

The Structure of Thallium(I) Tetraacetatohallate(III): When is the Lone Pair of Electrons on Tl^I Stereoactive?

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Abstract

Thallium(I) tetraacetatohallate(III), Tl[Tl(C₂H₃O₂)₄], C₈H₁₂O₈Tl⁺. Tl⁺, *M_r* = 2579, monoclinic, space group *P*2₁/*c*, *a* = 8.313 (2), *b* = 12.247 (6), *c* = 13.484 (4) Å, β = 90.31 (2)°, *D_x* = 3.12 Mg m⁻³, *Z* = 4. The structure was refined from 2716 diffractometer-measured X-ray reflections to *R_w* = 0.076. The structure consists of chelated [Tl^{III}(CH₃CO₂)₄]⁻ anions with approximate 4*mm* symmetry linked together in an hexagonal array by seven-coordinate Tl^I cations (Tl—O = 2.88–3.15 Å) in which the lone pair shows no stereoactivity. This is consistent with a model which predicts that Tl^I will form short bonds, have a low coordination number and a stereoactive lone pair when the counter ion is a strong base (strength > 0.22 valence units), but otherwise will form longer bonds and have a coordination number greater than 6.

Introduction

As part of a study on the structural chemistry of complexes of Tl^{III} we attempted to obtain crystals of the hydrated form of Tl^{III}(CH₃CO₂)₃ by dissolving thallium triacetate in a 1:1 mixture of glacial acetic acid and water. The solution was left for several weeks in a refrigerator at 278 K during which time colourless hexagonal plate-like crystals appeared. These crystals, which were later identified from the structure as the title compound, decomposed in air at room temperature over a period of several hours.

Experimental procedure

Precession photographs of a crystal mounted in a Lindemann-glass capillary showed that the crystal was monoclinic with systematic absences *h*0*l*: *l* = 2*n* + 1 and 0*k*0: *k* = 2*n* + 1 indicating the space group *P*2₁/*c*. A second crystal was ground into a cylinder 0.075 mm in radius and 0.30 mm long and was mounted without protection on a Syntex *P*2₁ diffractometer but to prevent decomposition it was kept in a stream of cool

dry nitrogen (243 ± 1 K). Lattice parameters were calculated from the settings of 15 well centred reflections with 20° ≤ 2θ ≤ 31° using monochromated Mo *K*α radiation (λ = 0.71069 Å). Intensities of 3544 reflections with 2θ < 55° were measured using a θ/2θ scan. Correction was made for absorption (cylinder with μ*r* ~ 1.75). Standard reflections (123 and 023) measured every 48 reflections showed systematic increases of 20% and 9% respectively during the course of the experiment. The intensities were therefore scaled by factors varying from 1.0 to 0.87 according to the time at which they were measured. Equivalent reflections were averaged to give the complete set of 2716 unique reflections. Of these, 1097 intensities that were less than three times the standard counting error were designated as unobserved. The Patterson function was used to find the Tl atoms and subsequent electron density maps were used to locate all the other atoms except H.

The positional and anisotropic temperature factors of all atoms were refined by least-squares calculations using the locally written program *CUDLS* to give *R₁* = 0.070 and *R_w* = {∑ *w*(|*F_o*| - |*F_c*|)²/∑ *w*|*F_o*|²}^{1/2} equal to 0.076 where *w* = [σ² + (k*F_o*)²]⁻¹, σ being the

Table 1. Atomic parameters (× 10⁴)

	<i>x</i>	<i>y</i>	<i>z</i>	⟨ <i>u_{ii}</i> ⟩ (Å ²)
Tl(1)	1088 (1)	3694 (1)	4006 (1)	491
Tl(3)	1685 (1)	956 (1)	2194 (1)	367
O(1)	2979 (18)	2599 (11)	2478 (11)	399
O(2)	2299 (21)	2230 (14)	939 (12)	546
O(3)	-911 (21)	1140 (15)	1618 (13)	594
O(4)	-515 (18)	1884 (13)	3065 (11)	483
O(5)	1846 (20)	-276 (13)	790 (11)	477
O(6)	4004 (20)	-45 (13)	1709 (12)	508
O(7)	2280 (23)	342 (15)	3759 (13)	596
O(8)	577 (20)	-660 (14)	2952 (11)	506
C(1)	2944 (23)	2878 (79)	1583 (16)	395
C(2)	3562 (35)	3968 (21)	1335 (22)	610
C(3)	-1416 (27)	1641 (17)	2377 (19)	418
C(4)	-3252 (29)	1926 (21)	2441 (22)	588
C(5)	3296 (30)	-531 (20)	1001 (17)	455
C(6)	4096 (43)	-1384 (22)	321 (20)	715
C(7)	1344 (32)	-546 (19)	3716 (18)	493
C(8)	1298 (31)	-1207 (18)	4587 (18)	492

