

Atom Transfer as a Preparative Tool in Coordination Chemistry. Synthesis and Characterization of Cr(V) Nitrido Complexes of Bidentate Ligands

Torben Birk and Jesper Bendix*

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

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The transfer of a terminal nitrido ligand from Mn^V(N)(salen) to Cr(III) complexes is explored as a new preparative route to Cr^V nitrido complexes. Reaction of Mn^V(N)(salen) with labile CrCl₃(THF)₃ in acetonitrile solution precipitates [Mn(Cl)(salen)]·(CH₃CN) and yields a solution containing a mixture of Cr^V nitrido species with only labile auxiliary ligands. From this solution Cr^V nitrido complexes with bidentate monoanionic ligands can be obtained in high yields. Five coordinate complexes of 8-hydroxyquinolate (quin), 1,3-diphenylpropane-1,3-dionate (dbm), and pyrrolidinedithiocarbamate (pyr-dtc) have been structurally characterized: Cr(N)(quin)₂ (**1**) crystallizes as compact orange prisms in the triclinic space group *P* $\bar{1}$ with cell parameters $a = 7.2450(6)$ Å, $b = 8.1710(4)$ Å, $c = 13.1610(12)$ Å, $\alpha = 80.519(6)^\circ$, $\beta = 75.721(7)^\circ$, $\gamma = 75.131(5)^\circ$, $V = 725.47(10)$ Å³, $Z = 2$. Cr(N)(dbm)₂ (**2**) crystallizes as green rhombs in the orthorhombic space group *Pbca* with cell parameters $a = 14.6940(6)$ Å, $b = 16.4570(18)$ Å, $c = 19.890(3)$ Å, $V = 4809.8(8)$ Å³, $Z = 8$. Cr(N)(pyr-dtc)₂ (**3**) crystallizes as orange prisms in the monoclinic space group *P21/c* with cell parameters $a = 14.8592(14)$ Å, $b = 8.5575(5)$ Å, $c = 11.8267(12)$ Å, $\beta = 106.528(7)^\circ$, $V = 1441.7(2)$ Å³, $Z = 4$. Complexes **2** and **3** represent new coordination environments for first row transition metal nitrido complexes. The d-orbital energy splitting in these systems with relatively weak equatorial donors differs significantly from the pattern in vanadyl and the previously known first row transition metal nitrido complexes. The d_{x²-y²} orbital in **2** and **3** is lower in energy and well resolved from the M–N π^* orbitals {d_{zx}, d_{yz}}.

Introduction

Atom- and group-transfer reactions are central to the chemistry of metal complexes with multiply bonded ligands. This is true for biological oxo-transfer reactions catalyzed by metalloenzymes¹ as well as for the reactivity of simple oxo-complexes toward organic substrates exemplified by the epoxidation with manganese(III) catalysts developed by Jacobsen and others.² The possibility of transferring a nitrogen atom between metal centers was discovered some 20 years ago by Bottomley and Neely, who found that the transfer of a nitrido ligand between Mn(V) and Cr(III) as well as between Mn(V) and Mn(III) is possible.³ All of the systems investigated by these authors contained porphyrin

ligands. This area was further developed by Woo et al. and the mechanistic details of the transfer reaction were clarified.⁴ The nitrogen atom transfer reaction was extended to Schiff-base complexes of manganese by Gray et al.⁵ Recently, nitrogen atom transfer chemistry has received considerable attention fueled by the facile preparation of [Mn(N)(salen)] developed by Carreira and the demonstration that this compound when activated by (CF₃CO)₂O allows stoichiometric aziridination of electron-rich olefins.^{6,14} With a few exceptions the studies of nitrogen atom transfer reactions have been fundamental, aiming at elucidating the mechanism and thermodynamics of the reactions and not exploring the preparative potential of this type of reactions.

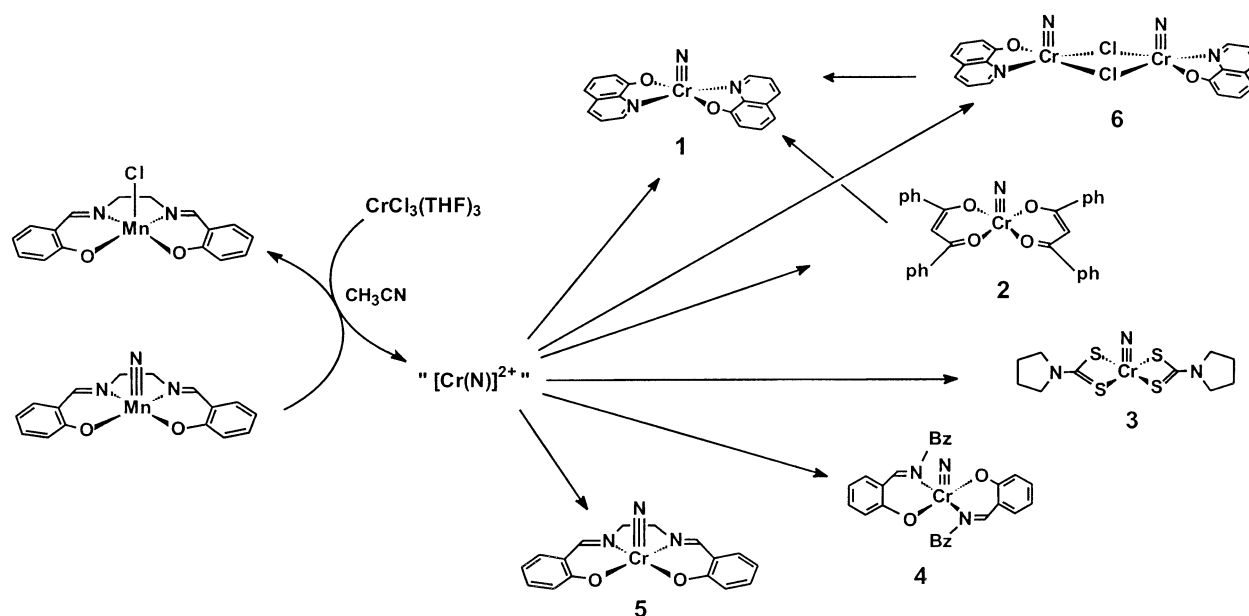
Common to the known nitrido complexes of Cr(V) is that they feature polydentate ligands (cyclam,⁷ tacn,⁸ porphyrins,⁹

* Author to whom correspondence should be addressed. E-mail: Bendix@kiku.dk.

