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FLUORINATED ANILIDES OF β-KETO ACIDS AND THEIR Cu(II) COMPLEXES

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SUMMARY

Pentafluoroanilides of acetoacetic and benzoylacetic acids and their α-SCF_3 substituted analogues have been synthesized from the respective β-keto esters. Cu(II) complexes of the compounds obtained as well as of anilide of α-(trifluoromethylthio)acetoacetic acid have been prepared and characterized. The structure of these compounds has been elucidated on the basis of the elemental analysis and IR, MS, ^1H and ^{19}F NMR spectra.

INTRODUCTION

Relatively little is known about Cu(II) complexes with ligands containing fluorine. Some studies have been published on Cu(II) complexes of fluorinated 1,3-diketonates [1] and hexafluorodiacetone alcohol [2,3]. As the anilides of β-keto acids form easily Cu(II) complexes [4] we decided to obtain their fluorinated analogues in order to prove whether they are equally suitable as complexing agents.

RESULTS AND DISCUSSION

Ligands

As we showed recently, α-SCF_3 substituted β-keto esters react easily with aniline to give respective anilides [5]. We wish now to present that pentafluoroaniline reacts with β-keto

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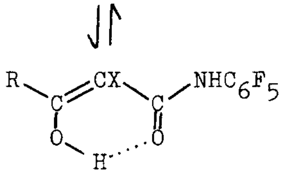
esters in a similar way providing compounds 1 - 4. Their structure was elucidated by elemental analyses, IR, MS, ^1H and ^{19}F NMR spectra. All these compounds show the presence of enolic forms (11% for 1, 8% for 2, 100% for 3, and 90% for 4, respectively); this was proved by ^1H NMR spectra taken in $CDCl_3$ at room temperature. Under the same conditions the ^1H NMR spectrum of benzoylacetanilide shows the presence of 23% of the enolic form. Comparing these data one can draw a conclusion that the CF_3S- substituent present in the molecule, due to its electronegativity, shifts the equilibrium to the enol direction, whereas the pentafluoroaniline residue causes the opposite shift. The latter effect could be explained by the electron-withdrawing influence of a pentafluorobenzene ring on nitrogen and thence the anilide carbonyl group. It eliminates the intramolecular hydrogen bonding that seems to be a driving force for enol formation. IR spectra are in a good agreement with this phenomenon. CF_3S- substituted anilides do not show the frequency characteristic of the free carbonyl group.

$$RCOCHXCOOC_2H_5 + C_6F_5NH_2 \longrightarrow RCOCHXCONHC_6F_5$$

1 R = CH_3 X = H
2 R = C_6H_5 X = H
3 R = CH_3 X = CF_3S
4 R = C_6H_5 X = CF_3S



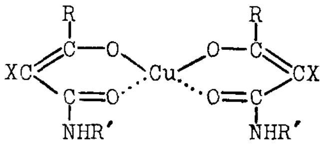
1 - 4

Mass spectra of the ligands 1 - 4 show the presence of molecular ions of small intensity and typical fragmentation pathways e. g., splitting of pentafluoroaniline, pentafluorophenyl fragment, benzoyl or acetyl fragments, respectively, or trifluoromethyl group.

Complexes

Ligands 1 - 4 react smoothly with copper (II) acetate in the molecular ratio 2 : 1 giving coloured complexes 5 - 8 :

$$2\ RCOCHXCONHR' + Cu(OCOCH_3)_2 \longrightarrow$$



5 - 9

5 R = CH_3 X = H R'= C_6F_5
6 R = C_6H_5 X = H R'= C_6F_5
7 R = CH_3 X = CF_3S R'= C_6F_5
8 R = C_6H_5 X = CF_3S R'= C_6F_5
9 R = CH_3 X = CF_3S R'= C_6H_5

Additionally α-(trifluoromethylthio)acetoacetanilide and α-(trifluoromethylthio)benzoylacetanilide [5] were used in an analogous process, but only the first one gave the respective complex 9. All the attempts to use the second anilide as complexing agent were unsuccessful. Structure elucidation for compounds 5 - 9 has been done by means of elemental analysis as well as IR and ^{19}F NMR spectra. In IR spectra of complexes 7, 8, and 9 very characteristic bands ascribed to ν N-H of non-bonded group are to be seen. All these compounds contain a relatively bulky $-SCF_3$ group that prevents possibly the formation of the external hydrogen bond.

