was applied. Azimuthal scans of several reflections for all complexes indicated no need for an absorption correction. All data were corrected for Lorentz and polarization effects. The crystallographic data and collection details are summarized in Table 1. The structure was solved by direct methods (SAPI 91)[10] and expanded using Fourier techniques.[11] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located on the calculated positions (C–H = 0.95 Å and U = 1.3 U(C)). Refinements were carried out by a full-matrix least-squares method on F. The final discrepancy factors (R and R_w) are listed in Table 1. Neutral atom scattering factors were taken from Cromer and Waber[12] and anomalous dispersion effects were included in F_{calc}.[13] All calculations were performed using the teXsan[14] crystallographic software package of Molecular Structure Corporation. The final positional and thermal parameter, full listing of the bond distances and angles, torsion angles, and the $F_o - F_c$ table have been deposited as Document No. 73039 at the Office of the Editor of Bull. Chem. Soc. Jpn. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 144096-144098.

Results and Discussion

Syntheses. The reaction between copper(II) nitrate trihydrate and potassium salts of the alkyl substituted hydrotris(pyrazolyl)borates, K[HB(3,5-*i*Pr$_2$pz)$_3$] or K[HB(3-*t*Bu-5-*i*Prpz)$_3$], in a mixed solvent, acetone/dichloromethane, at room temperature readily gave the corresponding nitratocopper(II) complexes, **1** and **3**, in high yield, in accordance with the following equations:

$$\mathrm{K[HB(3,5\text{-}\mathit{i}Pr_2pz)_3] + Cu(NO_3)_2{\cdot}3H_2O \xrightarrow{Me_2CO/CH_2Cl_2}} \tag{1}$$

$$\mathrm{[Cu(NO_3)\{HB(3,5\text{-}iPr_2pz)_3\}] + KNO_3}$$

(1)

$$\mathrm{K[HB(3\text{-}\mathit{t}Bu\text{-}5\text{-}\mathit{i}Prpz)_3] + Cu(NO_3)_2{\cdot}3H_2O \xrightarrow{Me_2CO/CH_2Cl_2}} \tag{2}$$

$$\mathrm{[Cu(NO_3)\{HB(3\text{-}\mathit{t}Bu\text{-}5\text{-}\mathit{i}Prpz)_3\}] + KNO_3}$$

(3)

However, in the case of methyl substitution, a coordinatively saturated copper(II) complex, [Cu{HB(3,5-Me$_2$pz)$_3$}$_2$],[1] is easily obtained.[15] No formation of the coordinatively saturated complexes ([Cu{HB(3,5-*i*Pr$_2$pz)$_3$}$_2$] or [Cu{HB(3-*t*Bu-5-*i*Pr$_2$pz)$_3$}$_2$]) were observed, owing to these bulkier ligands. Indeed, attempts to prepare the latter using a 2 : 1 ligand/copper(II) ratio were unproductive. Since the colors of both complexes were distinctly different, green in **1** and yellow in **3**, a critical structural change would be anticipated (vide infra).

The treatment of the nitrato complexes, **1** and **3**, with 0.2 mol dm^{-3} NaOH aqueous solution in dichloromethane yielded the hydroxo complexes (**2** and **4**), respectively, as shown in the Eqs. 3 and 4. As reported before, the structure of **2** is dinuclear di(μ-hydroxo)copper(II) complexes, [{Cu[HB(3,5-*i*Pr$_2$pz)$_3$]}$_2$(μ-OH)$_2$].[6] On the other hand, the structure of **4** does not have a dinuclear mode, because of the bulkier tertiary butyl group substitution at the 3-position of the pyrazole ring.

$$\mathrm{[Cu(NO_3)\{HB(3,5\text{-}\mathit{i}Pr_2pz)_3\}] + NaOH\ aq \xrightarrow{CH_2Cl_2}} \tag{3}$$

$$\mathrm{[\{Cu[HB(3,5\text{-}\mathit{i}Pr_2pz)_3]\}_2(\mu\text{-}OH)_2]}$$

(2)

$$\mathrm{[Cu(NO_3)\{HB(3\text{-}\mathit{t}Bu\text{-}5\text{-}\mathit{i}Prpz)_3\}] + NaOH\ aq \xrightarrow{CH_2Cl_2}} \tag{4}$$

$$\mathrm{[Cu(OH)\{HB(3\text{-}\mathit{t}Bu\text{-}5\text{-}\mathit{i}Prpz)_3\}]}$$

(4)

Structures of Complexes. A single-crystal X-ray diffraction study of [Cu(NO$_3$){HB(3,5-*i*Pr$_2$pz)$_3$}] (**1**), [Cu(NO$_3$){HB(3-*t*Bu-5-*i*Prpz)$_3$}] (**3**), and [Cu(OH){HB(3-*t*Bu-

5-*i*Prpz)$_3$}] (**4**) confirms that the nitrogen atoms of the hydrotris(pyrazolyl)borate ligands bind the copper(II) atoms as a facially coordinating tridentate ligand, forming mononuclear structures, as shown in Figs. 1, 2, and 3. Selected bond distances and angles for all complexes are given in Table 2.

