Deprotonation reactions of 2-thiouracil with [2-(pyridin-2-yl)-phenyl]mercury(II) acetate. Structural and spectroscopic effects

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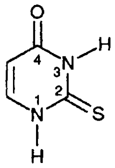
The reaction of [2-(pyridin-2-yl)phenyl]mercury(II) acetate with 2-thiouracil (H_2tuc) in 1:1 and 2:1 mole ratio in methanol solution afforded [Hg($C_6H_4C_5H_4N$)(H_2tuc)] and [{Hg($C_6H_4C_5H_4N$)}$_2$(tuc)] respectively. The bimetallic complex crystallizes in the monoclinic space group $P2_1/n$ with $a = 10.706(1)$, $b = 22.043(3)$, $c = 11.126(1)$ Å, $\beta = 117.01(1)°$ and $Z = 4$. The complex molecules are associated in centrosymmetric dimers by weak intermolecular pyridine N • • • Hg bond interactions. Of the two organometallic cations, one is bound to the thiouracil N(3) atom [Hg(1)–N(3) 2.12(1) Å] and the other is S-co-ordinated [Hg(2)–S 2.350(5) Å]. Atom Hg(1) also forms two weak intramolecular bonds with the O and S atoms and another secondary bond with the pyridine nitrogen of the Hg(1)($C_6H_4C_5H_4N$) moiety [Hg(1) • • • N 2.61(2) Å]. This last type of intramolecular bond is also present, though a little longer [Hg(2) • • • N 2.69(2) Å], in Hg(2)($C_6H_4C_5H_4N$), where Hg(2) is located 2.99(1) Å from the non-co-ordinated nitrogen atom of the tuc^{2-} anion [N(1)]. On the grounds of a vibrational study of the two complexes, a scheme for IR-based diagnosis of the co-ordination of the 2-thiouracilate anions is proposed. The ^{1}H and ^{199}Hg NMR spectra of the bimetallic complex in $CDCl_3$ solution indicate that the N- and S-bound Hg($C_6H_4C_5H_4N$) units interchange slowly, while the pyridine intramolecular N • • • Hg interactions remain in both $CDCl_3$ and $(CD_3)_2SO$ solutions.

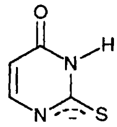
In recent years the identification of 2-thiouracil [2,3-dihydro-2-thioxo-(1*H*)-pyrimidin-4-one, H_2tuc] in several tRNAs of yeasts and *Escherichia coli*[1] has increased interest in the interaction of this molecule with metal ions. In spite of this there have been few structural studies of the resulting complexes.[2] Thiouracil crystallizes in the thione form[3] **Ia**, with two ionizable protons. The loss of the first (pK_{a_1} *ca.* 7.5 at 25 °C[4]) is usually assumed to affect the thioamide group HN(1)C(2)=S, and to afford the monoanion, **Ib**[5] but this is at odds with some of the existing solid-state structural data:[2] in the complex [Au(dppe)$_2$][Htuc]·H_2tuc[2e] (dppe = $Ph_2PCH_2CH_2PPh_2$) the bond distances in the Htuc$^-$ counter ion, which is not co-ordinated, suggest that the form **Ic** is an important resonance structure; while [{Ca(Htuc)$_2$(H_2O)(dmso)$_2$}$_2$][2f] (dmso = dimethyl sulfoxide) contains O- and O,N-bound Htuc$^-$ ions which appear to be of the forms **Ic** and **Id** respectively.

2-Thiouracil can also lose a second proton (pK_{a_2} = 12.7[5]), and the structure of the cationic cobalt(III) complex [Co(tuc)(en)$_2$]$^+$ (en = ethane-1,2-diamine) has recently been reported.[6] The dianion is N(3), S-co-ordinated, possibly because the intramolecular hydrogen bond between the tuc^{2-} oxygen atom and the amino group of one en ligand prevents N(1), S co-ordination. Although double deprotonation of H_2tuc occurs readily in the presence of monoorganomercury acetates, affording compounds such as [(HgPh)$_2$(tuc)],[7] there have been no X-ray studies of bimetallic complexes of the thiouracilate dianion.

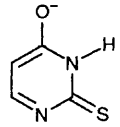
Noting that in certain novel organomercury derivatives of 2-phenylpyridine[8] the presence of the pyridine ring close to the metal centre must have both electronic and steric effects on the acceptor behaviour of the mercury atom, we treated H_2tuc with one such derivative, [2-(pyridin-2-yl)phenyl]mercury(II) acetate, in order to compare its deprotonation and metallation with the analogous reaction previously[7] carried out with phenylmercury acetate. The complexes [Hg($C_6H_4C_5H_4N$)(Htuc)] and [{Hg($C_6H_4C_5H_4N$)}$_2$(tuc)] were isolated and investigated in the solid state by vibrational spectroscopy and in solution (by ^{1}H and ^{199}Hg NMR spectroscopy), and the crystal structure of the bimetallic complex was determined by X-ray diffraction in order to clarify the co-ordination behaviour of the tuc^{2-} anion.



