Solid state NMR study of 1,3-imidazolidine-2-thione, 1,3-imidazolidine-2-selenone and some of their N-substituted derivatives

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Abstract. Solid-state NMR spectra were recorded for 1,3-imidazolidine-2-thione, 1,3-imidazolidine-2-selenone and some of their N-substituted derivatives. Spinning side-bands of thione and selenone carbons were analysed to yield chemical shift anisotropies for these carbons. The NMR spectrum of imidazolidine-2-thione (Imt) showed some evidence for the presence of thiol tautomer. Molecular computations were carried out for Imt and its N-methyl derivative to yield relative energies of various tautomers.

1. Introduction

There has been considerable interest in 1,3-imidazolidine-2-thiones (Imt), 1,3-imidazolidine-2-selenones (ImSe) and their derivatives, because of their ambidentate nature [1]. That is, they may coordinate to a metal through S (or Se), nitrogen or by various chelating modes. These penta-atomic ligands exist in a thiol $\rightleftharpoons$ thione equilibrium [2]. However, it has been established that the thione form dominates in the solid state of these complexes [3,4]. We have studied extensively the interaction of metal ions with Imt and its derivatives [5]. Most of the complexations with these ligands were carried out in solution and investigated by NMR spectroscopy. The X-ray structures of some of the complexes only show a specific unit for the ligand, i.e. thione form in the case of ligand and thiolate form in the case of complexation. This was explained as due to the weakening and elongation of the thione when bonded to metal, as demonstrated by IR [5].

In this study, we have carried out a solid state NMR studies of these penta-atomic ligands. Examination of solid state NMR of powder samples provides principal components of the chemical shift tensors, which potentially contain a wealth of structural information. Before embarking on a solid-state NMR study of Imt–metal and ImSe–metal complexes, it is important to understand the shielding tensors for the uncoordinated ligand. Towards this end we present the results of solid state ^{13}C NMR for Imt and various related ligands and some of their selenium counterparts.

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2. Experimental

2.1. Preparation of Imt and ImSe ligands

The thione ligands were synthesized according to the procedure described in the literature (by the addition of CS₂ to diamines in ether and then heating the resulting adduct at 100°C for 2–3 hrs, followed by its crystallization in methanol) [6,7].

The selenone ligands were synthesized according to the procedure described in the literature [8,9].

2.2. Solid-state NMR studies

Natural abundance ¹³C solid state NMR spectra were obtained on a JEOL LAMBDA 500 spectrometer operating at 125.65 MHz (11.74 T), at ambient temperature of 25°C. Samples were packed into mm zirconium oxide rotors. Cross polarization and high power decoupling were employed. Pulse delay of 7.0 s and a contact time of 5.0 ms were used in the CPMAS experiments. The magic angle spinning rates were from 2000 to 4000 Hz. Carbon chemical shifts were referenced to TMS by setting the high frequency isotropic peak of solid adamantane to 38.56 ppm. The CPMAS spectra of thione and selenone

Table 1
¹³C chemical shift tensors^a for the C=X (X = S or Se) carbons

Compound				δ_{iso}	σ_{11}	σ_{22}	σ_{33}	$\Delta\sigma$	η
	R ₁	R ₂	X						
1a	H	H	S	180.6	−270	−188	−84	145	0.85
1b	Me	H	S	181.4	−106	−170	−266	−127	0.75
1c	Et	H	S	180.9	−101	−176	−266	−227	0.36
1d	nPr	H	S	180.1	−87	−173	−280	−150	0.85
1e	iPr	H	S	180.8	−83	−176	−281	−152	0.92
1f	Me	Me	S	181.4	−111	−155	−278	−145	0.44
1g	Et	Et	S	180.1	−106	−164	−271	−136	0.64
1h	iPr	iPr	S	181.4	−103	−160	−281	−149	0.58
1i	H	H	Se	175.0	−271	−187	−67	163	0.78
1j	Me	H	Se	176.6	−276	−176	−70	156	0.96
1k	iPr	H	Se	175.6	−273	−183	−68	158	0.85
2a	H	H	S	175.6	−246	−201	−79	145	0.47
2b	H	OH	S	173.8	−241	−201	−80	140	0.42
2c	Et	H	S	176.2	−218	−185	−125	77	0.65
2d	H	H	Se	174.1	−257	−204	−61	169	0.47
2e	H	OH	Se	166.6	−340	−188	−42	314	0.80
3				188.4	−264	−207	−94	141	0.61

^aIsotropic shielding, $\sigma_i = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$; $\Delta\sigma = \sigma_{33} - \sigma_i$; $\eta = (\sigma_{22} - \sigma_{11})/\Delta$.

