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Structural Effects on Nitratocopper(II) Complexes of Tris(pyrazolyl)borates

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Some structural influences on nitratocopper(II) complexes ligated by a series of hydrotris(pyrazolyl)borates are described. The 5-position of pyrazole rings as well as the 3-position is important to provide coordination structure.

Tris(pyrazolyl)borate ligands have been applied to inorganic, bioinorganic, and organometallic chemistry owing to the fact that these anionic ligands take versatile coordination modes and are useful for the preparation of complexes of elements throughout the periodic table.[1] In 1986, the bulkier substitutions were introduced in the 3-position of pyrazole rings, $[HB(3\text{-}Rpz)_3]^-$ (R = Ph, Bu^t); the formation of the unreactive and coordinately saturated complex, $[M\{HB(3\text{-}Rpz)_3\}_2]$, was easily inhibited.[2] After then, many substituents, aliphatic or aromatic groups, in the 3- and/or 5- (and/or 4-) position(s) were inserted to obtain novel complexes. We also used this methodology by using $[HB(3,5\text{-}Pr^i_2pz)_3]^-$ (= hydrotris(3,5-diisopropyl-1-pyrazolyl)borate(1-)) to prepare peroxocopper(II) complexes,[3] alkylperoxocopper(II) complexes,[4] and thiolatocopper(II) complexes[5] as models for oxy-hemocyanin, copper containing monooxygenases, and blue copper proteins, respectively. Expanding this ligand system, we introduced *tert*-butyl group in the 3-position, $[HB(3\text{-}Bu^t\text{-}5\text{-}Pr^ipz)_3]^-$ (= hydrotris(3-*tert*-butyl-5-isopropyl-1-pyrazolyl)borate(1-)), to make mononuclear complexes selectively, and recently reported the structural influences on copper(II) complexes.[4,6] In our previous paper,[6] the nitrate ligand exhibited both unidentate and bidentate coordination modes. Therefore, observation of the structure of a nitratocopper(II) complex may provide a good indication as to the structural effects on tris(pyrazolyl)borate ligands. We report herein some structural researches on nitratocopper(II) complexes ligated by hydrotris(pyrazolyl)borates, $[HB(3,5\text{-}Me_2pz)_3]^-$: ($L^{Me,Me}$) (= hydrotris(3,5-dimethyl-1-pyrazolyl)borate(1-)),[7] $[HB(3\text{-}Ph\text{-}5\text{-}Mepz)_3]^-$: ($L^{Ph,Me}$) (= hydrotris(3-phenyl-5-methyl-1-pyrazolyl)borate(1-)),[8] $[HB(3\text{-}Bu^t\text{-}5\text{-}Mepz)_3]^-$: ($L^{tBu,Me}$) (= hydrotris(3-*tert*-butyl-5-methyl-1-pyrazolyl)borate(1-)),[9] $[HB(3,5\text{-}Pr^i_2pz)_3]^-$: ($L^{iPr,iPr}$),[3] $[HB(3\text{-}Ph\text{-}5\text{-}Pr^ipz)_3]^-$: ($L^{Ph,iPr}$) (= hydrotris(3-phenyl-5-isopropyl-1-pyrazolyl)borate(1-)),[10] $[HB(3\text{-}Bu^t\text{-}5\text{-}Pr^ipz)_3]^-$: ($L^{tBu,iPr}$).[10,11]

The nitratocopper(II) complexes were obtained from the reaction between copper(II) nitrate trihydrate and potassium salts of the substituted hydrotris(pyrazolyl)borates in a mixed solvent, Me_2CO/CH_2Cl_2, at room temperature in high yield (Scheme 1). The crystal structures of **4** and **6** have been reported.[6] All other nitratocopper(II) complexes are characterized by an X-ray diffraction method in the present work. An X-ray characterization of all nitratocopper(II) complexes reveals that three nitrogen atoms of the hydrotris(pyrazolyl)borate ligand bind the copper(II) atom as a facially coordinating tridentate ligand, forming a mononuclear structure.

