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$[Na(THF)_2Cr(N_3N)]$: The First Trigonal Monopyramidal Chromium(II) Complex

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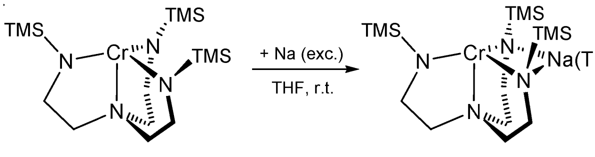
Reduction of $[Cr(N_3N)]$ (**1**) $\{(N_3N)^{3-} = ((SiMe_3NCH_2CH_2)_3N)^{3-}\}$ with sodium powder in THF affords the yellow, extremely air-sensitive amidochromate(II) $[Na(THF)_2Cr(N_3N)]$ (**2**) in good yield. Complex **2** has an effective magnetic moment of 5.1 μ_B indicative of a d^4 high-spin electronic configuration. ^1H NMR spectroscopy in solution and single-crystal X-ray crystallography show that compound **2** is composed of idealized C_s symmetric contact ion pairs, in which trigonal-monopyramidal $[Cr^{II}(N_3N)]^-$ anions are linked to the $[Na(THF)_2]^+$ countercations by two bridging amide ligands. DFT calculations of **1**, **2**, and the anion $[Cr(N_3N)]^-$ at the RI-BP86/TZVPP level of theory provide in combination with extended Hückel calculations a rationale for the observed structural changes from **1** to **2**.

Triamidoamine ligands, $[(RNCH_2CH_2)_3N]^{3-}$ ($R = SiR'_3$, aryl, alkyl), are an interesting class of tripodal ligands, which bind to transition metals in a tetradentate manner to form mostly complexes with a rigid, distorted trigonal-bipyramidal or trigonal-monopyramidal coordination geometry.[1] The salient feature of these ligands is their ability to create a sterically protected, 3-fold-symmetric pocket, in which two metal-centered π orbitals (approximately d_{xz} and d_{yz}) and a σ orbital (approximately d_{z^2}) are available for bonding to additional ligands. This stereoelectronic situation has enabled a variety of remarkable transformations at molybdenum and tungsten centers, such as the activation of dinitrogen[2] and carbon monoxide,[3] the C−C coupling of acetylide complexes and α,α-dehydrogenation of alkyl complexes to give metal alkylidynes,[4] or the synthesis of complexes with a metal−pnictogen triple bond.[5] In comparison, studies on related chromium complexes have been very rare so far.[6] We set out to explore the chemistry of chromium with triamidoamine ligands and discovered some marked differences from that of the heavier group 6 elements. For example, $[Cr(N_3N)]$ (**1**) is a very stable complex[7] and a useful starting material for the synthesis of Cr^{IV} triamidoamine complexes,[8] whereas no evidence was found so far for the existence of $[M\{(RNCH_2CH_2)_3N\}]$ (M = Mo, W).[1b,e,2b,d,3] Furthermore, complex **1** reacts with $Li[BEt_3H]$ to give the hydridochromate(III) $[Li(THF)Cr(N_3N)H]$,[9] which does not have any molybdenum or tungsten counterparts. In this paper, we provide another example for the diverse chemistry of chromium with the synthesis and full characterization of the trigonal-monopyramidal amidochromate(II) $[Na(THF)_2Cr(N_3N)]$ (**2**).

Reduction of $[Cr(N_3N)]$ (**1**) with 6 equiv of sodium powder in THF affords selectively the chromium(II) triamidoamine complex $[Na(THF)_2Cr(N_3N)]$ (**2**), which was isolated after crystallization from pentane as yellow, highly air-sensitive cubes in 67% yield (see equation). Complex **2** melts at 125−128 °C and is readily soluble in hydrocarbons, diethyl ether, and THF to give amber colored solutions, which turn instantaneously brown upon exposure to air. The amido-



1 TMS = $SiMe_3$ 2

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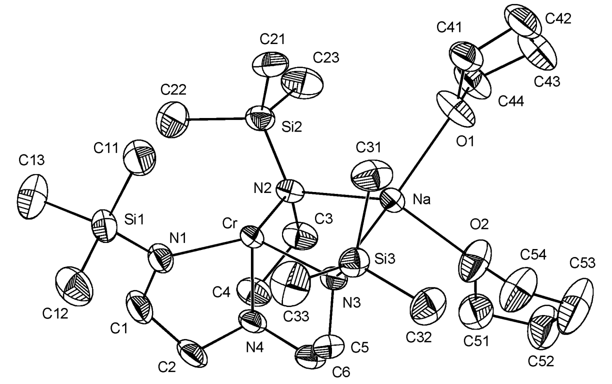

