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

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TABLE. Mössbauer Parameters

	δ^{a} (mm sec^{-1})	Δ^{b} (mm sec^{-1})	U_Z
$(p\text{-EtOC}_6H_4)_2$Te (L)	0.24	11.13	2.00
$CuCl{\cdot}L_2$	0.09	9.0	1.82
$CuBr{\cdot}L_2$	0.18	8.8	1.80
$CuI{\cdot}L$	0.15	9.2	1.84
$PdCl_2{\cdot}L_2$	0.31	7.61	1.70
$PdBr_2{\cdot}L_2$	0.29	6.78	1.64
$PtCl_2{\cdot}L_2$ (*cis*)	0.35	6.63	1.62
$PtCl_2{\cdot}L_2$ (*trans*)	0.12	6.61	1.62
$HgCl_2{\cdot}L$	0.32	5.96	1.57
$HgBr_2{\cdot}L$	0.37	6.00	1.57
$HgI_2{\cdot}L$	0.28	6.25	1.59

[a]±0.08 mm sec^{-1}, *vs.* ^{125}Sb/Cu. [b]±0.1 mm sec^{-1}.
(All compounds gave satisfactory elemental analysis).

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.

$$\begin{tikzcd}
mR_2Te\,(g) & + & MXn\,(g) \arrow[r, "\Delta H_4"] & MXn{\cdot}mR_2Te\,(g) \arrow[dd, "\Delta H_5"] & \\
& & & & MX_nmR_2Te(s) \arrow[ul, "\Delta H_6"'] \arrow[dl, "\Delta H_7"] \\
mR_2Te(\text{solvated}) \arrow[uu, "\Delta H_2"] & + & MX_n(\text{solvated}) \arrow[uu, "\Delta H_3"'] \arrow[r, shift left, "\Delta H_1"'] & MX_n{\cdot}mR_2Te(\text{solvated}) \arrow[l, shift left] &
\end{tikzcd}$$

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:

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

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

$$A(g) + B(g) \rightleftharpoons AB(g) \qquad (2)$$

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 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 ^{125}Te 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 $(p\text{-EtOC}_6H_4)_2Te$, $U_x = U_y = 1.07$. 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 influence 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 $(p\text{-EtOC}_6H_4)_2Te$:

$$\text{Hg (II)} > \text{Pt (II)} > \text{Pd (II)} > \text{Cu(I)}$$

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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