On the border between localization and delocalization: Tris(iminoxolene)titanium(IV)

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The tris(aminophenol) ligand tris(4-methyl-2-(3',5'-di-*tert*-butyl-2'-hydroxyphenylamino)phenyl)amine, MeClampH$_6$, reacts with Ti(O^{i}Pr)$_4$ to give, after exposure to air, the dark purple, neutral, diamagnetic complex (MeClamp)Ti. The compound is six-coordinate, with an uncoordinated central nitrogen (Ti–N = 2.8274(12) Å), and contains titanium(IV) and a doubly oxidized ligand, formally a bis(iminosemiquinone)-mono(amidophenoxide). The compound is unsymmetrical in the solid state, though the three ligands are equivalent on the NMR timescale in solution. *Ab initio* calculations indicate that the ground state is a multiconfigurational singlet, with a low-lying multiconfigurational triplet state. Variable-temperature NMR measurements are consistent with a singlet-triplet gap of 1200 ± 70 cm^{-1}, in good agreement with calculations. The distortion from threefold symmetry allows a low-lying, partially populated ligand-centered π nonbonding orbital to mix with largely occupied metal-ligand π bonding orbitals. The energetic accessibility of this distortion is inversely related to the strength of the metal-ligand π bonding interaction.

Introduction

The central problem posed by redox-active ligands when coordinated to redox-active metal centers is the oxidation state problem: Does the electron reside on the metal, on the ligand, or is it shared between the two? This ambiguity, absent with more common, redox-inert ligands, has given rise to the moniker "noninnocent" to describe redox-active ligands.[1] A frequently occurring secondary problem, if there are multiple redox-active ligands present, is whether any ligand-centered electrons are localized or delocalized among the ligands. One can view this problem in the language of mixed-valency:[2] are the electrons fully delocalized (Class III), fully localized on one ligand (Class I), or somewhere in between?[3] This question can be answered in many cases for specific compounds, but general principles that govern the degree of delocalization have not yet been clarified.

When redox-active ligands are bound to early transition metals, the first problem, of redox non-innocence, is usually unimportant. These electropositive metals have a high propensity to adopt their highest possible oxidation state, so when the complexes exhibit redox activity, it is unambiguously localized on the ligands.[4] The problem of localization of oxidation state among multiple redox-active ligands still remains, and even rather similar compounds may give divergent outcomes. Thus, a vanadium complex with three bis(arylimino)acenaphthylene ligands appears to be completely delocalized,[5] while a complex with three 3,6-di-*tert*-butylcatecholate ligands contains a fully localized semiquinonate ligand, as judged in the solid state by X-ray crystallography and in solution by EPR spectroscopy.[6]

We recently reported the encapsulating tris(aminophenol) ligand tris(4-methyl-2-(3',5'-di-*tert*-butyl-2'-hydroxyphenylamino)phenyl)amine, MeClampH$_6$, and described its seven-coordinate complex with molybdenum, κ^7-(MeClamp)Mo.[7] This complex is completely symmetrical, as expected for a compound whose electronic structure can be satisfactorily described as containing fully oxidized Mo(VI) and fully reduced amidophenoxides, albeit with substantial ligand-to-metal π donation and concomitant covalency in the metal-ligand bonds. Here we describe the air- and water-stable neutral complex (MeClamp)Ti, where a fully oxidized Ti(IV) oxidation state requires mixed oxidation states among the amidophenolate arms, either one amidophenolate and two iminosemiquinones or two amidophenolates and one iminoquinone. The complex appears to sit on the energetic border between a fully delocalized and a fully localized structure, thus offering the possibility of illuminating the factors that favor electronic localization or delocalization.

Experimental

General procedures

Where indicated, procedures were carried out under an inert atmosphere in a nitrogen-filled glovebox. When needed, chlorinated solvents were dried over 4 Å molecular sieves,

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followed by CaH_2. Deuterated solvents were obtained from Cambridge Isotope Laboratories, dried using the same procedures as their protio analogues, and stored in the drybox prior to use. All other reagents were commercially available and used without further purification. Routine NMR spectra were measured on Bruker Avance III HD 400 and 500 spectrometers, while variable temperature experiments were performed on a Varian Inova 500 instrument. Chemical shifts for ^{1}H NMR spectra are reported in ppm downfield of TMS, with spectra referenced using the chemical shifts of the solvent residuals. Infrared spectra were recorded on a JASCO FT/IR-6300 spectrometer. UV-visible-NIR spectra were measured in a 1-cm quartz cell on a Jasco V-670 spectrophotometer. ESI mass spectra were obtained using a Bruker micrOTOF-II mass spectrometer, and peaks reported are the mass number of the most intense peak of isotope envelopes. Samples were injected as acetonitrile solutions. In all cases, the observed isotope patterns were in good agreement with calculated ones. Elemental analyses were performed by Robertson Microlit Laboratories (Ledgewood, NJ, USA).

Synthesis

κ^6-[Tris(4-methyl-2-((3',5'-di-*tert*-butyl-2'-oxyphenyl)amido)phenyl)amine]titanium(IV), (MeClamp)Ti. In the drybox, 0.607 g MeClampH$_6$[7] (0.642 mmol) is dissolved in 8 mL of chloroform. To the stirred solution is added 285 µL $Ti(O^iPr)_4$ (0.964 mmol, 1.5 equiv), whereupon the solution turns dark red. After 45 min, the flask is opened to the air and stirred overnight to give a dark purple solution. The solution is filtered through a silica gel column with methylene chloride and the solvent is removed from the filtrate on the rotary evaporator to give a dark purple solid. The solid is slurried with a minimum of acetonitrile and filtered to give 0.448 g (MeClamp)Ti (71%). ^{1}H NMR (CD_2Cl_2, 23 °C): δ 1.25 (s, 27H, ^{t}Bu), 1.31 (s, 27H, ^{t}Bu), 2.08 (s, 9H, C*H*$_3$), 6.0 (v br, 3H, Ar*H*), 7.32 (v br, 3H, Ar*H*). ESI-MS: 987.5657 (M$^+$, calcd 987.5633). UV-Vis-NIR (CH_2Cl_2): λ_{max} = 347 nm (ε = 31600 L mol^{-1} cm^{-1}), 520 (11500), 829 (6780), 1331 nm (6870), 1961 nm (7680). Anal. Calcd for $C_{63}H_{78}N_4O_3Ti$: C, 76.65; H, 7.96; N, 5.68. Found: C, 76.42; H, 7.67; N, 5.72.