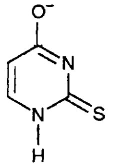
Ia



Ib



Ic



Id

Experimental

Materials and instrumentation

2-Thiouracil was obtained commercially (Aldrich). [2-(Pyridin-2-yl)phenyl]mercury(II) acetate was prepared as described elsewhere.[8] Elemental analyses were performed with a Carlo Erba 1108 microanalyser. Melting points were determined in a Büchi apparatus. Infrared (KBr discs) and Raman (polycrystalline samples) spectra were recorded on a Bruker IFS 66V spectrometer equipped with a Bruker FRA 106 accessory, ^{1}H and ^{199}Hg NMR spectra on a Bruker AMX 500 (500.14 and 89.58 MHz) spectrometer referenced to $SiMe_4$ and $HgMe_2$, respectively, and mass spectra on a Kratos MS50TC spectrometer connected to a DS90 data system and operating under FAB conditions [*m*-nitrobenzyl alcohol, Xe, 8 eV (*ca.* 1.28×10^{-15} J)]; all fragments were identified using DS90 software.

Syntheses

[Hg($C_6H_4C_5H_4N$)(Htuc)]. A stirred solution of H_2tuc (0.20 g, 1.56 mmol) in methanol (30 cm^3) was treated with a solution of [Hg($C_6H_4C_5H_4N$)(O_2CMe)] (0.65 g, 1.56 mmol) in methanol (40 cm^3). The mixture obtained was stirred for 7 h, and the precipitate then filtered off and dried *in vacuo*, m.p. 280 °C (Found: C, 37.3; H, 2.0; N, 8.7; S, 6.0. $C_{15}H_{11}HgN_3OS$ requires C, 37.3; H, 2.3; N, 8.7; S, 6.7%); m/z 484 (M + H, 100%).

[{Hg($C_6H_4C_5H_4N$)}$_2$(tuc)]. A stirred solution of [Hg(C_6H_4-C_5H_4N)(O_2CMe)] (0.40 g, 0.97 mmol) in methanol (30 cm^3) was treated with a solution of H_2tuc (0.06 g, 0.49 mmol) in methanol (20 cm^3). The microcrystalline solid immediately produced was filtered off and dried over P_4O_{10}. The filtrate was left to stand at room temperature and the solvent slowly evaporated, affording crystals suitable for X-ray study, m.p. 200 °C (Found; C, 37.6; H, 1.8; N, 6.8; S, 3.5. $C_{26}H_{18}Hg_2N_4OS$ requires C, 37.4; H, 2.2; N, 6.7; S, 3.8%); m/z 1190 [M + Hg($C_6H_4C_5H_4N$) − 2 H, 31], 837 (M + H, 100), 482 [M − Hg($C_6H_4C_5H_4N$) + 2 H, 42] and 356 [Hg($C_6H_4C_5H_4N$), 41%].

Crystallography

Crystal data. $C_{26}H_{18}Hg_2N_4SO$, M = 835.7, monoclinic, space group $P2_1/n$ (no. 14), a = 10.706(1), b = 22.043(3), c = 11.126(1) Å, β = 117.01(1)°, U = 2339.7(4) Å^3, Z = 4, D_c = 2.372 g cm^{-3}, F(000) = 1544. Colourless prismatic crystals, dimensions 0.30 × 0.2 × 0.05 mm, μ(Mo-Kα) = 132.25 cm^{-1}.

Data collection and processing. Data for structure determination were collected at room temperature (293 K) with a CAD-4 Enraf-Nonius automatic diffractometer and graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). The ω–2θ scan technique was used. Of 4485 reflections measured in the range 0–25° (h 0–12 k −26 to 0; l −13 to 11), 3666 were unique (R_{int} = 0.029 after numerical absorption correction) and 2711 had $I > 3\sigma(I)$.

Structure analysis and refinement. The structure was solved using direct methods[9] and subsequent Fourier-difference maps, and was refined on F by full-matrix least squares minimizing $\Sigma w(|F_o| - |F_c|)^2$. Hydrogen atoms were included as fixed contributors at geometrically calculated positions, all with a common isotropic thermal parameter B_{iso} refined to 6 Å.^{2} Refinements converged to final $R = \Sigma(|F_o| - |F_c|)/|F_o|$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ values of 0.052 and 0.054 respectively for 308 refined parameters. The weighting scheme was $[\sigma^2(F_o) + 0.0001|F_o|^2]^{-1}$. Atomic scattering factors were taken from Cromer and Mann.[10] Calculations were performed on a VAX 6420 computer using the programs SHELX 76[11] and SCHAKAL.[12]

Complete atomic coordinates, thermal parameters and bond lengths and angles, have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Results and Discussion

Structure of [{Hg($C_6H_4C_5H_4N$)}$_2$(tuc)]

Fig. 1 shows the SCHAKAL drawing of [{Hg($C_6H_4C_5H_4$-N)}$_2$(tuc)] and the atom numbering scheme used; fractional atomic coordinates are listed in Table 1, and selected bond distances and angles in Table 2.