Figure 1. DIAMOND plot of the molecular structure of **2** with thermal ellipsoids drawn at the 40% probability level. Hydrogen atoms and split positions (C44S and C54S) are omitted for clarity. Selected bond lengths (Å) and angles (deg) (see also Table 1): Na−N2 = 2.402(2), Na−N3 = 2.462(2), Na−O1 = 2.342(2), Na−O2 = 2.336(2), Cr−N2−Na = 88.06(8), Cr−N3−Na = 86.16(7), N2−Na−N3 = 80.97(7), O1−Na−O2 = 91.96(10), O1−Na−N3 = 145.79(9), O2−Na−N2 = 123.19(9).

chromate **2** is a strong reductant and behaves like a molecular source of metallic sodium being oxidized even by Teflon to give **1**.[10] Similarly, the reaction of **2** with $[(C_5Me_5)Ge][BF_4]$[11] affords only the electron-transfer reaction products **1** and $[Ge(C_5Me_5)_2]$.

Complex **2** was characterized by IR and NMR spectroscopy and single-crystal X-ray crystallography (Figure 1, Supporting Information).[12] The IR spectrum of **2** in Nujol resembles that of $[Li(THF)Cr(N_3N)H]$[9] in the fingerprint region, indicating the structural similarity of these compounds. The effective magnetic moment μ_{eff} of **2** was determined in C_6D_6 at 308 K using the Evans method[13] and was corrected for the underlying diamagnetism.[14] The mean value of 5.1 μ_B is close to the spin-only value of a d^4 high-spin electronic configuration (4.90 μ_B). Consequently, the ^1H NMR spectrum of **2** in C_6D_6 displays broadened and shifted signals for the protons of the triamidoamine and THF ligands (Supporting Information). On the basis of the relative intensities, line widths, and chemical shifts, the sharper, less shifted resonances at +2.98 and +1.49 ppm are assigned to the α- and β-protons of the THF ligands,[15] the broader, low-field shifted resonances at +36.1 and +30.1 ppm to the $SiMe_3$ groups, and the three very broad resonances at +46.8, −50.1, and −143 ppm to methylene protons of the triamidomine ligand backbone.[16] The integrating ratio of the $SiMe_3$ resonances of 1:2 and the high solubility of **2** in hydrocarbons suggest that overall C_s symmetric contact ion pairs are present in weakly coordinating solvents, as found in the solid state by X-ray crystallography.[17] In the $^{13}C\{^1H\}$ NMR spectrum of **2**, only two shifted and broadened resonances for the α- and β-carbons of the THF ligands are observed at 76.4 and 27.0 ppm, respectively.[15,18]

The crystal structure confirms that **2** is composed of C_1 (roughly C_s) symmetric contact ion pairs. Each ion pair contains a $[Cr^{II}(N_3N)]^-$ anion, that is linked to the sodium countercation through the nitrogen atoms of two bridging amido groups (Figure 1). Thereby, a puckered Cr−N2−Na−N3 ring results (folding angle N2−Cr−N3/N2−Na−N3 = 25.2°), with the sodium atom being inclined toward the vacant, apical coordination site at chromium. The tetrahedral coordination sphere of sodium is completed by two THF molecules and is strongly distorted as evidenced by the bonding angles at the Na atom and by the dihedral angle N2−Na−N3/O1−Na−O2 of 68.83°. The chromium center exhibits a trigonal-monopyramidal coordination geometry with the bridgehead amine nitrogen atom N4 residing at the apex of the pyramid. This coordination polyhedron is unprecedented in chromium(II) chemistry, all the other reported Cr^{II} amides displaying a trigonal-planar, square-planar, or square-pyramidal coordination geometry.[19] In general, most chromium(II) complexes are octahedral such as *trans*-$[CrMe_2(dmpe)_2]$,[20] or square-planar such as $[Li_2(tmeda)_2CrMe_4]$ (tmeda = $Me_2NCH_2CH_2NMe_2$).[21,22] The chromium atom in **2** is displaced from the equatorial plane defined of the three amide nitrogen atoms N1−N3 by 0.23 Å toward

