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¹³C AND ¹H NMR STUDY OF COMPLEXES OF 2-PYRIDINETHIONE AND 4-PYRIDINETHIONE WITH Zn(II), Cd(II) AND Hg(II) HALIDES

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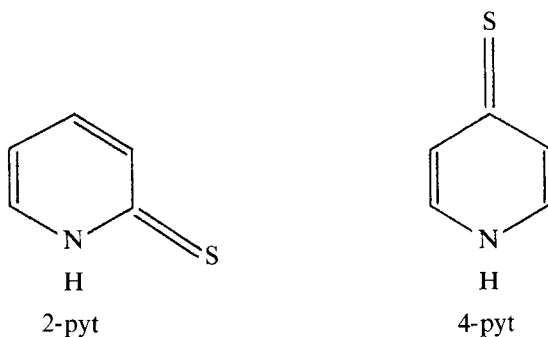
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Proton and carbon-13 NMR has been used to study complexes of 2-pyridinethione (in its basic and deprotonated forms) and 4-pyridinethione with zinc(II), cadmium(II) and mercury(II) halides. The variations in the carbon-13 and proton chemical shifts are discussed.

INTRODUCTION

Transition metal complexes of 2-pyridinethione (2-pyt) and 4-pyridinethione (4-pyt) were first prepared and studied in some detail before ¹³C and ¹H NMR were generally available.^{1,2} Thus, despite the fact that a substantial number of 2-pyt and 4-pyt complexes are known, no ¹³C and ¹H NMR data for these complexes have been reported. 2-pyt can be considered as a model compound for thiolated nucleosides such as 6-thioguanosine.³ This study by ¹³C and ¹H NMR was carried out in order to further elucidate the interaction of 2B metal ions with 2-pyt and 4-pyt.



EXPERIMENTAL

Commercially available high purity chemicals were employed. The complexes of deprotonated 2-pyt were obtained by reacting ethanolic solutions of the ligand with the metal acetate in a 2:1 molar ratio. The resulting complexes were washed with dry ether and dried *in vacuo*. The complexes of neutral 2-pyt and 4-pyt were obtained by following literature procedures.^{1,2} The complexes analysed satisfactorily for the stoichiometries shown in Tables I and II.

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TABLE I
¹³C NMR data for 2-pyt and 4-pyt and their complexes.

Compound	C(2)	C(3)	C(4)	C(5)	C(6)
<i>L</i> = 2-pyt	177.8	132.9	137.9	112.4	137.1
ZnL ₂ Cl ₂	176.0	132.7	138.0	113.5	138.0
ZnL ₂ Br ₂	175.4	132.5	138.2	113.9	138.2
CdL ₂ Cl ₂	174.0	132.5	138.7	114.7	138.5
CdL ₂ Br ₂	172.9	132.4	139.2	115.2	138.7
HgL ₂ Cl ₂	168.9	131.6	140.9	118.1	139.7
HgL ₂ Br ₂	167.5	131.4	141.4	118.5	140.0
Cd(L-H) ₂	166.0	124.7	136.0	115.6	146.6
Hg(L-H) ₂	164.0	123.4	136.8	119.3	148.0
<i>L'</i> = 4-pyt	133.2	129.3	190.2		
ZnL' ₂ Cl ₂	135.3	128.7	180.8		
CdL' ₂ Cl ₂	135.1	129.0	178.8		
HgL' ₂ Cl ₂	135.8	127.9	175.4		

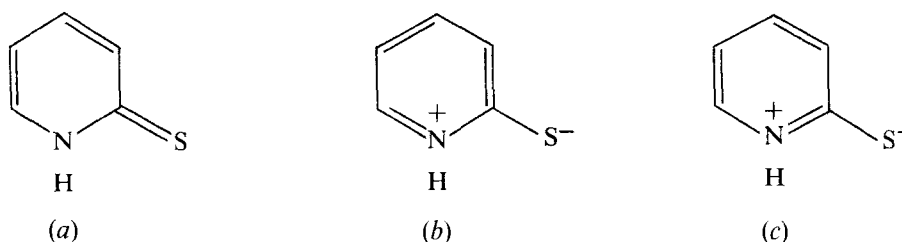
TABLE II
¹H NMR data for 2-pyt and 4-pyt and their Complexes.

