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Diamagnetic Group 6 Tetrakis(di-*tert*-butylketimido)metal(IV) Complexes

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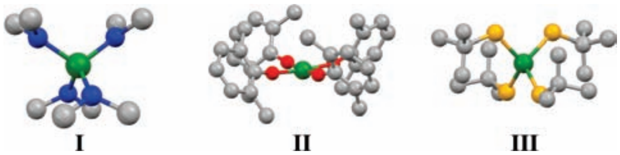
Abstract: The addition of 4 equiv of LiN═C-*t*-Bu_2 to $CrCl_3$, $MoCl_5$, and WCl_6 in diethyl ether produced the complexes M(N═C-*t*-$Bu_2)_4$ (M = Cr, Mo, W). Single-crystal X-ray diffraction studies revealed that the molecules have flattened tetrahedral geometries with virtual D_{2d} symmetry in the solid state. ^1H and ^{13}C NMR spectra indicated that the complexes are diamagnetic, and a qualitative MO analysis showed that the orthogonal π-donor and -acceptor orbitals of the ketimide ligand cooperatively split the d_{xy} and d_{z2} orbitals sufficiently to allow spin pairing in the d_{xy} orbital. A more sophisticated quantum-mechanical analysis of Cr(N═C-*t*-$Bu_2)_4$ using density functional/molecular mechanics methods confirmed the qualitative analysis by showing that the singlet state is 27 kcal/mol more stable than the triplet state.

Homoleptic four-coordinate chromium(IV) complexes with alkyl,[1−9] aryl,[10−13] and π-donor ligands, including the well-characterized complexes $Cr(NEt_2)_4$,[14,15] Cr(O-*t*-$Bu)_4$,[14,16−18] and Cr(OCH-*t*-$Bu_2)_4$[19] and heteroleptic Cr(O-*t*-$Bu)_3$(OSi(O-*t*-$Bu)_3$),[20] are paramagnetic. Single-crystal X-ray diffraction studies have been performed on several of these complexes,[5,7−10,13,19] including the alkoxide complexes Cr(OCH-*t*-$Bu_2)_4$ and Cr(O-*t*-$Bu)_3$(OSi(O-*t*-$Bu)_3$),[19,20] and the MX_4 cores in all cases are essentially tetrahedral. Molybdenum alkyl and aryl complexes are also paramagnetic and have tetrahedral cores.[21,22]

In contrast to the analogous chromium complexes, homoleptic molybedenum(IV) and tungsten(IV) complexes with π-donor ligands display structural diversity. While the MN_4 core in the amide complex $Mo(NMe_2)_4$, for example, has a nearly tetrahedral geometry (Chart 1, **I**),[23−25] the MO_4 cores in the alkoxide and aryloxide complexes Mo(OC(2-adamantylidiene)(mesityl)$)_4$ and W(O-2,6-$C_6H_3R_2)_4$ (R = Me, *i*-Pr) have severely flattened tetrahedral (Mo)[26] or nearly square-planar (W) geometries (Chart 1, **II**),[27,28] and the MS_4 cores in the thiolate complexes M(S-*t*-$Bu)_4$ [M = Mo (Chart 1, **III**), W][27,29] and Mo(S-2,4,6-C_6H_2-*i*-$Pr_3)_4$[30] have elongated and slightly flattened tetrahedral geometries, respectively. All of these Mo and W complexes are diamagnetic because of the ligand π-donor capability. In the tetrahedral and distorted tetrahedral complexes, the π-donor orbital(s) split the lowest-lying two-d-orbital set sufficiently to allow for spin pairing, while in the square-planar complex **II**, the aryloxide π-donor orbitals push the d_{xz}, d_{yz}, and d_{xy} orbitals up in energy, leaving the d_{z^2} orbital as the HOMO. The smaller d−d exchange energies for second- and third-row metals, whose *n*d orbitals are more diffuse than 3d orbitals of the first-row metals, and the greater spin−orbit coupling for the second- and third-row metals also favor spin pairing.

In this report, we describe the synthesis and structure of a *diamagnetic* four-coordinate homoleptic chromium(IV) ketimide complex and its molybdenum(IV) and tungsten(IV) congeners. In the new complexes, the ketimide orthogonal π-donor and -acceptor orbitals uniquely and cooperatively split the lowest-lying d orbitals to allow for spin pairing.

