

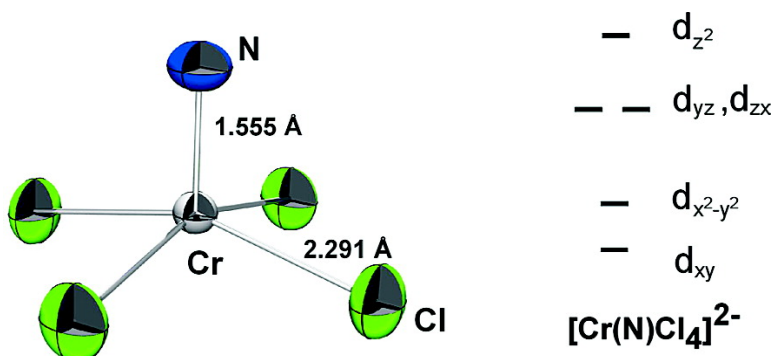
Communication

**[Cr(N)Cl<sub>4</sub>]: A Simple Nitrido Complex Synthesized by Nitrogen-Atom Transfer**

Jesper Bendix

*J. Am. Chem. Soc.*, **2003**, 125 (44), 13348-13349 • DOI: 10.1021/ja0371000 • Publication Date (Web): 09 October 2003

Downloaded from <http://pubs.acs.org> on March 30, 2009



**More About This Article**

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 6 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

## [Cr(N)Cl<sub>4</sub>]<sup>2-</sup>: A Simple Nitrido Complex Synthesized by Nitrogen-Atom Transfer

Jesper Bendix\*

Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100, Denmark

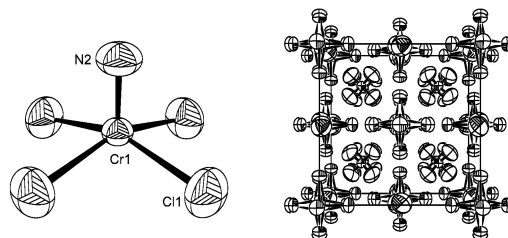
Received July 7, 2003; E-mail: bendix@kiku.dk

Contrary to almost all other ligands, the nitrido ligand (N<sup>3-</sup>) has a much more developed chemistry of second and third row transition metal (TM) ions than of first row TM ions.<sup>1</sup> The existing nitrido chemistry of the first row TM elements is largely confined to systems with a coordination sphere completed by polydentate ligands. Examples include Schiff-bases,<sup>2</sup> porphyrins,<sup>3</sup> corroles,<sup>4</sup> phthalocyanine,<sup>5</sup> as well as the spectroscopically more innocent tacn and cyclam from Wieghardt et al.<sup>6</sup> The prevalence of polydentate ligands in this chemistry arises from the synthetic routes, which require quite forceful conditions (photolysis of azido complexes by UV radiation or treatment with OCl<sup>-</sup>/NH<sub>3</sub>). These conditions are incompatible with monodentate ligands, and although the systems [M(N)(CN)<sub>4</sub>]<sup>2-</sup> and [M(N)(CN)<sub>5</sub>]<sup>3-</sup> (M = Cr, Mn)<sup>7</sup> represent notable exceptions to the above generalizations, they are from a synthetic point of view as much dead ends as the systems with polydentate ligands. In the search for a synthetic route applicable to systems with more labile coordination spheres, the nitrogen-atom transfer reactions described by Bottomley and Neely<sup>8</sup> and independently by Woo et al.<sup>9</sup> attracted our interest. These authors have shown that it is possible to transfer a terminal nitrido ligand from manganese(V) nitrido porphyrins to Mn(III) as well as to Cr(III) porphyrin systems. These studies were later extended by Neely and Bottomley<sup>8c</sup> and by Gray et al.<sup>10</sup> to encompass N-atom transfer between Schiff-base complexes.