Compound	3-H	4-H	5-H	6-H	N-H
<i>L</i> = 2-pyt	7.30	7.41	6.77	7.67	13.52
ZnL ₂ Cl ₂	7.36	7.44	6.79	7.69	13.52
CdL ₂ Cl ₂	7.38	7.46	6.80	7.70	13.52
HgL ₂ Cl ₂	7.95	7.95	7.33	8.22	
Zn(L-H) ₂	7.63	7.63	7.10	7.83	
Cd(L-H) ₂	7.33	7.20	6.79	7.87	
Hg(L-H) ₂	7.35	7.57	7.07	8.19	
<i>L'</i> = 4-pyt			7.18	7.66	
ZnL' ₂ Cl ₂			7.52	7.85	
CdL' ₂ Cl ₂			7.89	8.25	
HgL' ₂ Cl ₂			7.90	8.27	

The ¹H and ¹³C NMR spectra were recorded employing a Bruker WH 270 FT spectrometer operating at 270 and 67.87 MHz respectively with a deuterium internal lock. TMS was used as the internal reference with DMSO-*d*₆ as solvent. The ¹H and ¹³C chemical shifts are reported in ppm relative to TMS.

RESULTS AND DISCUSSION

The lactam-thione structure of 2-pyt has been confirmed by X-ray diffraction studies⁴ and the same tautomeric form is preserved in solution.⁵ Table I gives ¹³C chemical shifts for the metal complexes of 2-pyt and 4-pyt. The assignments for the free ligands are also listed for comparison. Charge-transfer features as well as bond-order parameters influence the ¹³C chemical shifts of six-membered heterocyclic nitrogen compounds.^{6,7} Theoretically, the addition of metal salts to a solution of a ligand should result in the downfield chemical shifts of the carbon resonances in the vicinity of the coordination site.^{8,9} However, the spectra of the 2-pyt complexes show that C(2), which is in the proximity of the presumed coordination sites, experiences an upfield shift which is somewhat larger than the upfield shift of the C(3) signal. The other carbon atoms show downfield chemical shifts of relatively smaller magnitude. It is easy to see that upon bonding of 2-pyt through sulfur, the canonical forms (b) and (c) contribute more to the bonding of 2-pyt, with the effect that charge density increases at the C(2) and C(3) positions and decreases at the remaining carbon sites. This is consistent with the observed chemical shifts. Furthermore, the relatively larger downfield chemical shifts for C(5) may also be predicted.¹⁰



In the spectra of the deprotonated 2-pyt complexes, a pertinent observation is the greater upfield shift of the C(2) and C(3) signals as well as the greater downfield shift of the C(6) resonance. Whereas in the complexes with neutral 2-pyt, the C(4) peak in the deprotonated 2-pyt complexes is consistent with the majority of the negative charge residing on sulfur. In addition, the shift also reflects the strength of the metal-nitrogen bond. The results show that Cd-N bonding should be stronger than Hg-N bonding. It may be noted that the coordination of 2-pyt solely through the nitrogen atom should produce downfield shifts of the C(4) and C(6) peaks and an upfield shift of the C(5) peak.¹¹

The ¹³C NMR spectra of the 4-pyt complexes are relatively simple. In the metal complexes, although both C(3) and C(4) signals are shifted upfield, C(4), which is adjacent to the coordination site, experiences more upfield shifts. In all the above complexes, the magnitudes of the shifts are larger for the mercury complexes. This is in accord with the preferences of mercury(II) for "soft" sulfur donors.

The ¹H chemical shifts for 2-pyt, 4-pyt and their complexes are listed in Table II. The bonding of 2-pyt to the metal ions through sulfur causes expected but negligible downfield shifts for the C-H protons. The shifts are pronounced only for the Hg(II) complexes. The N-H resonance occurs as a weak broad signal for the free ligand and is unshifted in the spectra of the Zn(II) and Cd(II) complexes. It is not discernable in the spectra of Hg(II) complexes. The changes in the chemical shifts are similar to those noted on protonation of the carbonyl oxygen of 2-pyridone.¹² Similar shifts are noted for the complexes with deprotonated 2-pyt. The fact that the shifts are larger for the Zn(II) complexes of deprotonated 2-pyt

suggests stronger bonding of Zn(II) to the ring nitrogen. In the spectra, the highfield shift of the H(4) proton in the Cd(L-H)₂ and Hg(L-H)₂ complexes relative to CdL₂Cl₂ and HgL₂Cl₂ (where L = 2-pyt) and the lowfield shift of H(4) in the Zn(L-H)₂ complex compared with ZnL₂Cl₂ is consistent with the higher electron density on sulfur in the former complexes and on the ring nitrogen in the latter complex. The results are also consistent with the ¹³C chemical shifts. The smaller net shifts of the ring protons are concordant with the smaller ring current and the decreased C=X group anisotropy shifts expected in pyridinethiones.⁵

In the spectra of the 4-pyt complexes, the C-H ring protons register significant downfield shifts in agreement with the bonding of 4-pyt through the sulfur atom. The N(H) resonance is not discernable in DMSO-*d*₆ solutions probably due to the fact the signal is very broad.

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