

Correlation between the Covalency and the Thallium-205 Nuclear Magnetic Resonance Chemical Shift in Oxides and Halides

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²⁰⁵Tl chemical shift measurements were carried out on thallium(I) oxides and halides. A correlation between the chemical shift and the stereochemical activity of the 6s² lone pair of Tl^I was established; the greater this activity, the greater the absolute value of the chemical shift. For the halides, optical and chemical shift measurements gave access to the Tl-X bond ionicity via Ramsey's equation. In thallium(I) halides the absolute value of the chemical shift increases with the covalency. The work of Glaser on thallium(III) halides showed the chemical shift to decrease with increasing covalency. An explication of this difference is proposed. The hyperfine coupling constant *A* of the paramagnetic compound Tl₄MnI₆ was determined by the study of the chemical shift as a function of the susceptibility. This constant *A* is seen to be weak ($-7 \text{ KG}/\mu_B$). © 1986 Academic Press, Inc.

Introduction

The influence of the Tl-X bond nature on the effective ionic radius of Tl^I has been discussed in a previous paper (1); this radius is seen to decrease, whatever the structure, when the covalency of the Tl-X bond increases. The Tl^I valence band has a 6s² electronic configuration and when this ion is engaged in a compound, the lone pair may manifest a certain stereochemical activity. The structure of several oxygen-thallium(I) compounds possessing such an activity has been determined: the lone-pair activity in these compounds results in an asymmetrical environment about thallium(I), the lone pairs being located either in tunnels or in layers. The compounds

which present an important lone-pair activity often contain thallium with a coordination number of 3: the three oxygens are placed in such a way that, with the help of VSEPR (2), the Tl^I environment can be described as a distorted tetrahedron, the lone pair being directed toward one of the four apexes. In this case Tl^I presents *sp*³ hybridization. In all the Tl-O-B systems studied there is a limiting value of the Tl:B ratio beyond which the lone-pair activity is null: the coordination is higher and thallium behaves as an alkali-metal.

The coordination number of thallium in the ternary halides studied, TlBX₃ and Tl₄BX₆, where *B* is a transition element, is higher than in the oxides. This indicates either an absence or very weak stereochemical activity of the lone pair. In the TlBX₃ halides the Tl^I coordination number is ei-

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ther 9 (trigonal prism tricapped by the halogen), 12, or between 9 and 12. In the Tl_4BX_4 compounds the trigonal prism is dicapped by the halide and monocapped by the thallium. For CsCl-type TLX halides ($X = Cl, Br, I$) the thallium coordination number is 8. In the low-temperature form of TII the thallium environment is a trigonal prism monocapped by the iodide and dicapped by the thallium.

Until now few attempts have been made to establish a correlation between the stereochemical activity indicated by structural determinations and certain physical measurements. Kolditz and Wahner (3), in their study of the Tl_2O/P_2O_5 system, showed that the thallium NMR chemical shift increases with the covalency. By measuring the ^{205}Tl peak position in NMR, this work hopes to broaden what is known about the influence

of the stereochemical activity and/or the covalency on the ^{205}Tl chemical shift.

Results

The NMR study was carried out on a BRUKER SXP spectrometer by a pulse method. The fixed frequency resonance signal is obtained by the Fourier transformation of the free precession signal after a $\pi/2$ pulse by means of a boxcar. A multichannel Nicolet mean calculator enables accumulation and thus a perceptible improvement in the signal-to-noise ratio. For certain compounds 50 or so accumulation cycles are needed. The temperature variation is obtained by passing a preheated or pre-cooled air flow about the sample.

