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A 'Direct' Relationship between E=Ti–L Bond Angle and Ti=E Bond Length can exist in $[\mathrm{Ti(E)L_4}]$ Complexes (E = Organoimido or Oxo)

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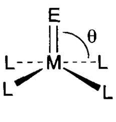
Evidence for a 'direct' relationship between E=Ti–L bond angle and Ti=E bond length in five-coordinate complexes $[\mathrm{Ti(E)L_4}]$ (E = organoimido or oxo) is presented and is supported by extended-Hückel molecular orbital calculations; the crystal structure of $[\mathrm{Ti(tmtaa)(NC_6H_3Me_2\text{-}2,6)}]$ is described ($\mathrm{H_2tmtaa}$ = tetramethyldibenzotetraaza[14]annulene).

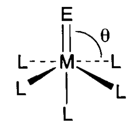
Complexes containing one or more transition metal–ligand multiple bonds have arguably been a focus of sustained activity for the last 15 years. Such complexes may be relevant to industrial processes, organic transformations and catalysis and substantial effort has been spent in exploring their structure, reactivity and bonding.[1–3] Two of the simplest structural types are based on the square-based pyramid $[\mathrm{M(E)L_4}]$ **I** and the corresponding pseudooctahedral arrangement $[\mathrm{M(E)L_5}]$ **II** (where E is a multiply bonded ligand such as organoimido, oxo, sulfido or nitrido, and L is predominantly σ donor in character).†

The E=M–L_{cis} angle (θ) in such complexes almost invariably exceeds 90°.[2] While this may reflect, in part, steric repulsion between the multiply bonded ligand and those *cis* to it,[4] it has been established from approximate density functional calculations[5] and other theoretical studies[6] that such angular 'distortions' are predominantly electronic in origin and may be traced to a rehybridisation of metal π orbitals giving enhanced multiple bonding. Angular distortions (*i.e.* increases in θ) in complexes $[\mathrm{M(E)L_4}]$ and $[\mathrm{M(E)L_5}]$ have thus far been considered to be 'inverse' in nature; *i.e.* an *increase* in θ is driven by an increase in multiple bond strength and a subsequent *decrease* in metal–ligand multiple bond length. A similar 'inverse' relationship has recently been recognised for metal–metal quadruply bonded complexes in which larger M–M–L angles are associated with shorter metal–metal bonds,[7] and has long been known in carbon chemistry.[8] However, in carbon chemistry a 'turnover point' may be reached at high angular distortions so that the relationship between distortion angle and carbon–element single bond length enters a 'direct' region where *increased* angles leads to an *increased* bond length.[8] We show here how five-coordinate transition metal–ligand multiply bonded complexes $[\mathrm{M(E)L_4}]$ may be forced into a 'direct' region at relatively modest θ values through the appropriate choice of ancilliary ligand set, $\mathrm{L_4}$.

In the course of our studies of imido titanium chemistry we structurally characterised the tetraazamacrocycle-supported *tert*-butyl imido derivative $[\mathrm{Ti(omtaa)(NBu^t)}]$ **1** ($\mathrm{H_2omtaa}$ = octamethyldibenzotetraaza[14]annulene).[9] This complex has the longest reported $\mathrm{Ti{=}NBu^t}$ bond length [1.724(4) Å] and an unusually large average $\mathrm{N{=}Ti{-}N_{macrocycle}}$ bond angle (111.3°). Other square-based pyramidal complexes have considerably shorter $\mathrm{Ti{=}NBu^t}$ bond lengths and smaller average N=Ti–L angles: $[\mathrm{Ti(NBu^t)Cl_2(tmen)}]$ [$\mathrm{Ti{=}NBu^t}$ 1.662(4) Å, av. N=Ti–L 103.5°],[10] $[\mathrm{Ti_2(NBu^t)_2(\mu\text{-}O_2P\{OR\}_2)_4}]$ [$\mathrm{Ti{=}NBu^t}$ 1.667(5) Å, av. N=Ti–L 107.1°],[11] $[\mathrm{Ti(NBu^t)Cl_2(dipeda)}]$ [dipeda = *N,N′*-diisopropylethylenediamine; $\mathrm{Ti{=}NBu^t}$ 1.681(7) Å, av. N=Ti–L 101.7°],[10] $[\mathrm{Ti(NBu^t)Cl_2(OPPh_3)_2}]$ [$\mathrm{Ti{=}NBu^t}$ 1.672(7) Å, av. N=Ti–L 105.4°].[12] The longer $\mathrm{Ti{=}NBu^t}$ bond length and large average $\mathrm{N{=}Ti{-}N_{macrocycle}}$ angle in **1** possibly suggest a 'direct' relationship between these two parameters. There is no clear correlation, however, among these latter four complexes between $\mathrm{Ti{=}NBu^t}$ bond length and N=Ti–L bond angle, but in these species steric factors vary significantly, as does the donor ability of the basal ligands.



