Some metal complexes of 1,3-diketone: syntheses, UV–Vis, IR, ^{1}H, ^{13}C and ^{19}F NMR spectral studies of the complexes of U(VI), Fe(III), V(V) and Ca(II) with 2-thenoyltrifluoroacetone (HTTA)

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Abstract

2-Thenoyltrifluoroacetone complexes with U(VI), Fe(III), V(V) and Ca(II) have been synthesized and investigated. Characterization was by elemental analysis, UV–Vis, IR (4000–200 cm^{-1}), ^{1}H, ^{13}C and ^{19}F NMR spectral analyses. The complexes were shown to be neutral with molecular formula M(TTA)$_n$X where n is the oxidation state of metal M. X is an adduct: H_2O for Ca(II), CH_3CH_2OH for U(VI) and HTTA for V(V). UV–Vis, IR (4000–200 cm^{-1}), ^{1}H, ^{13}C and ^{19}F NMR spectral data with assignments are presented and discussed.

Introduction

Research on β-diketones and their metal chelates has been stimulated for numerous reasons such as their versatile practical applications. A number of works [1–6] on the practical use of some metal β-diketonates as laser materials and NMR shift reagents have appeared. Brecher *et al.* [4], Nugent *et al.* [5] and Lempicki and Samuelson [6] have shown that laser activity is possible with the tetrakis chelates of the rare earths of which chelate of the benzoyltrifluoroacetone has been so far properly investigated. On the other hand Hinckley [2] has demonstrated that large isotropic shifts are possible in solutions containing some rare earth β-diketonates.

The chelating agent 2-thenoyltrifluoroacetone (HTTA) is an interesting ligand long known for its application in the extraction of metal ions from acid solutions [7]. In the course of our serial studies on the interaction of HTTA with metal ions in the aqueous phase, a number of the metal complexes have been isolated and characterized. Apart from extraction and spectrophotometric [8, 9] application of this ligand, data on the spectral properties of its chelates have not been well compiled. On the whole, we are interested in the general chemistry and structural elucidation of the chelates through UV–Vis, NMR and IR spectral studies.

Experimental

Reagents

Reagents of analytical grade (Aldrich or BDH) were used. They included the following: HTTA, $UO_2(NO_3)_2\cdot6H_2O$, $Fe(NO_3)_3\cdot9H_2O$, NH_4VO_3, HCl, $Ca(CH_3COO)_2$ and 95% ethanol. Distilled demineralized water was used throughout the experiment.

Preparation of metal complexes

Complexes of U(VI), Fe(III) and Ca(II) were prepared by the following general procedure. An aqueous solution of the metal ion prepared by dissolving 5 mmol of the metal salt in 50 ml of water with warming was added dropwise with stirring to 50 ml of warm ethanol solution containing 10 mmol of ligand when the precipitate of the metal complex separated. In the case of Fe(III) 15 mmol of ligand was used. The product obtained from Ca(II) did not separate immediately. This was left to stand in an open beaker for three days when the product separated. The product formed was filtered with suction, washed with water, dried in air and stored in a desiccator over fused calcium chloride.

The V(V) ion was generated in solution by dissolving 1 g of NH_4VO_3 in 20 ml of 10 M HCl and making up to 100 ml with water. The procedure stated above was used for preparing the V(V) complex in the metal:ligand mole ratio of 1:2. The product

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TABLE 1. Physical and microanalytical data of metal complexes

Molecular formula	Colour	Melting point (°C)	Yield (%)	Found (calc.) (%)	
				C	H
$UO_2(TTA)_2 \cdot CH_3CH_2OH$	orange	168	97	27.96 (28.50)	1.81 (1.86)
$Fe(TTA)_3$	wine-red	80	96	39.82 (40.07)	1.91 (1.68)
$VO_2(TTA) \cdot HTTA$	orange–brown	283	83	37.14 (36.48)	2.29 (2.11)
$Ca(TTA)_2 \cdot H_2O$	bone-white	>360	61	38.93 (38.40)	2.07 (2.01)