Thallium, with a nuclear spin $I = \frac{1}{2}$, does not exhibit a quadrupole effect and its

TABLE I
 ^{205}Tl CHEMICAL SHIFT IN OXIDES AND HALIDES

Compound	Chemical shift, $-\delta$ (ppm)		Tl ^I Environment	Refs.
$TlVO_3$		260	Irregular polyhedron made up of 10 oxygens	(4)
$Tl_2Ti_3O_7$		769	Environment unknown	(5)
$Tl_2Ti_4O_9$		840	{Tl(1) coordination 8 Tl(2) coordination 6	(6) (6)
$Tl_4V_2O_7$		1274	Environment close to that of Tl^+ in $TlVO_3$	(7)
$TlNbO_3$		1333	Chair form flattened octahedron D_{3d}	(7)
$TlTaO_3$		1451	Chair form flattened octahedron D_{3d}	(7)
Tl_3PO_4		1834	Tetrahedron O_3E	(8)
Tl_2TiO_3		2700	Tetrahedron O_3E	(9)
Tl_4O_3		2743	{ Tl^{3+} : distorted octahedron Tl^+ : tetrahedron O_3E	(10) (10)
Tl_2SnO_3		2781	Tetrahedron O_3E	(11)
$Tl_6Si_2O_7$		2842	Tetrahedron O_3E	(12)
$TlCl$	400	493	Cubic environment CsCl	
$TlBr$	850	957	Cubic environment CsCl	
$TlI \alpha$	1500	1600	Cubic environment CsCl	
$TlI \beta$	1950 (13)	1707	Asymmetric tricapped prism	
$TlGeI_3$		1116	Trigonal prism tricapped by I	(14)
Tl_4HgI_6		1234	} Trigonal prism dicapped by I and monocapped by Tl	(14)(15)
Tl_4CdI_6		1410		
Tl_4GeI_6		1704		

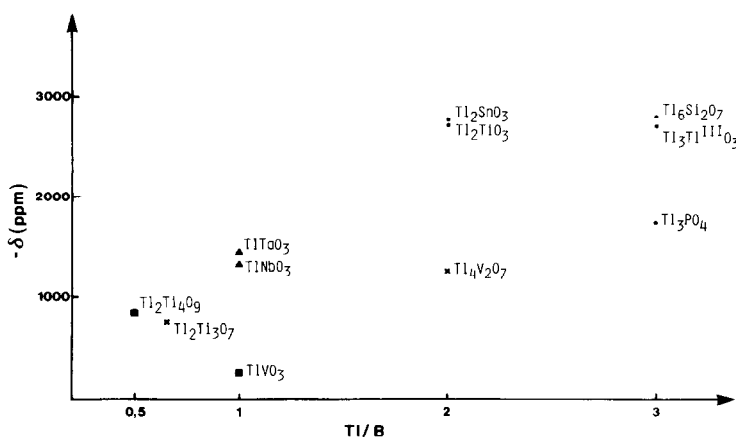


FIG. 1. Chemical shift evolution as a function of the Tl:B ratio in ternary oxides. (●) Important stereochemical activity, (▲) possible stereochemical activity, (■) no stereochemical activity, (×) structure unknown. (B: transition element.)

chemical shift is superior to that of lighter elements. Combined with a high Larmor frequency (+24.57 MHz at 10 kG) and a high natural abundance of ^{205}Tl (70.48%), these factors favor a good signal-to-noise ratio.

Measurements were effectuated at fixed frequency of 42 MHz. The reported chemical shifts are relative to thallium nitrate. The results obtained for the oxides and halides are given in Table I.

Discussion

Lone-Pair Stereochemical Activity and the Chemical Shift

Table I contains the chemical shifts and the thallium environment for several oxides and halides. The lone-pair stereochemical activity present in the thallium-rich oxides, particularly when the cation *B* has a high degree of oxidation, is weak or null in the halides and may be considered in terms of the thallium(I) polarization. This polarization decreases first when the *B*-anion bond covalency increases and second, for a given anion, when the number of *B*-anion bonds increases because of the resulting decrease

in the effective charge of anion. The anion's polarizing power decreases on passing from the oxides to the halides: for the same number of cations with given charge, there are two times as many anions in the halides. Thus the thallium(I) environment remains fairly symmetrical and the effect of covalency on the structure is only noticeable in the Tl-X distances.

The absolute values of the chemical shifts δ of oxides studied as a function of Tl:B ratio are given in Fig. 1. The highest values are obtained for Tl₆Si₂O₇, Tl₄O₃, Tl₂SnO₃, Tl₂TiO₃, and Tl₃PO₄ which have already been clearly shown to have lone-pair stereochemical activity. The TlTaO₃ and TlNbO₃ pyrochloric species, which may have a weak lone-pair activity, follow. The lowest absolute values of δ measured are for Tl₂Ti₄O₉ and TlVO₃ which show no stereochemical activity: these two species are isotopes of their alkali-metal homologs.

