Infrared investigations on the dithioformamidinium dihalides

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Abstract—The monohydrate dithioformamidinium dihalides $[(H_2N)_2CS-]_2X_2$. $H_2O(X = Cl, Br, I)$ and the anhydrous dibromide have been investigated by i.r. spectroscopy. The vNH and δNH_2 bands were identified from the deuterated dithioformamidinium di-iodide. With respect to thiourea the vNH and δNH_2 frequencies decrease and increase, respectively, as in other sulphur-bonded derivatives of thiourea, and the $v_{as}CN_2$ and vCS frequencies increase and decrease, respectively, in agreement with the increased CN double bond character and the formation of a C-S single bond.

INTRODUCTION

In previous works we investigated the crystal and molecular structure of 3, 5-diamino-1, 2, 4-dithiazolium bromide [1] and the i.r. spectra of the 3, 5diamino-1, 2, 4-dithiazolium salts [2] obtained by the oxidation of 2, 4-dithiobiuret. Some copper(I), silver(I) and mercury(II) halide complexes of the 3, 5-diamino-1, 2, 4-dithiazolium halides were prepared and investigated by i.r. spectroscopy, showing that in all these complexes the cyclic positively-charged electrondonor ligand is coordinated to the metal ion through the unprotonated ring nitrogen atom [3].

It is well known that thiourea is easily converted into dithioformamidinium (or formamidinium disulphide) salts by a variety of oxidizing agents. The crystal structure of the dibromide and diiodide was determined by X-ray diffraction methods [4]. Proton magnetic resonance and i.r. spectra have been recorded for the dichloride and the dinitrate [5] but the i.r. spectra were neither interpreted nor discussed. The kinetics of the oxidation of thiourea and N, N'-dialkylthioureas by hydrogen peroxide [6] and by hexachloroiridate (IV) ion [7] were also studied.

In preliminary investigations we succeeded in preparing some metal compounds containing the dithioformamidinium cation. For an interpretation of them we were therefore interested in the investigation of the i.r. spectrum and an assignment of the bands of this cation.

EXPERIMENTAL

The dithioformamidinium dihalides (Tu_2X_2) were prepared as follows.

Chloride

 H_2O_2 (0.1 mole in 10 cm³ of aqueous solution) was slowly added to an ice-cooled solution of thiourea (0.1 mole) in acetone (20 cm³) and concentrated HCl (0.1 mole in 10 cm³ of aqueous solution); the product crystallized immediately and was washed with acetone.

Bromide

An ethanolic solution of bromine was slowly added to an ice-cooled solution of thiourea (0.1 mole) in EtOH (160 cm³); the product crystallized immediately and was washed with EtOH. The compound was recrystallized anhydrous from MeOH and Et_2O and as monohydrate from water.

Iodide

Solid iodine (5 g) was slowly added to an ice-cooled solution of thiourea (3 g) in H_2O (25 cm³); the product crystallized in some hours from the ice-cooled solution and was rapidly washed with ice-cooled water in which it is fairly soluble.

By dissolving the dithioformamidinium di-iodide in acetone and adding ethyl ether and petroleum ether to the solution the compound is transformed in iodine and thiourea which precipitates as white pure crystals. This agrees with the fact that the equilibrium

Thiourea + Iodine = Dithioformamidinium iodide

is shifted to left in solvents of low ionizing power [4].

Infrared spectra were recorded on the solid compounds with a Perkin-Elmer 180 spectrophotometer in the 4000-250 cm⁻¹ region either as Nujol mulls on KBr disks or in KBr disks for thiourea and in KX (X = Cl, Br, I) disks for the dithioformamidinium dihalides in order to avoid exchange reactions.

Thiourea (1 mmole) was repeatedly deuterated for some time in hot D_2O (1 cm³) evaporating each time the solution *in vacuo* and then transformed with iodine in the deuteriated dithioformamidinium diiodide, as described above, in D_2O .