Variable-Temperature NMR of (MeClamp)Ti

^{1}H NMR spectra were acquired from –95 °C to 30 °C in CD_2Cl_2 solution. For those peaks that showed a significant dependence of the chemical shift on temperature and were observable over a sufficient temperature range, the chemical shifts were described by eq 1a, with the hyperfine coupling constants *A* in MHz, the absolute temperatures *T* in K, Δ*E* in kcal mol^{-1}, and chemical shifts in ppm. Due to the relatively small energy gap in this compound, the temperature-dependence of the diamagnetic chemical shift was neglected in the analysis.[8]

$$\delta_{obsd} = \delta_{dia} + \frac{2g\beta A}{(\gamma_H/2\pi)kT}(3+e^{\Delta E/RT})^{-1} \tag{1}$$ [9,10]

$$\delta_{obsd} = \delta_{dia} + (63150)\frac{A}{T}(3+e^{\Delta E/0.001987T})^{-1} \tag{1a}$$

Unweighted nonlinear least-squares fitting was carried out, optimizing one chemical shift and one hyperfine coupling per resonance and a single global value of Δ*E* for all resonances, using the Levenberg-Marquardt algorithm as implemented in the Solver routine of Microsoft Excel.[11] Uncertainties were estimated using established methods.[12]

Electrochemistry of (MeClamp)Ti

Electrochemical measurements were performed in the drybox using a Metrohm Autolab PGSTAT128N potentiostat. A three-electrode arrangement (glassy carbon working electrode, glassy carbon counter electrode, silver/silver chloride pseudo-reference electrode) was used. The electrodes were connected to the potentiostat through electrical conduits in the drybox wall. The sample solution contained 1 mM (MeClamp)Ti in CH_2Cl_2 with 0.1 M Bu_4NPF_6 as the electrolyte. Potentials were referenced to ferrocene/ferrocenium at 0 V,[13] with the reference potential established by spiking the test solution with a small quantity of decamethylferrocene (E° = –0.565 V in CH_2Cl_2[14]).

Theoretical Calculations

Correlation effects in the electronic structure of (Clamp)Ti (ClampH$_6$ = tris(2-(2'-hydroxyphenylamino)phenyl)amine) were investigated using RAS-CI.[15] The RAS-CI active space included the three orbitals derived from the redox-active orbitals on the amidophenoxide ligands and the five titanium *d* orbitals (2 occupied, 6 virtual). The RAS-CI calculations were performed using a 6-31G* basis set at geometries optimized by unrestricted DFT using the B3LYP functional and TZVP basis set. The unrelaxed RAS-CI triplet state energy was calculated at the DFT-optimized singlet geometry and the relaxed RAS-CI triplet state energy at the DFT-optimized triplet geometry. DFT calculations with B3LYP functionals and 6-31G* were performed to predict the geometries of simplified models in which the (MeClamp) is replaced by three catecholate, amidophenolate or benzenediamide ligands. To treat dynamical correlation, unrelaxed NEVPT2[16] calculations were also performed on (Clamp)Ti using an SVP basis set at geometries optimized by DFT with a B3LYP functional and SVP basis set. All DFT and RAS-CI calculations were performed using the *Q-Chem 4.0*[17] software package, while NEVPT2 calculations were carried out using *BAGEL*.[18]

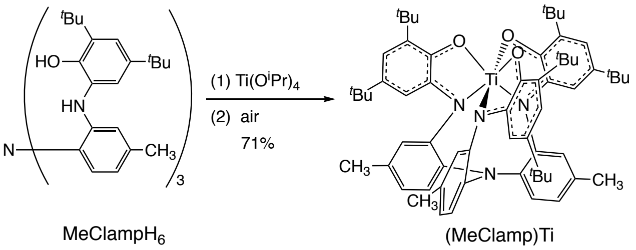
X-ray Crystallography

Crystals of (MeClamp)Ti • 2 CH_3CN were grown by dissolving the metal complex (as a crude oil) in a minimum of CH_3CN and allowing the solution to stand at room temperature. Crystals were placed in a mixture of DuPont Krytox GPL 105 PFPE lubricant and DuPont Krytox GPL205 grease before being transferred to the cold N_2 stream of the diffractometer. Data were reduced and corrected for absorption using the program SADABS. The structure was solved using direct methods. All non-hydrogen atoms not apparent from the initial solutions were found on difference Fourier maps, and all heavy atoms were refined anisotropically. Iminoxolene ring 1 was disordered in two different orientations (probably driven by the disorder of the tert-butyl group centered at C18, which is in two different orientations in the two ring orientations). All thermal parameters of the corresponding atoms in the two orientations were fixed as equal, and their occupancies were allowed to refine, giving a 57.8(2)% occupancy for the main orientation. No disorder was apparent for C11, and the two sites for C173 were so close that the refinement was only stable if their coordinates were fixed as equal. One of the acetonitriles of solvation was discerned in three different orientations. Thermal parameters of the corresponding atoms were fixed as equal and the sum of the occupancy factors constrained to 1.00; occupancies refined to 67.1(3), 23.7(5), and 9.2(5)%. All hydrogen atoms were placed in calculated positions, with their isotropic thermal parameters tied to the equivalent isotropic thermal parameters of the carbon atoms to which they were attached (1.2 × for aromatic and 1.5 × for methyl). Calculations used SHELXTL (Bruker AXS),[19] with scattering factors and anomalous dispersion terms taken from the literature.[20] Further details about the structure are given in Table 1.

Results and discussion

Preparation and Structure of (MeClamp)Ti

Titanium(IV) isopropoxide reacts with the tris(aminophenol) MeClampH$_6$[7] under a nitrogen atmosphere to form a red solution. *In situ* ^{1}H NMR spectroscopy (Fig. S1) indicates that one isopropoxide remains bound to the major titanium-containing product, which has no symmetry and is tentatively assigned as (MeClampH$_3$)Ti(O^{i}Pr). Presumably the isopropoxide groups deprotonate the phenols but are not sufficiently basic to deprotonate the diarylamines.[21] On exposure of this reaction mixture to the atmosphere, the remaining isopropoxide group is lost as isopropanol and a single titanium-containing product, dark purple (MeClamp)Ti, is formed (eq 2). This air-stable material can be purified by column chromatography on silica gel and is isolated as a crystalline solid in 71% yield.



(2)

The complete deprotonation of the ligand in the complex is confirmed by IR spectroscopy (no N-H or O-H stretches) and by X-ray crystallography, which shows trigonal planar environments for all the iminoxolene nitrogens (sum of angles at N > 356°; Fig. 1). The coordination geometry of titanium is octahedral, with no significant interaction of titanium with the central triarylamine nitrogen (Ti--N = 2.8274(12) Å). This situation contrasts with the seven-coordinate capped octahedral geometry shown by (MeClamp)Mo (Mo–N = 2.28 Å).[7] The absence of a bond between the triarylamine and titanium is presumably due to the smaller size and lower Lewis acidity of the titanium center. (MeClamp)Mo binds the triarylamine nitrogen despite the intrinsically low Lewis acidity of the tris(amidophenoxide)molybdenum(VI) fragment.[22]

Assignment of the oxidation state of titanium as +4 seems secure based on the air-stability of the complex and the difficulty of reducing titanium(IV) in oxygen-rich coordination environments. This oxidation state assignment is supported by analysis of the intraligand bond distances in the complex. Using established correlations to determine metrical oxidation state (MOS) values for each of the ligands[23] gives a total MOS for the three iminoxolenes of –3.85(7). The difference from –4

Table 1 X-ray crystallography of (MeClamp)Ti • 2 CH$_3$CN.

