Synthesis and Characterization of Six-Coordinate Nitrido Complexes of Vanadium(V), Chromium(V), and Manganese(V). Isolation of a Dinuclear, Mixed-Valent μ-Nitrido Chromium(III)/Chromium(V) Species

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Photolysis of a series of octahedral monoazido complexes of the type [LM^{III}(didentate ligand)(N$_3$)]$^{n+}$X$_n$ of vanadium(III), chromium(III), and manganese(III) in the solid state or in solution yields quantitatively the corresponding six-coordinate nitrido complexes [LM^{V}(didentate ligand)(N)]$^{n+}$X$_n$ and 1 equiv of dinitrogen. L represents the macrocycle 1,4,7-triazacyclononane or its N-methylated derivative (L′), the didentate ligands are pentane-2,4-dionate (acac), 2,2,6,6-tetramethylheptane-3,5-dionate (tacac), picolinate (pic), phenanthroline (phen), and oxalate (ox), and X$^-$ represents perchlorate or hexafluorophosphate. The following nitrido complexes were prepared: [LV^{V}(N)(acac)](ClO$_4$) (**6**), [LCr^{V}(N)(acac)](ClO$_4$) (**13**), [LCr^{V}(N)(tacac)](ClO$_4$) (**14**), [LCr^{V}(N)(pic)](ClO$_4$) (**15**), [LCr^{V}(N)(phen)](ClO$_4$)$_2$ (**16**), [LCr^{V}(N)(ox)] (**19**), [L′Mn^{V}(N)(acac)]PF$_6$ (**21**). Photolysis of [LCr^{III}(N$_3$)(ox)] (**17**) in the solid state produces the μ-nitrido-bridged mixed-valent species [L$_2$Cr$_2$(ox)$_2$(μ-N)](N$_3$) (**18**). The structures of the precursor complex [L′Mn(acac)(N$_3$)]BPh$_4$ (**20**), of **13**, and of [L′Mn^{V}(N)(acac)]BPh$_4$ (**21**) have been determined by X-ray crystallography. Complex **13** crystallizes in the orthorhombic space group *Pnma*, with cell constants $a = 27.187(5)$ Å, $b = 9.228(2)$ Å, $c = 7.070(1)$ Å, $V = 1773.7(6)$ Å^3, and $Z = 4$; complex **20** crystallizes in the triclinic space group $P\bar{1}$ with $a = 14.769(5)$ Å, $b = 16.83(1)$ Å, $c = 16.96(1)$ Å, $\alpha = 108.19(5)°$, $\beta = 105.06(4)°$, $\gamma = 99.78(4)°$, $V = 3719(2)$ Å^3, and $Z = 4$; and complex **21** crystallizes in the monoclinic space group $P2_1/n$ with $a = 10.443(3)$ Å, $b = 16.035(4)$ Å, $c = 21.463(5)$ Å, $\beta = 95.76(1)°$, $V = 3575.9(14)$ Å^3, and $Z = 4$. The Cr$^{V}\equiv$N and Mn$^{V}\equiv$N distances are short at 1.575(9) and 1.518(4) Å, respectively, and indicate a metal-to-nitrogen triple bond.

Introduction

First-row transition metal complexes containing a terminal nitrido ligand and a high-valent transition metal ion, M≡N, are quite rare.[2] This is in contrast to second- and third-row transition metal complexes of this type where the M≡N moiety is known to be thermodynamically quite stable. Since the nitrido ligand N^{3-} is one of the strangest π-donor ligands, a necessary prerequisite for the formation of stable nitrido species is in general the availability of suitable empty d orbitals at the metal ion. Thus the d^0, d^1, and d^2 electronic configurations of V(V), Cr(V), and Mn(V), respectively, should be ideally suited for *octahedral* complexes containing a terminal nitrido ligand. As follows from a simple qualitative MO scheme in Figure 1,[3] the t$_{2g}$ metal orbitals split into a set of doubly degenerate bonding π and antibonding π* orbitals whereas one b$_2$ orbital is nonbonding in character. This b$_2$ orbital is empty for V(V), half-filled in Cr(V), and filled in Mn(V) complexes. Due to an enormous structural trans-influence of the nitrido group, the ligand in a trans position is labilized to such an extent that nearly all complexes reported to date are five-coordinate, square pyramidal species with the nitrido group in the apical position (Table 1).[4−6] This is thought to be the reason that, to the best of our knowledge, no octahedral nitrido complexes of vanadium-

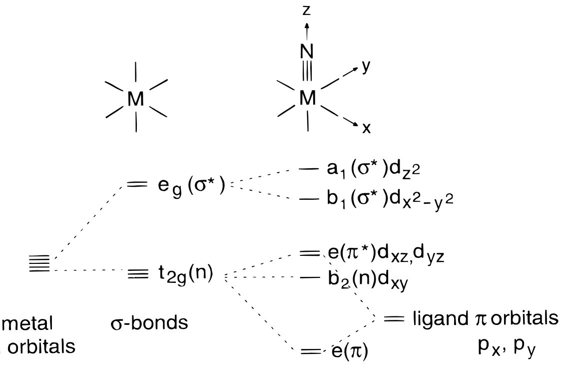

Figure 1. Partial qualitative molecular orbital scheme for octahedral complexes with one terminal nitrido ligand; adapted from ref 3, p 33.

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(5) References for nitridochromium(V) complexes follow. (a−d) Cr^{V}N(TTP) (TTP = *meso*-tetra-*p*-tolylporphinate(2−)): (a) Buchler, J. W.; Dreher, C. *Z. Naturoforsch.* **1984**, *39B*, 222. (b) Buchler, J. W.; Dreher, C.; Lay, K.-L.; Raap, A.; Gersonde, K. *Inorg. Chem.* **1983**, *22*, 879. (c) Groves, J. T.; Takahashi, T.; Butler, W. M. *Inorg. Chem.* **1983**, *22*, 884. (d) [Cr^{V}(bpb)N] (H$_2$bpb = 1,2-bis(2-pyridinecarboxamido)benzene): Che, C.-M.; Ma, J.-X.; Wong, W.-T.; Lai, T.-F.; Poon, C.-K. *Inorg. Chem.* **1988**, *27*, 2547. (e) Cr^{V}N(Pc(2−)) and Cr^{V}N(Pc(1−)) (Pc^{2-}, Pc$^-$ = phthalocyaninate(2−), -(1−)): Grunewald, H.; Homborg, H. *Z. Anorg. Allg. Chem.* **1992**, *608*, 81.

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Table 1. Summary of Structural, Spectroscopic, and Magnetic Data of Vanadium(V), Chromium(V), and Manganese(V) Complexes Containing a Terminal $M\equiv N$ Group

complex[a]	CN[b]	$M\equiv N$, Å	d, Å[c]	$\nu(M\equiv N)$, cm^{-1}	μ_{eff}, μ_B	ref
$VNCl_2(py)_2$	(5 + 1) (sp)	1.598(7) 1.571(7)		960	0.8	4b 4c
$VNCl_2(bpy)$	6 (?)			970	diamagnetic	4a
$VNCl_3^-$	4			1033	diamagnetic	4a
$VNCl_2(quin)_2$	5 (tbp)	1.568(19)		not assigned	diamagnetic	4c
CrN(TTP)	5 (sp)	1.565(6)	0.42	1017	not measured	5c
CrN(bpb)	5 (sp)	1.560(2)	0.51	1015	1.93	5d
MnN(TpMPP)	5 (sp)	1.515(3)	0.39	1036	"diamagnetic" (NMR)	6a
MnN(OEP)	5 (sp)	1.512(2)	0.43	1050	"diamagnetic" (NMR)	6c

[a] Ligand abbreviations: py = pyridine; TTP = 5,10,15,20-tetra-*p*-tolylporphinate(2−); H_2bpd = 1,2-bis(2-pyridinecarboxamido)benzene; TpMPP = tetrakis(*p*-methoxyphenyl)porphinate(2−); OEP = 5,15-dimethyl-2,3,7,8,12,13,17,18-octahethyl-*5H,15H*-porphinate(2−); quin = quinuclidine. [b] Coordination number; tbp = trigonal bipyramidal; sp = square-based pyramidal. [c] Distance of the metal ion from the mean basal plane of four equatorial ligands.

(V), chromium(V), or manganese(V) have been structurally characterized. By making use of the well-known kinetic stability of the facially coordinated tridentate macrocycle 1,4,7-triazacyclononane (L) and its N-substituted derivatives,[7] we have synthesized and characterized a series of octahedral nitrido complexes of V(V), Cr(V), and Mn(V) containing an $[LM(didentate)]^{2+}$ fragment.

Synthetically the most appealing precursor complexes are the corresponding azido complexes of the respective trivalent metal ion which undergo thermally or photochemically induced cleavage of dinitrogen, eq 1, with concomitant formation of

$$M^{III}-N_3 \xrightarrow[\substack{(1)\ \Delta H\\ (2)\ h\nu}]{-N_2} M^{V}\equiv N + N_2 \tag{1}$$

nitridometal(V) species. The photolysis of azidochromium(III) complexes yielding nitridochromium(V) species was reported in 1981 by Arzhankov and Poznyak[8] for the first time, but this reaction has not been used widely since.[9] Some five-coordinate Cr^VN and Mn^VN complexes have been prepared according to eq 1 but no V^VN species. Photolysis of $Fe^{III}-N_3$ complexes leads to mixed-valent nitrido-bridged $Fe^{IV}\equiv N-Fe^{III}$ species.[10] The very reactive intermediate $Fe^V\equiv N$ species has been involved in these reactions and has been characterized by resonance Raman spectroscopy at low temperatures.[11] Recently an in depth spectroscopic characterization (ESR, UV−vis) of the complex [*N,N′*-bis(pyridyl-2-carbonyl)-*o*-phenylenediamido]-nitridochromium(V)[5d] with a square-pyramidal CrN_5 chromophore was reported.[12]

Experimental Section

Caution! Although we have not encountered problems, it is noted that perchlorate salts are potentially explosive and should be handled only in small quantitaties with appropriate precautions.