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Scheme 1. Schematic Representation of the Synthetic Routes to the Nitrido Chromium(V) Complexes and the Labeling Scheme

salen¹⁰), the only exceptions being the tetra- and pentacyanonitridochromates.^{11,12} This is a consequence of the methods of preparation which have been either photolysis of Cr(III) azido complexes⁹ or ClO^- oxidation in the presence of NH_3 .⁵ These harsh conditions prevent synthesis of Cr(N) complexes which do not have a robust auxiliary coordination sphere. In this paper we present a protocol involving nitrogen atom transfer from Mn(N)(salen) to $CrCl_3(THF)_3$ yielding (a mixture of) Cr(V)(N) species with a very labile coordination sphere, from which a wide variety of chromium(V) nitrido complexes can be obtained. Here we exemplify the synthetic usefulness of the method by synthesizing and characterizing complexes with bidentate auxiliary ligands including the novel coordination environments $Cr(N)\{O\}_4$ and $Cr(N)\{S\}_4$.

Experimental Section

Materials. The compounds $CrCl_3(THF)_3$,¹³ $Mn(N)(salen)$,¹⁴ N,N' -ethylenebis(salicylideneamine)¹⁵ (salen), and 2-benzyliminomethylphenol were prepared by literature or standard procedures. $Mn(N)(salen)$ was purified by Soxhlet extraction with CH_2Cl_2 before use. Dibenzoylmethane (1,3-diphenylpropane-1,3-dione) 98% (Aldrich), 8-hydroxyquinoline 99+% (Aldrich), and ammonium-pyrrolidinedithiocarbamate (Merck) were used as received. All solvents used, acetonitrile (Lab-Scan), diethyl ether (Lab-Scan), and N -

methylformamide >99% (Merck-Schuchardt), were HPLC grade and were used without further purification.

Atom Transfer Reaction. The following procedure (cf. Scheme 1) was used for preparing the solution containing $\{Cr\equiv N\}^{2+}$ complexed by labile auxiliary ligands: $CrCl_3(THF)_3$ (0.906 g; 2.42 mmol) was dissolved in acetonitrile (20 mL) to give a purple solution. Addition of solid $Mn(N)(salen)$ (0.810 g; 2.42 mmol) was accompanied by an immediate color change to yield a dark brown solution with suspended solid material. The reaction mixture was stirred for 30 min under a N_2 atmosphere and filtered to give a dark brown crystalline precipitate and a yellow-brown solution (**sol. A**). The brown product was isolated and analyzed showing it to be essentially pure $Mn(Cl)(salen)\cdot CH_3CN$ (Anal. Calcd for $C_{18}H_{17}N_3O_2\cdot ClMn$ C, 54.36; H, 4.31; N, 10.56; Mn, 13.81; Cl, 8.92. Found C, 53.88; H, 4.23; N, 10.75; Mn, 12.99; Cl, 8.42). MS, FAB+: m/z 321 ($[Mn(salen)]^+$). In some preparations, improved yields were obtained by using an excess of manganese nitrido complex. In those cases, a 1:2 stoichiometry of Cr to Mn was realized by using 1.21 mmol of $CrCl_3(THF)_3$ as the only difference to the above procedure (**sol. B**).

Synthesis of Nitridobis(8-hydroxyquinoline)chromium(V) (1). A solution of 8-hydroxyquinoline (0.720 g; 4.832 mmol) in acetonitrile (6 mL) was added to **sol. B**, resulting in the immediate precipitation of an orange-brown crystalline product. The reaction mixture was stirred for 15 min and the product collected by filtration. The product was washed with H_2O (5×5 mL), H_2O/NMF (3:2; 1×5 mL), methanol (6×5 mL), and diethyl ether (1×5 mL). Yield: 0.318 g (75%). The product was recrystallized from boiling acetonitrile (200 mL) to give large orange-red crystals. Anal. Calcd for $C_{18}H_{12}N_3O_2Cr$: C, 61.02; H, 3.41; N, 11.86; Cr, 14.68. Found: C, 61.01; H, 3.27; N, 11.88; Cr, 13.96. MS, FAB+: m/z 355 ($\{M+H\}^+$, rel intensity 15%). EI: m/z 354 (M^+ , rel intensity 100%). IR: $\nu(Cr-N)$ 1015 cm^{-1} (vs). UV-vis (CH_2Cl_2 , room temperature), λ_{max} [nm] (ϵ) [$M^{-1} cm^{-1}$]: 403 (4080), 334 (1270), 315 (1670), 304 (1690), 264 (36000).

Synthesis of Nitridobis(1,3-diphenylpropane-1,3-dionate)chromium(V) (2). A solution of dibenzoylmethane (0.542 g, 2.42 mmol) in acetonitrile (4 mL) was added slowly to stirred **sol. B**, with immediate formation of a green precipitate. The reaction

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mixture was stirred for further 15 min, and the product was collected by filtration and washed with diethyl ether (2 × 5 mL), methanol (1 × 5 mL), and diethyl ether (2 × 5 mL). Yield: 0.315 g (51%). The product was recrystallized from a boiling mixture (240 mL) of toluene and *n*-heptane (2:1) giving green crystals (0.226 g, overall 37%). Anal. Calcd for C₃₀H₂₂NO₄Cr: C, 70.31; H, 4.33; N, 2.73; Cr, 10.15. Found: C, 70.08; H, 4.22; N, 2.69; Cr, 10.09. MS, FAB⁺: *m/z* 513 ({M + H}⁺, rel intensity 3%). EI: not observed. IR: $\nu(\text{Cr-N})$ 1007 cm⁻¹(s). UV-vis (CH₂Cl₂, room temperature), λ_{max} [nm] (ϵ) [M⁻¹ cm⁻¹]: 595 (26.4), 469 sh (93.3), 359 (37100), 271 (31500).

Synthesis of Nitridobis(pyrrolidinedithiocarbamate)chromium(V) (3). A solution of ammoniumpyrrolidinedithiocarbamate (0.986 g, 6.00 mmol) in methanol (70 mL) was added to stirred **sol. A**, resulting in immediate precipitation. The brown product was filtered off and washed repeatedly with cold methanol. The crude product was dissolved in CH₂Cl₂ (50 mL) and reprecipitated by dropwise addition of methanol (100 mL). Overall yield: 0.612 g (71%) of golden-brown plates. Anal. Calcd for C₁₆H₁₀N₃S₄Cr: C, 33.50; H, 4.50; N, 11.72; Cr, 14.50. Found: C, 33.46; H, 4.44; N, 11.52%. Cr, 13.96%. MS, FAB⁺: not observed; EI: *m/z* = 344 ({M - N}⁺, rel intensity 30%). IR: $\nu(\text{Cr-N})$ 991 cm⁻¹(vs). UV-vis (CH₂-Cl₂, room temperature), λ_{max} [nm] (ϵ) [M⁻¹ cm⁻¹]: 548 (54.5), 446 (221), 432 sh (212), 276 (17400). The procedure is applicable to a range of common dialkyldithiocarbamate ligands.