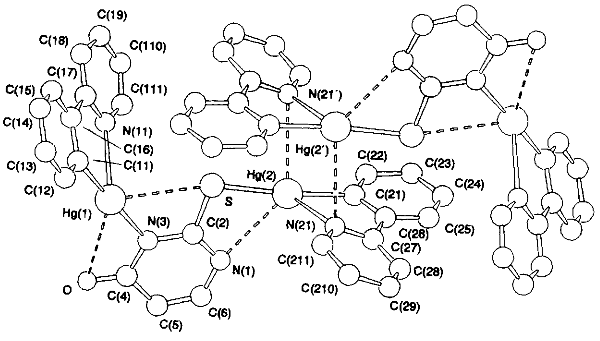


Fig. 1 Structure of [{Hg($C_6H_4C_5H_4N$)}$_2$(tuc)], with the atom-numbering scheme

Table 1 Fractional atomic coordinates for [{Hg($C_6H_4C_5H_4N$)}$_2$-(tuc)]

Atom	X/a	Y/b	Z/c
Hg(1)	0.0465(1)	0.6982(0)	0.8588(1)
Hg(2)	0.4476(1)	0.5270(0)	1.1238(1)
S	0.2594(5)	0.5900(2)	0.9868(4)
O	0.058(1)	0.7623(7)	1.111(1)
N(1)	0.355(1)	0.6299(6)	1.239(1)
N(3)	0.163(1)	0.6832(6)	1.069(1)
C(2)	0.264(2)	0.6387(8)	1.112(2)
C(4)	0.147(2)	0.7236(9)	1.153(2)
C(5)	0.248(2)	0.7144(9)	1.293(2)
C(6)	0.344(2)	0.6695(9)	1.325(2)
N(11)	−0.126(2)	0.6076(8)	0.753(2)
C(11)	−0.050(2)	0.7138(7)	0.653(2)
C(12)	−0.016(2)	0.7633(8)	0.599(2)
C(13)	−0.073(2)	0.7721(9)	0.461(2)
C(14)	−0.167(2)	0.729(1)	0.380(2)
C(15)	−0.203(2)	0.681(1)	0.426(2)
C(16)	−0.146(2)	0.6719(8)	0.568(2)
C(17)	−0.187(2)	0.6158(8)	0.616(2)
C(18)	−0.274(2)	0.574(1)	0.539(2)
C(19)	−0.296(3)	0.519(1)	0.594(3)
C(110)	−0.230(3)	0.512(1)	0.729(2)
C(111)	−0.149(2)	0.557(1)	0.802(2)
N(21)	0.691(2)	0.5586(8)	1.125(2)
C(21)	0.598(2)	0.4631(8)	1.243(2)
C(22)	0.557(2)	0.412(1)	1.283(2)
C(23)	0.656(2)	0.3671(9)	1.356(2)
C(24)	0.798(2)	0.378(1)	1.394(2)
C(27)	0.786(2)	0.5289(8)	1.233(2)
C(25)	0.834(2)	0.431(1)	1.357(2)
C(26)	0.740(2)	0.4745(9)	1.277(2)
C(28)	0.924(2)	0.548(1)	1.288(2)
C(29)	0.965(2)	0.595(2)	1.243(2)
C(210)	0.865(3)	0.628(1)	1.131(2)
C(211)	0.727(2)	0.608(1)	1.080(2)

In this complex one organometallic cation is N(3)-co-ordinated and the second is bound to the sulfur atom. Atom Hg(1) has two almost collinear bonds [Hg–C(11) and Hg–N(3), C(11)–Hg(1)–N(3) 174.8(6)°] and three weak interactions, two of which (Hg···O and Hg···S) are probably due to interatomic distances shorter than the sums of the van der Waals radii being imposed when the primary bonds form [see Table 2; the sums of the van der Waals radii for (Hg,O) and (Hg, S) are 3.23 and 3.53 Å respectively[13]]. The Hg(1)–N(11) distance suggests a stronger bond {stronger in fact than in [Hg($C_6H_4C_5H_4N$)(O_2CMe)], in which its length is 2.727(9) Å}.[14] Atom Hg(2) is co-ordinated to the sulfur atom and the phenyl carbon atom, again almost collinearly [S–Hg(2)–C(21) 173.3(5)°]. The Hg(2)–N(21) distance [2.69(2) Å], although a little longer than Hg(1)–N(11), still indicates significant bonding, and there is a secondary bond between Hg(2) and N(1) [Hg(2)–N(1) 2.99(1) Å; sum of the van der Waals radii, 3.28 Å[13]] which is analogous to those found in monoorganomercury(II) complexes with 2-sulfanyl-pyridine[15] or -pyrimidine.[16] In the case of [{Hg($C_6H_4C_5H_4N$)}$_2$(tuc)] this interaction results in Hg(2) lying only 0.03 Å out of the tuc^{2-} plane (χ^2 = 24.5), *i.e.* almost at the minimum that can be achieved by rotation about C(2)–S.

