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Mercury–Sulphur Bonding in Some Di(alkylthio)mercury(II) Compounds Studied by Means of Ultraviolet Photoelectron Spectroscopy

PAOLO BISCARINI

Istituto di Chimica Fisica e Spettroscopia dell'Università, Viale Risorgimento 4, Bologna, Italy

FRANCESCO PAOLO COLONNA, MAURIZIO GUERRA and GIUSEPPE DISTEFANO

Istituto dei composti del carbonio contenenti eteroatomi e loro applicazioni del CNR, Via Tolara di Sotto 89, Ozzano Emilia, Bologna, Italy

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The analysis of the photoelectron HeI spectra of the compounds $Hg(SR)_2$ *(R = Me, Et,* Pr^n, Pr^i, Bu^n, Bu^i *and* Bu^t*) and of the results of iterative extended Hückel calculations on selected members of the series suggests that in these compounds the Hg–S bonds have a partial double-bond character due to a weak π-interaction between the filled 3*p *sulphur orbitals and the empty 6*p *orbitals of mercury.*

Introduction

The nature of the mercury–sulphur bond in organothiomercury(II) compounds of the type $Hg(SR)_2$, *1*, and Hg(SR)X (X = Cl, Br, I), *2*, is not yet fully understood [1, 2]. In the IR and Raman spectra of some di(alkylthio)mercury(II) compounds, *1*, the frequency related to the strength of the mercury–sulphur bond, ν(S–Hg–S), decreases with increasing electron releasing ability of the alkylthio groups, but the absence of a strictly linear correlation did not allow the establishment of a definite bonding model [1].

From the study of compounds *2*, it was not possible to clarify if, in addition to the S–Hg σ bond, a π bond involving 5*d* orbitals of mercury and 3*d* orbitals of sulphur must be taken into account [2]. The involvement of this type of bonding was suggested for $Hg(SCN)_2$, but the weight of this factor depends on the relative energy of the *d* electrons of the metal and of the orbitals of the ligand groups [3,4].

Evidence of back-donation from the mercury 5*d* orbitals was obtained from the photoelectron spectra of Hg(CN)Me and $Hg(CN)_2$, whereas the spectrum of $Hg(SCF_3)_2$ showed only slight bonding participation of the mercury 5*d* electrons [5, 6]. According to UV and X-ray photoelectron (UPS and XPS) data and theoretical calculations on some difuryl and dithienyl derivatives, the central mercury atom acts as a slight π-acceptor [7]. In these compounds there is a small charge-transfer interaction between the ring π-orbitals and the empty $6p_\pi$ mercury atomic orbitals, which explains the observed π-orbital splitting, while the 5*d* atomic orbitals of mercury participate very little in bonding. This suggests that even in the $Hg(SR)_2$ series, mercury could operate as a π-electron acceptor. We have therefore undertaken a UPS and theoretical analysis of the series *1* compounds where R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^i and Bu^t in order to ascertain the involvement in bonding of the empty 6*p* and/or filled 5*d* AO's of mercury and the 3*p* and/or 3*d* AO's of sulphur. Calculations have been carried out at the iterative extended Hückel level (IEHMO) [7] on selected compounds.

Experimental and Calculations

The UPS spectra were obtained with a Perkin-Elmer photoelectron spectrometer using the HeI resonance line at 584 Å (21.22 eV) as ionizing radiation. The spectra were calibrated against argon and Xe lines. The reproducibility of the ionization energy (IE) values was ±0.05 eV. The di(alkylthio)-mercury(II) compounds were prepared and purified as described [1].

In the present IEHMO calculations the coulomb integrals were approximated as the negative of the valence orbital ionization potentials (VOIP) allowing for the effects of charge and configuration upon them [8]. $VOIP^q$ as a function of the atomic charges (q = 0, +1, −1) were taken from the literature [8, 9] except those for the mercury atom which were calculated from atomic term values (see Table I) [10]. The orbital exponents of Slater functions were taken from Clementi and Raimondi [11] except for that of the 3*d* orbital of sulphur [12] and for the orbitals of the mercury atom [13]. Geometric parameters were obtained from structural data [14] using standard geometric values for the alkyl groups.

TABLE I. VOIP (eV) for the Mercury Atom.