Table 1. Microanalyses gave the following results, found % (calcd. %)

	С	Н	N	S
C ₂ H ₈ N ₄ S ₂ Cl ₂ .H ₂ O	10.09(9.96)	4.19(4.18)	23.51 (23.53)	26.78 (26.59)
C ₂ H ₂ N ₄ S ₂ Br ₂	7.75(7.70)	2.72 (2.58)	17.46(17.95)	21.49 (20.55)
C,H,N,S,Br,H,O	7.54 (7.28)	3.11 (3.05)	16.91 (16.97)	19.85 (19.43)
$C_2H_8N_4S_2I_2.H_2O$	5.61 (5.66)	2.28 (2.38)	13.01 (13.21)	15.31 (15.12)

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Table 2.

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Assignments given for thiourea by AITKEN et al. [11]	Τu	Tu ₂ Cl ₂ H ₂ O	Tu ₂ Br ₂	Tu ₂ Br ₂ H ₂ O	Tu ₂ I ₂ H ₂ O	Tu ₂ I ₂ D ₂ O	۲ ^{D/V} H
vNH,(99.6)	3380 vs	3350 vs	3350 s	3350 sh	3360 s	2480 vs	0.74
		3300 s	3290 sh	3300 sh	3300 s	2415 wm	0.73
		3265 sh			3265 sh	2355 m	0.72
v _e NH ₂ (99.6)	3275 vs	3255 vs	3250 vs	3255 vs	3260 vs	2315 m	0.71
vNH (S)	3170 vs	3165 s	3165 s	3165 m	3160 m	2295 vs	0.70
VNH (S)	3095 w	3095 w	3090 sh	3080 sh	3080 m	2270 sh	0.74
δNH ₂ (96.1)	1612 vs	1654 vs	1653 vs	1656 vs	1653 vs	1172 vs	0.71
δNH ₂ (78.3), v _{as} CN ₂ (29.9)	1588 vs	1630 m	1630 sh	1625 sm	1628 sh	1138 vs	0.70
v _{ac} CN ₂ (61.7), õNH ₂ (21.8)	1472 vs*	1585 vs	1585 vs	1587 vs	1590 s	1600 vs	
v _s CN ₂ (55.3), vCS(22.3), pNH ₂ (24.8)	1413 vs*	1400 vs*	1400 vs*	1397 vs*	1405 s*		
pNH ₂ (58.3), v _s CN ₂ (34.4)	1083 s	1095 ms	1093 m	1097 ms	1095 wm	910 ms	
ρNH ₂ (77.5), v _s CN ₂ (14.6)	1040 w	1055 mw	1038 ms	1047 ms	1047 ms	810 m	
VCS(53.5), V _s CN ₂ (18.9), δCN ₂ (15.7)	728 s	718 vs	715 vs	715 vs	718 s		
•		660 ms	099 m	660 vs	662 ms		
β SCN ₂ and ν CS (Y)	630 sm	628 m	615 m	615 ms	598 mw		
		618 sh	605 sh	600 sh	588 sh		
	620 sh	574 wm	570 sh	560 mw	548 wm		
	515 sh	513 mw	513 mw	513 w	513 m		
δCN_2 (S, Y)	485 vs	470 vs	465 s	467 s	465 m		
δCN ₂ (60.6), vCS(25.1)	463 vs				440 w		
$\rho SCN_2(101.4), \ \rho NH_2(21.1)$	413 sh	408 mw	406 w	407 m	410 w		

(S) = STEWART [8] (Y) = YAMAGUCHI *et al.* [9] (*) recorded in KX disks.

RESULTS AND DISCUSSION

STEWART [8] has observed that the i.r. spectrum of thiourea recorded in Nujol mulls undergoes frequency shifts and splitting of bands when recorded in alkali halide disks. Therefore we report in Table 1 the spectra of thiourea and of the dithioformamidinium dihalides recorded as Nujol mulls. For the spectral regions obscured or disturbed by the Nujol bands we report, marked with an asterisk, the bands of the compounds recorded in KX disks.