The ligands 1,4,7-triazacyclononane (L) and its N-methylated derivative 1,4,7-trimethyl-1,4,7-triazacyclononane (L′) were synthesized according to published procedures.[13]

Vanadium Complexes. $LVCl_3$ (1). Vanadium trichloride (5.0 g; 31.8 mmol) in deaerated, dry acetonitrile (30 mL) was heated to reflux under an argon blanketing atmosphere until a light green, clear solution was obtained. To this solution was added at 40 °C a solution of 1,4,7-triazacyclononane (4.5 g; 34.8 mmol) in CH_3CN (20 mL). After heating of the mixture to reflux for 1 h, a green precipitate formed upon cooling to 10 °C, which was collected by filtration under argon. Yield: 8.3 g (91%).

$LV(O_3SCF_3)_3$ (2). To complex **1** (2.0 g; 11.1 mmol) was added dropwise under an argon blanketing atmosphere CF_3SO_3H (15 mL; 0.18 mol) with stirring at ambient temperature (*caution*: effervescence of HCl gas). The resulting green solution was stirred for 30 min, after which deaerated diethyl ether (200 mL) was added, initiating the precipitation of green microcrystals. Yield: 6.3 g (90%).

$[LV(acac)Cl]PF_6$ (3). To a solution of **1** (0.36 g; 2.0 mmol) in methanol/water (2:1 by volume) (20 mL) were added under argon Na(acac) (0.30 g; 2.5 mmol) and KPF_6 (0.6 g; 3.0 mmol). From the resulting clear brown solution a microcrystalline brown precipitate formed, which was recrystallized from oxygen-free acetone/acetonitrile (1:1 by volume). Yield: 0.37 g (40%).

$[LV(acac)(N_3)]X$ ($X = PF_6$, ClO_4) (4). Method A. To a deaerated acetonitrile solution (30 mL) of **2** (0.63 g; 1.0 mmol) were added Na(acac) (0.18 g; 1.5 mmol), NaN_3 (0.10 g; 1.5 mmol), and $NaClO_4$ (0.25 g; 2.0 mmol) with stirring under an argon atmosphere. From the resulting clear, red-brown solution a red-brown microcrystalline precipitate formed within a few hours. Yield: 0.06 g (15%).

Method B. To a deaerated acetonitrile solution (30 mL) of **3** (0.40 g; 0.90 mmol) was added $Ag(NO_3)$ (0.15 g; 0.90 mmol). The colorless precipitate of AgCl was removed by filtration under strictly anaerobic conditions. To the clear, red-brown solution were added NaN_3 (0.20 g; 2.0 mmol) and KPF_6 (0.60 g; 3.0 mmol). Red-brown microcrystals precipitated within a few hours at 10 °C. Yield: 0.084 g (20%).

$[LV(O)(acac)]X$ ($X = PF_6$, ClO_4) (5). When complex **3** or its perchlorate salt was dissolved in water containing CH_3CN in the presence of air, deep blue microcrystals formed in essentially quantitative yield.

$[LV(N)(acac)](ClO_4)$ (6). A finely powdered sample of **4**(ClO_4) was dispersed under argon on an aluminum foil in a thin layer. This sample was irradiated for 2−3 h with an Osram UV bulb (100−400 nm). The amount of N_2 liberated was measured manometrically (1 equiv of N_2/mol of **4**). During irradiation, the color of the sample changed from red-brown to nearly colorless.

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(6) References for nitridomanganese(V) complexes follow. (a, b) Mn^VN(TPP) (TPP = tetrakis(*p*-methoxyphenyl)porphinate): (a) Hill, C. L.; Hollander, F. J. *J. Am. Chem. Soc.* **1982**, *104*, 7318. (b) Reference 5a. (c) $Mn^VN(OEPMe_2)$ ($OEPMe_2$ = 5,15-dimethyl-2,3,7,8,12,13,17,18-octaethyl-5*H*,15*H*-porphinate): Buchler, J. W.; Dreher, C.; Lay, K.-L.; Lee, Y. J. A.; Scheidt, W. R. *Inorg. Chem.* **1983**, *22*, 888. (d) Mn^VN(Pc(2−)) (Pc = phthalocyaninate): Grunewald, H.; Homborg, H. *Z. Naturforsch.* **1990**, *45B*, 483. (e, f) Mn^VN(Pc(1−)): (e) Reference 5e. (f) Groves, J. T.; Takahashi, T. *J. Am. Chem. Soc.* **1983**, *105*, 2074.

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[LV(O)(acac)](ClO_4)$_2$ (7). Attempts to recrystallize **6** from "water-free" acetonitrile solutions resulted in the formation of colorless crystals of [LV(O)(acac)](ClO_4)$_2$ in quantitative yield.

Chromium Complexes. [LCrCl$_3$] (8). $CrCl_3 \cdot 6H_2O$ (5.0 g; 18.8 mmol) was added to dimethyl sulfoxide (dmso) (50 mL) containing two zinc granules, and the mixture was heated to 150 °C until a clear violet solution was obtained.[14] After cooling of the solution to 80 °C, 1,4,7-triazacyclononane (L) (2.5 g; 19.4 mmol) dissolved in methanol (30 mL) was added dropwise with stirring. The solution was heated to 110 °C for 30 min. Upon cooling, a green precipitate formed, which was collected by filtration. Yield: 4.8 g (89%).

[LCr^{III}(didentate ligand)(N_3)](ClO_4)$_n$. A suspension of **8** (1.0 g; 3.5 mmol), NaN_3 (0.5 g; 7.0 mmol), $NaClO_4$ (1.0 g; 8.2 mmol), and 5.4 mmol of the respective didentate ligand (Na(acac), 2,2,6,6-tetramethylheptane-3,5-dione (tacac), picolinic acid, 1,10-phenanthroline) in water (20 mL) was gently heated to ~80 °C with stirring until a clear red solution was obtained. Upon cooling of the solution to 10 °C, red microcrystalline precipitates formed, which were collected by filtration, washed with diethyl ether, and air-dried: [LCr(acac)(N_3)](ClO_4), **9** (yield 83%); [LCr(tacac)(N_3)](ClO_4), **10** (67%); [LCr(pic)(N_3)](ClO_4), **11** (84%); [LCr(phen)(N_3)](ClO_4)$_2$, **12** (62%). The complex [LCr(C_2O_4)(N_3)] (**17**) was prepared analogously in 80% yield by using $Na_2[C_2O_4]$ as didentate ligand. Complexes **9**−**12** and **17** were readily recrystallized from an acetone/acetonitrile mixture (1:1 vol %).

[LCr^V(N)(didentate ligand)](ClO_4)$_n$. Finely powdered solid samples of complexes **9**−**12** (2.0 g) were dispersed on an aluminum foil. This thin layer was irradiated with an Osram UV bulb (100−400 nm) for 4 h, during which the red color of the samples gradually changed to yellow with formation of dinitrogen. The reaction was complete when no $\nu(N_3)$ stretching mode at ~2070 cm^{-1} was detectable in the infrared spectrum of solid samples (KBr disk). The amount of N_2 liberated during irradiation was measured manometrically to be 1.0 ± 0.10 equiv/mol of starting complex. The resulting yellow complexes were recrystallized from hot saturated acetonitrile solutions: [LCr(N)(acac)](ClO_4), **13**; [LCr(N)(tacac)](ClO_4), **14**; [LCr(N)(pic)](ClO_4), **15**; [LCr(N)(phen)](ClO_4)$_2$, **16**.

[L$_2$Cr$_2$(C_2O_4)$_2$(μ-N)](N_3) (18). When [LCr(C_2O_4)(N_3)] (**17**) was treated in exactly the same fashion as described above for the synthesis of complexes **13**−**16**, it was found that, even upon irradiation up to 48 h, only 0.5 ± 0.1 equiv of N_2/mol of **17** formed. The resulting yellow-red solid material displays a $\nu(N_3)$ stretching frequency at 2073 cm^{-1} which does not lose intensity upon further irradiation.

[LCr(N)(C_2O_4)] (19). A solution of **17** (1.0 g; 3.2 mmol) in dmso (50 mL) was irradiated with mercury immersion lamp (100−400 nm) for 2 h, during which the red color of the solution changed to yellow with concomitant N_2 generation in the ratio 1:1. When this solution was allowed to stand in an open vessel for 2 days, yellow crystals precipitated in 77% yield (0.75 g).

Manganese Complexes. [L′Mn(N_3)(acac)]PF_6 (20). To a solution of [L′Mn^{III}(acac)(OC_2H_5)]PF_6[15] (3.3 g; 6.4 mmol) in water (60 mL) were added 10 drops of concentrated $HClO_4$. NaN_3 (1.5 g; 23.1 mmol) was added to the clear brown-yellow solution, which was stirred at ambient temperature for 10 min. Addition of 1.5 g of $NaPF_6$ initiated the precipitation of brown microcrystals, which were collected by filtration. Yield: 3.0 g (91%). Single crystals of [L′Mn(acac)(N_3)][BPh_4] were grown from an CH_3CN/CH_3OH (1:1 by volume) solution of **20** by addition of Na[BPh_4].

