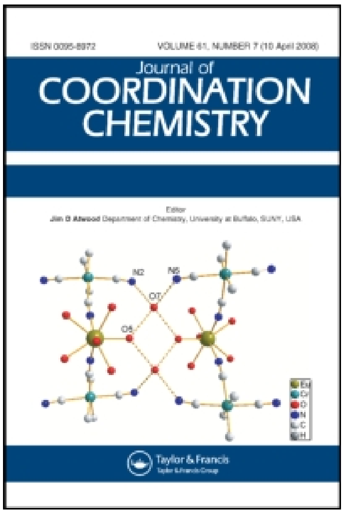

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MIXED IRON(III) β-DIKETONATES

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Note

MIXED IRON(III) β-DIKETONATES

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INTRODUCTION

Although studies on kinetics and stereochemical rearrangement of some mixed β-diketonate complexes of aluminium(III),[1,2] chromium(III) and cobalt(III)[3] have been investigated, very sparse information is available on mixed iron(III) β-diketonates.[4] In order to throw more light on the bonding and structural aspects of trivalent metal β-diketonates,[5-7] we have synthesized several new mixed β-diketonate complexes of iron(III) and investigated their magnetic and spectral properties.

EXPERIMENTAL

The ligands 1-(2-thienyl)-1,3-butanedione (Htbd), 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (Htftbd), 1-(2-furyl)-1,3-butanedione (Hfbd), 1-phenyl-1,3-butanedione (Hbzac),: 4,4,4-trifluoro-1-phenyl-1,3-butane-dione (Hbztfac) and 4,4,4-trifluoro-1-(2-naphthyl)-1, 3-butanedione (Htfnac) were obtained from Eastman Organic Chemicals Ltd. The complexes prepared were of the type $Fe[L_n L'_{3-n}]$ and FeLL′L″ (where n = 1 or 2 and L, L′, L″ are different β-diketones).

An aqueous solution (0.01 mol) of iron(III) chloride hexahydrate was immediately buffered by adding 5g of sodium acetate trihydrate for every 100 cm^3 of solution. The buffered aqueous Fe(III) solution was stirred with an alcoholic solution of the mixed β-diketones so as to maintain the metal/ligand ratio of 1:3. The product formed in each case was filtered and washed with 10% ethanol and recrystallized from petroleum ether. The recrystallized products were dried over phosphorous pentoxide in a vacuum desiccator. All the chelates obtained are red in colour except those containing naphthyl rings which appear darker but provide red solution in organic solvents. The complexes having three different β-diketones are extremely hygroscopic.

Analyses of the compounds were carried out in the microanalytical laboratories of the University of Ibadan and the results are summarized in Table I. IR spectra were recorded on a Perkin-Elmer model IR-577 spectrophotometer using KBr pellets (Table II) whilst the magnetic moments were determined on a Gouy balance at 303K. The method used for the electronic spectral measurements in chloroform solution has been described elsewhere.[5]

RESULTS AND DISCUSSION

Whereas mixed β-diketone complexes of the type Cu(AB) have been reported[9] to exhibit all the features present in the IR spectra of CuA_2 and CuB_2 complexes, the FeL_2L' and $FeLL'_2$ complexes do not strictly behave in the same manner. There is however a general

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broadening of the bands in the 1600-1550 cm^{-1} region for all the complexes. This broadening is due to strong multiple absorptions and hence a probable superimposition of bands in this region. Comparison of the IR spectral data for the FeL_2L' and $FeLL'_2$ complexes with their corresponding *tris*-chelates (FeL_3 and FeL'_3)$^{5-7}$ shows marked differences for band positions between 1600 and 1500 cm^{-1}. However, the region below 600 cm^{-1} appears to exhibit all the features present in the corresponding *tris*-chelates.

The electronic transitions reported in Table III for the mixed chelates are similar to those of the corresponding *tris*-chelates.