Complex **1** crystallized in the monoclinic space group $P2_1/a$. **1** consists of a copper core with three pyrazolyl nitrogen atoms and two bidentate oxygen atoms from NO_3^-, [Cu(NO$_3$){HB(3,5-*i*Pr$_2$pz)$_3$}]. Because this complex is neutral, the oxidation state of the copper ion is +2. The coordination around the copper(II) ion is essentially a square-pyramidal geometry with the basal plane comprising two nitrogen atoms (N11 and N21) from hydrotris(pyrazolyl)borate

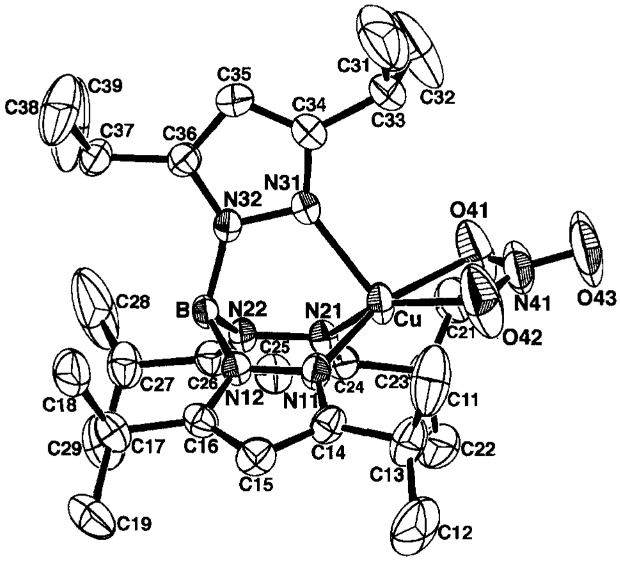


Fig. 1. An ORTEP drawing of [Cu(NO$_3$){HB(3,5-*i*Pr$_2$pz)$_3$}] (**1**) (40% probability) with an atomic labeling scheme. Hydrogen atoms are not shown for clarity.

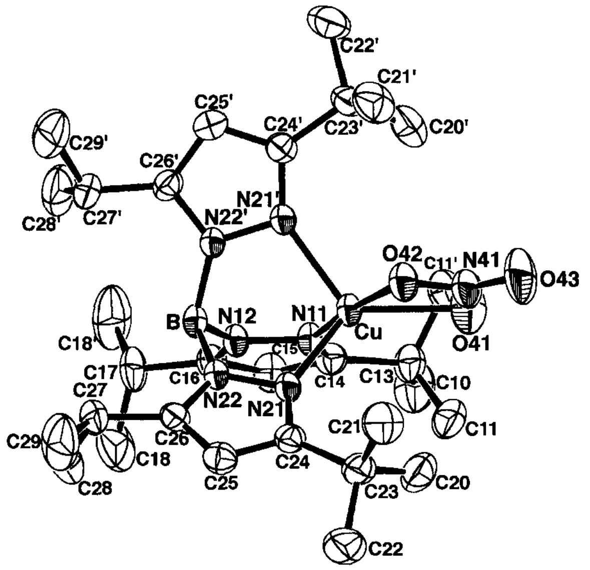


Fig. 2. An ORTEP drawing of [Cu(NO$_3$){HB(3-*t*Bu-5-*i*Prpz)$_3$}] (**3**) (50% probability) with an atomic labeling scheme. Hydrogen atoms are not shown for clarity.

