Inorg. Chem. **2002**, *41*, 6538–6540

Inorganic Chemistry
Communication

The Methanol–Methanolate $CH_3OH\cdots OCH_3^-$ Bridging Ligand: Tuning of Exchange Coupling by Hydrogen Bonds in Dimethoxo-Bridged Dichromium(III) Complexes†

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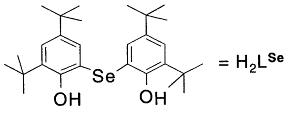
Received June 17, 2002

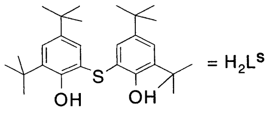
Two bis(μ-methoxo)dichromium(III) complexes, $[L^{Se}{}_2Cr_2(\mu\text{-}OCH_3)_2(CH_3OH)_2]$ **1** and $[L^{Se}{}_2Cr_2(\mu\text{-}OCH_3)_2(CH_3OH)(CH_3O)]^-$ **2**, where L^{Se} represents the dianion of 2,2′-selenobis(4,6-di-*tert*-butylphenol), have been reported to demonstrate the effect of hydrogen bonding on the exchange coupling interactions between the chromium(III) centers. The corresponding sulfur analogue of the ligand, i.e., 2,2′-thiobis(4,6-di-*tert*-butylphenol), also yields the analogous $[L^S{}_2Cr_2(\mu\text{-}OCH_3)_2(CH_3OH)_2]$ **3** and $[L^S{}_2Cr_2(\mu\text{-}OCH_3)_2(CH_3O)(CH_3OH)]^-$ **4**, which exhibit similar exchange coupling parameters. An acid–base dependent equilibrium between **1** and **2** or **3** and **4** has been established by electronic spectral measurements.

Polynuclear metal complexes[1] are increasingly attracting attention primarily because of the important functions polynuclear sites perform in biological systems. The importance of hydrogen bonds in modifying physical and chemical properties of active sites in biological systems is well-known.[2] On the other hand, it has been recently recognized that hydrogen bonds play a major role in the transmission of *ferromagnetic* interactions in organic ferromagnets.[3]

The hydrogen−oxide bridging ligand, $H_2O\cdots OH^-$, formed by means of a strong and symmetrical hydrogen bond between a hydroxo ligand coordinated to a metal center and an aqualigand of a neighboring metal ion, plays a fundamental role in the hydrolysis of aquated metal ions.[4] A similar important role is envisagable for the analogous methanol−methanolate, $CH_3OH\cdots OCH_3^-$, bridging anion in the methanolysis reactions of metal ions. We report here four complexes containing the bis(μ-methoxo)dichromium(III) core **1**−**4**, of which in **1** and **3** two coordinated methanol molecules are disposed in trans position, whereas **2** and **4** contain a bridging $CH_3OH\cdots OCH_3^-$ ligand. The ligands 2,2′-selenobis(4,6-di-*tert*-butylphenol)[5] H_2L^{Se} and 2,2′-thiobis(4,6-di-*tert*-butylphenol)[6] H_2L^S used for the synthesis of complexes[7] **1**−**4** are depicted with their labels.



for **1** and **2** $[L]^{2-} = [L^{Se}]^{2-}$



for **3** and **4** $[L]^{2-} = [L^S]^{2-}$

1, **2**, **3**, and **4** exhibit the effect of hydrogen bonding on the exchange coupling interactions between the chromium(III) centers in the two forms, which are otherwise electronically identical.

The six coordination sites of chromium ions in **1**[7,8] are occupied by two *cis*-methoxy bridging groups, one facially coordinated $[L^{Se}]^{2-}$ ligand providing the group $O\frown Se\frown O$ and a methanol molecule (Figure 1). Two methanol molecules in **1** are trans to each other. The $Cr(1)\cdots Cr(1)^{\ddagger}$ and Cr(1)−O(3) (methoxide) distances and the $Cr(1)-O(3)-Cr(1)^{\ddagger}$ angle of the bridging moiety are 3.093(2) and 1.972(2) Å and 103.58(6)°, respectively, which are comparable to the similar bis(alkoxy)-bridged dichromium(III) complexes.[9] The Cr_2O_2 bridging unit is strictly planar, there being a crystallographic inversion center in the middle of the dimer. The oxygen of the methanol molecule, O(4), coordinated to Cr(1),

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† This work was supported by the DFG (Priority Program "Radicals in the enzymatic catalysis").