All the complexes have magnetic moments in the range 5.74-5.90 B.M. indicative of a spin-free d^5 configuration except for Fe(bzac) (fbd) (tbd) and Fe(tfnac) (bzac) (tbd) complexes, which have low moments of 5.32 and 5.57 B.M. respectively. This is possibly

TABLE I
Physical and analytical data for the Fe(III) mixed β-diketonates.

Compound	M.P. (°C)	% C		% H		% Fe		$\mu_{eff.}$ (303K) B.M.
		Found	Calcd.	Found	Calcd.	Found	Calcd.	
Fe(fbd)$_2$(bzac)	202-203	60.23	60.13	4.46	4.46	10.72	10.75	5.78
Fe(fbd) (bzac)$_2$	184-186	63.20	63.53	4.97	4.76	10.24	10.55	5.74
Fe(tbd)$_2$(fbd)	218-219	52.88	53.24	4.20	3.91	10.30	10.32	5.74
Fe(tbd) (fbd)$_2$	222-224	55.30	54.87	4.02	4.03	10.59	10.63	5.90
Fe(bzac)$_2$(tftbd)	70-72	56.79	56.12	3.79	3.70	9.20	9.32	5.84
Fe(bzac) (tftbd)$_2$	78-80	47.24	47.37	2.53	2.60	8.44	8.47	5.87
Fe(bztfac)$_2$(tftbd)	94-96	46.88	46.88	3.60	3.64	7.79	7.79	5.80
Fe(bztfac) (tftbd)$_2$	128-129	43.57	43.78	1.96	1.98	7.50	7.83	5.90
Fe(tfnac)$_2$(tbd)	103-105	54.32	54.48	3.20	3.29	7.13	7.92	5.75
Fe(tfnac) (tbd)$_2$	78-80	54.94	54.97	3.35	3.38	8.22	8.52	5.75
Fe(tfnac)$_2$(bzac)	90-92	56.85	56.95	2.78	2.78	7.21	6.97	5.90
Fe(bzac) (fbd) (tbd)	204-206	58.33	58.33	4.53	4.33	9.85	10.43	5.32
Fe(tfnac) (bzac) (tbd)	58-60	58.70	58.86	3.70	3.71	7.84	8.18	5.57

TABLE II
Some relevant infrared bands (cm^{-1}).

Compound	ν_{asC-O}	ν_{asC-C}	ν_{M-O}	Ref.
Fe(fbd)$_2$(bzac)	1583	1550	467; 430	This work
Fe(fbd) (bzac)$_2$	1590	1550	458; 427	This work
Fe(tbd)$_2$(fbd)	1571	1550	450; 432	This work
Fe(tbd) (fbd)$_2$	1583	1544	463; 430	This work
Fe(bzac)$_2$(tftbd)	1592	1541	504; 433	This work
Fe(bzac) (tftbd)$_2$	1588	1542	550; 458	This work
Fe(bztfac)$_2$(tftbd)	1588	1571	538; 444	This work
Fe(bztfac) (tftbd)$_2$	1592	1575	525; 429	This work
Fe(tfnac)$_2$(tbd)	1574	1550	475; 429	This work
Fe(tfnac) (tbd)$_2$	1583	1567	475; 417	This work
Fe(tfnac)$_2$(bzac)	1575	1550	535; 467	This work
Fe(bzac) (fbd) (tbd)	1588	1560	446; 429	This work
Fe(tfnac) (bzac) (tbd)	1580	1562	470; 417	This work
Fe(fbd)$_3$	1598	1550	432; 360	5
Fe(bzac)$_3$	1595	1555	450; 432	6
Fe(tbd)$_3$	1600	1570	468; 430	7
Fe(tftbd)$_3$	1603	1575	465; 382	7
Fe(bztfac)$_3$	1600	1575	545; 450	6

TABLE III
Electronic spectra in chloroform solution (kK).[a]