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(12) Suitable greenish-yellow single crystals of **2** were grown upon slow cooling of a pentane solution from room temperature to −35 °C. The crystals were separated from the mother liquor in the glovebox, mounted in a glass capillary, and sealed under argon. Data were collected on a STOE IPDS diffractometer at 180 K using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Crystallographic data, collection parameters, and refinement parameters for $C_{23}H_{55}CrN_4NaO_2Si_3$ (578.97) follow: triclinic, space group $P\bar{1}$, $a = 10.464(2)$ Å, $b = 11.381(3)$ Å, $c = 15.994(3)$ Å, $\alpha = 87.74(3)°$, $\beta = 86.56(2)°$, $\gamma = 64.30(2)°$, $V = 1713.1(6)$ Å^3 ($Z = 2$), $d_{calcd} = 1.122$ g cm^{-3}, $2\theta_{max} = 51.0°$, $F(000) = 628$, 11662 collected reflections, 5958 unique reflections, 334 parameters, max/min residual electron density 0.655/−0.334 e Å^{-3}; R1 = 0.0428, wR2 = 0.1162 ($I > 2\sigma(I)$); R1 = 0.0532, wR2 = 0.1223 (for all data). The structure was refined by full-matrix least-squares on F^2. Hydrogen atoms were included isotropically using a riding model. The THF ligands were refined with a split model for C44 and C54 due to thermal disorder of the envelope conformation.

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(15) Two sets of signals would be expected for the inequivalent THF ligands of **2**, each set of ^1H NMR signals consisting of two resonances for the diastereotopic α-protons and two resonances for the diastereotopic β-protons in each methylene group. It is possible that signal broadening caused by the paramagnetism of **2** does not allow the four expected signals for the α- and for the β-protons, and the two expected signals for the α- and for the β-carbons of the THF ligands to be resolved. However, we cannot exclude the possibility that a rapid equilibration occurs between the ion pairs $[Na(THF)_xCr(N_3N)]$ ($x = 0-2$) and noncoordinated THF in C_6D_6 at room temperature.

(16) Six methylene proton signals would be expected for a C_s symmetric structure. We suggest that the three missing signals are too broad or shifted outside the range of +200 to −400 ppm to be observed. In the structurally related complexes $[Li(THF)Co(N_3N)]$ and $[TlCo(N_3N)]$, all six methylene proton resonances could be assigned: Schneider, S. Ph.D. Thesis, Humboldt University, Berlin, 2003.

(17) Attempts to separate the ions in **2** by using stronger complexing agents for the Na^+ ions have failed so far. The addition of 12-crown-4 to a pentane solution of **2** lead to the precipitation of an orange solid, which decomposed in diethyl ether during workup.

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Table 1. Selected Calculated Bond Lengths (Å) and Angles (deg) of **1**, $[Cr(N_3N)]^-$, and **2** at the RI-BP86/TZVPP Level of Theory[a]

	1		$[Cr(N_3N)]^-$	**2**	
	calcd	expt	calcd	calcd	expt
Cr−N1	1.889	1.870(3)	2.011	1.958	1.988(2)
Cr−N2	1.889	1.886(3)	2.024	2.083	2.063(2)
Cr−N3	1.889	1.874(3)	2.031	2.098	2.077(2)
Cr−N4	2.329	2.243(3)	2.358	2.282	2.251(2)
N1−Cr−N2	118.5	118.8(2)	118.8	124.8	124.94(9)
N1−Cr−N3	118.6	118.6(2)	129.3	132.4	131.78(9)
N2−Cr−N3	118.7	119.6(2)	105.6	98.3	99.46(8)
N1−Cr−N4	83.1	83.8(2)	82.2	83.7	84.03(8)
N2−Cr−N4	83.1	84.5(2)	82.1	83.0	83.38(7)
N3−Cr−N4	83.1	84.4(2)	80.7	82.7	83.43(8)

[a] The experimental values of **1** and **2** are also listed for comparison reasons.