[L′Mn(N)(acac)] PF_6 (21). A solution of **20** (1.5 g; 2.0 mmol) in dry acetonitrile (200 mL) was irradiated by a mercury immersion lamp (quartz) for 2−3 h in an ice/NaCl bath at −10 °C with a constant stream of argon gas bubbling through the reaction solution. A color change from brown to blue-green was observed. The volume of the solution was reduced to 60 mL by evaporation of the solvent. The resulting solution was added to an aqueous solution (500 mL) of KPF_6 (3.0 g), which initiated the precipitation of blue microcrystalline **21** (yield 0.9 g; 64%). Single crystals of [L′Mn(N)(acac)][BPh_4] were obtained from a methanol/acetone (1:1 by volume) solution of **21** by addition of the equivalent amount of Na[BPh_4]. Elemental analyses of complexes (C, H, N) are given in the Supporting Information.

Table 2. Crystallographic Data

	13	20	21
formula	$C_{11}H_{22}ClCrN_4O_6$	$C_{38}H_{48}BMnN_6O_2$	$C_{38}H_{48}BMnN_4O_2$
fw	393.8	686.6	658.6
a, Å	27.187(5)	14.769(5)	10.443(3)
b, Å	9.228(2)	16.83(1)	16.035(4)
c, Å	7.070(1)	16.96(1)	21.463(5)
α, deg	90.00	108.19(5)	90.00
β, deg	90.00	105.06(4)	95.76(1)
γ, deg	90.00	99.78(4)	90.00
V, Å^3	1773.7(6)	3719(2)	3575.9(14)
Z	4	4	4
space group	*Pnma*	$P\bar{1}$	$P2_1/n$
T, K	295	295	293
λ, Å	0.710 73	0.710 73	0.710 73
ρ_{calc}, g cm^{-3}	1.475	1.23	1.223
μ, mm^{-1}	0.828	0.38	0.407
R^a	0.074	0.064	0.051
$R_w{}^b$	0.079	0.055	0.041

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

X-ray Crystallography. Crystal data and data collection and refinement details are summarized in Table 2 (and corresponding tables in the Supporting Information). Graphite-monochromated Mo Kα X-radiation was used throughout. Intensity data were corrected in the usual fashion for Lorentz, polarization, and absorption effects (empirical ψ scans of seven reflections in the range $6 \le 2\theta \le 50°$). The structures were solved by conventional Patterson and difference Fourier (**20**) and direct (**13**, **21**) methods by using the SHELXTL-PLUS program package.[16] The function minimized during full-matrix least-squares refinement was $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(F) + 0.0002F^2$ (**13**, **21**) or $w^{-1} = \sigma^2(F)$ (**20**). Neutral-atom scattering factors and anomalous dispersion corrections for non-hydrogen atoms were taken from ref 17. The positions of the hydrogen atoms were placed at calculated positions (**13**, **20**) or located and refined (**21**) with isotropic thermal parameters. All non-hydrogen atoms were refined with anisotropic thermal parameters.

Physical Measurements. Infrared spectra of solid samples were recorded in the range 400−4000 cm^{-1} on a Perkin-Elmer 1720X FT IR spectrometer as KBr disks. Raman spectra of solid samples were measured in the range 100−3600 cm^{-1} on a Perkin-Elmer 1760X FT near-IR spectrometer connected to 180° backscattering FT Raman equipment. A Nd-YAG laser (λ = 1064 nm) was used. UV−vis spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer in the range 210−1100 nm. Temperature-dependent magnetic susceptibilities of powdered samples were measured by using the Faraday method (80−300 K) or a SQUID magnetometer (Quantum Design) at 1.0 T (2.0−300 K). Corrections for underlying diamagnetism were made by using tabulated Pascal constants. X-band EPR spectra of solid samples or solutions were recorded on a Bruker ER 200 spectrometer.

Results

Synthesis of Complexes. Vanadium. Scheme 1 summarizes the complexes synthesized. The reaction of monomeric octahedral LVCl$_3$ (**1**) with sodium pentane-2,4-dionate in a water/methanol mixture (1:2) under anaerobic conditions yields brown microcrystals of [LV(acac)Cl]PF_6 (**3**) upon addition of KPF_6. If a deaerated suspension of **1** and trifluoromethanesulfonic acid is carefully stirred at ambient temperature until the HCl gas evolution ceases, the addition of dry, deaerated diethyl ether initiates the precipitation of [LV^{III}(O_3SCF_3)$_3$] (**2**). Complexes **1**−**3** are octahedral vanadium(III) species (d^2). Their analogs containing the cyclic triamine 1,4,7-trimethyl-1,4,7-

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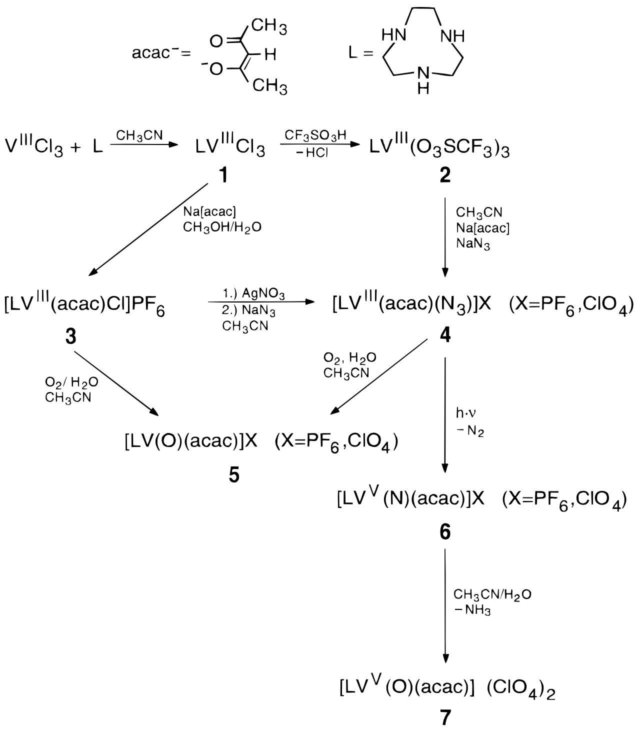
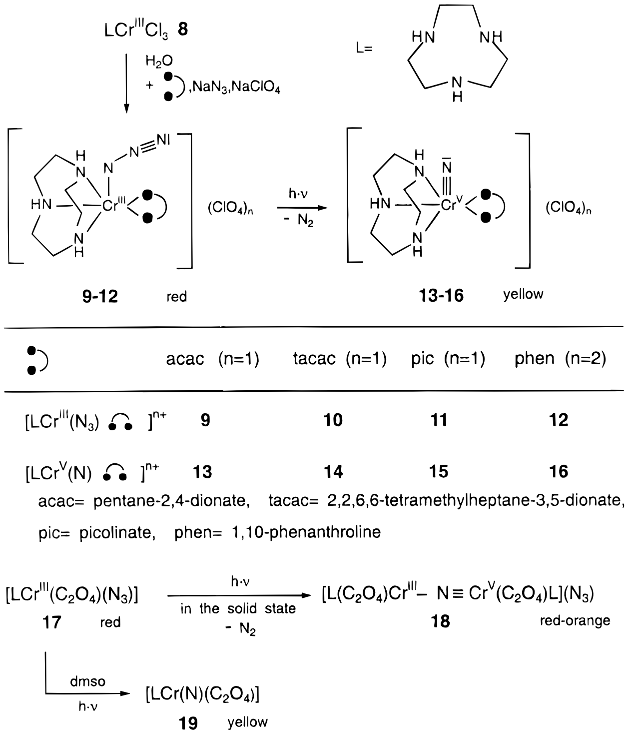
Scheme 1. Synthesis of Vanadium Complexes



triazacyclononane were described previously.[18] Since the color, magnetism, and spectroscopic properties are very similar to those of the present complexes, we refrain from reporting these data here.

Red-brown $[LV(acac)(N_3)]X$ **4**(X = CLO_4^- or PF_6^-) was prepared in only moderate yield (~20%) from **2** by reaction with Na(acac), NaN_3, and $NaClO_4$ (or KPF_6) in acetonitrile or from a deaerated acetonitrile solution of **3** by reaction with $AgNO_3$ to remove the chloro ligand as AgCl, followed by addition of NaN_3 to the acetonitrile solution. In CH_3CN solution complexes **3** and **4** are quite sensitive toward water and oxygen, as is judged from a rapid color change to deep blue. From such solutions blue crystals of $[LV^{IV}O(acac)]X$ **5** (X = ClO_4, PF_6) precipitated quantitatively. The structure of the 1,4,7-trimethyl-1,4,7-triazacyclononane derivative of **5** was reported previously.[18a] When red-brown microcrystals of the perchlorate salt of **4** were thinly dispersed on aluminum foil and irradiated with a UV lamp (100−400 nm), the color of the solid material slowly changed to nearly colorless (with a slight greenish appearance). This irradiation produced 1 equiv of gaseous dinitrogen/mol of vanadium ion (eq 1), as was judged by the loss of weight of the solid sample and quantitative volumetric determination of N_2. In the infrared spectrum of the colorless product **6** the $\nu(N_3)$ stretching mode is absent. Complex **6** is diamagnetic, and a new band in the infrared spectrum at 967 cm^{-1} is assigned to the $\nu(V{\equiv}N)$ stretching frequency. All attempts to recrystallizes **6** from a variety of suitable organic solvents failed because the V≡N moiety is extremely sensitive toward hydrolytic cleavage. Thus only colorless crystals of the oxovanadium(V) complex **7** and ammonia could be isolated and identified, respectively, from such solutions. In the infrared **7** displays a $\nu(V{=}O)$ stretching mode at 958 cm^{-1}. Complexes **6** and **7** also form a mixture in CH_3CN solution of **4** upon gentle heating (~50 °C). Thus the reaction in eq 1 may be either photolytically or thermally induced.

