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Photochromic Bisdithizonato Mercury(II): Resonance Raman Spectroscopy of the Orange and Blue Forms

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The Raman and resonance Raman spectra of the photochromic complex bisdithizonato mercury(II) has been recorded in solution using laser excitation in the range 457.9–647.1 nm. Resonance enhancement of bands attributed to normal modes of the orange and blue forms of the complex demonstrate how resonance Raman spectroscopy can provide a method for monitoring the structural changes to the components of a photochromic system. In particular, the resonance enhancement of bands associated with the –C=N–, C=S and –N=N– groups supports, for the light-induced blue form, a structure involving coordinated thiocarbonyl and hydrazyl groups.

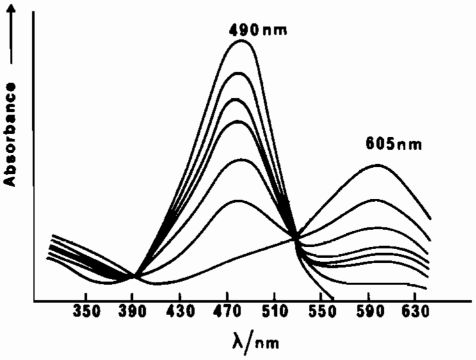

Fig. 2. The visible absorption spectrum of $Hg(HDz)_2$ in $CHCl_3$ solution measured at one minute intervals following irradiation using a 100 W tungsten lamp.

Introduction

Photochromic materials have been recorded and studied for almost a century [1] and for some years now they have been used as photochromic opthalmic glasses. However, it is their wide range of potential applications [2] which makes them materials of considerable current interest. A large number of organic and organometallic photochromes are of particular interest because of their favourable change in optical density on irradiation. Unfortunately, it is this class of photochrome which has proved unsuitable for reasons such as poor stability and high fatigue on recycling. In order to understand and improve on the properties of organic and organometallic photochromes it is necessary to determine the structures of the component molecules of a photochromic system and the mechanism by which the structural changes take place in the system.

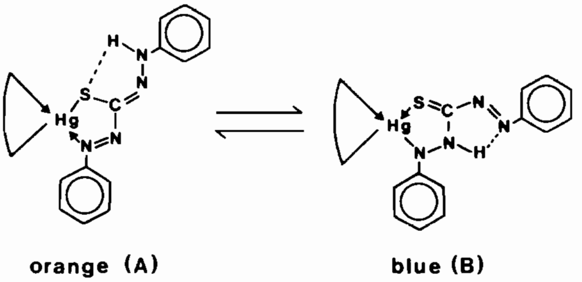

Fig. 1. The structures proposed for the orange (A) and blue (B) forms of $Hg(HDz)_2$ in $CHCl_3$ solution.

The photochromic mercury(II) derivative of the formazan commonly referred to as dithizone (diphenylthiocarbazone), $Hg(HDz)_2$, has been the subject of an earlier investigation [3] in which infrared absorption spectroscopy was used to study the stable orange (A) and metastable blue (B) forms in solution; a kinetic study of the thermal reaction led the authors to propose the structures described in Fig. 1. Using the photochromic $Hg(HDz)_2$ system we will show how resonance Raman spectroscopy can provide a valuable method for obtaining structural information on the components of a photochromic equilibrium.

The visible absorption spectrum of the stable, orange form of $Hg(HDz)_2$ has a band at 490 nm ($\epsilon = 7 \times 10^3$ m^2 mol^{-1}). After irradiation with visible light a second band develops at 605 nm (Fig. 2) due to the formation of the metastable blue form. We

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TABLE 1. Raman Bands and Assignments for $Hg(HDz)_2$ (this work) Compared to Those for $Ag(HDz) \cdot H_2O$ and the Dithizone Anion and to the Infrared Bands and Assignments for 1,3,5-Triphenylformazan. The Raman bands for $Ag(HDz) \cdot H_2O$ and the dithizone anion were obtained using 488.0 nm laser excitation.