Synthesis of Nitridobis(2-benzyliminomethylphenolato)chromium(V) (4). To stirred **sol. A** was added dropwise a solution of 2-benzyliminomethyl-phenol (2.114 g, 10.0 mmol) in acetonitrile (3 mL). After a few minutes crystallization commenced. The reaction mixture was cooled to 5 °C and the product consisting of red-brown needles was collected by filtration and washed repeatedly with methanol. Yield 0.81 g (69%). Anal. Calcd for C₂₈H₂₄N₃O₂-Cr: C, 69.13; H, 4.97; N, 8.64; Cr, 10.69. Found: C, 69.20; H, 4.97; N, 8.75; Cr, 10.33. MS, EI: *m/z* 486 (M⁺, rel intensity 25%). IR: $\nu(\text{Cr-N})$ 1016 cm⁻¹ (s). UV-vis (CH₂Cl₂, room temperature), λ_{max} [nm] (ϵ) [M⁻¹ cm⁻¹]: 552 (26.1), 362 (8400), 269 sh (24500).

Synthesis of Nitrido[N,N'-ethylenebis(salicylideneaminato)]chromium(V) (5). Stirred **sol. A** was heated to 70 °C and a solution of salen (0.648 g; 2.42 mmol) in acetonitrile (30 mL) was added dropwise. The hot solution was filtered and placed at 5 °C for 12 h. Precipitation of red crystals commenced after 30 min. The product was filtered off and washed by the mother liquor and methanol (4 × 10 mL). Yield: 0.147 g (18%). Anal. Calcd for C₁₆H₁₄N₃O₂Cr: C, 57.83; H, 4.25; N, 12.65. Found: C, 57.60; H, 4.15; N, 12.60. IR: $\nu(\text{Cr-N})$ 1011 cm⁻¹(s). The EPR spectrum was identical with the one reported in the literature.¹⁰

Synthesis of [Chloronitrido(8-hydroxyquinolinate)chromium(V)] Di- or Polymer (6). Dropwise addition over 15 min of a solution of 8-hydroxyquinoline (175 mg, 1.21 mmol) in acetonitrile (6 mL) to **sol B** resulted in formation of a green precipitate. The product was filtered off and washed repeatedly with H₂O, methanol, diethyl ether, and CH₂Cl₂. Yield: 37 mg (12%). Anal. Calcd for C₁₈H₁₂N₄O₂Cl₂Cr₂: C, 44.01; H, 2.46; N, 11.41. Found: C, 43.73; H, 2.39; N, 10.88. IR: $\nu(\text{Cr-N})$ 1023 cm⁻¹(vs).

Synthesis of 1 from 6. To a solution of 8-hydroxyquinoline (82 mg, 0.56 mmol) and acetonitrile (10 mL) was added solid **6** (11 mg, 0.022 mmol). The reaction mixture was boiled for ca. 5 min, converting the green suspension into an orange solution. The solution was filtered hot and cooled to deposit orange crystals. Yield 7.0 mg (44%). Anal. Found: C, 60.75; H, 3.24; N, 11.74.

Synthesis of 1 from 2. To a solution of 8-hydroxyquinoline (132 mg, 0.91 mmol) and acetonitrile (10 mL) was added **2** (30 mg, 0.059 mmol). Upon reflux for 5 min the color of the solution

changed from green to orange. Cooling of the filtered solution afforded orange crystals. Yield: 21 mg (100%). Anal. Found: C, 60.92; H, 3.25; N, 11.76.

Physical Measurements. UV/vis spectra were recorded on a Perkin-Elmer, Lambda 2 UV/vis spectrophotometer. EPR spectra were recorded on a Bruker ESP 300 equipped with a EIP 538B frequency counter and a ER035M NMR Gauss-meter. MCD spectra were recorded at room temperature on a Jasco J-710 spectropolarimeter equipped with an electromagnet providing a magnetic field of 1.6 T. The samples were measured with the field parallel and antiparallel to the light propagation direction, and the differences of these measurements are reported, thus giving an effective applied field of 3.2 T. The magnetic susceptibilities of powdered samples were measured by the Faraday method in the temperature range 50–300 K at a field strength of 1.3 T. The susceptibility data were corrected for diamagnetism by Pascal's constants. The magnetic field was calibrated with Hg[Co(NCS)].¹⁶ A more detailed description of the equipment has been published elsewhere.¹⁷ Fast atom bombardment (FAB, Xe ions, accelerated by 6 kV) and direct inlet (EI) mass spectra were recorded on a JEOL JMS-HX/HX110A tandem mass spectrometer (positive ion detection). Matrix for FAB: *m*-nitrobenzyl alcohol (*m*-NBA).

X-ray Crystallography. Crystal structure and refinement data for **1**, **2**, and **3** are summarized in Table 1. Details of the structure determinations are available in the Supporting Information. For all three compounds, all non-hydrogen atoms were refined with anisotropic temperature factors. The molecular structure diagrams were made with the ORTEP-II program.¹⁸ Crystals suitable for X-ray diffraction were obtained by the following procedures: slow evaporation of a filtered unsaturated solution of **1** in CH₂Cl₂ afforded orange prismatic X-ray quality crystals in 24 h. **2** (20 mg) was dissolved in a boiling mixture of toluene (10 mL) and heptane (5 mL). Slow cooling and partial evaporation afforded green block shaped crystals in 5 days. Complete dissolution of **3** in CH₂Cl₂ and slow evaporation over 24 h gave orange-brown prismatic crystals.