Orbital	Atomic charge, q		
	+1	0	−1
6s	18.75	10.43	4.32
6p	11.61	4.87	−1.36
5d	25.01	15.58	8.78

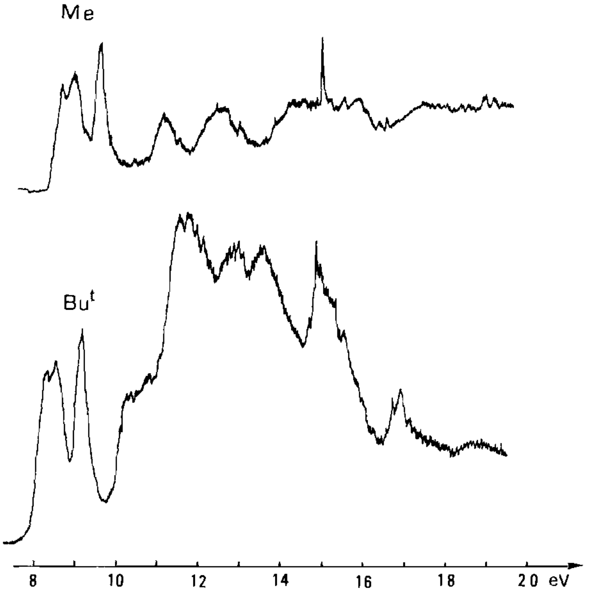

Fig. 1. Photoelectron HeI spectra of di(methylthio)- and di(t-Buthyltio)-mercury, $Hg(SR)_2$ (R = Me, Bu^t).

Results and Discussion

The HeI photoelectron spectra of representative compounds are shown in Fig. 1 and the first few experimental IE values are collected in Table II. The spectra show at low IE (<10 eV) two bands (largely overlapped when R = Et and Bu^n) the first of which is often partially split in two components. The intensity of these bands with respect to the following bands in the spectra decreases with increasing size of R. Ionization from MOs mainly localized at the substituent groups is in fact expected between 11 and 15 eV. Ionization of the mercury 5*d* AOs using HeI radiation gives rise to low intensity bands [7, 15] which are often hidden by bands arising from other photoprocesses. In addition, some thermal decomposition occurs (especially when R = Et) which produces atomic mercury. For these reasons, these ionizations are not further discussed.

To facilitate the analysis of the UPS data they are compared with those of the related symmetric dithiaalkanes, RS–SR, taken from the literature [16].

TABLE II. Experimental and Calculated (IEHMO, in parentheses) Ionization Energies (IE, eV) of Some Di(alkylthio)-mercury Derivatives, $Hg(SR)_2$.

R	IE_1 (n_s^-, B_g)^a	IE_2 (n_s^+, A_u)	IE_3 (σ, B_u)	IE_4 (σ, A_g)
Me	8.65	8.94	9.54	11.1
	(9.84)	(10.20)	(9.98)	(10.97)
Et	8.69	8.93	9.3	11.0
Pr^n	8.68		9.26	10.7
Pr^i	8.42	8.67	9.25	10.5
	(9.42)	(9.72)	(9.63)	(10.50)
Bu^n	8.60	8.82	9.18	10.6
Bu^i	8.64		9.27	10.4
Bu^t	8.32	8.58	9.15	10.3
	(9.38)	(9.69)	(9.53)	(10.47)
CF_3	10.2^b		11.4^b	12.3^b
	(12.06)	(12.40)	(12.21)	(13.23)

^{a}C_{2h} symmetry is assumed. ^{b}Values taken from Ref. 6.

Spatial interaction between the sulphur lone pairs in the latter causes splitting into an n^- and an n^+ combination (n^- above n^+, $\Delta = 0.2$–0.6 eV). The increase of the interatomic distance S····S by insertion of a mercury atom, reduces the 'through space' interaction [17] between the sulphur lone pairs and, therefore, their splitting. At the same time, however, 'through bond' interactions [17] with orbitals of the same symmetry class localized on the Hg atom should be operative thus providing an explanation for the splitting still observed ($\Delta = 0.2$–0.3 eV, see Fig. 1). By symmetry, n^- can be destabilized by interaction with the mercury $5d_\pi$ AO s, while n^+ can be stabilized by charge-transfer towards the empty $6p_\pi$ orbitals of mercury. In any case n^- will lie above n^+. The calculations (see Table II) reproduce the splitting between n^- and n^+ and their relative ordering. They indicate also that the splitting essentially derives from a sizeable participation of the $6p_\pi$ AO of mercury in n^+ (11–13%) and that the 5*d* AOs of mercury participate very little in bonding (~0.4%). These results are in agreement with previous conclusions reached in the study of some diarylmercury compounds [7].