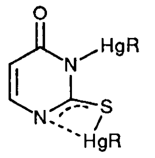
Table 2 Selected bond distances (Å) and angles (°) for $[\{Hg(C_6H_4C_5H_4N)\}_2(tuc)]$

Hg(1)–C(11)	2.07(1)	C(11)–C(12)	1.37(2)
Hg(1)–N(11)	2.61(2)	C(12)–C(13)	1.38(2)
Hg(1)–N(3)	2.12(1)	C(13)–C(14)	1.38(3)
Hg(1)–O	3.09(1)	C(14)–C(15)	1.31(3)
Hg(1)–S	3.158(5)	C(15)–C(16)	1.43(3)
C(2)–S	1.74(2)	C(16)–C(11)	1.39(2)
C(2)–N(1)	1.32(2)	C(16)–C(17)	1.43(3)
C(2)–N(3)	1.38(2)	C(17)–C(18)	1.31(3)
N(3)–C(4)	1.36(2)	C(18)–C(19)	1.43(4)
C(4)–O	1.20(3)	C(19)–C(110)	1.35(4)
C(4)–C(5)	1.45(2)	C(110)–C(111)	1.33(4)
C(5)–C(6)	1.35(3)	C(111)–N(11)	1.31(3)
C(6)–N(1)	1.34(2)	N(11)–C(17)	1.37(2)
Hg(2)–C(21)	2.10(2)	C(25)–C(26)	1.38(3)
Hg(2)–N(21)	2.69(2)	C(26)–C(21)	1.41(3)
Hg(2)–S	2.350(5)	C(26)–C(27)	1.46(3)
Hg(2)–N(1)	2.99(1)	C(27)–C(28)	1.38(3)
Hg(2)–N(21′)	3.11(2)	C(28)–C(29)	1.31(4)
C(21)–C(22)	1.36(3)	C(29)–C(210)	1.42(4)
C(22)–C(23)	1.41(3)	C(210)–C(211)	1.39(4)
C(23)–C(24)	1.40(4)	C(211)–N(21)	1.33(3)
C(24)–C(25)	1.35(3)	N(21)–C(27)	1.43(2)
N(3)–Hg(1)–C(11)	174.8(6)	Hg(1)–S–Hg(2)	165.9(2)
N(3)–Hg(1)–N(11)	108.6(5)	Hg(1)–S–C(2)	69.3(6)
N(11)–Hg(1)–C(11)	74.5(6)	Hg(1)–C(11)–C(12)	121.0(1)
N(11)–Hg(1)–O	119.2(5)	Hg(1)–C(11)–C(16)	90.0(7)
N(11)–Hg(1)–S	80.9(4)	Hg(1)–N(11)–C(17)	106(1)
C(11)–Hg(1)–S	121.3(5)	Hg(1)–N(11)–C(111)	134(1)
C(11)–Hg(1)–O	136.2(6)	Hg(2)–S–C(2)	98.1(6)
O–Hg(1)–N(3)	46.3(5)	Hg(2)–C(21)–C(22)	120(1)
O–Hg(1)–S	102.3(2)	Hg(2)–C(21)–C(26)	118(1)
S–Hg(1)–N(3)	56.0(4)	Hg(2)–N(21)–C(27)	103(1)
S–Hg(2)–C(21)	173.3(5)	Hg(2)–N(21)–C(211)	131(1)
S–Hg(2)–N(21)	113.1(4)	S–C(2)–N(1)	120(1)
N(21)–Hg(2)–C(21)	73.0(6)	S–C(2)–N(3)	115(1)
N(21)–Hg(2)–N(1)	108.1(5)	N(1)–C(2)–N(3)	124(1)
N(21)–Hg(2)–N(21′)	103.4(6)	C(2)–N(1)–C(6)	114(1)
N(21′)–Hg(2)–C(21)	94.2(6)	C(2)–N(3)–C(4)	124(1)
N(21′)–Hg(2)–N(1)	136.5(4)	N(3)–C(4)–C(5)	112(1)
N(21′)–Hg(2)–S	82.0(3)	N(3)–C(4)–O	122(1)
S–Hg(2)–N(1)	58.4(3)	C(5)–C(4)–O	126(1)
N(1)–Hg(2)–N(21)	108.1(5)	C(4)–C(5)–C(6)	119(1)
Hg(1)–N(3)–C(4)	118.0(1)	C(5)–C(6)–N(1)	126(1)
Hg(1)–N(3)–C(2)	118.0(1)		

Primed atoms are related to unprimed ones by $1 - x, 1 - y, 2 - z$.

