Binding polyprotic small molecules with second-sphere hydrogen bonds

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ABSTRACT
Second-sphere hydrogen bonds are known for playing significant roles in homogeneous catalysis and in biological processes with metal-containing molecules. In this work, we highlight a tetradentate asymmetric ether-sulfonamidate ligand that facilitates second-sphere hydrogen bonding in transition metal complexes. We explored its ability to bind mono-, di-, tri-, and tetra-protic ligands when supporting a cobalt(II) ion. The structures of three such cobalt complexes containing bound water, ammonia, and hydrazine are presented. Additionally, spectroscopic analysis of a strongly bound hydroxide ion complex is presented. A hydrogen-bonding configuration, not yet observed in crystal structures of this type, resulted in a bridging hydrazine complex with the two cobalt ions separated by a distance of 5 Å.

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1. Introduction
The impact of second-sphere hydrogen bonding in transition metal complexes has been well established in homogeneous catalysis [1–4] and biomimetic/bio-inspired synthesis [5–9]. Furthermore, the literature contains numerous examples of hydrogen bonding interactions that play a significant role in the study of metal complexes serving as models of reactive intermediates [10, 11] and in exploring reactivity with small molecules composed primarily of oxygen [12–15] or nitrogen [16–21]. Our research program is interested in second-sphere hydrogen bonding interactions with...
industrially relevant protic small molecules such as ammonia, hydrazine, and hydroxylamine. Sulfonamidate ligands are known for their ability to bind small protic molecules [10, 12, 21–23] and our exploration of ligands containing this functionality led us to [MeOtS]2− [24], which has been used by Mountford and coworkers to bind strongly electrophilic Group 3 and Group 13 metal ions such as TiIV, ZrIV, AlIII, and InIII in exploration of polymerization catalysts [25–27]. The Mountford group reports the crystal structure of the proteo-form of 1 [27], which displays intramolecular hydrogen bonding, and one crystal structure of an organometallic AlIII complex with second-sphere hydrogen bonding involving a bound oxyethylamine ligand [26]. However, exploration of this second-sphere hydrogen bonding with transition metals or with other protic molecules has not been reported. In this work, we report the synthesis of cobalt complexes supported by 1 (Scheme 1) that engage in second-sphere hydrogen bonding with mono-, di-, tri-, and tetra-protic ligands.

2. Results and discussion

2.1. Synthesis of ligand and cobalt complexes

The synthesis of 1 is accomplished by a tosylaziridine ring opening on methoxyethyamine. Stirring methoxyethyamine with a slight excess of tosylaziridine in acetonitrile for several days results in the clean formation of proteo-ligand 1. Complex 2−OH2 is formed by the reaction of 1 with stoichiometric equivalents of cobalt sulfate and excess potassium hydroxide in methanol under ambient conditions. After removing the methanol under reduced pressure, re-dissolving in dichloromethane, and filtering, the purple compound is crystallized by vapor diffusion of diethyl ether. Complexes 2−NH3 and 3 are formed by axial ligand metathesis from 2−OH2. Aqueous solutions of the axial ligand are added in stoichiometric excess to the cobalt complex in acetonitrile and then isolated by crystallization upon vapor diffusion of diethyl ether. Attempts to react 2−OH2 with hydroxylamine resulted in the decomposition of the metal complex.

2.2. Crystallographic and structural characteristics of cobalt complexes

The crystal structures of 2−OH2, 2−NH3, and 3 were refined with non-spherical electron configurations calculated from Hirshfeld-partitioned electron densities, not from standard spherical-atom scattering factors. The program NoSpherA2 [28], implemented in Olex2, calculates aspherical atom form factors from wavefunction-derived electron densities. The software Orca [29, 30] was used for the SCF calculations from the X-ray nuclear configurations by using PBE or PBE0 methods. Two types of methods were used to treat the hydrogen atoms. In the first case, the hydrogen atom positions were located from the electron densities and refined using Hirshfeld scattering factors without constraints. In the case of the crystal structure of 2−OH2, the hydrogens were refined with geometrical constraints but their distances were free to vary. In both cases, the Hirshfeld model was used for all the atoms. For suitable crystals (2−OH2 and 2−NH3), with adequate data to parameter ratios, the hydrogens were refined
with anisotropic temperatures. Rigid bond restraints were applied to the hydrogen atoms (and to their nearest neighbors).

