1994, ν(3,5-$Me_2C_6H_3HS$) 1601 (vs), and 1558 (s) ν(tpy) 1469 (vs), 1449 (vs), and 1390 cm^{-1} (vs); ν(^{14}NS) 1023 and ν(^{15}NS) 991 cm^{-1}; e) ^{1}H NMR data (δ = DMSO): 9.0–6.9 (m, 14 aromatic protons (11 H of tpy and 3 H of the aryl group)) 2.3 (s, 6H, methyl protons), 3.4 ppm (s, 1H, proton on the S atom); f) CCDC-177717 (**1**$^+$) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[7] **2**: a) Elemental analysis calcd (%) for $OsC_{23}H_{20}N_4SOCl_2$: C 41.76, H 3.05, N 8.47; found: C 42.07, H 3.08, N 8.19; b) cyclic voltammetry in 0.1 M Bu_4NPF_6/CH_3CN (V vs SSCE): $E_{1/2}$ ($Os^{VI/V}$) = 1.23 V, $E_{1/2}$ ($Os^{V/IV}$) = 0.30 V, $E_{1/2}$ ($Os^{IV/III}$) = −0.89 V, and $E_{1/2}$ ($Os^{III/II}$) = −1.19 V; c) UV/Vis spectra in CH_3CN λ_{max} [nm] (ε, $M^{-1} cm^{-1}$): 696 (3.17×10^3), 592 (2.79×10^3), 444 (9.16×10^3), 320 (1.32×10^4), 272 (2.07×10^4), 212 (2.73×10^4); d) IR (Nujol mull): $\tilde{\nu}$ = ν(3,5-$Me_2C_6H_3HS$) 1603 (vs) and 1578 (s), ν(tpy) 1477 (vs), 1449 (vs), and 1435 (vs), and ν(S=O) 1277 cm^{-1}; e) ^{1}H NMR (DMSO) δ = 8.95–8.91 (d, 6 and 6″-positions of tpy), 8.64–8.61 (d, 3 and 3″-positions of tpy), 7.83–7.81 (d, 3′ and 5′-positions of tpy), 7.48–7.42 (t, 5 and 5″-positions of tpy), 7.44–7.41 (q, 2 and 6-positions of benzene ring), 7.14–7.10 (t, 4 and 4″-positions of tpy), 6.97–6.94 (t, 4′-position of tpy), 6.90 (s, 4-position of benzene ring), and 1.71 ppm (d, 6 methyl protons on benzene ring).

[8] a) M. H. V. Huynh, P. S. White, T. J. Meyer, *Angew. Chem.* **2000**, *112*, 4267–4270; *Angew. Chem. Int. Ed.* **2000**, *39*, 4101–4104; b) Selected bond lengths and angles of the S-protonated *trans* isomer of the Os^{IV}–sulfilimido (*trans*-**1**$^+$) complex are listed for comparison: Os–N(tpy) 2.015(10), 2.108(9), and 2.129(9) Å (with the shortest Os–N(tpy) bond *trans* to the sulfilimido ligand); Os=N(sulfilimido) 1.906(10) Å; N(1)–S(1) 1.706(9) Å (single bond); ∢Os(1)-N(1)-S(1) 130.4(6)°; and ∢N(1)-S(1)-C(1) 101.6(5)°.

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[10] The oxygen produced was measured by a Thermal Orion Model 1230 waterproof dissolved oxygen meter both with and without salinity correction modes. Each measurement of dissolved oxygen was corrected against a blank air-saturated acidic CH_3CN solution.

A Structurally Characterized Chromium(III) Superoxide Complex Features “Side-on” Bonding[**]

