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BIS(PERFLUOROALKYL AND ARYL SUBSTITUTED ACETYLACETONATE)BERYLLIUM(II) CHELATES

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SUMMARY

The synthesis of eight beryllium chelates having substituted beta-diketone ligands, $\text{RCOCH}_2\text{COR}'$, is reported (R=methyl, 2'-thienyl, 2'-furyl, phenyl; R'=CF₃, C₂F₅, C₃F₇). ¹³C, ¹⁹F and ¹H NMR spectra data are compared to give a shielding order. These four-coordinate pseudo-tetrahedral complexes of idealized C₂ symmetry all give a more deshielded ring carbon than the corresponding ring carbon resonances of the same ligand in four-coordinate square planar complexes. Some dipole moment data are also presented.

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INTRODUCTION

We have recently reported on the synthesis, characterization of fluorinated- β -diketonate chelates of six-coordinate aluminum, gallium, indium, scandium, eight-coordinate zirconium, and four-coordinate palladium [1-5]. The latter complexes are square planar and exist as both cis and trans isomers. A literature survey of four-coordinate tetrahedral complexes of beryllium with unsymmetrical fluorinated- β -diketone ligands indicates that only the bis(1,1,1-trifluoro-2,4-pentanedionato)beryllium(II) and the bis(1,1,1-trifluoro-2,4-(2'-thienyl)propanedionato)beryllium(II) compounds have been reported. Work on these compounds includes their gas phase [6,7] and gel chromatographic [8-10] behavior, solvent extraction [11-14], stability constant determination [15] and sublimation studies [16]. Some ^1H NMR data has also been recorded [17].

We now report the synthesis and characterization of eight bis(fluorinated- β -diketonate)beryllium chelates, $\text{Be}(\text{RCOCHCOR}')_2$, of which six of these compounds are novel.

EXPERIMENTAL

Preparation of the β -diketones

The β -diketones ($\text{RCOCH}_2\text{COCF}_3$) with R as methyl, phenyl and 2'-thienyl were obtained from the commercial sources. Other β -diketones were prepared by Claisen condensation of the methyl ketone (RCOCH_3) and ethyl fluorocarboxylates ($\text{R}'\text{COOC}_2\text{H}_5$), catalyzed by sodium methoxide [18].

Preparation of the complexes

A solution of beryllium sulfate tetrahydrate (1 g; 5.65 mmol in 25 mL water) was added to the solution of β -diketone (11.3 mmol in 35 mL alcohol). The pH of the mixture was raised to about 5 by adding concentrated NH_3 and the solution was digested for 10-15 min. The mixture after

cooling in an ice bath for 1 h yielded a white product which was filtered and washed with ice-cold 50% alcohol/water.

The metal was determined by decomposing a 300 mg sample with five drops of concentrated H_2SO_4 and then strongly heating to BeO .

NMR data

The NMR spectra were recorded in CDCl_3 with the ^{19}F and ^{13}C NMR spectra taken on a JEOL-FX60Q NMR Spectrometer and the ^1H NMR spectra taken on a Varian EM360L NMR Spectrometer. The ^{13}C NMR chemical shifts (ppm). The ^{19}F NMR spectra were run at 56.3Hz with broad band decoupling using a sweepwidth of 15,150Hz and an internal reference of CFCl_3 . The carbon resonances of the C_3F_7 group were studied using a fluorine noise decoupling technique, $^{13}\text{C}\{^{19}\text{F}\}$, as previously described elsewhere [4].

Dipole moment data

The dipole moments were determined at 25°C in benzene dried with BDH molecular sieves (Type 4A) using a WTW dipolemeter and an Abbe 60 refractometer [19].

Molecular weight data

Molecular weights were determined in benzene by the Galbraith Laboratories, Inc.

RESULTS AND DISCUSSION

The reaction of beryllium sulfate tetrahydrate ($\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$) with the respective fluorinated- β -diketone afforded yields of the beryllium chelates of ca 50% or better except for the $\text{Be}(\text{CH}_3\text{COCHCOCF}_3)_2$ (18.4%) and $\text{Be}(2'\text{-C}_4\text{H}_3\text{SCOCHCOCF}_3)_2$ (28.5%) compounds. The analytical data for these compounds are presented in Table I. These BeL_2 complexes are highly soluble in absolute ethanol and other organic solvents.

Table I also shows dipole moment data for four of these compounds.