TABLE 2. Solubility data[a] of HTTA and metal complexes

Solvent	HTTA	U(VI)	Fe(III)	V(V)	Ca(II)
Water	i	i	i	i	i
Methanol	s	s	s	ss	i
Ethanol	vs	s	s	ss	i
Ether	vs	vs	vs	ss	i
Acetone	vs	vs	vs	vs	i
Toluene	vs	vs	vs	s	i
Chloroform	vs	vs	s	ss	ss
Xylene	vs	s	s	ss	i
THF	vs	vs	vs	s	i
CCl_4	s	s	s	ss	ss
DMSO	vs	vs	vs	vs	s
DMF	vs	vs	vs	vs	ss
Pyridine	vs	vs	vs	vs	s

[a]vs, very soluble; s, soluble; ss, sparingly soluble, i, insoluble.

formed was filtered with suction, washed with water and stored in a desiccator over fused calcium chloride.

The colour, melting points and analytical data of the complexes are presented in Table 1. The solubility data in various solvents are given in Table 2.

Physical measurements

Electronic spectra were recorded in chloroform with a Pye Unicam PU8700 series UV–Vis spectrophotometer. The IR spectra (4000–200 cm^{-1}) were obtained from a Perkin-Elmer 598 infrared spectrophotometer dispersed in Nujol mulls and CsI windows. NMR spectra were obtained from Bruker Data System WPAT80 and WUM 360 spectrometers in deuterated solvents. Chemical shifts are reported in δppm relative to TMS as an internal standard. That of ^{19}F is reported relative to $CFCl_3$ to 27 °C. Melting points were determined using an electrothermal melting point apparatus.

Elemental analyses

Microanalyses for C and H were performed by the Microanalytical Unit of the School of Chemistry and Molecular Sciences, University of Sussex, U.K.

Results and discussion

Analytical results and some physical properties of the chelates are listed in Table 1. The analytical data indicate that the complexes have the general molecular formula $M(TTA)_nX$ where n is the oxidation state of the metal M, and X is CH_3CH_2OH for the U(VI) complex, H_2O for the Ca(II) complex and HTTA for the V(V) complex. The iron complex is anhydrous and has no adduct. Table 2 shows that the Ca(II) complex is insoluble in most of the solvents both polar and non-polar. The other complexes are however, very soluble in polar solvents like acetone, DMF and DMSO, and non-polar solvents like toluene, ether and pyridine.

Electronic spectral analysis

Table 3 gives the UV spectral data of the ligands and chelates, and visible spectral data for chelates

TABLE 3. UV–Vis spectral data of HTTA and metal complexes

Compound	$\lambda_1$max (nm)	ϵ_1	$\lambda_2$max (nm)	ϵ_2	$\lambda_3$max (nm)	ϵ_3	$\lambda_4$max (nm)	ϵ_4
HTTA	228.8	6.060	326.4	12.480				
U(VI)	230.4	13.330	335.3	28.820	387.7	19.850		
Fe(III)	230.5	23.070	335.2	51.870	384.8	23.680	500	4.730
V(V)	251.7	10.720	355.2	33.190				
Ca(II)	265.4	6.850	340.5	18.780				

where applicable, in chloroform. Without quantum mechanical calculations assignment of the absorption bands to definite electronic transitions with complete certainty may not be possible. It is reasonable however, to assign the bands λ_1–λ_3 to $\pi \rightarrow \pi^*$ transitions. Similarly, the band λ_4 that appeared in the visible spectral region for the Fe(III) complex can be assigned to a ligand → metal charge transfer. It is also pertinent to mention that the molar absorptivities of the chelates are significantly different from that of the ligand by a factor greater than 2.

