TEMPO Coordination and Reactivity in Group 6; Pseudo-Pentagonal Planar ($(\eta^2\text{-TEMPO})_2CrX$) (X = Cl, TEMPO)

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TEMPO coordination and reactivity in Group 6; pseudo-pentagonal planar (η^2-TEMPO)$_2$CrX (X = Cl, TEMPO)

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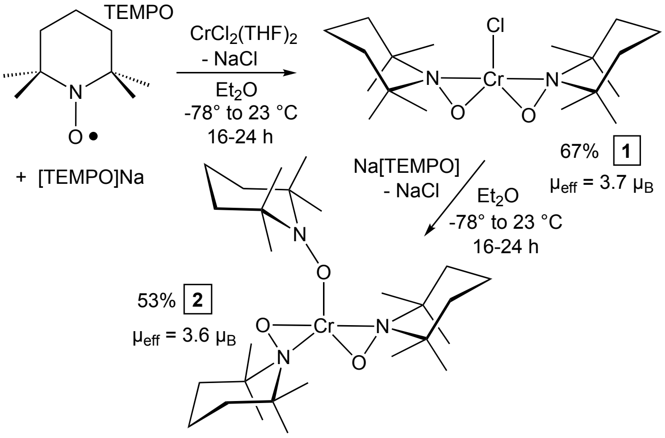
Abstract: The exposure of $CrCl_2(THF)_2$ to 1 equiv of TEMPO and 1 equiv [TEMPO]Na afforded (η^2-O,N-TEMPO)$_2$CrCl (1, 67%); addition of [TEMPO]Na to 1 yielded (η^2-O,N-TEMPO)$_2$Cr(TEMPO) (2). Both 1 and 2 exhibit pseudo-pentagonal planar (PPP) geometry, instead of myriad alternatives. Calculations and spectral studies suggest the solid-state geometry persists in solution.

TEMPO ((2,2,6,6-tetramethylpiperidin-1-yl)oxyl), the most common among stable nitroxyl radicals, has a diverse array of uses as an oxidant, including many examples of H-atom (HAT) and O-atom (OAT) transfer.[1-4] As a ligand for transition metals, κ^1-O-binding and bidentate η^2-O,N-ligation may be found. Crystallographic evidence reveals that TEMPO can ligate as an anion, TEMPO(-)[5-8] (d(N-O) ~ 1.40 Å),[9] or as a neutral radical ligand[10-13] (d(N-O) ~ 1.30 Å).[14] The scope of homoleptic TEMPO complexes is limited,[5-8] probably due to the innate possibility of OAT events. Investigations into preparing $(TEMPO)_xM$ complexes were initiated to discern whether the two types of binding could be observed within a single molecule. During this study, examples of pseudo-pentagonal planar (PPP) coordination are reported herein. Previously only observed in conformationally restricted chelate complexes,[15-18] the solid state,[19] and main group species,[20-23] they are rare additions to the lexicon of transition metal coordination environments.

Various TEMPO/[TEMPO]Na combinations were initially applied to $CrCl_2(THF)_2$,[24] and one resulted in crystalline material. ^{1}H NMR and EPR spectra were consistent with a ~1:1 mixture, and changing isolation times enabled one species to predominate, suggesting a straightforward synthesis. A 1:1 mixture of TEMPO and [TEMPO]Na,[14] when added to $CrCl_2(THF)_2$, generated lavender (η^2-O,N-TEMPO)$_2$CrCl (**1**) in 67% yield upon crystallization from Et_2O, as Scheme 1 illustrates. The addition of 2 equiv TEMPO to $CrCl_2(THF)_2$ in THF resulted in disproportionation to **1** and $CrCl_3(THF)_3$. The addition of [TEMPO]Na to **1** converted the chloride into the *tris*-TEMPO complex, (η^2-O,N-TEMPO)$_2$Cr(TEMPO) (**2**), as purple/yellow dichroic crystals from Et_2O in 53% yield. While **1** is stable for hours at 100°C in C_6D_6, **2** decomposes at 25°C (k ~ 0.02 s^{-1}) to afford some TEMPO, and unidentified products arising from apparent OAT. If TEMPO loss is irreversible, an upper limit of the Cr-(η^1-O) BDE is ~82 kJ/mol. Additional donors (e.g. PMe_3) failed to bind to **1** and **2**, and redox processes failed to yield isolable products.



Scheme 1. Synthetic procedure for obtaining pure (η^2-O,N-TEMPO)$_2$CrCl (**1**) and (η^2-O,N-TEMPO)$_2$Cr(TEMO) (**2**).

