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A Molecular Orbital Study of the *Cis* Influence in Substituted Octahedral Tellurium Hexafluoride Compounds

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The cis-influence in substituted tellurium hexafluoride compounds has been studied by a molecular orbital method. The calculations confirm the experimental observations that the fluorine atoms positioned cis to a ligand are more labile and, hence, more susceptible to replacement. The monosubstituted tellurium hexafluoride system, TeF_5X, was investigated for a series of ligands X and an order of increasing cis-influence for these ligands is found to be $H < OH < NH_2 < Cl < CH_3 < Br < SH \sim PH_2 < SiH_3$. Reasons are presented for the cis-directing properties within the system and for the order of the ligands.

Introduction

One of the most intriguing aspects of the chemistry of square planar transition metal complexes is the stereospecificity of the ligand replacement reactions. Consequently, there has been a plethora of experimental[1–3] and theoretical investigations into this phenomenon known as the *trans*-effect[4–6]. The result is a series of ligands ordered according to their ability to facilitate substitution of the ligand *trans* to their position. A rationale[6] of this classification has been constructed in terms of the *trans*-influence which involves bond weakening in the ground state of the complex, and also from a consideration of the structure of the five-coordinate intermediate which is especially stabilised by ligands containing low-lying vacant π-orbitals.

Related chemical phenomena also occur within the domain of non-transition-metal chemistry[7–11]. One of the most interesting is the substitution pattern of the mono- and di-substituted tellurium hexafluorides[7–9]. It is observed that in reactions of the type

$$TeF_5X + Y \rightarrow TeF_4XY + F \qquad (1)$$

$$TeF_4XY + Z \rightarrow TeF_3XYZ + F \qquad (2)$$

the probability of the entering ligand replacing a fluorine positioned *cis* to the substituent rather than *trans* is high in the first reaction. For the second reaction the mode of replacement is dependent upon the experimental conditions, although a *cis*-fluorine is usually substituted[7–9]. Hence it can be conjectured that in the case of the substituted tellurium hexafluorides the presence of a substituent weakens the *cis* Te–F *i.e.* a *cis*-effect is present. It is of considerable chemical interest to discover the electronic nature of this effect and so all-valence-electron-type calculations (CNDO/MO) were performed on several substituted compounds of tellurium hexafluoride.

The calculational framework has been fully described elsewhere[12, 13] and has proved successful in the interpretation of the *trans*-effect of substituted square-planar platinum complexes[6]. The dimensions of the molecules were constructed from information extracted from reference 14. The calculational input parameters for all the elements except Te have been previously tabulated[15], while for Te we used the valence-state ionisation potential[16] for the corresponding diagonal element of the core hamiltonian matrix and the value of the one-centre two-electron repulsion integral of Te was 9.77 eV.

In this investigation, particular attention was focused on the nature of the *cis*-influence and hence on the electronic composition of the molecules. This is obtained from the calculated electron densities and bond indices. The latter measure was recently defined[17, 18] and adjudged to be a reliable guide to the bond strength, with the advantage that the numerical values obtained were directly associated with bond multiplicity, *e.g.* the C–C bond index in C_2H_2, C_2H_4, and C_2H_6 is 3, 2, and 1, respectively[18]. In order to examine the *cis*-influence present in the tellurium hexafluoride derivatives, it is necessary to scrutinise the bond indices of the various Te–F bonds, as the bond with the lowest bond index will be the most prone to replacement.

Results and Discussion

As the theme of this investigation is concerned with mono- and di-substituted tellurium hexafluoride, it is pertinent to initially examine the electronic structure of TeF_6. The appropriate bond index and electron densities of TeF_6 are recorded in Table I. It can be readily seen that the valence electrons are polarised towards the fluorine atoms, resulting in a positive charge of 2.62 residing on the tellurium. These migrating electrons originate largely from the tellurium *p* orbitals. There is only a small electronic population in the 5*d* orbitals of Te, indicative of a modest back-bonding system. The Te–F bond index signifies partial single bonds are present in TeF_6. The Te*p*–F component accounts for nearly two thirds of the total, while the Te*d*–F fraction of the Te–F bond is 0.13. The nature of the bond is decidedly sigma in character, with the π-bond index contributing 21.2% of the total.

The Electronic Structure of the Mono- and Di-methoxy and Hydroxy Substituted Derivatives of Tellurium Hexafluoride

The electronic structure of TeF_5OCH_3, TeF_5OH, $TeF_4(OCH_3)_2$ and $TeF_4(OH)_2$ were chosen for examination because of the related practical interest of these compounds.[7,8] The calculated bond indices and electron densities are presented in Table II. It can be seen that the Te–F bonds *cis* to the substituted ligands are weaker than those which are *trans* to the Te–O bonds. Before examining in depth the reasons for the *cis*-influence, it is useful to glance cursorily through the electronic structures of the pentafluoro and tetrafluoro compounds. The addition of a Te–O bond reduces the strength of the bonds already present, while the positive charge on the tellurium is decreased and the fluorine atoms become more negatively charged. Hence, replacement of fluorine by a $-OCH_3$ or $-OH$ group results in an accumulation of charge on the fluorotellurium moiety, which is to be expected from electronegativity considerations.