Figure 1 clearly shows the relation between δ and the thallium(I) polarization for a given Tl:B ratio. Thus when Tl:B = 1 the absolute value of chemical shift increases in the order TlVO₃, TlNbO₃, TlTaO₃. The *B*(V) environment is tetragonal in the metavanadate where the *B*(V)-O bond is

very covalent, whereas it is octahedral in the niobate and the tantalate.

The oxides for which a stereochemical activity has been previously shown have absolute values of chemical shift greater than 1800 ppm, whereas of all the halides studied the highest value is 1707 ppm. This indicates clearly the correlation between high absolute values of δ and lone-pair stereochemical activity.

What quantitative information on Tl-X bond covalency can be found from chemical shift measurements in the halides will now be examined in further detail.

Tl-X Bond Covalency and the Chemical Shift

The diamagnetic and paramagnetic shielding constants' contributions to chemical shifts are not comparable. According to Ramsey (16) the diamagnetic contribution is negligible and the chemical shift δ is given by

$$\delta = -\frac{16}{3} \mu_B^2 \left\langle \frac{1}{r^3} \right\rangle (f/\Delta E)$$

where $\langle 1/r^3 \rangle$ is the mean radical part of the excited state wave function and ΔE is the energy difference between the ground and excited states. There are many approaches to the determination of this term (17, 18) but many authors (19) agree on ΔE as the near value of the energy gap as given by optical measurements. f indicates the nature and respective weighting of the cationic orbitals involved in hybridization. According to Hafner and Nachtrieb (20), for a cation with ns^2 configuration, f is the fraction of the p orbital involved in the hybridization: this fraction increases with covalency. μ_B is the Bohr magneton.

According to the results given below, the thallium(I) halides have a chemical shift of which the absolute value increases with the covalence, whereas results obtained by other authors for thallium(III) or copper(I)

compounds show that for these cations the chemical shift decreases when the covalency increases. An interpretation of this difference will be given later.

Covalency and the Chemical Shift in the TLX Series (X = Cl, Br, I)

In order to calculate f from δ in the TLX halides, the near value $\langle 1/r^3 \rangle$ of thallium(I) had to be determined. Yosida and Moriya (21) gave $\langle 1/r^3 \rangle$ the value of the isolated atom whereas Hafner and Nachtrieb (20), taking into account the electrical field effect caused by near neighbors, used an intermediate value between $\langle 1/r^3 \rangle$ Tl (11.8 au⁻³) and $\langle 1/r^3 \rangle$ Tl⁺ (18.3 au⁻³) (22). The average value of 15.1 au⁻³ was (rather arbitrarily) retained for this work. The results are listed in Table II: the ΔE values determined by optical measurements are in accord with those previously published (23).

The increase with covalency of the absolute value of the chemical shift of Tl(I) can be explained by an increase in the paramagnetic contribution σ_p which is a function of the orbital moment (24).

TlNO₃, taken as reference, has strong s character of the lone pair: the orbital moment is nearly null and the diamagnetic contribution, caused by the field induced by the spherical $6s^2$ electron density circulation, is no longer negligible.

The growing covalency in the series TlNO₃, TlCl, TlBr, TlI gives rise to an increasing mixing of s and p orbitals: the orbital moment is no longer null. This causes

TABLE II
RESULTS OBTAINED FOR THE SERIES TLX
(X = Cl, Br, I)

Compound	$-\delta$ (ppm)	ΔE (eV)	$f/\Delta E$	f
TlCl	493	3.3	0.022	0.073
TlBr	957	2.8	0.043	0.120
TlI β	1707	2.6	0.076	0.199

TABLE III
EVOLUTION OF THE CHEMICAL SHIFT FOR Tl_4BI_6

Compound	$-\delta$ (ppm)	ΔE (eV)	$f/\Delta E$	f
Tl_4GeI_6	1704	2.4	0.076	0.183
Tl_4CdI_6	1410	2.9	0.063	0.183
Tl_4HgI_6	1234	2.3	0.055	0.127

an increase in the paramagnetic contribution to the chemical shift, due to the field induced by the circulation of the no-longer-spherical electron density. Thus for thallium(I) compounds f measures the fraction of p orbitals involved in hybridization.