Scheme 2. Synthesis of Chromium Complexes



Chromium. Scheme 2 summarizes synthetic routes to chromium(III) and nitridochromium(V) complexes. Reaction of $[LCrCl_3]$ (**8**) suspended in water with a slight excess of NaN_3 and a suitable didentate ligand produces deep red solutions from which, upon addition of solid $NaClO_4$, the perchlorate salts $[LCr^{III}(N_3)(\text{didentate ligand})]^{n+}(ClO_4)_n$, precipitate in ~80% yield. The didentate ligands employed are pentane-2,4-dionate (acac), 2,2,6,6-tetramethylheptane-3,5-dionate (tacac), picolinate (pic), 1,10-phenanthroline (phen), and oxalate (ox), and the following complexes were isolated as air-stable but light-sensitive red solid materials: $[LCr^{III}(N_3)(acac)](ClO_4)$, **9**; $[LCr^{III}(N_3)(tacac)](ClO_4)$, **10**; $[LCr^{III}(N_3)(pic)](ClO_4)$, **11**; $[LCr^{III}(N_3)(phen)](ClO_4)_2$, **12**; $[LCr^{III}(N_3)(ox)]$, **17**. This series encompasses a neutral species **17**, the monocationic species **9**−**11**, and a dication in **12**. Some $[L'Cr^{III}(acac)X]PF_6$ (X = F^-, $O_2PF_2^-$) complexes containing the 1,4,7-trimethyl-1,4,7-triazacyclononane macrocycle were recently structurally characterized.[19]

Irradiation of microcrystals of **9**−**12** thinly dispersed on an aluminum foil with UV light (100−400 nm) for 5−6 h induces a gradual color change from red to yellow and formation of dinitrogen. The reaction was considered to be complete when the $\nu_{as}(N_3)$ stretching frequency in the infrared spectrum at ~2070 cm^{-1} had completely disappeared. From measurement of the loss of weight of the starting complex and volumetric determination of the amount of N_2 produced, it was readily established that, per mole of chromium(III) ion of complexes **9**−**12**, 1 equiv of N_2 is generated (eq 1). The resulting yellow materials were recrystallized from hot acetonitrile. The following complexes were isolated as air- and light-stable solids: $[LCr^V(N)(acac)](ClO_4)$, **13**; $[LCr^V(N)(tacac)](ClO_4)$, **14**; $[LCr^V(N)(pic)](ClO_4)$, **15**; $[LCr^V(N)(phen)](ClO_4)_2$, **16**. Complexes **13**−**16** are also stable in aqueous solution.

Interestingly, when the oxalate complex **17** was irradiated in the solid state in exactly the same manner as described above, only 0.5 equiv/mol of chromium(III) were generated. Pro-

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[18] (a) Knopp, P.; Wieghardt, K.; Nuber, B.; Weiss, J. *Z. Naturforsch.* **1991**, *46B*, 1077. (b) Knopp, P.; Wieghardt, K.; Nuber, B.; Weiss, J.; Sheldrick, W. S. *Inorg. Chem.* **1990**, *29*, 363. (c) Knopp, P.; Wieghardt, K. *Inorg. Chem.* **1991**, *30*, 4061.

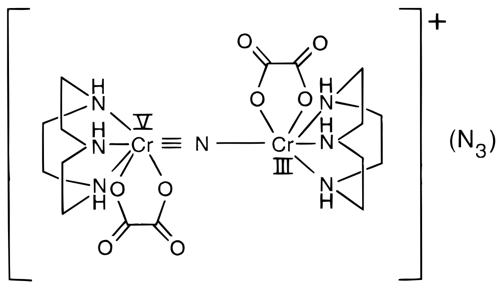
[19] Bossek, U.; Haselhorst, G.; Ross, S.; Wieghardt, K.; Nuber, B. *J. Chem. Soc., Dalton Trans.* **1994**, 2041.

Table 3. Selected Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for **13**

atom	*x*	*y*	*z*	*U*(eq)[a]
Cr(1)	1468(1)	2500	1089(3)	28(1)
N(1)	892(3)	1041(10)	949(12)	50(3)
N(2)	1256(4)	2500	−2132(15)	42(4)
N(3)	1517(3)	2500	3309(13)	40(3)
O(1)	1943(2)	1010(7)	452(8)	52(2)
C(1)	792(6)	483(16)	−967(16)	134(7)
C(2)	977(4)	1152(12)	−2499(16)	77(4)
C(3)	445(3)	1750(13)	1767(18)	100(5)
C(4)	2413(5)	1199(19)	316(14)	70(5)
C(5)	2640(7)	2500	375(27)	84(9)
C(6)	2700(5)	−240(20)	211(18)	120(7)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

longued irradiation up to 48 h did not change this ratio. The starting complex **17** displays a $\nu_{as}(N_3)$ stretching mode in the infrared at 2066 cm^{-1}, and the still red-orange product of its irradiation **18** exhibits a $\nu(N_3)$ band at 2073 cm^{-1}. In addition, a new band at 965 cm^{-1} indicates the presence of a $Cr^V{\equiv}N$ moiety. All spectroscopic data of **18** together with its magnetic properties (see below) are in agreement with the formulation as mixed-valent, μ-nitrido-bridged Cr^VCr^{III} complex **18**



As is shown in the EPR section, **18** is not stable in dimethyl sulfoxide (dmso) solution, and we have not been able to find another solvent from which **18** could be recrystallized.

When a red solution of **17** in dmso was irradiated with UV light for 2 h at room temperature, the color changed to yellow and 1 equiv of N_2/mol of chromium(III) ion was generated. From this solution yellow crystals of the neutral complex $[LCr^V(N)(ox)]$ (**19**) precipitated in 77% yield within 2 d.

Manganese. The synthesis and crystal structure of $[L'Mn^{III}(acac)(OC_2H_5)]PF_6$ where L′ represents 1,4,7-trimethyl-1,4,7-triazacyclononane were described previously.[15] When an aqueous solution of this complex was treated with a few drops of concentrated $HClO_4$ and NaN_3 was added, a clear brown solution was obtained. Addition of $NaPF_6$ initiated the precipitation of $[L'Mn(N_3)(acac)]PF_6$ (**20**).

Irradiation of an acetonitrile solution of **20** with UV light at −10 °C with a mercury immersion lamp generated, upon addition of an aqueous solution of KPF_6, blue crystals of $[L'Mn(N)(acac)]PF_6$ (**21**), eq 2.

$$\underset{\textbf{20}}{[L'Mn^{III}(N_3)(acac)]^+} \xrightarrow[CH_3CN]{h\nu} \underset{\textbf{21}}{[L'Mn(N)(acac)]^+} + N_2 \qquad (2)$$

Crystal Structure Determinations. The crystal structures of $[L'Mn^{III}(acac)(N_3)]\,BPh_4$ (**20**), $[L'Mn^V(acac)(N)]BPh_4$ (**21**), and $[LCr^V(acac)(N)](ClO_4)$ (**13**) have been determined by single-crystal X-ray crystallography. Tables 3−5 give the atom coordinates of the respective cations; Table 6 summarizes selected bond distances and angles of the cations, and Figures 2−4 display their structures.

Table 4. Selected Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **20**

atom	*x*	*y*	*z*	*U*(eq)[a]
Mn(1)	956(1)	3997(1)	2772(1)	46(1)
O(1)	−193(3)	4556(3)	2662(3)	64(2)
O(2)	1597(3)	4792(2)	3952(2)	52(2)
(1)	395(4)	3160(3)	1455(3)	53(3)
N(2)	2276(4)	3523(3)	2687(3)	57(3)
N(3)	1613(4)	4868(3)	2246(3)	50(3)
N(7)	384(4)	3066(3)	3120(4)	71(3)
N(8)	556(5)	3089(4)	3851(5)	81(4)
N(9)	745(7)	3063(6)	4543(5)	146(6)
C(1)	910(5)	2455(4)	1395(4)	72(4)
C(2)	2013(5)	2835(4)	1794(4)	72(4)
C(3)	2990(5)	4318(5)	2796(4)	66(4)
C(4)	2574(5)	4734(4)	2174(4)	66(4)
C(5)	858(5)	4613(4)	1356(4)	66(4)
C(6)	586(5)	3631(4)	868(4)	60(4)
C(7)	−680(4)	2751(4)	1186(4)	81(4)
C(8)	2652(5)	3210(4)	3400(4)	83(4)
C(9)	1757(5)	5811(4)	2777(4)	67(4)
C(71)	−1258(5)	5350(5)	3118(4)	86(4)
C(72)	−343(5)	5071(5)	3321(5)	60(4)
C(73)	303(5)	5400(4)	4185(4)	60(4)
C(74)	1210(5)	5280(4)	4457(4)	51(4)
C(75)	1866(4)	5747(4)	5393(4)	69(4)
Mn(2)	3795(1)	1432(1)	6739(1)	52(1)
O(3)	3414(3)	2489(3)	6720(3)	72(3)
O(4)	3379(3)	952(3)	5391(3)	77(3)
N(4)	4117(4)	282(3)	6871(4)	63(3)
N(5)	4015(4)	1784(4)	8158(3)	63(3)
N(6)	2385(4)	782(3)	6649(3)	55(3)
N(10)	5126(5)	1900(4)	6922(5)	91(4)
N(11)	5452(5)	2568(6)	6902(5)	106(5)
N(12)	5777(7)	3250(7)	6946(8)	191(8)
C(11)	4671(7)	520(6)	7804(6)	137(7)
C(12)	4506(6)	1182(5)	8441(5)	92(5)
C(13)	3040(6)	1674(6)	8213(5)	122(6)
C(14)	2266(5)	1089(6)	7512(5)	109(5)
C(15)	2331(6)	−154(5)	6342(6)	100(5)
C(16)	3196(6)	−378(5)	6595(6)	114(6)
C(17)	4694(6)	−42(5)	6319(5)	114(6)
C(18)	4617(6)	2682(5)	8707(5)	113(5)
C(19)	1593(5)	914(5)	6010(4)	88(5)
C(76)	3309(6)	3706(5)	6340(5)	126(6)
C(77)	3330(5)	2779(6)	6111(6)	81(5)
C(78)	3281(5)	2305(6)	5271(6)	88(6)
C(79)	3281(5)	1424(6)	4934(5)	73(5)
C(80)	3144(5)	975(5)	3980(5)	105(6)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

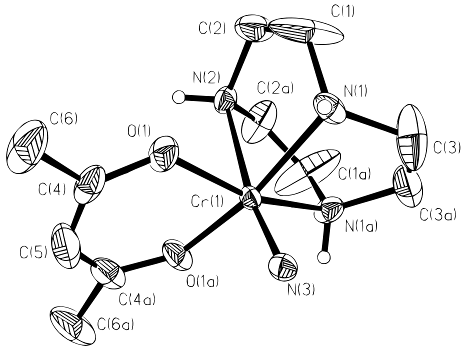


Figure 2. Structure of the monocation in crystals of **13**. Hydrogen atoms are omitted for clarity.