$Ag(HDz) \cdot H_2O$[a] CS_2 soln.	HDz-[b] 10^{-3} *M* in pH 12 soln.	Assignment	1,3,5-triphenylformazan[c]		Assignment	$Hg(HDz)_2$		Assignment
			trans-anti- CCl_4 soln.	*trans*-syn solid		$\tilde{\nu}_0$ = 20,400 cm^{-1} $CHCl_3$ soln.	$\tilde{\nu}_0$ = 16,600 cm^{-1} $CHCl_3$ soln.	
1624	1635	C=N				1603		C=N
1589	1598	ring	1570	1513	C=N	1590	1590	ring
1510	1511	asym N=C–N				1534	1534	NCS, NCN
1489								
1457	1468	N=N				1483	1483	NCS, NCN
						1442		
1415	1427	C–N						
1396								
1358	1379	sym N=C–N	1416	1351	N=N	1373	1430	N=N
1298	1307	ring-N–H				1316	1316	NCS, NCN
	1254	ring-N=N	1249	1234	C–N	1220	1220	C–N
1203	1208	NCS						
1188	1172	NCS				1170	1170	NCS, NCN
						1163	1163	NCS, NCN
1153	1156	NCS				1154	1154	NCS, NCN
	1119	NCS	1105	1043	N–N			
			1016	1018				
985	992	ring				998	998	ring
880								
	848							
	753	C–S						
718						621	621	C–N
590	595					602	607	C–S
						265	265	Hg–S

[a] See reference [7]. [b] See reference [6]. [c] See reference [5].

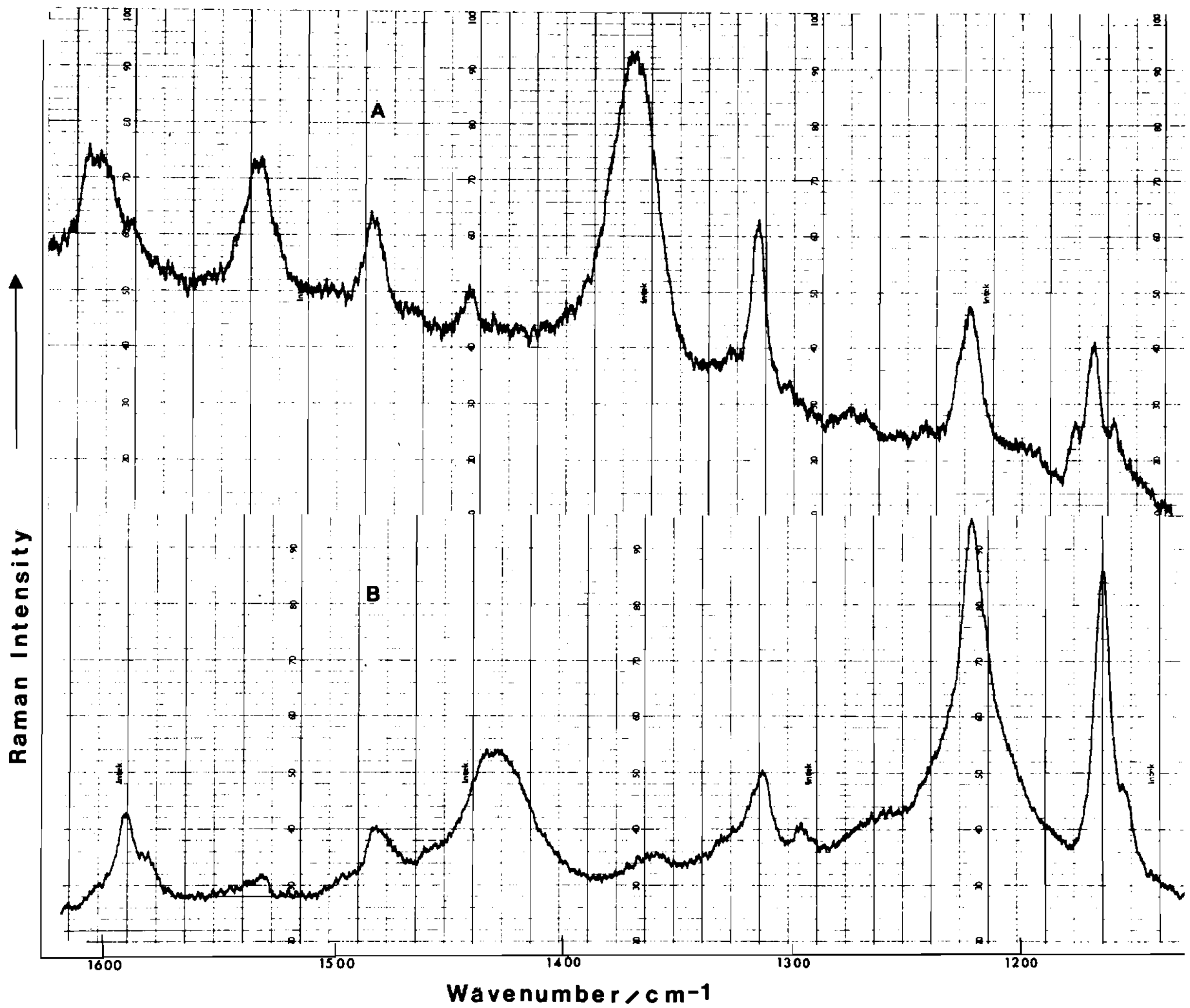

Fig. 3. Resonance Raman spectra of $Hg(HDz)_2$ obtained using 476.5 nm laser excitation (A) and 568.2 nm laser excitation (B).