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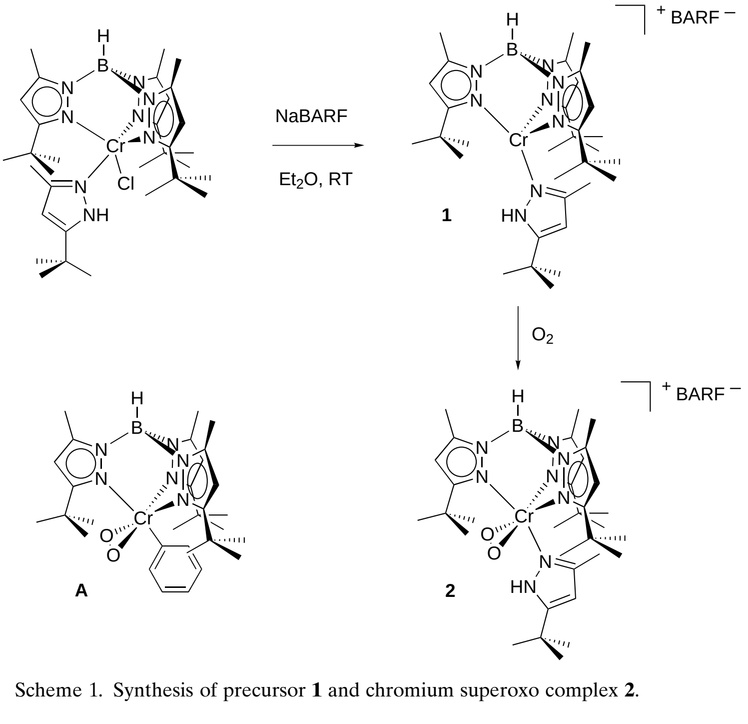
The coordination chemistry of dioxygen (O_2) is of interest in the context of bioinorganic chemistry and oxidation catalysis. Catalytic transformations utilizing O_2 as the oxidant are considered environmentally benign; however, they typically require “activation” of the dioxygen by a metal center. Whereas the chemistry of chromium—a common ingredient in oxidation reagents—is replete with high-valent oxo (O^{2-}) or peroxo (O_2^{2-}) compounds, there exist few superoxo complexes of chromium resulting from the binding of gaseous O_2, and none that have been structurally characterized.[1] In a recent report on the insertion of O_2 into the chromium–carbon bond of [$Tp^{tBu,Me}$-Cr-Ph] ($Tp^{tBu,Me}$ = hydrotris(3-*tert*-butyl-5-methylpyrazolyl)borate) we provided spectroscopic evidence for a reactive Cr^{III} superoxide intermediate (**A**, Scheme 1), and we proposed a “side-on” bonding mode for the superoxo ligand.[2] Herein we describe the synthesis and structural characterization of a stable Cr^{III} superoxide complex that supports our earlier assignment.

Key to our investigation was the synthesis of a coordinatively unsaturated Cr^{II} precursor that would not suffer insertion of a coordinated O_2, for example, into a chromium–carbon bond. Thus we prepared [$Tp^{tBu,Me}$Cr(pz’H)]BARF (**1**, pz’H = 3-*tert*-butyl-5-methylpyrazole, BARF = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) by reaction of [$Tp^{tBu,Me}$Cr(pz’H)Cl] with NaBARF (see Scheme 1). Complex **1** featured the characteristic *cis*-divacant octahedral structure of four-coordinate [$Tp^{tBu,Me}$CrX] derivatives;[3] hence it should be able to coordinate O_2. Indeed, exposure of a diethyl ether solution of **1** at −78 °C to excess O_2 caused a rapid color change from blue to red. Warming to room temperature followed by standard work-up of the reaction mixture yielded [$Tp^{tBu,Me}$Cr(pz’H)(O_2)]BARF (**2**) as a dark red solid in high yield. The solid-state IR spectrum of **2** showed an O–O stretching vibration at 1072 cm^{-1}. In the product of the reaction of **1** with $^{18}O_2$ this band was shifted to 1007 cm^{-1}. These values are consistent with an assignment as a superoxo complex of chromium(III).[4] The effective magnetic moment of **2** (μ_{eff}(295 K) = 2.8(1) μ_B) must result from strong



Scheme 1. Synthesis of precursor **1** and chromium superoxo complex **2**.

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antiferromagnetic coupling between the Cr^{III} ion (d^3, $S = 3/2$) and the coordinated superoxide radical ($S = 1/2$).

The most unambiguous method for determining the bonding mode of the dioxygen is of course X-ray crystallography. Fortunately **2** is rather stable and cooling of a CH_2Cl_2 solution to $-30\,^{\circ}C$ gave dark red crystals of $\mathbf{2}\cdot CH_2Cl_2$ suitable for a structure determination (Figure 1).[5] The most conspicuous feature is the "side-on" (or η^2-) coordination of the O_2 ligand.