Bathochromic shift is observed on chelation in all the chelates and this observation agrees with previous observations [10] on 1,3-diketonates. However, the spectra of the complexes and that of the ligand are identical in character indicating that the π-bonding system in the free ligand is almost intact in the ligand anion of the chelates. Thus only the oxygen atoms of the ligand are substantially involved in σ-bonding with the metal ion. This is achieved through displacement of the proton of the OH group and accepting an electron pair from the oxygen atom of the C=O group of the keto-enol form of the ligand shown in Fig. 1.

Infrared spectral analysis

The IR spectra of metal 1,3-diketonates in general have received considerable attention over the years [11–16]. In this present study of some chelates of 2-thenoyltrifluoroacetone the recent work by Okafor [15, 16] and other previous papers [11–14] were taken into consideration in the assignment of frequencies presented. The IR spectra of the keto-enol tautomer of the ligand shown in Fig. 1 is taken as reference.

The observed frequencies together with the approximate assignments are listed in Table 4. The absorption spectra may be divided into three main spectral regions namely: 4000–1800, 1800–1000 and 1000–200 cm^{-1}.

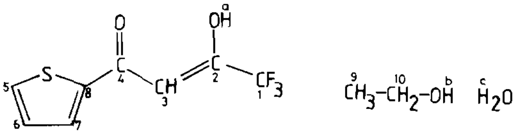

Fig. 1. Proton labelling.

4000–1800 cm^{-1} region

The broad band at 3400 cm^{-1} which is assigned to νOH...O of the enol tautomer of HTTA is absent in the spectra of the complexes. This fact implicates the removal of the hydroxyl proton during chelation [15]. The band at 3375 and 3340 cm^{-1} in the U(VI) and Ca(II) complexes, respectively is attributable to OH stretching frequencies of the ethanol and water adducts in the two complexes, respectively. The weak broad band centred at 3100 cm^{-1} for the V(V) complex is assigned to the stretching frequency of the coordinated OH group of the neutral HTTA adduct. The coordination of the neutral HTTA adduct to the V(V) ion is formulated as having occurred through the donation of an electron pair from the oxygen atom of the OH group of the free ligand to the vanadium(V) metal ion. This region is free of absorption in the case of the Fe(III) complex indicating the absence of coordinated water or ethanol [16] in the complex.

1800–1000 cm^{-1} region

Most of the bands observed in this region are attributable to oscillations of the thenoyl and chelate rings. Normal coordinate calculations [17, 18] and isotopic studies [19] on 1,3-diketones showed that νC=O occurs at a higher frequency than νC=C. Thus, the absorption bands occurring at 1630 and 1521 (HTTA), 1596 and 1540 (U), 1605 and 1538 (Fe), 1620 and 1535 (V), and 1620 and 1539 (Ca) cm^{-1} have been assigned to the C=O and C=C asymmetric stretching frequency modes, respectively, when compared with those reported for other 1,3-diketonates [11–15, 17, 18]. The shift of the C=O stretching frequencies of the ligand in the metal chelates indicates that C=O is involved in chelation [12, 16]. The C=O frequency bands of the chelates are of the order: U<F<V=Ca. It is pertinent to mention that all the absorption bands assigned to the C=C bond of the chelates occur at higher frequencies than that of the ligand. This may indicate the occurrence of delocalization of C=C—C to C=C=C in the metal complexes.

The strong absorption band near 1355 cm^{-1} in all the compounds has been assigned to ν_sC=O while

TABLE 4. Observed vibrational frequencies (cm^{-1}) of 2-thenoyltrifluoroacetone and metal complexes[a]