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10.1021/ic0204068 CCC: $22.00

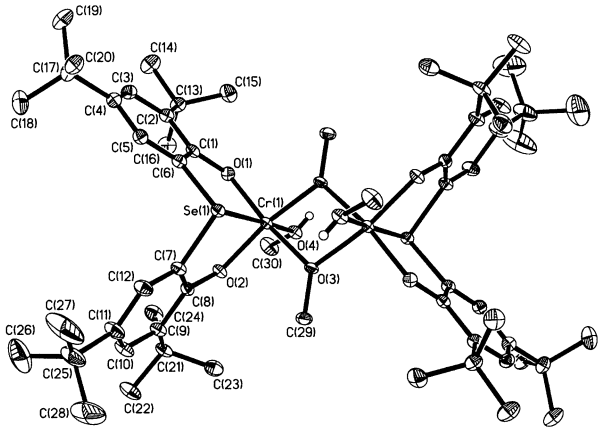

Figure 1. ORTEP drawing of $[L_2Cr_2(\mu\text{-}OMe)_2(MeOH)_2]$ **1** with the atom-labeling scheme. Bond lengths (Å) and angles (deg): Cr(1)−O(1) 1.934(2), Cr(1)−O(2) 1.9354(14), Cr(1)−O(3)#1 1.9638(14), Cr(1)−O(3) 1.972(2), Cr(1)−O(4) 2.036(2), Cr(1)−Se(1) 2.5008(5), Cr(1)#1−O(3)−Cr(1) 103.58(6), Cr(1)···Cr(1)‡ 3.093(2), O(1)−Cr(1)−O(2) 93.71(7), O(1)−Cr(1)−O(3)#1 95.70(6), O(2)−Cr(1)−O(3)#1 170.55(6), O(1)−Cr(1)−O(3) 171.16(6), O(2)−Cr(1)−O(3) 94.14(6), O(3)#1−Cr(1)−O(3) 76.42(6), O(1)−Cr(1)−O(4) 89.94(7), O(2)−Cr(1)−O(4) 90.51(7), O(3)#1−Cr(1)−O(4) 90.27(7), O(3)−Cr(1)−O(4) 94.05(6), O(1)−Cr(1)−Se(1) 85.42(5), O(2)−Cr(1)−Se(1) 85.03(5), O(3)#1−Cr(1)−Se(1) 94.95(5), O(3)−Cr(1)−Se(1) 91.22(5), O(4)−Cr(1)−Se(1), 173.33(5).

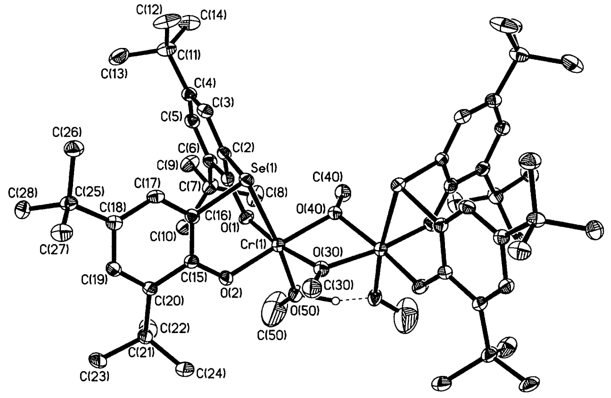

Figure 2. Molecular structure of the anion in **2**, $[L_2Cr_2(\mu\text{-}OMe)_2(OMe)(MeOH)]^-$, with the atom-labeling scheme. Bond lengths (Å) and angles (deg): Se(1)−Cr(1) 2.5390(8), Cr(1)−O(2) 1.923(3), Cr(1)−O(1) 1.930(3), Cr(1)−O(30) 1.972(3), Cr(1)−O(50) 1.982(3), Cr(1)−O(40) 1.989(3), Cr(1)*−O(30)−Cr(1) 101.7(2), Cr(1)*−O(40)−Cr(1) 100.5(2), Cr(1)···Cr(1)* 3.059(2), O(2)−Cr(1)−O(1) 94.26(14), O(2)−Cr(1)−O(30) 94.99(14), O(1)−Cr(1)−O(30) 170.66(13), O(2)−Cr(1)−O(50) 92.35(13), O(1)−Cr(1)−O(50) 91.28(12), O(30)−Cr(1)−O(50) 89.6(2), O(2)−Cr(1)−O(40) 170.72(14), O(1)−Cr(1)−O(40) 93.98(13), O(30)−Cr(1)−O(40) 76.69(14), O(50)−Cr(1)−O(40) 91.7(2), O(2)−Cr(1)−Se(1) 83.96(9), O(1)−Cr(1)−Se(1) 84.26(8), O(30)−Cr(1)−Se(1) 95.45(12), O(50)−Cr(1)−Se(1) 173.97(9), O(40)−Cr(1)−Se(1) 92.64(11).