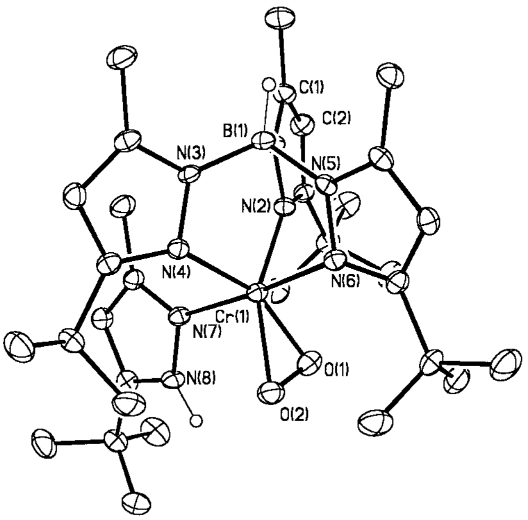

Figure 1. The molecular structure of **2**; the BARF anion has been omitted for clarity. Selected interatomic distances [Å] and angles [°]: Cr(1)-O(1) 1.861(4), Cr(1)-O(2) 1.903(4), O(1)-O(2) 1.327(5), Cr(1)-N(2) 2.069(4), Cr(1)-N(4) 2.080(5), Cr(1)-N(6) 2.080(4), Cr(1)-N(7) 2.063(5); O(1)-Cr(1)-O(2) 41.27(16), O(1)-Cr(1)-N(7) 88.48(18), O(2)-Cr(1)-N(7) 86.76(18).

At 1.861(4) and 1.903(4) Å, respectively, the Cr–O distances are essentially identical. The O(1)–O(2) bond length of 1.327(5) Å puts the ligand squarely into the superoxo category.[6] The trivalent nature of chromium is also supported by the metal–ligand bond distances. Thus the average $Cr-N_{Tp}$ distance of 2.08 Å is significantly shorter than the corresponding value in $[Tp^{tBu,Me}Cr^{II}(pz'H)(Cl)]$ (2.18 Å); the same holds for the $Cr-N_{pzH}$ bond (2.063(5) Å versus 2.144(7) Å). The orientation of the pyrazole ligand (perpendicular to the CrO_2 plane) puts its NH proton in a position to hydrogen bond to the oxygen atoms.[7] The relevant distances, namely 2.90 Å (N(8)–O(1)) and 2.80 Å (N(8)–O(2), are certainly short enough for N–H···O interactions.[8] However, the N-H-O angles (the hydrogen atom was located and its position refined) of 98.4° (N(8)-H-O(1)) and 109.8° (N(8)-H-O(2)) are rather acute for hydrogen bonds. Furthermore, the N–H stretching vibration of **2** appears as a sharp band at 3446 cm^{-1} in the IR spectrum, which is actually higher than $\nu_{N\text{-}H}$ of **1**. The evidence for substantial hydrogen bonding in **2** is thus ambiguous, and we hesitate to ascribe significant strengthening of the O_2 coordination to it.

Encouraged by the stability of **2**, and in the hopes of gauging electronic effects on the bonding of O_2 to Cr^{II} centers, we then investigated the reactivity of several analogous chromium complexes with dioxygen. Gratifyingly, $[Tp^{tBu,Me}Cr(py)]BARF$ (py = pyridine), $[Tp^{tBu,Me}CrCl]$, and $[Tp^{tBu,Me}CrOPh]$ all yielded isolable dioxygen complexes, which have been characterized by various methods, including IR spectroscopy of the $^{16}O_2$ and $^{18}O_2$ isotopomers. The results are listed in Table 1. The extent of electron transfer to the O_2 unit, as measured by $\nu_{O\text{-}O}$ stretching frequency data, parallels the donor strength of the changing ligand ($Ph^- > PhO^- > pz'H > py > Cl^-$). Based on the chemical analogy and their spectroscopic similarity, we assume that all of these complexes contain side-on bonded superoxide ligands.

To our knowledge, **2** is the first structurally characterized chromium superoxo complex; it is also a representative of the small, but growing, number of mononuclear "side-on" superoxide complexes.[9] We wish to suggest that this bonding mode may be more common than is generally assumed. The reactivity of this new class of O_2 complexes, especially with regard to dioxygen activation and oxidation reactions, is currently under investigation.

Table 1. O–O stretching frequencies of chromium(III) superoxo complexes.