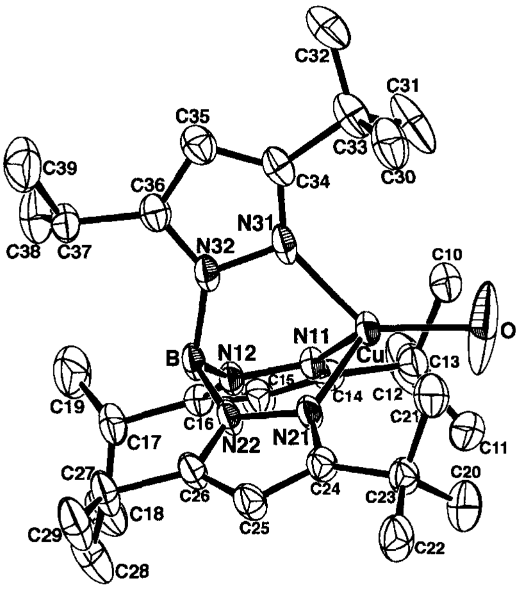


Fig. 3. An ORTEP drawing of [Cu(OH){HB(3-*t*Bu-5-*i*Prpz)$_3$}] (**4**) (50% probability) with an atomic labeling scheme. Hydrogen atoms are not shown for clarity.

Table 2. Selected Bond Distances (Å) and Angles (°) for Copper(II) Complexes Characterized by X-Ray Analysis[a)]

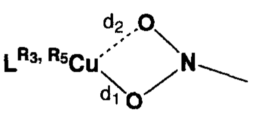
	[Cu(NO$_3$){HB(3,5-*i*Pr$_2$pz)$_3$}] (**1**)		
Cu–N11	1.956(3)	Cu–O41	2.021(4)
Cu–N21	2.000(3)	Cu–O42	1.989(4)
Cu–N31	2.083(3)		
N11–Cu–N21	92.1(1)	N21–Cu–O41	99.5(2)
N11–Cu–N31	91.5(1)	N21–Cu–O42	147.4(2)
N11–Cu–O41	160.8(2)	N31–Cu–O41	103.0(2)
N11–Cu–O42	102.1(2)	N31–Cu–O42	115.7(2)
N21–Cu–N31	92.8(1)	O41–Cu–O42	60.4(2)
	[Cu(NO$_3$){HB(3-*t*Bu-5-*i*Prpz)$_3$}] (**3**)		
Cu–N11	1.958(3)	Cu–O41	2.206(3)
Cu–N21	2.072(2)	Cu–O42	1.989(3)
N11–Cu–N21	91.0(1)	N21–Cu–O41	125.2(1)
N11–Cu–O41	110.9(1)	N21–Cu–O42	94.4(1)
N11–Cu–O42	171.3(1)	O41–Cu–O42	60.4(1)
N21–Cu–N21'	102.9(1)		
	[Cu(OH){HB(3-*t*Bu-5-*i*Prpz)$_3$}] (**4**)		
Cu–N11	2.061(4)	Cu–O	1.918(4)
Cu–N21	2.094(3)		
Cu–N31	2.004(4)		
N11–Cu–N21	95.4(1)	N11–Cu–O	121.7(2)
N11–Cu–N31	92.1(1)	N21–Cu–O	114.5(2)
N21–Cu–N31	92.7(1)	N31–Cu–O	131.9(2)

a) Numbers in parentheses are estimated standard deviations.

and two oxygen atoms (O41 and O42) from NO_3^-; the axial site is occupied by the resting nitrogen atom (N31) from hydrotris(pyrazolyl)borate. This coordination geometry is supported by the structural parameter τ, $\tau = (\alpha - \beta)/60°$, where α and β are the largest angles ($\alpha > \beta$) around a five-coordinate metal center, provided by Addison et al.[16] By using this parameter, for an ideally square-planar geometry τ is equal 0, while for a perfect trigonal-bipyramidal geometry it becomes 1. The application of this approach in **1** yields a value of 0.22. The deviation of copper(II) ion from the corresponding least-squares N_2O_2 plane toward the apical direction falls in 0.32 Å. The Cu–N distance at the apical position is slightly longer by 0.08—0.13 Å than those in the basal plane, as expected. The nitrato ligand in **1** is a moderately symmetric bidentate coordination mode (Cu–O41, 2.021(4) Å and Cu–O42 1.989(4) Å; ΔCu–O, 0.032 Å).