Compound	Band I $\pi-\pi^*$	Band II $\pi_3-\pi_4$	Band III (C.T)	Band IV (C.T)	Band V (C.T/d–d)	Ref.
Fe(fbd)$_2$(bzac)	37.00 (4.30)	31.00 (4.70)	26.70 (4.10)	23.80 (3.90)	20.80 (2.50)	This work
Fe(fbd) (bzac)$_2$	37.20 (4.42)	30.80 (4.80)	26.70 (4.20)	23.50 (3.92)	20.40 (2.69)	This work
Fe(tbd)$_2$(fbd)	37.20 (4.40)	31.00 (4.64)	27.00 (3.87)	23.53 (3.70)	21.00 (2.24)	This work
Fe(tbd) (fbd)$_2$	38.30 (4.41)	31.80 (4.72)	26.90 (3.99)	24.80 (3.76)	21.30 (2.60)	This work
Fe(bzac)$_2$(tftbd)	39.00 (4.24)	32.50 (4.70)	27.50 (4.00)	25.00 (3.80)	21.50 (2.65)	This work
Fe(bzac) (tftbd)$_2$	37.40 (4.50)	32.00 (4.60)	27.40 (4.25)	25.20 (3.96)	21.00 (2.30)	This work
Fe(bztfac)$_2$(tftbd)	37.00 (4.42)	31.25 (4.60)	25.70 (4.02)	–	20.00 (2.39)	This work
Fe(bztfac) (tftbd)$_2$	36.40 (4.29)	31.60 (4.52)	25.80 (3.63)	23.30 (2.38)	20.00 (2.00)	This work
Fe(tfnac)$_2$(tbd)	37.20 (4.59)	30.50 (4.58)	27.40 (4.22)	24.60 (3.98)	18.90 (2.28)	This work
Fe(tfnac) (tbd)$_2$	37.20 (4.64)	30.80 (4.74)	27.00 (4.23)	–	20.00 (2.00)	This work
Fe(tfnac)$_2$(bzac)	37.00 (4.33)	30.30 (4.38)	27.00 (4.11)	24.90 (3.74)	18.70 (1.69)	This work
Fe(bzac) (fbd) (tbd)	38.50 (4.33)	31.30 (4.66)	26.95 (4.05)	23.80 (3.57)	22.32 (3.00)	This work
Fe(tfnac) (bzac) (tbd)	37.45 (4.57)	31.20 (4.64)	26.90 (4.13)	25.00 (3.20)	19.70 (2.70)	This work
Fe(fbd)$_3$	37.04 (4.24)	30.78 (4.85)	26.67 (4.42)	23.53 (3.92)	20.41 (2.38)	5
Fe(bzac)$_3$	37.17 (4.40)	31.25 (4.40)	29.41 (4.00)	26.32 (3.55)	21.74 (2.30)	6
Fe(tbd)$_3$	40.00 (4.25)	30.77 (4.84)	26.67 (4.42)	23.81 (3.92)	20.83 (3.69)	7
Fe(tftbd)$_3$	41.32 (3.87)	29.41 (4.73)	27.80 (4.57)	25.38 (4.36)	21.28 (3.75)	7
Fe(bztfac)$_3$	38.46 (4.15)	32.26 (4.80)	27.78 (4.00)	25.64 (3.50)	21.98 (2.40)	6
Fe(tfnac)$_3$	37.50	30.40	29.00	25.30	20.40	8[b]

[a] 1kK = 1000 cm^{-1}; log ϵ values in parenthesis with units of M^{-1} cm^{-1}. [b] Spectrum determined in cyclohexane solution.

as the result of weak antiferromagnetic interactions. These low magnetic moments and the tendency of Fe(III) to achieve six-coordination suggest multinuclear Fe(III) centres having two bridging β-diketone molecules. Such bridging is known[10] to occur in the species $[L_2FeOR]_2$, where L is acetylacetone or dipivaloylmethane and R is CH_3, C_3H_5, i = C_3H_7, and which have alkoxide bridges.

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