Empirical formula	$C_{67}H_{84}N_6O_3Ti$
Temperature / K	120(2)
λ / Å	1.54178 (Cu Kα)
Crystal system	Orthorhombic
Space group	*Pbca*
Total data collected	180382
No. of indep reflns.	12331
R_{int}	0.0439
Obsd refls [I>2σ (I)]	11853
a / Å	22.8836(6)
b / Å	12.2462(3)
c / Å	45.2221(12)
α / °	90
β / °	90
γ / °	90
V / Å^3	12672.9(6)
Z	8
μ / mm^{-1}	1.511
Crystal size / mm	0.24 × 0.12 × 0.08
No. refined params	750
R indices [I > 2σ (I)]	*R*1 = 0.0406, *wR*2 = 0.1106
*R*1 indices (all data)	*R*1 = 0.0421, *wR*2 = 0.1118
Goodness of fit	1.039

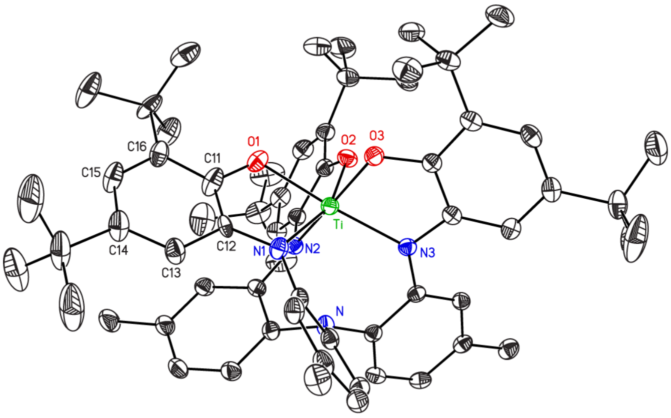


Fig. 1 Thermal ellipsoid plot of (MeClamp)Ti • 2 CH$_3$CN. Hydrogen atoms and solvent molecules are omitted, and only the major orientation of ring 1 is shown.

Table 2 Selected bond distances (Å) and metrical oxidation states (MOS) for the three iminoxolene rings (n = 1, 2, or 3) in (MeClamp)Ti • 2 CH_3CN.

	n = 1	*n* = 2	*n* = 3
Ti–O*n*	2.0069(10)	1.9693(10)	1.8961(9)
Ti–N*n*	2.1231(12)	2.1219(11)	2.0704(11)
O*n*–C*n*1	1.2952(19)	1.3141(16)	1.3367(16)
N*n*–C*n*2	1.361(11)[a]	1.3637(17)	1.3938(17)
C*n*1–C*n*2	1.449(11)[a]	1.4295(19)	1.4178(18)
C*n*2–C*n*3	1.414(11)[a]	1.4072(19)	1.4031(18)
C*n*3–C*n*4	1.373(6)[a]	1.382(2)	1.3874(19)
C*n*4–C*n*5	1.425(4)[a]	1.412(2)	1.405(2)
C*n*5–C*n*6	1.377(7)[a]	1.385(2)	1.392(2)
C*n*6–C*n*1	1.445(7)[a]	1.4177(18)	1.4075(19)
MOS	–0.95(8)	–1.27(3)	–1.63(5)
Ti--N	2.8274(12)		

[a] Ring 1 is disordered in two different orientations; the values given are the weighted averages of the two components.

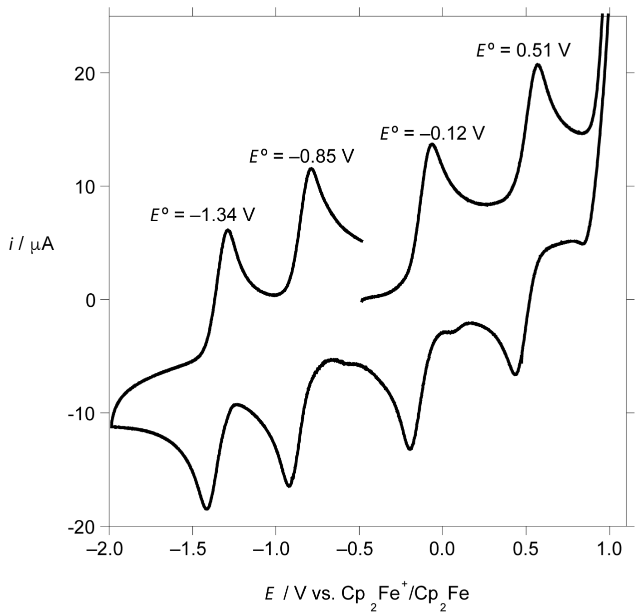


Fig. 2 Cyclic voltammogram of (MeClamp)Ti in CH_2Cl_2 (100 mM Bu_4NPF_6, 100 mV s^{-1}).

is only marginally significant, but may indicate a small amount of π donation from the iminoxolenes to titanium(IV), at least from ring 3, whose titanium-oxygen distance is longer than typical aryloxide-titanium distances (~1.85 Å) but shorter than those of non-π-donor oxygen anions such as acetylacetonate (~1.95 Å).[24–26] The bis(amidophenolate)titanium(IV) complex $(^tBuNC_6H_2{}^tBu_2O)_2Ti(THF)_2$ has an average MOS of –1.88(7).[27]

The iminoxolenes are thus formally in mixed oxidation states, nominally two iminosemiquinones and one amidophenolate. The isoelectronic complex based on bis(arylimino)acenapthenequinone, $Ti(C_{12}H_6[NAr]_2)_3$, shows a highly symmetric structure (crystallographic D_3 symmetry).[28] In contrast, (MeClamp)Ti shows a noticeably unsymmetrical coordination environment in the solid state (Table 2), as evidenced by the variation in metal-ligand bond distances (for example, Ti–O distances that range from 1.8961(9) to 2.0069(10) Å) and in intraligand distances (MOS values of –0.95(8), –1.27(3), and –1.63(5)). These values are most consistent with a structure that is neither fully delocalized (MOS = –1.33 for all three ligands) nor fully localized (MOS = –1 for two ligands and –2 for one ligand).

Characterization of (MeClamp)Ti

The cyclic voltammogram of (MeClamp)Ti shows four reversible one-electron redox waves, two oxidations and two reductions, between –2.0 V and +1.0 V vs. ferrocene/ferrocenium (Fig. 2). Given the difficulty of reducing titanium(IV) in oxygen-rich environments,[29] all of the redox events may be assigned as ligand-centered. The reduction waves at –0.85 V and –1.34 V are very similar to those shown by bis(aryliminobenzosemiquinone) complexes of group 10 metals[8,30–33] and are thus assigned to iminoxolene-centered reductions. The oxidations are more ambiguous, since both iminoxolenes (as in (MeClamp)Mo, *E*° = –0.17, +0.55 V)[7] and triarylamines are expected to show oxidation waves at these potentials. Tri-*p*-tolylamine itself oxidizes at +0.33 V,[34] and *ortho*-amino substitution is expected to lower this potential. However, triarylaminium ions have the aryl groups nearly coplanar with the coordination plane of the central nitrogen in order to allow delocalization of the positive charge. For example, tris(4-bromophenyl)aminium ion has an average angle of 36.7° between these planes, and lower-potential oxidants tend to have even smaller angles.[35] The constraints of the hexadentate chelate in (MeClamp)Ti require the aryl groups to align much closer to perpendicular to the NC_3 plane (average angle 55(3)°), which decreases the overlap between the nitrogen *p* orbital and the arene rings and makes the triarylamine harder to oxidize. The two oxidation waves in (MeClamp)Ti are thus tentatively assigned as iminoxolene-localized; the potentials observed are strikingly similar to those shown by (MeClamp)Mo.[7]