It should be underlined that complexes 7, 8, and 9 are the first examples of chelates containing the CF_3S- substituent known in the literature.

EXPERIMENTAL

Melting points are uncorrected. IR spectra were taken in KBr pellets on Zeiss UR 10 apparatus. Mass spectra of compounds 1, 3, and 4 were measured at 70 eV on LKB 9000S apparatus in Regional Laboratory for Physicochemical Analyses and Structural Research in Cracow and at 70 eV on Varian CH-5 at the Ruhr University in Bochum (F. R. G.) for compound 2; m/z, relative abundance in % and supposed assignment are given. ^1H NMR spectra were recorded in $CDCl_3$ with TMS as internal standard at the

Ruhr University Bochum on Bruker WP 80 spectrometer for compounds 1, 2, and 4, and on Bruker WM 250 for 3. ^{19}F NMR spectra were taken at the Ruhr Uniwersity Bochum in $CDCl_3$ on Bruker HX 60/5 with $CFCl_3$ as internal standard for compound 2, on Bruker WM 250 with C_6F_6 as internal standard for compounds 3 and 4, and in $CDCl_3$ + CF_3COOH with C_6F_6 as internal standard for compounds 7 - 9. Positive values of chemical shift are given upfield from $CFCl_3$.

Synthesis of ligands [6]

0.03 Mole of the respective unsubstituted or α-SCF_3 substituted β-keto ester was dissolved in 150 ccm of xylene and the solution was put into a 250 ccm flask equipped with distillation head having a dropping funnel instead of a thermometer. 0.03 Mole of pentafluoroaniline dissolved in 50 ccm xylene with 0.5 ccm pyridine was added dropwise to the boiling ester solution at the same spead at what a mixture of ethanol, pyridine and xylene distilled. Then the solution was concentrated to about 50 ccm, cooled down and the precipitate of the respective anilide was filtered off and purified by crystallization (1, 2, 4) or sublimation (3).

Synthesis of complexes

To a solution of 0.005 mole of the respective β-keto acid anilide in 50 ccm of methanol a solution of 0.0025 mole of $Cu(OCOCH_3)_2 \cdot H_2O$ in 30 ccm methanol was added and the mixture was boiled for 3 - 7 hrs. After cooling down the precipitate was filtered off and purified by crystallization.

Acetoacetpentafluoroanilide 1

Colourless needles (n-hexane). M. p. 68 - 70°C. Yield 19%. Analysis calc. for $C_{10}H_6F_5NO_2$ (267.146): 44.9% C, 2.3% H, 5.2% N; found: 44.9% C, 2.3% H, 5.2% N.
IR ν [cm^{-1}]: 3270 s, 3075 w, 3040 w, 3000 w, 1720 s, 1670 s, 1650 m, 1525 s, 1500 s, 1460 m, 1420 m, 1365 m, 1330 m, 1270 w, 1180 w, 1160 m, 1150 s, 1055 s, 1035 m, 1010 s, 960 m, 810 w, 730 w, 675 w, 680 w.

^{1}H NMR δ [ppm] : 2.2, s, (CH_3 enol); 2.3, s, (CH_3 ketone); 3.7, s, ($-CH_2-$); 5.0, m, ($-CH=$); 9.0, s, (NH); 11% of enol, 89% of ketone form.
MS: 267, 3.1, M^+; 183, 98.0, $C_6H_2F_5N^+$; 155, 15.1, $C_5F_5{}^+$; 85, 10.1, $C_4H_5O_2{}^+$; 43, 100.0, $C_2H_3O^+$.