Compound **3** crystallized as well-separated molecules in the $P2_1/m$ space group with a crystallographically imposed plane of symmetry containing one of the pyrazole rings, B, Cu, and the NO_3^- unit (Fig. 2). **3** also contains a copper core with three pyrazolyl nitrogen atoms and two bidentate oxygen atoms of NO_3^-; its oxidation state of the copper ion is +2, $[Cu(NO_3)\{HB(3\text{-}t\text{Bu-}5\text{-}i\text{Prpz})_3\}]$. The copper(II) center adopts a distorted trigonal-bipyramidal geometry with the basal plane comprising two nitrogen atoms (N21 and N21′) from hydrotris(pyrazolyl)borate and one oxygen atoms (O41) from NO_3^-; also the axial site is occupied by the resting nitrogen atom (N11) from hydrotris(pyrazolyl)borate and an oxygen atom (O42). The τ value in **3** is 0.77.[16] Further, the Cu–N11 distance at the apical position is much shorter, by 0.11 Å, than those in the basal plane. The Cu–O42 distance at the apical position is also much shorter, by 0.22 Å than the Cu–O41 in the basal plane. Therefore, the interaction between the copper(II) ion and the apical atoms is very strong, showing the d_{z^2} ground state, as expected. The nitrato ligand in **3** is an asymmetric bidentate coordination mode (ΔCu–O, 0.22 Å). As shown by the X-ray crystal structural results for the set of nitrato complexes presented in Fig. 4,[17] the nitrate binding mode shifts from symmetric bidentate (ΔCu–O = 0 Å) in $L^{t\text{Bu},\text{H}}$ and (ΔCu–O = 0.032 Å) in $L^{i\text{Pr},i\text{Pr}}$, to essentially asymmetric bidentate (ΔCu–O = 0.22 Å) in $L^{t\text{Bu},i\text{Pr}}$. These differences in the nitrate binding geometry can be viewed as a direct reflection of the divergent steric influences of the alkyl substituted hydrotris(pyrazolyl)borate ligand. These results also indicate that this steric influence affords both substitution positions, 3- and 5-position in the pyrazole rings.

Complex **4** crystallized in the triclinic space group $P\bar{1}$ (Fig. 3). The coordination environment about copper is a C_{3v}-distorted tetrahedral [average dihedral angle, 89.5°], as evidenced by the three small N(pyrazole)–Cu–N(pyrazole) bond angles (average, 93.3°), typical for hydrotris(pyrazolyl)borate copper(II) complexes, and three accordingly large O–Cu–N (pyrazole) bond angles (average, 122.7°).[4,18] The Cu–O distance (1.918(4) Å) is similar to those of terminal hydroxocopper(II) complexes (1.87—1.88 Å),[19,20] terminal alkoxocopper(II) complexes (1.85—1.93 Å),[21,22] and terminal aquacopper(II) complexes (1.93—2.01 Å).[19,21] Furthermore, evidence for the presence of the hydroxo ligand was provided by an IR study. Thus, **4** is a terminal hydroxocopper(II) complex, $[Cu(OH)\{HB(3\text{-}t\text{Bu-}5\text{-}i\text{Prpz})_3\}]$. To our knowledge, **4** is the first example of a four-coordinate terminal hydroxocopper(II) complex. On the other hand, only dinuclear μ-hydroxo dimers are observed with less sterically hindered ligands, $HB(3,5\text{-}i\text{Pr}_2\text{pz})_3^-$ and $HB(3,5\text{-Me}_2\text{pz})_3^-$. The averaged Cu–O distances are 1.94 Å (1.921(5) and 1.953(6) Å) in **2**[6] and 1.94 Å (1.917(7) and 1.965(5) Å) in $[\{Cu[HB(3,5\text{-Me}_2\text{pz})_3]\}_2(\mu\text{-OH})_2]$.[23]



$L^{R3,R5}$ [a]	d_1 (Å)	d_2 (Å)
$L^{iPr,iPr}$ [b]	2.021(4)	1.989(4)
$L^{tBu,iPr}$ [b]	2.206(3)	1.989(3)
$L^{tBu,H}$ [c]	2.042(3)	2.042(3)

Fig. 4. Comparison of X-ray structural data for $L^{R_3,R_5}Cu(NO_3)$ complexes. a: R3, R5 denotes 3 and 5 substitution position at pyrazole rings, respectively. b: this work. c: Ref. 17.

IR Spectroscopy. The coordination of the anion group is reflected by the IR spectra, as shown in Fig. 5.[24] From an X-ray analysis of nitrato complexes **1** and **3**, the NO_3^- group is coordinated to copper(II) ion as cheating bidentate. As compared with each hydroxo complex, **2** and **4**, two bands were observed for each of the asymmetric and symmetric