standard error in F_o derived from counting statistics. The factor k was chosen to be 0.05, a value which made the average value of $w(|F_o| - |F_c|)^2$ independent of the size of F_o . This procedure should lead to a correct absolute weighting scheme, so that the observed value of $\sum w(|F_o| - |F_c|)^2/P$ ($=1.004$, where P = number of degrees of freedom) indicates that the model accounts for all systematic information in the intensities. The maximum value of shift/error was 0.08. An extinction correction given by $F^* = F[1 + 0.24 \times 10^{-6} \beta(2\theta)F^2]^{1/2}$ (Larson, 1967) was applied. Atomic scattering factors corrected for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974). The largest features on a final difference synthesis were peaks of +2.5 and -2.5 e \AA^{-3} in the regions (0.23, 0.10, 0.28) and (0.30, 0.10, 0.23) respectively. The H atoms could not be clearly distinguished although positive density (~ 1 e \AA^{-3}) was found in all regions where H was expected. The final coordinates are given in Table 1.†

Description of structure

Bond lengths and angles are given in Table 2 and the structure is illustrated in Fig. 1. The structure consists of $[\text{Ti}^{\text{III}}(\text{CH}_3\text{CO}_2)_4]^-$ anions packed in hexagonal sheets perpendicular to the a axis with Ti^{I} cations in the triangular cavities within the sheets. The weak inter-sheet bonding is consistent with the hexagonal plate-like habit of the crystals.

† Lists of anisotropic thermal parameters, bond valences and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35259 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

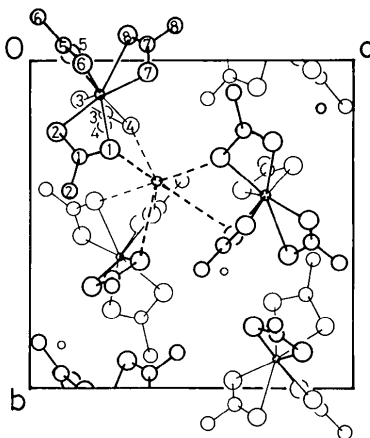


Fig. 1. The contents of one unit cell of $\text{Ti}[\text{Ti}(\text{CH}_3\text{CO}_2)_4]$. The circles in increasing order of size represent Ti, C and O. The bonds formed by one of the Ti^{I} ions are shown dashed, the solid lines indicate bonds within the $[\text{Ti}^{\text{III}}(\text{CH}_3\text{CO}_2)_4]^-$ ions.

Table 2. Bond distances (\AA) and angles ($^\circ$) with standard errors

2_1 denotes an atom related to that in Table 1 by $\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$ followed by any translation indicated; c similarly denotes the transformation $x, \frac{1}{2} - y, \frac{1}{2} + z$ and $\bar{1}$ denotes the transformation $-x, -y, -z$.

$[\text{Ti}^{\text{III}}(\text{CH}_3\text{CO}_2)_4]^-$ anion

	$a-b =$	1-2	3-4	5-6	7-8
Ti(3)-O(a)		2.31 (1)	2.30 (2)	2.42 (2)	2.29 (2)
Ti(3)-O(b)		2.36 (2)	2.46 (2)	2.38 (2)	2.41 (2)
O(a)-Ti(3)-O(b)		56.0 (5)	54.3 (6)	54.3 (5)	54.7 (6)
Ti(3)-O(a)-C(a)		94 (4)	95 (1)	92 (1)	96 (1)
Ti(3)-O(b)-C(a)		91 (3)	89 (1)	94 (1)	94 (2)
C(a)-O(a)		1.25 (3)	1.27 (3)	1.28 (3)	1.34 (3)
C(a)-O(b)		1.29 (6)	1.23 (3)	1.27 (3)	1.22 (3)
C(a)-C(b)		1.47 (9)	1.57 (3)	1.54 (4)	1.43 (3)
O(a)-C(a)-O(b)		119 (7)	122 (2)	119 (2)	116 (2)
O(a)-C(a)-C(b)		117 (5)	119 (2)	116 (2)	116 (2)
O(b)-C(a)-C(b)		123 (3)	120 (2)	124 (2)	128 (2)
O(1)-Ti(3)-O(7)		92.0 (6)		O(3)-Ti(3)-O(5)	81.6 (6)
O(2)-Ti(3)-O(8)		158.6 (5)		O(4)-Ti(3)-O(6)	167.5 (6)
O(2)-Ti(3)-O(6)		88.0 (6)		O(6)-Ti(3)-O(8)	90.3 (5)
O(8)-Ti(3)-O(4)		83.7 (5)		O(4)-Ti(3)-O(2)	101.6 (5)