The optical spectrum of (MeClamp)Ti (Fig. 3) shows an intense band in the UV, probably due to ligand-to-metal charge transfer (compare bis(amidophenoxide) complex $Ti(^tBuNC_6H_2{}^tBu_2O)_2(THF)_2$, λ_{max} 371 nm[27]). A series of moderately intense transitions in the visible region extending into the near-infrared is also observed. These bands are likely due to intraligand transitions, which are typically observed at long wavelengths in complexes containing iminosemiquinone ligands.[8]

(MeClamp)Ti is diamagnetic both in the solid state and in solution (by Evans method). Its ^1H NMR spectrum at ambient temperatures (Fig. 4), however, shows substantially broadened peaks due to the *tert*-butyl and methyl resonances, and two of the aromatic resonances. The other three aromatic resonances are apparently so broad as to be undetectable, though two more can be discerned at low temperature. Lowering the temperature causes all the resonances to change chemical shift towards their expected diamagnetic positions. At all temperatures, the presence of only two *tert*-butyl peaks and one methyl peak indicates that the asymmetry shown in the solid state is either lost in solution, or more likely is averaged by a rapid fluxional process.

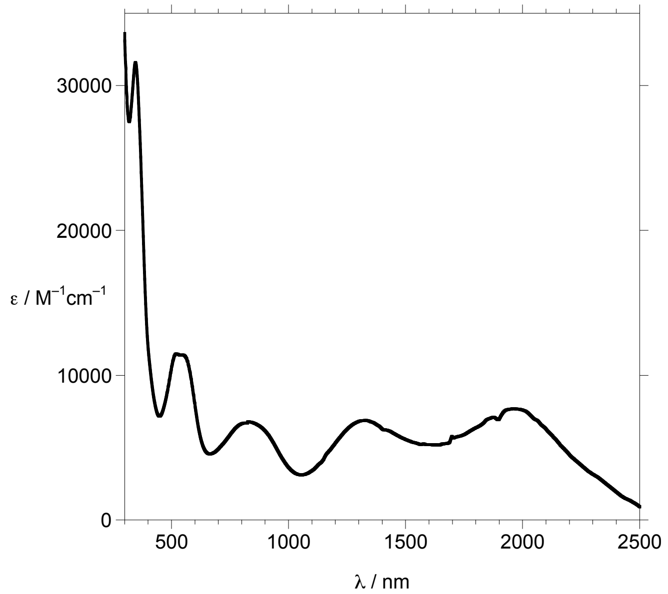


Fig. 3 UV-Vis-NIR spectrum of (MeClamp)Ti in CH_2Cl_2.

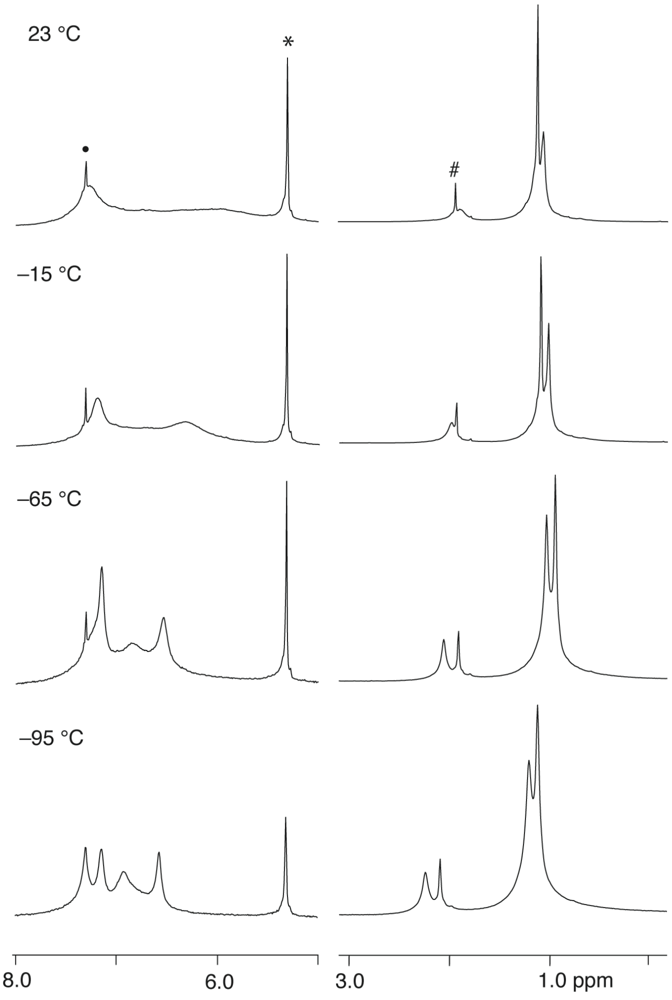


Fig. 4 ^1H NMR spectra of (MeClamp)Ti (CD_2Cl_2, 500 MHz). The solvent residual $CHDCl_2$ peak is marked with *; traces of C_6H_6 (•) and CH_3CN (#) are also discernible.

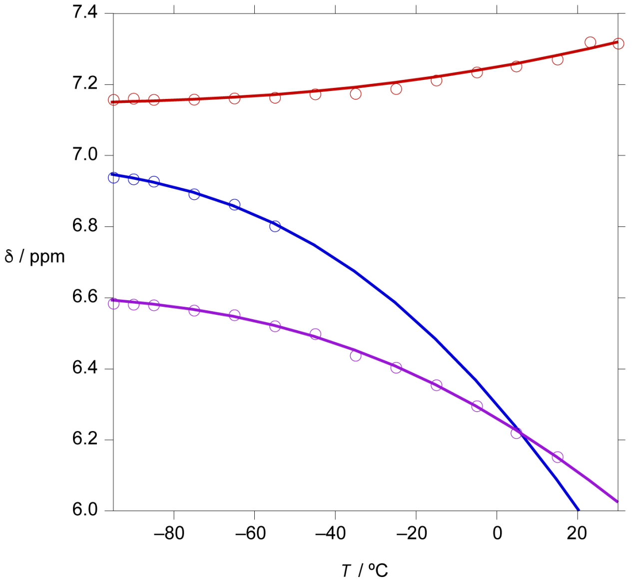


Fig. 5 Temperature-dependence of the ^1H NMR chemical shifts of the aromatic resonances of (MeClamp)Ti (CD_2Cl_2). Solid lines represent the best fit to eq 1a.