Figure 1 shows the crystal structure of 2–OH$_2$ with clear hydrogen bonding interactions between the two protons on the axially bound water molecule and a sulfonyl oxygen from each of the two sulfonamidate arms of the ligand. Similar interactions are observed in the crystal structure of 2–NH$_3$ where two of the protons on the axially bound ammonia molecule are hydrogen bonding with sulfonyl oxygen atoms from each of the two sulfonamidate arms of the ligand.

While the two published complexes of hydrazine with sulfonamidate complexes are both monodentate [12, 22], the Cambridge Structural Database (CSD) contains 46 unique examples of bridging molecular hydrazine complexes with transition metals. Consequently, formation of bridging hydrazine compound 3 was unexpected but not

Scheme 1. Synthesis of cobalt complexes.
unprecedented. Interestingly, crystallographic characterization of 3 displays an unusual hydrogen bonding pattern between the four protons on the hydrazine molecule and sulfonyl oxygen atoms. Unlike the proximal-distal configuration observed in monometallic species $\text{2-OH}_2$ and $\text{2-NH}_3$, the bridging hydrazine ligand of 3 adopts a “left-right” configuration where protons bound to the same nitrogen atom are hydrogen bonding with sulfonyl oxygen atoms on opposite sides of the bridging structure. In the CSD, there are currently only 138 unique structures containing molecular hydrazine bound to a transition metal including the 46 bridging hydrazine compounds. However, only one of these structures displays clear intramolecular hydrogen bonding: an organometallic palladium complex bearing toluenesulfonylmethide ligands [31]. The hydrogen bonding displayed by the palladium complex follows a proximal-distal configuration where the protons on the nitrogen atom proximal to one palladium ion are hydrogen bonding to sulfonyl oxygen atoms on the ligand bonding the opposite metal. Complex 3 is a relatively rare example of a bridging metal-hydrazine complex and, to our knowledge, the only structure with the observed “left-right” configuration of hydrogen bonding.

The solid-state structures $\text{2-OH}_2$, $\text{2-NH}_3$, and 3 all possess a slightly distorted trigonal bipyramidal molecular geometry. As shown in Table 1, the equatorial bond angles range between $109^\circ$ and $123^\circ$ and the sum of the equatorial angles for each complex is less than $360^\circ$ due to out-of-plane distortions of the metal ion. In each complex, the axial ligand binds to cobalt at bent angles ($166.7^\circ$–$173.2^\circ$), likely due to the influence of intramolecular hydrogen bonding interactions with sulfonyl oxygen atoms of the supporting ligand. Additional crystallographic data are included in the Supplementary Information.

### 2.3. Spectroscopic evidence for binding hydroxide

Complexes $\text{2-OH}_2$, $\text{2-NH}_3$, and 3 are purple and have very similar absorption spectra (Figure 2, top). However, exposure of $\text{2-OH}_2$ to potassium hydroxide in methanol leads to an immediate color change from purple to dark green, which is consistent
with the formation of a hydroxide complex in methanol solution. Attempts to obtain single crystals of this complex for crystallographic characterization have thus far proved unsuccessful. However, a spectrophotometric titration of $2\text{OH}_2$ with potassium hydroxide in methanol under anhydrous conditions indicates a clean transition to a species having an absorption spectrum with $\lambda_{\text{max}}$ values at 607 nm and 422 nm along with the disappearance of the peak belonging to $2\text{OH}_2$ (Figure 2, middle). Furthermore, FTIR analysis of dark green powder isolated from reactions of $2\text{OH}_2$ with excess potassium hydroxide exhibits a broad peak at 3492 cm$^{-1}$, which we assign to the OH stretch of bound hydroxide, and is distinct from IR spectra for $2\text{OH}_2$, $2\text{NH}_3$, and 3 in the OH/NH stretch region (Figure 2, bottom). These spectroscopic values are similar to known Co$^{II}$—OH compounds with a similar molecular geometry at cobalt [32–35].

3. Conclusions

The synthesis and characterization of three cobalt sulfonamidate complexes are reported with spectroscopic evidence of binding with hydroxide ion, which serves to demonstrate the great facility possessed by the asymmetric ether-sulfonamidate ligand $[\text{MeOTs}_2]^{-2}$ to engage in second-sphere hydrogen bonding when bound to cobalt(II). Furthermore, the bridging hydrazine complex displays a hydrogen bonding configuration not yet seen in published structures.