HTTA	U(VI)	Fe(III)	V(V)	Ca(II)	Approximate assignments
3400b			3100b		$\nu O=H$ of enol
	3375b			3340b	$\nu O=H$ of ethanol/water
1630s					$\nu_{as}C=O$ of enol form of ligand
	1596b	1605sh	1620b	1620b	$\nu_{as}C\overset{\cdots}{-}O$
1597s		1570b	1588s	1600sh	thenoyl ring stretch
1521m	1540s	1538m	1535s	1539w	$\nu_{as}C\overset{\cdots}{-}C\overset{\cdots}{-}C$
1421s	1405s	1403s	1402s	1411s	thenoyl ring stretch
1350s	1359s	1359m	1352s	1363m	$\nu_sC\overset{\cdots}{-}O$
1278s	1307s	1310s	1300b	1295b	$\nu_{as}CF_3$
1250sh	1253m	1250m	1250s	1251m	$\nu_sC\overset{\cdots}{-}C\overset{\cdots}{-}C$
1201s	1192s	1192s	1192s	1190s	$\beta_sC–H$
1163s	1140s	1137m	1140s	1170s	
1111s	1123s	1120sh	1124sh	1123m	ν_sCF_3
1064s	1066s	1064m	1062m	1065m	C=H in-plane deformation of thenoyl ring
1032m	1039m	1040w	1030w	987s	
979m	935s	933m	935m	938w	
	900s		(970m)		$\nu_{as}O=M=O$
861s	858w	861m	860m	862m	C=H out of plane deformation of thenoyl ring
801s	833w	795m	792s	791w	
	781m	774m	750sh	746m	
721s	726m	723sh	721s	720w	
681m	685w	688m	690m	681m	chelate ring deformation
642m	639s	647s	650s	640m	βCF_3
582m	588s	590s	600s	596w	
	497s	527m	522w	521w	chelate ring vibration
458w	470w		454w	478m	
	360w			457sh	$\nu(M=O+\text{chelate ring})$
	262m	377w	380w	390w	$\nu_{as}M=O$
	245m	338w	340w	315m	$\nu(M=O+\text{chelate ring})$
	224sh	275m	250w	262w	

[a] b, broad; w, weak; m, medium; s, strong; sh, shoulder; ν, stretching frequency; ν_{as}, asymmetric stretching frequency; ν_s, symmetric stretching frequency; β, bending or deformation.

$\nu_sC\overset{\cdots}{-}C$ is assigned to the medium absorption near 1250 cm^{-1}. Joshi and Pathak [12] have attributed the shift of the $C\overset{\cdots}{-}O$ and $C\overset{\cdots}{-}C$ stretching bands of the chelates to higher frequencies to the strong positive inductive effect of the CF_3 group which strengthens the $C\overset{\cdots}{-}O$ and $C\overset{\cdots}{-}C$ bonds.

1000–200 cm^{-1} region

The metal–ligand vibrations are expected below 700 cm^{-1} of this region, and they offer a means for correlating the stability order of the metal complexes and the strength of the M–O bond. The assignments made in this region were supported by the fact that absorptions associated with 1,3-diketone ring do change whenever chelation occurs with several metals, and the M–O absorption bands occur as unique bands that are not present in the region of absorption of that of the ligand. Taking previous work into consideration [13, 14] the strong absorption band at 900 (UO_2^{2+}) and 970 (VO_2^{+}) cm^{-1} has been assigned to the asymmetric stretching frequency of the O=M=O ions of the U(VI) and V(V) complexes.

The presence of bands between 300 and 500 cm^{-1} which are typical of 1,3-diketonates have been suggested by some workers [20] to be due to bonding to metal through the oxygen atom of the ligand. In the spectra of the chelates the peaks at 262 (U) [14], 377 (Fe), 380 (V) and 390 (Ca) cm^{-1} have been assigned to the M–O stretching mode. The M–O stretching frequencies follow the order: $U<Fe<V<Ca$.

