6306 *Inorg. Chem.* **1999,** *38,* 6306−6308

Notes

N,O-Polydentate Scorpionate Ligands

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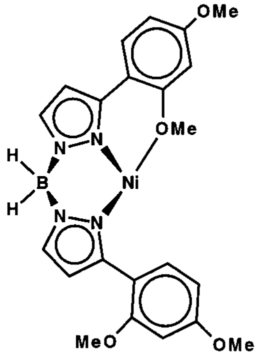
Received July 26, 1999

Introduction

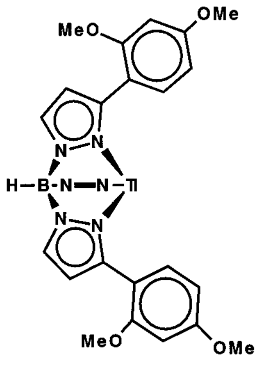
The scorpionate (polypyrazolylborate) ligand system has been known for over 33 years,[1] and more than 150 different ligands of this type have been prepared.[2] They contain a wide variety of substituents, modifying their coordination chemistry through steric and electronic effects in numerous ways. And yet, there have been no examples in which the coordination of the pz nitrogens was augmented by an oxy function from a pz substituent, thus expanding the scorpionate ligand denticity beyond the number of pz rings. Although the ligand HB[3-(2-OMePh)pz]$_3$, Tp$^{o\text{-An}}$, has been reported, its *o*-methoxy groups were found to be noncoordinating to the metal in the thallium complex TlTp$^{o\text{-An}}$,[3] nor were they coordinated in the trinuclear silver complex Ag$_3$(Tp$^{o\text{-An}}$)$_2$.[4] The thio analogue ligand HB[3-(2-SMePh)pz]$_3$, Tp$^{\text{Ph}(o\text{-SMe})}$, has also been reported recently, but no coordination of the MeS donor group was observed in the complex [Tp$^{\text{Ph}(o\text{-SMe})}$Cu(H$_2$O)]{PF$_6$}.[5]

On the other hand, N-based denticity expansion in polypyrazolylborates was demonstrated with the 2-pyridyl-substituted ligands Bp$^{\text{Py}}$ (dihydrobis[3-(2-pyridyl)pyrazol-1-yl]borate) and Tp$^{\text{Py}}$ (hydrotris[3-(2-pyridyl)pyrazol-1-yl]borate).[6,7] That the latter ligand is capable of hexadentate coordination was clearly proved for the icosahedral cationic complexes [U(Tp$^{\text{Py}}$)$_2$]$^+$ and [Sm(Tp$^{\text{Py}}$)$_2$]$^+$ by X-ray crystallography.[8] More recently, a related pyridine-derived ligand, Bp$^{\text{Bipy}}$, where Bipy = 6′-(2,2′-bipyridyl), has also been described.[9]

We report the synthesis of two new scorpionate ligands, including the first demonstrated oxygen-based example of expanded denticity, where the O-donor functionality resides on the pyrazolyl 3-substituent. These ligands are dihydrobis[3-(2,4-dimethoxyphenyl)pyrazol-1-yl]borate, Bp$^{(2,4(\text{OMe})_2\text{Ph})}$, and hydrotris[3-(2,4-dimethoxyphenyl)pyrazol-1-yl]borate, Tp$^{(2,4(\text{OMe})_2\text{Ph})}$, which have the capability to coordinate, in addition to the pyrazolyl nitrogens, through the *o*-methoxy groups on the phenyl rings.



Bp$^{(2,4(\text{OMe})_2\text{Ph})}$,
(as in the Ni complex)
only one of the two ligands is shown



Tp$^{(2,4(\text{OMe})_2\text{Ph})}$
(as in the Tl complex)
N—N represents the third,
hidden pz$^{(2,4(\text{OMe})_2\text{Ph})}$ group

The Bp$^{(2,4(\text{OMe})_2\text{Ph})}$ and Tp$^{(2,4(\text{OMe})_2\text{Ph})}$ ligands differ from Bp$^{\text{Py}}$ and Tp$^{\text{Py}}$ not only in being potentially tetradentate and hexadentate as N$_2$O$_2$ and N$_3$O$_3$, respectively, rather than N$_4$ and N$_6$, but also in having this secondary chelation occurring through a six-membered, rather than five-membered, ring (M−N−C−C−C−O sequence versus M−N−C−C−N).

Experimental Section

All chemicals were commercial reagent grade and were used as received. 2,4-Dimethoxyacetophenone was obtained from Aldrich. Elemental analyses were done by Microanalysis, Inc., Wilmington, DE. Infrared spectra were obtained as Nujol mulls with a Perkin-Elmer 1625 FTIR infrared spectrophotometer, using 16 scans. Proton NMR spectra were obtained with a Nicolet NT360WB spectrometer. The compounds were studied with typical conditions of 16K data points, a sweep width of 3000−4000 Hz, 90° pulse angles, and a recycle time of 4−5 s.