As Fig. 1 shows, two molecules of $[\{Hg(C_6H_4C_5H_4N)\}_2(tuc)]$ are associated in a centrosymmetric dimer due to intermolecular interactions which can be roughly described as bond interactions between the p_π orbital of the N(21) atom of each molecule and Hg(2) of the other. That this is not just a packing effect is shown (*a*) by the fact that because N(21) is pulled towards Hg(2′) the dihedral angle between the pyridine ring containing N(21) and its associated phenyl ring is 19 ± 2°, as against only 6 ± 4° in the other $Hg(C_6H_4C_5H_4N)$ unit, and (*b*) by the intramolecular N(21)–Hg(2) distance being slightly longer than N(11)–Hg(1), presumably because the intermolecular N(21) · · · Hg(2′) bond weakens N(21)–Hg(2).

Comparison with previous structural data on H_2tuc[3] and its complexes[2,6] shows that in $[\{Hg(C_6H_4C_5H_4N)\}_2(tuc)]$, as usual,[2] metallation of the H_2tuc sulfur atom elongates the C(2)–S bond (although not so much as sulfur methylation,[7] suggesting that some thione bond multiplicity remains). Metallation at N(3) seems not to induce enolization of the ring although the estimated standard deviations of the bond distances are large and prevent detailed discussion; the C(4)–O bond is not significantly longer than in free H_2tuc,[3] whereas it would be if an enol resonance form contributed significantly to the electron-density distribution of the tuc^{2-} anion. Thus the best description of $[\{Hg(C_6H_4C_5H_4N)\}_2(tuc)]$ is probably as in **II**. Formally, this co-ordination mode results from a simple replacement of hydrogen by HgR in monometalled **Ib**. The C–C [C(5)–C(6) short and C(4)–C(5) long] and C–N distances [C(2)–N(1) short and C(2)–N(3) long] are also in keeping with this description.



II

The main geometrical differences, between the tuc^{2-} ligands, in $[\{Hg(C_6H_4C_5H_4N)\}_2(tuc)]$ and the cationic mixed-ligand complex $[Co(tuc)(en)_2]^+$,[6] other than N(1), S and N(3), S co-ordination, affect the N(1)–C(2)(S)–N(3) part of the tuc^{2-} ring. In the cobalt(III) complex the chelating function of the S and N(3) atoms widens the N(1)–C(2)–S angle and narrows S–C(2)–N(3), and the internal ring angles N(1)–C(2)–N(3) and C(2)–N(3)–C(4) are also slightly modified.

It may be concluded that tuc^{2-} (and probably $Htuc^-$) functions as a versatile ligand the co-ordination behaviour of which is strongly tailored by the nature of the cation and the presence of competing ligands.

Vibrational spectra

Table 3 lists the main thiouracil IR bands of H_2tuc,[17] $[Hg(C_6H_4C_5H_4N)(Htuc)]$ and $[\{Hg(C_6H_4C_5H_4N)\}_2(tuc)]$, and the corresponding Raman bands of H_2tuc[17] and $[Hg(C_6H_4C_5H_4N)(Htuc)]$; we were unable to obtain the Raman spectrum of $[\{Hg(C_6H_4C_5H_4N)\}_2(tuc)]$ and that of $[Hg(C_6H_4C_5H_4N)(Htuc)]$ was of poor quality but suffices to support certain assignments. The $Hg(C_6H_4C_5H_4N)$ bands will not be described in detail here except to note that they are located at practically identical positions for $[Hg(C_6H_4C_5H_4N)(O_2CMe)]$, $[Hg(C_6H_4C_5H_4N)(Htuc)]$ and $[\{Hg(C_6H_4C_5H_4N)\}_2(tuc)]$, showing that in all three compounds the N atom of the pyridine ring is co-ordinated to the Hg as the X-ray study shows it to be in $[\{Hg(C_6H_4C_5H_4N)\}_2(tuc)]$ and $[Hg(C_6H_4C_5H_4N)(O_2CMe)]$.[14]

Table 3 shows that in the IR spectrum of $[Hg(C_6H_4C_5H_4N)(Htuc)]$ ν(C=O) has shifted slightly to lower wavenumbers than in the spectrum of free H_2tuc; there is a strong band at 1512 cm^{-1} [probably contributed to by β(N–H)], the intensity of ν(C=S) has decreased significantly and ν(ring), which lies at 1003 cm^{-1} for the free H_2tuc, has shifted to slightly lower wavenumbers, 982s cm^{-1}. These characteristics parallel those found for $[HgMe(H_2tuc)]$.[7] As for the latter compound, they are in keeping with the evolution of the thione form which predominates in free H_2tuc to the 'thiol' form present in *S*-methyl thiouracilate, and so suggest that the thiouracilate anion is primarily S-co-ordinated. In the spectrum of $[\{Hg(C_6H_4C_5H_4N)\}_2(tuc)]$ the shift of ν(C=O) is greater than for $[Hg(C_6H_4C_5H_4N)(Htuc)]$, and the bands lying at 1240 and 1003 cm^{-1} for free H_2tuc shift to higher wavenumbers (1308 and 1007 cm^{-1}).