the vacant coordination site. Coordination of the nitrogen atoms N2 and N3 to sodium reduces the local symmetry of the CrN_3N core from C_3 to C_1 and is accompanied by a pyramidalization of the bridging amide groups, a reduction of the N2−Cr−N3 angle to 99.46(8)° (cf. N1−Cr−N2 = 124.94(9)°, N1−Cr−N3 = 131.78(9)°) and an elongation of the Cr−N bonds of the bridging amide groups (Cr−N2 = 2.063(2) Å, Cr−N3 = 2.077(2) Å) with respect to the Cr−N bond of the terminal, planar amide group (Cr−N1 = 1.988(2) Å, sum of angles at N1 = 359.9°) (Table 1). The terminal $Cr-N_{amide}$ bond of **2** is considerably longer than those of **1** (1.877 Å (mean value)),[7] whereas the $Cr-N_{amine}$ bond length of **2** (2.251(2) Å) compares well with that of **1** (2.243(3) Å). Density functional theoretical calculations of **1**, **2**, and the anion $[Cr(N_3N)]^-$ were carried out at the RI-BP86/TZVPP level of theory to rationalize these structural trends (Supporting Information). Complex **1** was found to have a quartet ground state with C_3 symmetry, and $[Cr(N_3N)]^-$ and **2** have a quintet ground state with C_1 symmetry in full agreement with the experimental results (vide supra).[7] The lowest energy doublet excited state of **1** and triplet excited states of $[Cr(N_3N)]^-$ and **2** are 56.7, 89.5, and 95.3 kJ mol^{-1} higher in energy than the ground states, respectively. The geometrical parameters of the optimized minimum structures compare reasonably well with the experimental values (Table 1).

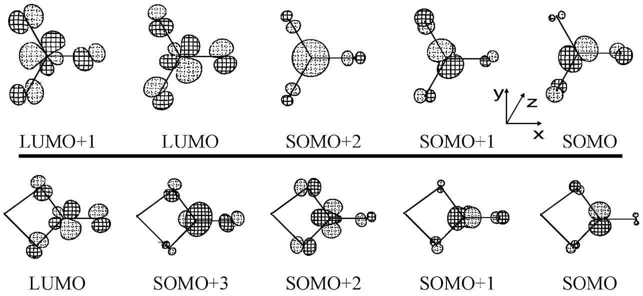

Figure 2. Frontier orbitals of **1** (top) and **2** (bottom) from extended Hückel calculations on the RI-BP86/TZVPP optimized structures.

The frontier orbitals of **1** are a pair of almost degenerate metal-based (mainly d_{xz} and d_{yz}) singly occupied molecular orbitals (SOMO, SOMO + 1), a metal-based (mainly d_{z^2}) singly occupied molecular orbital at higher energy (SOMO + 2), and a pair of degenerate LUMOs, resulting from the σ/π antibonding interaction of the metal d_{xy} and $d_{x^2-y^2}$ orbitals with the lone-pair orbitals of the N_{amide} atoms (Figure 2). Addition of one electron to **1** to give $[Cr(N_3N)]^-$ occurs at one of the degenerate LUMOs and causes a Jahn−Teller distortion, which lifts the degeneracy of the $d_{xy}/d_{x^2-y^2}$-based orbitals upon reduction of the N2−Cr−N3 angle from 118.7° (**1**) to 105.6°, and decreases thereby the energy of the corresponding SOMO ($d_{x^2-y^2}$ orbital). Coordination of $[Na(THF)_2]^+$ to the C_1 symmetric anion $[Cr(N_3N)]^-$ to give **2** mainly enforces the distortion by further reduction of the N2−Cr−N3 angle to 98.3° (Table 1), and shifts the $d_{x^2-y^2}$-based orbital (SOMO + 2) to even lower energy than the d_{z^2}-based orbital (SOMO + 3, Figure 2). Occupation of the $d_{x^2-y^2}$-based orbital with one electron in $[Cr(N_3N)]^-$ and **2** causes an elongation of the $Cr-N_{amide}$ bonds (cf. with **1**, Table 1) due to the $Cr-N_{amide}$ antibonding character of this orbital. Similarly, the presence of one electron in the d_{z^2}-based orbital, that is antibonding with respect to the $Cr-N_{amine}$ linkage, provides a rationale for the long $Cr-N_{amine}$ bonds of **1**, **2**, and the anion $[Cr(N_3N)]^-$ (Table 1, Figure 2).

Analogous molybdenum(II) and tungsten(II) triamidoamine complexes with **2** are presently unknown, underlining the peculiarity of chromium among the group 6 elements. Efforts are continued to uncover new reaction modes of chromium triamidoamine complexes.

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Supporting Information Available: Experimental section including the synthesis and characterization of **2**. Figure showing the ^1H NMR spectrum of **2**. X-ray crystallographic files in CIF format for **2**. Details of DFT and extended Hückel calculations. This material is available free of charge via the Internet at http://pubs.acs.org. The crystallographic data of **2** have also been deposited with the Cambridge Crystallographic Data Center under the file number CCDC-212962. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax (+44)1223−336033, e-mail deposit@ccdc.cam.ac.uk).

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