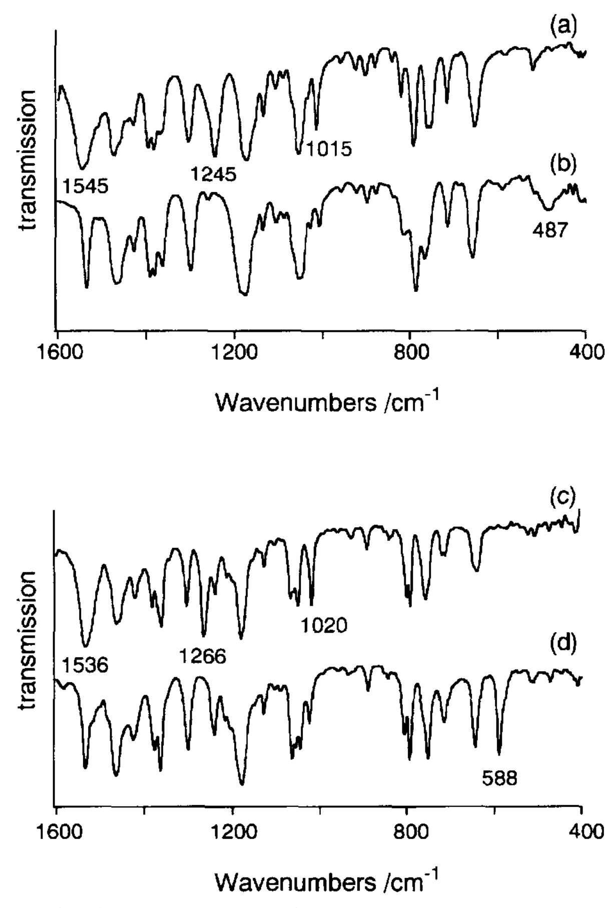


Fig. 5. IR spectra of **1**—**4**. (a) **1**, (b) **2**, (c) **3**, and (d) **4**.

nitrate stretching, $\nu_{as}(NO_3)$ 1545, $\nu_s(NO_3)$ 1245 cm^{-1} in **1** and $\nu_{as}(NO_3)$: 1536, $\nu_s(NO_3)$ 1266 cm^{-1} in **3**. Additionally, the $\nu(NO)$ band was observed at 1015 cm^{-1} in **1** and 1020 cm^{-1} in **3**.[24] The separation (Δ_{as-s}) between the $\nu_{as}(NO_3)$ and $\nu_s(NO_3)$ frequencies may be indicative of the nitrate binding mode. The Δ_{as-s} in **1** (300 cm^{-1}) is larger than that in **3** (270 cm^{-1}). From an X-ray analysis, the nitrate binding mode in **1** is more symmetrical than that in **3** (Fig. 4). Thus, its structural change in **1** and **3** reflects this Δ_{as-s}. This result indicates that the Δ_{as-s} is also characteristic for the nitrate binding mode in similar coordination compounds.

Evidence for the presence of a hydroxo group in **2** and **4** was provided by the $\nu(O\text{-}H)$ band at 3645 cm^{-1} in **2**[6] and 3667 cm^{-1} in **4**. This assignment in **4** was confirmed by an observation of the shift to 2704 cm^{-1} upon deuterium substitution $[Cu(OD)\{HB(3\text{-}t\text{Bu-}5\text{-}i\text{Prpz})_3\}]$ ($\nu(OH)/\nu(OD) = 1.35$). **4** had a characteristic band at 588 cm^{-1}, as compared with **3**. This band is assigned to Cu–O stretching. On the other hand, there was a very weak broad peak in **2** at around 487 cm^{-1}. This band may be assignable to Cu–O stretching. Sanders-Loehr and co-workers reported resonance Raman results of the μ-hydroxo-μ-phenolato-dicopper(II) complex $[Cu_2(\mu\text{-XYLO-1}:2\kappa^2O))(\mu\text{-OH})]^{2+}$.[25] This complex has a characteristic Raman shift at 465 cm^{-1} (ν_s(Cu–OH–Cu) mode), which is shifted to 453 cm^{-1} upon 18 oxygen substitution, $[Cu_2(\mu\text{-XYLO-1}:2\kappa^2O))(\mu\text{-}^{18}OH)]^{2+}$. However, **2** was not enhanced by the same resonance Raman condition.[25,26] Therefore, they conclude that only for the μ-OH bridged systems it is difficult to use resonance Raman spectroscopy to detect the bridging OH groups.[25] On the other hand, we can detect a resonance Raman shift in **4** at 589 cm^{-1} by using 386 nm laser excitation.[26] Therefore, this Cu–O stretching band is useful for a mononuclear (not dinuclear) hydroxo group, and can be applied as a good indicator for the presence of the mononuclear hydroxo intermediate during catalytic cycles in copper-containing enzymes.

