

Synthesis, Structure, and Properties of a Dimeric Chromium(II) Pyrazolato Complex with a Long Chromium–Chromium Distance. Maintenance of a Dimeric Structure in Solution and Interconversion between Dimeric and Monomeric Structures

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The synthesis, solid-state structure, and solution structure of $\text{Cr}_2(\text{tBu}_2\text{pz})_4$ are described. This complex is obtained by sublimation of the monomeric species $\text{Cr}(\text{tBu}_2\text{pz})_2(4\text{-tBupy})_2$ and contains long chromium–chromium distances that are enforced by the divergent nature of the pyrazolato ligands.

Complexes of the formula Cr_2L_4 , where L is a monoanionic bidentate donor ligand, have attracted considerable attention because of the presence of chromium–chromium bonds.¹ Much of the work to date has been directed toward exploring complexes containing short chromium–chromium distances. There are many examples of Cr_2L_4 complexes with chromium–chromium distances between 1.83 and 2.00 Å, with the shortest distance to date [1.828(2) Å] in dichromium tetrakis(2-methoxy-5-methylphenyl).² Recent emphasis has been focused on how long the chromium–chromium distances can be in Cr_2L_4 complexes. It is well established that coordination of donor ligands to the axial coordination sites in Cr_2L_4 leads to elongation of the chromium–chromium distance, and values of 2.21–2.69 Å have been documented in a variety of complexes.¹ Recently, “divergent” ligands, in which the lone pairs on the donor atoms do not point in parallel directions, have been evaluated for their ability to impose longer chromium–chromium bond lengths.³ Use of axial ligand coordination and a divergent ligand afforded a chromium–chromium distance of 2.688(2) Å in $[\text{Li}_2(\text{DMF})_6][\text{Cr}_2(\text{azin})_4\text{Cl}_2]$ (azin = 7-azaindolato).^{3a} This is the longest chromium–chromium distance in a complex containing a

Cr_2L_4 core. To date, all complexes of the formula Cr_2L_4 have employed bidentate ligands with nonadjacent donor atoms. Such ligands contain one or more spacer atoms separating the Lewis base sites. As part of our interest in chromium(II) complexes with nitrogen-based ligands⁴ and transition-metal pyrazolato complexes,⁵ we sought to explore the synthesis, structure, and properties of chromium(II) complexes containing pyrazolato ligands. The nitrogen atom lone pairs in pyrazolato ligands are highly divergent by virtue of the geometry imposed by the five-membered ring structure, and pyrazolato ligands do not contain spacer atoms between the two nitrogen atom donors.

Herein we report the synthesis, solid-state structure, and solution structure of $\text{Cr}_2(\text{tBu}_2\text{pz})_4$ (tBu_2pz = 3,5-di-*tert*-butylpyrazolato) as well as its reaction with 4-*tert*-butylpyridine (4-tBupy) to form the monomeric complex $\text{Cr}(\text{tBu}_2\text{pz})_2(4\text{-tBupy})_2$. Dimeric $\text{Cr}_2(\text{tBu}_2\text{pz})_4$ is remarkable for several reasons. It possesses the longest chromium–chromium distance of any dimeric chromium complex described to date, yet it does not contain axial donor ligands. The long chromium–chromium distance is attributable to the highly divergent nature of the tBu_2pz ligand. Despite the long chromium–chromium distance and presumably weak bond, $\text{Cr}_2(\text{tBu}_2\text{pz})_4$ retains a dimeric structure in a benzene solution. The results add new insights into the limits of long chromium–chromium bonds in Cr_2L_4 complexes.

Treatment of CrCl_2 with tBu_2pzK ⁶ in the presence of 4-tBupy in tetrahydrofuran at ambient temperature afforded $\text{Cr}(\text{tBu}_2\text{pz})_2(\text{tBupy})_2$ (**1**; 60%) as purple crystals after workup (eq 1). In this reaction, the 4-tBupy ligand served to increase the solubility of CrCl_2 , as well as to coordinate to the metal

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(1) For leading references, see: Cotton, F. A.; Murillo, C. A.; Walton, R. A. *Multiple Bonds between Metal Atoms*, 3rd ed.; Springer: New York, 2005; Chapter 3.