Benzoylacetpentafluoroanilide 2

Colourless needles (methanol). M. p. 131 - 132°C. Yield 51%.
Analysis calc. for $C_{15}H_8F_5NO_2$ (329.212): 54.7% C, 2.5% H, 4.3% N; found: 54.7% C, 2.7% H, 4.1% N.
IR ν [cm^{-1}] : 3280 m, 3070 w, 1690 s, 1670 s, 1650 w, 1525 s, 1490 s, 1450 m, 1400 w, 1330 m, 1290 w, 1220 s, 1180 w, 1150 m, 1040 m, 1015 s, 995 m, 960 m, 770 m, 675 m.
^{1}H NMR δ [ppm] : 4.2, s, ($-CH_2-$); 5.7, s, ($-CH=$); 7.4 - 8.1, m, (aromatic); 9.3, s, (NH); 13.5, s, (OH); 8% of enol, 92% of ketone form.
MS: 329, 3.5, M^+; 183, 48.0, $C_6H_2F_5N^+$; 155, 4.0, $C_5F_5{}^+$; 147, 32.0, $C_9H_7O_2{}^+$; 105, 100.0, $C_7H_5O^+$; 77, 51.0, $C_6H_5{}^+$; 69, 12.0, $CF_3{}^+$.

α-(Trifluoromethylthio)acetoacetpentafluoroanilide 3

Colourless crystals (sublimed). M. p. 78 - 80°C. Yield 42%.
Analysis calc. for $C_{11}H_5F_8NO_2S$ (367.206): 36.0% C, 1.4% H, 3.8% N, 8.7% S; found: 35.9% C, 1.3% H, 3.9% N, 8.7% S.
IR ν [cm^{-1}] : 3250 m, 1630 m, 1600 s, 1540 s, 1510 s, 1470 s, 1400 m, 1350 m, 1270 w, 1150 s, 1120 s, 1090 m, 1060 w, 1020 m, 1000 s, 950 w, 860 w, 720 w.
^{1}H NMR δ [ppm] : 2.4, s, (CH_3); 8.0, s, (NH); 15.3, s, (OH); 100% of enol form.
^{19}F NMR δ [ppm] : 45.8, m, (SCF_3).
MS: 367, 1.7, M^+; 183, 66.6, $C_6H_2F_5N^+$; 88, 17.0, $C_3H_4OS^+$; 69, 16.7, $CF_3{}^+$; 45, 11.0, CHS^+; 43, 100.0, $C_2H_3O^+$.

α-(Trifluoromethylthio)benzoylacetpentafluoroanilide 4

Colourless plates (ethanol/water). M. p. 114 -116°C. Yield 38%.
Analysis calc. for $C_{16}H_7F_8NO_2S$ (429.272): 44.8% C, 1.6% H,

3.2% N, 7.5% S; found: 44.3% C, 1.7% H, 3.3% N, 7.5% S.
IR ν [cm^{-1}]: 3390 w, 3330 m, 1640 m, 1610 m, 1550 m, 1530 s, 1500 s, 1490 s, 1460 m, 1350 m, 1270 w, 1250 w, 1160 m, 1140 s, 1110 s, 1090 s, 1000 s, 795 w, 760 m, 710 m, 640 w.
^1H NMR δ [ppm]: 5.8, s, ($COCH(SCF_3)CO$); 7.4 - 7,8, m, (aromatic); 8.3, s, (NH); 15.7, s, (OH); 90% of enol, 10% of ketone form.
^{19}F NMR δ [ppm]: 46.5, m, (SCF_3).
MS: 429, 1.0, M^+; 183, 35.3, $C_6H_2F_5N^+$; 155, 6.4, $C_5F_5^+$; 105, 100.0, $C_7H_5O^+$; 77, 86.2, $C_6H_5^+$; 69, 15.0, CF_3^+; 31, 10.2, CF^+.