UV-vis Spectroscopy. The UV-vis spectra of the nitrato complexes (**1** and **3**) and the hydroxo complexes (**2** and **4**) are shown in the upper and bottom side of Fig. 6, respectively. Both nitratocopper(II) complexes had characteristic absorption bands (293 nm in **1** and 297 nm in **3**), which are assigned to the NO_3^- → copper(II) charge transfer band. In the ligand field region, the d → d transition band in **1** (773 nm (12.9×10^3 cm^{-1})) had a higher energy than that in **3** (797 nm (12.6×10^3 cm^{-1})). This d → d band shift is consistent with its coordination geometry from X-ray structures, in which **1** is a square-pyramidal geometry and **3** is a distorted trigonal-bipyramidal geometry (Fig. 6). This structural difference affects the d → d band energy. A similar behavior is also observed in our chlorocopper(II) complexes.[27] The d → d band of the square-pyramidal five-coordinate chlorocopper(II) complex, $[Cu(Cl)\{HB(3,5\text{-}i\text{Pr}_2pz)_3\}(dmf)]$, is 758 nm ($13.2\times10^3$ cm^{-1}) and that of the distorted tetrahedral four-coordinate chlorocopper(II) complex, $[Cu(Cl)\{HB(3,5\text{-}i\text{Pr}_2pz)_3\}]$, is 1003 nm ($9.97\times10^3$ cm^{-1}).[27]

Both hydroxocopper(II) complexes have characteristic absorption bands (335 nm in **2**[6] and 373 nm in **4**), which are assigned to the OH^- → copper(II) charge transfer band. This assignment in **2** is consistent with the μ-hydroxo-μ-phenolatodicopper(II) complex,[25] which has an absorption band at 340 nm. The assignment of **4** was also confirmed by a resonance Raman result with 386 nm excitation. A ligand field band shift was also observed. The d → d transition band in **2** is 653 nm (15.3×10^3 cm^{-1}),[6] which is typically five-coordinate dinuclear copper(II) complexes.[25] The d → d band in **4** is 830 nm (12.1×10^3 cm^{-1}). This band in **4** shifts to the lower energy side than that in **2**. This indicates that the d → d transition shift is essential to the coordination geometry and environment in the copper(II) center due to steric effects on the hydrotris(pyrazolyl)borate ligands.

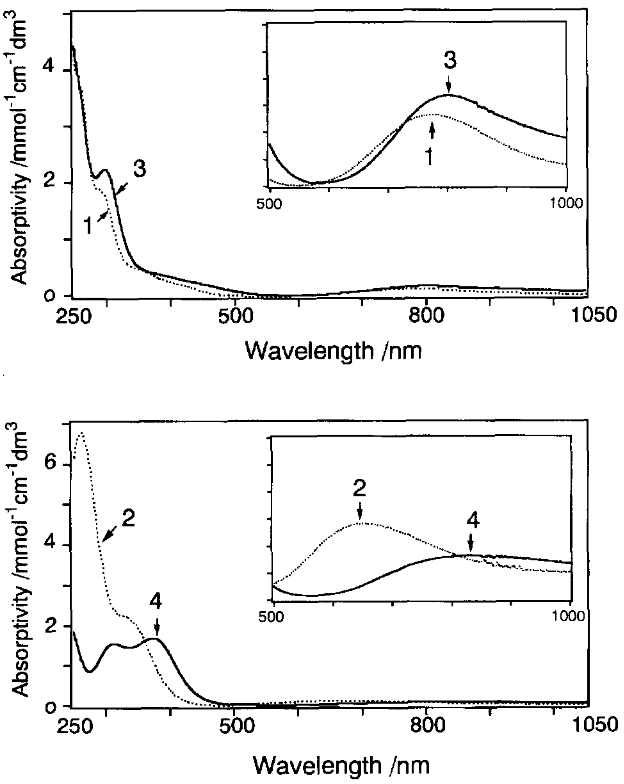


Fig. 6. UV-vis spectra of **1**—**4**. upper: nitrato complexes solid line (**3**), and dash line (**1**). bottom: hydroxo complexes; solid line (**4**), and dash line (**2**). inset: d → d transition region of **1**—**4**.