Bonds around the Ti^{I} cation

Ti(1)-O(2)c	3.01 (2)	Ti(1)-O(5) 2_1	2.76 (2)
Ti(1)-O(1)	2.92 (2)	Ti(1)-O(5)c	3.15 (2)
Ti(1)-O(3) 2_1	3.12 (2)	Ti(1)-O(8) 2_1	3.08 (2)
Ti(1)-O(4)	2.88 (2)		

Possible C-H...O interactions

	C-H...O	C-C...O
C(2)-O(6) $2_1(100)$	3.53 (3)	110 (2)
C(2)-O(7)c(001)	3.72 (3)	109 (2)
C(2)-O(7) $2_1(100)$	3.85 (3)	136 (3)
C(4)-O(1)(100)	3.24 (3)	178 (2)
C(4)-O(6)(100)	3.46 (3)	118 (2)
C(6)-O(2) $\bar{1}(100)$	3.60 (4)	147 (2)
C(6)-O(6) $\bar{1}(100)$	3.62 (3)	108 (2)
C(6)-O(3) $\bar{1}$	3.72 (4)	93 (2)
C(8)-O(4) $\bar{1}(001)$	3.34 (3)	158 (2)
C(8)-O(2) $2_1(0\bar{1}0)$	3.62 (3)	100 (2)
C(8)-O(3) $2_1(0\bar{1}0)$	3.65 (3)	98 (1)
C(8)-O(7) $\bar{1}(001)$	3.88 (3)	110 (2)

The $[\text{Ti}^{\text{III}}(\text{CH}_3\text{CO}_2)_4]^-$ anions have approximate $\bar{4}mm$ symmetry with pairs of acetate ions lying opposite each other in the same plane. Although the errors in individual distances and angles are fairly large, averaging chemically equivalent dimensions gives the idealized picture of the ion shown in Fig. 2. The acetate groups are asymmetrically bonded with the weaker bonds lying near the equatorial plane, as is also observed in $[\text{Ti}(\text{H}_2\text{O})_3(\text{NO}_3)_3]$ (Faggiani & Brown, 1978). The angles at the carboxyl C atom are different from those expected (Brown, 1980). The O-C-O angle of 119° is much smaller than the 124° predicted from the bond lengths and the methyl groups are bent more towards the pseudo $\bar{4}$ axis than would be expected (the O-C-C angles are 117 and 124° rather than the expected 118 and 119°). Since these effects are shown by all four acetate groups it is unlikely that they result from experimental error.

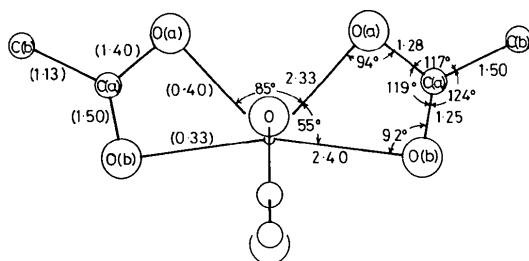


Fig. 2. An idealized view of the $[\text{Ti}(\text{CH}_3\text{CO}_2)_4]^-$ ion. Bond distances (Å) and angles are shown on the right, bond valences (in parentheses) on the left.

The anions are packed in hexagonal layers with Tl^{I} ions occupying half the triangular cavities within each layer. Each Tl^{I} is bonded to O atoms only from the three neighbouring anions in the same plane. All other interionic interactions are van der Waals contacts or weak $\text{C}-\text{H}\cdots\text{O}$ bonds. When these latter bonds are taken into account, satisfactory bond valence sums (Brown, 1978) are obtained around all atoms with the exception of O(7) [valence = 1.63 (11)] and Tl^{I} [valence = 0.88 (1)]. A search of the difference synthesis for a water molecule between O(7) and Tl^{I} revealed no significant peak.*

The Tl^{I} ion shows seven-coordination with little or no indication of stereoactivity of the lone pair. Such coordination is consistent with the principles discussed below.