Compound	$\nu(^{16}O-^{16}O)$	$\nu(^{18}O-^{18}O)$
$[Tp^{tBu,Me}Cr(Ph)(O_2)]$[a]	1027 cm^{-1}	969 cm^{-1}
$[Tp^{tBu,Me}Cr(OPh)(O_2)]$	1068 cm^{-1}	1009 cm^{-1}
$[Tp^{tBu,Me}Cr(pz'H)(O_2)]BARF$ (**2**)	1072 cm^{-1}	1007 cm^{-1}
$[Tp^{tBu,Me}Cr(py)(O_2)]BARF$	1083 cm^{-1}	1025 cm^{-1}
$[Tp^{tBu,Me}Cr(Cl)(O_2)]$	1104 cm^{-1}	1044 cm^{-1}

[a] Data from ref. [2].

Experimental Section

1: $[Tp^{tBu,Me}Cr(pz'H)Cl]$[2] (0.530 g 0.82 mmol) was dissolved in Et_2O (30 mL). An Et_2O solution of NaBARF (0.704 g 0.80 mmol) was added at room temperature. The mixture was stirred at room temperature for 48 h. After the solvent was removed, the solid was washed three times with pentane, and then extracted with Et_2O to yield a deep blue solution. Cooling the solution to $-30\,^{\circ}C$ overnight produced blue crystals (1.00 g, 80% yield) of **1**. ^1H NMR (250 MHz, CD_2Cl_2): $\delta = 81.0$ (br, 3H), 48.9 (br, 9H), 32.4 (br, 3H), 10.9 (br, 27H), 7.8, 7.6 (12H), 2.8 (9H), −13.9 (1H), and −24.9 ppm (1H); IR (KBr): $\tilde{\nu} = 3435$ (s, N-H), 2972 (s), 2805 (w), 2556 (w, B-H), 1610 (m), 1541 (s), 1473 (s), 1424 (s), 1354 (vs), 1276 (vs), 1137 (vs), 1063 (s), 887 (s), 838 (s), 806 (m), 716(s), 682 cm^{-1} (s); UV/Vis (Et_2O): $\lambda_{max}(\varepsilon) = 282$ (4000), 669 nm (329); m.p.: 186 °C; μ_{eff} (295 K) = 5.0(1) μ_B. elemental analysis calcd (%) for $C_{64}H_{66}B_2CrF_{24}N_8$: C 52.05, H, 4.50, N 7.59; found: C 51.75, H 4.66, N 7.53.

2: Compound **1** (0.445 g 0.3 mmol) dissolved in Et_2O (10 mL) was charged into an ampoule. This solution was degassed and cooled to $-78\,^{\circ}C$. Then 1 atm of dry O_2 was admitted into the ampoule while the solution inside was stirred. The deep blue solution turned dark red within 5 min. The solution was kept under the O_2 atmosphere at $-78\,^{\circ}C$ overnight. Then the solvent was removed under vacuum, and the remaining solid was extracted with cold CH_2Cl_2. After cooling the concentrated solution to $-30\,^{\circ}C$ overnight, 0.325 g (70% yield) of dark red crystals of **2** were obtained. ^1H NMR (250 MHz, CD_2Cl_2): $\delta = 31.3$ (br, 3H), 7.7, 7.6 (s, 12H), 3.5 (br, 27H), 1.7 (br, 9H), −8.9 ppm (br, 9H); IR (KBr): $\tilde{\nu} = 3446$ (s, N-H), 3020 (w), 2971 (s), 2876 (w), 2565 (w, B-H), 1609 (m), 1546 (s), 1481 (s), 1423 (s), 1354 (vs), 1277 (vs), 1182 (vs), 1128 (vs), 1072 (s), 1046 (m), 1029 (w), 886 (s), 839 (s), 811 (s), 713 (s), 671 cm^{-} $(s)^1$; UV/Vis (Et_2O): $\lambda_{max}(\varepsilon) = 279$ (6150), 445 (714), 566 (407), 624 (264), 926 nm (274); m.p.: 125 °C; μ_{eff} (295 K) = 2.8(1) μ_B; elemental analysis calcd (%) for $C_{64}H_{66}B_2CrF_{24}N_8O_2$: C 50.94, H 4.41, N 7.42; found: C 50.29, H 4.19, N 6.90.