Bis-(acetoacetpentafluoroanilide) Cu(II) complex 5

Light green plates (benzene). M. p. 244 - 246°C. Yield 42%.
Analysis calc. for $C_{20}H_{10}F_{10}N_2O_4Cu$ (595.818): 40.3% C, 1.7% H, 4.7% N; found: 39.1% C, 1.7% H, 3.7% N.
IR ν [cm^{-1}]: 3245 m, 3000 w, 1680 s, 1660 m, 1610 m, 1540 s, 1510 s, 1470 m, 1290 m, 1255 w, 1120 w, 1060 m, 1020 s, 990 s, 905 w, 740 w.

Bis-(benzoylacetpentafluoroanilide) Cu(II) complex 6

Green needles (acetone/methanol). M. p. 303 - 304°C. Yield 78%.
Analysis calc. for $C_{30}H_{14}F_{10}N_2O_4Cu$ (719.948): 50.0% C, 2.0% H, 3.8% N; found: 49.9% C, 2.6% H, 3.4% N.
IR ν [cm^{-1}]: 3110 m, 1605 s, 1570 s, 1530 s, 1500 s, 1460 s, 1305 s, 1220 s, 1120 m, 1040 m, 1030 m, 1020 s, 985 s, 770 s, 710 m.

Bis-[α-(trifluoromethylthio)]-acetoacetpentafluoroanilide Cu(II) complex 7

Green needles (chloroform). M. p. 188 - 190°C. Yield 69%.
Analysis calc. for $C_{22}H_8F_{16}N_2O_4S_2Cu$ (795.986): 33.1% C, 1.0% H, 3.5% N, 8.0% S; found: 33.1% C, 1.0% H, 3.5% N, 8.1% S.
IR ν [cm^{-1}]: 3365 m, 1600 s, 1580 s, 1540 s, 1510 s, 1470 s, 1415 s, 1255 m, 1165 s, 1150 s, 1130 s, 1100 s, 1060 m, 1005 s, 760 m.
^{19}F NMR δ [ppm]: 46.0, m, (SCF_3).

Bis-[α-(trifluoromethylthio)]-benzoylacetpentafluoroanilide Cu(II) complex 8

Light green needles (benzene). M. p. 235 -238°C. Yield 38%.
Analysis calc. for $C_{32}H_{12}F_{16}N_2O_4S_2Cu$ (920.068): 41.8% C, 1.3% H, 3.0% N, 6.9% S; found: 42.3% C, 1.9% H, 2.8% N, 7.3% S.
IR ν [cm^{-1}] : 3400 m, 1580 s, 1540 s, 1510 s, 1460 s, 1430 s, 1400 s, 1280 m, 1260 m, 1180 m, 1140 m, 1130 s, 1095 s, 1020 s, 1005 s, 800 m, 770 m, 760 m.
^{19}F NMR δ[ppm] : 46.8, m, (SCF_3).

Bis-[α-(trifluoromethylthio)]-acetoacetanilide Cu(II) complex 9

Green needles (acetone). M. p. 244 - 246°C. Yield 83%.
Analysis calc. for $C_{22}H_{18}F_6N_2O_4S_2Cu$ (616.046): 42.9% C, 2.9% H, 4.5% N, 10.4% S; found: 42.7% C, 2.9% H, 4.5% N, 10.4% S.
IR ν [cm^{-1}] : 3380 m, 1610 s, 1580 s, 1540 s, 1455 s, 1415 s, 1340 m, 1250 m, 1160 s, 1140 s, 1130 s, 1100 m, 1080 m, 1050 w, 1000 w, 760 s, 700 m, 685 m.
^{19}F NMR δ[ppm] : 46.6, m, (SCF_3).

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