Factors affecting the coordination of Tl^{I}

Thallium(I) is found in different compounds with every coordination number between 3 and 12. The lower coordination numbers (3–5) are invariably associated with stereoactivity of the lone pair of electrons, but this activity, evidenced by a pronounced asymmetry in the coordination polyhedron, can also be found with high coordination numbers [e.g. in $\text{Tl}_{0.3}\text{WO}_3$, in which the 12-coordinate Tl atom is displaced along the sixfold axis of a hexagonal prism (Labbé, Goreaud, Raveau & Monier, 1978)]. Verbaere, Marchand & Tournoux (1978) have pointed out that in ternary oxides of the form $\text{Tl}_x\text{M}_y\text{O}_z$, where the M belongs to the fourth or fifth groups of the Periodic Table, the cation ratio $\gamma = y/x$ can be used as an indicator of Tl–O bond lengths and lone-pair activity. Compounds with $\gamma < 1$ typically have three or four short (primary) Tl–O bonds (<2.9 Å) on one side of the Tl atom and only very long (secondary) bonds (>3.1 Å) on the other. For compounds with $\gamma > 1$ the coordination numbers are greater than 6 with most bonds distributed uniformly around the Tl, and with bond lengths lying in the range 2.9 to 3.2 Å.

* Bond valences have been deposited. See previous footnote.

Table 3. Base strengths and coordination in Tl^{I} compounds

Compound	Anion base strength (v.u.)	γ	Coordination number of Tl	Reference (year, coden, volume, page)
Tl_2O	0.5	0	3+0	71 ZAACAB 381 266
$\text{Tl}_2(\text{TiO}_3)$	0.5	0.33	3+0 3+1 3+2	73 CHDCAQ 277 863
KTiO	0.5	0.5	3+0	78 ZAACAB 438 213
RbTiO	0.5	0.5	3+0	
CsTiO	0.5	0.5	3+0	
Tl_2BO_3	0.33	0.33	3+0	73 CHDCAQ 276 177
Tl_2SnO_3	0.33	0.5	3+3 4+0	74 JSSCBI 11 184
$\text{Tl}_2\text{Ge}_2\text{O}_{14}$	0.31	0.62	3+0 3+2 3+2 3+2	79 ACBCAR 35 810
Tl_2TiO_3	0.28	0.5	3+1 3+1	74 JSSCBI 11 60
Tl_2PO_4	0.25	0.33	3+2	73 CHDCAQ 276 1755
Cysteinato Tl	0.23	—	4+2	77 ACBCAR 33 2690
$\text{Tl}_2\text{CO}_3\text{F}$	0.22	0.33	4+3 4+3 4+3	73 ACBCAR 29 498
Tl_2CO_3	0.22	0.5	5+2 4+2	75 CJCHAG 53 2454
$\text{Tl}_2\text{Na}(\text{SO}_3)_2$	0.22	1.0	6 9	77 JRPSCD 1977 138
TiH_2PO_4	0.18	—	7	79 ACBCAR 35 542
$\text{Tl}_2\text{S}_2\text{O}_7$	0.17	0.5	9 9	76 ACBCAR 32 2225
$\text{Tl}_2[\text{Cu}(\text{H}_2\text{O})_6](\text{SO}_4)_2$	0.17	1.5	7	72 CSCMCS 1 371
$\text{Tl}_2\text{Cu}(\text{SO}_3)_2$	0.17	1.5	9	73 ACSAA4 27 345
TlInB_3O_8	0.17	3.0	4+2	74 ACBCAR 30 1181
$\text{Tl}[\text{H}_2(\text{PO}_3)_2]$	0.15	—	6	78 ACBCAR 34 3510
TlVO ₃	0.14	1.0	10	74 CJCHAG 52 3539
$\text{Tl}_2[\text{Hg}_2(\text{SO}_4)_2\text{Cl}]$	0.13	1.67	10 9 7	76 ACAPCT 30 241
$\text{TlNO}_3\cdot\text{III}$	0.11	1.0	10	75 ACBCAR 31 365
$\text{Tl}[\text{ZnSO}_3\text{Cl}]$	0.09	2.0	5+4	76 ACBCAR 32 2044
$\text{Tl}_2[\text{Mo}_6\text{O}_{13}]$	0.07	2.0	9 10	78 ACBCAR 34 3547
Tl picrate	0.05	—	11	77 ACBCAR 33 649
Tl_2WO_3	0.05	3.3	6+6	78 ACBCAR 34 1433
$\text{Tl}_2[\text{Mo}_2\text{O}_{11}]$	0.04	3.5	5+3	76 ACBCAR 32 1859