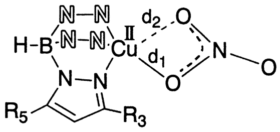
In the case of phenyl substituted ligand at the 3-position ($L^{Ph,iPr}$), the structural values of **5** (ΔCu–O = 0.074 Å, τ value[12] = 0.70) are intermediate between those of **4** with $L^{iPr,iPr}$ and **6** with $L^{tBu,iPr}$, which has many differences in their structural parameters (ΔCu–O, τ value) and physicochemical properties (Scheme 2 and Table 1).[6] This result can be summarized by the following series according to effective steric bulkiness at a complexed metal center in the 3-position substituted ligand system: Bu^t > Ph > Pr^i.

In the methyl substituted complexes at the 5-position (**1–3**), **1** has a crystallographically imposed plane of symmetry containing one of pyrazole rings, B Cu, N41 and O42 of the NO_3^- unit. Therefore, two Cu–O distances are exactly the same (ΔCu–O = 0). As the substituent in the 3-position ($L^{Me,Me}$ (**1**), $L^{Ph,Me}$ (**2**), $L^{tBu,Me}$ (**3**)) become bulkier, the ΔCu–O distance is

$$K[HB(3\text{-}R_3\text{-}5\text{-}R_5pz)_3] + Cu(NO_3)_2\cdot 3H_2O \xrightarrow{Me_2CO/CH_2Cl_2} [Cu(NO_3)\{HB(3\text{-}R_3\text{-}5\text{-}R_5pz)_3\}] + KNO_3$$

$R_3 = Me, R_5 = Me$; (**1**) $R_3 = Pr^i, R_5 = Pr^i$; (**4**)[6]
$R_3 = Ph, R_5 = Me$; (**2**) $R_3 = Ph, R_5 = Pr^i$; (**5**)
$R_3 = Bu^t, R_5 = Me$; (**3**) $R_3 = Bu^t, R_5 = Pr^i$; (**6**)[6]

Scheme 1.



Scheme 2.

Table 1. Comparison of Structural Data $L^{R_3,R_5\ a)}$ $Cu(NO_3)$ Complexes

$L^{R_3,R_5\ a)}$		d_1 (Å)	d_2 (Å)	ΔCu–O (Å)	$\tau^{e)}$	Cu···N (Å)
$L^{Me,Me}$	(**1**)	2.030(9)	2.030(9)	0	0	2.38(2)
$L^{Ph,Me}$	(**2**)	2.033(2)	2.011(2)	0.022	0.38	2.416(3)
$L^{tBu,Me\ b)}$	(**3**)	2.16(2)	1.99(1)	0.17(2)	0.55(1)	2.47(2)
$L^{iPr,iPr\ c)}$	(**4**)	2.021(4)	1.989(4)	0.032	0.22	2.413(4)
$L^{Ph,iPr}$	(**5**)	2.072(4)	1.998(4)	0.074	0.70	2.427(5)
$L^{tBu,iPr\ c)}$	(**6**)	2.206(3)	1.989(3)	0.217	0.77	2.493(3)
$L^{tBu,H\ d)}$		2.042(3)	2.042(3)	0	0	—

a) R_3, R_5 denotes 3- and 5-substitution position at pyrazole rings, respectively. b) There are two independent molecules in the unit cell. c) Ref. 6. d) Ref. 13. e) Ref. 12.

longer (0, 0.022, 0.17) and the τ value is also larger (0, 0.38, 0.55). Such facts suggest that the bulkiness of the substituent in the 3-position is effective in coordination environments.

As can be seen from Table 1, some influences on the structural data in the 5-position substituent (**2** vs. **5** and **3** vs. **6**) are also observed. The $\Delta(\Delta\text{Cu–O})$ distances and $\Delta\tau$ values are 0.052 and 0.32 (**2** vs. **5**), 0.047 and 0.22 (**3** vs. **6**), whereas those are 0.017 and 0.55 (**1** vs. **3**), and 0.185 and 0.55 (**4** vs. **6**). Therefore, the bulkiness of substituent in the 5-posision (**2** vs. **5** and **3** vs. **6**) is smaller than that in the 3-position (**1** vs. **3** and **4** vs. **6**). From the τ value and the distance between copper(II) ion and N41 (Table 1), the coordination of the nitratocopper(II) ligated by more bulkier substituent(s) in 3 and/or 5 position(s) has a more distorted geometry. In the case of the difference between methyl (**1**) and isopropyl (**4**) groups in the 3- and 5-positions, there are slight changes about ΔCu–O distances and τ values. In addition, $\mathrm{L}^{t\mathrm{Bu,H}}$ ligand has almost the same bulkiness as $\mathrm{L}^{\mathrm{Me,Me}}$ in nitratocopper(II) complexes. From these results, the substituent in the 5-position as well as that in the 3-position are also effective in the metal center environment. And the bulkiness order of nitratocopper(II) complexes is as follows: $\mathrm{L}^{\mathrm{Me,Me}}$ (**1**) < $\mathrm{L}^{i\mathrm{Pr},i\mathrm{Pr}}$ (**4**) < $\mathrm{L}^{\mathrm{Ph,Me}}$ (**2**) < $\mathrm{L}^{\mathrm{Ph},i\mathrm{Pr}}$ (**5**) < $\mathrm{L}^{t\mathrm{Bu,Me}}$ (**3**) < $\mathrm{L}^{t\mathrm{Bu},i\mathrm{Pr}}$ (**6**). Further research is proceeding on these structural effects on metal center in other ligand systems.