A common feature of these structures is the five-coordinate LM(acac) fragment which consists of the facially coordinated tridentate amine 1,4,7-triazacyclononane (**13**) or its N-methylated derivative (**20**, **21**) and the didentate ligand pentane-2,4-dionate(1−). The sixth coordination site is occupied by a terminal azido ligand in **20** or a terminal nitrido ligand in **13**

Table 5. Selected Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for **21**

atom	*x*	*y*	*z*	*U*(eq)[a]
Mn(1)	1962(1)	1805(1)	4900(1)	40(1)
O(1)	2188(4)	1030(3)	5601(2)	60(2)
O(2)	2173(4)	917(3)	4302(2)	56(2)
N(1)	2233(5)	2654(3)	4208(2)	55(2)
N(2)	4173(4)	1889(3)	5010(2)	52(2)
N(3)	2197(5)	2829(3)	5490(2)	53(2)
N(4)	503(4)	1858(3)	4827(2)	54(2)
C(1)	3529(7)	2510(5)	3990(3)	97(4)
C(2)	4553(6)	2403(4)	4491(3)	76(3)
C(3)	4438(6)	2303(4)	5624(3)	79(3)
C(4)	3581(7)	2994(5)	5709(3)	98(4)
C(5)	1679(7)	3541(4)	5086(3)	83(3)
C(6)	2149(8)	3514(4)	4457(3)	91(4)
C(7)	1256(7)	2541(5)	3659(3)	85(3)
C(8)	4830(6)	1076(4)	5031(4)	90(3)
C(9)	1431(7)	2758(4)	6036(3)	83(3)
C(10)	1939(6)	249(5)	5544(4)	65(3)
C(11)	1739(7)	−175(5)	4980(5)	71(4)
C(12)	1927(6)	150(4)	4406(4)	66(3)
C(13)	1908(9)	−215(5)	6150(4)	122(4)
C(14)	1885(9)	−403(5)	3834(4)	124(4)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

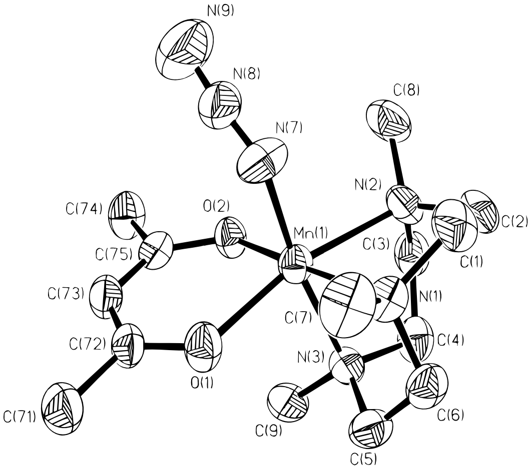


Figure 3. Structure of one of the crystallographically independent monocations in crystals of **20**.

and **21**. In all three structures, the monocations are well separated from the anions (ClO_4^- or BPh_4^-).

As has been observed in all crystal structures of complexes containing the LM or L′M fragment, the three five-membered chelate rings $\overline{\text{M−N−C−C−N}}$ adopt either ($\lambda\lambda\lambda$) or ($\delta\delta\delta$) conformation. Since all complexes investigated here crystallize in centric space groups (Table 2), both enantiomers are present in equal amounts in the unit cell. The monocation in **13** lies on a crystallographic mirror plane which bisects the LCr fragment. Consequently, the ethylene carbon atoms are disordered. This disorder results in physically meaningless large anisotropic thermal parameters of the carbon atoms and unrealistically short C−C and N−C bonds of the coordinated macrocycle. In the structures of **20** and **21**, these distances are normal and the above problem is not encountered.

The structure of **20** consists of two crystallographically independent monocations; their metrical details differ slightly. Both monocations display an elongated Jahn−Teller axis along one amine-to-manganese and one oxygen-to-manganese bond which are trans to each other (O(1)−Mn(1)−N(2) and O(4)−Mn(2)−N(5)). This renders the coordinated acac ligand asymmetric in both instances. Interestingly, the Mn−N_{azido} bond distances at 1.975(7) and 1.893(7) Å are quite similar to those reported for the Mn(IV) species $[Mn(N_3)_4(bpy)]$, which are on average 1.914(8) Å (trans to the bpy ligand) and 1.965(7) Å (cis to the bpy ligand).[20] The dimensions of the LMn^{III}(acac) fragment are very similar to those reported for $[L'Mn(acac)(OC_2H_5)]BPh_4$, where the same elongated Jahn−Teller axis is clearly detectable.[15]

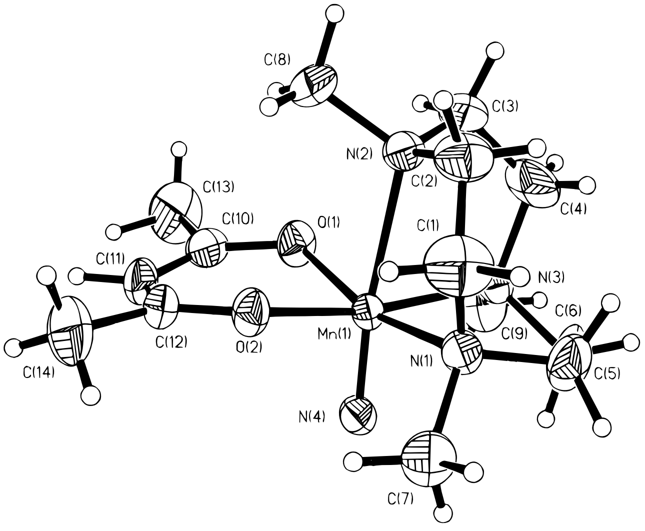


Figure 4. Structure of the monocation in crystals of **21**.

Complex **13** consists of $[LCr^V(N)(acac)]^+$ monocations and well-separated perchlorate anions. The Cr^V ion is in a distorted octahedral environment composed of the tridentate amine, the didentate acac ligand, and a terminal nitrido ligand. The $Cr^V{\equiv}N$ distance of 1.575(9) Å is very short and indicative of a triple bond. This bond length is similar to those reported for two five-coordinate square-based pyramidal nitrido chromium(V) complexes (Table 1). The Cr≡N group exerts a pronounced trans influence on the Cr−N_{amine} bond in the trans position as is documented by the Cr−N_{amine} bond length difference Δ([Cr−N_{trans}]−[Cr−N_{cis}]) of 0.29 Å. Furthermore, the Cr^V ion is 0.30 Å above the mean plane of the equatorial ligand atoms O(1), O(1a), N(1), and N(1a), which is to be compared with 0.42 and 0.51 Å determined for the two five-coordinate square-based pyramidal complexes in Table 1.[5c,d]

It is instructive to compare the metrical details of the coordination polyhedra of the isomorphous complexes **13** and $[LCrCl(acac)](ClO_4)$[21] shown in Figure 5. In the latter, the chromium(III) ion is also displaced above the mean plane toward the chloro ligand of the acac oxygen atoms and two amine nitrogen atoms by 0.167 Å but the Cr^{III}−N_{amine} bonds are within experimental error identical. As is to be expected, the chloro ligand does not exert a significant trans influence. Rather surprisingly, the Cr−N_{amine} and the Cr−O_{acac} bond lengths in the equatorial plane are virtually identical in both complexes, despite the fact that in **13** the chromium ion possesses the formal oxidation state +V whereas in $[LCrCl(acac)](ClO_4)$ it is only +III.

The structure of the monocation $[L'Mn(N)(acac)]^+$ in crystals of **21** is very similar to that of **13**. The Mn≡N bond is very short at 1.518 (4) Å and is in perfect agreement with the two five-coordinate nitridomanganese(V) complexes in Table 1. The

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(20) Dave, B. C.; Czernuszewicz, R. S. *J. Coord. Chem.* **1994**, *33*, 257.

(21) The crystal structure of $[LCrCl(acac)](ClO_4)$ has been determined by X-ray crystallography. It crystallizes in the orthorhombic space group *Pnma* with cell constants $a = 17.872(4)$ Å, $b = 9.285(2)$ Å, $c = 10.898(2)$ Å, $V = 1808.5(7)$ Å^3, and $Z = 4$ and has been fully refined to $R = 0.063$ and $R_w = 0.066$. Full details of the synthesis and structure determination will be reported elsewhere.