ASTM codens: ACAPCT *Acta. Chem. Scand. Ser. A*; ACBCAR *Acta Cryst. B*; ACSAA4 *Acta Chem. Scand.*; CHDCAQ *C.R. Acad. Sci. Sér. C*; CJCHAG *Can. J. Chem.*; CSCMCS *Cryst. Struct. Commun.*; JRPSDC *J. Chem. Res. (S)*; JSSCBI *J. Solid State Chem.*; ZAACAB *Z. Anorg. Allg. Chem.*

Unfortunately, the ratio γ is not easy to calculate for compounds such as $\text{Tl}[\text{Ti}(\text{CH}_3\text{CO}_2)_4]$, and while γ correlates directly with coordination number for Tl^{I} , it correlates inversely with coordination number for V^{V} , As^{V} and Ge^{IV} (Shannon, Chenevas & Joubert, 1975). A more general approach is therefore needed to provide insight into the factors that determine the stereochemistry of Tl^{I} .

One such factor is the base strength of the anion. Strong bases will form strong and hence short bonds with Tl, resulting in smaller coordination numbers that are stabilized when the lone pair of electrons occupies space within the coordination sphere, while weak bases correspondingly produce weak bonds resulting in larger coordination numbers. Thus, in compounds with strong bases the lone pair of electrons is invariably stereoactive; in compounds with weak bases, however, the lone pair is no longer required to be stereoactive but nevertheless may be so if the arrangement of neighbouring atoms is appropriate.

One measure of Lewis acid and base strength is the valence (or bond strength) of a typical bond formed by the ion (Brown, 1978). For most ions this will be the atomic valence (or formal charge) divided by the average coordination number (CN). Thus the acid strength of Be is $2/4 = 0.5$ valence units (v.u.) and Si is $4/4 = 1.0$ v.u. Because Tl^{I} has such a variable coordination, its Lewis acid strength can range between

0.08 v.u. (CN = 12) and 0.33 v.u. (CN = 3); the particular value which occurs in a given compound will be such as to form the best match with the base strength of the anion. Calculating the base strength of the anions is a little more complex (see Appendix), but generally, small highly charged anions like O^{2-} and BO_3^{3-} have high base strengths (>0.33 v.u.), whereas large anions with low charge, such as the picrate ion or $[Mo_7O_{22}]^{2-}$, have low base strengths.

Table 3 lists the anion base strengths and coordination numbers found in a representative selection of Tl^I compounds. All $Tl-O$ bonds shorter than 3.5 Å have been included and where primary (<3.1 Å) and secondary (>3.1 Å) bonds can be clearly distinguished and when all the primary bonds lie on the same side of the Tl atom, *i.e.* when the lone pairs are stereoactive, the two types of bond have been listed separately as '(primary) + (secondary)'. For comparison, the ratio γ is also given where it can be calculated. These results are shown graphically in Fig. 3, with a cross for compounds with inert lone pairs and a circle for those with stereoactive lone pairs. The solid curve indicates the coordination number that would be expected if all the bonds to Tl had valences exactly equal to the anion base strength.

While the coordination number decreases as the base strength increases, the effect is not as great as the solid curve would suggest. The observed and predicted coordination numbers are equal at 9, corresponding to a base strength of 0.11 v.u. For stronger bases the observed coordination numbers lie above the curve indicating that the O coordination numbers must be greater than 4 (the coordinate number of O assumed in calculating the base strength, see Appendix), while for weaker bases the observed points lie below the curve indicating an O coordination number less than 4. A fairly dramatic change in stereochemistry occurs at a