have investigated the Raman spectrum of $Hg(HDz)_2$ at wavelengths which include the absorption maxima for the orange (A) form and blue (B) form in order to see whether resonance enhancement of bands due to the vibrations of the chromophores are observed.

The observation of resonance enhancement for Raman bands of the orange and blue forms can help to identify those bands which are due to normal modes of each chromophore. This in turn provides a method of monitoring the structural changes of the orange form as it converts to the metastable blue form.

Experimental

Raman spectra of $Hg(HDz)_2$ were obtained from a chloroform solution in a spinning cell in order to prevent decomposition of the sample.

A Spex 1401 spectrometer was used to record the Raman spectra, which were excited by laser lines in the range 457.9 nm to 647.1 nm from Coherent Radiation model 52 argon ion and krypton ion lasers and a Coherent Radiation model 490 dye laser in conjunction with rhodamine 6G. Detection of the scattered radiation was by standard photon counting techniques using a thermoelectrically cooled RCA C31034 photomultiplier.

Band wavenumber measurements were calibrated using the emission spectrum of neon and band intensities, determined as the products of peak height and full-width-at-half-maximum (F.W.H.M.), were corrected for the spectral response of the spectrometer.

Electronic absorption spectra were obtained from a chloroform solution in a silica cuvette using a Cary 14 spectrometer. The blue (B) form of $Hg(HDz)_2$ was generated by irradiating the cuvette for one minute using a 100 W tungsten lamp.

The $Hg(HDz)_2$ was prepared by shaking an aqueous solution of the metal ion, maintained at pH = 5, with a chloroform solution of purified dithizone

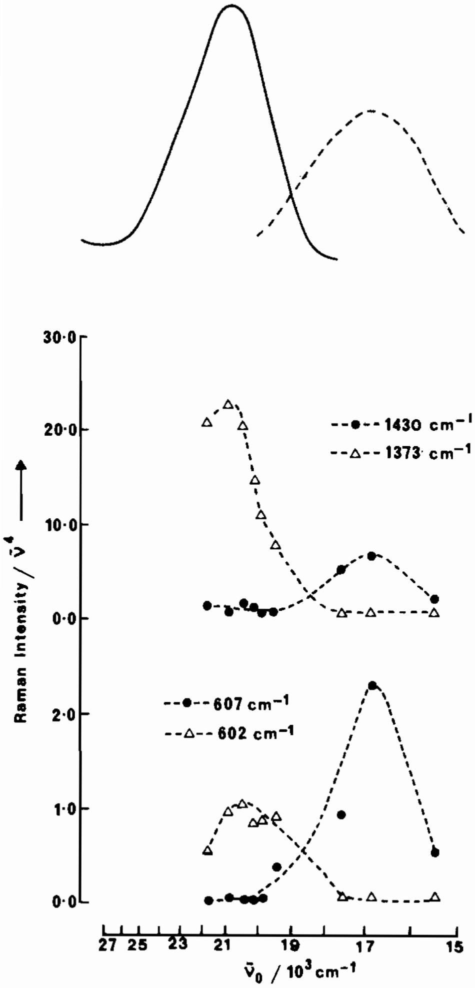

Fig. 4. Excitation profiles for the Raman bands of $Hg(HDz)_2$ at 1430, 1373, 607 and 602 cm^{-1} compared to the electronic absorption spectra of the orange (——) and blue (------) forms of the complex in $CHCl_3$ solution.

