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Do Metal–Metal Multiply-Bonded “Ligands” Have a *trans* Influence? Structural and Magnetic Comparisons of Heterometallic Cr≡Cr···Co and Mo≡Mo···Co Interactions

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Reported here are two new compounds containing either a Cr≡Cr···Co [**1**, CrCrCo(dpa)$_4$Cl$_2$, dpa = 2,2′-dipyridylamide] or a Mo≡Mo···Co [**2**, MoMoCo(dpa)$_4$Cl$_2$] framework both having a multiply-bonded unit (Cr≡Cr in **1**, Mo≡Mo in **2**) in close proximity to the Co^{2+} ion and *trans* to a Co–Cl bond. Variable temperature magnetic susceptibility measurements reveal **1** to have a temperature-dependent spin equilibrium between a low-spin (S = 1/2) and high-spin (S = 3/2) state, whereas the Co^{2+} ion in **2** exists solely in its high-spin state. The crystal structures of **1** and **2** were determined. Variable temperature crystallographic data of **1** at 100 K and at room temperature reveal that the spin-transition affects not only the Co–ligand bond lengths but also the terminal Cr–ligand bond lengths. Whereas the Cr···Co distance becomes shorter by 0.13 Å in the low-spin form, the Co–Cl distance becomes longer by 0.2 Å. These observations, along with the crystal structure of **2**, suggest that the multiply-bonded M≡M group has a *trans* influence on the Co^{2+} ion.

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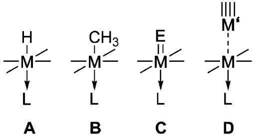
Introduction

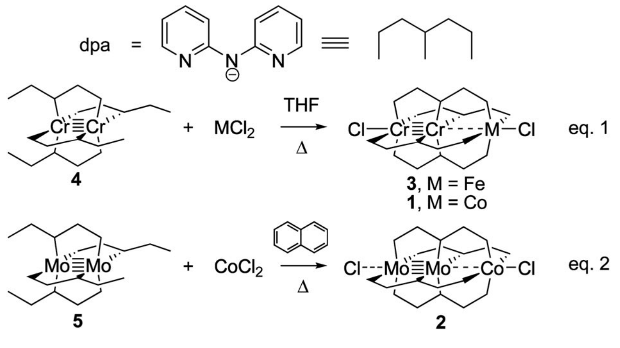
The “*trans* influence” describes the ability of a ligand to weaken the metal–ligand bond *trans* to itself.[1] Ligands such as hydride (**A**) or methyl (**B**) have long been known to have a significant *trans* influence,[1] as have M=E metal–ligand multiply-bonded species (**C**).[2] We have recently suggested that a metal–metal multiply-bonded group may be considered as a “ligand” to a third metal atom in heterometallic chains of the type M′≡M′···M (**D**) (Scheme 1).[3] In order to probe this hypothesis, we have initiated a systematic synthetic investigation of such species with various metals M and M′. Surprisingly, we have found in results presented here that a multiply-bonded M′≡M′ group appears to have a significant *trans* influence on M.



Scheme 1. *trans* influence of ligands on a metal center.

Results and Discussion

The first molecule of type **D** was synthesized in the reaction of Cr$_2$(dpa)$_4$ (**4**, dpa = 2,2′-dipyridylamide) with FeCl$_2$ yielding CrCrFe(dpa)$_4$Cl$_2$ (**3**, Scheme 2).[3] It was previously suggested that the preparative route using dinuclear M′$_2$ species such as **4**[4] and mononuclear starting materials may be expanded to include other transition metals.[3] That is indeed the case, and reported herein is the preparation of CrCrCo(dpa)$_4$Cl$_2$ (**1**), containing a linear Cr≡Cr···Co core, as well as a significant expansion of this chemistry to a new second-row analog of **1** that contains a Mo≡Mo multiply-bonded group that is appended to a high-spin Co^{2+} ion, MoMoCo(dpa)$_4$Cl$_2$ (**2**). It should also be mentioned that related Ru≛Ru···M complexes (M = Ni, Cu) have been recently reported by Peng et al.[5]



Scheme 2. Synthesis of **1** and **2**.

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The dichromium complex $Cr_2(dpa)_4$ (**4**) is a good synthon for the preparation of heterotrinuclear compounds, as exemplified by the synthesis of **1** and **3** shown in Equation (1). Similarly, the dimolybdenum analog of **4**, $Mo_2(dpa)_4$ (**5**), was chosen for the attempted synthesis of Mo≡Mo···M complexes. Although **5** had been previously synthesized in yields up to 83% and crystallographically characterized,[6] we have developed an efficient new method for preparing **5** in excellent purity and nearly quantitative yield from the reaction of Li(dpa) with $Mo_2(OAc)_4$ in THF. The intensely red-colored **5** precipitates from THF solution and can be easily isolated by filtration. Elemental analysis (EA) and matrix-assisted laser desorption ionization time of flight (MALDI-TOF) mass spectrometry verify the identity of this red solid as **5**.

