An Infrared Spectroscopic Study on Imidazolidine-2-thione and -2-selone

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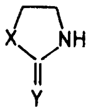
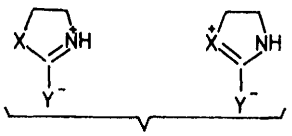
The i.r. spectrum of imidazolidine-2-thione in the range 4 000—200 cm^{-1} has been re-examined, and compared directly with that of the 2-selone. The CS and CSe groups give rise to typical absorptions below 600 cm^{-1}. The principal bands are assigned by comparisons with the i.r. spectra of *N*-deuterio-compounds, *S*- or *Se*-methiodides, and *S*- or *Se*-bonded metal complexes.

WE have recently studied the i.r. spectra of some heterocyclic penta-atomic rings with general formula $HN\cdot[CH_2]_2\cdot X\cdot CY$, where X = O or S and Y = O, S, or Se. It was pointed out that in the solid state the contribution of the dipolar resonating structures (2)



(1)



(2)

increases as Y is changed from O to Se.[1] This trend has also been recognized by other authors [2-5] in studies on several amides and thio- and seleno-amides by various methods.

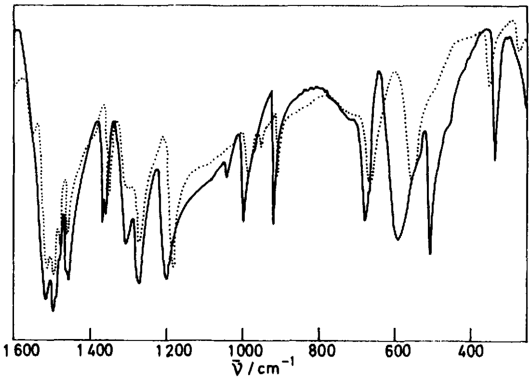
When X is NH, in imidazolidine-2-thione, the contribution of structures (2) is enhanced, as showed by an *X*-ray crystal structure investigation,[6] which revealed the presence of *ca.* 80% of such structures. In contrast, many i.r. studies [7-9] assign the ν_{CS} vibration to a band at 1 204 cm^{-1}, denoting a high π-bond order in the carbon–sulphur linkage.

We have now re-examined the i.r. spectrum of imidazolidine-2-thione (ImS) in the range 4 000—200 cm^{-1} in order to identify the thiocarbonyl vibrations. For this purpose the corresponding 2-selone (ImSe), the *S*- or *Se*-methiodides, the *N*-deuterio-derivatives and some *S*- or *Se*-bonded metal complexes have been used.

RESULTS AND DISCUSSION

In contrast with $\nu_{C:O}$, $\nu_{C:S}$ values fall in a wide range,[10] with an upper limit of *ca.* 1 300 cm^{-1} corresponding to a π-bond order close to unity.[11] Mecke *et al.*[7] assigned ν_{CS} in the spectrum of ImS to a very strong band at 1 204 cm^{-1}. To check this assignment, the spectrum of ImS was compared with that of ImSe; the effect of substitution of selenium for sulphur would be expected to resemble an isotope effect.[12]

The superimposed spectra of ImS and ImSe in the range 1 600—250 cm^{-1} are shown in the Figure. The band at 1 204 cm^{-1} for ImS is displaced to 1 190 cm^{-1} for ImSe; the shift of 14 cm^{-1} is much smaller than



Superimposed i.r. spectra of imidazolidine-2-thione (——) and -2-selone (· · · ·) in the range 1 600—250 cm^{-1} (KBr discs)

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would be expected. On methylation of ImS (see Table 2) the band at 1 204 cm^{-1} is practically unchanged; on deuteriation it disappears. We conclude that this band cannot arise from a predominantly CS stretching vibration.

TABLE 1

Tentative assignments of the i.r. bands of imidazolidine-2-thione (ImS) and -2-selone (ImSe) in KBr solid phase in the range 4 000—200 cm^{-1}

ImS	ImSe	Approximate description *
3 250vs	3 250vs	$\nu_s(NH) + \nu_{as}(NH)$
1 520vs	1 515vs	$\nu_{as}(CN) + \delta_{as}(NH)$
1 500vs	1 500vs	
1 204vs	1 190vs	$\nu_s(NH) + \nu_s(CN) + \delta_s(CNC)$
1 044mw		Overtone
	958w	Combination band
675s	668s	$\Delta_{as}(NH)$
590vs	558vs	$\Delta_s(NH)$
507vs		$\nu(CY) + \delta(NCY) + \delta(NCN)$
	357m	
337s		$\Delta(CS)$
	276ms †	$\Delta(CSe)$

* Only the predominant contributions assigned. † This band is not evident in the Figure.

Displacement more appropriate to the replacement of S by Se is shown by the weak bands at 1 044 and 958 cm^{-1} for ImS and ImSe, respectively. However, on deuteriation of ImSe the band at 958 cm^{-1} is lost, and so cannot arise from a CSe vibration. Possible assignments for these bands are in Table 1; these are in accord with the small shifts shown in the spectra of the derived metal complexes, ML_2X_2 (M = Zn, Cd, or Hg, L = ImS or ImSe, X = Cl, Br, or I). In fact, for zinc(II), cadmium(II), and mercury(II) chlorides, the band at 1 044 cm^{-1} for ImS is shifted to 1 035m, 1 040m, and 1 033mw cm^{-1} and the band at 958 cm^{-1} for ImSe to 956w, 957mw, and 955w cm^{-1}, respectively. The displacements of the i.r. bands for the ImSe complexes are similar to those for the ImS complexes, which are known to possess *S*–metal co-ordination.[13] It may be inferred that the ImSe complexes possess *Se*–metal bonds.