3-(2,4-Dimethoxyphenyl)pyrazole. This compound was synthesized from 2,4-dimethoxyacetophenone by the method used for making 3-phenylpyrazole,[10] and was obtained in 58% yield. Mp: 132−133 °C (from toluene/heptane). ^{1}H NMR: δ 7.59 (d, J = 8.4 Hz, 1H, H6′), 7.58 (d, J = 1.9 Hz, 1 H, H5), 6.57 (dd J = 8.4, 2.4, 1H, H5′), 6.56 (d, J = 2.4, 1H, H3′), 6.54 (d, J = 1.9, 1H, H4), 3.90 (s, 3H, OMe), 3.80 (s, 3 H, OMe). Anal. Calcd for C$_{11}$H$_{12}$N$_2$0$_2$: C, 64.7, H, 5.88, N, 13.7. Found: C, 64.9, H, 6.08; N, 13.8. The ^{13}C NMR has already been reported.[11]

The [Bp$^{(2,4(\text{OMe})_2\text{Ph})}$] Ligand. This ligand was synthesized by refluxing a mixture of 3-(2,4-dimethoxyphenyl)pyrazole and KBH$_4$ (2.5:1 mol ratio) in dry DMF until the theoretical amount of hydrogen was evolved. Hydrogen evolution was measured by a wet-test-meter protected by a −80 °C trap. Aliquots of the cooled solution were used directly for the preparation of complexes.

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10.1021/ic990881e CCC: $18.00

Table 1. Crystallographic Data for $\mathrm{Ni[Bp^{(2,4(OMe)_2Ph)}]_2}$ (**1**) and $\mathrm{Tl[Tp^{(2,4(OMe)_2Ph)}]}$ (**2**)

	1	**2**
formula	$C_{44}H_{48}B_2N_8NiO_8$	$C_{33}H_{34}BN_6O_6Tl$
fw	825.8	897.23
space group	*C*2/*c*	$R\bar{3}$
a, Å	19.0070(4)	19.398(5)
b, Å	8.7536(2)	
c, Å	25.3958(8)	15.773(6)
β, deg	92.0350(10)	
V, Å^3	4222.7(2)	5140(3)
Z	4	6
cryst color, habit	pale green block	colorless block
D(calc), g cm^3	1.411	1.595
μ(Mo Kα), cm^{-1}	5.24	47.47
temp, °C	−50(2)	24(2)
diffractometer	Siemens P4/CCD	Siemens P4
radiation	Mo Kα ($\lambda = 0.710\ 73$ Å)	
R(*F*) %^{a}	3.71^b	4.11^a
R(w*F*^{2}), %^{a}	10.31^{b,c}	4.49^a

^{a} Quantity minimized $= \sum\Delta^2$; $R = \sum\Delta/\sum(F_o)$; $R(w) = \sum\Delta w^{1/2}/\sum(F_o w^{1/2})$, $\Delta = |(F_o - F_c)|$. ^{b} Quantity minimized $= R(\mathrm{w}F^2) = \sum[w(F_o^2 - F_c^2)^2]/\sum[(\mathrm{w}F_o^2)^2]^{1/2}$; $R = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c)|$. $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + \mathrm{Max}(F_o,0)]/3$. ^{c} $R(\mathrm{w}F^2)$, %.

$\mathrm{Ni[Bp^{(2,4(OMe)_2Ph)}]_2}$ (1). This complex was prepared by stirring 2 equiv of the DMF solution of the ligand with aqueous $NiCl_2$. After dilution with more water, the blue-green product was extracted with methylene chloride, the extracts were washed with water several times to remove DMF, and the solution was chromatographed on alumina, collecting the blue-green band. Evaporation of the solvent produced the Ni complex in 53% yield. It was purified further by recrystallization from toluene/heptane. Mp: 185−188 °C dec. IR: BH at 2429, 2411, 2355, and 2301 cm^{-1}. Anal. Calcd for $C_{44}H_{48}B_2N_8O_8$: C, 58.9; H, 5.35; N, 12.5. Found: C, 59.3, H, 5.49; N, 12.3.

