One- *vs* Two-Electron Reduction of N_2O Promoted by a Divalent Chromium Macrocyclic Complex

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Reaction of $[Cr(ORPG)Li_2(THF)_4]$ (**1**) [ORPG = octaalkylporphyrinogen R = Et (**a**), *n*-Pr (**b**)] with N_2O gave two different products depending on the solvent employed. While a deoxygenation reaction was observed in toluene with formation of the Cr(IV) complex $[(THF)(ORPG)Cr(O)(LiTHF)_2]$ (**2**), reactions carried out in THF yielded a Cr(III) species $[Cr(ORPG)(THF)_2][Li(THF)_4]$ (**3**) where only one electron was transferred to N_2O. The structures of **1b**, **2a**, and **3a** have been elucidated by X-ray crystal structures. Crystal data are as follows. **1b**: $C_{60}H_{96}O_4CrN_4Li_2$, monoclinic $P2_1/c$, $a = 20.504(2)$ Å, $b = 12.347(1)$ Å, $c = 22.524(1)$ Å, $\beta = 94.56(1)°$, $Z = 4$. **2a**: $C_{48}H_{72}O_4CrN_4Li_2$, monoclinic $P2_1/n$, $a = 11.687(1)$ Å, $b = 20.273(3)$ Å, $c = 19.467(3)$ Å, $\beta = 100.27(1)°$, $Z = 4$. **3a**: $C_{60}H_{96}O_6CrN_4Li$, monoclinic $P2_1/c$, $a = 13.884(1)$ Å, $b = 16.170(1)$ Å, $c = 25.514(2)$ Å, $\beta = 90.59(1)°$, $Z = 4$.

Introduction

The ability of transition metal complexes to interact with NO by either forming complexes with a variety of bonding modes[1] or to perform deoxygenation reactions[2] is well established for many metals and oxidation states. However, much less is known about the reactivity of the other nitrogen oxides. This is mainly due to the exceptional stability of nitrosyl complexes or of the transition metal oxo derivatives, which are obtained as result of the reaction of a transition metal complex with nitrogen oxides, and which provides a formidable obstacle to the further development of the reactivity of these species. In this perspective, the recently described "denitrogenation" of N_2O[3] and NO[4] to form reactive metal-nitrides, rather than the expected metal oxides, may be considered as a landmark toward the understanding of the chemistry of NO_x with transition metals. With this respect, Cr(II) derivatives, are particularly interesting reagents due to their relatively low affinity for oxygen and high reactivity. In addition, the corresponding Cr(IV) species which hopefully might form as a result of the deoxygenation of NO_x performed by divalent chromium complexes, are usually unstable toward reduction or disproportionation.[5] Therefore, there is the possibility that the initial divalent state may be restored under a mild reaction condition with consequent closure of a catalytic cycle.

In this paper we describe the deoxygenation of N_2O performed by Cr(II) porphyrinogen complexes $[(ORPG)Cr]Li_2(THF)_4$ [ORPG = octaalkylprophyrinogen, R = Et,[6] *n*-Pr[7]] to form the corresponding Cr(IV)−oxo species. The choice of these macrocyclic ligands was suggested by their moderately flexible and polydentate geometry which, in addition to providing chemical stability to the complexes, makes their derivatives promising substrates for the preparation of reactive Cr═O species. In addition, the large chelating effect of these tetradentate ligands makes unwanted demetallation reactions unlikely to occur.

Herein we describe our findings.

Experimental Section

All operations were performed under inert atmosphere in a nitrogen-filled drybox (Vacuum Atmospheres) or by using standard Schlenk techniques. *n*-BuLi, styrene, styrene oxide and Li_2O were purchased (Aldrich) and used as received. N_2O and O_2 (Air Products) were dried over P_2O_5 prior to use. $CrCl_2(THF)_2$.[8] $CrCl_3(THF)_3$,[9] $ORPGH_4$ [R = Et,[6] *n*-Pr[7]], and the corresponding lithium salts $ORPG(LiTHF)_4$ were prepared according to published procedures.[10] Infrared spectra were recorded on a Mattson 9000 FTIR instrument from Nujol mulls prepared in a drybox. Samples for magnetic susceptibility measurements were weighed inside a drybox equipped with an analytical balance and sealed into calibrated tubes. Magnetic measurements were carried out with a Gouy balance (Johnson Matthey) at room temperature. The magnetic moment was calculated following standard methods,[11] and corrections for underlying diamagnetism were applied to the data.[12] Elemental analyses were carried out with a Perkin-Elmer PE 2400 CHN analyzer.

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Ratios between heavy atoms were determined by X-ray fluorescence by using a Philips XRF 2400 instrument.

Preparation of [Cr(ORPG)Li_2($THF)_4$] (1). $CrCl_2(THF)_2$ (4.1 g, 15.3 mmol) was added to a solution of [(ORPG)$Li_4(THF)_4$] (15.3 mmol) in toluene (250 mL). The resultant greenish slurry gradually changed colour to yellow, and after being stirred for 12 h the mixture was filtered to remove LiCl. The volume of the solution was reduced to *ca*. 50 mL and the resulting solution allowed to stand at −30 °C for 24 h, upon which dark yellow crystals of **1** separated.

1a [R = Et]. Yield: 8.6 g, 9.65 mmol, 63%. IR (cm^{-1}): 3093 (w), 1622 (m), 1323 (w), 1153 (s), 1061 (s), 958 (m), 779 (s), 737 (s). Anal. Calcd (found) for $C_{52}H_{80}O_4N_4Li_2Cr$: C, 70.09 (69.91); H 9.05 (8.97); N, 6.29 (6.22). $\mu_{eff} = 4.83\ \mu_B$.

1b [R = Pr]. Yield: 10.5 g, 10.4 mmol, 68%. IR (cm^{-1}): 3095 (w), 3064 (m), 1621 (m), 1315 (w), 1172 (s), 1061 (s), 1020 (sh), 960 (m), 753 (s), 730 (s). Anal. Calcd (found) for $C_{60}H_{96}O_4N_4Li_2Cr$: C, 71.83 (71.77); H, 9.64 (9.59); N, 5.58 (5.50). $\mu_{eff} = 4.87\ \mu_B$.

