

¹²⁵Te Mössbauer Spectra of Metal Halide Complexes of Di-(*p*-ethoxyphenyl)telluride: a Possible Scale of Lewis Acidity

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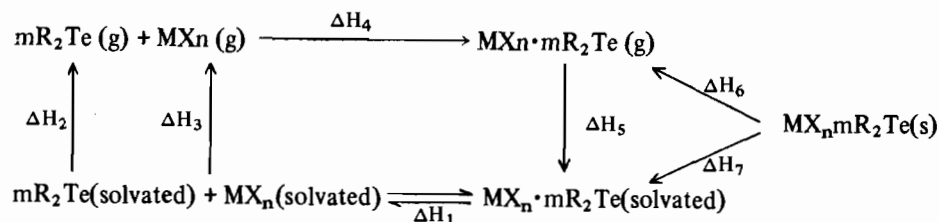
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The concept of even a semi-quantitative scale of Lewis acidity and basicity has always been attractive to co-ordination chemists [1, 2]. The formation of a complex between a diorganotelluride (Lewis base) and a metal halide (Lewis acid) may be illustrated by the simple enthalpy cycle following Drago [3]:

SCHEME.

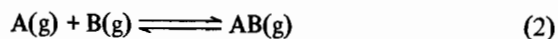


Of the terms indicated, only ΔH_4 can be considered to derive from electronic effects resulting from co-ordination of the base to the acid, and quite frequently the solvation and lattice terms are of the same order of magnitude.

Generally, it is the term ΔH_1 that is most readily accessible experimentally, hence the problem becomes one of predicting trends in ΔH_4 from known trends in ΔH_1 . Drago *et al.* [4] proposed that enthalpy changes in the gas phase could be expressed by the equation:

$$-\Delta H = E_A E_B + C_A C_B \quad (1)$$

where A (acid) and B (base) relate to reacting species such that:



and where the E and C parameters relate to electrovalent ("hard") and covalent ("soft") character. The significant feature of equation (1) is that the fact that "hardness" and "softness" [2] are not mutually exclusive properties, is emphasised [3]. The E and C parameters may be derived empirically to form a

TABLE. Mössbauer Parameters

	δ^a (mm sec ⁻¹)	Δ^b (mm sec ⁻¹)	U_Z
(<i>p</i> -EtOC ₆ H ₄) ₂ Te (L)	0.24	11.13	2.00
CuCl•L ₂	0.09	9.0	1.82
CuBr•L ₂	0.18	8.8	1.80
CuI•L	0.15	9.2	1.84
PdCl ₂ •L ₂	0.31	7.61	1.70
PdBr ₂ •L ₂	0.29	6.78	1.64
PtCl ₂ •L ₂ (<i>cis</i>)	0.35	6.63	1.62
PtCl ₂ •L ₂ (<i>trans</i>)	0.12	6.61	1.62
HgCl ₂ •L	0.32	5.96	1.57
HgBr ₂ •L	0.37	6.00	1.57
HgI ₂ •L	0.28	6.25	1.59

^a±0.08 mm sec⁻¹, vs. ¹²⁵Sb/Cu. ^b±0.1 mm sec⁻¹.
 (All compounds gave satisfactory elemental analysis).

self consistent set which may then be used predictively. However, the design of an experimental method which yields a quantity which is primarily influenced by the term ΔH_4 (scheme) is attractive.

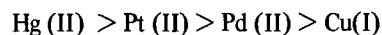
The ¹²⁵Te Mössbauer parameters of organotellurium derivatives of Te(II) and Te(IV) are very much dominated by lone pair effects. The studies currently made of the Mössbauer spectra of organotellurium compounds [5–7] may be analysed to self consistency if it is assumed (a) that covalent bonding to tellurium involves primarily p-orbitals and that one pair of electrons remains in an orbital of largely s-character. (b) That quadrupole splitting data (Δ) is conveniently analysed using Towns–Dailey theory [8] which, in essence, relates the magnitude of the splitting to an imbalance in occupation of the p-orbitals. The domination of lone pair effects is such that any variation in Mössbauer parameters across a series of complexes of metal halides with a particular diorganotelluride is likely to reflect a variation in ΔH_4 across the series, *despite the fact that measurements are made for a solid complex*. To test this hypothesis, we have synthesised a range of complexes of di(*p*-

ethoxyphenyl)telluride [9]. This base was selected due to the ease of synthesis, purification and handling of the white crystalline material. The Table gives Mössbauer parameters of a range of complexes with metal halides of the class B acceptor type [1] (tellurides complex rather exclusively with class B acceptors).

The chemical isomer shift (δ) is seen, within the error of the measurement, to be very insensitive to complex formation. This implies that we may reasonably assume that the p- lone pair is primarily involved in the donation to the acceptor – more particularly we may exclude significant rehybridisation at tellurium (which should significantly lower δ by direct removal of s electron density from the nucleus). Nor is there compelling evidence, from the data, that backbonding to tellurium d-orbitals is a major feature of the bonding – certainly the large experimental error on δ does not allow this point to be pursued.

The more informative parameter is Δ . From our earlier work [5] we may define U_x , U_y and U_z as the occupation numbers of the p_x , p_y and p_z orbitals. Thus, assuming that bonding to carbon involves pure tellurium p orbitals, and placing $U_z = 2.00$, we calculate for $(p\text{-EtOC}_6\text{H}_4)_2\text{Te}$, $U_x = U_y = 1.07$. Using this figure for U_x and U_y we may then calculate U_z for the complexes from the observed quadrupole splitting (Table). We argue that Δ is primarily influenced by the donor–acceptor interaction of telluride with metal halide and that trends in its measured value reflect trends in ΔH_4 (scheme). The values of U_z express this in a different way and suggest that the actual drift of electrons to the Lewis acid is quite small even in the most favourable case. If

we average sets of U_z numbers for each metallic element, we arrive at an order of Lewis acidity relative to $(p\text{-EtOC}_6\text{H}_4)_2\text{Te}$:



There is nothing surprising in the series, but perhaps that is reassuring. Experiments continue to investigate the possibility that finer distinctions in Lewis acidity may be detected.

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