The above data, together with those previously reported,[7] suggest the following tentative scheme for IR-based diagnosis of the co-ordination of 2-thiouracilate ions: (*a*) the monodeprotonated, primarily S-co-ordinated ion produces strong bands around 1675, 1270 and 990 cm^{-1}; (*b*) the dideprotonated, primarily S,N(3)-co-ordinated ion with additional M–O interaction produces strong bands around 1625, 1315 and 1010 cm^{-1}. However, further crystallographic and vibrational data are necessary to confirm these patterns and to take into account other secondary interactions.

Besides the bands listed in Table 3, the IR spectra of both complexes {and the Raman spectrum of $[Hg(C_6H_4C_5H_4N)$-

Table 3 Most significant thiouracil IR and Raman bands in H_2tuc and its complexes

H_2tuc		[Hg($C_6H_4C_5H_4N$)(Htuc)]		[{Hg($C_6H_4C_5H_4N$)}$_2$(tuc)]	
IR	Raman	IR	Raman	IR	Assignment
3086s	3084w	3059w	3061w	3057w	ν(C–H)
2928s		2978m			ν(N–H)
		2913m			
		2874m			
1686vs	1682s	1682vs		1616vs	ν(C=O)
		1672vs			
		1660vs	1663w		
1628m	1627m	1630m[a]		1632s[a]	ν(ring) + β(N–H)[b]
1566vs (br)	1555m	1590m[a]	1588s[a]	1588s[a]	
1530 (sh)		1512s	1578s[a]	1550m	
			1508m		
1451m	1442m	1452m		1443vs	ν(ring)
1421m		1420 (sh)		1420 (sh)	β(C–H)
1395m	1397m	1388m	1387m	1381m	ν(ring)
1240s	1255m	1267vs[a]	1264m[a]	1308vs	ν(ring) + β(N–H)[b]
1215vs	1222vs	1213w	1212vs	1207m	ν(C=S)
1177s		1177s	1173m	1173m	β(C–H)
1160s	1157w	1155m	1150m	1155s	
1073m		1068m	1068w	1066m	ν(ring)
1003m	998w	982s		1007vs	
	963w				γ(C–H)
912m		924m[a]	924m[a]	925 (sh)	γ(C–H)
895m	893w	896m			γ(N–H)
837m	839w	823m		821m	α(ring)
760m		746s[a]		756s[a]	γ(N–H)
736m		736 (sh)		733m	γ(C=O)
710m	718vs	708w	707m	710w	ν(ring)
648m		658m	662m[a]	665m[a]	α(ring)
580m					β(C=O)
548vs	539m	563w		579w	α(ring)
526s		513w			δ(ring)
454m	454m	453m	450w	460w	β(C=S)
413m	416w	422	425w	437w	δ(ring)
305m		315m		318m	γ(C=S)
	285m				δ(ring)

v = Very, s = strong, m = medium, w = weak, sh = shoulder, br = broad. [a] Vibration of $C_6H_4C_5H_4N$. [b] Not in [{Hg($C_6H_4C_5H_4N$)}$_2$(tuc)].

(Htuc)]} exhibit several other bands in the range 400–100 cm^{-1} at positions close to those of bands exhibited by H_2tuc and by the Hg($C_6H_4C_5H_4N$) moiety of [Hg($C_6H_4C_5H_4N$)(O_2CMe)]. Some of these bands may be due to ν(Hg–S), ν(Hg–C) and ν(Hg–N). Identification of ν(Hg–S) and ν(Hg–N) is hindered by the lack of Raman data for [{Hg($C_6H_4C_5H_4N$)}$_2$(tuc)] and by the complexity of the spectra, but a weak, broad band at 255 cm^{-1} in the Raman spectrum of [Hg($C_6H_4C_5H_4N$)(Htuc)] and a strong band at 255 cm^{-1} in that of [{Hg($C_6H_4C_5H_4N$)}$_2$(tuc)] may be attributed to ν(Hg–C) (t mode). In keeping with previous findings for phenylmercury compounds[18,19] we attribute the difference between the intensities of this band for the two complexes to the strong additional Hg–N bonds *trans* to the Hg–C bond in the dimetallated compound.

