Evidence from the Photoelectron Spectra of some Mercury(II) Compounds for the Involvement of the Inner 5*d* Electrons in Covalent Bonding

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Summary Structure corresponding to ionisation of the inner 5*d* electrons, observed in the He-I photoelectron spectra of $HgMe_2$, MeHgCN, and $Hg(CN)_2$, provides evidence for $d_\pi \rightarrow \pi^*$ back-donation in the Hg–CN bond; d_{z^2}–s hybridisation is apparently not a strong effect.

THE filled penultimate subshells, $(nd)^{10}$, of B metal atoms are normally regarded as being essentially core-like, though there are two respects in which it is sometimes supposed that the inner *d* electrons may be involved in chemical bonding. One hypothesis[1] is that in compounds with unsaturated ligands there is a significant donation of *d* electron density from the metal atom into low-lying antibonding π orbitals on the ligand group (so called $d_\pi \rightarrow \pi^*$ 'back-bonding'). The other,[2] advanced to explain the preference for linear 2-co-ordination shown by many $(nd)^{10}$ cations,[3] concerns the *d* electrons of σ symmetry: a covalent effect, formally equivalent to $nd_{z^2}/(n+1)s$ hybridisation at the metal atom, was postulated. We report the He-I photoelectron spectra† of some mercury(II) compounds, in particular $HgMe_2$,‡ MeHgCN, and $Hg(CN)_2$ (the last two compounds involving a ligand species that is generally supposed to be a good π acceptor[4]). We show that high resolution photoelectron spectroscopy provides novel information about the nature of the inner *d* electrons.

The 5*d* structure evident in the He-I spectrum of $HgMe_2$ (Figure 1) is quite similar to that observed for the dihalides HgX_2 (X = Cl, Br, and I)[5,6a] and for the methylmercury halides MeHgX.[5,7] Three well resolved band systems are observed, two of which (the higher ionisation energy bands) appear to represent overlapping structure corresponding in each case to two distinct ionisation processes. The form of this 5*d* structure is of course dominated by the effects of spin–orbit coupling in the molecular ion (*cf.* the widely separated multiplets, $^2D_{5/2}$ and $^2D_{3/2}$, observed for the atomic mercury 'impurity' structure Y in the $Hg(CN)_2$ spectrum, Figure 1). Even so, the influence of the molecular field, whatever its nature, is clearly significant since each of the five multiplet states ($^2\Sigma_{1/2}$, $^2\Pi_{1/2,3/2}$, and $^2\Delta_{3/2,5/2}$) expected for the C^*_∞ spinor group can apparently be observed in the $HgMe_2$ photoelectron spectrum.§ A close comparison of this spectrum with those of the dihalides, together with model calculations¶ of the energy levels of the perturbed $5d^9$ configuration,[8] suggests that the sequence of multiplet states in the molecular ions $HgMe_2^+$ and HgX_2^+ is $^2\Delta_{5/2} < {}^2\Pi_{3/2} \sim {}^2\Sigma_{1/2} < {}^2\Delta_{3/2} \sim {}^2\Pi_{1/2}$. (The mixing effect of spin–orbit coupling is of course considerable

