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The ^{1}H and ^{13}C NMR Spectra of some Monothio-β-diketonate Chelates having Phenyl and Methyl Substituents

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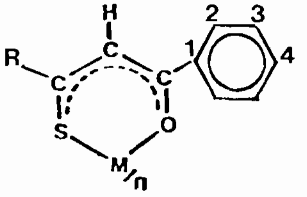
Introduction

Our previous ^{13}C and ^{19}F NMR studies of metal chelates of monothio-β-diketones, $RCSCH_2COR'$, have included a number of metals from the first, second and third row transition series. The R-substituents have been phenyl, aryl, 2′-naphthyl and 2′-thienyl and the R′-substituents being difluoromethyl, trifluromethyl, pentafluoroethyl and heptafluoropropyl [1–6]. Chemical shift ^{13}C NMR data indicates a geometry and a metal dependence on the diketonate ring carbon resonances and ^{19}F NMR chemical shift data is also related to the geometry of the complex.

This paper reports a ^{13}C NMR study of some nickel, palladium, zinc and cobalt chelates of $C_6H_5CSCH_2COC_6H_5$ and $CH_3CSCH_2COC_6H_5$ (see below). The rhodium complex, $Rh(C_6H_5CSCHCOC_6H_5)_3$ is also included for comparative purposes. Assignments of all the carbons have been made and their chemical shifts are compared to those in the monothio-β-diketone ligands, $CH_3CSCH_2COC_6H_5$ and $C_6H_5CSCH_2COC_6H_5$ [7] and the β-diketone ligands, $CH_3COCH_2COC_6H_5$ and $C_6H_5COCH_2COC_6H_5$.



R: CH_3, C_6H_5

M/n: Ni/2, Pd/2, Zn/2, Co/3

Experimental

The complexes were prepared according to the published procedures [8, 9]. The NMR were recorded in chloroform-d$_1$ and were taken on a JEOL-FVX600 NMR spectrometer. The ^{13}C NMR proton decoupled spectra were run over a 4000 Hz sweep width using 8 K and 16 K data points and the ^{1}H NMR spectra were run over a 1000 Hz sweep width using 8 K data points. Chemical shift data are recorded as downfield from tetramethylsilane (TMS).

Results and Discussion

The ^{13}C NMR chemical shift data for the metal complexes of $CH_3CSCH_2COC_6H_5$ and $C_6H_5CSCH_2$-

TABLE I. Chemical Shift Data (ppm) on Metal Chelates of $CH_3CSCH_2COC_6H_5$ (L–H) and $C_6H_5CSCH_2COC_6H_5$ (L′–H).

Complex	CS	CO	CH	C-1	C-2	C-3	C-4
NiL_2	181.1	179.4	114.9	137.4	127.1	128.2	131.4
PdL_2	181.9	177.3	115.4	138.1	127.4	128.2	131.5
ZnL_2	189.5	187.2	115.2	139.2	127.9	128.1	132.1
CoL_3	184.4	181.6	112.0	139.6	127.4	128.0	131.2
NiL'_2	181.9	178.3	114.2	137.7[a]	127.1	128.4	131.5
				141.6[b]	126.5	128.0	129.7
PdL'_2	182.8	177.0	115.1	138.8[a]	127.6	128.3	131.7
				142.5[b]	126.9	128.0	129.7
ZnL'_2	190.1	185.4	115.3	139.5[a]	128.0	128.2	132.3
				146.8[b]	126.9	128.0	129.7
CoL'_3	185.2	181.1	112.0	139.8[a]	127.4	128.0	131.3
				141.8[b]	126.8	127.9	129.4

[a] 1st row, R′-phenyl carbons. [b] 2nd row, R-phenyl carbons.

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TABLE II. Chemical Shift Data (ppm) for the Ligands $RCSCH_2COR'$ and $RCOCH_2COR'$.

Ligand	CS	CO	CH	C-1	C-2	C-3	C-4
$CH_3CSCH_2COC_6H_5$	197.0	180.6	112.2	135.7	126.9	128.4	132.1
$C_6H_5CSCH_2COC_6H_5$[a]	202.6	179.3	110.3	135.4[b] 145.1[c]	126.9 126.4	128.4 128.1	132.2 130.7
$CH_3COCH_2COC_6H_5$	–	193.0[d] 182.2[e]	96.4	134.5	126.6	128.1	131.8
$C_6H_5COCH_2COC_6H_5$[f]	–	185.3	93.0	135.4	126.9	128.3	132.0

[a] Data taken from ref. 7. [b] 1st row, R'-phenyl carbons. [c] 2nd row, R -phenyl carbons. [d] R-carbonyl resonance. [e] R'-carbonyl resonance. [f] Data taken from ref. 7.