Preparation of [(THF)(ORPG)Cr(O)(LiTHF)$_2$] (2). Method A. A suspension of **1** (1.0 mmol) in toluene (50 mL) was exposed to anhydrous N_2O. The dark yellow suspension immediately changed color to red, and all of the solid dissolved. The resultant dark red solution was stirred under an atmosphere of N_2O for additional 10 h. The volume of the solution was then reduced to *ca*. 10 mL *in vacuo* and then layered with hexane (20 mL). After this mixture was allowed to stand for 24 h at room temperature, dark red microcrystals of **2** were obtained.

2a [R = Et]. Yield: 0.36 g, 0.43 mmol, 43%. IR (cm^{-1}): 3101 (w), 1568 (s), 1279 (s), 1238 (m), 1140 (m), 1063 (s), 999 (s), 968 (m), 921 (m), 844 (m), 756 (s). Anal. Calcd (found) for $C_{48}H_{72}O_4N_4Li_2Cr$: C, 69.04 (68.92); H, 8.69 (8.65); N, 6.71 (6.66). $\mu_{eff} = 2.81\ \mu_B$.

2b [R = Pr]. Yield: 0.54 g, 0.55 mmol, 55%. IR (cm^{-1}): 3074 (w), 1570 (s), 1304 (s), 1275 (s), 1222 (m), 1142 (m), 1061 (vs), 1041 (sh), 1013 (sh), 883 (s), 807 (m), 773 (m), 767 (m). Anal. Calcd (found) for $C_{56}H_{88}O_4N_4Li_2Cr$: C, 71.01 (70.89); H, 9.36 (9.28); N, 5.91 (5.86); $\mu_{eff} = 2.77\ \mu_B$.

Method B. A suspension of **1** (1.0 mmol) in toluene (75 mL) prepared under N_2 atmosphere was exposed to dry O_2. The color of the solution immediately changed to dark red and the resulting suspension was allowed to stir at room temperature. After 24 h the mixture was filtered, the volume of the solution was reduced to *ca*. 20 mL, and the flask was cooled to −30 °C. After this was allowed to stand for 2 days at −30 °C, microcrystalline **2** was formed in yields comparable to those from Method A.

Preparation of [Cr(ORPG)(THF)$_2$][Li(THF)$_4$] (3). Method A. A solution of complex **1** (2.0 mmol) in THF (75 mL) was exposed to N_2O. The dark yellow solution gradually changed color to orange-brown and after 30 min became an intense green. Stirring was continued for 12 h, after which the volume of the solution was reduced to *ca*. 15 mL. The resulting solution was layered with hexane (40 mL) and allowed to stand at room temperature for 3 d, upon which well-formed crystals of **3** were obtained.

3a [R = Et]. Yield: 0.67 g, 0.65 mmol, 33%. IR (cm^{-1}): 3090 (w), 3064 (w), 1573 (w), 1345 (m), 1297 (s), 1270 (m), 1178 (m), 1145 (m), 1108 (w), 1045 (s), 889 (s), 781 (m), 729 (s). Anal. Calcd (Found) for $C_{60}H_{96}O_6N_4LiCr$: C, 70.08 (69.93); H, 9.41 (9.37); N, 5.45 (5.38). $\mu_{eff} = 3.76\ \mu_B$.

3b [R = Pr]. Yield: 0.8 g, 0.70 mmol, 35%. IR (cm^{-1}): 3089 (w), 3066 (w), 1549 (w), 1344 (m), 1311 (s), 1277 (m), 1240 (m), 1176 (m), 1145 (m), 1064 (sh), 1041 (s), 922 (sh), 882 (s), 777 (m), 728 (s). Anal. Calcd (Found) for $C_{68}H_{112}O_6N_4LiCr$: C, 71.61 (71.58); H, 9.90 (9.58); N, 4.91 (4.80). $\mu_{eff} = 3.81\ \mu_B$.

Method B. $CrCl_3(THF)_3$ (1.87 g, 5.0 mmol) was dissolved in THF (100 mL), giving a purple solution. The addition of solid ORPG(LiTHF)$_4$ (5.0 mmol) immediately changed the color to dark green. The mixture was stirred for 12 h, and the volume of the solution was reduced to 30 mL. After filtration to remove LiCl, hexane (60 mL) was layered onto the mother liquor, and green crystals of **3** were obtained upon allowing the resulting mixture to stand for 3 d at room temperature. Yield: **3a**, 57%; **3b**, 65%.

Table 1. Crystal Data and Structure Analysis Results

	1b	**2a**	**3a**
formula	$C_{60}H_{96}O_4N_4CrLi_2$	$C_{48}H_{72}N_4O_4CrLi_2$	$C_{60}H_{96}N_4O_6CrLi$
fw	1003.32	833.98	1028.38
space group	$P2_1\backslash c$ (No. 14)	$P2_1\backslash n$ (No. 14)	$P2_1\backslash c$ (No. 14)
a, (Å)	20.504(2)	11.687(1)	13.884(1)
b, (Å)	12.347(1)	20.273(3)	16.170(1)
c, (Å)	22.524(1)	19.467(3)	25.514(2)
β (deg)	94.56(1)	100.27(1)	90.59(1)
V ($Å^3$)	5684(1)	4538(2)	5728(1)
Z	4	4	4
radiation (Mo Kα) (Å)	0.710 69	0.710 69	0.710 69
T (°C)	−160	−160	−150
D_{calcd} (g cm^{-3})	1.172	1.221	1.192
μ_{calcd} (cm^{-1})	2.41	2.90	2.43
R, R_w[a]	0.056, 0.073	0.063, 0.075	0.069, 0.082

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

Table 2. Selected Bond Distances (Å) and Angles (deg)