EPR Spectroscopy. The EPR spectra of all complexes recorded for frozen solutions at 140 K are shown in Fig. 7. These spectral features are very consistent with their crystal structures. The EPR spectrum of **2** is silent because of highly antiferromagnetic coupling between two copper(II) ions.[6] The g values in **1** were $g_{//} \gg g_{\perp} > 2.00$, having a large $A_{//}$ value. The EPR spectrum of **1** is typically tetragonal copper(II) complexes, having a $d_{x^2-y^2}$ ground state, which is consistent with its X-ray structure, showing that the τ value is equal to 0.22. However, the EPR spectra of **3** and **4** are dramatically changed from the EPR spectrum of **1**.

The spectrum of **3**, which has a trigonal-bipyramidal structure, exhibited a slightly rhombic splitting (Δg_{12} and Δg_{23} are ca. 0.15), $g_1 > g_2 > g_3 > 2.00$, and a g_3 value (2.01)

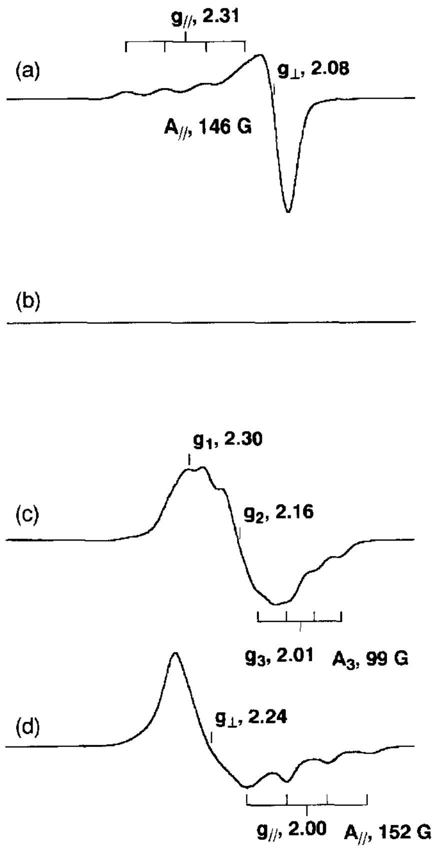


Fig. 7. EPR spectra of **1**—**4** at 140 K CH_2Cl_2 frozen. (a) **1**, (b) **2**, (c) **3**, and (d) **4**.

barely perturbed from the free-electron value (2.0023), and the largest copper hyperfine splitting in the highest field component (g_3). This feature is quite distinct from the typical copper(II) complexes, and is instead consistent with a ground state having a substantial d_{z^2} character.[28,29] Recently, the spectral features have been reported for some copper(II) complexes containing N_3O_2[18] and N_4Cl[30,31] ligand donor sets.

The spectrum of **4**, which has a distorted tetrahedral structure, exhibited a distinctly rhombic splitting ($g_\perp \gg g_{//} =$ 2.00), suggesting that the unpaired electron of copper(II) resides mainly in a d_{z^2} orbital. This hydroxo oxygen atom in **4** lies close to the copper(II) ion (1.918(4) Å). Therefore, the energy of the d_{z^2} orbital is raised so that the unpaired electron resides mostly in this orbital. Qualitatively similar spectra have been measured for the distorted tetrahedral sites in some blue copper proteins,[32] copper(II)-substituted insulin hexamer containing exogenous thiolate,[33] and copper(II) complexes containing benzo-crown ligands.[34] These EPR data in **3** and **4** are also supported by the X-ray structure and the d → d transition energy. This result also indicates that these structural changes affect the EPR parameters.

Conclusions

From these results, alkyl substitution at the close 3-position of the hydrotris(pyrazolyl)borates in the nitrato complexes (**1** and **3**) and the hydroxo complexes (**2** and **4**) plays an important role in modifying the coordination environment about the copper center. These structural distortions have been effective for their physicochemical properties. This explanation of the observed structural changes as well as differences in their physicochemical properties could be modified by increased repulsions between the alkyl groups in the 3-position and the copper(II) ion.

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References

1 Abbreviations used: HB(3,5-*i*Pr$_2$pz)$_3^-$ = hydrotris(3,5-diisopropyl-1-pyrazolyl)borate(1−), HB(3-*t*Bu-5-*i*Prpz)$_3^-$ = hydrotris(3-tertiary-butyl-5-isopropyl-1-pyrazolyl)borate(1−), HB(3,5-Me$_2$pz)$_3^-$ = hydrotris(3,5-dimethyl-1-pyrazolyl)borate(1−).