Scheme 1.

Table 2

Optimized total energies, relative energies, dipole moments (Debye) and rotational constants (MHz) for the various tautomers calculated at B3LYP/6-311+G**

	Total energy (Hartrees)	Relative energy (kJ/mol)	Dipole moment (D)	Rotational constants		
				A	B	C
R = H						
T1	−625.727275	0.000	5.81	7799	2045	1667
T2	−625.699648	72.534	2.30	7704	2023	1646
T3	−625.699648	72.534	2.30	7703	2024	1646
R = CH ₃						
T1	−665.046944	0.000	5.64	3386	2021	1305
T2	−665.016859	78.990	2.48	3442	1996	1303
T3	−665.012176	91.282	4.13	3387	1984	1291

carbons were analysed using a program based on Maricq and Waugh [10] and developed by Durham University, UK, and run on a unix platform. The calculated chemical shift tensors are given in Table 1.

2.3. Molecular computations

Using the Gaussian 98 program system [11], calculations at the density functional theory (DFT) [12] levels using Becke's nonlocal three-parameter exchange and correlated functional with Lee–Yang–Parr correlation (B3LYP) [13] functional methods were performed. The optimized molecular geometries and energies were obtained using 6-311+G** basis sets. Imidazolidine-2-thione (and its N-methyl derivative) has three expected tautomers, Scheme 1. These tautomers could be classified as the thione form (T1) and two thiol tautomers, where the S–H bond maybe eclipse the C=N bond (T2) or being anti to it (T3). The B3LYP/6-311+G** optimized total energies, relative energies, dipole moments and rotational constants are listed in Table 2. The calculated energies suggest the higher stability of the T1 relative to the other tautomeric forms. In Imt, the *cis* (T2) and *trans* (T3) thiol tautomers are found to be of equal energy that is about 72.5 kJ/mol higher than that of the thione form. However, in N-methylimidazolidine-2-thione, the stability order based on the calculated relative energies of the three tautomers is T1 < T2 < T3.

The optimized structural parameters, namely, intermolecular bond lengths and angles for the three tautomers of both the molecules are listed in Tables 3 and 4 and are compared to the X-ray data for N,N-dimethyl-2-imidazolidinethione [14]. The geometries calculated by this method are expected [15] to have rms errors of ca. 0.006 Å for the bond lengths and ca. ±4 kJ/mol for the energies. It is clear that the X-ray data agrees well with the calculated results for the thione tautomer (T1). In Imt, the C3–N1

Table 3
Optimized Parameters for 2-imidazolidinethione calculated at B3LYP/6-311+G**

	T1	T2	T3	Exp.
Bond length (Å)				
C2-N1	1.463	1.476	1.476	1.449
C3-N1	1.369	1.394	1.394	1.342
H-N1	1.008	1.011	1.011	
C-C	1.540	1.551	1.551	1.517
S-C	1.666	1.775	1.775	1.673
N7-C3	1.369	1.275	1.275	1.334
H-S/H-N1	1.008	1.347	1.347	
Bond angles (°)				
C3N1C2	111.6	105.2	105.2	112.1
HN1C2	122.8	117.8	117.8	
CCN1	100.8	100.7	100.7	102.7
SCN1	126.6	117.3	117.3	126.4
NCN	106.8	117.6	117.6	108.9
HSC/ HN7C	118.3	93.6	93.6	
Dihedral angles (°)				
HN1C2C3	149.3	133.2	133.2	
CCNC	24.4	20.7	20.7	
SCN1C	169.9	167.7	167.7	
N7CN1S	180.0	177.4	177.4	
HSCN1/HNCN	199.0	5.5	182.8	

X-ray data for N,N-dimethyl-2-imidazolidinethione taken from [14].

and S–C bond lengths in T1 were about 1.369 (Å) and 1.666 (Å), respectively, these values changed to 1.275 (Å) and 1.775 (Å) in T2 and T3 due to the formation and/or disappearance of double bonds. The calculated dihedral angles showed that the molecule is non-planar.