1b	**2a**	**3a**
Cr1−N1 = 2.018(4)	Cr1−N1 = 2.050(7)	Cr1−N1 = 2.042(5)
Cr1−N2 = 2.025(5)	Cr1−N2 = 2.071(7)	Cr1−N2 = 2.057(5)
Cr1−N3 =2.030(4)	Cr1−N3 = 2.067(7)	Cr1−N3 = 2.043(5)
Cr1−N4 = 2.033(5)	Cr1−N4 = 2.012(7)	Cr1−N4 = 2.044(5)
Li1−N4 = 2.39(1)	Cr1−O1 = 1.990(6)	Cr1−O5 = 2.033(4)
Li1−C16 = 2.37(1)	Cr1−O2 = 2.082(6)	Cr1−O6 = 2.048(4)
Li1−C17 = 2.27(1)	Li1−O1 = 1.88(2)	Li1−O1 = 1.92(1)
Li1−C18 = 2.29(1)	Li2−O1 = 1.89(2)	Li1−O2 = 1.95(2)
Li1−C19 = 2.38(1)	Li2−N3 = 2.24(2)	Li1−O3 = 1.93(1)
Li1−O1 = 1.96(1)	Li2−C8 = 2.28(2)	Li1−O4 = 1.91(2)
Li1−O2 = 1.95(1)	Li2−C9 = 2.44(2)	N1−Cr1−N2 = 89.3(2)
N1−Cr1−N2 = 92.3(2)	Li2−C10 = 2.51(2)	N1−Cr1−N3 = 177.9(2)
N1−Cr1−N3 = 172.2(2)	Li2−C11 = 2.35(2)	N1−Cr1−N4 = 90.3(2)
N1−Cr1−N4 = 88.1(2)	N1−Cr1−N2 = 88.5(3)	N2−Cr1−N4 = 177.8(2)
N2−Cr1−N4 = 178.4(2)	N1−Cr1−N3 =176.3(3)	O5−Cr1−O6 = 178.8(2)
O1−Li1−O2 = 96.3(5)	N1−Cr1−N4 = 90.2(3)	O1−Li1−O2 = 99.0(6)
	N2−Cr1−N4 = 178.1(3)	
	O1−Cr1−O2 = 177.4(3)	
	Li1−O1−Cr1 = 89.5(6)	
	Li1−O1−Li2 = 135.2(8)	

X-ray Crystallography. Data were collected in the temperature range −145 to −160 °C for complexes **1b**, **2a**, and **3a**. The $\omega-2\theta$ scan technique was used for suitable air-sensitive crystals mounted on glass fibers. Cell constants and orientation matrices were obtained from the least-squares refinement of 25 centered reflections. The intensities of three standard reflections, measured after every 150 reflections, showed no statistically significant decay over the duration of the data collections. Data were corrected for Lorentz and polarization effects but no absorption correction was applied to the data. The structures of **1b**, **2a**, and **3a** were solved by direct methods resulting in locating all the non-hydrogen atoms. Their positions were refined anisotropically. Hydrogen atom positions were calculated but not refined. The data were processed using the TEXSAN and NRCVAX software packages on a Digital VAX and Silicon Graphics workstations. Refinements were carried out by using full-matrix least-squares techniques on F minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$ and F_o and F_c are the observed and calculated structure factors. Atomic scattering factors and anomalous dispersion terms were taken from the usual sources (Cromer and Waber).[13] Details on the data collections and structure refinements are listed in Table 1. The final atomic coordinates are given as Supporting Information. Selected bond distances and angles are given in Table 2. Listings of significant final atomic coordinates are given in Tables 3−5 for **1b**, **2a**, and **3a**, respectively.

Results

The preparation of [Cr(ORPG)$Li_2(THF)_4$] (**1**) [R = Et (**a**), *n*-Pr (**b**)] was carried out in toluene by reacting stoichiometric

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Table 3. Listing of Significant Fractional Atomic Coordinates for **1b**