4. Materials and methods

4.1. General

Reagents were purchased from Sigma-Aldrich, Oakwood Chemicals, or Ambeed and used without purification. Experiments run under anaerobic and anhydrous conditions were conducted in a VAC Genesis glovebox with solvents degassed under vacuum and dried using activated 3 Å molecular sieves. NMR data were collected on a Bruker 400 MHz instrument and referenced to residual solvent peaks. IR spectra were obtained using a Nicolet 6700 FT-IR with ATR attachment. Magnetic susceptibility was measured with an Evans balance. Electronic absorption data for characterization of isolated compounds were collected on a Shimadzu UV-2600 double-beam spectrophotometer using

| Table 1. Select crystallographic values for cobalt complexes. |
|---------------------------------------------------------------|
| Geometric values at cobalt                                     |
| N1 – Co – L$_{ax}$ (Å)  | N2 – Co – O$_{eq}$ (Å)  | N3 – Co – O$_{eq}$ (Å)  | N2 – Co – N3 (Å)  | $\Sigma$ Eq. Angles  |
| 2 – OH$_2$          | 173.2(3)$^\circ$   | 119.8(3)$^\circ$   | 111.8(3)$^\circ$   | 122.7(3)$^\circ$   | 354.3$^\circ$   |
| 2 – NH$_3$          | 170.99(2)$^\circ$  | 109.75(2)$^\circ$  | 120.53(2)$^\circ$  | 121.22(2)$^\circ$  | 351.5$^\circ$  |
| 3                 | 166.67(5)$^\circ$  | 117.27(5)$^\circ$  | 117.83(5)$^\circ$  | 117.29(5)$^\circ$  | 352.4$^\circ$  |

| Bond lengths to cobalt                                      |
|---------------------------------------------------------------|
| Co – L$_{ax}$ (Å)   | Co – N$_{1ax}$ (Å)  | Co – N$_{2eq}$ (Å)  | Co – N$_{3eq}$ (Å)  | Co – O$_{eq}$ (Å)  |
| 2 – OH$_2$          | 2.107(6)           | 2.148(7)           | 1.998(7)           | 1.989(7)           | 2.057(5)           |
| 2 – NH$_3$          | 2.1031(6)          | 2.1600(5)          | 2.0179(5)          | 2.0460(5)          | 2.1417(5)          |
| 3                 | 2.1218(13)         | 2.1776(13)         | 2.0037(13)         | 2.0191(13)         | 2.1142(11)         |
1 cm pathlength quartz cuvettes. Electronic absorption data for photometric titrations were collected on a StellarNet BLACK-Comet-SR spectrometer with DP400-UVIS-SR transmission dip probe fitted with a 10 mm path length tip. Crystal diffraction data were collected by Emory University Department of Chemistry X-Ray Crystallography Center. Additional crystallographic characterization information is included in the supplementary information. The precursor compounds N-(2-chloroethyl)-4-methylbenzene-1-sulfonamide [36] and para-toluenesulfonyl aziridine [37] have been previously characterized and

**Figure 2.** Absorption spectra for cobalt complexes (top), anhydrous photometric titration of 2–OH₂ with a total of 1.5 equivalents of potassium hydroxide (middle), and FTIR spectrum of cobalt complexes (bottom).
published, but our modified synthetic procedures for these compounds are included here with select spectroscopic data for convenience.

4.2. Synthesis and characterization details

4.2.1. N-(2-Chloroethyl)-4-methylbenzene-1-sulfonamide (ClEATs)
One molar equivalent of chloroethylamine hydrochloride (18.40 g, 0.15 mol), 1.05 equivalents of para-toluenesulfonyl chloride (31.80 g, 0.17 mol), and 2.2 equivalents of triethylamine (36.16 g, 0.36 mol) were dissolved in 250 mL of dichloromethane (DCM). The reaction mixture was stirred vigorously for 24 h. The resulting yellow solution was washed three times with water (100 mL), twice with aqueous saturated sodium bicarbonate (100 mL), and once with saturated sodium chloride (100 mL). The organic layer was dried with magnesium sulfate and then vacuum-filtered through celite. The solvent was removed on the rotary evaporator to afford a yellow oil, which was dissolved in 200 mL of DCM and crystallized with 160 mL of pentane at 4°C. The colorless solid was filtered from the supernatant. Drying under vacuum yielded pure product (29.77 g, 80% yield). Characterization data of the dried product agrees with published material [36]. ¹H-NMR (400 MHz, CDCl₃): δ 7.78 (d, 2H, J = 8.5 Hz, Ar-H), 7.35 (d, 2H, J = 7.96 Hz, Ar-H), 4.95 (t, 1H), 3.56 (t, 2H), 3.33 (t, 2H), 2.46 (s, 3H).