I



II

We sought firmer structural evidence for a 'direct' bond angle/bond length relationship for imido titanium complexes where the ancilliary ligand set varies by a smaller extent. Woo and coworkers have recently described the crystal structure of the ttp ($\mathrm{H_2ttp}$: tetratolylporphyrin) arylimido derivative $[\mathrm{Ti(ttp)(NPh)}]$ [Ti=NPh 1.703(2) Å, average $\mathrm{N{=}Ti{-}N_{macrocycle}}$ 104.3°].[13] Because it may not be appropriate to compare the Ti=NPh bond length in $[\mathrm{Ti(ttp)(NPh)}]$ with the $\mathrm{Ti{=}NBu^t}$ bond length in $[\mathrm{Ti(omtaa)(NBu^t)}]$ **1** owing to the different electronic influence of N-aryl and N-*tert*-butyl organic substituents, we determined the crystal structure of the 2,6-dimethylphenyl imido analogue of **1**, namely $[\mathrm{Ti(tmtaa)(NC_6H_3Me_2\text{-}2,6)}]$ **2** (Fig. 1; $\mathrm{H_2tmtaa}$ = tetramethyldibenzotetraaza[14]annulene).‡ The average $\mathrm{N{=}Ti{-}N_{macrocycle}}$ bond angle (111.3°) and Ti=N bond length [Ti(1)–N(5) 1.720(4) Å] in **2** are both significantly larger than the corresponding values for $[\mathrm{Ti(ttp)(NPh)}]$ and point to a 'direct' relationship between Ti=N bond length and $\mathrm{N{=}Ti{-}N_{macrocycle}}$ bond angle.

To see if a 'direct' relationship between Ti=N bond length and $\mathrm{N{=}Ti{-}N_{macrocycle}}$ bond angle would be predicted by molecular orbital theory we carried out a number of extended-Hückel[14,15] calculations on simple model complexes $[\mathrm{Ti(E)L_4}]^{2-}$ where E is either NH or O and L is a σ-only, one-electron ligand.§ Fig. 2 shows a plot of computed net Ti–N overlap population and total energy (sum of one-electron energies) *vs.* N=Ti–L angle θ over the range $90 \leqslant \theta \leqslant 120°$ for the model complex $[\mathrm{Ti(NH)L_4}]^{2-}$. Between the geometries labelled **A** and **B** the net Ti–N overlap population *increases* with increasing N=Ti–L bond angle. This means that in a real complex, the Ti=N bond should shorten and so **A** $\longrightarrow$ **B**