TABLE 1

Analytical and dipole moment data of $\text{Be}(\text{RCOCHCOR}')_2$ chelates

R	R'	MP °C	Yield %	%Found		%Calculated		Dipole Moment (Debye)
				C	H	C	H	
methyl	CF ₃	110-112	18.4	38.08	2.68	38.10	2.56	4.28(2.55)*
phenyl	CF ₃	138-140	49.3	54.55	2.83	54.69	2.76	5.29(3.07)*
2'-thienyl	CF ₃	167-169	28.5	42.49	2.07	42.57	2.23	5.74(3.57)*
2'-furyl	CF ₃	172-173	47.5	45.73	2.01	45.84	1.92	6.05
phenyl	C ₂ F ₅	141-142	52.5	49.01	2.29	49.00	2.24	1.67
2-thienyl	C ₂ F ₅	171-172	54.9	39.09	1.47	39.21	1.46	1.63
phenyl	C ₃ F ₇	110-113	50.8	44.95	2.06	45.10	1.89	1.41
2-thienyl	C ₃ F ₇	99-101	52.4	36.86	1.31	36.87	1.24	1.38

* The values in parenthesis are the dipole moments of the zinc complexes of the corresponding ligand, RCSCHCOCF_3 [29]. The dipole moment of $\text{Zn}(\text{CH}_3\text{CSCHCOCF}_3)_2$ was reported by mistake in reference 29

as 3.37D. The correct value is 2.55D.

The parent compound, $\text{Be}(\text{acac})_2$, has been shown by X-Ray crystal [20,21] and molecular beam [22] studies to have a slightly distorted pseudo-tetrahedral D_{2d} structure. $\text{Be}(\text{acac})_2$ has zero dipole moment in the gas phase and a moments of 1.17D and 0.77D have been reported in benzene [23-25]. The lack of a nonzero dipole moment in the centrosymmetric $\text{Be}(\text{acac})_2$ chelate has been attributed to anomalously high atom polarizations [24]. It has also been suggested that symmetry destroying low-lying vibrational modes may be responsible [26,27]. The dipole moments of the four compounds reported in Table I are due to the two unsymmetric bidentate ligands arranged in a pseudo-tetrahedral environment plus the possibility of some contribution from the above described effects. Our dipole moment value of $\text{Be}(\text{CH}_3\text{COCHCOCF}_3)_2$ agrees with that reported by Holm and Cotton, 4.25D [28]. The formal symmetry of the beryllium complexes reported herein is lowered from the D_{2d} symmetry of $\text{Be}(\text{acac})_2$ to C_2 , thus rendering these chelates dissymmetric.

Table I also shows dipole moment data for zinc complexes of the monothio- β -diketone ligand, $\text{RCSC}_2\text{COCF}_3$, where R is methyl, phenyl or 2'-thienyl. While both metal complexes have pseudo-tetrahedral geometry, the BeO_4 core complexes have a higher dipole moment than their corresponding ZnS_2O_2 core complexes. The lower dipole moment of the ZnS_2O_2 core complexes are a result of the lower electronegativity of sulfur versus oxygen and/or the larger size of zinc compared to that of beryllium; covalent radii, 1.31Å and 0.9Å, respectively. The possibility of polymerization of the BeL_2 chelates can be discarded as the compounds $\text{Be}(\text{CH}_3\text{COCHCOCF}_3)_2$ and $\text{Be}(\text{C}_6\text{H}_5\text{COCHCOCF}_3)_2$ gave molecular weights (benzene) of 315 and 430 as compared to the respective theoretical values of 315 and 439.

Table 2 presents ^{13}C NMR chemical shift and coupling constant data for the $\text{R}-\underline{\text{C}}-\text{O}$, $\underline{\text{C}}-\text{H}$ and $\text{R}'-\underline{\text{C}}-\text{O}$ carbons. Several observations are apparent from this data and it agrees with ^{13}C NMR chemical shift data taken

TABLE 2

^{13}C NMR chemical shift (ppm) and coupling constant (Hz) data for $\text{Be}(\text{RCOCHCOR}')_2$ chelates

R ^a	R'	R- <u>C</u> -O	<u>C</u> -H ^b	R'- <u>C</u> -O ^c
CH ₃	CF ₃ ^d	201.0	97.9(2.0)	171.6(35.6)
C ₆ H ₅	CF ₃	190.8	93.8(2.0)	172.6(35.6)
2'-C ₄ H ₃ S	CF ₃	183.3	93.7(2.1)	171.5(35.6)
2'-C ₄ H ₃ O	CF ₃	178.4	93.4(2.3)	172.2(35.6)
C ₆ H ₅	C ₂ F ₅ ^e	190.3	95.4(2.5)	173.7(25.6)
C ₆ H ₅	C ₃ F ₇ ^f	190.3	95.6(3.4)	173.7(25.1)
2'-C ₄ H ₃ S	C ₂ F ₅	182.8	95.2(2.9)	172.5(25.4)
2'-C ₄ H ₃ S	C ₃ F ₇	182.8	95.5(3.5)	172.5(25.6)

^a CH₃, 27.4 ppm; C₆H₅, 134.6, 134.2, 128.6(2x) ppm; 2'-C₄H₃S, 140.6, 135.9, 133.8, 128.6 ppm; 2'-C₄H₃O, 150.5, 148.1(2x) ppm.

^b $^3J_{\text{C-F}}$, quartets for CF₃, triplets for C₂F₅ and C₃F₇.

^c $^2J_{\text{C-F}}$, quartets for CF₃, triplets for C₂F₅ and C₃F₇.