Results and Discussion

Synthesis. In agreement with the finding of Woo et al. that nitrogen atom transfer from Mn(V) to Cr(III) proceeds via a dissociative mechanism, we have found that a labile Cr(III) substrate is a prerequisite for turning N-atom transfer into a preparatively useful reaction. Labile Cr(III) complexes are scarce, but CrCl₃(THF)₃ was found to be well suited for our purpose. Addition of green [Mn(N)(salen)] to a violet solution of CrCl₃(THF)₃ in acetonitrile results in an instantaneous color change giving a yellow-brown solution and a brown precipitate of Mn(Cl)(salen)·(CH₃CN). Other Cr(III) substrates were investigated, but all were inferior to CrCl₃(THF)₃ with regard to the rate of reaction and/or the solubility in suitable solvents. The yellow-brown solution contains {Cr≡N}²⁺ complexed only by labile ligands and is an excellent precursor for the synthesis of Cr(V) nitrido complexes (Scheme 1). Here we have demonstrated the general applicability of this protocol by synthesizing the new compounds **1–4**. In addition, we have confirmed that this thermal route extends to polydentate ligand systems by

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Table 1. Crystallographic Data for Compounds

	1	2	3
empirical formula	C ₁₈ H ₁₂ CrN ₃ O ₂	C ₃₀ H ₂₂ CrNO ₄	C ₁₀ H ₁₆ CrN ₃ S ₄
fw (g/mol)	354.31	512.49	358.51
temp (K)	122(1)	122(1)	122(1)
wavelength (Å)	0.71073	0.71073	0.71073
space group	<i>P</i> $\bar{1}$ (No. 2)	<i>Pbca</i> (No. 62)	<i>P21/c</i> (No. 14)
crystal size (mm ³)	0.351 × 0.20 × 0.120	0.261 × 0.233 × 0.223	0.28 × 0.15 × 0.14
unit cell dimensions			
<i>a</i> (Å)	7.2450(6)	14.6940(6)	14.8592(14)
<i>b</i> (Å)	8.1710(4)	16.4570(18)	8.5575(5)
<i>c</i> (Å)	13.1610(12)	19.890(3)	11.8267(12)
α (deg)	80.519(6)		
β (deg)	75.721(7)	106.528(7)	
γ (deg)	75.131(5)		
<i>V</i> (Å ³)	725.47(10)	4809.8(8)	1441.7(2)
<i>Z</i>	2	8	4
<i>d</i> _{calc} (g/cm ³)	1.622	1.415	1.652
μ (mm ⁻¹)	0.805	0.514	1.357
<i>F</i> (000)	362	2120	740
θ range for data collection (deg)	2.59–40.00	2.05–30.00	1.43–34.95
no. reflns collected	69245	193667	53523
no. of unique reflns, <i>R</i> _{int}	8981, 0.0315	7007, 0.0878	6327, 0.0374
no. of data/restraints/params	8264/0/217	5608/0/325	5383/0/163
final <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)] ^a	0.0246, 0.0709	0.0334, 0.0805	0.0308, 0.0727
final <i>R</i> ₁ , <i>wR</i> ₂ (all data) ^a	0.0287, 0.0745	0.0475, 0.0872	0.0416, 0.0793
goodness of fit on <i>F</i> ²	1.106	0.873	1.052

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR_2 = [\sum \{w(|F_o|^2 - |F_c|^2)^2\} / \sum \{w(|F_o|^2)^2\}]^{1/2}.$$

preparing the previously reported [Cr(N)(salen)] (**5**), which had previously only been obtained by photolysis of the corresponding chromium(III) azide complex.

Using a 1:1 stoichiometry between Cr(V) and 8-hydroxyquinoline allows for the isolation of a product of composition [Cr(N)(quin)Cl]_{*n*} in place of **1**. This product could be formulated as either a dimer or a chain polymer. Characterization of this species is hampered by its insolubility and a clear distinction between the di- and polymeric structures has not been achieved. However, vibrational spectroscopy shows clearly the presence of a terminal nitrido ligand (Table 4 and Supporting Information), which rules out involvement of the nitrido ligand in bridging. This finding agrees with the previously reported low nucleophilicity of the nitrido ligand in Cr^V(N) and Mn^V(N) complexes.^{11,19} The formulation of **6** as a di- or polymer is supported by its magnetic properties; there is a clear antiferromagnetic interaction in **6** (cf. Figure 1). We tentatively formulate **6** as a chloride bridged dimer (cf. Scheme 1). This accounts for the antiferromagnetism by direct overlap of the *d*_{xy} orbitals of the Cr centers. However, considering the low solubility and the intermediate magnitude of the antiferromagnetic interaction, a chloride bridged chain structure remains a possibility.

X-ray Crystallography. The molecular structures of the Cr(V)nitrido complexes **1**, **2**, and **3** have been determined from single-crystal X-ray diffraction. The structures are shown in Figures 2–4. Selected bond lengths and angles are listed in Table 2. The structures are similar, consisting of square-pyramidal five-coordinate Cr(V) centers with a short bond to the apical nitrido ligand. The equatorial coordination sphere in **1** consists of the same donor atoms ({O}₂{N}₂) as those in the known Cr(V) nitrido complexes

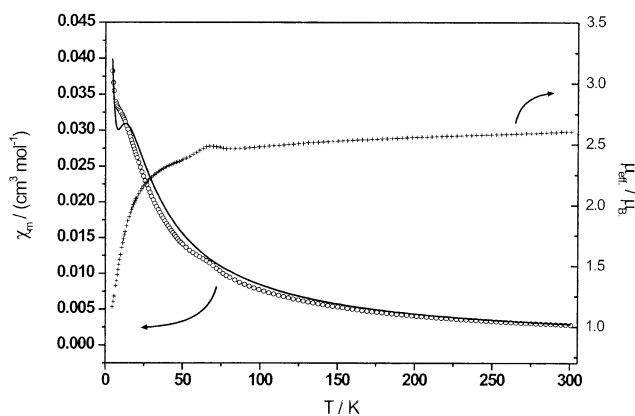


Figure 1. Temperature variation of magnetic susceptibility (○) and magnetic moment (+) of **6**. The solid line is a fit to the susceptibility ($g = 1.97$ fix; $J = -21$ cm⁻¹; $H = -2J(S_1 \cdot S_2)$). The irregularity around 60 K is due to an oxygen leak in the setup.

of tetradentate Schiff-base complexes. However, **1** differs in nature from the known systems by having the two 8-hydroxyquinolinato ligands trans oriented relative to each other leading to a system with an expected higher degree of rhombicity. The coordination environments of the chromium nitrido moiety in **2** and **3** are unprecedented in the nitrido chemistry of first row transition metals.

Crystal packing of the molecules in all three compounds is determined by shape and π -stacking of the equatorial ligands (cf. Figure 2). There are no close contacts involving the nitrido ligands. This is the most common situation, although examples exist where five-coordinate molecular nitrido complexes stack head-to-tail to form infinite chains.²⁰ The notion of isolated molecular units agrees with the completely temperature independent (50–300 K) magnetic moments measured for **1–3** (cf. Supporting Information).