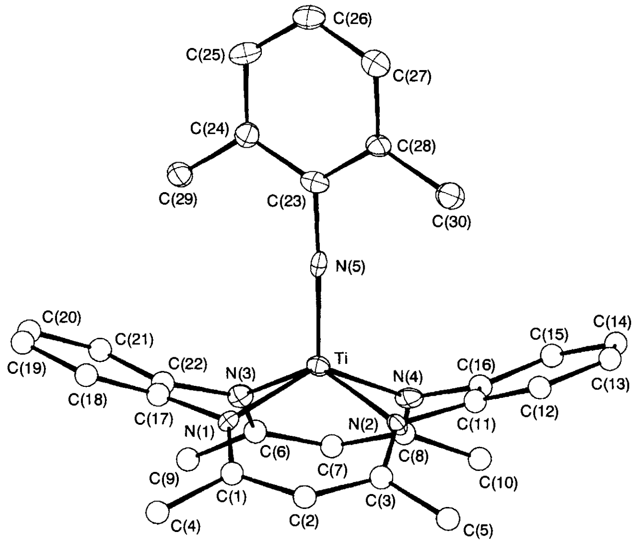


Fig. 1 Molecular structure of $[\mathrm{Ti(tmtaa)(NC_6H_3Me_2\text{-}2,6)}]$ **2**. Hydrogen atoms and $\mathrm{H_2NC_6H_3Me_2\text{-}2,6}$ molecule of crystallisation omitted for clarity. Selected distances (Å) and angles (°): Ti–N(5) 1.720(4), Ti–N(1) 2.064(4), Ti–N(2) 2.060(4), Ti–N(3) 2.084(4), Ti–N(4) 2.078(4), $\mathrm{Ti\cdots N_4}$(least squares plane) 0.75, C(27)–N(5)–Ti 175.4(4), N(5)–Ti–N(1) 109.7(2), N(5)–Ti–N(2) 109.9(2), N(5)–Ti–N(3) 113.0(2), N(5)–Ti–N(4) 112.4(2).

represents the usual 'inverse' region. From **B** → **C** the net Ti–N overlap population *decreases* with increasing θ. In a real complex the Ti=N bond length should lengthen, and hence this represents a 'direct' relationship between bond angle and bond length. The variations in net Ti–N overlap population may be traced predominantly to an enhancement, and a subsequent diminution, in π bonding as θ is gradually increased. Similar plots were obtained for model oxo complexes $[Ti(O)L_4]^{2-}$. It should be noted that the location of the minima and maxima in the curves shown in Fig. 2 can move by 2–3° in θ depending on the nature of L and the basis sets chosen. However, the key features remain the same and we can be confident of the existence of both an 'inverse' and a 'direct' region, with a turnover point (**B**) as shown in Fig. 2.

Additional support for our proposal of a 'direct' relationship between Ti=E bond length and E=Ti–L angle comes from a range of isolobal, crystallographically characterised macrocycle-supported oxotitanium complexes. For example, an oxo analogue of **1** and **2**, namely [Ti(tmtaa)(O)], has previously been structurally characterised and this also has an unusually long titanium–oxygen multiple bond [Ti=O 1.653(3) Å] and large average $O=Ti-N_{macrocycle}$ bond angle (111.6°).[16] This average $O=Ti-N_{macrocycle}$ angle is comparable to the average $N=Ti-N_{macrocycle}$ angles found in **1** and **2**. Table 1 lists Ti=O bond lengths and average O=Ti–N bond angles for [Ti(tmtaa)(O)] and three other different tetraazamacrocycle-supported oxotitanium complexes.[17–19] Fig. 3 shows a plot of average O=Ti–N angle *vs.* Ti=O bond length for all four complexes. In these four tetraazamacrocyclic complexes the steric and bonding requirements of the basal (macrocylic) ligand set remains essentially constant and the O=Ti–N angle is determined by the radius of the N_4 cavity. The Ti=O bond length therefore is 'tuned' by the O=Ti–N angle imposed by the {Ti(macrocycle)} fragment, and not *vice versa*. Fig. 3 shows that the Ti=O bond length increases with increasing average O=Ti–N bond angle for these complexes. Thus the bond angle/bond length relationship for the complexes listed in Table 1 is 'direct', rather than 'inverse' in nature.

We made a further numerical test of the 'direct' relationship between Ti=E bond length and the $E=Ti-N_{macrocycle}$ angle. We calculated net Ti–O overlap populations for *model* complexes $[Ti(O)L_4]^{2-}$ with *fixed* Ti=O bond lengths but using the *real* $O=Ti-N_{macrocycle}$ bond angles taken from the oxotitanium complexes listed in Table 1. A plot of the *computed* net Ti–O