In order to see in more detail how the substitution of a methoxy or hydroxy group for a fluorine atom affected the bonding patterns, it is necessary to examine the component bond indices of the mono-substituted compound which are displayed in Table II. The largest difference between the components of the two Te–F bonds occurs with Te*s*–F and, in particular, with the Te*s*–F*p* constituents. The Te*p*–F and Te*d*–F fractional bond indices are both larger for the *cis*-bond but the differences are not as great as those between the aforementioned Te*s*–F components, which favour the *trans*-bond. The Te–F π-bond ingredient is altered upon substitution whereupon the *trans*-bond content is increased, while the magnitude of the *cis*-bond π-fraction is decreased. A similar inspection of the Te–O bond TeF_5OCH_3 and TeF_5OH reveals that the bond index is much larger that the replaced Te–F bond. This emanates from a large Te–O σ-bond character accompanied by a π-bond component which is larger and smaller, in the case of the hydroxy and methoxy compound respectively, than the corresponding Te–F π-bond character. Increase in the σ-bonding due to substitution causes an increase in the *trans* Te*s*–F σ-bond. Furthermore, increased participation by the

TABLE I. The Valence Electronic Structure of TeF_6.

Electron Densities					
Te	*s*	1.195	F	*s*	1.782
	p	1.917		*p*	5.654
	d	0.270		*Total*	7.436
	Total	3.382			
Bond Index					
	Te*s*–F	0.160			
	Te*p*–F	0.435			
	Te*d*–F	0.088			
	Te–F	0.683			
	π(Te–F)	0.145			

TABLE II. The Valence Electronic Distribution in TeF_5OH, TeF_5OCH_3, $TeF_4(OH)_2$ and $TeF_4(OCH_3)_2$.

Electron Densities	TeF_5OH	TeF_5OCH_3	$TeF_4(OH)_2$	$TeF_4(OCH_3)_2$
Te	3.476	3.514	3.564	3.619
F *cis*	7.457	7.471	7.481	7.508
F *trans*	7.438	7.445	7.458	7.475
O	6.426	6.404	6.442	6.430

Bond Indices	TeF_5OH		TeF_5OCH_3		$TeF_4(OH)_2$		$TeF_4(OCH_3)_2$	
	Te–F *cis*	Te–F *trans*	Te–F *cis*	Te–F *trans*	Te–F *cis*	Te–F *trans*	Te–F *cis*	Te–F *trans*
Te*s*–F	0.146	0.163	0.137	0.161	0.135	0.150	0.126	0.142
Te*p*–F	0.424	0.420	0.422	0.416	0.404	0.408	0.390	0.403
Te*d*–F	0.090	0.088	0.085	0.086	0.089	0.090	0.076	0.085
Te–F	0.660	0.671	0.644	0.663	0.628	0.648	0.592	0.630
π(Te–F)	0.140	0.147	0.135	0.146	0.133	0.143	0.117	0.137

tellurium p-orbital in the σ-bonding scheme will ensure a decreased share by the same p-orbital in the trans Tep–F σ-bond and *cis* Tep–F π-bonds. The change in the π-bonding scheme due to the introduction of a Te–O bond with a relatively large π-bond component results in an increase in the *trans* Te–F π-bond component and, at the same time, there is a reduction in the *cis* Tep–F σ-bond as it uses the same Tep orbital. These are the two main components present in a very complicated process involving many small secondary effects.

The electronic structures of the di-methoxy and di-hydroxy tellurium tetrafluoride compounds are presented in Table II. Rationalisation of the calculated bond indices was not attempted, as of the two unique Te–F bonds present in the tetrafluorides, one is *cis* and *trans* to the Te–O bonds, while the other is *cis* to both the Te–O bonds. The calculated bond index of the latter bond is lower than the former and can be correlated with experimental findings[9]. The difference between the two types of Te–F bond indices is larger for the di-substituted case than for the mono-substituted molecule and so the weakening of the Te–F bond appears to be largely reinforced by the presence of a further *cis* Te–O bond. Concentration on the electronic structure of the molecules and on the prediction of particular bond breaking upon ligand attack is essentially related to the mechanistic aspects of ligand substitution. It is also possible to present a guide to the thermodynamics of ligand substitution by calculating the relative stabilities of the *cis*- and *trans*-substituted products. The *trans*-isomer is computed to be more stable, although the energy difference is very small. Therefore, if a suitable transition state can be easily formed during the ligand substitution, then the formation of the *trans*-product cannot be discounted.