*Chemical Shift Evolution in Tl_4BI_6
Ternary Compounds ($B = \text{Ge}, \text{Cd}, \text{Hg}$)*

The results for these three isostructural compounds are given in Table III. The Tl-I covalency is approximately the same as Tl_4GeI_6 and Tl_4CdI_6 and less in Tl_4HgI_6 . By correlation the Ge-I and Cd-I bonds are less covalent than the Hg-I bond. Chemical shift measurements associated with optical methods form an experimental approach to the ionicity of a bond which is more precise than the value obtained by simple differences in electronegativity; as in the latter

the next nearest neighbors are not taken into account.

*Comparative Study of the Chemical Shift of the $nd^{10}(n+1)s^2\text{Tl}^I$ and $nd^{10}\text{Tl(III)}$,
Cu(I) Cations*

Thallium(I) is a bulky cation with a coordination number greater than or equal to 9 in ternary halides; the smaller thallium(III) adopts lower coordination: octahedral in $\text{Cs}_2\text{TlCl}_5 \cdot \text{H}_2\text{O}$ (25), $\text{K}_3\text{TlCl}_6 \cdot 2\text{H}_2\text{O}$ (26), trigonal bipyramidal in $\text{TlBr}_3 \cdot 4\text{H}_2\text{O}$ (27), or tetragonal in $\text{KTlBr}_4 \cdot 2\text{H}_2\text{O}$ (28),

The recent chemical shift measurements of Glaser (29) are reproduced in Table IV. They were taken to establish a correlation between δ and the environmental geometry in the thallium(III) halides and were not the object of an investigation as to the evolution of δ with covalency. The reported chemical shifts are relative to an aqueous solution of TlClO_4 . A decrease in the chemical shift is observed when, for a given coordination, the sequence chloride, bromide, iodide is followed. This evolution is in the opposite sense to that observed for the thallium(I) halides. This difference can be explained qualitatively by the nature of the external electronic orbitals.

For the thallium(I) cation of $5d^{10}6s^2$ configuration, the covalency implies a mixture

TABLE IV
CHEMICAL SHIFTS OF Tl(III) HALIDES ACCORDING TO GLASER

Compound	Chemical shift, δ (ppm)	Tl ^{III} Environment	Refs.
$\text{Tl}(\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$	2175	Regular octahedron $\text{Tl}(\text{H}_2\text{O})_6^{3+}$	(30)
$\text{TlCl}_3 \cdot 4\text{H}_2\text{O}$	2051	Trigonal bipyramid $\text{TlCl}_3(\text{H}_2\text{O})_2$	(27)
KTlCl_4	2716	Tetrahedron TlCl_4^-	(31)
$\text{Cs}_2\text{TlCl}_5 \cdot \text{H}_2\text{O}$	2022	Octahedron $\text{TlCl}_5(\text{H}_2\text{O})^{2-}$	(25)
$\text{Na}_3\text{TlCl}_6 \cdot 12\text{H}_2\text{O}$	1972	Octahedron TlCl_6^{3-}	(32)
$\text{K}_3\text{TlCl}_6 \cdot 2\text{H}_2\text{O}$	2007	Octahedron TlCl_6^{3-} and $\text{TlCl}_5(\text{H}_2\text{O})^{2-}$	(26)
$\text{Cs}_3\text{Tl}_2\text{Cl}_9$	1926	Distorted octahedron TlCl_6^{3-}	(33)
$\text{TlBr}_3 \cdot 4\text{H}_2\text{O}$	1098	Trigonal bipyramid $\text{TlBr}_3(\text{H}_2\text{O})_2$	(27)
$\text{KTlBr}_4 \cdot 2\text{H}_2\text{O}$	1262	Tetrahedron TlBr_4^-	(28)
$[\text{NBu}_4]\text{TlI}_4$	-1560	Distorted tetrahedron TlI_4^-	(34)

of 6s and 6p orbitals and an increase in orbital moment. For thallium(III) with $5d^{10}$ configuration, the covalency implies on the contrary, a decrease in orbital moment caused by the mixture of 5d and 6s or 5d and 6p orbitals. When the orbital moment decreases so does the paramagnetic contribution σ_p and thus the chemical shift δ .