^d $\underline{\text{C}}\text{F}_3$: 118.2 ppm, $J_{\text{C-F}}$ 281.4 Hz.

^e C₂F₅:CF₂, 108.7 ppm, $^1J_{\text{C-F}}$ 242.2 Hz (t), $^2J_{\text{C-F}}$ 38.4 Hz (q); $\underline{\text{C}}\text{F}_3$, 118.1 ppm, $^1J_{\text{C-F}}$ 298.1 Hz (q), $^2J_{\text{C-F}}$ 35.6 Hz (t).

^f C₃F₇: CF₂CF₂CF₃, 110.2 ppm, CF₂ $\underline{\text{C}}\text{F}_2$ CF₃, 109.3 ppm; $\underline{\text{C}}\text{F}_2$ CF₂ $\underline{\text{C}}\text{F}_3$, 117.4 ppm.

on similar ligands in various geometries [1-5]. The effect of the more electronegative perfluoroalkyl group (R') causes the resonance of the carbonyl carbon adjacent (R'-C-O) to the R' group to be more shielded than the carbonyl carbon's resonance of the R' substituent (R'-C-O). Spin-spin coupling to the methine carbon (C-H) and the R'-C-O carbonyl carbon resonance is observed only for the fluorine of the CF₃ and the

CF₂ fluorines of the perfluoroethyl (CF₂CF₃) and perfluoropropyl (CF₂CF₂CF₃) group. The R-C=O carbonyl carbon resonance is R-group dependent with the order of shielding being methyl < aryl < 2'-thienyl < 2'-furyl. This again appears to be an electronic effect. The methine (C-H) carbon resonance is more dependent on the R'-group than the R-group with the CF₃ group causing a more shielded resonance, except for CH₃ group (R-group), than the C₂F₅ or C₃F₇ groups.

The carbon resonances of the R and R'-group substituents are also shown in Table 2. The perfluoropropyl carbon resonances were lost in the baseline and as described in the Experimental, they were recorded by a ¹³C{¹⁹F} noise decoupling technique. By this technique the C-H resonance was recorded at 173.7 and 172.6 ppm for Be(C₆H₅COCHCOC₃F₇)₂ and Be(2'-C₄H₃SCOCHCOC₃F₇)₂, respectively, with ¹J_{C-H} 168.5Hz. These perfluoroalkyl carbon resonances are in agreement with our previous work [4].

¹⁹F NMR spectra data of the R' fluorines and the ¹H NMR spectra data of the methine proton are presented in Table 3. The CF₂ fluorines adjacent to the carbonyl carbon do not show spin-spin coupling for the C₂F₅ and C₃F₇ substituents. The ¹H NMR data for the C-H proton show a more deshielded resonance when R is phenyl or aryl as compared to a methyl substituent. This the reverse order of shielding for the C-H carbon resonance (Table 2).

Finally, a comparison of the ¹³C NMR chemical shift data of four-coordinate beryllium chelates with four-coordinate palladium chelates having the identical ligands show a more shielded R-C=O and R'-C=O carbonyl carbon resonance for the tetrahedral-beryllium chelates versus the square planar-palladium chelates [5]; this shielding order has also been observed for monothio-β-diketonate chelates of tetrahedral-zinc and square planar-nickel palladium and platinum complexes [31-35].

TABLE 3

 ^1H and ^{19}F NMR chemical shifts of $\text{Be}(\text{RCOCHCOR}')_2$ chelates

R	R'	C-H	CF_3	CF_2CF_3	$\text{CF}_2\text{CF}_2\text{CF}_3$
CH_3	CF_3	6.1	-76.3	--	--
C_6H_5	CF_3	6.8	-76.0	--	--
$2' \text{-C}_4\text{H}_3\text{S}$	CF_3	6.6	-75.9	--	--
$2' \text{-C}_4\text{H}_3\text{O}$	CF_3	6.7	-76.1	--	--
C_6H_5	C_2F_5	6.8	--	-123.7, -83.2	--
C_6H_5	C_3F_7	6.8	--	--	-127.3, -121.4(9.2Hz, q), -81.1(9.2Hz, t)
$2' \text{-C}_4\text{H}_3\text{S}$	C_2F_5	6.6	--	-123.8, -83.2	--
$2' \text{-C}_4\text{H}_3\text{S}$	C_3F_7	6.6	--	--	-127.4, -121.5(9.2Hz, q), -81.1(9.2Hz, t)

The preparation of these new fluorinated substituted acetylacetonate beryllium chelates should promote an interest in studies of their chromatographic, solution and sublimation behavior. Of particular interest would be the resolution of the optical antipodes of these complexes as only the enantiomers of bis(1-phenyl-2,4-butanedionato)beryllium(II) have been separated on optically active quartz [36] and on the potassium salt of the heteropolyacid, $\text{H}_5[\text{BW}_{12}\text{O}_{40}] \cdot 28\text{H}_2\text{O}$ [37].

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