Chart 1. Ball-and-Stick Structures of $Mo(NMe_2)_4$ (**I**), W(O-2,6-$C_6H_3Me_2)_4$ (**II**), and Mo(S-*t*-$Bu)_4$ (**III**)



Chromium trichloride was allowed to react with LiN═C-*t*-Bu_2 in diethyl ether to produce Cr(N═C-*t*-$Bu_2)_4$ as dark-amber crystals in 49% yield. Similar procedures using $MoCl_5$ and WCl_6 produced, respectively, blue and blue-green crystals of M(N═C-*t*-$Bu_2)_4$ [M = Mo (76%), W (64%)]. The formation of high-valent group VI complexes via nonstoichiometric reactions, such as the reactions in these examples, has been observed previously.[15,23] The chromium and molybdenum complexes sublime cleanly under vacuum (92−94 and 84−86 °C, respectively, at 55 Torr), while the tungsten analogue decomposes when heated under vacuum to form an unidentified yellow material. Each complex revealed a sharp, unshifted singlet resonance in the ^1H NMR spectrum attributable to the *tert*-butyl protons and sharp, unshifted resonances arising from the ketimide and *tert*-butyl carbon atoms in the $^{13}C\{^1H\}$ spectra. The NMR data are consistent with diamagnetic complexes.

Single-crystal X-ray diffraction studies were performed on the Cr (Figure 1), Mo (Figure 2), and W complexes. The tungsten complex was severely disordered and is not shown; the final structural model for the tungsten complex was chosen to correspond closely to the molybdenum structure. In the solid state, the complexes have virtual D_{2d} symmetry with flattened tetrahedral MN_4 cores. In the cores, the two opposite large N−M−N angles average 136, 133, and 129° and the four smaller angles average 98, 99, and 100° for the complexes with M = Cr, Mo, and W, respectively. The M−N bond lengths, which vary only slightly within each molecule, are 1.78, 1.88, and 1.88 Å for M = Cr, Mo, and W, respectively. In contrast to the flattened tetrahedral structures found in these d^2 complexes, the d^0 complex Hf(N═C-*t*-$Bu_2)_4$ has an undistorted tetrahedral MN_4 core.[31]

If the complexes had tetrahedral cores and the ligands had no π-donor or -acceptor capability, a two-below-three splitting of the d orbitals and a triplet ground state would be expected. The ketimide ligand, however, is both a single-faced π-donor and -acceptor ligand in which the π-donor and -acceptor orbitals are orthogonal to each other (Chart 2, **IV**). In D_{2d} symmetry and with the orientation of the ketimide ligand substituents found in the solid state, the ligand π-donor orbital interacts with d_{z^2}, pushing it up in energy relative to d_{xy}, while the ligand π-acceptor orbital interacts with d_{xy}, pushing it down in energy relative to d_{z^2}. The net result is a splitting between d_{z^2} and d_{xy}, with the former higher in energy (Chart 2, **V**). Because the NMR data indicate that all three complexes are diamagnetic, the splitting must be large enough to allow spin pairing of the two

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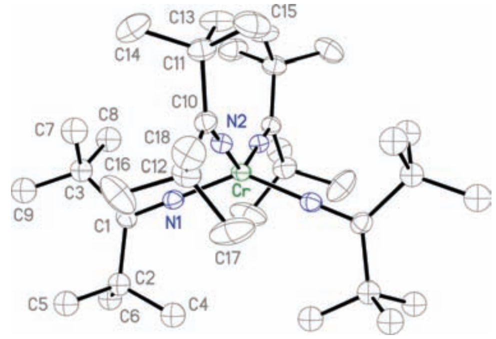


Figure 1. Molecular structure of Cr(N═C-*t*-Bu$_2$)$_4$. The thermal ellipsoids are 40% equiprobability envelopes, and hydrogen atoms have been omitted. Only one orientation of each disordered *tert*-butyl group is shown. Selected bond lengths (Å) and angles (deg): Cr−N1, 1.7840(17); Cr−N2, 1.7850(17); N1−C1, 1.265(3); N2−C10, 1.262(3); N1−Cr−N1′, 136.09(11); N2−Cr−N2′, 136.16(10); N1−Cr−N2, 98.21(7); N1−Cr−N2′, 97.84(7).

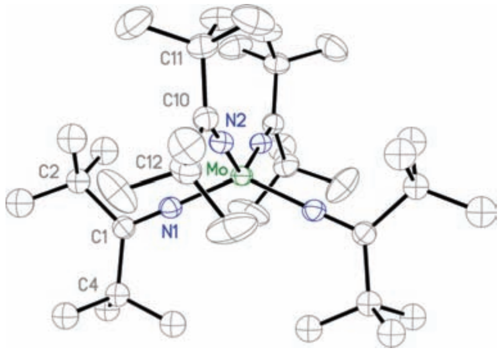
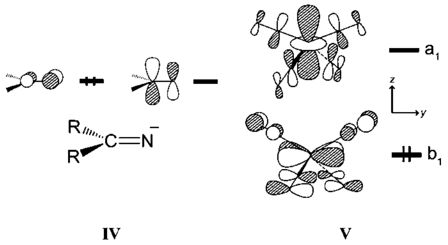