4.2.2. Para-toluenesulfonyl aziridine
One molar equivalent of ClEATs (16.57 g, 0.07 mol) was dissolved in 200 mL of toluene. Ten equivalents of a 20% aqueous potassium hydroxide solution (200 mL) were added and stirred for 30 min. The aqueous and organic solvents were separated from each other. The colorless solution in toluene was washed with water (100 mL) and with aqueous saturated sodium chloride (100 mL). The organic layer was dried with magnesium sulfate and then vacuum-filtered through celite. The solvent was removed on the rotary evaporator to afford a colorless solid, which was dissolved in 50 mL of DCM and crystallized with 200 mL of pentane at 4°C. The colorless solid was filtered from the supernatant. Drying under vacuum yielded pure product (9.23 g, 66% yield). Characterization of this product agrees with published values [37]. ¹H-NMR (400 MHz, CDCl₃): δ 7.85 (d, 2H, J = 8.44 Hz, Ar-H), 7.38 (d, 2H, J = 8.44 Hz, Ar-H), 2.48 (s, 3H), 2.39 (s, 4H), 1.60 (s, 3H). ¹³C-NMR (100 Hz, CDCl₃): δ 144.7, 134.9, 129.8, 128.0, 27.4, 21.7.

4.2.3. (2-Methoxyethyl)bis[2-[(2-(4-methylbenzenesulfonyl)ethyl)amino]ethyl]amine (1, H₂MeOTs²)
The synthesis of H₂MeOTs² was adapted from the previously published procedure [24]. One molar equivalent of 2-methoxyethyamine (1.49 g, 0.020 mol) and 2.1 equivalents of para-toluensulfonyl aziridine (7.48 g, 0.038 mol) were dissolved in 8 mL of acetonitrile. The reaction mixture was stirred vigorously for 24 h. A colorless solid was precipitated from the reaction mixture by the addition of cold diethyl ether (30 mL) and collected via vacuum filtration. The solid was dissolved in 40 mL of heated acetonitrile and recrystallized with diethyl ether (60 mL). The colorless solid was collected by vacuum filtration and residual solvent was removed under vacuum to yield a pure product (5.55 g, 65% yield). Characterization of this product agree with published values
$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.78 (d, 4H, $J = 8.28$ Hz, Ar-H), 7.34 (d, 4H, $J = 7.96$ Hz, Ar-H), 5.73 (s, 2H), 3.47 (s, 3H), 3.38 (t, 2H), 2.56 (t, 2H), 2.50 (t, 2H), 2.45 (s, 3H). $^{13}$C-NMR (100 Hz, CDCl$_3$): $\delta$ 143.2, 136.9, 129.7, 127.2, 70.5, 58.9, 53.4, 52.5, 41.0, 21.5. IR (FT-ATR, cm$^{-1}$): 3210, 2969, 2884, 2829, 1738, 1596, 1494, 1472, 1455, 1426, 1396, 1379, 1365, 1233, 1300, 1293, 1230, 1201, 1151, 1119, 1091, 1058, and 1008.

4.2.4. [CoMeOTs$_2$]$^2$–OH$_2$ (2–OH$_2$)

One equivalent of 1 (4.0 g, 7.35 mmol), one equivalent of cobalt(II) sulfate heptahydrate (2.38 g, 8.47 mmol), and 2.1 equivalents of potassium hydroxide (1.09 g, 19.4 mmol) were dissolved in 120 mL of methanol. The reaction mixture was stirred vigorously for 24 h. The dark brown solution was diluted with 120 mL of dichloromethane and filtered through celite, which removed a dark solid and afforded a purple solution. The solvent was removed under rotary evaporation to yield a purple solid. The solid was dissolved in 25 mL dichloromethane and crystallized with 50 mL of pentane at 4 °C. The purple crystals were collected by vacuum filtration and residual solvent was removed under vacuum (3.15 g, 68%). UV/VIS (DCM, $\varepsilon$ in M$^{-1}$cm$^{-1}$): 521 (41), 682 (12). IR (FT-ATR, cm$^{-1}$): 3203, 3066, 3030, 2961, 2917, 2918, 2890, 2852, 1596, 1494, 1472, 1450, 1397, 1323, 1301, 1291, 1258, 1246, 1201, 1152, 1127, 1200, 1076, 1040, 1018. Magnetic susceptibility (Evan’s balance): $\mu_{\text{obs}} = 3.79$ B.M.