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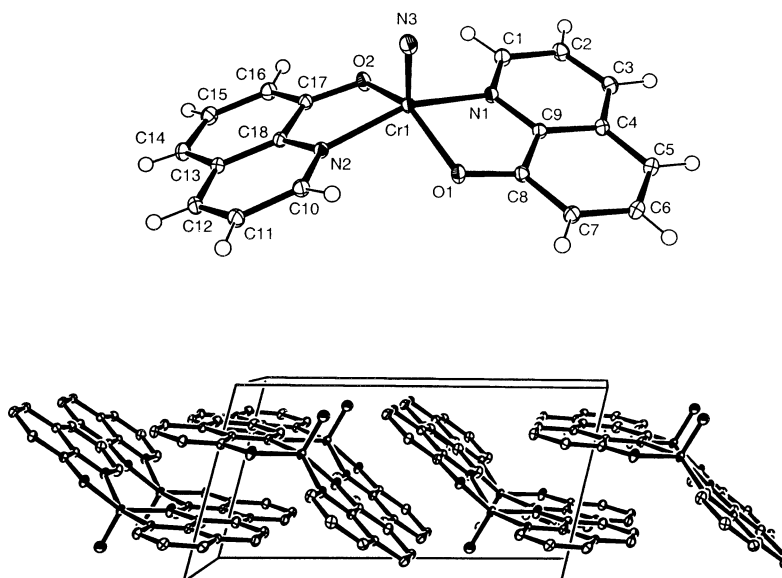


Figure 2. Top: Molecular structure and atom labeling for **1** with thermal ellipsoids (50% probability). Cf. Table 2 for metrical details. Bottom: Crystal packing in **1**.

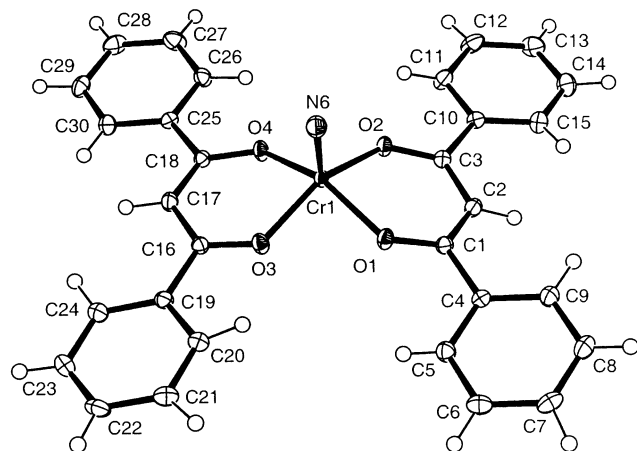


Figure 3. Molecular structure and atom labeling for **2** with thermal ellipsoids (50% probability). Cf. Table 2 for metrical details.

The Cr–N bond length in five-coordinate Cr(V) nitrido complexes is at $(1.555 \pm 0.011 \text{ \AA})$, almost independent of the nature of the remaining coordination sphere (cf. Table 3), making it justified to consider $\{\text{Cr}\equiv\text{N}\}^{2+}$ as an integrated moiety. With the large variation of the equatorial ligands encompassed by **1–3**, this is a much stronger statement than what could be concluded from existing data. Comparison with the six-coordinate systems in Table 3 shows that coordination of a sixth ligand trans to the nitrido ligand invariably elongates the Cr–N bond.

In **1** and **2** the Cr ion is displaced out of the plane of the equatorial ligands toward the nitrido ligand by ca. 0.5 \AA . This is in line with findings for other five-coordinate nitrido complexes (cf. Table 3) and a distinctly larger displacement than found in six-coordinate complexes. In **3** there is an even larger degree of pyramidalization (cf. Figure 4) leaving the Cr center more than 0.72 \AA out of the plane of the sulfur donor atoms. This is by far the largest out-of-plane distance for any first row transition metal nitrido complex, but it is almost identical in magnitude to the 0.727 \AA found for

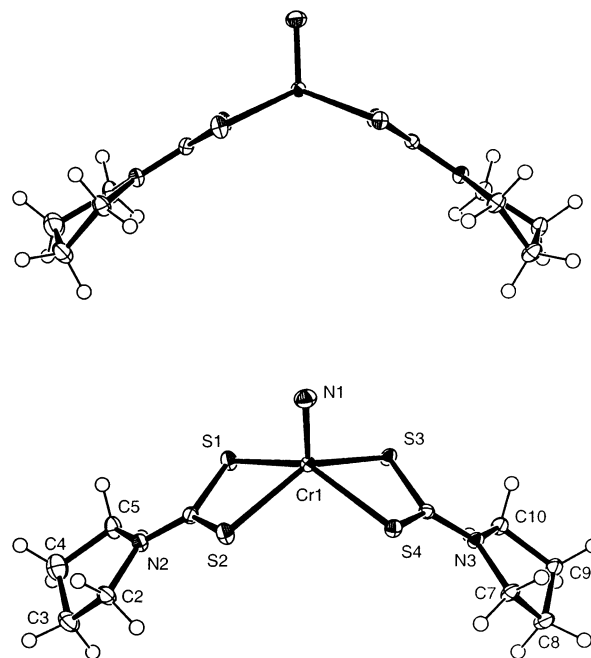


Figure 4. Molecular structure and atom labeling for **3** with thermal ellipsoids (50% probability). Cf. Table 2 for metrical details. The top view emphasizes the pronounced pyramidalization of the molecule with Cr displaced 0.725 \AA out of the least-squares plane of the four sulfur donor atoms.

$[\text{Re}(\text{N})(\text{S}_2\text{CN}(\text{Et})_2)_2]^{21}$ and appears thus to be property governed by the dithiocarbamate ligands. The bond lengths to the equatorial ligands in **1–3** are invariably shorter than those found in Cr(III) complexes of the same ligands: Cr^{III}(quin) (Cr–N, $1.947\text{--}1.964 \text{ \AA}$; Cr–O, $2.082\text{--}2.093 \text{ \AA}$),²² Cr^{III}(dbm) ($1.958\text{--}1.961 \text{ \AA}$),²³ and Cr^{III}(pyr-dtc) (2.392--

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compounds **1**, **2**, and **3**