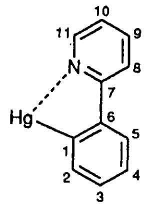
Proton and ^{199}Hg NMR spectra

Despite the very dissimilar solubilities of the two complexes in $CHCl_3$ and dmso {while [Hg($C_6H_4C_5H_4N$)(Htuc)] is soluble in dmso, [{Hg($C_6H_4C_5H_4N$)}$_2$(tuc)] is only slightly soluble in this solvent but very soluble in $CHCl_3$}, it was possible to record the ^{1}H and ^{199}Hg NMR spectra of both compounds in both solvents. Table 4 lists their most significant signals, together with those of free H_2tuc, assigned on the basis of previous work.[7,8] The spectra of the complexes in $CDCl_3$ are shown in Fig. 2. As expected, the NH signal in the ^{1}H NMR spectrum of [Hg($C_6H_4C_5H_4N$)(Htuc)] [at δ 12.59 in $(CD_3)_2SO$] does not appear in that of [{Hg($C_6H_4C_5H_4N$)}$_2$(tuc)].

In the spectrum of [{Hg($C_6H_4C_5H_4N$)}$_2$(tuc)] in $CDCl_3$, C(11)H appears at room temperature as two very broad signals, suggesting that, although some exchange is probably occurring in the solution, N-bound Hg(1) and S-bound Hg(2) are still distinguishable on the NMR time-scale. Further, the difference between the positions of the two signals can be plausibly attributed to the persistence of the Hg$\cdots$N ($C_6H_4C_5H_4N$) interaction in $CDCl_3$ solution, since this would ensure that the C(11)H proton is close enough to the metal to be affected by the difference between the co-ordination spheres of Hg(1) and Hg(2). This hypothesis is confirmed by the spectrum recorded at 223 K, which instead of the two broad signals shows two sharp doublets (Fig. 2). Furthermore, at 223 K, all the $C_6H_4C_5H_4N$ signals except the triplet at δ 7.49 are split, showing that the whole $C_6H_4C_5H_4N$ unit is affected by the difference between the environments of the two mercury atoms.

In $(CD_3)_2SO$ the ^{1}H NMR spectrum of [{Hg($C_6H_4C_5H_4N$)}$_2$(tuc)] at room temperature shows only a single broad signal for C(11)H, probably because exchange is faster in this solvent, although it is slow enough to give two different signals [one for S-bonded Hg(2) at δ −953.0 and the other for N(3)-bonded Hg(1) at δ −1147.3] in the ^{199}Hg NMR spectrum of this complex, as occurs in $CDCl_3$ [Table 4, Fig. 2(*e*)]. The difference between this behaviour and that of [(HgPh)$_2$(tuc)],[7] where only a single broad signal at a position between those of the [{Hg($C_6H_4C_5H_4N$)}$_2$(tuc)] signals is observed, may be due to the Hg($C_6H_4C_5H_4N$) group being less mobile than HgPh because of its greater bulk. The fact that the ^{199}Hg signals of the Hg($C_6H_4C_5H_4N$) derivatives lie downfield from those of the HgPh derivatives[7] suggests that intramolecular Hg$\cdots$N($C_6H_4C_5H_4N$) interaction persists in $(CD_3)_2SO$ as well as in $CDCl_3$: as Black *et al.*[8] pointed out, an increase in the co-ordination

Table 4 Main ^1H and ^{199}Hg NMR[2] signals (δ)[a] of H_2tuc and its complexes



Compound	Solvent	^1H											^{199}Hg
		NH	C(5)H	C(6)H	C(2)H[b]	C(3)H[b]	C(4)H[b]	C(5)H[b]	C(8)H[b]	C(9)H[b]	C(10)H[b]	C(11)H[b]	
H_2tuc	$(CD_3)_2SO$	12.36 (br s)	5.81 (d)	7.40 (d)									
$[Hg(C_6H_4C_5H_4N)(Htuc)]$	$CDCl_3$	10.50 (vbr s)	6.16 (d)	7.50 (d)	7.68 (d)	7.51 (t)	7.44 (t)	7.06 (d)	7.98 (t)	7.84 (t)	7.34 (d)	8.55 (d)	−904.4
	$(CD_3)_2SO$	12.59 (br s)	5.95 (d)	7.45 (d)	7.93 (d)	7.93 (t)	7.37–7.48 (m)	7.37–7.48 (m)	8.13 (d)	7.93 (t)	7.37–7.48 (m)	8.47 (d)	−925.1
$[\{Hg(C_6H_4C_5H_4N)\}_2(tuc)]$	$CDCl_3$		6.34 (d)	7.55 (d)	7.71 (d)	7.50 (t)	7.44 (t)	8.06 (d)	7.98 (d)	7.83 (t)	7.33 (t)	8.57 (vbr s), 8.80 (vbr s)	−915.6, −1127.9
	$CDCl_3$[c]		6.36 (d)	7.56 (d)	7.67 (d), 7.71 (d)	7.49 (t)	7.42 (t), 7.45 (t)	8.03 (d), 8.07 (d)	7.94 (d), 7.98 (d)	7.83 (t), 7.84 (t)	7.31 (t), 7.36 (t)	8.47 (d), 8.78 (d)	
	$(CD_3)_2SO$		6.13 (d)	7.53 (d)	7.95 (d)	7.40–7.50 (m)	7.40–7.50 (m)	8.16 (d)	8.16 (d)	7.95 (t)	7.40–7.50 (m)	8.61 (br d)	−953.0, −1147.3

[a] S = Singlet, d = doublet, t = triplet, m = multiplet, br = broad, v = very. [b] See numbering scheme for $Hg(C_6H_4C_5H_4N)$. [c] Spectrum recorded at 223 K.