To further generalize the N-atom transfer, and with the aim of turning it into a tool for synthesis, reaction with various substrates having only labile ligands was attempted. Letting violet CrCl<sub>3</sub>·(THF)<sub>3</sub> react with green Mn<sup>V</sup>(N)(salen) results in a fast reaction yielding yellow-brown solutions. An EPR spectrum of such a reaction mixture shows an intense broad featureless absorption around *g* = 1.98 indicative of Cr(V). When acetonitrile was chosen as solvent for the reaction, [Mn<sup>III</sup>(salen)(Cl)]·(CH<sub>3</sub>CN) precipitates and can be filtered off nearly quantitatively. The resulting solution is an excellent source of the {Cr≡N}<sup>2+</sup> moiety. Addition of N(CH<sub>3</sub>)<sub>4</sub>Cl or N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>Cl·H<sub>2</sub>O to this solution causes precipitation of bright yellow crystals shaped like octahedra and of size up to several millimeters.<sup>11</sup> The products [N(CH<sub>3</sub>)<sub>4</sub>]<sub>2</sub>[Cr(N)Cl<sub>4</sub>]·H<sub>2</sub>O (**1**) and [N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>]<sub>2</sub>[Cr(N)Cl<sub>4</sub>] (**2**) are stable for months in the solid when dry, but they are hydrolyzed by moisture and turn green in hours when left in the atmosphere. Compounds **1** and **2** are insoluble in acetone and less polar solvents. In acetonitrile and CH<sub>3</sub>NO<sub>2</sub>, **2** is quite soluble, but **1** is almost insoluble. Both salts are soluble in the lower alcohols and water where they undergo solvolysis.

The crystal structure of **1** is shown in Figure 1.<sup>12</sup> [Cr(N)Cl<sub>4</sub>]<sup>2-</sup> is accommodated in the cubic structure by a slight displacement from *m-3m* positions resulting in systematic disorder with six different orientations. The Cr–N bond length of 1.555(19) Å lies within the range observed for Cr<sup>v</sup>–nitrido bonds.<sup>6,7</sup>

UV–vis and MCD spectra of [Cr(N)Cl<sub>4</sub>]<sup>2-</sup> are shown in Figure 2. The low-energy, low intensity absorption band at 12 900 cm<sup>-1</sup> is the d<sub>xy</sub> → d<sub>x<sup>2</sup>-y<sup>2</sup></sub> transition and involves thus only orbitals which

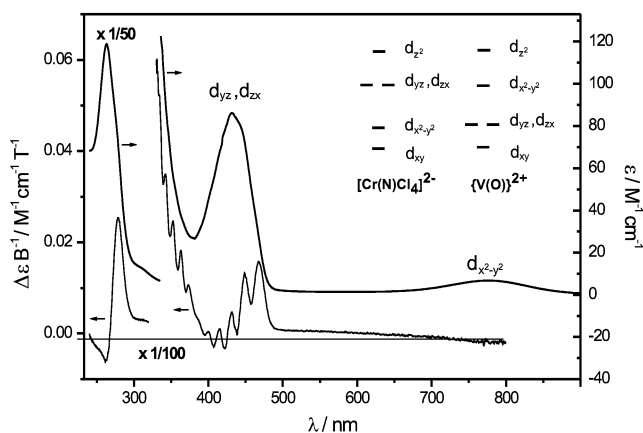


**Figure 1.** Structure of the [Cr(N)Cl<sub>4</sub>]<sup>2-</sup> anion with 35% probability ellipsoids and the crystal packing in **1**. All positions of the disordered anion and the disordered water molecule are shown in the packing, but hydrogens are omitted. Bond lengths: Cr–N, 1.555(19) Å, Cr–Cl, 2.2912(16) Å; N–Cr–Cl 101.24(4)°.

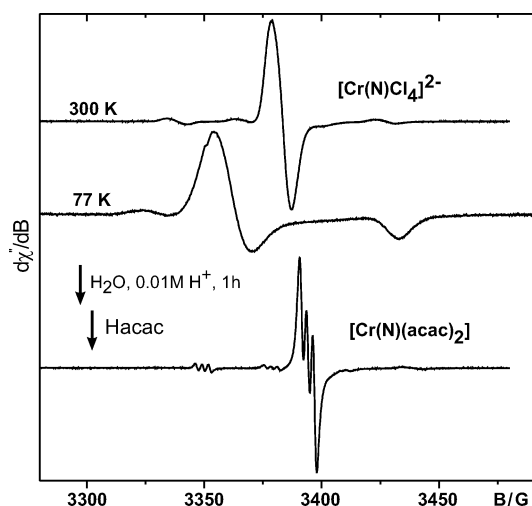
interact with the chloride ligands. Its low intensity agrees with it being the only dipole forbidden d–d transition in C<sub>4v</sub> symmetry. Two factors contribute to the low energy of this absorption (even lower than Δ = 13 800 cm<sup>-1</sup> in CrCl<sub>3</sub>).<sup>13</sup> There is a reduction in σ-overlap with the chloride ligands of ca. 7% due to the chromium being displaced out of the Cl<sub>4</sub>-plane.<sup>14</sup> Second, the charge on the formally chromium(V) center, as calculated by DFT, is close to +0.7, and on N it is as high as –0.3.<sup>15</sup> The chlorides may thus be considered ligands to the {Cr≡N}<sup>2+</sup> unit rather than to a Cr(V) center, justifying their low spectrochemical parameters.