Cr(N)(quin) ₂ (1)			
Cr1–N3	1.5549(7)		
Cr1–N1	1.9300(5)	N3–Cr1–N1	102.86(3)
Cr1–N2	1.9303(5)	N3–Cr1–N2	103.39(3)
Cr1–O1	2.0380(6)	N3–Cr1–O1	106.85(3)
Cr1–O2	2.0399(6)	N3–Cr1–O2	107.85(3)
N1–Cr1–O1	81.67(2)	N1–Cr1–O2	89.01(2)
N1–Cr1–N2	153.73(2)	O1–Cr1–O2	145.25(3)
Cr(N)(dbm) ₂ (2)			
Cr1–N6	1.5491(14)		
Cr1–O1	1.9319(10)	N6–Cr1–O1	103.69(6)
Cr1–O2	1.9450(10)	N6–Cr1–O2	105.06(6)
Cr1–O3	1.9222(11)	N6–Cr1–O3	103.32(6)
Cr1–O4	1.9283(10)	N6–Cr1–O4	103.65(6)
O1–Cr1–O2	88.60(4)	O1–Cr1–O3	83.53(5)
O1–Cr1–O4	152.60(5)	O2–Cr1–O3	151.59(5)
Cr(N)(S ₂ CNC ₄ H ₈) ₂ (3)			
Cr1–N1	1.5490(13)		
Cr1–S1	2.3811(4)	N1–Cr1–S1	106.38(5)
Cr1–S2	2.3763(5)	N1–Cr1–S2	109.00(5)
Cr1–S3	2.3689(5)	N1–Cr1–S3	107.14(5)
Cr1–S4	2.3842(4)	N1–Cr1–S4	108.52(5)
S1–Cr1–S2	75.209(15)	S1–Cr1–S3	94.513(16)
S1–Cr1–S4	145.099(16)	S2–Cr1–S3	143.853(17)

Table 3. Structurally Characterized Cr(V) Nitrido Complexes

complex	C.N.	Cr–N (Å)	Cr out of plane (Å)	ref
1	5	1.5549(7)	0.5193(3)	<i>a</i>
2	5	1.5491(14)	0.4652(6)	<i>a</i>
3	5	1.5490(13)	0.7251(3)	<i>a</i>
[Cr(N)(salen)]	5	1.544(3)	0.499(3)	34
[Cr(N)(tpp)]	5	1.565(6)	0.42	9
[Cr(N)(bpb)]	5	1.560(2)	0.51	35
[(Me ₃ tacn)Cr(N)(acac)](ClO ₄)	6	1.575(9)	0.30	8
<i>trans</i> -[Cr(N)(cyclam)(NCCCH ₃) ²⁺	6	1.561(3)	0.265	7
<i>trans</i> -[Cr(N)(CN) ₄ (py)] ²⁻	6	1.570(3)	0.261(2)	11
[Cr(N)(CN) ₅] ³⁻	6	1.594(9)	0.255	12

^a This work.

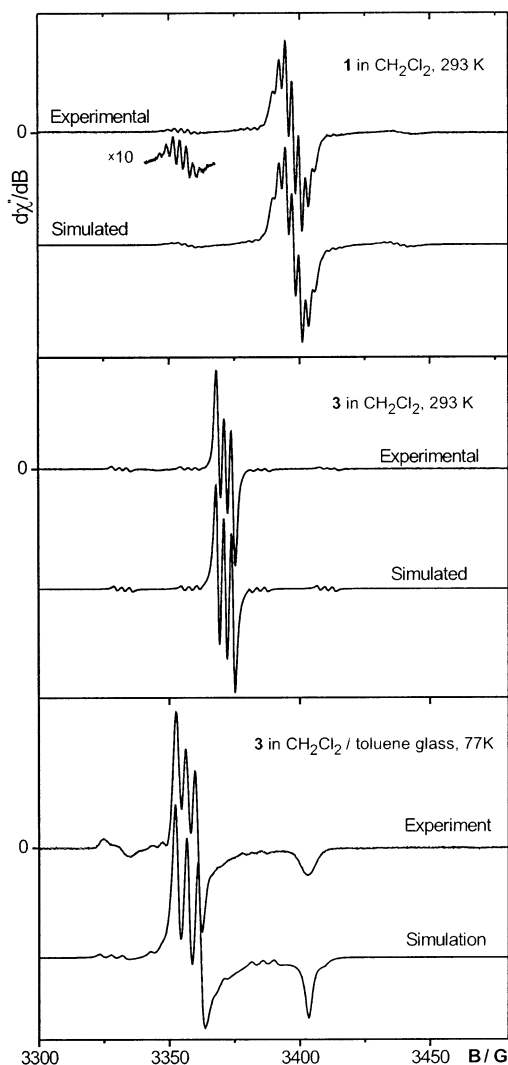
2.412 Å)²⁴ (dbm = 1,3-diphenylpropane-1,3-dionate, pydtc = pyrrolidinedithiocarbamate). However, the difference is in most cases quite small, only ca. 0.02 Å, despite a difference of two units in formal oxidation state of the chromium central ion. The small difference can be taken as evidence of the high degree of charge leveling within the {Cr≡N}²⁺ unit found previously in calculations. The previous data are supplemented by a recent calculation on [Cr(N)Cl₄]²⁻, which places charges of +0.70 and –0.34 on Cr and N, respectively.²⁵

Vibrational Spectroscopy. Cr–N stretching frequencies of the new compounds and some reference systems are given in Table 4. All new compounds, except **3**, have $\nu(\text{Cr–N})$ in the normal range 1000–1025 cm⁻¹ for five-coordinate Cr(V) nitrido systems. In **3** $\nu(\text{Cr–N})$ is significantly lower and in the range normally observed for six-coordinate systems. This is counter-intuitive when considering the relatively weak ligand field from the dithiocarbamates (*vide supra*), but may be correlated to the pyramidal geometry.

EPR Spectroscopy. In solution at room temperature complexes **1–4** exhibit sharp isotropic signals with $g \approx 1.98$

(24) Sinn, E. *Inorg. Chem.* **1976**, *15*, 369.(25) Bendix, J. *J. Am. Chem. Soc.* Submitted for publication.**Table 4.** IR Data for Cr(V) Nitrido Complexes

complex	$\nu_{\text{Cr–N}}$ (cm ⁻¹)	ref
1	1015	<i>a</i>
2	1007	<i>a</i>
3	991	<i>a</i>
4	1016	<i>a</i>
6	1023	<i>a</i>
[Cr(N)(salen)]	1012	10
[Cr(N)(tpp)]	1017	9
Cs ₂ Na[Cr(N)(CN) ₅]	972	11
[PPh ₄] ₂ [Cr(N)(CN) ₄ (py)]	995	11
<i>trans</i> -[Cr(N)(cyclam)(CH ₃ CN)](ClO ₄) ₂	996	7

^a This work.**Figure 5.** Experimental and simulated EPR spectra of **1** and **3**. Cf. Table 5 for simulation parameters.