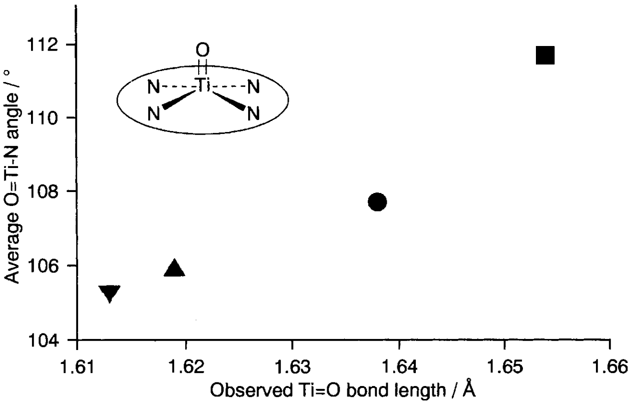


Fig. 3 Plot of average $O=Ti-N_{macrocycle}$ angle *versus* Ti=O bond length for [TiL(O)] where H_2L = octaethylporphyrin (▼), α,γ-dimethyl-α,γ-dihydrooctaethylporphyrin (▲), phthalocyanine (●) (data are an average of 2 independent structure determinations) or H_2tmtaa (■). See Table 1 for references.

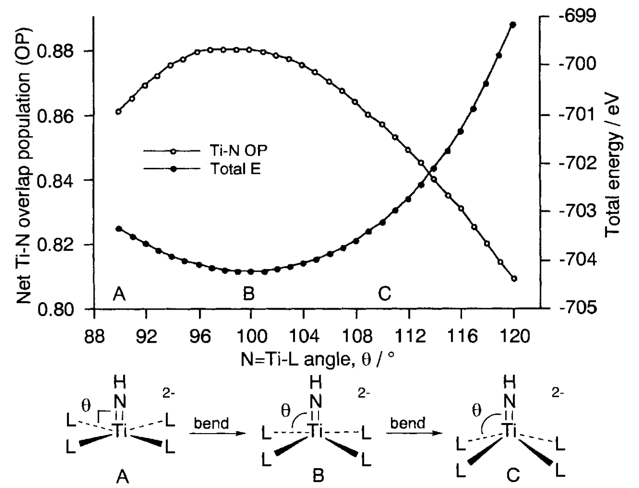


Fig. 2 Net Ti–N overlap population (OP) and total energy (sum of one-electron energies) *versus* θ for $[Ti(NH)L_4]^{2-}$

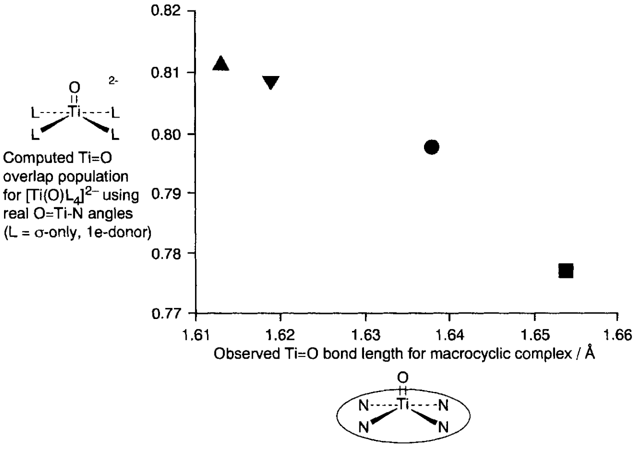


Fig. 4 Plot of computed net Ti–O overlap population for model complexes $[Ti(O)L_4]^{2-}$ with O=Ti–L angles taken from real tetraazamacrocycle-supported oxotitanium complexes *versus* the observed Ti=O bond length for the corresponding real complexes with labels as in Fig. 3

Table 1

Compound [TiL(O)], H_2L =	Ti=O/Å	Average[b] O=Ti–N/°	Ref.
Octaethylporphyrin (▼)	1.613(5)	105.2	19
α,γ-Dimethyl-α,γ-dihydrooctathylporphyrin (▲)	1.619(4)	105.9	18
Phthalocyanine[c] (●)	1.626(7)	107.8	17
	1.650(4)	107.6	17
H_2tmtaa (■)	1.653(3)	111.6	16