is hydrogen-bonded to a noncoordinated methanol molecule with a O···O distance of 2.652(5) Å. There is a hydrogen-bonding network between the three other noncoordinated methanol molecules.

The coordination geometry of the chromium center Cr(1) in **2** (Figure 2)[7,8] is distorted octahedral with three donor atoms,O(1), Se(1), and O(2), from the facially coordinated $[L^{Se}]^{2-}$ ligand, two oxygen atoms, O(40) and O(30), from the cis-bridging methoxide groups, and a methanol molecule, O(50), resulting in the CrO_5Se core as that in **1**. The presence of the cation Bu_4N^+ in **2** dictates, on account of charge balance, loss of one proton from the coordination sphere of the chromium(III) centers. The distance between the symmetry-related atoms O(50)···O(50)* of 2.43(1) Å is clearly indicative of a strong hydrogen-bond interaction, suggesting

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(7) Complex **1**: To the pale yellow solution containing H_2L^{Se} (0.245 g; 0.5 mmol) and Bu_4NOMe (2.5 mL of a 20% methanolic solution) in dry methanol (20 mL) was added $CrCl_2$ (0.065 g; 0.5 mmol), and the resulting light green solution was refluxed under argon for 1 h and then in air for another 1 h. On cooling, a green microcrystalline solid of **1** was isolated by filtration and air-dried. Yield: 0.13 g (43%). Anal. Calcd for $C_{60}H_{94}O_8Se_2Cr_2$: C, 59.79; H, 7.86; Cr, 8.63. Found: C, 59.3; H, 8.2; Cr, 8.1. MS-EI: (*m*/*z*) 1140 $[M - 2MeOH]^+$. UV−vis in CH_2Cl_2/CH_3OH (λ, nm; ϵ M^{-1} cm^{-1}): 622 (214), ∼400sh (∼1190). X-ray quality crystals of **1** were grown from a solvent mixture (1:1) of dichloromethane and methanol. Complex **2**: The ligand H_2L^{Se} (0.245 g; 0.5 mmol) and sodium methoxide (0.11 g; 1 mmol) were dissolved in dry methanol (25 mL) under argon to yield a yellow solution, which was charged with solid $CrCl_2$ (0.065 g; 0.5 mmol). The resulting light green solution was refluxed under argon for 2 h and for a further 3 h in air. After addition of Bu_4NPF_6 (0.19 g; 0.5 mmol), X-ray quality green platelike crystals were isolated. Yield: 0.27 g (73%). Anal. Calcd for $C_{76}H_{129}O_8NSe_2Cr_2{\cdot}CH_3OH$: C, 61.01; H, 9.28; N, 0.89; Cr, 6.60. Found: C, 61.1; H, 8.7; N, 0.9; Cr, 6.3. MS-ESI positive in CH_2Cl_2: (*m*/*z*) 242.3 $[Bu_4N]^+$. MS-ESI negative (*m*/*z*) in CH_2Cl_2: 1171.9 $[M - MeOH]^-$. UV−vis in CH_2Cl_2/CH_3OH (λ, nm; ϵ M^{-1} cm^{-1}): 635 (197). **2** can also be prepared from **1** by dissolving **1** (0.1 g; 0.083 mmol) in dichloromethane (5 mL), to which Bu_4NOMe (0.5 mL of a 20% methanolic solution) was added. To the resulting deep green solution was added methanol (5 mL). After 2 days, a deep green crystalline solid of **2** was isolated by filtration and air-dried. Yield: 70 mg (68%). The sulfur analogues of **1** and **2**, i.e., complexes **3** and **4**, were obtained by protocols which are very similar to those for **1** and **2**, respectively. Complex **3**: yield 40%. Anal. Calcd for $C_{60}H_{94}S_2O_8Cr_2{\cdot}CH_3OH$: C, 64.07; H, 8.64; Cr, 9.06. Found: C, 62.6; H, 8.5; Cr, 9.2. MS-EI: *m*/*z* 1047 [M − 2MeOH]. UV−vis in CH_2Cl_2/CH_3OH (λ, nm; ϵ M^{-1} cm^{-1}): 605 (255), ∼400sh (∼1160). Complex **4**: yield 78%. Anal. Calcd for $C_{76}H_{129}O_8NS_2Cr_2{\cdot}CH_3OH$: C, 66.76; H, 9.69; N, 1.01; Cr, 7.51. Found: C, 66.3; H, 10.1; N, 1.0; Cr, 7.5. MS-ESI positive in CH_3CN: (*m*/*z*) 242.3 $[Bu_4N]^+$. MS-EI negative in CH_3CN: (*m*/*z*) 1077.5 $[M - MeOH]^-$. UV−vis in CH_2Cl_2/CH_3OH (λ, nm; ϵ M^{-1} cm^{-1}): 626 (112). The electronic spectra for **1** and **3** were measured in the presence of perchloric or trifluoromethane sulfonic acid, whereas the spectra for **2** and **4** were taken in the presence of *n*-Bu_4NOCH_3.