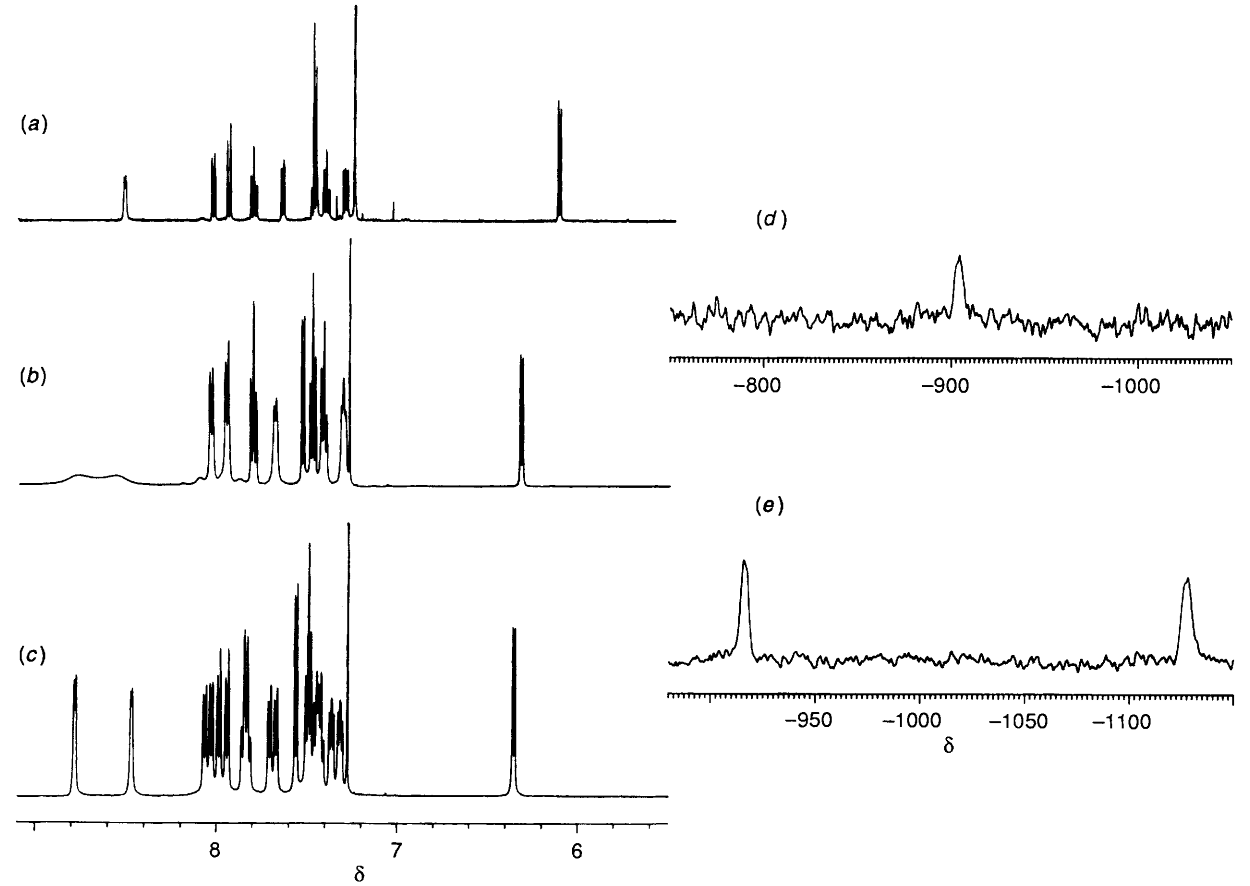


Fig. 2 Proton NMR spectra of [Hg($C_6H_4C_5H_4N$)(Htuc)] at r.t. (*a*), [{Hg($C_6H_4C_5H_4N$)}$_2$(tuc)] (*b*) at r.t. and [{Hg($C_6H_4C_5H_4N$)}$_2$(tuc)] at 223 K (*c*) and ^{199}Hg NMR spectra of [Hg($C_6H_4C_5H_4N$)(Htuc)] (*d*) and [{Hg($C_6H_4C_5H_4N$)}$_2$(tuc)] (*e*) at r.t

number of mercury due to the nitrogen atom of the pyridine ring should shift the ^{199}Hg signal significantly downfield, whereas in the absence of this interaction the relative rotation of the phenyl and pyridine rings about the C(6)–C(7) bond to reduce inter-ring H,H repulsion would shift the ^{199}Hg signal upfield.

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