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[5] **2**: monoclinic, $P2_1/c$, $a = 19.1562(15)$, $b = 19.6372(15)$, $c = 19.2621(14)$ Å, $\beta = 99.919(2)^\circ$, $V = 7137.6(9)$ Å^3, $\rho_{\text{calcd}} = 1.483\ \text{g cm}^{-1}$, $\theta = 1.73-27.00^\circ$, $\text{Mo}_{\text{K}\alpha}$, $\lambda = 0.71073$ Å, $T = 173$ K, 33900 reflections, 13653 independent, *SADABS* absorption correction, $\mu = 0.347\ \text{mm}^{-1}$, max and min transmission: 0.9338 and 0.9338, solved by direct methods and refined by full-matrix least-squares procedures using SHELXTL (5.1), 945 parameters, $R = 0.0749$, $wR = 0.1943$, largest difference peak and hole: 1.027 and $-1.301\ \text{e Å}^{-3}$. CCDC-179035 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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Parallels in Cation and Anion Coordination: A New Class of Cascade Complexes[**]

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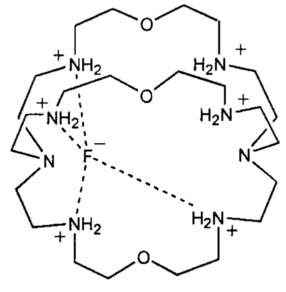
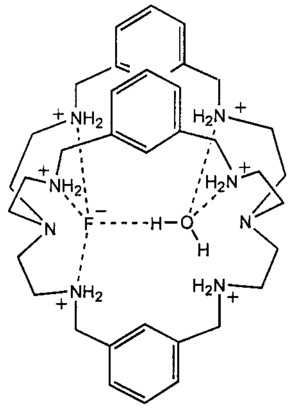
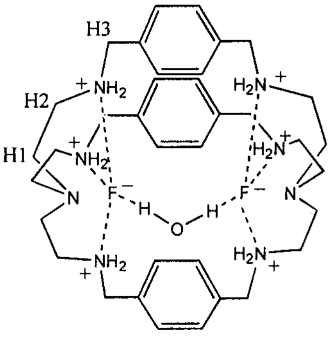
For a number of years it has been speculated that azacryptands capable of binding two metal ions could also serve as hosts for two discrete anions. In the early 1980s Lehn and co-workers proposed that a simple bicyclic azacryptand (bis-tren) derived from two tren (tris(2-aminoethyl)amine) units might be capable of encapsulating a bifluoride ion.[1] Although not considered as "discrete" ions in that regard, bifluoride does consist of two fluoride ions linked by a hydrogen bridge. However, a crystal structure revealed only a single fluoride ion sitting to one side of the cavity (**A**). In 1998 we observed ditopic anion binding behavior, namely, two discrete encapsulated nitrate ions, for a related azacryptand, MEAcryp.[2, 3] Our subsequent attempt to sequester either a bifluoride ion or two discrete fluoride ions in the MEAcryp cavity was not successful, although crystallographic results did indicate two residents in the cavity: a molecule of water and a fluoride ion (**B**).[4, 5]



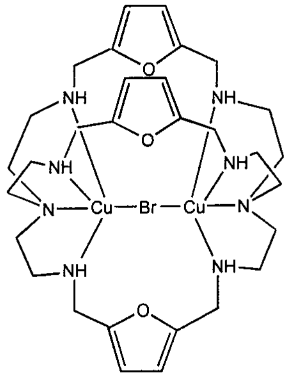
bis-tren(F)
A



MEAcryp(F)(H$_2$O)
B



PEAcryp(F)$_2$(H$_2$O)
C



FuEAcryp(Cu)$_2$(Br)
D

By very slightly enlarging the cavity size with a *p*-xylyl spacer to give PEAcryp (**L**),[2] we have at last succeeded in capturing two fluoride ions inside the cavity (**C**), to provide the first example of an azacryptand with two encapsulated fluoride ions. Rather than being linked by a single hydrogen atom, as for a bifluoride ion (F-H-F$^-$), a water molecule bridges the two halide ions (F$\cdots$H-O-H$\cdots$F^{2-}). This additional structural feature adds another dimension to the finding, thus making this complex the first example of an "anion-based cascade complex," where two spherical anions play the topological role of the two metal ions in traditional cascade complexes. These findings serve to expand the

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