Broadening of NMR spectra has been observed in other complexes with redox-active ligands due to traces of one-electron oxidized material which is in rapid exchange with the neutral, diamagnetic species.[7,36,37] Partial oxidation does not appear to be the explanation for the behavior of (MeClamp)Ti. Its NMR spectrum is reproducible from sample to sample, and is unaffected by addition of a reducing agent such as decamethylferrocene (which causes spectra to sharpen in case of adventitious oxidation). Furthermore, the peaks of paramagnetic species become increasingly shifted as the temperature is lowered, while those of (MeClamp)Ti shift toward their diamagnetic values.

Instead, the pattern of nonlinearly increasing chemical shift with temperature is most consistent with a singlet-triplet equilibrium. Such a situation was studied by Cotton and coworkers in metal-metal quadruply bonded dimers[9,10] and has been subsequently observed in other chemical contexts,[38-41] including in complexes containing redox-active ligands.[8,42,43] The temperature dependence of the chemical shifts (Fig. 5) is well described by the model of a thermally populated triplet, with a measured singlet-triplet gap of 1200 ± 70 cm^{-1}.

Electronic Structure of (MeClamp)Ti

A qualitative starting point for understanding the electronic structure of (MeClamp)Ti is that of (MeClamp)Mo, which has been described in detail.[7] The three ligand orbitals that are important are the high-lying ligand redox-active orbitals (the HOMOs of the fully reduced amidophenolates, corresponding to the B_1-symmetry combination of heteroatom lone pair orbitals in catecholates[44]). The E-symmetry combinations of these ligand π orbitals (in C_3 symmetry) interact strongly with two of the metal $d\pi$ orbitals (essentially d_{xy} and $d_{x^2-y^2}$), while the A-symmetry combination is roughly nonbonding because of its poor overlap with the d_{z^2} orbital.

There are three critical differences in the bonding of (MeClamp)Ti that distinguish it from (MeClamp)Mo. First, the titanium compound is pseudo-octahedral and lacks the M-N10 interaction present in (MeClamp)Mo, removing the σ* character from the d_{z^2} orbital in (MeClamp)Ti and lowering its energy. Second, titanium(IV) is substantially more electropositive than molybdenum(VI),[45,46] which increases the separation of the metal and ligand orbitals. The increase in the energy gap between metal and ligand orbitals, in concert with the lesser spatial extension of the 3*d* orbitals of Ti, is expected to significantly decrease the extent of ligand-to-metal π bonding in the titanium complex. Experimentally, the structural effect of π bonding is more modest in the bis(amidophenolate)titanium(IV) complex *cis*-$({}^tBuNC_6H_2{}^tBu_2O)_2Ti(THF)_2$ (MOS = –1.88(7)[27]) than in the bis(amidophenolate)molybdenum(VI) complex *cis*,α-$({}^tBuClip)Mo(O^iPr)_2$ (MOS = –1.50(10)[47]).

Third, and most importantly, (MeClamp)Ti has two fewer electrons than (MeClamp)Mo. In the molybdenum complex, the principally ligand-based orbitals are completely filled, there is a sizable energy gap between them and the principally metal-based orbitals, and single-determinant methods suffice to give a reasonable representation of the molecule's electronic structure. In contrast, (MeClamp)Ti is anticipated to have four electrons among the three delocalized ligand-centered orbitals. While there should be an appreciable stabilization of the two metal-ligand π bonding combinations relative to the ligand-localized π_{nb} orbital, for the reasons discussed above this gap will be smaller than the 7600 cm^{-1} gap observed in (MeClamp)Mo.[7] Other systems with partially occupied ligand π levels, even in the presence of significant splitting, have appreciable multireference character.[48–51]

Figure 6 shows the RAS-CI natural orbitals of the ground state of (MeClamp)Ti, constrained to C_3 symmetry, and their occupation numbers. The RAS-CI calculation shows considerable multireference character in the ground singlet state, with the major configurations being $(e)^4(a)^0(e^*)^0$ (36%) and $(e)^2(a)^2(e^*)^0$ (12%). There is a clear predominance of occupation of the ligand-centered π bonding orbitals, but there is also a significant contribution of configurations with the π-nonbonding orbital populated as well. The population of the metal-centered *A*-symmetry orbital (essentially d_{z^2}) is negligible despite its low energy, presumably because it contains so little ligand character that it does not couple well to the ligand-centered *E*-symmetry orbitals that have the majority of the electron density.

Symmetry Breaking in (MeClamp)Ti

The spatial symmetry of the (multiconfigurational) ground state of C_3-symmetric (Clamp)Ti is *A*, so the compound is not susceptible to (first-order) Jahn-Teller distortion. However, distortion along an *E* vibrational coordinate that shortens one Ti-ligand distance at the expense of the other two allows the *A*-symmetry ligand-centered orbital to mix with the ligand-centered *E*-symmetry orbitals and, given partial occupancy of the three orbitals, can lead to net stabilization of the complex. Such second-order Jahn-Teller distortions have been shown to be strongly stabilizing in certain 4π-electron organic diradicals such as cyclopentadienyl cation,[52,53] though these systems differ significantly from (Clamp)Ti in that the *A*-symmetry MO in the organic systems is invariably lower in energy than the *E* combination.[54] In the present system, both Kohn-Sham and correlated calculations predict that the C_3 geometry of Ti(Clamp) is unstable relative to a C_1 structure with one short and two longer sets of ligand-metal bonds (Figs. S2-S3). However, the energetic driving force for distortion is small, 0.04 eV in a RAS-CI calculation with a 6-31G* basis set and 0.14 eV in a NEVPT2 calculation with a SVP basis set.

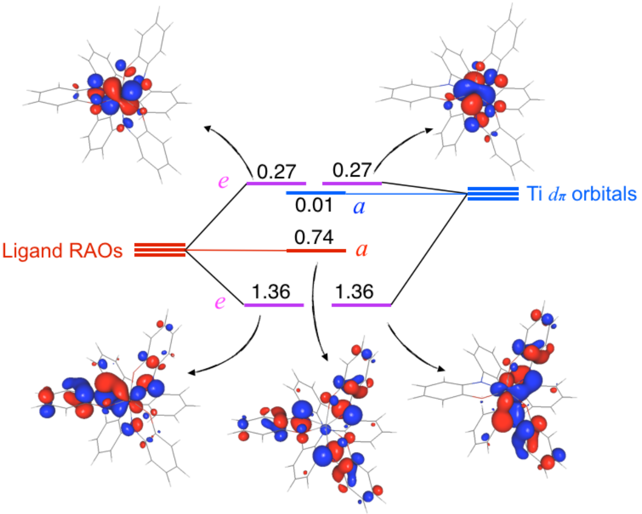


Fig. 6 Shape, symmetry, and occupation number of RAS-CI natural orbitals of ground-state singlet (Clamp)Ti, constrained to a C_3-symmetric geometry.