The work of Becker and Schafgen on $3d^{10}$ Cu(I) compounds (35), for which the same evolution is observed, confirms this interpretation. For Tl(I), f measures the fraction of the p orbital involved in bonding and which increases with covalency. For Cu(I), on the contrary, f designates the fraction of the d orbital not involved in bonding and which decreases with covalency, as would seem to also be the case of Tl(III).

Temperature-Dependent Paramagnetism and Isotropic Paramagnetic Shift: the Compound Tl_4MnI_6

The diamagnetic compounds discussed in the previous paragraphs exhibit a ^{205}Tl chemical shift which is temperature independent. The compound Tl_4MnI_6 , an isotype of $\alpha-Tl_4CrI_6$, presents a temperature-dependent magnetic behavior, and is paramagnetic up to 4 K (36). The molar susceptibility obeys the Curie-Weiss law:

$$\chi_M = \frac{C}{T - \theta}$$

where $\mu = 5.8 \mu_B$ and the Curie-Weiss temperature $\theta = 5$ K. The paramagnetic shift as a function of the susceptibility is given by (37)

$$K = K_{orb} - A \frac{\gamma_c}{\gamma_n} \frac{1}{N(g\mu_B)^2} \chi_M.$$

In the case of Tl_4MnI_6 , nuclear spin is carried by the Tl(I) and free electrons by the Mn^{2+} . The constant A is called transferred hyperfine field. As the Tl-Mn distance is quite long (4.26 Å), exchange takes place via the iodine. The paramagnetic shift K as

a function of the molar susceptibility is given in Fig. 2: the slope of this straight line curve allows determination of the constant $A = 7$ kG/ μ_B .

Transferred hyperfine fields are generally weaker than polarization hyperfine fields, those existing in compounds where the nuclear and electronic spins are carried by the same cation. These interatomic hyperfine fields are of the order of 100 kG/ μ_B in the Fe group, 375 kG/ μ_B in the Pd group, and 90 kG/ μ_B for the rare earth metals (38, 39).

It should be noted that the measurements were taken for the powder, and demagnetizing field calculations were not taken into account.

Conclusion

Thallium(I), often considered as a pseudo-alkali, has a high polarizability (5.11 \AA^3) which results in a distinctive behavior. For the oxides this is translated by a stereochemical activity which is favored by a high Tl : B ratio, and, for a given Tl : B ratio, by a low degree of oxidation in B. The stereochemical activity gives rise to high absolute values of the chemical shift (greater than 1800 ppm).

For the halides, the strong polarizability of Tl(I) results in important covalency ef-

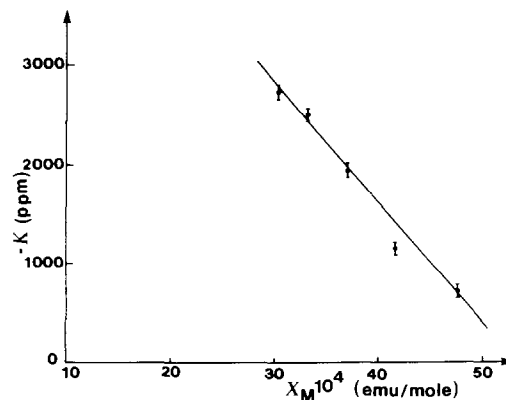


FIG. 2. Paramagnetic shift evolution as a function of susceptibility for Tl_4MnI_6 .

fects. The absolute value of the chemical shift increases with the covalency. The opposite trend is noticed in the Tl(III) halides. In both cases the explanation lies in the thallium orbital mixture involved in hybridization.

Finally, the investigation of the chemical shift of thallium in Tl₄MnI₆ has shown evidence of a hyperfine interaction coupling the Mn(II) free electrons with the nuclear spin of Tl(I). The hyperfine field thus transferred is $-7 \text{ kG}/\mu_B$.

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