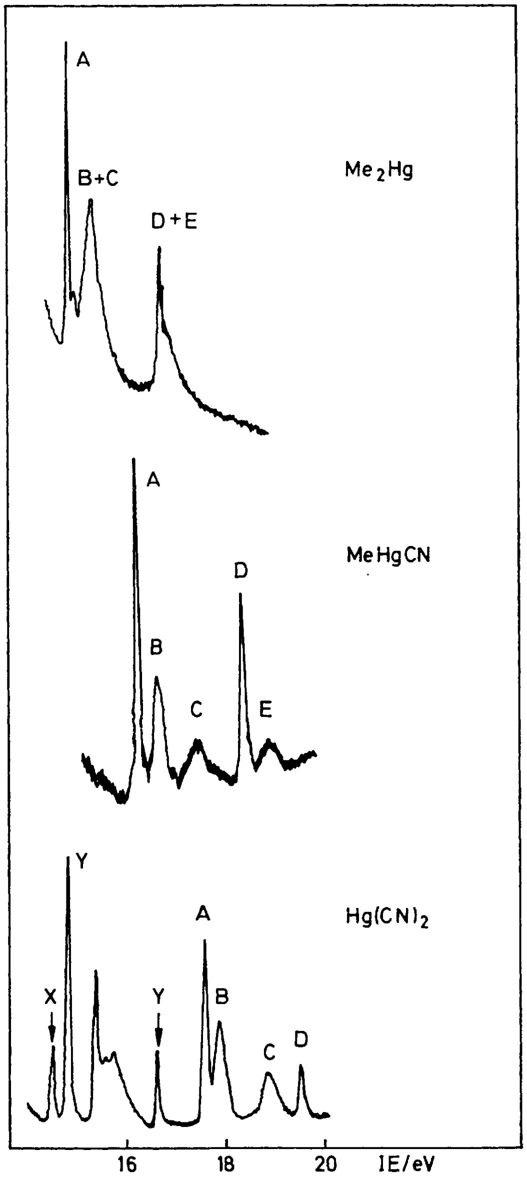

FIGURE 1. A comparison of the 5*d* regions of the He-I photoelectron spectra of $HgMe_2$, MeHgCN, and $Hg(CN)_2$ (see text).

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† The He-I (21·2 eV) spectra of $HgMe_2$ and $Hg(CN)_2$ in Figure 1 were obtained using a Perkin-Elmer PS 16/18 instrument while that of MeHgCN was measured on a spectrometer built in this laboratory.[6] Spectra of MeHgCN recorded on the PS 16/18 are in good agreement with those in Figure 1. The measurements on $Hg(CN)_2$ required a sample temperature of around 220 °C when partial decomposition, as evidenced by structure attributable to atomic mercury (Y) and cyanogen (X), proved unavoidable. Separate measurements on the other spectrometer, modified to take a Perkin-Elmer heated probe, substantiate the spectrum of $Hg(CN)_2$ shown in Figure 1. The *X*-ray photoelectron spectra (Figure 2), excited with Al-K_α radiation, were recorded on an AEI ES 200 spectrometer, the Hg^{II} compounds being sublimed directly on to the cooled sample probe.

‡ The He-I spectrum of $HgMe_2$ (together with spectra of other Hg^{II} compounds) has been reported by Eland:[5] the 5*d* ionisations were, however, not fully characterised in these earlier spectra.

§ We have not found it necessary to admit the possibility that any part of the 5*d* structure is due to 'shake up' (K. Siegbahn *et al.* 'ESCA Applied to Free Molecules,' North Holland, Amsterdam) (many-electron) processes.

¶ These calculations employ adjustable parameters both for the orbital energies of the σ, π, and δ type *d* electrons and for the average spin–orbit coupling constant ξ_{5d}. The model takes into account the mixing effects of the spin-orbit interaction.

and the term parentages given for the $\frac{3}{2}$ and $\frac{1}{2}$ multiplets indicate only the majority orbital character.) The relative sharpness of the first 5*d* band (A) in a range of Hg^{II} compounds[5–8] substantiates its assignment to ionisation of the (necessarily) non-bonding $\delta(d)$ electrons. In the particular case of $HgMe_2$ the similarity of the vibrational structure observed for the first and fourth 5*d* ionisations (bands A and D in Figure 1) suggests that the latter relates to the $^2\Delta_{3/2}$ multiplet state, rather than $^2\Pi_{1/2}$.

The sequence of ion multiplet states deduced above implies (by Koopmans' theorem[9]) the *orbital* energy ordering $\delta > \pi > \sigma$ (where the d_σ electrons are the most tightly bound) which is not that expected for a crystal field effect.[10] This conclusion is in sharp contrast to that reached on the basis of an analysis of the 3*d* structure that we have observed in the He-I spectra of the zinc dihalides ZnX_2 and $ZnMe_2$,[11] which can be understood in terms of the *d* orbital sequence $\sigma > \pi > \delta$, expected for a simple electrostatic perturbation of the 3*d* subshell. The orbital energy sequence inferred for $HgMe_2$ (and the dihalide species HgX_2) indicates that covalent interactions outweigh the electrostatic terms which appear to be dominant in the zinc compounds. The apparent stabilisation of the d_σ electrons is consistent with the hypothesis of d_{z^2}–*s* hybridisation,[2] though the effect is hardly dramatic.