The next absorption band is the excitation to the degenerate set of π-antibonding orbitals {d<sub>xz</sub>, d<sub>yz</sub>}. The weakening of the Cr–N bond is evident by a vibronic progression barely detectable in the absorption spectrum, but clear in the MCD spectrum. The spacing of the lines is not completely equidistant. It varies between 810 and 906 cm<sup>-1</sup> with a clear tendency toward smaller spacing at higher energies. This variation may be due to anharmonicity. The spacing, which is a measure of the vibrational frequency in the excited state, is comparable to the values of 880 cm<sup>-1</sup> found for [Cr(N)(CN)<sub>4</sub>]<sup>2-</sup> and 876 cm<sup>-1</sup> for matrix-isolated Fe<sup>V</sup>(N) systems.<sup>7a,16</sup> The excitation to d<sub>z<sup>2</sup></sub> is obscured by a LMCT (Cl to Cr, ε = 5950 M<sup>-1</sup> cm<sup>-1</sup>), but a weak shoulder (λ = 310 nm, ε ≈ 600 M<sup>-1</sup> cm<sup>-1</sup>) may be a possible assignment. The extreme orbital splitting scheme derived from Figure 2 is distinctly different from that applicable to vanadyl complexes and to other chromium and manganese nitrido complexes with stronger field equatorial ligands.<sup>6,7</sup> In [Cr(N)Cl<sub>4</sub>]<sup>2-</sup>, the π perturbation from the nitrido ligand dominates the σ perturbation from the chloride ligands. The appropriate reference geometry for [Cr(N)Cl<sub>4</sub>]<sup>2-</sup>, which has both δ(C<sub>∞v</sub>) orbitals energetically far below the π(C<sub>∞v</sub>) and σ(C<sub>∞v</sub>) orbitals, is, thus, linear geometry rather than a distorted octahedron.

When redissolved, the complexes show characteristic Cr(V) EPR spectra with a single resonance close to *g* = 2 surrounded by a low intensity quartet of hyperfine lines arising from the 9.5% <sup>53</sup>Cr with *I* = 3/2 (cf. Figure 3). The superhyperfine coupling to the terminal nitrido ligand is not resolved, probably due to broadening arising from the nuclear spin of the chlorine nuclei (*I* = 3/2, 100%). The EPR spectrum of a frozen solution yields the *g*-anisotropy as



**Figure 2.** UV-vis (top) and MCD (bottom) spectra of **2** in  $\text{CH}_3\text{CN}$  at room temperature.  $\lambda_{\text{max}}$  [nm] ( $\epsilon$ ) [ $\text{M}^{-1} \text{cm}^{-1}$ ]: 776 (6.8), 431 (86), 311 sh. (600), 263 (5950). The inset illustrates the difference in orbital ordering for  $[\text{Cr}(\text{N})\text{Cl}_4]^{2-}$  and vanadyl.



**Figure 3.** Top: Solution ( $\text{CH}_3\text{CN}$ ) and frozen glass ( $\text{CH}_3\text{CN}/\text{C}_3\text{H}_7\text{CN}$ ) EPR spectra of **2**. Fitted parameter values:  $g_{\text{iso}} = 1.978$ ,  $A_{\text{iso}}^{\text{Cr}} = 3.03$  mT,  $g_{\parallel} = 1.948$ ,  $g_{\perp} = 1.993$ ,  $A_{\perp}^{\text{Cr}} = 2.20$  mT. Bottom: EPR spectrum of hydrolyzed **2** (in 0.01 M  $\text{HClO}_4$ ) with an added excess of acetylacetone. Fitted parameter values:  $g_{\text{iso}} = 1.972$ ,  $A_{\text{iso}}^{\text{Cr}} = 2.93$  mT,  $A_{\text{iso}}^{\text{N}} = 0.27$  mT.

well as the hyperfine coupling constant in the perpendicular direction  $A_{\perp}^{\text{Cr}}$ . The  $g$ -anisotropy is the largest one observed for any  $\text{Cr}(\text{V})$ -nitrido complex<sup>7b,17</sup> in good agreement<sup>18</sup> with the large splitting between  $d_{x^2-y^2}$  and  $\{d_{zx}, d_{yz}\}$ .