Table 6. Selected Bond Lengths (Å) and Angles (deg)

Complex **13**

Cr(1)−N(1)	2.069(9)	Cr(1)−N(2)	2.350(11)
Cr(1)−N(3)	1.575(9)	Cr(1)−O(1)	1.938(6)
O(1)−C(4)	1.30(1)	C(4)−C(6)	1.54(2)
C(4)−C(5)	1.35(2)		

N(1)−Cr(1)−N(2)	76.6(3)	N(1)−Cr(1)−N(3)	96.4(3)
N(2)−Cr(1)−N(3)	170.5(4)	N(1)−Cr(1)−O(1)	91.8(3)
N(2)−Cr(1)−O(1)	86.5(3)	O(1)−Cr(1)−O(1a)	90.4(4)
N(1)−Cr(1)−N(1a)	81.2(5)		
N(1)−Cr(1)−O(1a)	162.7(3)		

Complex **20**[a]

Mn(1)−O(1)	2.071(5)	Mn(1)−O(2)	1.899(3)
Mn(1)−N(1)	2.083(4)	Mn(1)−N(2)	2.249(6)
Mn(1)−N(3)	2.162(6)	Mn(1)−N(7)	1.975(7)
O(1)−C(72)	1.280(9)	O(2)−C(74)	1.307(8)
N(8)−N(9)	1.15(1)	N(7)−N(8)	1.18(1)
C(71)−C(72)	1.50(1)	C(72)−C(73)	1.397(9)
C(73)−C(74)	1.37(1)	C(74)−C(75)	1.495(7)

O(1)−Mn(1)−O(2)	91.0(2)	O(1)−Mn(1)−N(1)	93.0(2)
O(2)−Mn(1)−N(1)	173.8(2)	O(1)−Mn(1)−N(2)	167.4(2)
O(2)−Mn(1)−N(2)	93.3(2)	N(1)−Mn(1)−N(2)	81.8(2)
O(1)−Mn(1)−N(3)	87.9(2)	O(2)−Mn(1)−N(3)	92.6(2)
N(1)−Mn(1)−N(3)	82.8(2)	N(2)−Mn(1)−N(3)	80.1(2)
O(1)−Mn(1)−N(7)	97.2(2)	O(2)−Mn(1)−N(7)	93.8(2)
N(1)−Mn(1)−N(7)	90.5(2)	N(2)−Mn(1)−N(7)	94.3(3)
N(3)−Mn(1)−N(7)	171.8(2)	Mn(1)−N(7)−N(8)	125.6(4)
N(7)−N(8)−N(9)	175.4(9)		

Mn(2)−O(3)	1.961(5)	O(3)−C(77)	1.26(1)
Mn(2)−O(4)	2.050(5)	O(4)−C(79)	1.27(1)
Mn(2)−N(4)	2.134(7)	N(10)−N(11)	1.16(1)
Mn(2)−N(5)	2.211(6)	N(11)−N(12)	1.14(2)
Mn(2)−N(6)	2.126(6)	C(77)−C(76)	1.49(1)
Mn(2)−N(10)	1.893(7)	C(77)−C(78)	1.37(1)
		C(78)−C(79)	1.41(1)
		C(79)−C(80)	1.50(1)

Complex **21**

Mn(1)−O(1)	1.948(4)	Mn(1)−O(2)	1.943(4)
Mn(1)−N(1)	2.055(5)	Mn(1)−N(2)	2.301(4)
Mn(1)−N(3)	2.073(5)	Mn(1)−N(4)	1.518(4)
O(1)−C(10)	1.283(9)	O(2)−C(12)	1.280(8)
C(10)−C(11)	1.38(1)	C(10)−C(13)	1.50(1)
C(11)−C(12)	1.37(1)	C(12)−C(14)	1.51(1)

O(1)−Mn(1)−O(2)	91.7(2)	O(1)−Mn(1)−N(1)	165.1(2)
O(2)−Mn(1)−N(1)	88.6(2)	O(1)−Mn(1)−N(2)	85.1(2)
O(2)−Mn(1)−N(2)	86.1(2)	N(1)−Mn(1)−N(2)	80.0(2)
O(1)−Mn(1)−N(3)	92.0(2)	O(2)−Mn(1)−N(3)	165.7(2)
N(1)−Mn(1)−N(3)	84.3(2)	N(2)−Mn(1)−N(3)	80.5(2)
O(1)−Mn(1)−N(4)	99.1(2)	O(2)−Mn(1)−N(4)	98.8(2)
N(1)−Mn(1)−N(4)	95.7(2)	N(2)−Mn(1)−N(4)	173.4(2)
N(3)−Mn(1)−N(4)	94.3(2)		

[a] For the second crystallographically independent cation only bond distances are given.

Mn≡N bond exerts again a strong influence on the Mn−N$_{amine}$ bond in the trans position (Δ[(Mn−N$_{trans}$)−(Mn−N$_{cis}$)] = 0.24Å).

Magnetic Properties of Complexes. Table 7 gives effective magnetic moments of complexes at 293 K which were derived from temperature-dependent susceptibility measurements on solid samples in the range 80−293 K by using the Faraday method. For complexes **1**−**4** these measurements have not been carried out, since their 1,4,7-trimethyl-1,4,7-triazacyclononane analogs have been fully characterized previously.[18]

Complex **5**(ClO_4) displays a temperature-independent magnetic moment (81−293 K) of 1.75 μ_B, which is typical for a vanadium(IV) species (d^1), whereas complexes **6** and **7** are diamagnetic (d^0). The azidochromium(III) precursor complexes **9**−**12** and **17** have magnetic moments in the range 3.6−3.9 μ_B, characteristic of octahedral chromium(III) complexes (d^3).

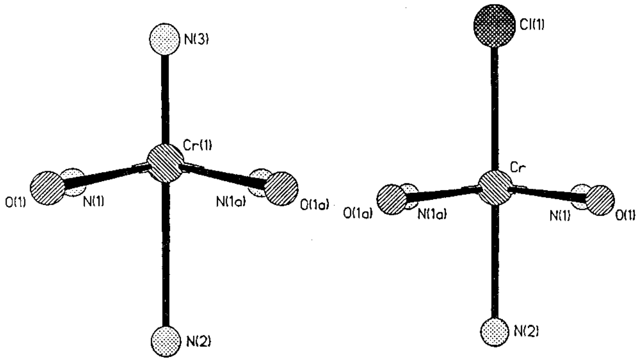


Figure 5. Comparison of the coordination polyhedra of the monocations [LCr^V(N)(acac)]$^+$ in crystals of **13** (left) and [LCr^{III}Cl(acac)]$^+$ (right) in the corresponding perchlorate salt. Selected bond distances (Å) of the latter: Cr(1)−N(1), 2.085(6); Cr(1)−N(2), 2.079(8); Cr(1)−O(1), 1.928(6); Cr(1)−Cl, 2.302(3).

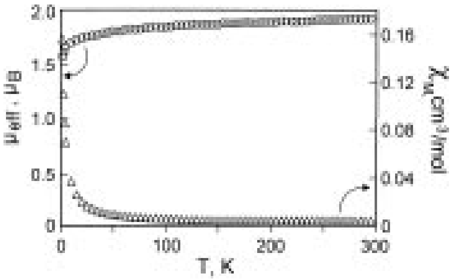


Figure 6. Temperature dependence of the molar susceptibility and of the magnetic moment of the neutral complex **19**.

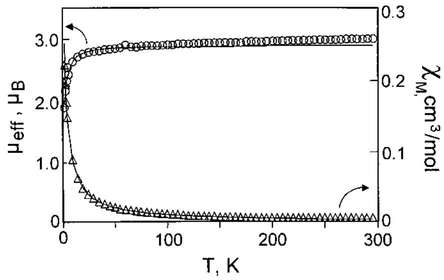


Figure 7. Temperature dependence of the molar susceptibility and of the magnetic moment of the neutral moment of **18** (calculated per dinuclear unit). The solid line represents a fit to the data (see text).

For the nitridochromium(V) species **13**, **15**, **16**, and **19**, effective magnetic moments between 1.74 and 1.9 μ_B have been determined at 293 K. The temperature dependence of the susceptibility (1.8−293 K, SQUID) and of the effective magnetic moment of the neutral complex **19** is shown in Figure 6. Spin−orbit coupling decreases μ_{eff} with decreasing temperature.

Figure 7 shows the temperature dependence of the magnetic moment and of the susceptibility of **18** (calculated per dinuclear unit). In the temperature range 40−295 K, the effective magnetic moment increases from 2.83 to 3.01 μ_B/dinuclear unit. Below 40 K, it drops to 1.88 μ_B at 2 K. From this it is concluded that **18** has an $S = 1$ ground state, which is in agreement with the fact that **18** is EPR silent at 10 K. An $S = 1$ ground state can be achieved by intramolecular antiferromagnetic coupling between a chromium(V) (d^1) and chromium(III) (d^3) ion. The solid line in Figure 7 shows a fit to the data by using the Heisenberg−Dirac−van Vleck isotropic spin-coupling model with $H = -2J\vec{S}_1\cdot\vec{S}_2$ ($S_1 = {}^3/_2$, $S_2 = {}^1/_2$). Numerical values are $J = -122$ cm^{-1} and $g = 1.98$. No paramagnetic impurity, zero-field splitting, or spin−orbit coupling has been taken into account. Since the fit is reasonably good using only the two

Table 7. Electronic Spectral Data and Magnetic Properties

complex	solvent	λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})	μ_{eff}(293 K), μ_B
5(ClO_4)	CH_3CN	697 (39), 537 (13), 403 (58), 319 (8.0×10^3), 271 (4.1×10^3)	1.75
8	solid state[a]	704, 588, 446	3.7
9	CH_3CN	521 (100), 380 (260), 340 (4.3×10^3), 280 (7.2×10^3), 260 (6.9×10^3)	3.7
10	CH_3CN	522 (89), 364 (241), 340 (3.7×10^3), 279 (5.1×10^3), 259 (5.1×10^3)	3.8
11	CH_3CN	511 (93)	3.7
12	CH_3CN	512 (94), 400 (sh), 340 (sh), 266 (6.0×10^3)	3.6
13	CH_3CN	421 (42), 400 (sh), 324 (4.1×10^3), 258 (2.4×10^3)	1.74
14	CH_3CN	423 (66), 301 (4.2×10^3), 252 (2.3×10^3)	not measd
15	CH_3CN	407 (82), 265 (3.5×10^3)	1.8
16	CH_3CN	450 (sh, 94), 262 (18.1×10^3), 226 (20×10^3)	1.8
17	solid state[a]	519	3.9
18	solid state[a]	~550, 420	3.0 (see text)
19	solid state[a]	425	1.9
20	CH_3CN	422 (2.6×10^3), 317 (8.4×10^3), 263 (9.3×10^3)	4.9
21	CH_3CN	647 (56), 580 (52), 400 (sh), 320 (sh), 293 (6.5×10^3)	0.4−1.1

[a] Reflectance spectrum.