Experimental

Measurement. Elemental analyses were performed in the analytical facility at the Research Laboratory of Resource Utilization, Tokyo Institute of Technology and the Analysis Center of the University of Tsukuba.

Preparation. All the complexes were prepared by the methods described in previous papers.[6] Yield and elemental analyses of new nitratocopper(II) complexes are as follows: **1** (yield 72%) Found: C, 42.37; H, 5.40; N, 23.67%. Calcd for $C_{15}H_{22}N_7BCuO_3$: C, 42.62; H, 5.25; N, 23.19%.; **2** (yield 84%) Found: C, 58.74; H, 4.21; N, 16.05%. Calcd for $C_{30}H_{28}N_7BCuO_3$: C, 59.17; H, 4.63; N, 16.10%.; **3** (yield 76%) Found: C, 52.51; H, 7.34; N, 17.86%. Calcd for $C_{24}H_{40}N_7BCuO_3$: C, 52.96; H, 7.27; N, 17.94%.; **5** (yield 79%) Found: C, 62.36; H, 5.89; N, 14.22%. Calcd for $C_{36}H_{40}N_7BCuO_3$: C, 62.38; H, 5.82; N, 14.15%.

Crystallography. The diffraction data were measured on a Rigaku automated four-circle diffractometer with graphite-monochromated Mo $K\alpha$ ($\lambda = 0.71069$ Å) radiation. The data were collected at 23 ± 1 °C. The unit-cell parameters of each crystal were obtained from a least-squares refinement. The crystallographic data and collection details are summarized in Table S1. The non-hydrogen atoms were refined anisotropically. Refinements were carried out by a full-matrix least-squares method on *F*. Some important crystal data are as follows: **1** orthorhombic space group $Cmc2_1$ (No. 36), $Z = 4$, $D_{\mathrm{calc}} = 1.44$, 532 observed reflections [$I > 1.00\sigma(I)$] used in the refinements, $R = 0.056$, $R_{\mathrm{w}} = 0.061$ and GOF = 1.59 for 133 variable parameters; **2** triclinic space group $P\bar{1}$ (No. 2), $Z = 2$, $D_{\mathrm{calc}} = 1.41$, 3201 observed reflections [$I > 2.00\sigma(I)$] used in the refinements, $R = 0.030$, $R_{\mathrm{w}} = 0.045$ and GOF = 1.43 for 379 variable parameters; **3** orthorhombic space group $Pca2_1$ (No. 29), $Z = 8$, $D_{\mathrm{calc}} = 1.28$, 4124 observed reflections [$I > 2.00\sigma(I)$] used in the refinements, $R = 0.051$, $R_{\mathrm{w}} = 0.057$ and GOF = 1.26 for 649 variable parameters; **5** triclinic space group $P\bar{1}$ (No. 2), $Z = 2$, $D_{\mathrm{calc}} = 1.25$, 3828 observed reflections [$I > 2.00\sigma(I)$] used in the refinements, $R = 0.059$, $R_{\mathrm{w}} = 0.065$ and GOF = 1.40 for 433 variable parameters using the teXsan crystallographic software package.[14] The final positional and thermal parameters, full listing of the bond distances and angles, torsion angles, and ORTEP drawings, and the *F*o-*F*c table of **1**–**3** and **5** have been deposited as Document No. 74037 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 159121–159124.

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