When the  $[\text{Cr}(\text{N})\text{Cl}_4]^{2-}$  ion is hydrolyzed for 1 h, an EPR spectrum (not shown) of the resulting pale green solution shows a distinctly shifted  $g$ -value (1.964), but is otherwise similar to that of the chloro complex, with no superhyperfine coupling resolved. When the EPR-active species is assumed to be an aqua complex, this could be due to broadening from the nuclear spin of the hydrogens in coordinated water molecules. An alternative explanation could be that the nitrido ligand was hydrolyzed off by the treatment to yield an oxo chromium(V) complex. However, addition of acetylacetone to the solution from the hydrolysis reaction produces a more intensely green solution with an EPR spectrum featuring a well-resolved superhyperfine triplet, unequivocally demonstrating the presence of the nitrido ligand. This spectrum,

which has the same integrated intensity as that of the chloro complex immediately after dissolution, demonstrates the stability of the  $\{\text{Cr}\equiv\text{N}\}^{2+}$  unit toward hydrolysis. Simultaneously, it hints at the preparative scope of this chemistry.

Work in progress has established this procedure to be applicable to the synthesis and isolation of  $\text{Cr}(\text{V})$  nitrido complexes with a wide variety of ligands including phosphines, pyridines, thiocyanate, water, dithiocarbamates, and amines.

**Acknowledgment.** Aid in crystallographic work by Scott R. Wilson and discussions with C. E. Schäffer are greatly appreciated.