Geometrically, the distortion results in a 0.06 Å shortening of the Ti–N bonds to one ligand and a 0.02-0.04 Å lengthening of the other two, with a similar pattern in the Ti–O bonds, though the changes are smaller in magnitude (Table 3). The calculated MOS values behave accordingly, with two becoming more positive by 0.1 units and the third becoming more negative by 0.2 units. The calculated C_1-symmetric structure is in reasonable agreement with the solid-state structure of (MeClamp)Ti, though the calculated distortions are more uniform than those observed in the solid, possibly due to crystal packing effects. Significantly, even in the calculated C_1-symmetric structure, the redox states of the ligands are not fully localized, with the iminosemiquinone-like ligands in particular showing MOS values that are two standard deviations away from –1.00.

In the triplet state of (Clamp)Ti, the lowest-energy configuration of the C_3-symmetric compound would be expected to be $(e)^3(a)^1$, which would be unstable to a first-order Jahn-Teller distortion. Indeed, calculations on triplet (Clamp)Ti confirm an unsymmetrical minimum-energy geometry. Both the metal-ligand distances and the calculated MOS values (Table 3) indicate that the triplet is more localized than the singlet, with greater distortion from C_3 symmetry. The MOS values are consistent with an essentially localized

Table 3. Calculated structural features of Ti complexes.

Complex	Level of theory	Ti–O, Å	Ti–N, Å	MOS
Singlet (Clamp)Ti, C_3	B3LYP/TZVP	1.922	2.176	–1.29(9)
Singlet (Clamp)Ti, C_1	B3LYP/TZVP			
Ring 1		1.948	2.198	–1.18(9)
Ring 2		1.932	2.213	–1.18(9)
Ring 3		1.889	2.116	–1.53(9)
Triplet (Clamp)Ti, C_1	B3LYP/TZVP			
Ring 1		1.964	2.224	–1.12(11)
Ring 2		1.938	2.252	–1.11(10)
Ring 3		1.863	2.078	–1.73(9)
Singlet $(cat)_3Ti$, C_2	B3LYP/6-31G*			
Rings 1 and 2		2.018 2.060	n/a	–1.04(6)
Ring 3		1.878	n/a	–1.82(8)
Singlet *fac*-$(ap)_3Ti$, C_1	B3LYP/6-31G*			
Ring 1		1.986	2.103	–1.02(9)
Ring 2		1.960	2.098	–1.09(9)
Ring 3		1.914	2.040	–1.40(9)
Singlet $(bd)_3Ti$, D_3	B3LYP/6-31G*	n/a	2.058	n/a

geometry, and the spin density of the triplet (Clamp)Ti (Fig. 7) indicates that the spins are indeed essentially localized on the two ligands with longer metal-ligand bonds and MOS values close to –1 (that is, the two iminosemiquinone ligands). The triplet still has considerable multireference character, with major configurations in the RAS-CI calculation of $(e_1)^1(e_2)^1(a)^1(e_1^*)^1(e_2^*)^0$ (36%) and $(e_1)^1(e_2)^2(a)^1(e_1^*)^0(e_2^*)^0$ (24%). The calculated singlet-triplet gap is 320 cm^{-1} in relaxed RAS-CI (480 cm^{-1} in unrelaxed RAS-CI) and 1100 cm^{-1} in NEVPT2, in good agreement with the experimental value of 1200(70) cm^{-1}.

In order to clarify the features that favor localization or delocalization, we considered computationally the octahedral tris(ligand) complexes with O,O (catecholate, cat), N,O (amidophenolate, ap), and N,N (benzenediamide, bd) donors (Table 3). The lowest-energy structures of the catecholate and amidophenolate ligands are both unsymmetrical. The catecholate structure is appreciably less symmetrical than the amidophenolate, as judged both by the differences in MOS values and the differences in Ti–O distances. The minimum-energy structure of the benzenediamide complex is C_3-symmetric. There is thus a clear trend that the degree of asymmetry in the complexes decreases as oxygen donors are replaced by nitrogen donors in the ligands.

This trend is consistent with the limited experimental data available for early metal tris-ligand complexes. No neutral titanium tris(dioxolene) complexes have been characterized experimentally. The tris(iminoxolene) (MeClamp)Ti described here is unsymmetrical in the solid state, while a tris(bis(arylimino)acenaphthylene)titanium complex $Ti(C_{12}H_6[NAr]_2)_3$ has a symmetrical structure,[28] as does the isoelectronic vanadium cation.[5] While the neutral vanadium compounds are not strictly comparable, having one more electron, the available data are informative as well. The tris(dioxolene) complex $V(3,6\text{-}^t Bu_2C_6H_2O_2)_3$ is essentially localized in the solid state, with MOS values of –1.05(7) for the crystallographically unique (semiquinonate) ligand and –1.61(4) each for the other two crystallographically equivalent (catecholate) ligands.[23] Further evidence for the propensity of this compound to adopt a localized electronic structure is provided by the room-temperature solution EPR spectrum, which shows hyperfine coupling to only a single dioxolene ligand.[6] The neutral tris(iminoxolene)vanadium complex, $V(OC_6H_2\text{-}4,6\text{-}^t Bu_2\text{-}2\text{-}NPh)_3$, has been prepared and characterized.[55] Since this compound is observed as the meridional isomer, it cannot strictly speaking exhibit any symmetry. Nevertheless, the very similar MOS values exhibited by the three ligands (–1.17(10), –1.26(7), and –1.33(6), with a total span of only 0.16 units) suggest a considerable delocalization of the electronic structure, certainly more than is exhibited in the experimental structure of (MeClamp)Ti (span of MOS values of 0.68 units) or calculated (Clamp)Ti (0.35 span of MOS) or *fac*-$(ap)_3Ti$ (0.38 span of MOS). The fully nitrogen-ligated $V(C_{12}H_6[NAr]_2)_3$ is again completely symmetrical in the solid state.[5]

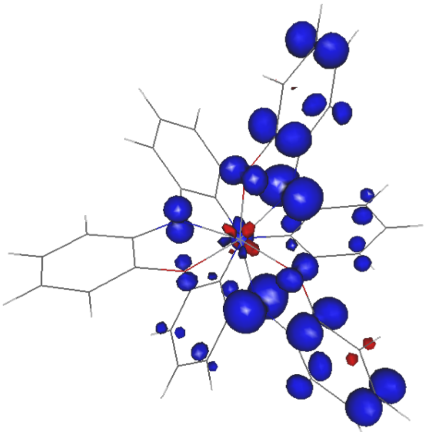


Fig. 7 Calculated spin density of triplet (Clamp)Ti.

A second-order Jahn-Teller distortion is expected to be more favorable the smaller the energy difference between the lower-lying ligand-centered E orbitals and the higher-lying, less highly occupied, A orbital. This correlation is observed in the calculations on $(cat)_3Ti$, *fac*-$(ap)_3Ti$, and $(bd)_3Ti$, where in the structures constained to C_3 symmetry, the Kohn-Sham HOMO-LUMO gaps are 0.84 eV, 1.25 eV, and 1.55 eV, respectively. Since the HOMO levels are metal-ligand π bonding in character while the LUMO orbitals are essentially nonbonding, the energy differences must be due to increasing π interaction in the nitrogen donor ligands compared to oxygen donor ligands. For early transition metals such as titanium and vanadium, the ligand levels are lower in energy than the metal orbitals, so decreasing the electronegativity of the donor atom improves the energy match between metal and ligand and hence increases the strength of the π interaction. The greater ability of amidophenolates compared to catecholates to donate to early transition metals has been documented.[23] Vanadium, because of its greater electronegativity and hence better orbital energy match with the ligands compared to titanium, is expected to have stronger π interactions than titanium. This difference in π bonding may in part explain the apparently higher propensity of the tris(iminoxolenes) of vanadium to adopt a delocalized structure, though the additional electron present in the vanadium complex, which would be expected to decrease the favorability of second-order Jahn-Teller distortion due to the greater occupancy of the *A*-symmetry orbital, may also play a role.