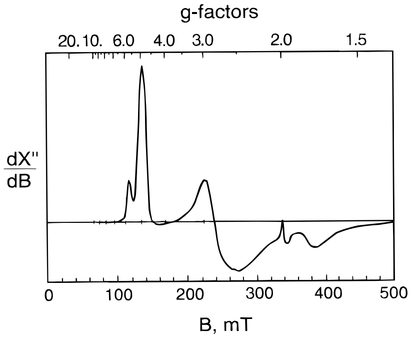


Figure 8. X-band EPR spectrum of **9** in frozen acetonitrile at 10 K.

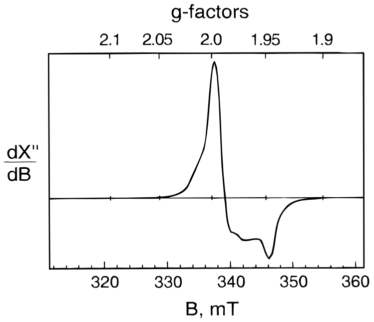


Figure 9. X-band EPR spectrum of **13** in frozen acetonitrile at 10 K.

variables above, we feel confident that **18** is to be described as a mixed-valent μ-nitrido-bridged Cr^VCr^{III} dinuclear complex.

The manganese(III) complex **4** has a magnetic moment of 4.9 μ_B, indicating a high-spin d^4 electronic configuration. The nitridomanganese(V) species **21** is expected to be diamagnetic (d^2), as has been reported for the five-coordinate species given in Table 1. It is noted that for these latter complexes no susceptibility measurements have been reported. Their “diamagnetism” was established by the observation of “normal” ^1H NMR spectra in solution. We have measured the susceptibility of different samples of **21** in the range 2−300 K using a SQUID magnetometer. In all samples we found residual paramagnetism after correcting the data for underlying diamagnetism of the order 1.1−0.49 μ_B/Mn^V. The smallest value was obtained for a sample which was carefully recrystallized three times. Further recrystallization steps did not reduce this residual paramagnetism. As always in cases like this, there remains the possibility of a cocrystallizing paramagnetic impurity (~1%; $S = 2$) but there is also the possibility of genuine Pauli paramagnetism (temperature-independent paramagnetism). It is noted that Dehnicke et al.[4b] have reported similar magnetic behavior for [$V^VNCl_2(pyr)_2$], for which they found 0.8 μ_B/V.

EPR Spectra of Chromium Complexes. The azidochromium complexes **9**−**12** and **17** are distorted octahedral chromium(III) species with a d^3 electronic configuration (^4F ground state in O_h symmetry). Figure 8 shows the rhombic X-band EPR spectrum of **9** in acetonitrile (frozen) solution at 10 K. The values $g_y = 4.8$, $g_x = 2.8$, and $g_z = 1.9$, with rhombicity $E/D = 0.18$, were established. This is a typical ESR spectrum for an octahedral chromium(III) complex of rather low symmetry. Figure 9 shows the corresponding spectrum of the chromium(V) complex **13** in frozen acetonitrile at 10 K. An axial spectrum with $g_\perp = 1.99$ and $g_\parallel = 1.955$ with no hyperfine splitting is observed. Similar spectra have been reported for [Cr(OEP)(N)] in toluene at 77 K ($g_\perp = 1.994_5$, $g_\parallel = 1.958_3$). The solid state spectrum of [Cr(salen)(N)] displays an isotropic signal at $g = 1.98$, whereas in a frozen 1-butanol/dmso mixture an axial signal ($g_\perp = 1.993$, $g_\parallel = 1.960$) has been observed.[8b] This is indicative for a large splitting between the d_{xy} and the d_{xz}, d_{yz} orbitals and of the fact that the unpaired electron is localized in the d_{xy} orbital (b_2 in Figure 1).

The EPR spectrum at 10 K of pure **19** dissolved in dmso displays an axial spectrum with $g_\perp = 1.995$ and $g_\parallel = 1.955$, whereas a powdered sample shows an isotropic signal at $g = 1.99$. It is now significant that the solid state UV-irradiation product of **17** yielding complex **18** were only 0.5 equiv of N_2/chromium(III) is produced is EPR silent at 10 K. In contrast, when **18** is dissolved in the dark in dmso, the EPR spectrum shown in Figure 10 is observed, which displays two signals at $g = \sim 5$ and ~ 2. Clearly, a mixture of a chromium(III) and of a chromium(V) species is produced. When this solution was irradiated with UV light at room temperature for ~2 h, the signal at $g \sim 5$ disappeared and only the axial spectrum of **19** at $g \sim 2$ (Figure 9) was observed. These observations are in excellent agreement with the formation of an antiferromagnetically coupled $Cr^{III}Cr^V$ mixed-valent complex **18** ($S_t = 1$) which dissociates in dmso into mononuclear Cr(III) and Cr(V) species. The Cr(III) species probably reacts with azide to give **17**, which upon irradiation forms **19** as the sole product (Scheme 3).

Electronic Spectra. Table 7 summarizes the electronic spectral data of complexes which were measured in acetonitrile solution or recorded as reflectance spectra on solid samples. For complexes **9**−**12** and **17**, a typical d−d transition of low intensity ($\epsilon \sim 100$ M^{-1} cm^{-1}) in the visible region in the range 511−522 nm is observed which is assigned to the $^4A_{2g} \rightarrow {}^4T_{2g}$ transition (in O_h symmetry).

The octahedral nitridochromium(V) complexes **13**−**16** and **19** display a single d−d transition in the range 407−425 nm of low intensity. It is tempting to assign this band to the $^2B \rightarrow {}^2E$ ($d_{xy} \rightarrow d_{xz}$, d_{yz}) transition of a d^1 system in C_{4v} symmetry, but

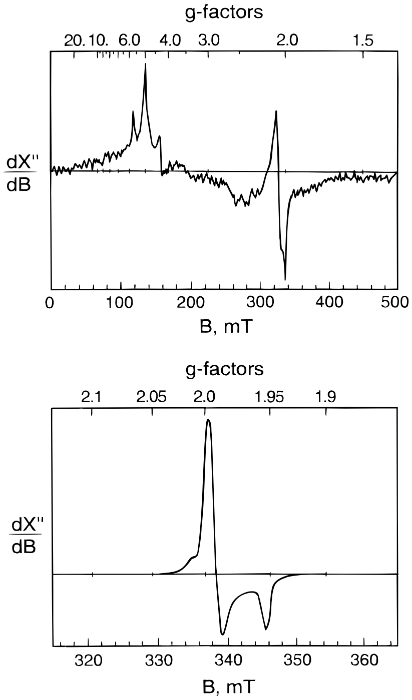
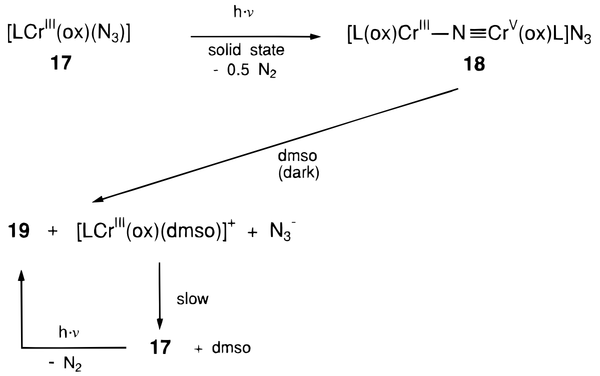


Figure 10. X-band EPR spectra of (a) **18** in frozen dmso at 10 K (top) (the sample was carefully protected from light) and (b) the same solution after illumination for 2 h with UV light (bottom).

Scheme 3



see the controversial discussion in refs 22 and 23 for $[M^V(O)Cl_4]^-$ ions (M = Cr,Mo), for which two low-energy transitions at $\sim$13 000 cm^{-1} ($\sim$770 nm) and $\sim$18 000 cm^{-1} (555 nm) have been reported and assigned to the $^2B \rightarrow {}^2E$ transition at lower energy in the chromium(V) case. Such low-energy transitions are not observed for octahedral complexes **13**−**16** and **19**, and the d−d transition at $\sim$420 nm is assigned to $^2B_2 \rightarrow {}^2E_1$ (and $^2A_1$) ($d_{xy} \rightarrow d_{x^2-y^2}$ and d_{z^2}) transitions. Figure 11 displays a comparison of reflectance spectra of solid samples of **17**−**19**. The azidochromium(III) complex exhibits the typical d−d transition ($^4A_{2g} \rightarrow {}^4T_{2g}$) at 519 nm, which is absent in the spectrum of the nitridochromium(V) species **19**, where only the d−d transition at 425 nm is observed. In the spectrum of **19**, both bands are detectable at $\sim$550 and 420 nm, which is in agreement with our proposal of a mixed-valent μ-nitrido-bridged Cr^VCr^{III} moiety. Note that the spectrum of **18** is not a simple superposition of those of **17** and **19**, which is taken as evidence against the assumption that an equimolar amount of **17** and **19** is present in **18**.