(cf. Figure 5). The spectra have an intense central resonance line due to the chromium isotopes with $I = 0$ (90.5%), surrounded by a weak hyperfine quartet arising from coupling to ⁵³Cr (9.5%, $I = 3/2$). In addition, superhyperfine coupling to coordinated nitrogens can be observed for all systems. The spectra of **2** (not shown) and **3** have a simple appearance with all lines split into triplets due to coupling to the nitrido ligand (¹⁴N, ≈100%, $I = 1$). In **1** and **4** the superhyperfine coupling results in a septet with intensities corresponding to almost equally strong coupling to the nitrido ligand and the

Table 5. EPR Parameters for Cr(V) Nitrido Complexes

complex	g_{iso}	g_{\parallel}	g_{\perp}	$A_{\text{iso}}^{\text{N}}$ [mT]	A_{\perp}^{N} [mT]	$A_{\text{iso}}^{\text{Cr}}$ [mT]	A_{\perp}^{Cr} [mT]	ref
1	1.976	1.948	1.992	0.25		2.70	1.8	<i>a</i>
2	1.971	1.935	1.989	0.25	0.45	3.03	1.9	<i>a</i>
3	1.985	1.966	1.993	0.27	0.45	2.60	1.9	<i>a</i>
4	1.977	1.944	1.993	0.25		2.70	1.8	<i>a</i>
[Cr(N)(CN) ₅] ³⁻	1.990	1.9755	1.9990	0.29	0.36	2.49	1.5	12
<i>trans</i> -[Cr(N)(cyclam)(CH ₃ CN)] ²⁺	1.9856	1.965	1.997	0.23		2.80	1.6	7
[Cr(N)(salen)]	1.987	1.951	1.991	0.25		2.83	1.98	10
[Cr(N)(tpp)]	1.9825	1.9583	1.9945	0.277	0.37 ^{<i>b</i>}	2.827	2.24	9

^{*a*} This work. ^{*b*} Determined by ENDOR.

equatorial ligands. This near degeneracy of the Fermi contact interactions is a general feature of Cr(V) nitrido complexes and has been discussed before.^{26,27} The EPR spectra observed in a frozen glass at 77 K are characteristic of axially symmetric systems. In the solid-state spectra of **2** and **3**, the anisotropies of the hyperfine and superhyperfine couplings are directly observable. This is a uniquely advantageous situation, brought about by the simple coordination sphere without ligands with nuclear spin. Normally it requires dilute single-crystal spectra or ENDOR to obtain the anisotropy of the superhyperfine interaction. EPR parameters from simulations of the solution and solid-state EPR spectra are collected and compared with literature data in Table 5. All the parameters lie in the ranges of previously reported data.^{7,9,10,12}

UV/vis Spectroscopy. UV/vis and MCD spectra of **2** and **3** are shown in Figure 6. In both cases, a weak absorption is located between 540 and 600 nm. A similar absorption ($\lambda = 552$ nm, $\epsilon = 26.1$ M⁻¹ cm⁻¹) is found for **4**. In the spectrum of **3**, a second (slightly split) band at $\lambda = 446$, 432 (sh) nm is observed. In all cases we assign the low-energy band to be the $d_{x^2-y^2} \leftarrow d_{xy}$ transition. The band system at ca. 440 nm in **3** is the transition $\{d_{zx}, d_{yz}\} \leftarrow d_{xy}$, slightly split due to the large deviation from 90° bite angles in the dithiocarbamate ligands. In these assignments, the relative band intensities in the spectrum of **3** agree with the selection rules in (idealized) C_{4v} symmetry, where the $d_{x^2-y^2} \leftarrow d_{xy}$ is the only electrical dipole forbidden d-d transition and is thus expected to be fairly weak. The assignment of the second band system in **3** as $\{d_{zx}, d_{yz}\} \leftarrow d_{xy}$ is further corroborated by the MCD spectrum where, in agreement with previous findings, this band is clearly observed. On the basis of the experimental coordination geometry of **3**, the following AOM expression²⁸ is obtained for the position of the first band: $E(d_{x^2-y^2}) - E(d_{xy}) = 2.31e_{\sigma}^S - 3.40e_{\pi\parallel}^S + 0.34 e_{\pi\perp}^S$. And for the splitting of the $\{d_{zx}, d_{yz}\}$ set of orbitals $E(d_{yz}) - E(d_{zx}) = 0.18e_{\sigma}^S - 0.07e_{\pi\parallel}^S + 0.50e_{\pi\perp}^S$.²⁹ From these

(26) Hori, A.; Ozawa, T.; Yoshida, H.; Imori, Y.; Kuribayashi, Y.; Nakano, E.; Azuma, N. *Inorg. Chim. Acta* **1998**, *281*, 207.

(27) It is possible to distinguish the nitrido ligand from the equatorial nitrogen donors in simulations of the EPR spectra of **1** and **4**. A complete reproduction of the intensity distribution in the septet is only possible if a slightly smaller $A_{\text{iso}}^{\text{N}} = 0.24$ mT is employed for the equatorial N-donors.

(28) (a) Schäffer, C. E. *Struct. Bonding* **1968**, *5*, 93. (b) Bendix, J. In *Comprehensive Coordination Chemistry II*; Meyer, T. J., McCleverty, J. A., Ed.; Elsevier, in press Chapter 9.4.

(29) Parallel and perpendicular refers to the plane of the dithiocarbamate ligand and not to the Cr-N axis, where the designations would have been interchanged.