atom	*x*	*y*	*z*	*B*(eq) (Å)[a]
Cr1	0.25004(5)	0.03013(7)	0.24434(4)	1.28(4)
O1	0.5058(2)	0.1969(3)	0.1544(2)	2.6(2)
O2	0.3698(2)	0.2642(3)	0.1346(2)	2.2(2)
O3	0.0008(2)	0.2016(3)	0.3485(2)	2.3(2)
O4	0.1378(2)	0.2597(3)	0.3635(2)	2.1(2)
N1	0.2200(2)	0.0253(4)	0.1569(2)	1.5(2)
N2	0.1570(2)	0.0293(4)	0.2684(2)	1.3(2)
N3	0.2824(2)	0.0131(4)	0.3314(2)	1.3(1)
N4	0.3437(2)	0.0266(4)	0.2208(2)	1.3(2)
C1	0.2480(3)	−0.0337(5)	0.1146(2)	1.7(3)
C2	0.2035(3)	−0.0532(5)	0.0666(2)	1.7(3)
C3	0.1447(3)	−0.0045(5)	0.0797(2)	1.7(3)
C4	0.1559(3)	0.0430(5)	0.1354(2)	1.6(3)
C5	0.1103(3)	0.1124(5)	0.1715(2)	1.6(3)
C6	0.1022(3)	0.0578(5)	0.2314(2)	1.3(3)
C7	0.0456(3)	0.0236(5)	0.2563(2)	1.7(3)
C8	0.0668(3)	−0.0297(5)	0.3106(2)	1.9(3)
C9	0.1348(3)	−0.0247(5)	0.3173(2)	1.3(3)
C10	0.1792(3)	0.0825(5)	0.3651(2)	1.6(3)
C11	0.2481(3)	−0.0379(5)	0.3753(2)	1.3(3)
C12	0.2907(3)	−0.0494(5)	0.4255(2)	2.1(3)
C13	0.3516(3)	−0.0035(5)	0.4132(2)	2.1(3)
C14	0.3448(3)	0.0337(5)	0.3558(2)	1.5(3)
C15	0.3907(3)	0.0984(5)	0.3197(2)	1.3(3)
C16	0.3980(3)	0.0463(5)	0.2595(2)	1.5(3)
C17	0.4521(3)	0.0063(5)	0.2345(2)	1.5(1)
C18	0.4314(3)	−0.0389(5)	0.1783(2)	1.6(3)
C19	0.3643(3)	−0.0263(5)	0.1710(2)	1.4(3)
C20	0.3197(3)	0.0752(5)	0.1208(2)	1.6(3)
C21	0.1458(3)	−0.0799(5)	0.4244(2)	1.8(3)
C22	0.1364(3)	0.0317(6)	0.4513(2)	2.3(3(3)
C23	0.1081(4)	0.0274(6)	0.5113(3)	3.4(4)
C24	0.1812(3)	−0.2033(5)	0.3439(2)	1.7(3)
C25	0.3168(3)	−0.2005(5)	0.1326(2)	2.1(3)
C26	0.3494(3)	−0.0620(5)	0.0604(2)	1.7(1)
C27	0.3554(3)	0.0530(5)	0.0381(2)	2.2(3)
C28	0.0421(3)	0.1232(5)	0.1371(2)	2.0(3)
C29	0.0376(3)	0.1928(6)	0.0806(2)	2.5(3)
C30	−0.0246(3)	0.1687(6)	0.0413(3)	3.5(4)
C31	0.1431(3)	0.2255(5)	0.1797(2)	1.8(3)
C32	0.1056(3)	0.3131(5)	0.2104(3)	2.3(3)
C33	0.1412(3)	0.4203(5)	0.2126(3)	2.8(3)
C34	0.4590(3)	0.1037(5)	0.3550(2)	1.8(3)
C35	0.4666(3)	0.1754(5)	0.4106(3)	2.2(3)
C36	0.5280(4)	0.1479(6)	0.4501(3)	3.9(4)
C37	0.2878(3)	−0.2344(5)	0.1892(3)	2.3(3)
C38	0.2851(4)	−0.3574(6)	0.1954(3)	3.6(4)
C39	0.3628(3)	0.2150(5)	0.3122(2)	1.5(3)
C40	0.4031(3)	0.3019(5)	0.2843(3)	2.0(3)
C41	0.3892(3)	0.0600(6)	−0.0195(3)	2.8(3)
C42	0.3704(3)	0.4119(6)	0.2862(3)	3.2(4)
C43	0.2125(3)	−0.2852(5)	0.3878(3)	2.2(3)
C44	0.2139(4)	−0.3988(6)	0.3639(3)	3.6(4)
C45	0.5357(3)	0.1517(6)	0.1046(3)	3.0(3)
C46	0.5967(3)	0.2176(6)	0.0991(3)	3.4(4)
C47	0.6182(3)	0.2415(5)	0.1634(3)	2.5(3)
C48	0.5544(3)	0.2541(6)	0.1909(3)	3.9(4)
C49	0.3956(4)	0.3519(7)	0.1016(4)	5.1(5)
C50	0.3418(4)	0.4174(7)	0.0774(3)	4.6(4)
C51	0.2811(3)	0.3527(7)	0.0837(4)	4.6(4)
C52	0.2996(3)	0.2749(6)	0.1324(3)	2.6(3)
C53	−0.0443(3)	0.1456(5)	0.3830(3)	2.7(3)
C54	−0.1068(3)	0.2111(6)	0.3779(3)	3.5(4)
C55	−0.1044(3)	0.2687(6)	0.3197(3)	3.3(4)
C56	−0.0318(4)	0.2908(6)	0.3187(3)	3.8(4)
C57	0.2071(3)	0.2694(5)	0.3587(3)	2.5(3)
C58	0.2382(3)	0.2863(6)	0.4205(3)	3.1(3)
C59	0.1819(3)	0.3189(6)	0.4573(3)	3.2(3)
C60	0.1233(3)	0.3295(6)	0.4122(3)	2.9(3)
Li1	0.4191(5)	0.1456(8)	0.1733(5)	2.5(5)
Li2	0.0849(5)	0.149(1)	0.3257(4)	2.5(5)

[a] $B(eq) = (8\pi/3)\mathbf{U}_{ij}A_i{}^*A_j{}^*A_iA_j$.

Table 4. Listing of Significant Fractional Atomic Coordinates for **2a**

atom	*x*	*y*	*z*	*B*(eq) (Å)[a]
Cr1	0.52378(12)	0.36325(7)	0.23504(7)	1.75(6)
O1	0.5359(5)	0.2660(3)	0.2484(3)	2.5(3)
O2	0.5032(5)	0.4645(3)	0.2194(3)	2.6(3)
O3	0.5680(6)	0.1674(3)	0.1260(3)	3.3(3)
O4	0.4427(7)	0.1737(3)	0.3486(4)	4.8(4)
N1	0.6829(6)	0.3627(3)	0.2046(4)	1.9(3)
N2	0.4479(6)	0.3445(3)	0.1324(4)	1.8(3)
N3	0.3625(6)	0.3574(4)	0.2643(4)	2.4(4)
N4	0.6012(6)	0.3470(4)	0.1366(4)	2.0(4)
C2	0.6189(8)	0.3803(4)	0.0761(5)	2.2(4)
C3	0.4879(8)	0.3724(5)	0.0760(5)	2.3(4)
C4	0.3982(8)	0.3874(5)	0.0228(5)	2.6(4)
C5	0.2931(8)	0.3681(5)	0.0460(5)	2.7(5)
C6	0.3262(8)	0.3422(5)	0.1115(5)	2.3(4)
C7	0.2510(8)	0.3021(4)	0.1537(5)	2.5(5)
C8	0.2776(8)	0.4067(4)	0.3858(5)	2.6(4)
C13	0.5497(8)	0.4066(5)	0.3861(5)	2.6(5)
C14	0.6323(9)	0.4328(5)	0.4374(5)	3.2(5)
C15	O.7417(9)	0.4168(6)	0.4206(5)	2.7(1)
C16	0.7205(8)	0.3851(4)	0.3573(5)	2.4(4)
C17	0.8136(8)	0,2989(5)	0,2076(5)	2.7(5)
C20	0.7897(8)	0.3074(4)	0.1379(4)	2.0(4)
C21	0.6445(8)	0.4563(5)	0,0786(5)	218(5)
C22	0.7711(9)	0.4753(5)	0.0790(6)	4.0(6)
C23	0.6448(9)	0.2843(6)	-0.0130(6)	3.2(5)
C24	0.6079(10)	0.2843(6)	-0.0.0130(6)	4.4(6)
C25	0.2708(9)	0.1779(10)	0.1633(11)	3.5(5)
C26A	0.2546(16)	0.2071(10)	0.0653(11)	2.9(9)
C26B	0.2012(19)	0.1779(10)	0.1633(11)	3.6(10)
C27	0.1210(8)	0.3206(5)	0.1258(6)	3.4(5)
C28	0.0863(91	0.4789(5)	0.3665(5)	3.5(5)
C30	0.2399(10)	0.4881(6)	0.3638(6)	4.8(6)
C31	0.3993(9)	0.3921(5)	0.4602(5)	3.6(5)
C32	0.4504(11)	0,3242(6)	0.4904(6)	4.8(6)
C33	0.8557(9)	0.2874(5)	0.3682(5)	3.2(5)
C34	0.7642(10)	0.2333(6)	0.3698(6)	4.2(6)
C35	0.9240(8)	0.3961(5)	0.3325(5)	3.3(5)
C36	0.9052(8)	0.4595(5)	0.2916(6)	3.7(5)
C37	0.6769(9)	0.1379(5)	0.1558(5)	3.4(5)
C38	0.7168(11)	0.1045(6)	0.0939(6)	4.9(6)
C39	0.6068(13)	0.0875(7)	0.0477(7)	7.1(8)
C40	0.5105(10)	0.1269(6)	0.0698(6)	4.5(6)
C41	0.4926(12)	0.1204(6)	0.3137(7)	6.0(7)
C42	0.4352(12)	0.0594(6)	0.3316(7)	5.9(8)
C43	0.4193(13)	0.0723(6)	0.4064(7)	5.9(7)
C44	0.4055(13)	0.1480(6)	0.4086(6)	5.9(7)
C45	0.4029(8)	0.4967(5)	0.1782(5)	3.0(5)
C46	0.4236(11)	0.5685(5)	0.1887(6)	5.2(7)
C47	0.5388(12)	0.5785(6)	0.2231(10)	9.5(11)
C48	0.5899(9)	0.5121(5)	0.2520(6)	3.7(5)
Li1	0.5445(15)	0.2561(8)	0.1533(9)	3.1(8)
Li2	0.4175(17)	0.2560(9)	0.3027(8)	3.5(9)