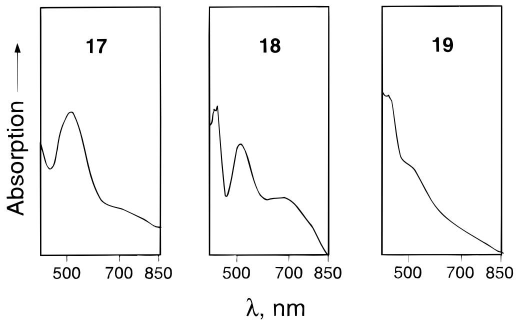


Figure 11. Solid state reflectance spectra of **17** (left), **18** (middle), and **19** (right).

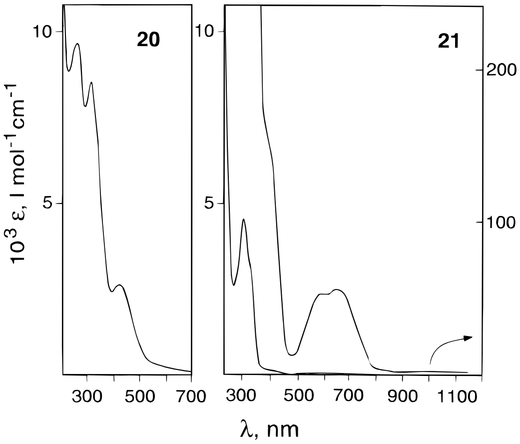


Figure 12. Electronic spectra of **20** (left) and **21** (right) in acetonitrile solution.

Table 8. Selected Vibrational Spectroscopic Data

complex	IR,[a] cm^{-1}	assgnt	Raman,[b] cm^{-1}	assgnt
4(ClO_4)	2062	$\nu_{as}(N_3)$		
5(ClO_4)	968	ν(V=O)		
5(PF_6)	979	ν(V=O)		
6(ClO_4)	967	ν(V≡N)		
7($ClO_4)_2$	958	ν(V=O)		
7($PF_6)_2$	958	ν(V=O)		
9	2074	$\nu_{as}(N_3)$		
10	2069			
11	2057			
12	2084			
13	not detected	ν(Cr≡N)	967	ν(Cr≡N)
14	943		962	
15	953		967, 974	
16	969		not measd	
17	2066	$\nu_{as}(N_3)$		
18	2073	$\nu_{as}(N_3)$		
	965	ν(Cr≡N)		
19	963	ν(Cr≡N)	968	ν(Cr≡N)
20(PF_6)	2050	$\nu_{as}(N_3)$		
21(PF_6)	983	ν(Mn≡N)		

[a] KBr disks. [b] Solid samples.

Figure 12 shows the electronic spectra of **20** and **21** in CH_3CN solution. The two low-energy absorptions at 647 and 580 nm of **21** are tentatively assigned to the $^2B \rightarrow {}^2E$ ($d_{xy} \rightarrow d_{xz}$, d_{yz}) transition with the assumption that, due to the lower than C_{4v} symmetry of the $[LMn(N)(acac)]^+$ cation, the degeneracy of the ^2E level is lifted.

Vibrational Spectroscopy. Table 8 gives selected vibrational data for the complexes. All mononuclear azido complexes (**4**, **9**−**12**, **17**, **20**) display a very strong $\nu_{as}(N_3)$ stretching mode in the infrared spectra in the range 2050−2084 cm^{-1} [24] which

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disappears upon irradiation with UV light. The nitrido complexes **6**, **14**−**16**, **19**, and **21** exhibit the $\nu(M{\equiv}N)$ stretching frequency in the range 943−983 cm^{-1}, which is considerably lower than for the five-coordinate complexes (>1010 cm^{-1}) compiled in Table 1. The $M-N_{amine}$ bond trans to the $M{\equiv}N$ bond obviously weakens the $M{\equiv}N$ bond.

The assignments of $\nu_{as}(N_3)$ and $\nu(M{\equiv}N)$ stretching modes have been corroborated by investigation of the isotopomer mixtures $M-{}^{14}N-{}^{14}N-{}^{15}N$ and $M-{}^{15}N-{}^{14}N-{}^{14}N$ of **9** and **20** and $M{\equiv}{}^{14}N$ and $M{\equiv}{}^{15}N$ of **13** and **21**. The 1:1 isotopomer mixtures were generated by synthesizing the azido complexes with isotopically labeled $Na[{}^{14}N{}^{14}N{}^{15}N]$. Photolyzing these mixtures produces a 1:1 mixture of $M{\equiv}{}^{14}N$ and $M{\equiv}{}^{15}N$ nitrido species.

Unlabeled **9** exhibits a sharp $\nu_{as}(N_3)$ mode at 2074 cm^{-1} whereas for the isotopomer mixture a broader band at 2065 cm^{-1} is observed in the infrared spectrum. In contrast, for unlabeled **20** (PF_6) a sharp $\nu_{as}(N_3)$ mode at 2050 cm^{-1} is observed in the IR which splits into two bands of equal intensity at 2050 and 2036 cm^{-1} upon labeling. Similar effects have been reported for azido(porphinato)manganese(III) complexes.[24]

For the nitrido complexes, identification of the $\nu(M{\equiv}N)$ stretching frequency in the IR proved to be difficult due to the low intensity of this mode and neighboring ligand bands of the coordinated amine. Thus, for complex **13**, we have not been able to unambiguously identify this mode in the infrared, but in the Raman spectra a $\nu(Cr{\equiv}N)$ band has been observed at 967 cm^{-1} for the unlabeled complex which splits into two bands at 970 and 940 cm^{-1} upon labeling.

Similar problems have been encountered in the infrared spectrum of **21**(PF_6), where the $\nu(Mn{\equiv}N)$ stretch is probably hidden under a ligand band at 1004 cm^{-1}. The labeled compound displays two new weak bands at 988 and 976 cm^{-1}, which we tentatively assign to $\nu(Mn{\equiv}{}^{14}N)$ and $\nu(Mn{\equiv}{}^{15}N)$ modes, respectively.

Interestingly, for complex **18**, a $\nu_{as}(N_3)$ and a $\nu(Cr{\equiv}N)$ stretching mode are observed at 2073 and 965 cm^{-1}, respectively. From these data alone, the proposed dinuclear μ-nitrido bridging structure cannot be deduced.

Discussion

Photolysis of the isostructural series of azidometal(III) complexes $[LM^{III}(N_3)(acac)](ClO_4)$ in the solid state or in CH_3CN solution generates the corresponding nitridometal(V) species $[LM^V(N)(acac)](ClO_4)$ and 1 equiv of dinitrogen where M is vanadium, chromium, and manganese. The nitrido complexes **13** and **21** are the first structurally characterized octahedral species containing a terminal $M{\equiv}N$ group.

The observed very short $Cr{\equiv}N$ and $Mn{\equiv}N$ distances clearly indicate a triple bond. The nitrido ligand is a very potent π-donor ligand which exerts a pronounced structural trans-influence on the $M-N_{amine}$ bond trans to the $M{\equiv}N$ moiety. On the other hand, the presence of this trans $M-N_{amine}$ bond weakens the $M{\equiv}N$ bond somewhat, as is deduced from the observation that the $\nu(M{\equiv}N)$ stretching mode is in all cases observed at lower frequencies than for five-coordinate square-based pyramidal complexes with an $M{\equiv}N$ group in the apical position.

The reactivity of the $[LM(N)(acac)]^+$ ions in aqueous solution is remarkably different for the vanadium complex **6** as compared to the chromium and manganese species **13** and **21**. The former is rapidly hydrolyzed to yield the monooxovanadium(V) complex **7** and NH_3 whereas the latter two are stable in water.

Photolysis of red $[LCr(ox)(N_3)]$ (**17**) in the solid state produces only 0.5 equiv of dinitrogen/chromium(III) ion, and the resulting red-orange material **18** is most probably a mixed-valent, μ-nitrido-bridged Cr^VCr^{III} dinuclear species. A similar mixed-valent complex $[VBr_2(N_3)(dmpe)(\mu\text{-}N)VBR(dmpe)_2]$ (dmpe = 1,2-bis(dimethylphosphino)ethane) was recently structurally characterized,[25] where the μ-nitrido bridge is asymmetric with a short V(IV)−N bond at 1.65(2) Å and a longer one V(III)−N at 1.97(1) Å. This species displays an intramolecular antiferromagnetic coupling between the V(III) (d^2) and the V(IV) (d^1) ions, yielding an $S_t = 2$ ground state. Consequently, we propose for **18** a similar asymmetric μ-nitrido bridge with antiferromagnetic exchange coupling between a Cr(V) (d^1) and a Cr(III) (d^3) ion, yielding the observed $S_t = 1$ ground state. Since the $Cr^{III}-N_{nitrido}$ bond is expected to be rather weak, this bond is hydrolytically unstable and in strong donor solvents, the mononuclear species **19** and $[LCr^{III}(acac)(solvent)]^{2+}$ are generated.

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Supporting Information Available: Tables listing elemental analyses (C, H, N) of the complexes, details of the crystal data collection, atom coordinates, anisotropic thermal parameters, calculated positional parameters for the hydrogen atoms, and bond distances and angles (30 pages). Ordering information is given on any current masthead page.

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