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Synthesis and X-ray Structure of the First Dinuclear Homoleptic Chromium(II) Amide, $\{[(i\text{-Pr})_2N]Cr[\mu\text{-}(i\text{-Pr})_2N]\}_2$

Although mononuclear and dimeric species without metal–metal bonds are well-known in the chemistry of Cr(II),[1] the majority of the well-defined complexes are dominated by the presence of Cr–Cr quadruple bonds of unusual shortness.[2,3] With only two exceptions,[4] the occurrence of this interesting functionality seems restricted to a class of complexes where the special geometry of bridging three-center chelating ligands is able to form five-membered rings with the two chromium atoms.[5] In order to identify some possible role played by the ligands in this respect, we have recently studied the structural features of new classes of Cr(II) complexes (alkyls, amides, alkoxides) bearing ligands with most diverse geometries.[6c] In the case of $X_8Cr_2M_4$ systems (X = Me, OR; M = Li, Na) for example, it is possible to break up the supershort Cr–Cr bond and keep intact the molecular frame at the same time, simply by changing the nature of the donor atom.[6] This suspected ability of the ligand of enforcing or inhibiting the formation of the supershort Cr–Cr bond[6,7] prompted us to extend this study to Cr(II) complexes in which ligands were bonded by using donor atoms different from the carbon and oxygen of the already known alkyl-[4b] and aryloxide[6,8] derivatives. In our expectation, nitrogen should have interesting intermediate properties in this respect.

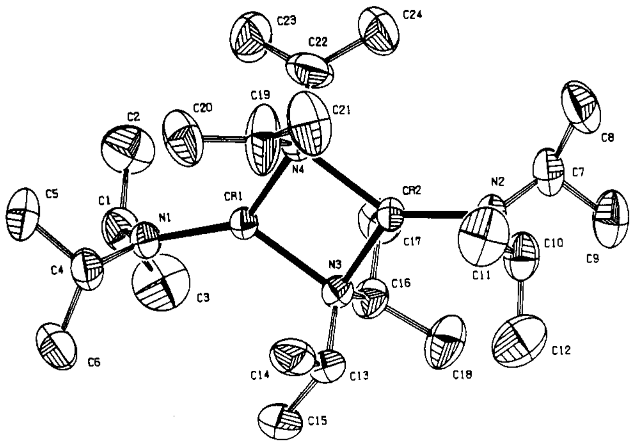

Figure 1. Thermal motion ellipsoid plot of **1** (40% probability level). Selected interatomic distances (Å) and angles (deg) (estimated standard deviations in parentheses): Cr(1)–N(1) = 1.927 (3); Cr(1)–N(3) = 2.065 (3); Cr(1)–N(4) = 2.077 (3); N(1)–Cr(1)–N(3) = 129.2 (1); N(1)–Cr(1)–N(4) = 138.3 (1); N(3)–Cr(1)–N(4) = 92.4 (2); Cr(1)···Cr(2) = 2.8657 (9).

We found that the quadruply bonded dimer $Me_8Cr_2Li_4 \cdot 4thf$[4] reacts vigorously in toluene with an excess of $(i\text{-Pr})_2NH$, resulting in the evolution of methane and formation of emerald green solutions, from which the complex $\{[(i\text{-Pr})_2N]Cr[\mu\text{-}N(i\text{-Pr})_2]\}_2$ (**1**) can be isolated in good yield (68%)[9] (eq 1). Complex **1** can

$$Me_8Cr_2Li_4 \cdot 4thf + 8(i\text{-Pr})_2NH \rightarrow \underset{\textbf{1}\ \text{(green)}}{\{[(i\text{-Pr})_2N]Cr[\mu\text{-}N(i\text{-Pr})_2]\}_2} + 8CH_4 + 4(i\text{-Pr})_2N_2Li \quad (1)$$

also be conveniently synthesized by reaction of $Mes_2Cr(thf)_3$[10a]