[a] $B(eq) = (8\pi/3)\mathbf{U}_{ij}A_i{}^*A_j{}^*A_iA_j$.

amounts of $CrCl_2(THF)_2$ with the corresponding $ORPG(LiTHF)_4$ salt (Scheme 1). Complexes **1** were isolated in moderately high yield and in crystalline form as extremely air sensitive, somewhat pyrophoric compounds, soluble in THF, partially soluble in toluene, and insoluble in hexane. Both complexes are paramagnetic with magnetic moments as expected for the high spin d^4 electronic configuration of Cr(II). As with most Cr(II) compounds, these species showed poorly solved and uninformative EPR spectra. The infrared spectra shows the characteristic resonances of the porphyrinogen ligand as rather broad resonances at 3093 and 1622 cm^{-1} for **1a**, and at 3095 and 1621 cm^{-1} for **1b**. Analytical data consistent with the proposed formulations were obtained for both compounds.

In the case of the octapropyl derivative **1b** it was possible to grow crystals of suitable size to undertake an X-ray crystal structure and to clarify the chemical connectivity. The Cr atom

Table 5. Listing of Significant Fractional Atomic Coordinates for **3a**

atom	x	y	z	B(eq) (Å)^a
Cr1	0.31099(7)	0.16662(7)	0.13874(4)	1.52(4)
O1	0.6932(3)	0.2090(3)	0.4102(2)	3.0(2)
O2	0.8404(4)	0.1147(4)	0.3528(2)	4.0(3)
O3	0.8501(4)	0.1509(4)	0.4809(2)	4.6(3)
O4	0.9293(4)	0.2732(4)	0.3988(2)	4.3(3)
O5	0.3381(3)	0.2496(3)	0.1969(2)	1.9(2)
O6	0.2809(3)	0.0824(3)	0.0809(2)	1.8(2)
N1	0.4228(4)	0.2106(3)	0.0955(2)	1.8(2)
N2	0.2220(4)	0.2528(3)	0.1040(2)	1.4(2)
N3	0.1983(4)	0.1193(4)	0.1800(2)	1.9(3)
N4	0.4014(4)	0.0845(3)	0.1751(2)	1.6(2)
C1	0.6281(6)	0.2709(5)	0.3910(3)	3.8(4)
C2	0.5510(7)	0.2250(6)	0.3610(3)	4.8(5)
C3	0.5483(6)	0.1401(5)	0.3859(3)	3.7(4)
C4	0.6358(6)	0.1372(5)	0.4230(3)	3.6(4)
C5	0.7750(7)	0.1086(7)	0.3086(4)	5.9(6)
C6	0.8258(6)	0.0657(6)	0.2658(4)	5.0(5)
C7	0.8977(6)	0.0143(6)	0.2954(3)	4.2(5)
C8	0.9239(6)	0.0671(6)	0.3413(3)	4.4(5)
C9	0.8021(6)	0.1814(6)	0.5273(3)	4.6(5)
C10	0.7874(7)	0.1052(7)	0.5598(3)	5.4(6)
C11	0.8709(7)	0.0478(6)	0.5461(3)	4.7(5)
C12	0.9166(7)	0.0910(7)	0.5001(3)	5.2(5)
C13	1.019(1)	0.274(1)	0.4258(4)	9.6(8)
C14	1.0857(7)	0.3279(7)	0.3988(4)	5.8(6)
C15	1.0459(7)	0.3312(6)	0.3439(4)	5.0(5)
C16	0.9398(7)	0.3190(6)	0.3510(4)	5.5(6)
C17	0.4992(4)	0.1604(4)	0.0804(2)	1.8(3)
C18	0.5314(5)	0.1861(4)	0.0317(2)	2.3(3)
C19	0.4751(5)	0.2544(5)	0.0163(3)	2.6(3)
C20	0.4111(5)	0.2689(4)	0.0568(2)	2.0(3)
C21	0.3503(5)	0.3448(4)	0.0645(3)	2.0(3)
C22	0.2520(5)	0.3281(4)	0.0869(2)	1.9(3)
C23	0.1776(5)	0.3838(4)	0.0903(3)	2.6(4)
C24	0.0967(5)	0.3404(5)	0.1089(3)	2.4(3)
C25	0.1245(5)	0.2610(4)	0.1169(2)	1.8(3)
C26	0.0603(4)	0.1873(4)	0.1267(2)	1.9(3)
C27	0.1024(5)	0.1202(4)	0.1606(2)	1.9(3)
C28	0.0559(5)	0.0541(5)	0.1833(3)	2.4(3)
C29	0.1199(5)	0.0130(5)	0.2163(3)	2.4(3)
C30	0.2054(5)	0.0536(4)	0.2138(2)	1.8(2)
C31	0.2911(5)	0.0433(4)	0.2509(2)	1.9(3)
C32	0.3882(4)	0.0553(4)	0.2258(2)	1.7(3)
C33	0.4765(5)	0.0381(5)	0.2490(3)	2.3(3)
C34	0.5468(5)	0.0549(4)	0.2109(3)	2.3(3)
C35	0.5006(5)	0.0818(4)	0.1664(3)	2.0(3)
C36	0.5440(5)	0.0930(4)	0.1126(2)	2.0(3)
C37	0.6536(5)	0.1125(5)	0.1188(3)	2.7(4)
C38	0.6751(5)	0.1946(5)	0.1451(3)	3.5(4)
C39	0.5329(5)	0.0104(4)	0.0810(3)	2.3(3)
C40	0.5739(6)	−0.0671(5)	0.1063(3)	3.3(4)
C41	−0.0353(5)	0.2161(5)	0.1514(3)	2.7(3)
C42	0.0346(5)	0.1536(5)	0.0702(3)	2.7(3)
C43	0.2899(5)	−0.0442(5)	0.2753(3)	2.8(4)
C44	0.3043(5)	−0.1142(5)	0.2368(3)	3.5(4)
C45	0.2829(5)	0.1072(5)	0.2967(2)	2.5(3)
C46	0.1865(6)	0.1092(6)	0.3239(3)	3.9(4)
C47	0.4319(5)	0.2644(4)	0.2215(3)	2.3(3)
C48	0.4149(6)	0.3339(6)	0.2578(4)	5.2(5)
C49	0.3184(6)	0.3510(8)	0.2601(5)	8.9(8)
C50	0.2652(5)	0.3037(5)	0.2190(3)	2.6(3)
C51	0.2857(5)	0.0985(5)	0.0249(3)	2.3(3)
C52	0.2322(5)	0.0271(5)	−0.0001(3)	2.7(4)
C53	0.2540(5)	−0.0429(5)	0.0382(3)	2.6(3)
C54	0.2529(5)	−0.0021(4)	0.0910(3)	2.2(3)
C55	0.4052(5)	0.4028(4)	0.1032(3)	2.5(3)
C56	0.5089(6)	0.4253(5)	0.0888(3)	3.6(4)
C57	0.2781(6)	0.3457(5)	−0.0299(3)	3.6(4)
C58	0.3362(5)	0.3909(4)	0.0117(3)	2.5(3)
C59	−0.0317(6)	0.0800(6)	0.0645(3)	3.8(4)
C60	−0.0236(5)	0.2543(5)	0.2064(3)	3.5(4)
Li1	0.831(1)	0.193(1)	0.4107(5)	3.9(7)