Compared with $HgMe_2$, the 5*d* structure in the He-I spectrum of MeHgCN (Figure 1) shows the overall shift to higher ionisation energy that would be expected on the basis of an increased effective positive charge on the mercury atom. For example, the first band (A), which is again very sharp, has shifted by some 1·34 eV relative to $HgMe_2$. More significant, however, is the observation of a differential shift of the various 5*d* bands, leading to complete resolution of all five elements. In the light of our previous discussion, the MeHgCN spectrum is most naturally interpreted in terms of the multiplet sequence[2] $\Delta_{5/2} < {}^2\Sigma_{1/2} < {}^2\Pi_{3/2} < {}^2\Delta_{3/2} < {}^2\Pi_{1/2}$. The sharpness of the first (A) and fourth (D) bands argues strongly for assignment to $^2\Delta_{5/2}$ and $^2\Delta_{3/2}$, respectively, the latter band having apparently shifted by 1·43 eV. Similarly, the rather broad bands, C and E, which are displaced by 1·97 and 1·88 eV, respectively, relative to their apparent counterparts in the $HgMe_2$ spectrum, are most obviously assigned to the $^2\Pi$ multiplet states. The second band (B), of intermediate width and shifted by 1·25 eV, we take to represent the $^2\Sigma_{1/2}$ state.**

This interpretation is confirmed by a comparison of the He-I spectra of MeHgCN and $Hg(CN)_2$ (Figure 1). However, a satisfactory correspondence between these spectra depends on the assumption that the fifth 5*d* ionisation of $Hg(CN)_2$, corresponding to band E in the MeHgCN spectrum has not been detected. The 5*d* region of the *X*-ray photoelectron spectra of these compounds supports this hypothesis for, in the case of $Hg(CN)_2$, a weak shoulder, absent in the spectra of the dihalides HgX_2, is discernible on the high ionisation energy side of the 5*d* band system (Figure 2). Our interpretation of the He-I spectrum of $Hg(CN)_2$ is then such that, compared with the spectrum of $HgMe_2$, the first 5*d* band ($^2\Delta_{5/2}$) is displaced a further 1·37 eV to higher ionisation energy, while the subsequent three bands (B—D) show additional shifts of 1·27, 1·54, and 1·38 eV, respectively. These shifts are in line with those observed on passing from the spectrum of $HgMe_2$ to that of MeHgCN (though the $^2\Pi_{3/2}$ band, C, is less dramatically affected) and, extrapolating on the basis of our assignment, the missing $^2\Pi_{1/2}$ band is expected to occur at *ca.* 20·2 eV ionisation energy (that is, with *ca.* 1·5 eV shift relative to MeHgCN). This is indeed beyond the limits of detection, for such a weak and probably rather diffuse band. We cannot reliably estimate the ionisation energy of the $^2\Pi_{1/2}$ band from the *X*-ray spectrum since it is not clear how it should be mapped on to the He-I spectrum.

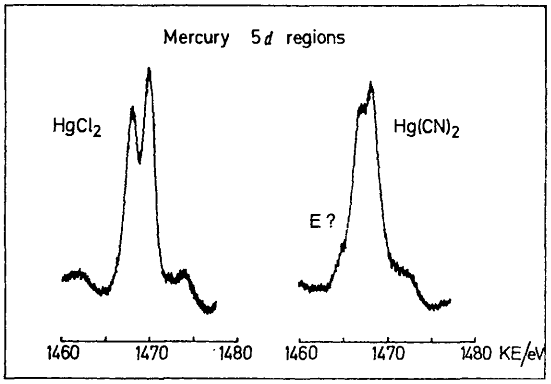

FIGURE 2. The valence regions of the *X*-ray photoelectron spectra of $HgCl_2$ and $Hg(CN)_2$.

We conclude that there appears to be a preferential stabilisation of the $\pi(d)$ level on substitution of Me by CN in $HgMe_2$ and MeHgCN. This effect, substantial for MeHgCN, we attribute to back-donation of electron density from the d_π orbitals of the inner 5*d* subshell to the antibonding π orbitals of cyanide. We believe this to be the first reasonably direct evidence for $d_\pi \rightarrow \pi^*$ back-bonding in compounds involving formally d^{10} cations of the B subgroup elements.

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** The small shift of the $^2\Sigma_{1/2}$ band (B), in relation to the other 5*d* bands, presumably reflects the diminished σ donor properties of CN as compared with Me.

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