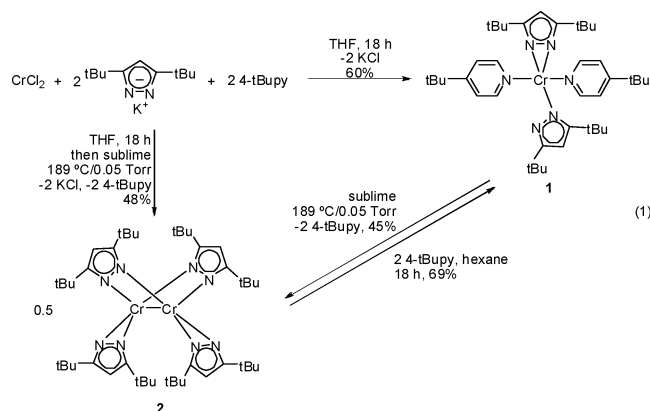
(2) Cotton, F. A.; Koch, S. A.; Millar, M. *Inorg. Chem.* **1978**, *17*, 2084.

(3) For Cr complexes, see: (a) Cotton, F. A.; Murillo, C. A.; Zhou, H.-C. *Inorg. Chem.* **2000**, *39*, 3728. (b) Alfaro, N.; Cotton, F. A.; Daniels, L. M.; Murillo, C. A. *Inorg. Chem.* **1992**, *31*, 2718. (c) Cotton, F. A.; Falvello, L. R.; Schwotzer, W. *Inorg. Chim. Acta* **1991**, *190*, 89. (d) Edema, J. J. H.; Gambarotta, S.; Meetsma, A.; van Bulhuis, F.; Spek, A. L.; Smeets, W. J. J. *Inorg. Chem.* **1990**, *29*, 2147. (e) Cotton, F. A.; Wang, W. *Polyhedron* **1985**, *4*, 1735.

(4) Sadique, A. R.; Heeg, M. J.; Winter, C. H. *J. Am. Chem. Soc.* **2003**, *125*, 7774.

(5) For recent selected references, see: (a) Arachchige, S. M.; Heeg, M. J.; Winter, C. H. *J. Organomet. Chem.* **2005**, *690*, 4356. (b) Gust, K. R.; Knox, J. E.; Heeg, M. J.; Schlegel, H. B.; Winter, C. H. *Eur. J. Inorg. Chem.* **2002**, 2327. (c) Gust, K. R.; Knox, J. E.; Heeg, M. J.; Schlegel, H. B.; Winter, C. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 1591. (d) Perera, J. R.; Heeg, M. J.; Schlegel, H. B.; Winter, C. H. *J. Am. Chem. Soc.* **1999**, *121*, 4536.

(6) Yélamos, C.; Heeg, M. J.; Winter, C. H. *Inorg. Chem.* **1998**, *37*, 3892.



center to prevent oligomerization. Sublimation of **1** at 189 °C and 0.05 Torr afforded $\text{Cr}_2(\text{tBu}_2\text{pz})_4$ (**2**; 45% based on CrCl_2) as purple crystals (eq 1). Treatment of **2** with 2 equiv of 4-*t*BuPy afforded **1** in 69% yield. The structural assignments for **1** and **2** were based upon ^1H NMR and IR spectroscopy, microanalyses, magnetic moment determinations, and X-ray structure determinations.⁷ Complexes **1** and **2** are paramagnetic and exhibited broad resonances in the ^1H NMR spectra in benzene-*d*₆. The magnetic moment (μ_{eff}) values of **1** in the solid state and a benzene solution were 4.61 and 4.85 μ_{B} , respectively, which are close to the spin-only magnetic moment expected for the four unpaired electrons of a high-spin chromium(II) center ($\mu_{\text{eff}} = 4.90 \mu_{\text{B}}$). The μ_{eff} values of **2** were 1.67 and 1.58 μ_{B} per dimer in the solid state and a benzene solution, respectively. Freezing point depression molecular weight determinations of a 0.070 M solution of **2** in benzene revealed molecular weights of 803 and 843 g mol^{-1} , which are within the experimental error ($\pm 10\%$) of the molecular weight of 821 g mol^{-1} for dimeric **2**. Thus, complex **2** maintains a dimeric structure in solution.

