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NMR STUDIES ON SOME MONOTHIO-β-DIKETONATE COMPLEXES AND THE CORRESPONDING β-DIKETONES CONTAINING A PERFLUOROPROPYL GROUP

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SUMMARY

The ^{13}C and ^{19}F NMR spectra of nine metal complexes containing a monothio-β-diketone ligand with a perfluoropropyl group have been recorded in chloroform-d. The chelates are of the type $(MRCSCHCOC_3F_7)_n$ where M is nickel, palladium and cobalt and n is 2 (Ni, Pd) and 3 (Co). The R-substituent is 2'-thienyl (C_4H_3S), phenyl (C_6H_5) or 2'-naphthyl $(C_{10}H_7)$. Correlations between the chemical shifts of the complexes' and ligands' respective carbon and fluorine resonances are presented. The data shows a metal dependence on the diketonate carbon ring resonances when the R-substituent is kept constant. Correlations in the chemical shift data of the β-diketone carbon resonances are also present. ^{19}F noise decoupled ^{13}C NMR spectral data, $^{13}C\{^{19}F\}$, assisted in assigning the perfluoropropyl carbon resonances.

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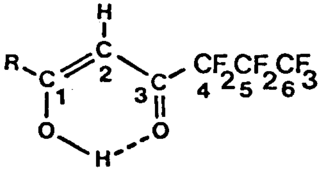
INTRODUCTION

Our ^{13}C nuclear magnetic resonance studies of various monothio-β-diketonate complexes, $M[RCSCHCOR']_n$ where the R-group is alkyl, phenyl aryl or 2'-thienyl and the R'-group is CHF_2, CF_3 or C_2F_5, show that the chemical shift of the diketonate rings carbons to be metal and/or geometry dependent. Similarly, ^{19}F NMR chemical shift data of the R'-group fluorines show a geometry relationship [1-4].

Now we have extended these NMR studies to include metal chelates of monothio-β-diketones having a perfluoropropyl substituent, $RC(SH)=CHCOC_3F_7$ (L-H). We have previously reported dipole moment data on these complexes where R is phenyl, 2'-naphthyl or 2'-thienyl [5]. The nickel and palladium complexes, ML_2, have a high dipole moment which definitely indicates a *cis*-square planar geometry while the dipole moment of the cobalt complexes, ML_3, tends to support a *facial* octahedral configuration. In this study we have also included NMR data on the corresponding β-diketones, $RC(OH)=CHCOC_3F_7$ (see below).



EXPERIMENTAL

The monothio-β-diketone ligands 1,1,1,2,2,3,3-heptafluoro-6-mercapto-6-(2'-thienyl)hex-5-en-4-one, 1,1,1,2,2,3,3-heptafluoro-6-mercapto-6-(phenyl) hex-5-en-4-one and 1,1,1,2,2,3,3-heptafluoro-6-mercapto-6-(2'-naphthyl)hex-5-en-4-one and their metal chelates of nickel(II), palladium(II) and cobalt(III were prepared as previously described [5].

The ^{13}C and ^{19}NMR spectra were taken on a JEOL-FX60Q NMR spectrometer. All samples were run in $CDCl_3$. The ^{13}C proton noise decoupled spectra, $^{13}C\{H\}$, were run over a 4000 Hz sweep width using 16K data points. Fluorine noise decoupled spectra [6], $^{13}C\{^{19}F\}$, were run on the monothio-β-diketonate ligands and on the nickel(II), palladium(II) and cobalt(III) complexes of $C_6H_5C(SH)$=$CHCOC_3F_7$. To obtain the weak perfluoropropyl carbon resonances of the metal chelates it was necessary to use the frequency domain accumulation (FYDAC) mode in the JEOLCO software. The major peaks in the spectrum were overflowed and 25 to 50 blocks of 1000 scans were run and signal averaged. The ^{19}F proton noise decoupled spectra, $^{19}F\{'H\}$, were run at 56.3 MHz over a 15,150 Hz sweep width. Chemical shift data are recorded downfield from TMS (^{13}C) and upfield from $CFCl_3$ (^{19}F).

RESULTS AND DISCUSSION

^{13}C chemical shift and coupling constant data for the three β-diketone, $RC(OH)$=$CHCOC_3F_7$ are presented in Table 1. The carbonyl carbons of the R-substituted phenyl and 2'-naphthyl ligands are more deshielded than the R-substituted 2'-thienyl ligand and the reverse shielding trend is observed for the methine carbon resonance. Similar shielding results were obtained for the same ligands having trifluoromethyl and perfluoroethyl substituents [1-4].