The dihedral angle CCNC shows nonplanarity of about 24.4° out of the plane. Furthermore, in the *cis* (T2) and *trans* (T3) tautomers, the HSCN dihedral angle shows a deviation from nonplanarity by about 5.5° in T2 and about 3° in the T3.

3. Results and discussion

The solid-state CPMAS ¹³C spectrum Imt (**1a**) is shown in Fig. 1. Based on the gas phase calculation, we expect only two isotropic peaks for this compound in its thione form. However, there is an extra set of peaks which can only be explained in terms of a tautomeric isomer. This phenomenon was not observed in any of the other compounds studied. Imt was prepared three times independently, and spectra recorded showed similar pattern indicating the reproducibility of the result. The splitting observed in the high field region cannot be attributed to the second order quadrupolar effects due to the nitrogen nuclei as this was not observed in any of the other related molecules. Moreover, at the high fields (11.74 T) used in our experiment, this effect is expected to be very low. The second order effect due to two equivalent nitrogens should result in a 4 : 4 : 1 triplet for the thione carbon. However, we do not observe any splitting. So we can safely assume that the second order effects are negligible in these case.

A similar tautomerism has been suggested in imidazoline in its coordination compounds [16]. The tautomers present in five-membered rings that contain nitrogen (azoles) have been reported [17]. In spite

Table 4

Optimized parameters for N-methyl-2-imidazolidinethione calculated at B3LYP/6-311+G**

	T1	T2	T3	Exp.
Bond length (Å)				
C2-N1	1.462	1.477	1.473	1.449
C3-N1	1.373	1.279	1.278	1.342
C-C	1.536	1.544	1.540	1.517
S-C	1.670	1.779	1.777	1.673
H-S /H-N	1.008	1.347	1.347	
N7-C3	1.367	1.391	1.400	1.334
N7-R	1.448	1.453	1.452	1.459
Bond angles (°)				
C3N1C2	111.4	105.6	106.0	112.1
CCN1	100.6	105.3	105.0	103.3
SCN1	125.0	123.6	118.7	124.7
HSC/ HN1C	122.2	92.8	97.8	
NCN	107.3	117.7	117.3	108.9
RN7C3	124.0	123.2	124.2	125.8
Dihedral angles (°)				
C3N1C2C4	-24.7	-14.5	-15.5	
SC3N1C2	192.0	182.8	185.8	
HSCN1		2.1	190.2	
N7C3N1C2	180.1	177.5	175.1	
RN7C3C4	-203.0	-220.3	-221.8	

X-ray data for N,N-dimethyl-2-imidazolidinethione taken from [14].

Fig. 1. CPMAS spectrum of Imt. *Denotes spinning side-bands.

Scheme 2.

of the higher energy of the thiol tautomer in the gas phase, the stability of the thiol tautomer in the solid state may be explained due to the hydrogen bonding possible in the solid state (Scheme 2).

The Imt (**1a**) peaks are broader than the peaks in the other compounds and this can be explained due to the interproton transfer [17,18] possible in the catenation form shown above. This also explains the fact that N-mono substituted Imt compounds do not show tautomerism, due to the absence of the stabilizing H bonding possible in these compounds. This would imply we have got mixed crystals rather than having the two tautomers in the same unit cell. A similar situation where two crystal forms of a tetrazole containing compound was observed [19].

In the IR spectrum the S–H stretching is generally expected to be weak around $2550\text{--}2600\text{ cm}^{-1}$. The IR spectrum of solid Imt (**1a**) does show a weak peak at 2575 cm^{-1} , confirming the presence of thiol form in the solid state. The solution C-13 NMR spectrum of **1a** in DMSO, on the other hand, showed only two peaks at 183.4 ppm and 44.1 ppm corresponding to the thione structure. This indicates that the hydrogen bonded structure of the thiol form breaks down in solution giving rise to near 100% thione form.

The chemical shift tensors, anisotropy and asymmetry factors for the compounds studies are given in Table 1. The shielding tensor component 3 is defined as the one farthest from the isotropic value and component 2 is the closest to the isotropic. When the component 2 is more shielded than the isotropic value the anisotropy will be negative, as observed in the compounds **1b–1g**. At the same time components 1 and 3 appear to swap. There seem to be only a minor effect in the tensors by the substitution on the nitrogen atoms in the Imt moiety. The thione carbon peaks (isotropic as well as side-bands) of compound **1d** are 1 : 1 doublets, indicating two non-equivalent molecules in the unit cell.

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