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Three-co-ordinate Mercury Complex: Photochromism and Molecular Structure of Phenylmercury(II) Dithizonate

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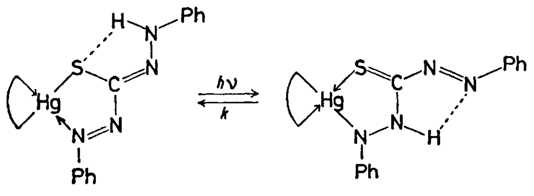
Summary Solutions in organic solvents of 1 : 1 complexes between organomercury(II) cations and dithizone (and its *p*-tolyl analogue) undergo reversible photo-isomerisation (yellow ⇌ blue) at conveniently measurable rates; the structure of the crystalline yellow form of phenylmercury(II) dithizonate involves irregular three-co-ordination about the mercury atom, that of the blue form being deduced from spectroscopic measurements on irradiated solutions.

Irradiation by visible light of solutions of mercury(II) bis(dithizonate) [**1**, $Hg(HDz)_2$] in organic solvents induces a colour change from yellow to blue.[1-4] This, and the thermal reverse reaction, proceed sufficiently slowly ($t_{\frac{1}{2}}$ of the order of minutes) for kinetic measurements to be made,[2,3,5] and spectrophotometric data[3,6,7] point to the equilibrium shown in equation (1), where the conformation of only one of the dithizone residues is shown in detail. Photochromism occurs with all metal dithizonates[2] but the reverse reactions are inconveniently fast except in the case of mercury complexes.



(1)

(1) yellow (2) blue

We have now prepared† by established routes[2,7,8] a series of solid complexes from organomercury(II) cations and dithizone [RHg(HDz); R = Me, Ph, *p*-tolyl, or 2,6-dimethylphenyl], as well as the corresponding complexes with *p*-tolyldithizone. These all display similar photochromism (yellow ⇌ blue) when suitably irradiated in organic solvents, with forward and back reactions proceeding at conveniently measurable rates. Moreover, whereas the low concentration (*ca.* 10^{-3} M) of even a saturated solution of $Hg(HDz)_2$ in CCl_4[9] restricts reliable measurements by n.m.r. spectroscopy,[6] the newly prepared complexes with a single chelated ligand are 100-times more soluble. Investigation by i.r. and ^1H n.m.r. spectroscopy of solutions in the dark or under simultaneous irradiation by visible light supports the conformations of the chelate rings in the yellow and blue forms postulated for $Hg(HDz)_2$ [*cf.* (**1**) and (**2**)]. Details will be reported in the full paper.

It has not proved possible to isolate a specimen of the blue isomer by irradiating crystals of the stable yellow form: photo-isomerisation does not appear to proceed at a measurable rate in the absence of a solvent. Nor has it proved possible to secure crystals of the blue form by carefully and slowly concentrating a solution kept in the blue form by constant and intense illumination: only the stable yellow form crystallizes out. Whereas it has only been possible to assign the structure of the blue isomer [as (**2**)] of phenylmercury(II) dithizonate, PhHg(HDz), from measurements on irradiated solutions, that of the yellow form, as fragile needles, has been established unambiguously by *X*-ray crystallography. *Crystal data:* $C_{19}H_{16}HgN_4S$, M_r 533·03, monoclinic, space group $P2_1/c$,

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† All new compounds reported are crystalline solids for which satisfactory elemental analyses and the usual range of spectroscopic data have been obtained.

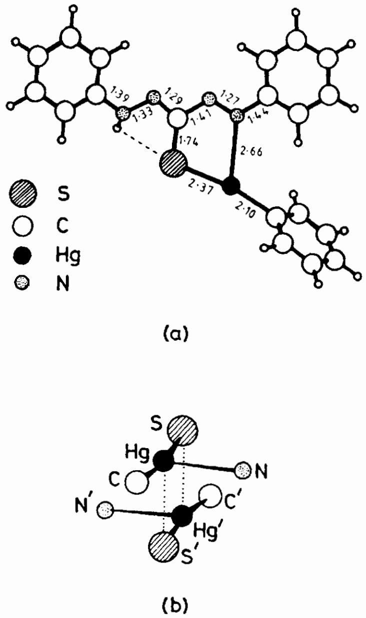

FIGURE. (a) The molecular geometry of phenylmercury(II) dithizonate, showing selected bond lengths (Å; all e.s.d.'s are <0·03 Å). Co-ordinate bond angles: S–Hg–C, 168·0(7); S–Hg–N, 73·6(4); and N–Hg–C, 118·4(8)°. The dashed line indicates a hydrogen bond. The molecule is virtually planar except for the Hg-phenyl ring which is twisted out of this plane by *ca.* 60°. (b) The co-ordination spheres of the Hg atoms in molecules at x, y, z and $-x, 1-y, -z$. The closest interaction (dotted line) is Hg · · · S' (3·69 Å).

$a = 5{\cdot}991(3)$, $b = 20{\cdot}68(1)$, $c = 17{\cdot}129(9)$ Å, $\beta = 99{\cdot}40(5)°$, $U = 2094(2)$ Å^3, $D_m = 1{\cdot}63$ (by flotation), $D_c = 1{\cdot}69$ g cm^{-3}, $Z = 4$, $F(000) = 1016$. The structure was determined by Patterson and Fourier methods using the SHELX[10] program system from data collected by the ω—2θ scan technique in the range $3 \leqslant \theta \leqslant 20°$ on a Philips PW 1100 four-circle diffractometer with graphite-monochromated Mo-K_α radiation [$\lambda = 0{\cdot}7107$ Å, μ(Mo-K_α) = 7·17 mm^{-1}]. Refinement by full-matrix least-squares gave $R = 0{\cdot}058$ for 1354 observed reflections with $I_{\text{rel}} > 2\sigma I_{\text{rel}}$.‡ The Figure [a; *cf.* also (**1**)] gives a perspective view of the molecule in which three atoms may be considered bonded to mercury. The Hg–C bond length is 2·10(2) Å and Hg–S is 2·37(1) Å, with an S–Hg–C angle of 168·0(7)°. These strong bonds and the near linear angle are typical of *sp*-hybridized mercury. However, the Hg–N distance of 2·66(2) Å is 0·34 Å shorter than the sum of the van der Waals radii and constitutes a weak bond.[11] The mercury atom thus exhibits planar, irregular three-co-ordination,[11] the geometry at the mercury atom being approximately T-shaped. Apart from the primary three-co-ordination there is a weak secondary interaction between the Hg atom in the molecule at x, y, z and the sulphur atom of the molecule at $-x, 1-y, -z$ [Figure (b)]. This Hg · · · S' distance is 3·69 Å, which is 0·34 Å larger than the van der Waals sum; thus according to Grdenić's criterion[11] S' is outside the co-ordination sphere of Hg. There are no other secondary interactions. Relatively few examples of three-co-ordinate mercury complexes have been reported[12] and the present structure presents a striking contrast to mercury(II) bis(dithizonate), where a rather distorted tetrahedral co-ordination [as (**1**)] is found, although the conformations of the dithizone residues are identical, *viz. anti*, s-*trans*.[13]

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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