As compared to **4**, the formation of heterotrinuclear species using **5** is energetically more demanding. For example, the reaction of **4** with $CoCl_2$ in refluxing THF solution furnishes **1** in 67% yield, which can be isolated and recrystallized from dichloromethane/hexanes mixtures yielding brown crystals of **1**·CH_2Cl_2. No reaction is observed between **5** and metal dihalides in refluxing THF or even in refluxing toluene, DMSO, *o*-dichlorobenzene, or methanol. Instead, it was found that higher temperatures were necessary, and that the reaction of **5** with $CoCl_2$ proceeds in molten naphthalene solution (180 °C) to produce **2** [see Equation (2)]. Dark green X-ray quality crystals of **2** were grown from dichloromethane/hexane mixtures and were isolated in 67% yield. The compositions of **1** and **2** were verified by means of EA and MALDI-TOF experiments. Despite the similarities in the crystal structures of **1** and **2** (shown in Figure 1 and discussed below), their magnetic susceptibilities (χ) are quite different. Whereas **2** is high spin with $\chi \cdot T = 3.00$ emu K mol^{-1} at room temperature ($S = 3/2$ with significant orbital contribution to $\chi \cdot T$), variable-temperature measurements on **1** reveal a low-temperature plateau of $\chi \cdot T$ ca. 0.5 emu K mol^{-1} between 4 and 50 K, with an S-shaped curve at higher temperatures indicative of a low-spin/high-spin equilibrium (Figure 2). At temperatures below ca. 50 K, the low-spin configuration ($S = 1/2$) is dominant and raising the temperature allows for the high-spin configuration ($S = 3/2$) to be populated. The variable temperature data for **1** were modeled using previously reported methods[7] and the parameters derived from the fitting, shown in Figure 2, are comparable to those obtained for spin transitions in homonuclear tricobalt analogs of **1**.[7]

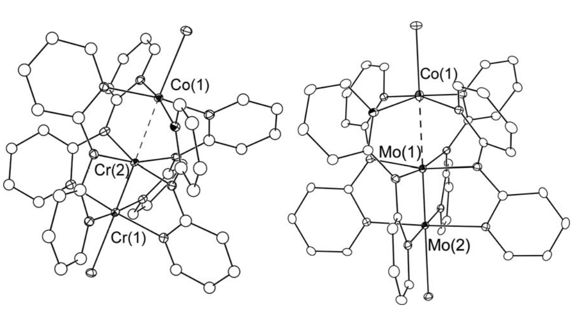

Figure 1. Molecular structures of **1** (low-spin) (left) and **2** (right). Thermal ellipsoids are drawn at the 30% probability level; interstitial CH_2Cl_2 molecules and hydrogen atoms have been omitted.

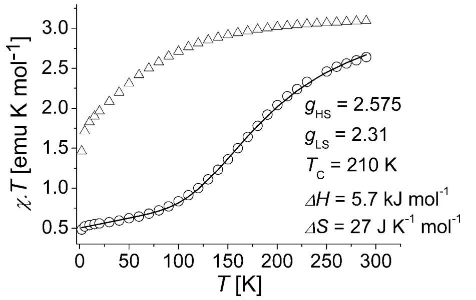

Figure 2. Variable temperature magnetic susceptibility plots of the experimental data of **1** (circles) and **2** (triangles). The given parameters (inset) were obtained by simulating $\chi \cdot T$ values of **1** (line).

In mononuclear, pseudo-octahedral Co^{2+} compounds, spin crossover is accompanied by structural changes. The most pronounced change involves elongation of Co–ligand bond lengths upon achieving the high-spin form.[8] We studied the spin-transition-induced structural changes in **1**·CH_2Cl_2, by determining the crystal structure from data collected at room temperature as well as at 100 K (Figure 1) and found interesting non-standard structural changes. Both structures are isomorphous in the space group *Pnn*2, and a crystallographic twofold axis passes through the center of the molecule normal to the Cr≡Cr···Co axis, resulting in disorder in the positions of the metal atoms, as has been previously discussed.[9]