The complexes exhibit magnetic moments (**1**, μ_{eff} = 3.7 μ_B; **2**, μ_{eff} = 3.6 μ_B) consistent with near spin-only S = 3/2 Cr(III) centers. The ^{1}H NMR spectrum of (η^2-O,N-TEMPO)$_2$CrCl (**1**) reveals only one type of TEMPO, and spans ~20 ppm (δ -1 -> δ 19). In contrast, (η^2-O,N-TEMPO)$_2$Cr(TEMPO) (**2**) manifests a more complex ^{1}H NMR spectrum with broader signals and greater shift dispersity (δ -5 -> δ 65 ppm; see Supplementary Information). Due to the thermal sensitivity of **2**,

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and the symmetry evident in **1**, it was not possible to obtain information regarding any η^2- to η^1-interconversion. EPR spectra (Fig. 1) obtained at 100K in 2-Me-THF show pseudo-axial symmetry for **1**, with g_{iso} = 2.00 and D = 2.25 cm^{-1} (E/D = 0.03), while **2** exhibits rhombic symmetry, with g_{iso} = 1.97, D = 2.01 cm^{-1} and E/D = 0.17). The pseudo-axial symmetry in **1** suggests that an η^2-O,N-TEMPO ligand manifests the same perturbation as a chloride, and that pentagonal planar coordination is similar to a trigonal field.[25]

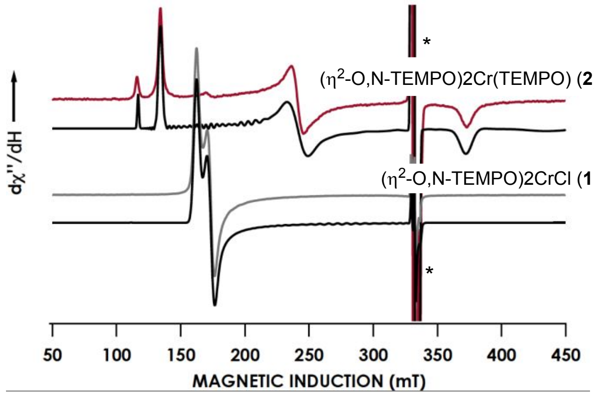


Fig 1. Experimental (2-Me-THF, 100K, red, gray) and simulated (black) EPR spectra of (η^2-O,N-TEMPO)$_2$CrCl (**1**, bottom; g = [2.01, 2.00, 2.01], D = 2.25 cm^{-1}, E/D = 0.03) and (η^2-O,N-TEMPO)$_2$Cr(TEMPO) (**2**, top; g = [1.90, 2.04, 1.97], D = 2.01 cm^{-1}, E/D = 0.17). TEMPO(*) is a ~1% and 10% impurity in **1** and **2**, respectively.

As Fig. 2 illustrates, (η^2-O,N-TEMPO)$_2$CrCl (**1**) displays PPP coordination, and C$_{2v}$ symmetry. The Cl-Cr-N1 and -N2 angles of 95.98(3)° and 95.37(3)°, the (h^2-O,N-) bite angles of 41.18(4)° (N1) and 41.21(4)°, and the O1-Cr-O2 angle of 86.45(3)° sum to 360.2°. Chromium bond distances to the two oxygens (O1, 1.8974(9) Å; O2, 1.8972(9) Å) are consistent with anionic TEMPO ligands, as are the O1-N1 and O2-N2 bond lengths of 1.3987(12) Å and 1.4115(13) Å,[14] respectively. Chromium-nitrogen distances (N1, 2.0569(10) Å; N2, 2.0611(10) Å) clearly reveal donor bonds, and the d(CrCl) of 2.3191(3) is typical for chromic species.

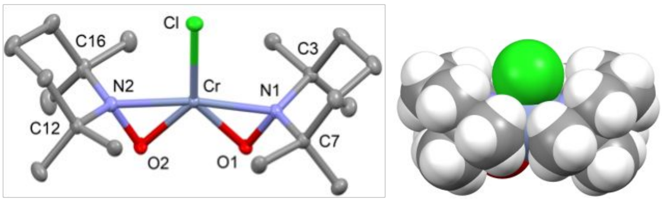


Fig. 2. Molecular and space filling views of (η^2-O,N-TEMPO)$_2$CrCl (**1**). Selected distances (Å) and angles (°): CrCl, 2.319s1(3); CrO1, 1.8974(9); CrO2, 1.8972(9); CrN1, 2.0569(10); CrN2, 2.0611(10); ClCrO1, 137.02(3); O1-N1, 1.3987(12); O2-N2, 1.4015(13); ClCrO2, 136.52(3); ClCrN1, 95.9893); ClCrN2, 95.37(3); O1CrN1, 41.18(4); O1CrO2, 86.45(3); O1CrN2, 127.49(4); O2CrN1, 127.45(4); O2CrN2, 41.21(4); N1CrN2, 168.65(4); CrO1N1, 75.54(6); CrO2N2, 75.68(5); CrN1O1, 63.28; CrN2O2, 63.11(5); CNC, 118.3(4) ave; CNO, 111.06(8) ave; CNCr, 119.3(6) ave.