(8) Crystal data for **1**: $C_{68}H_{126}Cr_2O_{16}Se_2$, M_f = 1461.61, triclinic, a = 11.3263(9) Å, b = 13.1581(9) Å, c = 13.6913(9) Å, α = 82.59(1)°, β = 86.84(1)°, γ = 87.92(1)°, V = 2019.5(2) Å^3, T = 100(2) K, space group $P\bar{1}$, Z = 1, 13113 independent reflections used for solution and refinement (SHELX-97) by full-matrix least-squares on F^2, absorption correction by using the program SADABS (G. M. Sheldrick 1994). Final R indices: $R_w(F^2)$ = 0.115, R_w (all data) = 0.125. Crystal data for **2**: $C_{76}H_{129}O_8NSe_2Cr_2{\cdot}CH_3OH$, M_f = 1462.74, monoclinic, a = 10.2757(8) Å, b = 29.351(3) Å, c = 13.910(10) Å, β = 108.88(1)°, V = 3970(3) Å^3, T = 100(2) K, space group $P2(1)/m$, Z = 2, 7907 independent reflections used for solution and refinement (SHELX-97) by full-matrix least-squares on F^2, Gaussian, face indexed, absorption correction. Final R indices: $R_w(F^2)$ = 0.1285, R_w (all data) = 0.1915. Disorder was observed in the carbon position of the bridging methanolate (C(30) 44%; C(30X) 56%). Crystal data for **3**: $C_{68}H_{126}O_{16}S_2Cr_2$, M_f = 1367.81, triclinic, a = 11.3458(9) Å, b = 12.9930(10) Å, c = 13.5770(10) Å, α = 82.99(1)°, β = 86.35(1)°, γ = 87.86(1)°, V = 1981.6(3) Å^3, T = 100(2) K, space group $P\bar{1}$, Z = 1, 10271 independent reflections used for solution and refinement (SHELX-97) by full-matrix least-squares on F^2, no absorption correction. Final R indices: $R_w(F)$ = 0.068, R_w (all data) = 0.0999. Crystal data for **4**: $C_{76}H_{129}O_8NS_2Cr_2{\cdot}2CH_3CN$, M_f = 1435.03, orthorhombic, a = 22.610(2) Å, b = 29.393(3) Å, c = 26.450(3) Å, V = 17578(6) Å^3, T = 100(2) K, space group $Cmca$, Z = 8, crystal dimensions 0.13 × 0.13 × 0.11 mm. R_1 = 0.152. The crystal structure determination is of mediocre quality.

