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The Isolation and Characterization of some Iron(III) Complexes with Mixed Uni-, Bi-, and Tridentate Ligands

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Ligand substitution in the $Fe(diketo)_3$ *(diketo = the anion of either acetylacetone (Hacac), benzoylacetone (Hbzac), or dibenzoylmethane (Hdbzac)), by its 1:1 molar ratio reaction with either pyridine-2,6-dicarboxylic acid* (H_2pdc)*, picolinic acid (Hpc), or with chloroacetic acids (HR;* R_A, R_B, R_C *= mono-, di-, or trichloroacetate respectively) produced the mixed iron(III) complexes (diketo)Fe(pdc) (diketo = acac, bzac, or dbzac),* $(diketo)_2Fe(pc)$ *(diketo = acac or dbzac), and* $(acac)_2Fe(R)\cdot nH_2O$ *(for R =* R_A *and* R_C*, n = 1 and for R =* R_B*, n = 0) respectively. The reaction of the latter (R =* R_C*; 1:1 molar ratio) with either HR(R =* R_B *or* R_A*) afforded the mixed complex* $(acac)Fe(R_C)(R_B)\cdot H_2O$ *and* $(acac)Fe(R_C)(R_A)\cdot H_2O$ *respectively, while its reaction with* H_2pdc *(1:1) led to the formation of (acac)Fe(pdc). The acetylacetonate anion in the complex could be replaced by oxinate and trichloroacetate in its reaction with oxine (1:1) or* HR_C *(1:5), whereas (acac)Fe(pdc)·urea was obtained from the reaction of the complex with urea (1:2). The tridentate (pdc), bidentate (diketonate, pc,* R_C, R_B, R_A*, and oxinate) and monodentate (urea, Fe–O bonding) coordinations of the ligands and the suggested polymerization of the (pdc) mixed ligand complexes are based on analytical, spectral and magnetic moment evidence.*

Introduction

It was deduced [1] from the X-ray structural determination of the neutral acetylacetonato- iron(III) complex that the Fe–O distances are identical and the O–Fe–O angle was found to be 89.5° which is the nearest to 90° for the trivalent metal acetylacetonate [2] complexes. Thus the metal ion is surrounded by a fairly regular octahedral arrangement of the chelate oxygens. A mass spectral study has shown that the iron(III) complex will lose one acetylacetonate radical at low pressures [3]. The reaction of either sodium ethoxide [4] or picric acid [5] with iron(III) acetylacetonate led to the cleavage of one of the coordinated ligands. The ligand exchange reaction in aluminium acetylacetonate was reported [6, 7] to be catalyzed by acids and the oxygen atom of the ligand is protonated as the first step. It was recently argued [8] that the protonation site is the carbon atom. Both sites were considered [9] for the protonation of 1,3-dicarbonyl compounds.

We wish to report an investigation concerning the reactivity of some β-diketonate-iron(III) complexes which is aimed at isolating mixed ligands complexes of iron(III) with mono- (urea), di- (β-diketonate, haloacetates and picolinate) and tridentate (pyridine-2,6-dicarboxylate) ligands.

Experimental

Reagent grade chemicals were used. $Fe(diketonate)_3$ complexes (diketonate = acetylacetonate, monobenzoylacetonate, or dibenzoylmethanate) were prepared by literature methods [10]. The electronic spectra were carried out with a Unicam SP 800. The infrared spectra of the metal complexes were measured as nujol mulls using a Perkin-Elmer 580 spectrophotometer (4000–200 cm^{-1}). Magnetic susceptibilities were measured at room temperature (296 K) by the Faraday method. Mercuric tetrathiocyanatocobaltate(II) was used as the magnetic susceptibility standard. Diamagnetic corrections were effected by employing Pascal's constants [11]. Magnetic moments were calculated from the equation $\mu_{eff} = 2.84 \sqrt{\chi_M^{cor}\cdot T}$. Carbon and hydrogen were determined at the University of Cairo. Nitrogen and chlorine analyses were performed at the analytical unit of our chemistry department. A standard method was used for the metal determination. All metal complexes were dried under vacuum over phosphorus pentoxide.

Preparation of Metal Complexes

(i) Preparation of (acac)Fe(pdc), (bzac)Fe(pdc), and (dbzac)Fe(pdc)

Hacac, Hbzac, and Hdbzac refer to acetylacetone, benzoylacetone, and dibenzoylmethane respectively;

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H_2pdc = pyridine-2,6-dicarboxylic acid. The ethyl alcohol solution (100 ml) of the acid (0.0057 mol) was added to that (50 ml) of the equimolar concentration of the complex. The resulting solution was boiled for 4 hr, filtered, and left to cool. The precipitated complex was filtered off, washed with benzene followed by ethyl alcohol, and dried.

(ii) Reaction of (acac)Fe(pdc) with oxine

The ethyl alcohol solution (20 ml) of oxine (0.0031 mol) was added to the warm solution (50 ml) of the equimolar concentration of the iron(III) complex. The resulting dark solution was boiled for 1 hr and left overnight. The formed complex was filtered off, washed with ethyl alcohol, and dried.