Conclusions

The air- and moisture-stable neutral tris(iminoxolene) (MeClamp)Ti contains titanium(IV) and mixed oxidation states of the iminoxolenes. The compound is diamagnetic, but NMR studies indicate that the triplet state is only 1200 cm^{-1} higher in energy than the singlet ground state. Crystallographic and computational studies show that the compound is unsymmetrical, with a structure intermediate between the fully localized (two iminosemiquinones and one amidophenolate) and the fully delocalized (three ligands with oxidation states of –1.33) limits. The distortion from C_3 symmetry can be explained as a second-order Jahn-Teller effect caused by mixing of the nominally filled *E*-symmetry iminoxolene-titanium π bonding orbitals with the nominally empty *A*-symmetry iminoxolene-localized π nonbonding orbitals. The driving force force for distortion is inversely related to the strength of π bonding, with stronger π donor ligands (such as diamidobenzenes) fostering a symmetrical structure and weaker π donor ligands (such as catecholates) fostering a localized structure. The amidophenolates in the MeClamp ligand are intermediate in their π donor ability, so (MeClamp)Ti sits on the border between a localized and a delocalized structure.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references

1 P. J. Chirik, *Inorg. Chem.*, 2011, **50**, 9737–9740.
2 M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, 1968, **10**, 247–422.
3 K. D. Demadis, C. M. Hartshorn and T. J. Meyer, *Chem. Rev.*,

2 M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, 1968, **10**, 247–422.
3 K. D. Demadis, C. M. Hartshorn and T. J. Meyer, *Chem. Rev.*, 2001, **101**, 2655–2685.

4 R. F. Munhá, R. A. Zarkesh and A. F. Heyduk, *Dalton Trans.*, 2013, **42**, 3751-3766.
5 J. Bendix and K. M. Clark, *Angew. Chem. Int. Ed.*, 2016, **55**, 2748–2752.
6 A. M. Morris, C. G. Pierpont and R. G. Finke, *Inorg. Chem.*, 2009, **48**, 3496–3498.
7 T. Marshall-Roth and S. N. Brown, *Dalton Trans.*, 2015, **44**, 677–685.
8 K. M. Conner, A. L. Perugini, M. Malabute and S. N. Brown, *Inorg. Chem.*, 2018, **57**, 3272–3286.
9 F. A. Cotton, J. L. Eglin, B. Hong and C. A. James, *Inorg. Chem.*, 1993, **32**, 2104–2106.
10 F. A. Cotton, J. Su, Z. S. Sun and H. Chen, *Inorg. Chem.*, 1993, **32**, 4871–4875.
11 D. C. Harris, *J. Chem. Educ.*, 1998, **75**, 119–121.
12 R. de Levie, *J. Chem. Educ.*, 1999, **76**, 1594–1598.
13 N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877–910.
14 D. Lionetti, A. J. Medvecz, V. Ugrinova, M. Quiroz-Guzman, B. C. Noll and S. N. Brown, *Inorg. Chem.*, 2010, **49**, 4687–4697.
15 P. M. Zimmerman, F. Bell, M. Goldey, A. T. Bell and M. Head-Gordon, *J. Chem. Phys.*, 2012, **137**, 164110-164121.
16 C. Angeli, R. Cimiraglia, S. Evangelisti, T. Leininger and J.-P. Malrieu, *J. Chem. Phys.*, 2001, **114**, 10252–10264.
17 Y. Shao, Z. Gan, E. Epifanovsky, A. T. B. Gilbert, M. Wormit, J. Kussmann, A. W. Lange, A. Behn, J. Deng, X. Feng, D. Ghosh, M. Goldey, P. R. Horn, L. D. Jacobson, I. Kaliman, R. Z. Khaliullin, T. Kuś, A. Landau, J. Liu, E. I. Proynov, Y. M. Rhee, R. M. Richard, M. A. Rohrdanz, R. P. Steele, E. J. Sundstrom, H. L. Woodcock, P. M. Zimmerman, D. Zuev, B. Albrecht, E. Alguire, B. Austin, G. J. O. Beran, Y. A. Bernard, E. Berquist, K. Brandhorst, K. B. Bravaya, S. T. Brown, D. Casanova, C.-M. Chang, Y. Chen, S. H. Chien, K. D. Closser, D. L. Crittenden, M. Diedenhofen, R. A. DiStasio, H. Do, A. D. Dutoi, R. G. Edgar, S. Fatehi, L. Fusti-Molnar, A. Ghysels, A. Golubeva-Zadorozhnaya, J. Gomes, M. W. D. Hanson-Heine, P. H. P. Harbach, A. W. Hauser, E. G. Hohenstein, Z. C. Holden, T.-C. Jagau, H. Ji, B. Kaduk, K. Khistyaev, J. Kim, J. Kim, R. A. King, P. Klunzinger, D. Kosenkov, T. Kowalczyk, C. M. Krauter, K. U. Lao, A. D. Laurent, K. V. Lawler, S. V. Levchenko, C. Y. Lin, F. Liu, E. Livshits, R. C. Lochan, A. Luenser, P. Manohar, S. F. Manzer, S.-P. Mao, N. Mardirossian, A. V. Marenich, S. A. Maurer, N. J. Mayhall, E. Neuscamman, C. M. Oana, R. Olivares-Amaya, D. P. O'Neill, J. A. Parkhill, T. M. Perrine, R. Peverati, A. Prociuk, D. R. Rehn, E. Rosta, N. J. Russ, S. M. Sharada, S. Sharma, D. W. Small, A. Sodt, T. Stein, D. Stück, Y.-C. Su, A. J. W. Thom, T. Tsuchimochi, V. Vanovschi, L. Vogt, O. Vydrov, T. Wang, M. A. Watson, J. Wenzel, A. White, C. F. Williams, J. Yang, S. Yeganeh, S. R. Yost, Z.-Q. You, I. Y. Zhang, X. Zhang, Y. Zhao, B. R. Brooks, G. K. L. Chan, D. M. Chipman, C. J. Cramer, W. A. Goddard, M. S. Gordon, W. J. Hehre, A. Klamt, H. F. Schaefer, M. W. Schmidt, C. D. Sherrill, D. G. Truhlar, A. Warshel, X. Xu, A. Aspuru-Guzik, R. Baer, A. T. Bell, N. A. Besley, J.-D. Chai, A. Dreuw, B. D. Dunietz, T. R. Furlani, S. R. Gwaltney, C.-P. Hsu, Y. Jung, J. Kong, D. S. Lambrecht, W. Liang, C. Ochsenfeld, V. A. Rassolov, L. V. Slipchenko, J. E. Subotnik, T. Van Voorhis, J. M. Herbert, A. I. Krylov, P. M. W. Gill and M. Head-Gordon, *Mol. Phys.*, 2015, **113**, 184–215.
18 T. Shiozaki and S. Hirata, *J. Chem. Phys.*, 2010, **132**, 151101–151105.
19 G. M. Sheldrick, *Acta Crystallogr. A*, 2008, **64**, 112–122.