A perspective view of **1** is shown in Figure 1. The chromium atom in **1** is bound to two pyrazolato ligands and two 4-*t*BuPy ligands. One of the two pyrazolato ligands is coordinated in a slipped η^2 fashion, with chromium–nitrogen bond lengths of 2.043(2) and 2.351(2) Å. The second pyrazolato ligand coordinates to the chromium center in a η^1 fashion with a chromium–nitrogen bond length of 2.044(2) Å. The two coordinated pyridine ligands are trans to each other and have chromium–nitrogen bond lengths of 2.113(2) and 2.141(3) Å.

A perspective view of **2** is shown in Figure 2. There are two independent molecules in the unit cell. The bond distances and angles are similar within experimental uncertainty in both molecules, with the exception of the chromium–chromium distances. Complex **2** exists as a dimer, and each chromium atom is bonded to the nitrogen atoms of one *t*Bu₂pz ligand in a terminal, chelating η^2 fashion and to the nitrogen atoms of two *t*Bu₂pz ligands with μ_2 interactions. The μ_2 ligands are cis within the dimer to make room for the η^2 -pyrazolato ligands. The chromium–chromium distances are 2.6722(7) and 2.7591(7) Å [avg = 2.7156(7) Å]. The η^2 -*t*Bu₂pz ligands have chromium–nitrogen bond lengths

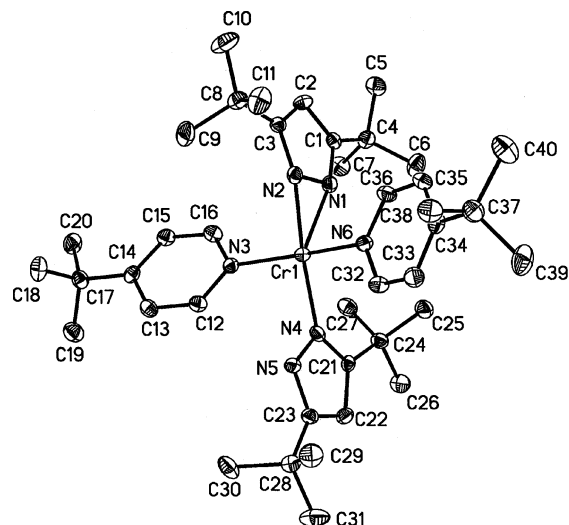


Figure 1. Perspective view of **1**. Selected bond lengths (Å) and angles (deg): Cr–N1, 2.351(2); Cr–N2, 2.043(2); Cr–N3, 2.113(3); Cr–N4, 2.044(2); Cr–N5, 2.893(3); Cr–N6, 2.141(3); N1–N2, 1.382(3); N4–N5, 1.379(3); N1–Cr–N2, 35.82(8); N1–Cr–N3, 96.85(9); N1–Cr–N4, 132.61(9); N1–Cr–N6, 94.85(9); N2–Cr–N3, 89.47(10); N2–Cr–N4, 168.15(10); N2–Cr–N6, 91.85(10); N3–Cr–N4, 90.25(9); N3–Cr–N6, 162.63(9); N4–Cr–N6, 91.94(10).

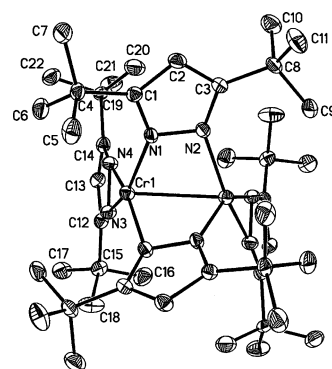


Figure 2. Perspective view of **2**. Selected bond lengths (Å) and angles (deg): Cr1–Cr1', 2.6722(7); Cr2–Cr2', 2.7591(7); Cr1–N1, 2.042(2); Cr1–N2', 2.042(2); Cr1–N3, 2.023(2); Cr1–N4, 1.981(2); N1–N2, 1.380(2); N3–N4, 1.395(3); N1–Cr1–N3, 146.88(8); N1–Cr1–N4, 106.69(8); N3–Cr1–N4, 40.78(7); N1–Cr1–Cr1', 70.43(5); N2'–Cr1–Cr1', 71.02(5); N3–Cr1–Cr1', 110.17(5); N4–Cr1–Cr1', 110.46(6).

of 1.981(2), 2.009(2), 2.022(2), and 2.023(2) Å, while the related values for the μ_2 -*t*Bu₂pz ligands are 2.038(2), 2.042(2), 2.043(2), and 2.044(2) Å.