**Supporting Information Available:** Crystallographic data for **1** in CIF format. Magnetic susceptibility data at 4–300 K for **1** and **2**. IR spectra of **1** and **2** and Raman spectrum of **1**. Details of the DFT calculations (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) (a) Griffith, W. P. *Coord. Chem. Rev.* **1972**, *8*, 369. (b) Dehnicke, K.; Straehle, J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 955. (c) Che, C.-M. *Pure Appl. Chem.* **1995**, *67*, 225. (d) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; John Wiley & Sons: New York, 1988.
- (2) (a) Arshankow, S. I.; Poznjak, A. L. *Z. Anorg. Allg. Chem.* **1981**, *481*, 201. (b) Du Bois, J.; Hong, J.; Carreira, E. M.; Day, M. W. *J. Am. Chem. Soc.* **1996**, *118*, 915. (c) Du Bois, J.; Tomooka, C. S.; Hong, J.; Carreira, E. M. *Acc. Chem. Res.* **1997**, *30*, 364.
- (3) Groves, J. T.; Takahashi, T. *J. Am. Chem. Soc.* **1983**, *105*, 2073.
- (4) Golubkov, G.; Bendix, J.; Gray, H. B.; Mahammed, A.; Goldberg, I.; DiBilio, A. J.; Gross, Z. *Angew. Chem., Int. Ed.* **2001**, *40*, 2132.
- (5) Grunewald, H.; Homborg, H. *Z. Naturforsch., B* **1990**, *45*, 483.
- (6) (a) Niemann, A.; Bossek, U.; Haselhorst, G.; Wieghardt, K.; Nuber, B. *Inorg. Chem.* **1996**, *35*, 906. (b) Meyer, K.; Bendix, J.; Metzler-Nolte, N.; Weyhermüller, T.; Wieghardt, K. *J. Am. Chem. Soc.* **1998**, *120*, 7260. (c) Meyer, K.; Bendix, J.; Bill, E.; Weyhermüller, T.; Wieghardt, K. *Inorg. Chem.* **1998**, *37*, 5180.
- (7) (a) Bendix, J.; Meyer, K.; Weyhermüller, T.; Bill, E.; Metzler-Nolte, N.; Wieghardt, K. *Inorg. Chem.* **1998**, *37*, 1767. (b) Bendix, J.; Deeth, R. J.; Weyhermüller, T.; Bill, E.; Wieghardt, K. *Inorg. Chem.* **2000**, *39*, 930.
- (8) (a) Bottomley, L. A.; Neely, F. L. *Inorg. Chem.* **1997**, *36*, 5435. (b) Bottomley, L. A.; Neely, F. L. *J. Am. Chem. Soc.* **1989**, *111*, 5955. (c) Neely, F. L.; Bottomley, L. A. *Inorg. Chim. Acta* **1992**, *192*, 147.
- (9) Woo, L. K.; Goll, J. G.; Czapla, D. J.; Hays, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 8478.
- (10) Chang, C. J.; Low, D. W.; Gray, H. B. *Inorg. Chem.* **1997**, *36*, 270.
- (11) All manipulations were performed under  $\text{N}_2$  to exclude moisture.  $\text{CrCl}_3 \cdot (\text{THF})_3$  (1.30 g, 3.47 mmol) was dissolved in  $\text{CH}_3\text{CN}$  (30 mL).  $\text{Mn}(\text{N})$ -(salen) (1.20 g, 3.58 mmol) was added, and the suspension immediately changed color from violet to yellow-brown. After the mixture was stirred for 1 h, brown  $[\text{Mn}(\text{Cl})(\text{salen})](\text{CH}_3\text{CN})$  (1.4 g, 3.5 mmol) was filtered off. To the resulting solution was added  $[(\text{CH}_3)_4\text{N}]\text{Cl}$  (Fluka) (1.6 g, 14 mmol) in  $\text{CH}_3\text{CN}/\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}$  (15:14:1) (30 mL) causing immediate precipitation of yellow **1**, which was filtered off, washed with  $\text{CH}_3\text{CN}$ , and dried. Yield 0.92 g (71%). Anal. Calcd for  $\text{C}_8\text{H}_8\text{N}_2\text{OCl}_2\text{Cr}$ : C, 25.68; H, 7.00; N, 11.23; Cl, 37.91. Found: C, 26.49; H, 6.89; N, 11.64; Cl, 37.08. Magnetic susceptibility by the Faraday method yielded  $\mu_{\text{eff}}$  varying from 1.69 (4 K) to 1.90  $\mu_{\text{B}}$  (300 K).  $\nu(\text{Cr}-\text{N})$  1009  $\text{cm}^{-1}$  (IR), 1008  $\text{cm}^{-1}$  (Raman). **2** was prepared by the same method adding  $[(\text{C}_2\text{H}_5)_4\text{N}]\text{Cl}$  (Aldrich) (2.5 g 14 mmol) directly to the filtrate and reducing the volume to 10 mL and cooling to 5 °C. Yield 0.84 g (52%) of large yellow crystals, which were washed with acetone/water (20:1). Anal. Calcd for  $\text{C}_{16}\text{H}_{40}\text{N}_3\text{Cl}_4\text{Cr}$ : C, 41.03; H, 8.61; N, 8.97; Cr, 11.10. Found: C, 40.73; H, 8.75; N, 8.81; Cr, 10.92.  $\mu_{\text{eff}}$  varies from 1.69 (4 K) to 1.79  $\mu_{\text{B}}$  (300 K).  $\nu(\text{Cr}-\text{N})$  1007  $\text{cm}^{-1}$  (IR).
- (12) Crystallographic data for **1**:  $\text{C}_8\text{H}_8\text{N}_2\text{OCl}_2\text{Cr}$ , cubic,  $Fm-3m$ , yellow octahedra,  $a = 12.3488(14)$  Å,  $Z = 4$ ,  $T = 122$  K,  $R = 0.0703$  ( $F^2 > 2\sigma$ ),  $wR2 = 0.2184$ ,  $\text{GOF} = 1.195$ .
- (13) Schäffer, C. E.; Jørgensen, C. K. *J. Inorg. Nucl. Chem.* **1958**, *8*, 143.
- (14) Based on a simple angular overlap model calculation.
- (15) Mulliken charges calculated with ADF version 2002.03, TZ2P basis. Functionals: LDA, VWN; GGA, Becke-Perdew.
- (16) Wagner, W.-D.; Nakamoto, K. *J. Am. Chem. Soc.* **1988**, *110*, 4044.
- (17) Hori, A.; Ozawa, T.; Yoshida, H.; Imori, Y.; Kuribayashi, Y.; Nakano, E.; Azuma, N. *Inorg. Chim. Acta* **1998**, *281*, 207.
- (18) Hare, C. R.; Bernal, I.; Gray, H. B. *Inorg. Chem.* **1962**, *1*, 831.

JA0371000