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that one of the methanol molecules is deprotonated and coordinates as a methoxide ligand. Indeed, a difference Fourier in the refinement stages did reveal a peak assignable to a single proton, appearing equidistant from the two oxygen atoms, and this was included in the final refinement cycle. The oxygen−oxygen separation in the bridging $CH_3O\cdots H\cdots OCH_3^-$ anion of 2.43 Å is comparable with that in the $HO\cdots H\cdots OH^-$ anion, $H_3O_2^-$, bridging two metal ions (2.44−2.50 Å).[10] It is noteworthy that the oxygen−oxygen distance is significantly shorter in the noncoordinated $H_3O_2^-$ anion (2.27 Å)[4,11] or in the cation $(CH_3OH)_2H^+$ (2.23 Å).[12] The Cr(1)···Cr(1)*, Cr(1)−O(40), and Cr(1)−O(30) (methoxide) distances and the angles Cr(1)−O(40)−Cr(1)* and Cr(1)−O(30)−Cr(1)* of the bridging moiety are 3.059(2), 1.989(3), and 1.972(3) Å, 100.5(2)°, and 101.7(2)°, respectively, which are not significantly different from those of **1** and other similar complexes.[9] The Cr_2O_2 bridging unit is folded with an angle of 24.8° between the two Cr−O−Cr planes. That the coordination geometry of Cr(1) in **2** is very similar to that of the chromium centers in **1** is indicated by the O−Cr−O angles lying in the range 94.3(1)−89.6(2)° and the O(30)−Cr(1)−O(40) angle with 76.7(1)°. Thus the metrical parameters for **1** and **2** are very similar, irrespective of different geometrical dispositions of the methanol/methanolate molecules.

X-ray structures of **3** and **4** containing the sulfur analogue of the ligand were also determined (Supporting Information).

Magnetic data (SQUID) with $H = 1$ T for polycrystalline samples of **1**−**4** are displayed in Figures S1 and S2 (Supporting Information) as μ_{eff} vs T. On lowering the temperature, the effective magnetic moments decrease monotonically for both complexes. This arises from antiparallel spin coupling between two chromium(III) centers with $S = {}^3/_2$. Simulation ($\hat{H} = -2J\hat{S}_1\cdot\hat{S}_2$) of the data yielded $J = -9.0$ cm^{-1}, $g = 1.94$ for **1** and $J = -1.96$ cm^{-1}, $g = 1.89$ for **2**. The corresponding sulfur analogues, **3** and **4**, yield the following evaluated magnetic data: $J = -8.30$ cm^{-1}, $g = 1.83$ for **3** and $J = -0.49$ cm^{-1}, $g = 1.90$ for **4**. **2** and **4** exhibit the weakest exchange interactions between the chromium(III) centers in bis-alkoxo/bis-phenoxo-bridged compounds reported until now.[9]

An empirical model relating the magnitude of the coupling to the Cr−O−Cr angle, the Cr−O bond length, and the angle θ between the bridging plane and the O−R vector of the bridging group has been proposed to explain antiferromagnetic coupling in edge-shared biooctahedral dichromium(III) complexes.[13] In a second approach[14] for magnetostructural correlation in a number of chromium(III) dimers containing a Cr_2O_2 bridging network, the energy separation between the singlet and the triplet levels originating from the exchange interaction was found to be correlated to the ratio between the Cr−O−Cr bond angle (ϕ) and the Cr−O bond length (r). Regrettably, none of these two models can satisfactorily explain the trend of the exchange interactions in the present complexes.

The crystallographic data for the bridging angles and distances in **1** and **2** are very similar and therefore do not provide a basis for an explanation of the different magnetic behaviors. A qualitative rationale for the trend of the exchange interactions, i.e., the strength of antiferromagnetic coupling is stronger in **1** ($J = -9.0$ cm^{-1}) than that in **2** ($J = -1.96$ cm^{-1}), can be provided by considering a third bridging unit in **2**, a hydrogen bond between two cis-situated methanolates $CH_3O\cdots H\cdots OCH_3$ which is absent in **1**. The folding of the Cr_2O_2 core in **2** lowers the magnitude of the antiferromagnetic interaction in this plane (which dominates exchange coupling between the two Cr(III) units) due to loss of orbital overlap. Evidence for transmission of ferromagnetic interactions through hydrogen bonds in nitroxide radicals has also recently been put forward.[3]

That complexes **1** and **2** in solution are present in an acid/base dependent equilibrium has been established by the electronic spectra.

Supporting Information Available: Simulated magnetic data for **1**−**4** (Figures S1 and S2), an ORTEP representation of **3**, and tables of crystallographic data. Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0204068

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