A rare ether-bridged cobalt complex which gives rise to an unusual 'serpentine' metal-ligand binding motif

Garry Mund, Andrea J. Gabert, Raymond J. Batchelor, James F. Britten and Daniel B. Leznoff* Department of Chemistry, Simon Fraser University, 8888 University Drive, Burnaby, B.C, Canada V5A 1S6. E-mail: dleznoff@sfu.ca; Fax: 1-604-291-3765; Tel: 1-604-291-4887

Received (in Purdue, IN, USA) 22nd August 2002, Accepted 25th October 2002 First published as an Advance Article on the web 13th November 2002

An unusual metal-ligand binding motif is found in dimeric cobalt(n) complexes coordinated by diamidoether ligands that bridge the metals in a 'serpentine' fashion through the ether donors of the ligand backbone rather than the amido groups.

Chelating diamidodonor ligands have been shown to be excellent ligands for high-valent metal centres.¹⁻⁸ This is not only due to their ease of steric and electronic modification but more importantly due to their strong π -donating ability. Neutral donors that have been incorporated into the ligand backbone include amino,¹ phosphino,² thio^{3,4} or weaker ether donors.^{3,5} In general, the amido donors chelate the metal centre with the neutral donor playing an important electronic role.⁶ The few reported bimetallic diamidodonor complexes all contain amidogroups that bridge the metal centres as expected.^{8,9} The neutral donor in the backbone has not been observed to do so. In particular, weakly basic ether donors rarely bridge metal centres.¹⁰ The bridging role for THF, one of the most utilized ether-type ligands, is very uncommon in the solid state.11-14 $[Co(acac)_2(PhHgOHgPh)(THF)]_2$,¹² $[(C_5H_4Me)TiF_3]_2$ ·THF,¹³ and [Rh₂(O₂CCF₃)₄(THF)]¹⁴ are among the few known THFbridged transition-metal complexes. We have been exploring diamido ligands incorporating a neutral ether donor, termed [NON], as supporting ligands for paramagnetic first-row transition metals.^{7,8} Through the use of a flexible [NON] ligand, we hereby report an unusual dimeric cobalt(II) complex in which the cobalt atoms of the dimer are bridged in a 'serpentine' fashion through the *ether* moieties of the ligand rather than the stronger amido donors.

We have considered two [NON] ligand backbones: (1) a short silicon-derived backbone, {[RN(SiMe₂)]₂O}²⁻ (R = ${}^{t}Bu, {}^{7-9}$ 2,4,6-Me₃Ph,⁸ and 2,6- ${}^{t}Pr_{2}Ph^{8}$) and (2) a more flexible carbon-based framework, {[RN(CH₂CH₂)]₂O}²⁻ (R = 2,4,6-Me₃Ph, {}^{15} 2,6- ${}^{t}Pr_{2}Ph^{3}$). Reaction of the appropriate dilithio diamidoether ligands with CoCl₂ at -78 °C resulted in an immediate colour change from aqua blue to dark green. From these solutions, the paramagnetic and air-sensitive {Co[Me₃PhN(SiMe₂)]₂O}₂ (1),⁸ {Co[${}^{t}BuN(SiMe_{2})$]₂O}₂ (2),⁸ {Co[Me₃PhN(CH₂CH₂)]₂O}₂ (3) and {Co[${}^{t}Pr_{2}PhN(CH_{2}CH_{2})$]₂O}₂ (4) complexes were isolated in moderate to high yield.¹⁶

The single-crystal X-ray structures of 1 and 4 are shown in Figs. 1 and 2, respectively.¹⁷ In the dimeric $cobalt(\pi)$ complex (1) with the short silicon-containing [NON] ligand backbone, (Fig. 1) the cobalt atoms have a roughly trigonal geometry: each cobalt atom is bound by one terminal and two bridging amido groups. The tert-butyl substituted amido system (2) has a similar structure.8 Both bridging and terminal amido bond lengths are comparable to other cobalt-amido systems such as $Co(CH_2Ph)[N(SiMe_2CH_2PPh_2)_2]^{18}$ and $\{Co_2[N(SiMe_3)_2]_4\}$.¹⁹ The cobalt atoms of the dimer are held in close proximity by the bridging amido ligands with Co1-Co1* distances of 2.468(3) and 2.5682(13) Å in 1 and 2, respectively, suggesting metalmetal interactions. The dimeric cobalt(II) complex (4) with the longer and more flexible carbon-based [NON] ligand backbone has a remarkably different ligand coordination environment (Fig. 2). The molecule is non-centrosymmetric with approximate D_2 symmetry. In this case it is the *ether* atom of the diamidoether ligand that bridges the cobalt atoms of the dimer rather than the more strongly basic amido group. Each cobalt centre is four-coordinate and displays a distorted see-saw geometry: each ligand binds *via* a terminal amido group, bridges the cobalt atoms through the oxygen donor in the backbone and finally swings around in a 'serpentine' fashion and binds to the other cobalt atom through another amido group. The Co1–Co2 distance of 3.716(1) Å precludes any bonding interaction between the metal centres.