The changes in the coordination sphere of the Co^{2+} ion from 100 K (low-spin) to room temperature (high-spin) are somewhat unusual and deserve some discussion. While the change in Co–N bond lengths from low-spin [2.054(2) Å] to high-spin [2.125(3) Å] is in accord with what would be expected for the $d_{x^2-y^2}$ orbital being populated in the latter case but not in the former, the change in Co–Cl bond lengths is counter to expectation. The Co–Cl bond in the low-spin structure [2.567(5) Å] is ca. 0.2 Å *longer* than that in the high-spin structure [2.370(1) Å]. Additionally, the Cr···Co distance of 2.623(5) Å in the high-spin structure decreases more than 0.13 Å to 2.491(1) Å in the low-spin form, which is the shortest Cr···Co distance reported for any compound to date {0.2 Å shorter than the Cr···Fe distance in **3** [2.715(2) Å]} and very similar to the Cr···Cr distance reported in the homometallic analog of **1**, $Cr_3(dpa)_4Cl_2$ [2.477(4) Å].[9] We note that the axial distortion of the octahedral geometry of the low-spin Co^{2+} ion in **1** may partially be attributed to a Jahn–Teller effect, but this effect cannot account for the very short Cr···Co distance. Since this difference is significantly greater than the difference in ionic radii (0.085 Å)[10] for low-spin vs. high-spin Co^{2+}, this result is a clear indication that direct bonding between Cr and Co must be considered.

In support of this consideration, close inspection of the high- and low-spin structures of **1** indicate that the changes in metal–ligand bond lengths are not limited solely to the

Co^{2+} ion. There are also significant elongations of the metal–ligand bonds by ca. 0.05 Å for the terminal Cr ion in the high-spin structure.

Heterometallic interactions must also be considered for **2**, the structure of which features a very short Mo···Co distance of 2.6170(7) Å. To put this distance in perspective, it is similar to the Cr···Co distance in the high-spin form of **1**, despite the difference in size between Mo and Cr! The Mo···Co distance in **2** is also notably shorter than the Mo···M distances (2.69–2.75 Å) observed in the structurally similar tri- or tetranuclear complexes synthesized by Mashima, where M = Rh, Pd, Ir, or Pt.[11] This Mo···Co distance also represents the shortest known Mo···Co distance ever determined for any compound that does not have a single atom bridge between the Mo and Co atoms. Addition of $CoCl_2$ to **4** elongates the Cr≡Cr multiple bond (1.943 Å in **4**)[4] to 2.036 Å in the low-spin form of **1** and to 2.067 Å in its high-spin configuration. In contrast, the Mo≡Mo distances in **5** (2.097 Å) and **2** (2.103 Å) are very similar.

The Co–Cl bond length in **2** (2.430 Å) like that in **1** is also noticeably long as compared to typical Co–Cl bond lengths for other high-spin Co^{2+} compounds, and it is now possible to observe that for the structures reported here, the Co–Cl bond lengths are roughly inversely proportional to the heterometallic M···Co separation (M = Cr or Mo). It appears that the Co–Cl bonds are lengthened because the Co^{2+} ion must share its d_{z^2} orbital between making the Co–Cl bond and a Co···M σ interaction.

Conclusions

We may conclude from this data that the M≡M group has a *trans* influence on the Co–Cl bond. Also, since the Co^{2+} ion in **1** is able to achieve a low-spin ground state, it appears that the Cr≡Cr multiply-bonded group is a stronger field "ligand" than the Mo≡Mo moiety. It should be noted here that an analogous compound to **1** with a Cl–Co–Co···Co–Cl chain has also been structurally characterized in its low- and high-spin forms.[12] The tricobalt species also undergoes non-standard structural changes as a function of spin-state, and these changes are similar but less pronounced than those in **1**. This observation indicates that, in comparison to the Co–Co moiety, the Cr≡Cr group has a stronger *trans* influence.

This phenomenon has significance in many areas of chemistry where heterometallic interactions are important, such as in heterogeneous catalysis,[13] alloys,[14] and in the active sites of many metalloproteins.[15] In particular, we note the potential relevance of Mo···Co interactions to widely used Mo/Co hydrodesulfurization catalysts[16] and Mo/Co catalysts for hydroprocessing of biofuels.[17]

Experimental Section

General: All reactions were carried out under dry N_2 using Schlenk techniques. Solvents tetrahydrofuran (THF) and hexanes were purified using a Vacuum Atmospheres solvent purification system. Dichloromethane was freshly distilled under N_2 over CaH_2 prior to use. Naphthalene was purchased from Sigma–Aldrich. MeLi solution in diethyl ether was purchased (Sigma–Aldrich), anhydrous $CoCl_2$ was prepared from $CoCl_2 \cdot xH_2O$ in refluxing thionyl chloride[18] and the ligand dpaH (2,2′-dipyridylamine from Sigma–Aldrich) was recrystallized from hot hexanes prior to use. Molybdenum acetate $Mo(OAc)_4$[19] and $Cr_2(dpa)_4$[3] were synthesized according to published methods.