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(9) Neat $(i\text{-Pr})_2NH$ (1.04 g, 10.2 mmol) was added to a solution of $Me_8Cr_2Li_4(thf)_4$ (0.703 g, 1.28 mmol) in toluene (15 mL). The resulting green solution was evaporated to dryness and the residual solid redissolved in pentane (10 mL). After filtration and concentration to a very small volume, deep green crystals separated on cooling at −80 °C (0.45 g, 0.90 mmol, 70% yield). Anal. Calcd (found) for $C_{12}H_{28}N_2Cr$: C, 57.14 (57.09); H, 11.11 (11.19); N, 11.11 (11.48); Cr, 20.63 (20.46). IR (KBr, Nujol mull, cm^{-1}): 1375 (s), 1360 (s), 1335 (m), 1310 (w), 1155 (s), 1150 (m), 1100 (s), 990 (m), 970 (w), 920 (s), 840 (m), 805 (m), 635 (m), 550 (m), 500 (w), 480 (w), 460 (w), 420 (w), $\mu_{eff} = 2.30\ \mu_B$.

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(Mes = 2,4,6-mesityl) with stoichiometric amounts of $(i\text{-Pr})_2NH$ or by reaction of $CrCl_2(thf)_2$[10b] with 2 equiv of $(i\text{-Pr})_2NLi$. The reaction is quite general, and the result is affected by the nature of the alkyl substituents of the amide moiety. While a complex isostructural with **1** has been isolated in the case of the bulky Cy_2N–(Cy = cyclohexyl), only monomeric square-planar species ($(R_2N)_2CrL_2$ and $(R_2N)_4CrLi_2L_2$: R = ethyl; L = 2 thf, py) have been obtained in the case of smaller substituents.[6c]

Complex **1** crystallizes in the triclinic space group $P\bar{1}$.[11] The unit cell contains two amide-bridged dimers (Figure 1). Each dimer has a slightly puckered central core of two chromium and two nitrogen atoms (deviation from the least-squares plane 0.012 (1) and 0.012 (3) Å). The geometry of the three-coordinated chromium atoms is severely distorted trigonal planar, and the two terminally bonded nitrogen atoms lie approximately in the same molecular plane. The molecular arrangement is quite similar to that of the previously reported $[(RO)Cr(\mu\text{-}OR')]_2$.[8] The Cr–N bond distances for the terminal and the bridging amido groups are quite different (Cr(1)–N(1) = 1.927 (3) Å, Cr(1)–N(3) = 2.065 (3) Å), in agreement with the two different coordination geometries (tetrahedral versus trigonal), which suggest a different nature of bonding to chromium. The trigonal-planar geometry of N(3) and N(4) indicates a strong nitrogen $\rightarrow$ metal π-interaction for the terminally bonded amino groups. In contrast, in the case of the bulky and monomeric $[(Me_3Si)_2N]_2Cr(thf)_2$[12b] and isostructural $\{[(Me_3Si)_2N]Mn[\mu\text{-}N(SiMe_3)_2]\}$,[12a] no such interaction has been claimed and the planarity of the nitrogen atoms has been explained in terms of nitrogen $\rightarrow$ silicon strong π-bonding interactions.

The value of the Cr···Cr intermetallic distance (Cr···Cr = 2.8657 (9) Å) falls between those observed for $Me_8Cr_2Li_4$[4b] and $(RO)_8Cr_2Na_4$[6] (1.98 and 3.634 Å, respectively) and indicates the presence of a Cr–Cr single bond only.[13] However, the magnetic properties of **1** support the idea that no real Cr–Cr bond actually occurs, in spite of the short intermetallic separation. The magnetic susceptibilities showed in fact a dependence on the temperature in the range 120–298 K, in agreement with the Curie–Weiss law. The presence of a strong antiferromagnetic interaction can be diagnosed by the large negative value of Θ ($\Theta = -101$ K).[14] The value of μ_{eff} ($\mu_{eff} = 2.30\ \mu_B$) is significantly lower than expected for a low-spin d^4 electronic configuration (μ_{eff} spin-only value 2.83 μ_B). These results can be explained by assuming either a low-spin d^4 electronic configuration of chromium (with only a strong antiferromagnetic interaction between the two metal centers) or a d^4 high-spin configuration with the two metal centers linked by a Cr–Cr double bond. Considering the high value of the intermetallic distance, this second possibility seems quite improbable.