$\mathrm{Tl[Tp^{(2,4(OMe)_2Ph)}]}$ (2). The $[\mathrm{Tp^{(2,4(OMe)_2Ph)}}]$ ligand was prepared by refluxing a mixture of 3-(2,4-dimethoxyphenyl)pyrazole and KBH_4 (3.5:1 mole ratio) in 4-methylanisole, until the theoretical amount of hydrogen was evolved. The solvent was distilled out at reduced pressure, and the residue was dissolved in THF and stirred with a slight excess of aqueous $TlNO_3$ solution. The product was extracted with methylene chloride, and was purified by being passed through a bed of alumina. After evaporation of the solvent, the residue was stirred with methanol, and was filtered. The white solid was washed with methanol, to remove excess 3-(2,4-dimethoxyphenyl)pyrazole, and was air-dried. $\mathrm{Tl[Tp^{(2,4(OMe)_2Ph)}]}$ was obtained in 57% yield, and it was recrystallized from toluene. Mp: 209−212 °C dec. IR: BH 2416 cm^{-1}. ^{1}H NMR: δ 7.74 (d, $J = 1.9$, 1H, H5), 7.44 (d, $J = 7.8$, 1H, H6′), 6.50 (dd, $J = 7.8$, 0.9, 1H, H5′), 6.48 (d, $J = 0.9$, 1H, H3′), 6.40 (d, $J = 1.9$, 1 H, H-4), 3.79 (s, 3H, OMe), 3.65 (s, 3H, OMe). Anal. Calcd for $C_{33}H_{34}BN_6O_6$: C, 63.8; H, 5.48; N, 13.5. Found: C, 64.0; H, 5.56; N, 13.2.

Crystallographic Structural Determination. Crystal data collection and refinement parameters are given in Table 1. The data for $\mathrm{Ni[Bp^{(2,4(OMe)_2Ph)}]_2}$ (**1**) were collected on a Siemens P4 diffractometer equipped with a SMART/CCD detector.

Systematic absences in the diffraction data for $\mathrm{Tl[Tp^{(2,4(OMe)_2Ph)}]}$ (**2**) were consistent with the rhombohedral space groups *R*3, $R\bar{3}$, *R*3*m*, *R*32, and $R\bar{3}m$, and diffraction symmetry suggested the lower Laue group. For **1**, systematic absences in the diffraction data were consistent for the C-centered monoclinic space groups *Cc* and *C*2/*c*. The chemical composition and the value of *Z* suggested the space group $R\bar{3}$ for **2** and *C*2/*c* for **1**. Solution in the respective space groups yielded chemically reasonable and computationally stable results of refinement. The structures were solved by direct methods, completed by subsequent difference Fourier syntheses and refined by full-matrix, least-squares procedures. **2** lies on a 3-fold axis, and **1** lies on a 2-fold axis. Semiempirical absorption corrections were applied to the data of **2**, and empirical absorption corrections were applied to the data of **1**. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms on boron were located from the difference map and allowed to refine. All other hydrogen atoms were treated as idealized contributions.

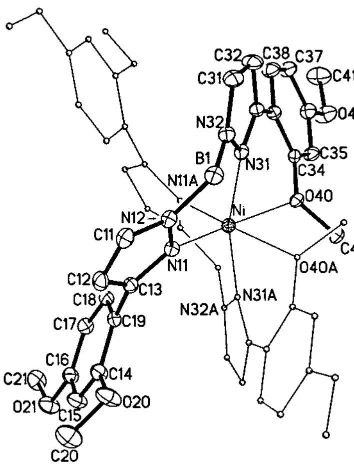

Figure 1. Molecular structure of complex of **1**, $\mathrm{Ni[Bp^{(2,4(OMe)_2Ph)}]_2}$. Selected bond lengths (Å) and angles (deg): Ni−N(31) 2.0071(14), Ni−N(11) 2.096(2), Ni−O(40) 2.2710(14); N(31)−Ni−N(11) 95.23(6); N(31)−Ni−O(40) 79.14(5).

All software and sources of the scattering factors are contained in either the SHELXTL PLUS (Version 4.2) or the SHLXTL (5.03) program library (G. Sheldrick XRD, Madison, WI).

Results and Discussion

The ligands $[\mathrm{Bp^{(2,4(OMe)_2Ph)}}]^-$ and $[\mathrm{Tp^{(2,4(OMe)_2Ph)}}]^-$ were prepared from 3-(2,4-dimethoxyphenyl)pyrazole and KBH_4 in conventional fashion, and the latter ligand was characterized as the Tl salt. The ligand $[\mathrm{Bp^{(2,4(OMe)_2Ph)}}]^-$ formed a blue-green Ni(II) complex, $\mathrm{Ni[Bp^{(2,4(OMe)_2Ph)}]_2}$, judged to be octahedral on the basis of its color, and this was confirmed by an X-ray crystallographic structure determination, which showed that one *o*-methoxy group per ligand was coordinated to nickel. The nickel ion was in an octahedral environment, with each $\mathrm{Bp^{(2,4(OMe)_2Ph)}}$ ligand coordinating through two pyrazolyl nitrogen atoms, and one methoxy group (Figure 1). The Ni−N distances were 2.096 and 2.007 Å, respectively, the shorter distance being associated with the N,O-chelated pyrazolyl group. These values were in the shorter range of the reported scorpionate Ni−N bond distances. For instance, in the heteroleptic complex $\mathrm{Tp^{iPr,4Br}NiTp^*}$ the Ni−N bond distances averaged 2.14 Å for $\mathrm{Tp^{iPr,4Br}}$ and 2.07 Å for Tp*.[12] In the asymmetric TpNi(η^3-allyl) complex the two Ni−N bonds were 1.978 Å, while the axial Ni−N bond was 2.153 Å.[13] The O−Ni distance in $\mathrm{Ni[Bp^{(2,4(OMe)_2Ph)}]_2}$ was 2.271 Å, and thus longer than the values found for Ni complexes with ethers (2.147−2.176 Å).[14]