Preparation of $CrCrCo(dpa)_4Cl_2$ (1): In a typical reaction, solid orange $Cr_2(dpa)_4$ (200 mg, 0.255 mmol) and a slight excess of blue anhydrous $CoCl_2$ (40 mg, 0.31 mmol) were combined and THF (25 mL) was added via cannula. The suspension was then heated to reflux for at least 4 h after which a complete color change to brown had occurred and a crystalline solid precipitate was observed. The mixture was concentrated to ca. 10 mL and the solid was collected by filtration and washed with hexanes (30 mL). The product was extracted with CH_2Cl_2 (40 mL) and the dark brown solution was layered with hexanes (60 mL). Brown, block shaped crystals of **1**·CH_2Cl_2 suitable for single crystal X-ray diffractometry were obtained within 1 d. Crystalline yield: 170 mg (67%). $C_{41}H_{34}Cl_4CoCr_2N_{12}$ (999.12): calcd. C 49.27, H 3.43, N 16.82, Co 5.90; found C 48.62, H 3.50, N 17.06, Co 5.81. MALDI-Mass spectrum: *m*/*z* = 878 [**1** – Cl]$^+$. IR (KBr): ṽ = 1606 (m), 1594 (m), 1468 (s), 1430 (s), 1363 (m), 1316 (w), 1166 (w), 1152 (m), 1016 (w), 877 (w), 764 (m), 734 (w) cm^{-1}.

Preparation of $Mo_2(dpa)_4$ (5): The ligand dpaH (2.192 g, 12.80 mmol) was dissolved in THF (70 mL) and cooled to –78 °C. Upon addition of one equivalent of MeLi (1.6 M solution in ethyl ether) a white suspension resulted which was warmed to room temperature. The white suspension was added via cannula to solid bright yellow $Mo(OAc)_4$ (0.921 g, 2.15 mmol) resulting in the immediate formation of a red precipitate. The mixture was heated to reflux for at least 6 h, after which the solid was collected by filtration and washed with methanol (3 × 30 mL) and ethyl ether (1 × 50 mL) and dried under vacuum. Yield: 1.68 g (90%). $C_{40}H_{32}Mo_2N_{12}$ (872.28): calcd. C 55.05, H 3.70, N 19.26; found C 55.39, H 3.28, N 18.85. MALDI-Mass spectrum: *m*/*z* = 873.1 [**5**]$^+$, 726 [**5** – dpa + Na]$^+$, 703 [**5** – dpa]$^+$. IR (KBr): ṽ = 1600 (m), 1578 (s), 1477 (s), 1455 (s), 1422 (s), 1370 (m), 1302 (m), 1283 (w), 1250 (m), 1150 (m), 1015 (m), 986 (w), 852 (w), 769 (m), 755 (m), 732 (m), 618 (w) cm^{-1}.

Preparation of $MoMoCo(dpa)_4Cl_2$ (2): Solid red $Mo_2(dpa)_4$ (**5**) (190 mg, 0.218 mmol) and blue anhydrous $CoCl_2$ (40 mg, 0.31 mmol) were combined with naphthalene (2.30 g, 18.0 mmol) in a Schlenk flask equipped with a reflux condenser. The flask was set whilst stirring into a sand bath preheated to 180 °C. The nitrogen inlet stream was reduced to a minimum to avoid sublimation of naphthalene into the condenser and naphthalene sublimed on the flask walls was melted using a heat gun. After 10 min at 180 °C the color changed to brown and the mixture was cooled to room temperature. Hexanes (50 mL) were then added and the mixture was again heated to reflux. The hot hexanes were then filtered off and the solid residue was extracted with CH_2Cl_2 (40 mL). The resulting green solution was layered with hexanes and crystals of **2·CH_2Cl_2** were obtained after 1 d. Yield: 160 mg, 67%. $C_{40}H_{32}Cl_2CoMo_2N_{12}$ (1002.11): calcd. C 47.92, H 3.22, N 16.77; found C 47.57, H 3.22, N 16.29. MALDI-Mass spectrum: *m*/*z* = 966.6 [**2** – Cl]$^+$. IR (KBr): ṽ = 1602 (m), 1592 (m), 1464 (s), 1419 (s), 1353 (m), 1310 (m), 1284 (w), 1261 (w), 1154 (m), 1015 (w), 855 (w), 764 (m), 739 (w) cm^{-1}.

CCDC-695975 (for **1**), -695976 (for **2**), -695977 (for **5**) contain the supplementary crystallographic data for this paper. These data can

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be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Crystallographic and physical measurement details for compounds **1**, **2**, and **5** are available online in the Supporting Information.

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