20 A. J. C. Wilson, *International Tables for Crystallography*, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1992, vol. C.

21 S. Pritchett, D. H. Woodmansee, P. Gantzel and P. J. Walsh, *J. Am. Chem. Soc.*, 1998, **120**, 6423–6424.

22 A. N. Erickson and S. N. Brown, *Dalton Trans.*, 2018, **47**, 15583-15595.

23 S. N. Brown, *Inorg. Chem.*, 2012, **51**, 1251–1260.

24 P. H. Bird, A. R. Fraser and C. F. Lau, *Inorg. Chem.*, 1973, **12**, 1322–1328.

25 K. C. Fortner, J. P. Bigi and S. N. Brown, *Inorg. Chem.*, 2005, **44**, 2803–2814.

26 T. Schroeder, V. Ugrinova, B. C. Noll and S. N. Brown, *Dalton Trans*, 2006, 1030–1040.

27 K. J. Blackmore, M. B. Sly, M. R. Haneline, J. W. Ziller and A. F. Heyduk, *Inorg. Chem.*, 2008, **47**, 10522–10532.

28 K. M. Clark, J. Bendix, A. F. Heyduk and J. W. Ziller, *Inorg. Chem.*, 2012, **51**, 7457–7459.

29 L. T. Dulatas, S. N. Brown, E. Ojomo, B. C. Noll, M. J. Cavo, P. B. Holt and M. M. Wopperer, *Inorg. Chem.*, 2009, **48**, 10789–10799.

30 C. Mukherjee, T. Weyhermüller, E. Bothe and P. Chaudhuri, *Inorg. Chem.*, 2008, **47**, 11620–11632.

31 S. Kokatam, T. Weyhermüller, E. Bothe, P. Chaudhuri and K. Wieghardt, *Inorg. Chem.*, 2005, **44**, 3709–3717.

32 X. Sun, H. Chun, K. Hildenbrand, E. Bothe, T. Weyhermüller, F. Neese and K. Wieghardt, *Inorg. Chem.*, 2002, **41**, 4295–4303.

33 P. Chaudhuri, C. N. Verani, E. Bill, E. Bothe, T. Weyhermüller and K. Wieghardt, *J. Am. Chem. Soc.*, 2001, **123**, 2213–2223.

34 S. Amthor, B. Noller and C. Lambert, *Chem. Phys.*, 2005, **316**, 141–152.

35 M. Quiroz-Guzman and S. N. Brown, *Acta Crystallogr. C*, 2010, **66**, m171–m173.

36 M. Quiroz-Guzman, A. G. Oliver, A. J. Loza and S. N. Brown, *Dalton Trans.*, 2011, **40**, 11458–11468.

37 S. Wanniarachchi, B. J. Liddle, B. Kizer, J. S. Hewage, S. V. Lindeman and J. R. Gardinier, *Inorg. Chem.*, 2012, **51**, 10572–10580.

38 C. E. Kriley, P. E. Fanwick and I. P. Rothwell, *J. Am. Chem. Soc.*, 1994, **116**, 5225–5232.

39 R. L. Miller, K. A. Lawler, J. L. Bennett and P. T. Wolczanski, *Inorg. Chem.*, 1996, **35**, 3242–3253.

40 S. Pfirrmann, C. Limberg, C. Herwig, C. Knispel, B. Braun, E. Bill and R. Stösser, *J. Am. Chem. Soc.*, 2010, **132**, 13684–13691.

41 J. Rittle, C. C. L. McCrory and J. C. Peters, *J. Am. Chem. Soc.*, 2014, **136**, 13853–13862.

42 B. Le Guennic, T. Floyd, B. R. Galan, J. Autschbach and J. B. Keister, *Inorg. Chem.*, 2009, **48**, 5504–5511.

43 T. J. Steiman and C. Uyeda, *J. Am. Chem. Soc.*, 2015, **137**, 6104–6110.

44 D. J. Gordon and R. F. Fenske, *Inorg. Chem.*, 1982, **21**, 2907–2915.

45 R. T. Sanderson, *Inorg. Chem.*, 1986, **25**, 3518–3522.

46 R. T. Sanderson, *J. Chem. Educ.*, 1988, **65**, 112–118.

47 J. A. Kopec, S. Shekar and S. N. Brown, *Inorg. Chem.*, 2012, **51**, 1239–1250.

48 D. Herebian, K. E. Wieghardt and F. Neese, *J. Am. Chem. Soc.*, 2003, **125**, 10997–11005.

49 K. Ray, T. Weyhermüller, F. Neese and K. Wieghardt, *Inorg. Chem.*, 2005, **44**, 5345–5360.

50 H. Fukui, R. Kishi, T. Minami, H. Nagai, H. Takahashi, T. Kubo, K. Kamada, K. Ohta, B. Champagne, E. Botek and M. Nakano, *J. Phys. Chem. A*, 2008, **112**, 8423–8429.

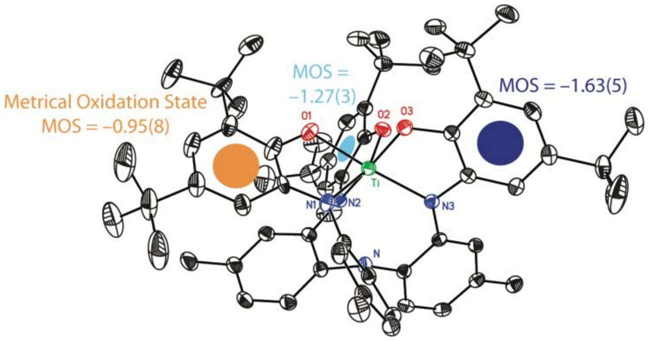
51 F. Alary, J.-L. Heully, A. Scemama, B. Garreau-de Bonneval, K. I. Chane-Ching and M. Caffarel, *Theor. Chem. Acc.*, 2010, **126**, 243–255.

52 E. R. Davidson and W. T. Borden, *J. Chem. Phys.*, 1977, **67**, 2191–2195.

53 W. T. Borden and E. R. Davidson, *J. Am. Chem. Soc.*, 1979, **101**, 3771–3775.

54 W. T. Borden and E. R. Davidson, *Acc. Chem. Res.*, 1981, **14**, 69–76.

55 H. Chun, C. N. Verani, P. Chaudhuri, E. Bothe, E. Bill, T. Weyhermüller and K. Wieghardt, *Inorg. Chem.*, 2001, **40**, 4157–4166.



An air-stable tris(iminoxolene)titanium(IV) complex is a ground state singlet best described as intermediate between fully localized and fully delocalized.