4.2.5. [CoMeOTs$_2$]$^2$–NH$_3$ (2–NH$_3$)

Crystalline 2–OH$_2$ (0.49 g, 0.89 mmol) was dissolved in 15 mL of acetonitrile. Two equivalents (130 $\mu$L) of 14.5 M aqueous ammonia were added to the purple solution and a slight darkening in color was observed. The product was crystallized via vapor diffusion with diethyl ether. The purple crystals were collected by vacuum filtration and residual solvent was removed under vacuum (0.23 g, 46%). UV/VIS (DCM, $\varepsilon$ in M$^{-1}$cm$^{-1}$): 471 (31.6), 539 (80.0), 720 (15.7). IR (FT-ATR, cm$^{-1}$): 1017, 1032, 1069, 1078, 1106, 1126, 1158, 1244, 1269, 1450, 1494, 1598. Magnetic susceptibility (Evan’s Balance): $\mu_{\text{obs}} = 3.84$ B.M.

4.2.6. [CoMeOTs$_2$]$^2$–NH$_2$NH$_2$–[CoMeOTs$_2$] (3)

Crystalline 2–OH$_2$ (0.48 g, 0.88 mmol) was dissolved in 15 mL of acetonitrile. Two equivalents (160 $\mu$L) of 35% aqueous hydrazine were added to the purple solution and a slight darkening in the solution color was observed. The solution was placed in vapor diffusion with diethyl ether. The product was crystallized via vapor diffusion with diethyl ether. The purple crystals were collected by vacuum filtration and residual solvent was removed under vacuum (0.095 g, 20%). UV/VIS (DCM, $\varepsilon$ in M$^{-1}$cm$^{-1}$): 527 (80.0), 690 (17.1). IR (FT-ATR, cm$^{-1}$): 3267, 3161, 2970, 2956, 2900, 2859, 1738, 1597, 1578, 1494, 1468, 1447, 1397, 1382, 1348, 1288, 1261, 1187, 1176, 1157, 1128, 1096, 1075, 1040, 1019, 1005. Magnetic susceptibility (Evan’s Balance): $\mu_{\text{obs}} = 3.82$ B.M.

4.3. Reaction of 2–OH$_2$ with KOH procedure

Crystalline 2–OH$_2$ (0.32 g, 0.59 mmol) was dissolved in 4 mL of methanol. Two molar equivalents of potassium hydroxide dissolved in methanol (0.23 M, 5.6 mL) were added
and a color change from purple to dark green was observed. The solution was concentrated to a green oil via rotary evaporation. The remainder of the solvent was removed under a high vacuum to yield a fine green powder. The powder is extremely hygroscopic, but an IR spectrum was collected on the green solid while minimizing exposure to air. IR (FT-ATR, cm$^{-1}$): 3492, 2855, 1661, 1651, 1599, 1494, 1450, 1397, 1351, 1245, 1136, 1110, 1076, 1019, 976, 914, 813, 740, 710, 658, 602, 539, 528, 519, 512, 505, 502.

4.4. Photometric titration procedure

In a nitrogen-filled glovebox, a solution of 2-OH$_2$ (7.0 mM, 10.0 mL) was added to a two-neck round-bottom flask. One neck was sealed with a rubber septum and the other with a glass stopper before removing from the glovebox. The glass stopper was replaced with a spectrometer dip probe while flushing nitrogen through the other neck. A solution of 0.21 M potassium hydroxide (KOH) solution in anhydrous methanol was dispensed in 50 $\mu$L increments (0.15 M equivalents) via gas tight syringe and spectra were collected after each addition. A total of 500 $\mu$L of KOH solution (1.5 M equivalents) was added. The absorption spectra in Figure 2 (middle) were adjusted to account for dilution.

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Disclosure statement

The authors report there are no competing interests to declare.

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