The average value of the first two ionization energies $\overline{IE}_{1,2}$ decreases slightly in the n-alkyl series (8.80 eV when R = Me and Et and 8.7 eV when R = Pr^n and Bu^n), while it changes more significantly with the branching of the alkyl chain (R = Bu^n: 8.71, R = Bu^t: 8.45 eV) in agreement with the increasing hyperconjugative interaction between the alkyl groups and the lone pair of the sulphur atoms. IE_3 decreases steadily with the length of the n-alkyl chain (9.54–9.15 eV) but it is not sizeably influenced by its branching suggesting that this IE is to be related to a σ-MO mainly localized at the Hg–S bonds. The first σ-MO occurs in fact at 9.5 eV in dimethylmercury

TABLE III. Calculated (IEHMO) Net Charges on Atoms or Groups of Some Di(alkylthio)mercury Derivatives $Hg(SR)_2$, with σ (q_σ) and π (q_π) Electronic Charge Transfer away from the Mercury Atom.

R	2S	2R	Hg	q_σ	q_π
CH_3[a]	−0.1992	−0.0280	+0.2272	+0.4818	−0.2546
CH_3	−0.2540	+0.0223	+0.2317	+0.4853	−0.2536
$CH(CH_3)_2$	−0.3149	+0.0920	+0.2229	+0.4651	−0.2422
$C(CH_3)_3$	−0.3237	+0.1059	+0.2178	+0.4604	−0.2426
CF_3	+0.1058	−0.4771	+0.3713	+0.5773	−0.2060

[a] In the first calculation the sulphur 3*d* AO s are not included.

[18] and 9.6 eV in bis-3-thienylmercury [7]. According to the calculations the third uppermost MO is highly localized at the sulphur $3p_\sigma$ orbitals (~90%). IE_4 decrease with increase in both the size and branching of R indicating that it originates from a MO with significant localization at R. The correlation of IE_4 to the fourth calculated MO is supported by the increasing localization at R of this MO (11–16%).

The experimental $\overline{IE}_{1,2}$ values of the mercury derivatives are smaller than those of the corresponding disulphides (except for R = Et in which case the two values are equal [16]). This destabilization could derive from a mesomeric and/or inductive [7, 18] effect of mercury which would release negative charge towards the sulphur atoms. In fact the calculations indicate that, despite the charge-transfer towards its $6p_\pi$ AO, mercury bears a total positive charge indicating that the polarization towards the sulphur atoms of the σ-Hg–S bonds is the prevailing effect. These two interactions are synergic: the highest positive charge on mercury is associated with the strongest $S_{3p} \rightarrow Hg_{6p}$ π-bonding (see Table III). Increasing the size of R, the positive charge slowly decreases on mercury, and significantly increases on the two R substituents, while sulphur becomes steadly more negative.

The inclusion of the sulphur 3*d* AO s in the calculations does not modify the charge on mercury but rather those on sulphur and on the R groups. These AOs participate very little in the various MOs even if their participation slightly increases with the size of R (0.4–1.1%).

Conclusions

Changing R has only a minor influence on the bonding between mercury and the sulphur atoms in di(alkylthio)mercury(II) compounds. The Hg–S bonds have a partial double-bond character due to a weak π-interaction between the filled 3*p* sulphur orbitals and the empty 6*p* orbital of mercury. The back-donation from the filled 5*d* orbitals of mercury to the empty 3*d* orbitals of sulphur is not important on the basis of the present results.

The increasing donor power of the alkyl groups augments the electronic charge on sulphur. This effect, decreasing the difference between the electronegativity of mercury and sulphur, reduces the degree of polarization towards sulphur of the σ-Hg–S bonds. As a consequence, the strength of the synergic $S_{3p} \rightarrow Hg_{6p}$ π-bond decreases giving an explanation of the reduced force constant of the Hg–S bond observed [1] on increasing the size of R. On the other hand, even a strong electron-withdrawing substituent such as CF_3 apparently reduces the force constant of the Hg–S bonds [2]. This finding can be rationalized on the basis of the calculated charge distribution in $Hg(SCF_3)_2$. It is due to the sizeable decrease of the basicity of the sulphur atoms in this compound (see Tables II and III).

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