Fig. 3 displays a molecular view of (η^2-O,N-TEMPO)$_2$Cr(TEMPO) (**2**), a PPP complex consisting of one monodentate and two bidentate (η^2-O,N-TEMPO)$^-$ anions. The molecule is asymmetric, as the bidentate TEMPO ligands are rotated with respect to each other (d(N2-N3) = 3.90 Å) to keep all three tetramethylpiperidinyl (TMP) groups roughly equidistant (d(N1-N2) = 4.30 Å; d(N1-N3) = 4.20 Å). As in the preceding chloride (**1**), the sum of relevant core angles is 360.1°. The metrics indicate that core distances in **2** are slightly longer than in **1**, perhaps a modest consequence of sterics. Chromium-oxygen distances also reveal binding of TEMPO anion (O1, 1.9037 Å; O2, 1.9083(13) Å; O3, 1.9223(14) Å), which is corroborated by the d(N-O) of 1.4403(19) Å (N1), 1.414(2) Å (N2), and 1.407(2) Å (N3).[14] Note that these PPP complexes are unique, as all previous conformationally locked examples were of Ag$^+$, a metal lacking the potential for ligand field stabilization.[15-18]

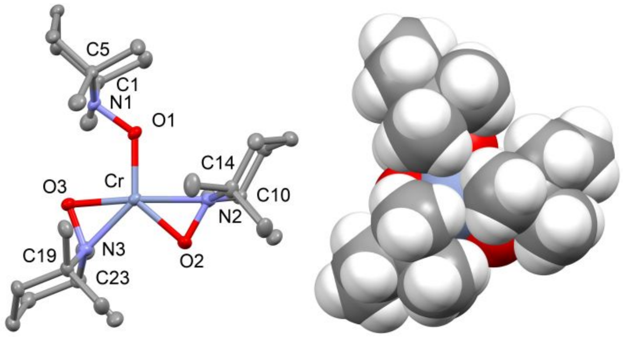


Fig 3. Molecular and space filling views of (η^2-O,N-TEMPO)$_2$Cr(TEMPO) (**2**). Selected distances (Å) and angles (°): CrO1, 1.9037(13); CrO2 1.9083(13); CrO3 1.9223(14); CrN2, 2.1250(16); CrN3, 2.0375(16); O1N1, 1.4403(19); O2N2, 1.414(2); O3N3, 1.407(2); O1CrO2, 131.15(6); O1CrO3, 93.69(6); O1CrN2, 90.56(6); O1CrN3, 135.15(6); O2CrO3, 135.16(6); O2CrN3, 93.68(6); N2CrN3, 134.29(6); CrO1N1, 125.86(11); CrO2N2, 77.96(9); CrO3N3, 73.63(9); CrN2O2, 61.43(8); CrN3O3, 64.86(15); O2-Cr-N2, 40.61(6); O3-Cr-N3, 41.51(6).

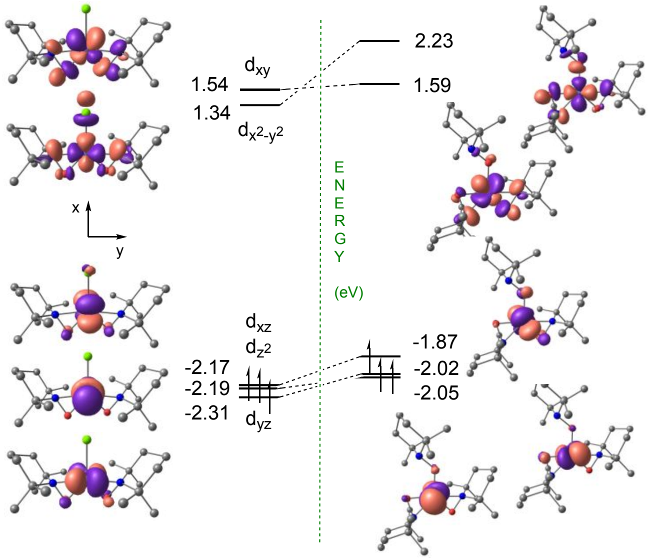
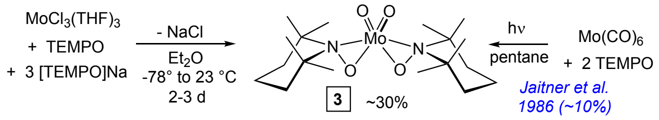


Fig. 4. RO-wB97xD/def2-tzvpp orbitals (isovalues = 0.045) for (η^2-O,N-TEMPO)$_2$CrCl (**1**, left) and (η^2-O,N-TEMPO)$_2$Cr(TEMO) (**2**, right). Orbital energies are in eV.