[a] The character in parentheses following the compound name corresponds to that used in Figs. 3 and 4. [b] The individual $O=Ti-N_{macrocycle}$ angles fall in the range: (▼) 104.2(2)–106.3(2)°; (▲) 105.05(7)–106.65(7)°; (●) 106.9(4)–108.8(4) and 106.3(2)–109.2(2)°; (■) 110.2(2)–113.5(2)°. [c] Two different crystal phases (triclinic and monoclinic) were found.[17] Although the Ti=O distances are slightly different, the average $O=Ti-N_{macrocycle}$ angle and average Ti–N distances [2.066(4) and 2.066(8) Å] are nearly identical. In Figs. 3 and 4 we use the average Ti=O bond length and average O=Ti–N bond angle for both structures.

overlap populations *versus* the *observed* Ti=O bond length in the real complexes is shown in Fig. 4. The lengthening of Ti=O bond correlates very well with decreasing Ti–O overlap population and is a very nice demonstration of the validity of our extended-Hückel calculations, serving to reveal the importance of θ in setting the Ti=O bond length.

In conclusion, we have shown for the first time that a 'direct' relationship can exist between metal–ligand multiple bond length and the angle subtended at the metal between the multiply bonded ligand and the ancilliary ligands. Further experimental and theoretical studies of **1**, **2** and related macrocycle-supported, early transition metal complexes are underway to probe further the consequences of this 'direct' relationship. For example, we note that there is significant effort currently being spent in designing so-called 'π loaded' complexes in which a single metal carries two or more multiply bonded ligands.[20] The desired effect is to labilise the M=N π bonding and give imido ligands with a greater negative charge on the nitrogen atoms in the hope of achieving greater reactivity. Our results suggest that design of the appropriate σ framework towards the 'direct' region of the bond length/bond angle relationship might also give the desired effect.

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Footnotes

† Although for ease of representation all titanium–imido and –oxo linkages are drawn Ti=E, the formal Ti–E bond order in complexes [Ti(E)L_n] described herein is best thought of as three (pseduo-σ^2 π^4; triple bond) rather than as two.[1]

‡ [Ti(tmtaa)($NC_6H_3Me_2$-2,6)] **2** was prepared from [Ti(tmtaa)(NBu^t)] and an excess of $H_2NC_6H_3Me_2$-2,6 in dichloromethane.[21] Layering of the mixture with hexane afforded orange–red crystals of **2**·$H_2NC_6H_3Me_2$-2,6 as shown by ^1H NMR spectroscopy. *Crystal data* for **2**·$H_2NC_6H_3Me_2$-2,6: M = 630.69, triclinic, space group $P\bar{1}$, a = 11.132(1), b = 11.822(16), c = 12.450(3) Å, α = 99.31(10), β = 91.87(2), γ = 92.58(2)°, U = 1613.8 Å^3, Z = 2, D_c = 1.298 g cm^{-3}, $F(000)$ = 668, T = 150 K. All crystallographic measurements were made using a FAST area detector diffractometer and Mo-Kα radiation, following previously described procedures.[22] The structure was solved by direct methods (SIR92) and 251 parameters were refined by full-matrix least squares (CRYSTALS 386) on F^2 for 4324 unique data to final conventional R values of 0.064 [$F_o > 4\sigma(F_o)$, 1287 observed data] and 0.146 (4324 unique data), and to R_w = 0.131 (Chebychev weighting scheme, 4324 unique data). Owing to the weakly diffracting nature of the crystal, only Ti, the four coordinated nitrogen atoms of the tmtaa ligand and the non-hydrogen atoms of the $NC_6H_3Me_2$-2,6 ligand were subject to anisotropic refinement. The other non-hydrogen atoms were refined in the isotropic approximation. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ Extended-Hückel calculations were performed using the CACAO program.[14,15] Atomic parameters for Ti, N, O and H were taken from the list contained within the program and gave satisfactory charges. The one-electron, pseudo-ligands L carry a single 1s orbital with $H_{ii} = -16.60$ eV and $\varsigma = 1.300$. Bond lengths used: Ti–L 1.70, Ti=N 1.70, Ti=O 1.65, N–H 1.0 Å.

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