The temperature (*T*) dependence of the magnetic susceptibility (χ_m) of 1–4 were measured from 2–300 K. Plots of μ_{eff} vs. *T* per cobalt atom for 1, 2 and 4 are shown in Fig. 3. Both 1 and 2 show a significant decrease in μ_{eff} as *T* decreases, indicative of antiferromagnetic coupling between the metal atoms of the dimer.²⁰ However, 4 shows a considerably smaller drop in μ_{eff} with temperature—there is much less coupling between the cobalt atoms of the ether-bridged dimer. The greater coupling



Fig. 1 Molecular structure of **1** (ORTEP view, 33% probability ellipsoids are shown; methyl groups on aryl ring excluded for clarity). Selected bond lengths (Å) and angles (°): Co1–Co1* 2.468(3), Co1–N1 1.912(7), Co1–N2 2.007(8), Si1–O1 1.645(8), Si1–N1 1.720(9), Si2–O1 1.617(7), Si2–N2 1.780(9); N1–Co1–N2 120.0(4), N1–Co1–N2* 139.3(4), N2–Co1–N2* 95.0(4), Si2–O1–Si1 145.6(6). * = -x, y, -z + 1/2.



Fig. 2 Molecular structure of 4 (ORTEP view, 33% probability ellipsoids are shown; isopropyl groups excluded for clarity). Selected bond lengths (Å) and angles (°): Co1–Co2 3.716(1), Co1–N1 1.827(4), Co1–N2 1.832(4), Co2–N3 1.841(4), Co2–N4 1.850(4), Co1–O1 2.279(4), Co1–O2 2.423(4), Co2–O1 2.415(4), Co2–O2 2.306(4); N2–Co1–N1 162.83(17), N2–Co1–O1 79.61(16), O1–Co1–O2 76.08(13), N1–Co1–O2 77.70(15), N3–Co2–N4 158.42(16).



Fig. 3 Plots of magnetic moment (μ_{eff}) vs. temperature (K) for 1, 2 and 4.

observed in amido-bridged **1** and **2** *vs.* ether-bridged **4** is likely the result of the much shorter metal–metal distances that are supported by amido-bridges. Importantly, **3** shows minimal coupling, implying that this carbon-containing [NON] ligand system still appears to form an ether-bridged dimer as opposed to an amido-bridged one, despite having the same amido Rgroup as **1**. Below 20 K, the sharp drop in μ_{eff} is attributable to zero-field splitting (ZFS) effects common in Co(II) systems. The simultaneous presence of ZFS and antiferromagnetic coupling impeded accurate modeling of the data.²¹

Why do rather similar diamidoether ligands give rise to such different metal-ligand binding motifs? The length and rigidity alterations in the ligand backbone provide a plausible explanation. The silicon-containing [NON] backbone consists of a short, five-atom chain that is sterically hindered around the silylether donor. Alternatively, the carbon-containing [NON] system is two atoms longer and is sterically unhindered at the diethyl ether donor, yielding a more flexible ligand that may be more apt to bridge metal atoms through the ether donor. The stronger Lewis basicity of the latter may also assist in etherbridging. The size of the resulting metallacycle that is formed could also account for the unusual ether atom bridging motif. The silylamido-bridged cobalt system gives rise to stable sixmembered rings. An amido-bridged system featuring the carbon-containing [NON] ligand would give rise to less stable eight-membered metallacycles; ether-bridging allows for more stable five-membered rings to form.

In conclusion, a series of dinuclear cobalt complexes containing diamidoether ligands has been reported, in which an amido-bridged system is favoured by the short, rigid silicon-[NON] backbone whereas ether-bridging is favoured by the longer, more flexible carbon-[NON] backbone. Further investigation of these [NON]-ligand systems with other metal centres is underway. This new binding motif may have implications for the use of diamidodonor ligands in alkene polymerization catalyst design.^{3,5,22}

We are grateful to NSERC of Canada (D. B. L.) and Simon Fraser University for financial support.