2 S. Trofimenko, *Chem. Rev.*, **93**, 943 (1993).

3 S. Trofimoenko, *Prog. Inorg. Chem.*, **34**, 115 (1986).

4 N. Kitajima and W. B. Tolman, *Prog. Inorg. Chem.*, **43**, 419 (1995).

5 G. Parkin, *Adv. Inorg. Chem.*, **42**, 291 (1995).

6 N. Kitajima, K. Fujisawa, C. Fujimoto, Y. Moro-oka, S. Hashimoto, T. Kitagawa, K. Toriumi, K. Tatsumi, and A. Nakamura, *J. Am. Chem. Soc.*, **114**, 1277 (1992).

7 S. Imai, K. Fujisawa, T. Kobayashi, N. Shirasawa, H. Fujii, T. Yoshimura, N. Kitajima, and Y. Moro-oka, *Inorg. Chem.*, **37**, 3066 (1998).

8 K. Fujisawa, M. Tanaka, Y. Moro-oka, and N. Kitajima, *J. Am. Chem. Soc.*, **116**, 12079 (1994).

9 D. D. Perrin, W. L. Armarego, and D. R. Perrin, "Purification of Laboratory Chemicals," 2nd ed, Pergamon, New York (1980).

10 H. -F. Fan, "SAPI 91: Structure Analysis Programs with Intelligent Control," Rigaku Corporation, Tokyo, Japan (1991).

11 P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel, and J. M. M. Smits, "DIRDIF 94, The DIRDIF-94 Program System," Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands (1994).

12 D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography," The Kynoch Press, Birmingham, England (1974), Vol. 4, Table 2.2A.

13 J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, **17**, 781 (1964).

14 "teXsan: Single Crystal Structure Analysis Package, Version 1.9," Molecular Structure Corporation, The Woodlands, TX (1998).

15 N. Kitajima, Y. Moro-oka, A. Uchida, Y. Sasada, and Y. Ohashi, *Acta Crstallogr., Sect. C*, **C44**, 1876 (1988).

16 A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn, and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, **1984**, 1349.

17 R. Han, A. Looney, K. McNeill, G. Parkin, A. L. Rheingold, and B. S. Haggerty, *J. Inorg. Biochem.*, **49**, 105 (1993).

18 C. E. Ruggiero, S. M. Carrier, W. E. Antholine, J. W. Whittaker, C. J. Cramer, and W. B. Tolman, *J. Am. Chem. Soc.*, **115**, 11285 (1993).

19 a) S. C. Lee and R. H. Holm, *J. Am. Chem. Soc.*, **115**, 11789 (1993). b) S. C. Lee and R. H. Holm, *J. Am. Chem. Soc.*, **115**, 5833 (1993).

20 a) L. M. Berreau, S. Mahapatra, J. A. Halfen, V. G. Young, Jr., and W. B. Tolman, *Inorg. Chem.*, **35**, 6339 (1996). b) M. Harata, K. Jitsukawa, H. Masuda, and H. Einaga, *Chem. Lett.*, **1996**, 813.

21 A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson, and R. Taylor, *J. Chem. Soc., Dalton Trans.*, **1989**, S1.

22 N. N. Murthy, M. Mahroof-Tahir, and K. D. Karlin, *J. Am. Chem. Soc.*, **115**, 10404 (1993).

23 N. Kitajima, T. Koda, S. Hashimoto, T. Kitagawa, and Y. Moro-oka, *J. Am. Chem. Soc.*, **113**, 5664 (1991).

24 K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, Inc., New York (1997), Vol. 2, p. 87.

25 J. Ling, A. Farooq, K. D. Karlin, T. M. Loehr, and J. Sanders-Loehr, *Inorg. Chem.*, **31**, 2552 (1992).

26 E. I. Solomon and K. Fujisawa, unpublished observation.

27 N. Kitajima, K. Fujisawa, and Y. Moro-oka, *J. Am. Chem. Soc.*, **112**, 3210 (1990).

28 B. J. Hathaway, *Struct. Bond.*, **57**, 55 (1984).

29 B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, **5**, 143 (1970).

30 F. Jiang, K. D. Karlin, and J. Peisach, *Inorg. Chem.*, **32**, 2576 (1993).

31 A. W. Addison, H. M. J. Hendriks, J. Reedijk, and L. K. Thompson, *Inorg. Chem.*, **20**, 103 (1981).

32 E. I. Solomon, M. J. Baldwin, and M. D. Lowery, *Chem. Rev.*, **92**, 521 (1992).

33 M. L. Brader, D. Borchardt, and M. F. Dunn, *J. Am. Chem. Soc.*, **114**, 4480 (1992).

34 Y. Li, K. Tajima, K. Ishizu, and N. Azuma, *Bull. Chem. Soc. Jpn.*, **60**, 557 (1987).