While there have been some N,N,O-bonding scorpionates reported, they were all of the structure $\mathrm{(RO)Bp^xML}$, and were synthesized in most cases by inserting a C═O bond from an aldehyde or ketone into the B−H bond of the precursor $\mathrm{Bp^xML}$ complex. Examples of such alkoxy-containing complexes include $\mathrm{[(RO)Bp^{tBu}]ZnEt}$ (R = Me, Et, ^{i}Pr),[15] $\mathrm{[(MeO)Bp^{tBu,iPr}]ZnMe}$,[16] $\mathrm{[(Ph_2CHO)Bp^{tBu,iPr}]ZnI}$,[17] and $\mathrm{[(HCOO)Bp^{tBu,iPr}]ZnCl}$,[18]

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obtained via the addition of CO_2. All these complexes were tetrahedral. The only octahedral complex reported was the structurally characterized $[(^{i}PrO)Bp^{*}]Mo(CO)_2NO$, but the mechanism of its formation has remained obscure.[19]

The structure of $Tl[Tp^{(2,4(OMe)_2Ph)}]$ (Figure 2) shows the ligand coordinating to Tl(I) in symmetrical fashion through the three pyrazolyl nitrogens. There is no additional coordination through the *o*-methoxy groups. In fact, they are pointing away from Tl, as they also do in the case of $TlTp^{o\text{-}An}$. The phenyl rings are twisted by 35.4° with respect to the pz plane. In the crystal, two $Tl[Tp^{(2,4(OMe)_2Ph)}]$ molecules are paired up head-to-head, with a Tl−Tl distance of 3.995 Å, being positioned in such a manner that the "dimer" exhibits D_{3d} symmetry. This is in contrast to the known structures of $Tl[Tp^{Py}]$,[20] and of other known $TlTp^{x}$ complexes which show monomeric molecules in the crystal. The only exceptions are $TlTp^{Tol}$, which is also "dimeric" with a Tl−Tl distance of 3.86 Å,[21] and $TlTp^{Cpr}$, which is tetrameric, and contains a tetrahedron of Tl atoms, capped at each apex by a Tp^{Cpr} ligand.[22] The Tl−N distances in $Tl[Tp^{(2,4(OMe)_2Ph)}]$ are all identical (2.584 Å) and are thus significantly shorter than in $Tl[Tp^{Py}]$ (average 2.670 Å), and slightly shorter than the average of 2.593 Å found in $Tp^{o\text{-}An}$.

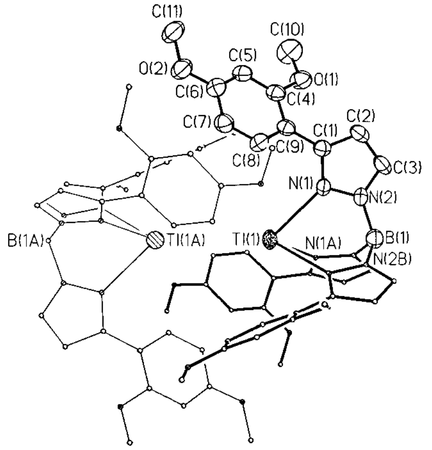

Figure 2. Molecular structure of complex of **2**, $Tl[Tp^{(2,4(OMe)_2Ph)}]$. Selected bond lengths (Å) and angles (deg): Tl−N(1) 2.584(8), Tl−N(1A) 2.584(6), Tl−N(1B) 2.584(6); N(1)−Tl−N(1A) 74.9(2), N(1)−Tl−N(1B) 74.9(2), N(1A)−Tl−N(1B) 74.9(2).

In summary, novel Bp and Tp ligands with expanded denticity via potential oxygen donors on the 3-phenyl substituent were synthesized, and it was demonstrated through structural characterization of the complex $Ni[Bp^{(2,4(OMe)_2Ph)}]_2$ that coordination through the *o*-methoxy substituent does indeed occur. These ligands may be particularly useful in lanthanide and actinide coordination chemistry.

Supporting Information Available: Tables of detailed crystallographic data, atomic position parameters, and bond lengths and angles for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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