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- 15 The synthesis of {[RNH(CH₂CH₂)]₂O} (R = 2,4,6-Me₃Ph) follows the procedure for R = 2,6-Me₂Ph as described in ref 3. Yield: 1.41 g (76%). Anal. Calc. for $C_{22}H_{32}N_2O$: C: 77.60, H: 9.47, N: 8.23. Found: C: 77.48, H: 9.23, N: 8.00%. ¹H NMR (C_6D_6): δ 6.78 (s, 4H, H_{aryl}), 4.03 (br, 2H, NH), 3.22 (t, 4H, OCH₂), 3.01 (t, 4H, NCH₂), 2.24 (s, 12H, 2,6-*Me*Ar) 2.17 (s, 6H, 4-*Me*Ar). MS: *m/z* 340 (M⁺).
- 16 Synthesis of 3: a white powder of {[(Me₃PhNH(CH₂CH₂)]₂O} (0.20 g, 0.59 mmol) was dissolved in 10 mL of THF and two equivalents of 1.6 M "BuLi in hexanes (0.12 mL, 1.18 mmol) were added dropwise at -78 °C. After stirring for 1 h at room temperature, the resulting solution was added dropwise to anhydrous CoCl2 (0.76 g, 0.59 mmol) in 30 mL of THF at -78 °C, yielding a dark green solution. After 1 h, the solvent was removed *in vacuo*, the product was extracted with toluene and filtered through Celite[®]. Removal of the toluene *in vacuo* gave dark green {Co[Me₃PhN(CH₂CH₂)]₂O}₂ (3). Yield: 0.12 g (56%). Anal. Calc. for C44H60N4C02O2: C: 66.49, H: 7.61, N: 7.05. Found: C: 66.58, H: 7.51, N: 6.94%. UV-vis (C₇H₈): $\lambda = 579$ nm ($\varepsilon = 118$ M⁻¹ cm⁻¹). MS: m/z 397 (M⁺, monomer unit). For 4, a similar procedure was used. Yield: 1.2 g (80%). Single crystals suitable for X-ray analysis were obtained by a slow evaporation of a toluene solution. Anal. Calc. for C56H84N4C02O2: C: 69.82, H: 8.80, N: 5.82. Found: C: 69.62, H: 8.68, N: 5.62%. UV-vis (C₇H₈): $\lambda = 422 \text{ nm} (\varepsilon = 98 \text{ M}^{-1} \text{ cm}^{-1})$. MS: m/z481 (M⁺, monomer unit).
- 17 Crystal data for 1: $C_{44}H_{68}Co_2N_4O_2Si_4$, M = 915.24, monoclinic, space group C2/c, a = 18.132(11), b = 13.972(8), c = 19.761(12) Å, $\beta =$ $107.854(10)^{\circ}$, V = 4765(5) Å³, Z = 4, μ (Mo-K α) = 0.8 mm⁻¹, T =153(2) K, 3068 unique reflections, 1756 observed ($I_o > 2.0\sigma(I_o)$). The final $R(F^2) = 0.0986$ and $wR(F^2) = 0.1868$ (observed data). The sample was a multiple crystallite. Crystal data for 4: $C_{56}H_{84}Co_2N_4O_2$, M =931.18, triclinic, space group $P\overline{1}$, a = 10.899(2), b = 15.104(3), c = 10.899(2)18.012(2) Å, $\alpha = 88.90(1)$, $\beta = 84.64(2)$, $\gamma = 69.22(2)^{\circ}$, V =2759.8(9) Å³, Z = 2, μ (Mo-K α) = 0.6 mm⁻¹, T = 293 K, 9759 unique reflections, 4528 observed ($I_0 > 2.5\sigma(I_0)$). The final $R_F = 0.050$ and $R_{wF} = 0.052$ (observed data). Structure solution and refinement for 4 was performed using CRYSTALS (D. J. Watkin, C. K. Prout, J. R. Carruthers, P. W. Betteridge and R. I. Cooper, CRYSTALS Issue 11, Chemical Crystallography Laboratory, University of Oxford, Oxford, England, 1999). CCDC 195025 and 195120. See http://www.rsc.org/ suppdata/cc/b2/b208221g/ for crystallographic data in CIF format.
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