Although the nature of the Cr–Cr interaction in complex **1** is not clarified by these results, an indication of the role played by the electron-donor ability of the bridging atom in affecting the size of the intermetallic separation emerges.

Further work to verify this point and to study the chemistry of Cr(II) amides is in progress at the moment.

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Supplementary Material Available: Tables of crystal data, positional and isotropic thermal parameters of non-hydrogen atoms, anisotropic thermal parameters of non-hydrogen atoms, positional parameters and isotropic thermal parameters of hydrogen atoms, bond distances, bond angles, and torsional angles (8 pages); a table of observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

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(11) X-ray diffraction data were collected on an Enraf-Nonius CAD4 diffractometer for a crystal (0.5 × 0.5 × 0.5 mm) sealed in a Lindemann glass capillary: Zr-filtered Mo Kα radiation; triclinic, space group $P\bar{1}$, $a = 9.755$ (1) Å, $b = 10.731$ (1) Å, $c = 15.011$ (2) Å, $\alpha = 93.34$ (1)°, $\beta = 101.83$ (1)°, $\gamma = 100.18$ (1)°, $V = 1506.5$ (3) Å^3, $Z = 2$, $d_{calcd} = 1.113$ g cm^{-3}; $F(000) = 552$, μ(Mo Kα) = 7.2 cm^{-1}. The structure was solved with Patterson techniques (SHELXS 86) and refined with full-matrix least squares (SHELX 76) to a final $R = 0.049$ ($R_w = 0.071$, $S = 0.91$, $w = 1/\sigma^2(F_o)$, $\rho_{max} = 0.38$ e Å^{-3}, maximum shift/error = 0.2; 309 parameters (including anisotropic thermal parameters for the non-hydrogen atoms and two isotropic thermal parameters for the hydrogen atoms), 3784 reflections with $I > 2.5\sigma(I)$). Hydrogen atoms were introduced on calculated positions. One of the two isopropyl groups bonded to N(4) is probably disordered.

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Use of Bis(2,2'-bipyridyl-d_8)ruthenium(II) Dichloride To Facilitate NMR Structural Assignments in Complexes with Diimine Ligands

Over the past decade the field of ruthenium polypyridine chemistry has seen explosive growth due largely to the promise of such systems to act as effective photoredox catalysts.[1] Many of the complexes examined in this regard are of the general type $Ru(bpy)_2LL'^{2+}$ where LL' is an unsymmetrical dimine ligand.[2] These complexes are relatively simple to prepare by treating the appropriate ligand LL' with $Ru(bpy)_2Cl_2$ in refluxing aqueous ethanol. Characterization of the resulting complex by ^1H NMR spectroscopy is complicated by its lack of symmetry in that the two bpy ligands will give rise to 16 nonequivalent protons in addition to those associated with LL'. This problem has been recognized by previous workers, and a significant effort has been directed toward interpretation of these spectra[3] or the employment of two-dimensional techniques to facilitate assignments.[4]

We have recently developed a simple and straightforward solution to this problem: the utilization of bpy-d_8 as an auxiliary ligand in place of its protio analogue. This perdeuterio species can be prepared[5] simply by treatment of the corresponding di-*N*-oxide with NaOD in D_2O.[6] If 1.88 g of 2,2'-bipyridine

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(5) This material is also commercially available from MSD Isotopes, 2.5 g/$925.00.

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