^{a} $B(\mathrm{eq}) = (8\pi/3)\mathbf{U}_{ij}A_i{}^*A_j{}^*A_iA_j$.

was located in the center of the porphyrinogen ring, which adopted the characteristic saddle shape geometry, with two pyrrole rings, occupying the opposite positions of the macrocycle, lying on staggered planes (Figure 1). The coordination geometry around the chromium atom is slightly distorted square planar with the metal center only slightly elevated above the plane bound by the four N atoms of the macrocycle. The Cr−N distances [Cr1−N1 = 2.018(4) Å, Cr1−N4 = 2.033(5) Å], and N−Cr−N angles [N1−Cr1−N2 = 92.3(2)°, N1−Cr1−N3 = 172.2(2)°, N1−Cr1−N4 = 88.1(2)°, N2−Cr1−N4 = 178.4(2)°] are in the expected range. Two Li atoms are bound in an η^5-mode to two pyrrole rings placed in opposite positions of the macrocycle, lying on the same side of the macrocyclic ligand plane. Each Li atom is further coordinated to two THF molecules.

Exposure of toluene solutions of **1** to N_2O (1 atm, room temperature) caused an immediate color change from dark yellow to dark red. New crystalline complexes **2** were isolated in moderate yield upon layering the toluene mother liquors with hexane. Complexes **2** are soluble in most nonpolar organic solvents, and the infrared spectrum of **2** shows intense resonances at 844 cm^{-1} for **2a** and 883 cm^{-1} for **2b** which may be tentatively attributed to a Cr═O stretching vibration.[14] The characteristic absorptions of both the porphyrinogen ligand and THF were also clearly identified in the spectra as resonances at 3101 and 1568 cm^{-1} for **2a** and at 3074 and 1570 cm^{-1} for **2b**. Both complexes are paramagnetic with magnetic moments as expected for the d^2 electronic configuration of a high-spin Cr(IV) metal center. The fact that complex **2** was obtained in comparable yield by exposing a toluene solution of **1** to dry oxygen, indicated that deoxygenation occurred during the reaction with N_2O and that the complex was probably a Cr(IV) oxo derivative. However, it should be mentioned that the three examples of porphyrine−Cr^{IV}═O species reported so far in the literature are diamagnetic.[14,15] The yield of the crude product, obtained by complete removal of the solvent from the reaction mixture, was essentially quantitative in both cases, and **2** was obtained as a red powder of acceptable purity. However, recrystallization resulted in lower yield due to the rather high solubility of these two compounds. Analytical data in agreement with the formulation [(THF)(ORPG)Cr(O)(LiTHF)$_2$] (**2**) were obtained in both cases.

For a complete structural analysis to be undertaken, crystals of **2a** were grown from a toluene/hexane mixture in a layering tube. The crystal structure showed one chromium atom placed in the center of an ideal octahedron (Figure 2). The equatorial plane is defined by the four nitrogen atoms of the macrocyle [N1−Cr1−N2 = 88.5(3)°, N1−Cr1−N3 = 176.3(3)°, N1−Cr1−N4 = 90.2(3)°] with rather regular Cr−N distances [Cr1−N1 = 2.050(7) Å, Cr1−N2 = 2.071(7) Å]. The axial positions are occupied by one oxygen of one THF molecule [Cr1−O2 = 2.082(6) Å] and one oxo− oxygen atom [Cr1−O1 = 1.990(6) Å][15] forming an almost linear O−Cr−O array [O1−Cr1−O2 = 177.4(3)°]. Two lithium atoms were found attached in a η^5-mode to two contiguous pyrrole rings on the same side of the macrocycle. The two lithium cations are also connected to the oxo oxygen atom [Li1−O1 = 1.88(2) Å, Li1−O2 = 1.89(2) Å] forming a bent Li−O−Li array [Li1−O1−Li2 = 135.2(8)°].