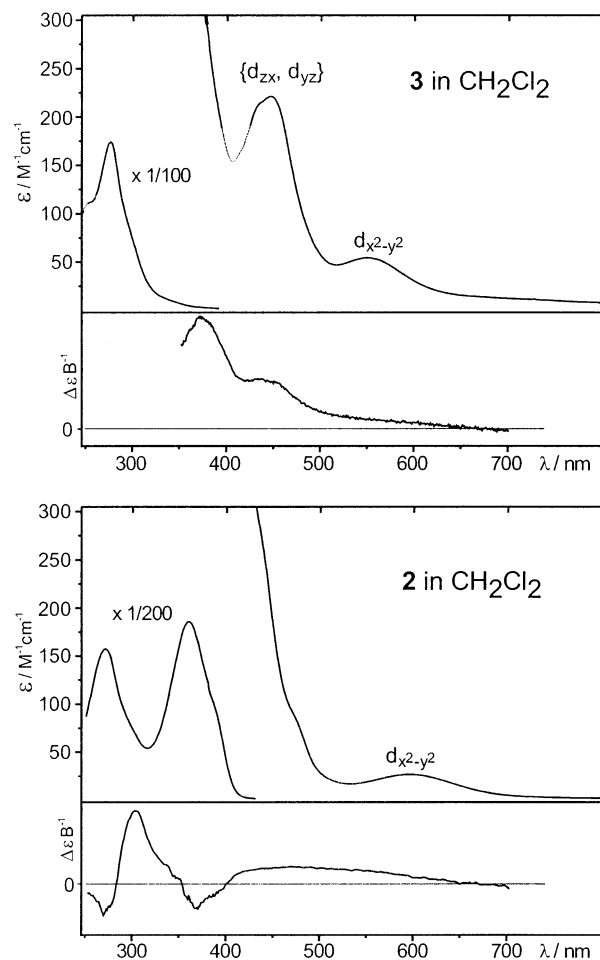


Figure 6. UV-vis and MCD spectra of **3** (λ_{max} [nm] (ϵ) [M⁻¹ cm⁻¹]: 548 (54.5), 446 (221), 432 sh, (212), 276 (17 400)) and **2** (λ_{max} [nm] (ϵ) [M⁻¹ cm⁻¹]: 595 (26.4), 469 sh, (93.3), 359, (37 100), 271 (31 500)).

expressions and the experimental position of the first band one can calculate in a σ -only model a splitting of the $\{d_{zx}, d_{yz}\}$ set of 1400 cm⁻¹. Since the experimental value of this splitting is less (although quite uncertain), and since it is normal from bonding considerations to assume $e_{\pi\perp}^S > e_{\pi\parallel}^S$ in planar bidentate ligands, it follows that π -donation from the dithiocarbamates is small. Considering that the sulfur ligand has to π -donate to the same orbitals as the nitrido ligand, the result of this simple analysis appears reasonable. The first spin-allowed bands in Cr(III) complexes provide (for ortho-axial ligation) a direct measure of $\Delta_o = 3e_{\sigma} - 4e_{\pi} = 3e_{\sigma}^{\text{Equatorial}} - 4e_{\pi}^{\text{Equatorial}}$. The positions of the first band in the spectra of **2** and **3** can thus be compared to data for Cr(III) complexes of the same ligands. In the spectrum of

Cr(V) Nitrido Complexes of Bidentate Ligands

Cr(acac)₃ the ${}^4A_2 \rightarrow {}^4T_2$ transition is located at 17 860 cm⁻¹,³⁰ and in the spectrum of Cr(S₂CN(Et)₂)₃ it is found at 15 500 cm⁻¹.³¹ Again the very small difference between Cr(III) and Cr(V) is noteworthy and emphasizes the usefulness of thinking in terms of a {Cr≡N}²⁺ unit. The data also show that there is a reversal of the spectrochemical ordering of the O and S donor ligands upon going from Cr(III) to Cr(V). Possible explanations could be that the low Δ_o for dithiocarbamate coordinated to Cr(III) reflects a relatively large π-donation, which is suppressed in the nitrido complexes in line with the above discussion. However, the reversal may also be due to a slightly better fit of the smaller Cr(V) center to the narrow bite angle of the dithiocarbamate ligands.

The first Cr(V) nitrido complexes to be prepared all featured conjugated organic ligand systems such as salen and porphyrins. Accordingly, d–d spectra were not observed and d-orbital splittings had to be inferred indirectly from EPR data. Later, systems with spectroscopically more innocent ligands such as cyclam, tacn, and cyanide were prepared and their d–d spectra were analyzed. Common to these systems were thus a coordination sphere completed by strong donor ligands. The outcome of these studies was an orbital splitting diagram reminiscent of the one devised for vanadyl systems early on by Ballhausen and Gray³² and independently Jørgensen³³ (cf. Figure 7). Conceptually, the splitting pattern is normally conceived as a strong tetragonal compression of an octahedral reference system. In the nitrido complexes the π* orbitals were found to be higher in energy than in {VO}²⁺ and nearly degenerate with the d_{x²-y²} orbital. Of the systems presented here, **2** and **3** are fairly spectroscopically transparent and represent with their relatively weakly donating equatorial ligands a qualitatively different d-orbital splitting pattern where the d_{x²-y²} orbital lies well below the π* orbitals (cf. right hand side of Figure 7). This splitting pattern with the two δ orbitals (d_{x²-y²} and d_{xy}, quantization along the Cr–N axis) lowest in energy approaches the situation for a linear system, where the two δ orbitals are degenerate and lowest in energy. It may be conceptually useful to consider these new complexes not as strongly perturbed octahedral systems, but rather as less strongly perturbed linear systems.

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(31) Jørgensen, C. K. *J. Inorg. Nucl. Chem.* **1962**, *24*, 1571.

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(35) Che, C.-M.; Ma, J.-X.; Wong, W.-T.; Lai, T.-F.; Poon, C.-K. *Inorg. Chem.* **1988**, *27*, 2547.

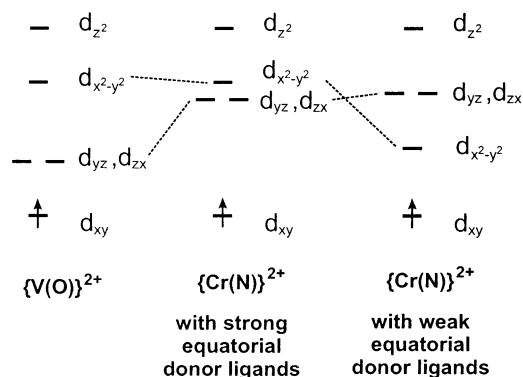


Figure 7. d-orbital energy diagrams illustrating the variation in splitting pattern going from vanadyl systems via {Cr≡N}²⁺ with strongly donating auxiliary ligands to (pseudolinear, see text) {Cr≡N}²⁺ complexes with weak equatorial donors.

Conclusion

A new general route to nitrido complexes of Cr(V) based on nitrogen atom transfer from Mn(N)(salen) to labile CrCl₃(THF)₃ has been developed. By this approach, four members of the hitherto unknown class of Cr(N) nitrido complexes with bidentate auxiliary ligands have been synthesized and characterized. The mild conditions of this protocol allow for the first time for the introduction of weak donor ligands in {Cr(N)}²⁺ coordination chemistry. Consequently, the orbital energies of these systems become completely dominated by the nitrido ligand. Work in progress has established the present procedure to be applicable also to the synthesis and isolation of Cr(V) nitrido complexes with a wide variety of monodentate ligands including phosphines, pyridines, thiocyanate, and chloride.

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Supporting Information Available: Crystallographic data (CIF format), magnetic moment data for **1–3**, and experimental and simulated EPR spectra of **1** (77 K), **2** (77, 293 K), and **4** (77, 293 K). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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