COC_6H_5 are presented in Table I. Dipole moment data on these chelates have indicated a *cis*-square planar configuration for the nickel and palladium complexes and a tetrahedral configuration for the zinc chelates [8, 9]. Dipole moment data of the cobalt complex indicates a *facial* octahedral rather than a *meridional* configuration [8]. The ^{13}C NMR spectra data on $Co(CH_3CSCHCOC_6H_5)_3$ and $Co(C_6H_5CSCHCOC_6H_5)_3$ supports the *facial* octahedral geometry as only one set of resonances is observed for each respective carbon; whereas a *meridional* structure would have three resonances for each respective carbon. The *facial* octahedral isomer has C_3 axis of symmetry which is absent from the *mer-*

Table II includes chemical shift data on the ligands $CH_3CSCH_2COC_6H_5$, $CH_3COCH_2COC_6H_5$, $C_6H_5CSCH_2COC_6H_5$ and $C_6H_5COCH_2COC_6H_5$. The thiocarbonyl carbons of the chelates are all more shielded for all of the complexes as compared to this resonance in the ligands. The zinc and cobalt complexes show a more deshielded carbonyl carbon resonance as compared to the corresponding resonance in the ligands; whereas, the nickel and palladium complexes show a more shielded resonance. The methine carbon resonance is shift downfield as compared to this carbon in the ligands. This deshielding of the C–H carbon has been related to the quasi-aromatic character of the diketone ligand on coordination to the metal [10, 11]. Although, this shift appears to have a small dependence on the metal complexed, the cobalt chelate gives the smallest chemical shift difference. We have reported this observation on other monothio-β-diketonate complexes [2]. Also as previously reported the carbonyl and thiocarbonyl carbon resonances are geometry related with the chemical shift order being tetrahedral > octahedral > square planar [4, 6].

The replacement of the less electronegative sulfur than for oxygen in the diketone ring of the ligand causes the thiocarbonyl and methine carbon resonance to be more deshielded and the carbonyl carbon resonance to be more shielded (Table II). The monothio-β-diketone ligand is believed to involve a enol–enethiol equilibrium [12]; whereas, a quasi-aromatic structure for the diketone ligand is proposed [13]. In the latter structure the enol-proton is bonded to both carbonyl oxygens, O–H–O. Electronic and infrared spectra support a tautomeric enol–enethiol equilibrium mixture for the monothio-β-diketone ligand which interconverts very rapidly on the NMR time scale. Our ^{13}C NMR data supports the enol structure as no methylene carbon resonance is observed.

The assignments of the phenyl carbons (Tables I and II) were based on intensity, an off resonance study and on previous work [14]. One notes that these phenyl resonance of the diketone and monothio-β-diketone ligands show little change in substitution of a sulfur atom for an oxygen atom. Furthermore on coordination the only phenyl carbon resonance which experiences a change is the deshielding of the C-1 resonance of the R'-phenyl carbons and a shielding of this carbon (except the Zn chelate) in the R-substituent. The phenyl carbon resonances of the metal complexes of $C_6H_5CSCH_2COC_6H_5$ and its corresponding ligand are based on the assignments for the phenyl carbons of the diketone $CH_3CSCH_2COC_6H_5$ and its metal complexes. The R'-phenyl carbons are all more deshielded than the corresponding R-phenyl carbons except the quaternary C-1 carbon resonances which are more shielded.

The effect of complexation on the shielding of the C-1 carbon of the R-substituent is also seen in the chemical shift of the methyl carbon resonance of the $CH_3CSCH_2COC_6H_5$ ligand and its chelates. These occurred at chemical shifts (ppm) of 35.5, 29.3, 30.1 36.4, 29.0 for the ligand, Ni, Pd, Zn and Co species, respectively. The smaller chemical shifts of the square planar and octahedral complexes have been reported in previous work [3]. A similar trend in the chemical shift (ppm) of the methyl protons of the corresponding species is observed from ^1H NMR spectra: 2.54, 2.32, 2.50, 2.58, 2.39.

^{1}H NMR chemical shift data of the methine proton in a complex shows a shift to lower field as compared with the ligand $CH_3C(SH)=CHCOC_6H_5$ and its Ni, Pd, Zn, and Co complexes. These resonances occurred at 6.99, 7.08, 7.01, 7.20 and 7.08 ppm, respectively.

Finally, our NMR studies show that the chemical shift of the diketone carbons are effected by the R and R$'$ substituents as well as configuration and the metal complexed. While the latter two effects have been referred to in our earlier studies, it now seems possible to draw several generalizations regarding the effect of the R and R$'$-substituents. The chemical shift of the thiocarbonyl carbon is larger when the R group is alkyl as compared to phenyl or aryl provided the R$'$ group is kept constant. The methine and carbonyl carbons resonances are more shielded when the R$'$ group is a fluorinated alkyl group (CHF_2, CF_3, C_2F_5, C_3F_7) as compared to a phenyl group. This ordering of the monothio-β-diketone ring carbon resonances appears to hold for not only the first row transition metal complexes but also for second an third transition metal complexes [5]. For example the chemical shifts of the C–S, C–O and C–H carbon resonance are 190.8, 172.6, 109.5 ppm respectively for the $Rh(C_6H_5CSCHCOCF_3)_3$ complex [5] and 183.9, 180.8 and 114.0 (ppm) for the $Rh(C_6H_5CSCHCOC_6H_5)_3$. The latter complex also show J(C–Rh) spin coupling of 1.5 Hz and 2.0 Hz for the C–H and C–O carbons, respectively.

The high soubility of these phenyl substituted monothio-β-diketonate complexes should make these compounds more favorable for solution studies as compared to the corresponding β-diketonate complexes. The monothio-β-diketonate complexes are anhydrous, monomeric and soluble in organic solvents whereas the β-diketonate complexes are solvated, polymeric and insoluble in organic solvents [15].

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