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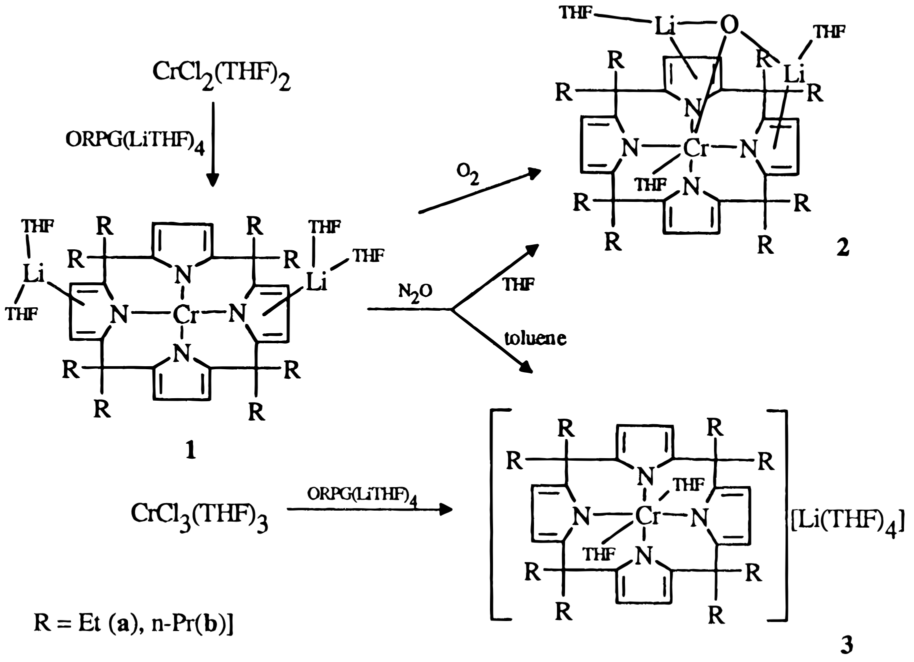
[14] (a) Groves, J. T.; Kruper, W. J.; Haushalter, R. C.; Buthler, W. M. *Inorg. Chem.* **1982**, *21*, 1363. (b) Liston, D. J.; West, B. O. *Inorg. Chem.* **1985**, *24*, 1568. (c) Buchler, J. W.; Lay, K. L.; Castle, L.; Ulrich, W. *Inorg. Chem.* **1982**, *21*, 842.

[15] The Cr−O distance is remarkably longer than in porphyrine Cr═O [1.57−1.62 Å]: (a) Buchler, J. W. Lay, K. L.; Castle, L.; Ulrich, V. *Inorg. Chem.* **1982**, *21*, 842. (b) Budge, J. R.; Gatehouse, B. M. K.; Nesbit, M. C.; West, B. O. *J. Chem. Soc., Chem. Commun.* **1981**, 370.

Scheme 1



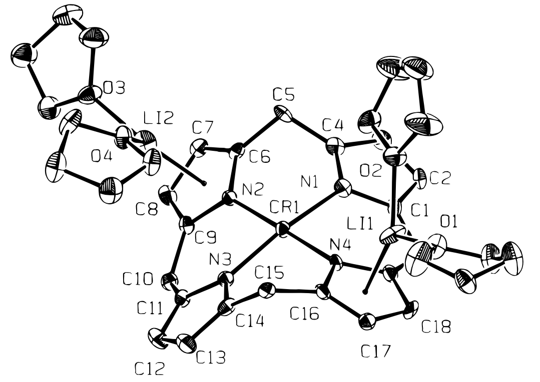


Figure 1. ORTEP plot of **1b**. Thermal ellipsoids are drawn at the 50% probability level. Alkyl groups have been removed for clarity.

One molecule of THF completes the coordination geometry of each Li atom [Li1−O3 = 1.91(2) Å].

The reaction of **1** with N_2O was remarkably dependent on the nature of the solvent. When a similar reaction under analogous reaction conditions was carried out in THF, in place of toluene, a comparatively slower reaction occured. The color changed from dark yellow to dark orange and finally to dark green, and a new crystalline green complex **3** was obtained by layering a concentrated THF solution of the product with hexane. The infrared spectrum of **3** indicates the presence of the porphyrinogen ligand and THF, while the paramagnetism of the complex precluded the use of NMR spectroscopy. Combustion analysis data suggested the formulation $[(THF)_2Cr(ORPG)][Li(THF)_4]$ [R = Et (**3a**), *n*-Pr (**3b**)] while the magnetic moment, calculated on the basis on this formulation, was in agreement with a high-spin d^3 electronic configuration of a Cr(III) atom. The attribution of the oxidation state was further confirmed by the fact that it was possible to obtain good yield of complex **3** directly from the reaction of $CrCl_3(THF)_3$ with $Li_4(ORPG)(THF)_4$ in THF.

Green crystals of **3a,** suitable for X-ray diffraction, were grown by slow diffusion of hexane into a concentrated THF solution of the complex. The compound is ionic and is composed of an $[Cr(OEPG)(THF)_2]^-$ anion and a $[Li(THF)_4]^+$ cation (Figure 3). In the anionic fragment the slightly distorted octahedral Cr atom is surrounded by four N atoms [Cr1−N1 = 2.042(5) Å, Cr1−N2 = 2.057(5) Å, Cr1−N3 = 2.043(5) Å] from the porphyrinogen ligand, which bound the equatorial plane [N1−Cr1−N2 = 89.3(2)°, N1−Cr1−N3 = 177.9(2)°, N1−Cr1−N4 = 90.3(2)°]. Two oxygen atoms of two THF molecules occupy the two axial positions [Cr1−O5 = 2.033(4) Å, Cr1−O6 = 2.048(4) Å], forming an almost linear O−Cr−O array [O5−Cr1−O6 = 178.8(2)°]. As a common feature to other porphyrinogen complexes reported in this work, the ORPG ligand deviates from planarity and adopted a saddle-shape conformation. The cationic moiety is formed by a slightly distorted tetrahedral Li cation coordinated to four THF molecules, with O−Li−O bond angles ranging from 99.0(6) to