Figure 2. Molecular structure of Mo(N═C-*t*-Bu$_2$)$_4$. The thermal ellipsoids are 40% equiprobability envelopes, and hydrogen atoms have been omitted. Only one orientation of each disordered *tert*-butyl group is shown. Selected bond lengths (Å) and angles (deg): Mo−N1, 1.880(2); Mo−N2, 1.885(2); N1−C1, 1.270(3); N2−C10, 1.271(3); N1−Mo−N1′, 132.26(13); N2−Mo−N2′, 132.67(13); N1−Mo−N2, 99.43(9); N1−Mo−N2′, 99.27(9).

electrons in d$_{xy}$ even in the case of the chromium complex. On the basis of the MO analysis, the experimentally observed distorted tetrahedral geometry is a compromise of competing interactions, with the ligand π-donor−d$_{z^2}$ interaction favoring a tetrahedral geometry and the ligand π-acceptor−d$_{xy}$ interaction favoring a square-planar geometry. In related studies, Wolczanski, Cundari, and co-workers[32] attributed the contrasting structures found in the heteroleptic complexes (*t*-Bu$_3$SiO)$_3$MX (trigonal monopyramidal for M = Mo and X = Cl or Et but flattened tetrahedral for M = W and X = Cl or Me) to stronger nd$_{z^2}$−(n + 1)s mixing for W than for Mo. Only (*t*-Bu$_3$SiO)$_3$WCl was found to have a singlet ground state.

Density functional calculations were performed to confirm the qualitative MO analysis.[33−37] For the geometry-optimized model compound Cr(N═CH$_2$)$_4$, the calculations showed that the singlet state is 20 kcal/mol more stable than the triplet. Both states have D_{2d} geometries; the N−Cr−N angles were found to be 121 and 114° for the singlet and triplet states, respectively. Similarly, for Cr(N═C-*t*-Bu$_2$)$_4$, quantum mechanics/molecular mechanics (QM/MM) calculations[38] showed that the singlet state is 27 kcal/mol more stable than the triplet state with the optimized singlet geometry very close to the flattened tetrahedral geometry found in the solid state (average N−Cr−N angles = 136 and 98° and Cr−N distance = 1.76 Å). The optimized geometry for the triplet state is similar to the singlet-state geometry, with average N−Cr−N angles of 127 and 102° and a Cr−N distance of 1.82 Å. Consistent with the qualitative MO analysis, in both Cr(N═CH$_2$)$_4$ and Cr(N═C-*t*-Bu$_2$)$_4$ the ground-state HOMO and LUMO are d$_{xy}$ and d$_{z^2}$, respectively. There are substantial HOMO−LUMO gaps in both cases (2.0 and 1.9 eV for Cr(N═CH$_2$)$_4$ and Cr(N═C-*t*-Bu$_2$)$_4$, respectively).

Chart 2. Orthogonal π-Donor and π-Acceptor Orbitals of the Ketimide Ligand (**IV**) and the HOMO and LUMO of D_{2d} M(N═C−*t*-Bu$_2$)$_4$ Complexes (**V**)



In the ^{1}H NMR spectra of the M(N═C-*t*-Bu$_2$)$_4$ complexes, the *tert*-butyl groups give rise to a sharp singlet. If the D_{2d} solid-state structures were retained in solution, the *tert*-butyl groups should give rise to two singlets. An ^{1}H NMR spectrum recorded at −70 °C for a toluene-d_8 solution of Cr(N═C-*t*-Bu$_2$)$_4$ showed only broadening of the resonance arising from the *tert*-butyl groups. Rotation about the MN bonds is one possible mechanism to account for the fast exchange of the *tert*-butyl groups. A meshed-gear-like rotation about two or more M−N bonds is probable to accommodate the large *tert*-butyl substituents. Alternatively, a $D_{2d} \rightarrow D_{4h} \rightarrow D_{2d}$ (i.e., flattened tetrahedral → square-planar → flattened tetrahedral) mechanism also accounts for the observed spectra. Preliminary QM/MM calculations on Cr(N═C-*t*-Bu$_2$)$_4$ have suggested that a geared rotation about two Cr−N bonds is the lower-energy pathway. There is ample precedent, however, for square-planar geometries that are energetically accessible for low d-electron counts: d^2 W(O-2,6-C$_6$H$_2$R$_2$)$_4$ (R = Me or *i*-Pr),[27,28] d^3 Re(N═C-*t*-Bu$_2$)$_4$,[31] and d^3 M(N═C-*t*-Bu$_2$)$_4$ (M = Fe and Os)[31,39] all have square-planar geometries.

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Supporting Information Available: Experimental procedures, complete ref 33, and crystallographic data (CIF) for M(N═C-*t*-Bu$_2$)$_4$ (M = Cr, Mo, W). This material is available free of charge via the Internet at http://pubs.acs.org.

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