The d-orbital splitting diagrams of (η^2-O,N-TEMPO)$_2$CrX (X = Cl, **1**; TEMPO, **2**) are illustrated in Fig. 4, and are most easily understood by assigning the z-axis perpendicular to the core-atom plane. Since the η^2-O,N-TEMPO bite angles approach 45°, ligand perturbations at roughly 0°, 90°, and 270° impact d_{x2-y2}, while interactions at ~135° and ~225° involve d_{xy}. Ligand orbitals at all five positions overlap with the torus of d_{z2}. Restricted open-shell (Fig. 4) and unrestricted orbitals of **2** reveal little difference in spin density, which is predominantly on Cr (ρ_{spin} ~ 3.2 e-; <0.07 e^- on N and O); chloride **1** has related values. The crystallographic geometries were well matched by calculation, and optimized structures and unrestricted calculations are available in Supplementary Information.

The d-orbital splitting diagrams in Fig. 4 reveal a nearly σ-only bonding pattern reminiscent of a trigonal complex,[25] with minor O(pp*)-components affecting the energies of d_{xz} and d_{yz}. To estimate field strengths, TDDFT calculations performed on **1** and **2** (see Supplementary Information) reveal the lowest d-d transitions at 662 and 759 nm, respectively, with miniscule oscillator strengths. The UV-vis spectrum of **1** is commensurate with that calculated, including an absorption at 640 nm (50 $M^{-1}cm^{-1}$ with intensity stealing); no low energy features could be discerned in spectra of **2**. The calculated spectra afford a rough estimate of the field strength, and show **1** modestly greater than **2** (15,105 cm^{-1} vs. 13175 cm^{-1}).

The hapticity of TEMPO was computationally tested by constraining Cr-O-N angles during geometry optimizations. Sequential η^2- to η^1-dissociations in **2** resulted in calculated ΔG° penalties of ~29 and ~38 kJ/mol, and in neither case were minima found for the 4- and 3-coordinate products. Rotating each η^2-O,N-TEMPO ligand has deleterious steric consequences, and the small bite angles of the η^2-O,N-TEMPO ligands negate any potential enthalpic advantage. In essence, PPP coordination of (η^2-O,N-TEMPO)$_2$CrX (X = Cl, **1**; TEMPO, **2**) stems from: 1) favorable binding from the N-donor components; 2) favorable sterics, as evident in the space-filling views in Figs. 2 and 3; and 3) small bite angles of the η^2-O,N-TEMPO that hamper orbital overlaps in out-of-plane configurations. The enthalpic consequences are reminiscent of pentagonal mono- and bi-pyrimidal geometries found for isoelectronic vanadium diperoxide species.[26]



Scheme 2. Halide and carbonyl methods yielding (η^2-O,N-TEMPO)$_2$MoO$_2$ (**3**).

The extension of this geometry to the heavier group 6 elements was not observed. Previously, thermolyses[27] and photolyses of $M(CO)_6$ (M = Mo, W) with TEMPO afforded oxides (η^2-O,N-TEMPO)$_2$MoO$_2$ (M = Mo, **3**, x-ray)[27,28] and $W_3(TEMPO)_5(O)_5$ (FAB MS).[29] Reasoning the use of group 6 halides would lessen the possibility of OAT, the addition of 3 equiv Na[TEMPO] and 1 equiv TEMPO to $MoCl_3(THF)_3$ was conducted, and **3** was isolated in ~30% yield. Similar experiments with the W(III) chloride dimer, $[W_2Cl_7(THF)_2][Na(THF)_3]$,[30] and other halide starting materials failed to produce crystalline material.

The apparent structural dichotomy between the 1st and 2nd/3rd row transition metal complexes lies with the greater covalent capacity of the latter as manifested in multiple bond formation. A preliminary survey of 1st row TEMPO complexes suggests that homoleptic species is of greater scope than originally thought, but the kinetic instability witnessed in **2** must be harnessed to avoid OAT akin to the heavier congeners.[31]

Author Contributions

All synthetic and most spectroscopic work was conducted by AKK; MMB and KML conducted the EPR spectroscopy; TRC is responsible for calculations, and SNM is the crystallographer. Conception of the project and management is the purview of PTW.

Conflicts of interest

Support from the National Science Foundation (PTW, CHE-1953884; KML, CHE-1954515; MMB, Fellowship) and Cornell University is gratefully acknowledged. Special thanks to Profs. Santiago Alvarez and Roald Hoffmann for a helpful perspective. There are no competing financial or otherwise conflicts of interest

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