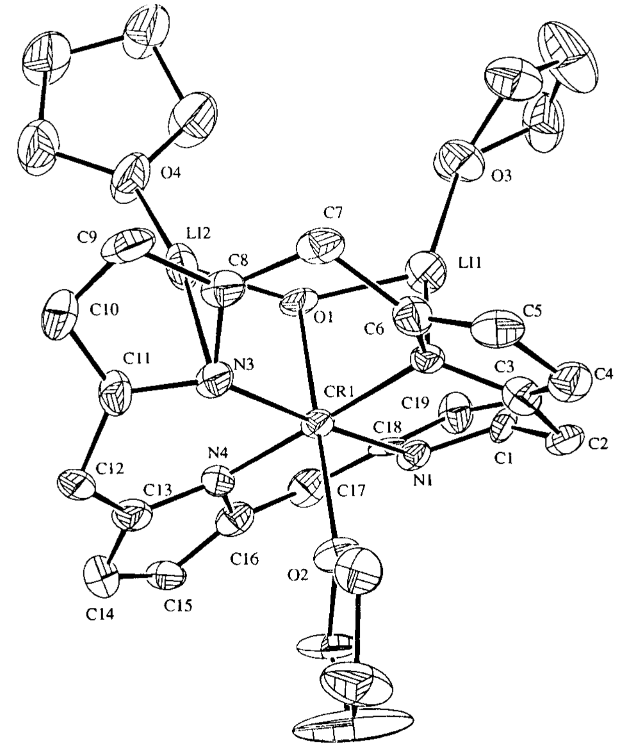


Figure 2. ORTEP plot of **2a**. Thermal ellipsoids are drawn at the 50% probability level. Alkyl groups have been removed for clarity.

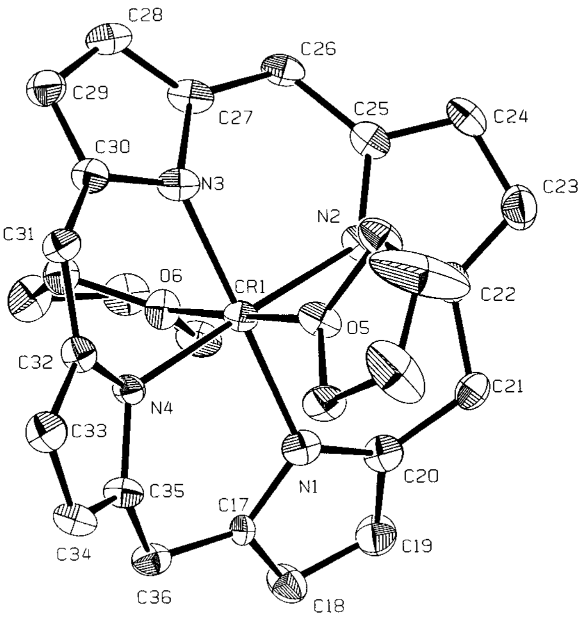
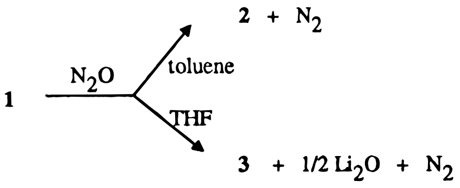


Figure 3. ORTEP plot of **3a**. Thermal ellipsoids are drawn at the 50% probability level. Alkyl groups have been removed for clarity.

Scheme 2



128.5(8)°. The Li−O bond distances in the tetrahedral $Li(THF)_4$ cation are all similar and fall in the expected range [Li1−O1 = 1.92(1) Å].

The marked solvent dependence of the reaction of **1** with N_2O implies that the nature of the solvent determines the extent of oxidation of the metal and of the electron transfer from the metal to the N_2O substrate (Scheme 2). From the formal point of view, two electrons are required by N_2O in order to eliminate the oxygen atom and to form N_2 and O^{2-}. In this respect, the result obtained in the case of the reaction in toluene, where the two electrons necessary for the deoxygenation of N_2O are formally obtained from one Cr(II) atom, may be regarded as a rather straightforward formation of a rare example of Cr(IV) chromyl species.[14,15] However, in contrast to the other example of Cr=O derivative reported in the literature,[14] the very long Cr−O distance [Cr1−O2 = 1.99 Å] suggests that in the present case the complex may also be regarded as the result of the addition of Li_2O to a (ORPG)Cr^{IV} compound. The fact that a similar reaction of **1** with N_2O produced, while carried out in THF, the ionic Cr(III) porphyrinogen derivative **3** as the major product, indicates that in a polar solvent only one electron was transferred by the metal to the N_2O substrate. While N_2 was always recovered almost quantitatively (91−98%) during Toepler pump experiments, the balance of the masses requires that a Li cation would be eliminated during the reaction. It is tempting at this stage to envision a process where two molecules of **1** provide the two electrons and the two lithium cations to form one equiv of Li_2O. The solvation of both Li_2O and the coordination to the high-spin Cr(III) atom by THF probably provide the necessary thermodynamic driving force to prevent further oxidation of the metal center to the less stable +IV oxidation state. However, other possibilities such as that the reaction proceeds through the formation of a highly reactive [$O^{\bullet}$] intermediate cannot be ruled out at this stage.

With this study we have shown that the extent of electron transfer to N_2O may be controlled by the nature of the solvent. In particular, the reaction of **1** with N_2O is rather promising for further studies since mild condition reactions can be anticipated for the reduction of **3** to **1** and consequent closure of a catalytic cycle. The ability of compound **2** to perform epoxydation reactions is currently under examination.

Acknowledgment. This work was supported by the National Science and Engineering Council of Canada (NSERC) through a strategic and operating grant.

Supporting Information Available: Full list of atomic coordinates, anisotropic thermal parameters, bond distances and angles and drawings of the complexes for **1b**, **2a** and **3a** (67 pages). Ordering information is given on any current masthead page.

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