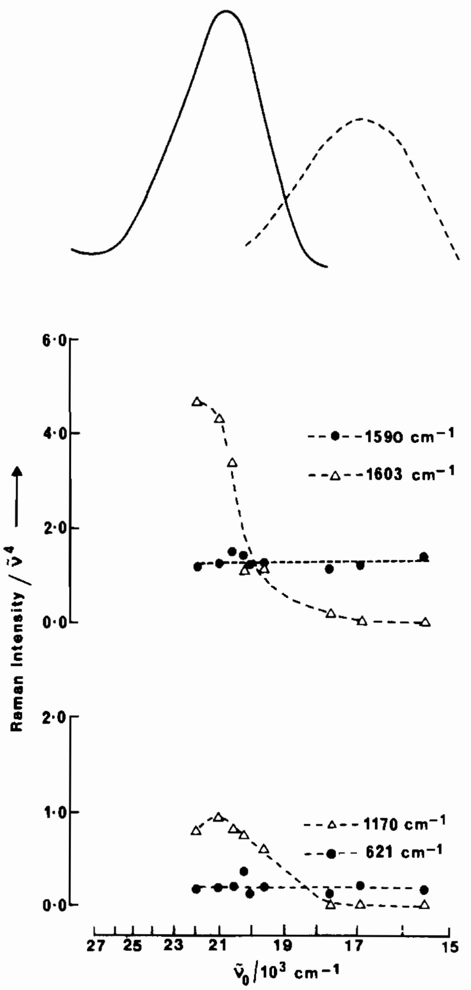

Fig. 5. Excitation profiles for the Raman bands of $Hg(HDz)_2$ at 1603, 1590, 1170 and 621 cm^{-1} compared to the electronic absorption spectra of the orange (——) and blue (------) forms of the complex in $CHCl_3$ solution.

for 30 minutes. The separated solid was filtered and recrystallised from chloroform.

Results

The resonance Raman spectra of a solution of $Hg(HDz)_2$ in chloroform were recorded using laser excitation in the range 457.9–647.1 nm. Sample spectra recorded at 568.2 nm and 476.5 nm are shown in Fig. 3 and band wavenumber measurements and assignments are presented in Table I.

Resonance Raman excitation profiles were constructed for all of the bands listed in Table I using the 667 cm^{-1} band of chloroform as an internal intensity standard. Excitation profiles for bands at 1430, 1373, 607 and 602 cm^{-1} assigned to the azo and thiocarbonyl groups are shown in Fig. 4. Excitation profiles for bands at 1603, 1534, 1483, 1316, 1170 and 1163 cm^{-1} showing maximum resonance enhancement at 490 nm are shown in Figs. 5 and 6. The remaining bands listed in Table I show no apparent resonance enhancement. See for example the excitation profiles for the ring mode at 1590 cm^{-1} and the weak band at 621 cm^{-1} shown in Fig. 5.

Bands observed below 600 cm^{-1} are weak and broad with the exception of a strong band at 265 cm^{-1} which is masked by the solvent band at 262 cm^{-1}. In acetonitrile solution and in the solid state a strong band occurs at 258 and 265 cm^{-1} respectively, for laser excitation at 514.5 nm.

Discussion

Vibrational Assignments

Previously, assignments have been made for vibrational bands of $Hg(HDz)_2$ by Meriwether *et al.* [3]

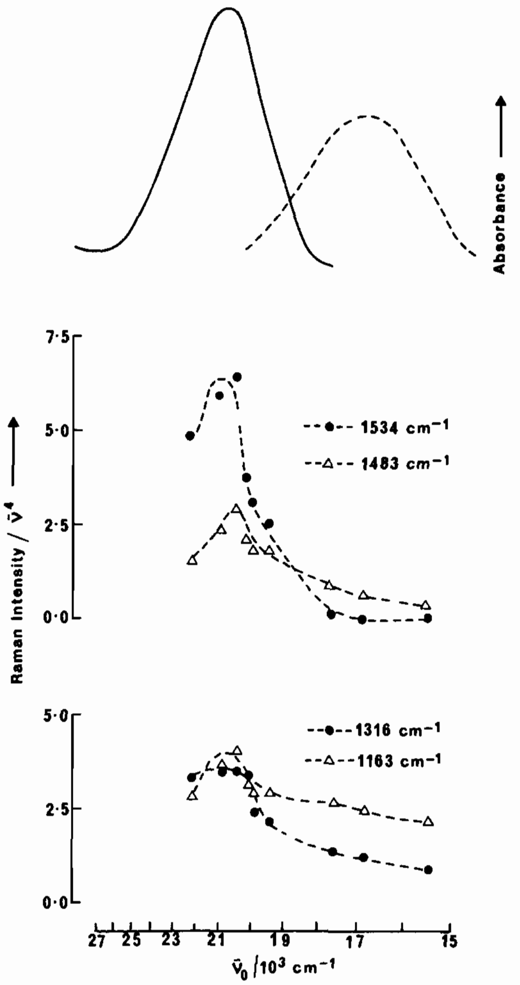

Fig. 6. Excitation profiles for the Raman bands of $Hg(HDz)_2$ at 1534, 1483, 1316 and 1163 cm^{-1} compared to the electronic absorption spectra of the orange (———) and blue (------) forms of the complex $CHCl_3$ solution.

and for those of formazans by Otting and Neugebauer [4, 5]. More recently Pemberton and Buck have made assignments for the parent ligand dithizone in acid and base solution [6] and for the silver complex [7], although there is some disagreement between their two sets of published results. Our assignments are listed along with those of the earlier workers in Table I.