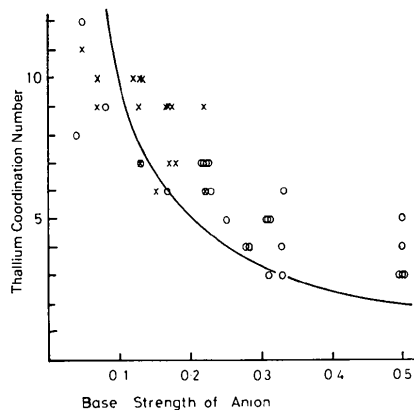


Fig. 3. Observed coordination numbers of Tl^I as a function of the base strength of the anion. Circles represent coordination polyhedra in which the lone pair is stereoactive, crosses polyhedra in which it is inert. The line represents the coordination number expected if all Tl^I bonds had a valence exactly equal to the anion base strength.

base strength of 0.22 v.u. Bases with strengths greater than 0.22 v.u. crystallize with Tl coordination numbers of 6 or less and stereoactive lone pairs, while bases with strengths less than 0.22 v.u. crystallize with Tl coordination numbers of 6 or more with or without a stereoactive lone pair.

The base strength of the $[Ti(CH_3CO)_4]^-$ ion is 0.09 v.u. (see Appendix) for which the solid curve would predict a Tl^I coordination number of 11. In practice, neglecting the $C-H \cdots O$ bonds, each O atom forms only two or three bonds rather than the four assumed and consequently the Tl^I atom forms only seven bonds, in agreement with the observation that for weak bases a coordination less than that indicated by the solid curve will be found.

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APPENDIX Calculation of base strength

The strength of groups that act as Lewis bases is defined as the strength of a typical base bond formed by the group. Since such groups frequently have rather complex structures (*e.g.* the acetate ion), the calculation is not always straightforward. Two methods can be used. In the first the valence of a typical bond is obtained by dividing the total negative charge on the group by the number of base bonds it forms:

$$\begin{aligned} \text{base strength} &= \frac{\text{total negative charge of the group}}{\text{number of base bonds formed by the group}} \\ &= (Q + \sum S_a) / (\sum (v_b - v_i)), \end{aligned}$$

where Q is the formal negative charge of the group (*e.g.* 1 for acetate, 0 for H_2O); $\sum S_a$ is the sum of the formal positive charges associated with Lewis acid functions of the group [*e.g.* 0.1 for the CH_3 group in the acetate ion (Brown, 1980) and 0.4 for the two H atoms in H_2O (Brown, 1976)]; v_b is the total coordination number of each base atom within the anion, assumed to be 4 for O unless O forms two strong bonds (*e.g.* $C-O-H$, $B-O-Nb$) in which case it is 3; v_i is the number of internal bonds formed between the base atom and other atoms *within* the group (*e.g.* 1 for terminal O atoms, 2 for bridging O atoms).

An alternative method is to determine at each base atom the residual valence, that is, the valence remaining after all the internal bonds have been satisfied. This must then be divided by the number of bonds required to raise the coordination number of the base atom to 3 or 4 as above.

The second method is necessary when the base atoms of the group are expected to have different

strengths, but it requires a greater knowledge of the internal structure of the group. The first method also requires some knowledge of the internal structure of the group but a good estimate can usually be made from a knowledge only of the composition and likely values for the coordination numbers of the constituent atoms.

In calculating the base strengths quoted in Table 3, the 'group' was assumed to be all the atoms in the crystal apart from Tl^I and other weak Lewis acids such as alkali metals. For consistency the first method outlined above was used.

The two methods can be illustrated for $[Tl^{III}(CH_3CO_2)_4]^-$. The formal charge on this anion is 1.0, which must be augmented by the positive charge associated with the methyl groups (each equal to 0.1; Brown, 1980) to give a total negative charge of 1.4. There are eight O atoms each capable of forming four bonds, two of which will be used internally (C—O and Tl—O). Therefore, the number of base bonds that can be formed = $8 \times (4 - 2) = 16$. The base strength is thus $1.4/16 = 0.09$.

Alternatively, the residual valence on each O atom can be found by subtracting the valences of the internal bonds (see Fig. 2) from the atomic valence of O (= 2.0)

and dividing by the number of external bonds each O must form to give it a coordination number of 4 (in this case two). The base strengths of the two chemically distinct O atoms are therefore $(2.0 - 1.4 - 0.4)/2 = 0.10$ and $(2.0 - 1.5 - 0.33)/2 = 0.08$. The two methods thus give the same average base strength but the latter method suggests that the equatorial O atoms will be slightly weaker bases than the axial ones.

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