The metal (geometry) dependence on the chemical shift of the ring carbons in the monothio-β-diketonate complexes is shown in Table 2. The square planar nickel and palladium complex, ML_2, give a more shielded thio-carbonyl and carbonyl carbon resonances than the octahedral cobalt complexes. The methine carbon resonance is more shielded in the octahedral cobalt complexes than in the nickel and palladium square planar complexes. These shielding results are in consort with our previously reported data [1-4].

TABLE I

^{13}C NMR Chemical Shift (ppm) and Coupling Constant Data (Hz) of the β-Diketones, $RC(OH)=CHCOC_3F_7$ (L-H)

R	C-1	C-2	C-3	C-4	C-5	C-6
C_6H_5	185.6	93.8(3.4)[a]	178.8(26.6)[b]	109.4[c]	108.7[d]	117.7[e]
2'-$C_{10}H_7$	185.0	93.9(3.4)[a]	178.3(26.2)[b]	109.2[c]	108.4[d]	117.6[e]
2'-C_4H_3S	181.9	95.0(3.5)[a]	172.8(26.9)[b]	109.5[c]	108.5[d]	117.6[e]
$C^{13}\{^{19}F\}$[f]	-	-	-	109.1	108.3	117.3

[a] $^3J_{C-F}$, [b] $^2J_{C-F}$

[c] $^1J_{C-F} = 262.7 \pm 0.5$ Hz; $^2J_{C-F} = 31.4 \pm 0.1$ Hz

[d] $^1J_{C-F} = 263.2 \pm 0.0$ Hz; $^2J_{C_5-F_6} = 38.6 \pm 0.0$ Hz; $^2J_{C_5-F_4} = 34.4 \pm 0.2$ Hz

[e] $^1J_{C-F} = 287.6 \pm 0.0$ Hz; $^2J_{C-F} = 33.5 \pm 0.0$ Hz

[f] ^{19}F noise decoupled ^{13}C NMR spectra (Avg. Value)

TABLE 2

^{13}C NMR Chemical Shifts (ppm) and Coupling Constants (Hz) of Metal Complexes of $RC(SH){=}CHCOC_3F_7$ (L-H)

Complex	R	C-S(1)	C-O(2)	C-H(3)
NiL_2	2'-thienyl	176.8	171.3(23.9)[a]	108.8(2.9)[b]
PdL_2	2'-thienyl	176.2	172.4(24.1)	108.8(2.9)
CoL_3	2'-thienyl	179.4	174.5(23.9)	105.4(2.7)
NiL_2[c]	phenyl	187.9	171.8(24.9)	111.9(3.0)
PdL_2[c]	phenyl	187.0	172.4(24.8)	111.8(2.9)
CoL_3[c]	phenyl	191.0	175.0(24.9)	108.5(2.9)
NiL_2	2'-naphthyl	187.5	171.6(24.9)	111.9(2.9)
PdL_2	2'-naphthyl	186.8	172.4(24.2)	111.9(2.8)
CoL_3	2'-naphthyl	190.8	171.5(24.9)	108.7(2.9)

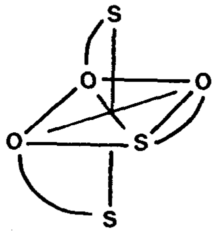
[a] $^2J_{C-F}$, [b] $^3J_{C-F}$

[c] $^{13}C\{^{19}F\}$ for C-4, 109.6 ± 0.3; C-5, 108.1 ± 0.1; C-6, 117.2 ±0.0 ppm

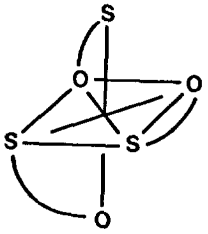
Since the perfluoropropyl group is a ten spin system of the type $ABCX_3Y_2Z_2$, it was necessary to use a ^{19}F noise decoupling technique, $^{13}C\{^{19}F\}$, to obtain these carbon resonances. This procedure aided in the interpretation of the ^{19}F coupled ^{13}C NMR spectra of the ligands and in the assignment of their perfluoropropyl carbons resonances (Table 1). The assignments of the C-1 to C-6 carbons varied at the most by 0.2 ppm by this procedure from those assigned by spectral interpretation. No $^3J_{C-F}$ coupling between the alkyl carbons of the diketone ligand is observed. Table 2 also shows these ^{19}F noise decoupled ^{13}C resonances of the Ni, Pd and Co complexes of $C_6H_6C(SH)=CHCOC_3F_7$. Under the normal condition these perfluoropropyl carbon resonances in the complexes are lost in the baseline and as described in the experimental section it was necessary to use the frequency domain accumulation (FYDAC) mode to obtain these resonances. These alkyl carbon resonances are in good agreement with those assigned for the diketone ligand (Table 1) using both the noise decoupling technique and spectral interpretation. The R-group substituent has no electronic effect on the chemical shift of the alkyl carbons of the C_3F_7 group which also supports our previous data on the carbon resonances of the R' groups CHF_2, CF_3 and C_2F_5 in RC(OH)=CHCOR' and RC(SH)=CHCOR' ligands [2,3]. The decoupled ^{13}C spectra give a $^1J_{C-H}$ for the methine carbon of 168.9 ppm which is a typical coupling constant for this type of carbon-hydrogen spin coupling [7].