Cis-series of Ligands

It is of some interest to examine a series of mono-substituted tellurium hexafluoride compounds, TeF_5X, and attempt to correlate the changes in the calculated Te–F bond indices with the structure of ligand X, and hence compile a *cis*-series of ligands. The ligands chosen were –H, $-CH_3$, $-NH_2$, –OH, –Cl, –Br, $-SiH_3$, $-PH_2$, and –SH, and the details of the resulting electronic structures are presented in Table III. It is found that all the ligands are *cis*-directing except –H, which produces a weaker Te–F *trans*-bond. The absence of any tellurium–ligand π-bonds must be a direct factor in the

TABLE III. Electronic Structures of Mono-substituted Tellurium Hexafluoride Compounds, TeF_5X.

X =	Electronic Charge				Bond Indices			
	Te	F	F	X	Te–F	Te–F	Te–X	π(Te–X)
		cis	*trans*		*cis*	*trans*		
–F	2.62	–0.44	–0.44	–0.44	0.683	0.683	0.683	0.145
–H	2.35	–0.46	–0.43	–0.08	0.668	0.648	0.858	–
$-CH_3$	2.39	–0.50	–0.44	–0.30	0.625	0.658	0.989	0.180
$-NH_2$	2.46	–0.48	–0.44	–0.40	0.636	0.662	0.937	0.203
–OH	2.52	–0.46	–0.44	–0.43	0.659	0.671	0.835	0.183
–Cl	2.40	–0.44	–0.43	–0.20	0.634	0.662	1.173	0.343
–Br	2.30	–0.45	–0.42	–0.10	0.625	0.665	1.150	0.291
$-SiH_3$	2.21	–0.49	–0.42	0.09	0.583	0.644	1.210	0.227
$-PH_2$	2.31	–0.48	–0.43	–0.23	0.589	0.645	1.322	0.311
–SH	2.31	–0.47	–0.43	–0.12	0.599	0.655	1.289	0.343

Partial Bond Indices

	TeF_5H		TeF_5CH_3		TeF_5NH_2		TeF_5Cl	
	trans	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*
Tes–F	0.197	0.137	0.165	0.116	0.165	0.132	0.179	0.145
Tep–F	0.352	0.439	0.407	0.415	0.409	0.413	0.397	0.404
Ted–F	0.099	0.093	0.086	0.094	0.088	0.091	0.086	0.085
Te–F	0.648	0.669	0.658	0.626	0.662	0.636	0.662	0.634
π(Te–F)	0.147	0.124	0.151	0.134	0.149	0.135	0.150	0.125

	TeF_5Br		TeF_5SiH_3		TeF_5PH_2		TeF_5SH	
	trans	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*
Tes–F	0.187	0.132	0.184	0.091	0.182	0.113	0.183	0.119
Tep–F	0.394	0.407	0.381	0.404	0.382	0.389	0.387	0.392
Ted–F	0.084	0.085	0.079	0.088	0.081	0.087	0.084	0.087
Te–F	0.665	0.625	0.644	0.583	0.645	0.589	0.654	0.598
π(Te–F)	0.148	0.124	0.146	0.116	0.150	0.115	0.149	0.121

formation of stronger *cis* bonds The best *cis* directing group is $-SiH_3$ while $-PH_2$ and $-SH$ moieties are also powerful *cis* directors All these groups form strong σ and π bonds with tellurium especially π bonds which means that the *cis* Te–F bonds are weakened correspondingly All the ligands examined form a stronger bond to the tellurium than fluorine and so the charge on the tellurium is reduced by the presence of a more covalent bond The electron density of the *cis* fluorine atom becomes greater while the charge on the *trans* fluorine decreases by the introduction of a ligand into the TeF_5 unit The rationale applied above to the substitution pattern of methoxy and hydroxy derivatives is confirmed by the results in Table III Weaker *cis* Te–F π bonds are found in the presence of a stronger Te–ligand σ bonds Furthermore weaker *cis* Te–F σ bonds are obtained when strong Te–ligand π bonds occur Finally the ligands can be arranged in an order of increasing *cis* influence

$$-H < -OH < -NH_2 < -Cl < -CH_3 < -Br < -SH \sim -PH_2 < -SiH_3$$

The disposition of these ligands is somewhat related to the arrangement of ligands with increasing *trans* influence in Pt^{II} square complexes[6] It appears that in both series the presence of low lying vacant *d* orbitals on a ligand reinforces the bonding between the ligand and the central metal atom and strengthens the directing properties of the ligand

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