TABLE 2

All bands in the range 2 500—250 cm^{-1} in *N*-deuteriated derivatives and *S*- or *Se*-methiodides (solid phase)

$DN[CH_2]_2NDCS$	$DN[CH_2]_2NDCSe$	$HN[CH_2]_2NHCSMeI$	$HN[CH_2]_2NHCSeMeI$
2 420vs	2 425vs	1 563vs	1 555vs
1 490vs	1 492vs	1 548vs	1 530vs
1 452vs	1 455s	1 469m	1 467s
1 430vs	1 432vs	1 415ms	1 413m
1 300sh	1 278vs	1 370ms	1 365s
1 275vs	1 190s	1 327m	1 320s
1 207w	1 115w	1 318m	1 298vs
1 192w	1 007vw	1 295s	1 280vs
1 035w	990vw	1 240w	1 195vs
883s	882s	1 210s	1 026s
850ms	850s	1 030s	995m
705mw	705mw	1 004w	955s
643m	560m	978w	915s
505s	435s	940s	904m
450s	354m	908m	670vs
400sh	276w	680s	560vs
325ms		580vs	
		475w	

At still lower frequencies, the bands at 507 cm^{-1} for ImS and at 357 cm^{-1} for ImSe show characteristics that are in accord with those expected for C–S and C–Se vibrations. Both are largely unaffected on *N*-deuteriation, and both are absent from the spectrum of the *S*-methyl or *Se*-methyl derivatives. In the spectra of the metal complexes, the two bands are displaced towards lower energies by *ca.* 16 cm^{-1} for ImS and *ca.* 11 cm^{-1} for ImSe, in accord with an almost single bond character.

It is not surprising that a CS vibration for an NH–CS–NH skeleton does not appear in the region 1 300—800 cm^{-1}. Jensen and Nielsen[12] compared the spectra of several thio- and seleno-ureas and showed that they differ substantially only below 650 cm^{-1}. On the basis of normal co-ordinate calculations,[14-16] bands at 729 and 640 cm^{-1} are assigned to vibrations involving substantial CS and CSe stretching in thiourea and selenourea, respectively. From these analyses it is probable that in ImS and ImSe the vibrations at 507 and 357 cm^{-1}, respectively, have a common origin, arising from coupled ν_{CY}, δ_{NCY}, and δ_{NCN} modes.

In the spectrum of ImS a strong band at 337 cm^{-1}, which moves to 325 cm^{-1} on *N*-deuteriation and is absent from the spectrum of the *S*-methyl derivative, may also have some contribution from ν_{CS}. The corresponding band at 276 cm^{-1} for ImSe is modified on *N*-deuteriation. Both bands occur at higher frequencies in the spectra of the corresponding metal complexes.

When X = NH the penta-atomic rings $NH{\cdot}[CH_2]_2{\cdot}X{\cdot}CY$ exhibit stronger crystal forces than when X = O or S. This is shown by the high m.p.s of ImS (198 °C) and ImSe [232 °C (decomp.)] (whereas 1,3-oxazolidine-2-thione, for example, has m.p. 98—99 °C)

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and by the observation that on *N*-deuteriation of ImS or ImSe almost all the bands move. The removal of the crystal forces would allow a better investigation of all the vibrational bands, but the low solubilities of the compounds in convenient solvents prevent us from carrying out solution studies.

EXPERIMENTAL

Imidazolidine-2-thione and -2-selone were obtained according to literature procedures.[17,18] Their *S*- and *Se*-methiodides were synthesized by refluxing in absolute ethanol with methyl iodide (1.1 mol. equiv.). Crystalline *products* were obtained by cooling in an ice-bath (Found: C, 19.55; H, 3.75; I, 52.05. $C_4H_9N_2SI$ requires C, 19.7; H, 3.7; I, 52.0%) (Found: C, 16.45; H, 3.2; I, 43.55. $C_4H_9N_2SeI$ requires C, 16.5; H, 3.1; I, 43.6%). The *N*-deuterio-derivatives were obtained by recrystallizing the compounds from D_2O.

The ImS complexes with Zn^{II}, Cd^{II}, and Hg^{II} chlorides were prepared according to the literature.[13] The analogous *complexes* with ImSe were prepared in the same way (Found: C, 16.7; H, 2.8; Zn, 15.1. $C_6H_{12}Cl_2N_4Se_2Zn$ requires C, 16.6; H, 3.0; Zn, 15.05%) (Found: C, 15.0; H, 2.83; Cd, 24.4. $C_6H_{12}CdCl_2N_4Se_2$ requires C, 15.0; H, 2.5; Cd, 23.4%) (Found: C, 12.7; H, 2.3; Hg, 35.2. $C_6H_{12}Cl_2HgN_4Se_2$ requires C, 12.65; H, 2.1; Hg, 35.2%).

The i.r. spectra were recorded with a Perkin-Elmer 325 instrument in the range 4 000—200 cm^{-1}. The samples were recorded for KBr discs (4 000—400 cm^{-1}) and for Nujol mulls between CsI discs (450—200 cm^{-1}).

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