Proton magnetic resonance (PMR) spectral analysis

The PMR spectral data for the ligand and some of the chelates are shown in Table 5. Assignments of the proton resonances in accordance with the proton labelling of Fig. 1 have been made. The PMR spectra provided additional evidence that the Ca(II) complex is hydrated. It also revealed the presence of proton signals attributable to the ethanol adduct present in the U(VI) complex. Extensive broadening

TABLE 5. ^{1}H NMR chemical shifts of HTTA and metal complexes in δ (ppm) relative to TMS (see Fig. 1 for proton labelling)

Compound	Proton no.									Solvent
	a	b	c	3	5	6	7	9	10	
HTTA	11.34(s)			6.82(s)	7.98–8.23(m)	7.31(t)	7.98–8.23(m)			acetone-d
U(VI)		4.46(s)		7.04(s)	8.18(d)	7.42(t)	8.50(d)	1.18(t)	3.71(q)	acetone-d
HTTA	14.00(s)			6.43(s)	7.64–7.86(m)	7.22(t)	7.64–7.86(m)			$CDCl_3$
Ca(II)			3.25(s)	6.35(s)	7.71(t)	7.12(t)	7.71(t)			$CDCl_3$

[a] s, singlet; d, doublet; t, triplet; q, quartet; b, broad; m, multiplet.

TABLE 6. ^{13}C NMR assignments (see Fig. 1)

Compound	Carbon no.										Solvents
	1	2	3	4	5	6	7	8	9	10	
HTTA	116.05 119.11	182.78	93.55	171.34	132.73	128.88	135.30	139.45	–	–	$CDCl_3$
U(VI)	118.96 122.10	186.74	96.35	173.79	133.59	129.08	135.78	143.46	17.86	64.07	$CDCl_3$

of the NMR signals was observed for the Fe(III) complex; this may be due to huge paramagnetic shifts.

The features of interest from the PMR spectra are:

(i) The proton resonance signals of the hydroxyl proton of the ligand obtained in $CDCl_3$ and acetone-d solutions, which occur downfield in the 11–4 ppm region, are absent in the spectra of the chelates showing that the hydroxyl proton was lost during chelation.

(ii) The proton labelled 3 has the resonance signal downfield in the U(VI) complex relative to that of the ligand; this indicates that the methylene proton is deshielded. It is, however, shifted upfield in the Ca(II) complex showing that it is shielded in this complex.

(iii) The proton resonance spectral signal appearing as a multiplet at 7.98–8.23 ppm (acetone-d) has been assigned to the protons labelled 5 and 7. The signals due to these two unequivalent protons are, however, well separated in the U(VI) complex with each signal appearing as a doublet. One of the signals appearing farther downfield at 8.50 ppm (U(VI) complex) is assigned to the proton labelled 7 because the methylene proton is situated in a position in the compound where it will be more deshielded than the proton labelled 5, by the mesomeric interaction between the thenoyl ring and the chelate ring.

^{13}C NMR spectral analysis

The ^{13}C NMR spectral data for the ligand and U(VI) complex is shown in Table 6 together with the assignments made. Previous assignments [15, 20] were taken into consideration. The assignment of the signals of the carbon atoms of the U(VI) complex follow quite easily from those of HTTA. The ^{13}C NMR spectra of the Ca(II) complex is weak due to insolubility of the Ca(II) complex.

The following features of the ^{13}C NMR spectral data are of interest:

(i) Spin-coupling with the fluorine atom was observed for the CF_3–carbon atom of both the ligand and U(VI) complex.

(ii) The carbon atoms labelled 2, 3 and 4 (Fig. 1) which are part of the chelate ring resonate downfield (by differences of ~3 ppm) relatlve to those of the ligand, indicating that they are deshielded in the U(VI) complex. This trend is in agreement with observations on the PMR signal of the proton labelled 3 already stated.

(iii) The presence of the ethanol adduct in the U(VI) complex is indicated by the ^{13}C resonance peaks at 64.07 (CH_2–) and 17.86 (CH_3–) ppm.

^{19}F NMR spectral analysis

The ^{19}F NMR chemical shifts of the trifluoromethyl group for HTTA and its U(VI) complex obtained in acetone-d revealed a single peak at −77.3 (HTTA) and −70.20 (U(VI) complex) ppm. The presence of one geometric isomer in each case may be inferred from the single fluorine resonance peak [15]. It also appears reasonable to state that the chemical shift of the trifluoromethyl group is appreciably metal dependent.

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