The assignment of the 1603 cm^{-1} band to the C=N stretch and of the bands at 1590 and 998 cm^{-1} to ring modes are in agreement with those of Pemberton and Buck.

We assign the strong Raman band at 1373 cm^{-1} in the orange A form to the azo stretching vibration and its counterpart in the blue B form we believe is the band at 1430 cm^{-1}. This agrees with the infrared studies of isotopic formazans by Otting and Neugebauer who concluded that, in trans-syn-1,3,5-triphenylformazan, the azo stretch occurs at 1351 cm^{-1} while in the *trans*-anti-isomer it occurs at 1416 cm^{-1}. Moreover, in the resonance Raman spectra of *p*-hydroxyazobenzene and of its ring-deuterated derivatives, a very strong Raman band observed in the range 1396 to 1442 cm^{-1} using 488.0 nm laser excitation has been assigned to the azo stretching vibration [8].

We assign the band at 602 cm^{-1} in the orange A form to a mode involving the C–S stretching vibration and in the blue B form this mode shifts to 607 cm^{-1}. The band at 1220 cm^{-1} and possibly that at 621 cm^{-1} can be assigned to the C–N stretching vibration on the basis that neither shows any strong resonance enhancement for the range of excitation wavelengths used in this study. The former assignment is also in agreement with that of Otting and Neugebauer who assign a similar band observed in the formazans to a C–N stretching vibration.

The strong band observed at 265 cm^{-1} has been assigned to the Hg–S stretching vibration. The solvent band at 262 cm^{-1} may have masked any resonance enhancement or wavenumber shift of this band with excitation wavelength.

We do not believe that there is sufficient evidence to make further firm assignments, although we agree with Pemberton and Buck that the normal modes giving rise to bands at 1534, 1170, 1163 and 1154 cm^{-1} probably involve the NCS and N–C=N fragments on the basis of their observed resonance enhancement which reaches a maximum for laser excitation at 490 nm ($\tilde{\nu}_0$ = 20,400 cm^{-1}). Such modes would be expected to give rise to resonance enhanced bands since the associated normal coordinates would be involved in the A → B structural change (small displacement approximation) [9].

Excitation Profiles and the Structure of Form B

The orange A form of $Hg(HDz)_2$ shows strong resonance enhancement at $\tilde{\nu}_0$ = 20,400 cm^{-1} for the band at 1373 cm^{-1} assigned to the azo stretching vibration, together with enhancement of the bands at 1603 cm^{-1} assigned to the C=N stretch, at 602 cm^{-1} assigned to the C–S stretch and at 1534, 1483, 1316, 1170, 1163 and 1154 cm^{-1} assigned to normal modes involving the NCS and N–C=N groups. The maximum in the excitation profile of each of these bands occurs at the same wavenumber as the absorption band maximum for orange $Hg(HDz)_2$.

The 1430 cm^{-1} band, assigned to the azo stretching vibration, of the blue B form of $Hg(HDz)_2$ shows most resonance enhancement using $\tilde{\nu}_0$ = 16,600 cm^{-1} excitation. The maximum in the excitation profile of this band matches the absorption band maximum for blue $Hg(HDz)_2$. A shift to higher wavenumber for the azo stretching vibration parallels that observed by Otting and Neugebauer for the two isomers of 1,3,5-triphenylformazan and agrees with our resonance Raman data for a number of isomeric formazans [10]. For the *trans*-syn-formazans with a strong intramolecular hydrogen bond the azo stretch occurs at a lower wavenumber than for the more open *trans*-anti-isomer. In the orange A form of mercury dithizonate the azo group is coordinated to the mercury atom. A shift to higher wavenumber for the azo stretch in the blue form of mercury dithizonate supports structure B.

The other band showing resonance enhancement for $\tilde{\nu}_0$ = 16,600 cm^{-1} is that assigned to the C–S stretch at 607 cm^{-1}. The small shift to higher wavenumber for the C–S stretching vibration of the blue relative to the orange form of $Hg(HDz)_2$, together with the apparent absence of a band attributable to a C=N stretching vibration, gives further support for structure B as originally proposed by Meriwether, Breitner and Colthup.

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