One of the chromium–chromium distances in an independent molecule of **2** is the longest in any Cr_2L_4 complex reported to date. The μ_2 -coordination mode is the most common in transition-metal pyrazolato complexes,^{5c,8} because of the divergent nature of the nitrogen atom lone pairs. The divergent *t*Bu₂pz ligand must promote the long chromium–chromium distances in **2** because there are no axial donor ligands present. Complex **2** does not adopt the paddlewheel structure that is commonly observed in Cr_2L_4 complexes and instead has two μ_2 -*t*Bu₂pz and two terminal η^2 -*t*Bu₂pz ligands. The only other reported chromium complex with a similar structure is $\text{Cr}_2(\text{tBuNC}(\text{CH}_3)\text{NEt})_4$ (**3**), but this complex exhibited a short chromium–chromium bond [1.9601(12) Å] despite the unusual structure.⁴ The fact

(7) Experimental procedures and spectral and analytical data are contained in the Supporting Information.

(8) La Monica, G.; Ardizzioia, G. A. *Prog. Inorg. Chem.* **1997**, *46*, 151.

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that two different chromium–chromium distances are observed in the solid-state structure of **2** suggests that these interactions are controlled by crystal packing forces and thus probably constitute weak bonds. Solution molecular weight measurements demonstrate that **2** maintains a dimeric structure in solution. This result contrasts with that of **3**, which was found to convert to monomeric species upon dissolution in benzene.⁴ The contradictory solution structures of **2** and **3** could be due to the relative energies of the resultant monomeric species. In the same paper describing **3**, it was demonstrated that $\text{Cr}(\text{RNC}(\text{CH}_3)\text{NR})_2$ ($\text{R} = \text{tBu}$, iPr) adopted monomeric structures in the solid state.⁴ Thus, it is likely that monomeric $\text{Cr}(\text{tBuNC}(\text{CH}_3)\text{NEt})_2$ is close in energy to **3**, allowing solvation to favor the monomeric structures in solution. In the present work, monomeric $\text{Cr}(\text{tBu}_2\text{pz})_2$ is probably too high in energy, relative to **2**, to exist in detectable concentrations in solution. Hence, a dimeric solution structure is favored. Only in the presence of a good donor ligand such as 4-tBupy is a monomeric structure favored. Finally, the magnetic moment values of **2** suggest similar structures in solution and the solid state. The ^1H NMR spectra of **2** exhibited broad resonances at δ 4.2 and 1.4 between -80 and $+20$ °C and did not change with temperature. Such behavior is not consistent with a thermally

populated low-lying triplet state in **2**⁹ because the ^1H NMR resonances should sharpen and move as the temperature is lowered. The μ_{eff} values of **2** are similar to those observed in $\text{Cr}_2(\text{O}_2\text{CCF}_3)_4\text{L}_2$ complexes ($\mu_{\text{eff}} = 1.15 \mu_{\text{B}}$ per Cr atom for $\text{L} = \text{PO}(\text{OEt})_3$ vs $\mu_{\text{eff}} = 1.12 \mu_{\text{B}}$ per Cr atom for **2**).¹⁰ These $\text{Cr}_2(\text{O}_2\text{CCF}_3)_4\text{L}_2$ complexes also have long chromium–chromium bond lengths [$2.541(1)$ Å in $\text{L} = \text{Et}_2\text{O}$].¹¹ Finally, it may be possible to achieve even longer chromium–chromium distances in complexes of the formula $\text{Cr}_2(\text{tBu}_2\text{-pz})_4\text{L}_2$ ($\text{L} = \text{axial donor}$).

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Supporting Information Available: Synthetic procedures and analytical and spectroscopic data for **1** and **2** (PDF) and X-ray crystallographic files for **1** and **2** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (9) Cotton, F. A.; Chen, H.; Daniels, L. M.; Feng, X. *J. Am. Chem. Soc.* **1992**, *114*, 8980.
(10) Bilgrien, C. J.; Drago, R. S.; O'Connor, C. J.; Wong, N. *Inorg. Chem.* **1988**, *27*, 1410.
(11) Cotton, F. A.; Extine, M. W.; Rice, G. W. *Inorg. Chem.* **1978**, *17*, 176.