Several assignments of the thiourea bands have been published [8–11]. The most recent and complete assignments of AITKEN *et al.* [11] based on normal coordinate analysis are reported in Table 2 together with Even if the vCN₂ bands have some contribution from NH₂ or ND₂ vibration modes, it is surprising that the deuteration of thiourea decreases the vCN₂ $(-324 \text{ and } -226 \text{ cm}^{-1})$ much more than the δ NH₂ modes $(-240 \text{ and } -113 \text{ cm}^{-1})$.

The δND_2 assignments given by YAMAGUCHI et al. [9] are therefore preferable. All the frequencies of the bands recorded in Nujol mulls for the iodide and reported in Table 2 as vND and δND_2 modes have normal v_D/v_H ratios (0.74–0.70).

The $v_{as}CN_2$ band of thiourea (1472 cm⁻¹) having a significant δNH_2 contribution shows, in the dithioformamidinium dihalides, frequencies significantly greater than those of thiourea, owing to the electronic shifts:



some other assignments for the bands not considered by these authors.

In the dithioformamidinium dihalides most of the vNH frequencies decrease in agreement with the fact that a partial positive charge likely decreases the NH bond strength.

The δNH_2 bands were located at 1678–1650 and 1661–1642 cm⁻¹ for the thiouronium cation, at 1640 and 1620 cm⁻¹ for the S-bonded thiourea complexes and at 1645 cm⁻¹ for the S-methyl-thiouronium iodide [12]. The thiouronium cation shows a sharp and rather intense vSH band at 2570–2375 cm⁻¹ indicating that the protonation occurs on the sulphur atom [12]. In all these S-bonded compounds the δNH_2 frequencies significantly increase with respect to those of thiourea.

In the dithioformamidinium dihalides the bands at 1656–1653 and 1630–1625 cm⁻¹ may therefore be assigned to δNH_2 modes. For the iodide these bands disappear in the deuterated derivative while the very strong band observed for this compound at 1600 cm⁻¹ and the corresponding bands observed at 1590–1595 for the Tu₂X₂ compounds are assigned to a $v_{as}CN_2$ mode.

There is a disagreement in the literature about the assignments of the δND_2 frequencies for thiourea. On the basis of normal coordinate calculations YAMAGUCHI et al. [9] located the ND₂ bending frequencies at 1190 and 1143 cm⁻¹ having normal v_D/v_H ratios (0.73 and 0.71) with the corresponding NH₂ bending frequencies (1625 and 1610 cm⁻¹) given by these authors.

On the contrary AITKEN et al. [11] gave the following correspondences for thiourea:

this last structure being in agreement with the proton magnetic resonance measurements [5].

A frequency increase of the vCN_2 bands was observed too in other S-bonded thiourea derivatives: at 1570-1547 and 1451-1443 cm⁻¹ in the thiouronium cation, at 1524 and 1429 cm⁻¹ in the S-methylthiouronium iodide and at 1510 and 1430 cm⁻¹ in the S-bonded thiourea complexes [12].

The $v_s CN_2$ band of thiourea (1413 cm⁻¹) has important vCS and ρNH_2 contributions which may be responsible for the fact that this band remains practically unchanged in the Tu₂X₂ derivatives showing only a very light frequency decrease.

The thiourea composite band at 728 cm⁻¹, having a predominant vCS contribution, is split for the dithioformamidinium dihalides into two bands at 718–715 and 660 cm⁻¹, this last band being assignable to the stretching mode of the new C-S single bond. Also the bands at 632 and 620 cm⁻¹, to which vCS contributions were assigned, show a frequency decrease in agreement with the presence of a C-S single bond whose stretching frequency generally appears in the 720–570 cm⁻¹ range [13].

The vS-S mode, generally giving rise to a weak band in the 500-400 cm⁻¹ region [13], could not be identified probably because superimposed or coupled with other thiourea modes.

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Table 3	ble 3
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δNH ₂		δHD ₂		SC(NH ₂) ₂	_	SC(ND ₂) ₂	
1628	+	1388	v _{as} CN ₂	1470	+	1146	cm ⁻¹
1620	→	1507	v _s CN ₂	1415	-	1189	cm ⁻¹

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