The ^{19}F NMR spectra of the ligands shows no spin coupling of the C-4 fluorines and only spin coupling between the C-5 and C-6 fluorines. The chemical shifts of these fluorines relative to $CFCl_3$ are:
$^4CF_2$(s, -127.1 ± 0.0 ppm); $^5CF_2$(q, -121.8 ± 0.1 ppm, $^3J_{F-F}$ 8.8 ± 0.2 Hz); $^6CF_3$(t, -81.1 ppm, $^3J_{F-F}$ 8.6 ± 0.3 Hz). The ^{19}F NMR of the metal chelates also showed spin coupling of the C-5 and C-6 fluorines and no spin coupling of the C-4 fluorines. Only the $^5CF_2$ fluorine resonances of the β-diketone ligand changed on coordination as a monothio-β-diketonate ligand:
$^4CF_2$(s, -126.9 ± 0.1 ppm); $^5CF_2$(q, -118.8 ± 0.2 ppm, $^3J_{F-F}$7.1 ± 1.6 Hz); $^6CF_3$(t, -81.1 ± 0.1 ppm, $^3J_{F-F}$ 7.8 ± 0.4 Hz). The square planar and octahedral complexes do not exhibit the metal (geometry) relationship described in our previous work for monothio-β-diketonate complexes with R'-CF_3 and R'C_2F_5 substituents [1-4]. Possibly the increased inductive effect of the perfluoropropyl fluorines cancels any shielding change of the $^4CF_2$ fluorine resonance due to metal coordination and/or configuration.

The cobalt complexes, CoL_3, can have either a *facial* or *meridional* octahedral configuration (see below). The evidence from dipole moments



trans(mer)



cis(fac)

suggest a *facial* geometry [5]. Our ^{13}C NMR spectra all show one resonance for each specific carbon in the complex. A *meridional* configuration would have three resonance for each carbon since the C_3 axis of symmetry present in the *facial* configuration is absent in the *meridional* configuration. Our previous reports on other cobalt(III) and rhodium(III) complexes also support a *facial* geometry [1-4]. Preferential formation of the *cis*-structure is probably due to d_π- d_π bonding between the cobalt and the three sulfur atoms which are at right angles for the cobalt [8]. An alternate explanation for the *cis* structure is that it may be due to weak nonbonded S····S interactions [9].

Finally our ^{13}C NMR spectral data indicates that the enol form of the β-diketonate ligand dominates in solution. No methylene carbon resonance and only one resonance for each carbonyl carbon are observed. These data are in accord with ^1H NMR data and our previously reported ^{13}C NMR data on β-diketonate and monothio-β-diketonate ligands [2,3,10]. While it was generally believed that the β-diketone ligand exists in solution as two tautomeric enol forms which interconvert very rapidly on the NMR time scale, Shapet'ko has presented ^1H and ^{13}C NMR data which suggests that an enol-enolic tautomerism is absent in β-diketones. A quasi-aromatic structure in which the hydrogen atom is bonded to both carbonyl oxygens (O--H--O) is proposed [11-13]. Duus has shown from IR and UV spectral data that monothio-β-diketones exist as an equilibrium mixture of the tautomeric enol-enethiol forms which convert very rapidly on the NMR time scale. [14-16].

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NOTE ADDED IN PROOF

Uhlemann [17] has recently shown from ^1H NMR and quantum chemical PCILO calculations that monothio-β-diketones, $RCSCH_2COR'$, exist in solution as different isomers depending on the R and R' substituents, solvent and temperature. In solvents of low dielectric constants the hydrogen-bridged *cis* enol form predominates and is in a fast equilibrium down to at least -100°C with the nonchelated *trans* enol form. This study also reports no indication for the presence of chelated and nonchelated enethiol isomers.

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