(iii) Reaction of (acac)Fe(pdc) with trichloroacetic acid

The benzene solution (50 ml) of the acid (0.016 mol) was added to the powdered iron complex (0.0031 mol) and the reaction solution was left for 3 days. The formed complex was filtered off, washed with benzene, and dried.

(iv) Reaction of (acac)Fe(pdc) with urea

This was carried out as described in (*i*) except that the molar ratio of urea to the iron(III) complex (0.0031 mol) was 2 to 1.

(v) Preparation of $(acac)_2Fe(pc)$ and $(dbzac)_2Fe(pc)$

Hpc = picolinic acid. These complexes were prepared as described in (*i*) from the reactions of picolinic acid with the corresponding $Fe(diketonate)_3$ complex.

(vi) Preparation of $(acac)_2Fe(CO_2R)$; R = CCl_3, $CHCl_2$, and CH_2Cl

The benzene solution (20 ml) of the chloroacetic acid (0.0062 mol) was added to that (70 ml) of the equimolar concentration of the iron(III) complex. The reaction solution was refluxed for 2 hr and concentrated to 30 ml. The complex was precipitated by petroleum ether, filtered off, and washed with petroleum ether.

(vii) Reaction of $(acac)_2Fe(CO_2CCl_3)$ with either dichloro- or monochloroacetic acid

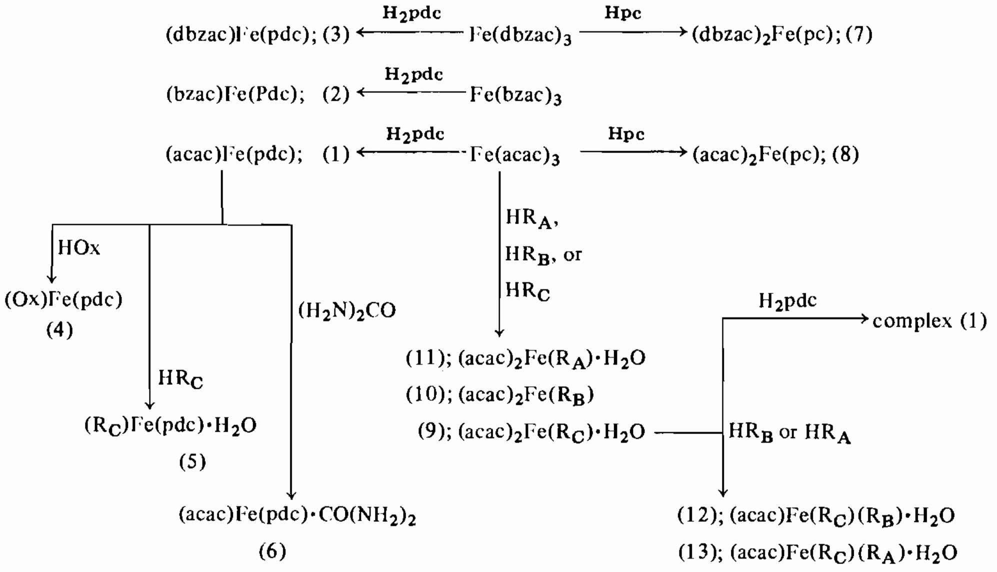
This reaction was carried out as described in (*vi*) using equimolar concentration of the acid (0.0062 mol) and the iron(III) complex.

(viii) The preparation of (acac)Fe(pdc) from the reaction of $(acac)_2Fe(CO_2CCl_3)$ with H_2pdc

This reaction was carried out as described in (*i*) using equimolar concentration of the acid (0.0031 mol) and the iron(III) complex.

Results and Discussion

The reactions that led to the formation of the iron(III) complexes 1–13 are illustrated in the accompanying schematic representation. The substitution of two diketonate anions, in the $Fe(diketonate)_3$ complexes, by one of the tridentate (pdc)



Scheme 1

A schematic representation that illustrates the reactions of metal complexes (abbreviations have the same significance as in experimental section).

TABLE I. Suggested Formulations, Elemental Analyses, Colour, and Effect of Heat for the Metal Complexes.

Metal Complex	Suggested Formulation (C) = Calculated (F) = Found		Elemental Analyses (%)					Colour	Effect of Heat (°C) melting starts = m.s.
			C	H	N	Cl	Fe		
1	(acac)Fe(pdc)	(C)	45.03	3.15	4.38	–	17.45	brownish-red	darkens at 240
	$C_{12}H_{10}NO_6Fe$	(F)	44.71	3.02	4.38	–	17.63		
2	(bzac)Fe(pdc)	(C)	53.43	3.17	3.67	–	14.61	brownish-red	darkens at 205, m.s. at 225
	$C_{17}H_{12}NO_6Fe$	(F)	53.80	3.23	3.72	–	14.39		
3	(dbzac)Fe(pdc)	(C)	59.49	3.18	3.15	–	12.57	red	darkens above 200, m.s. at 260
	$C_{22}H_{14}NO_6Fe$	(F)	59.66	3.30	3.20	–	12.71		
4	(Ox)Fe(pdc)	(C)	52.64	2.48	7.67	–	15.29	dark brown	no change till 300
	$C_{16}H_9N_2O_5Fe$; Ox = oxinate	(F)	52.34	2.51	7.63	–	15.07		
5	$(CCl_3CO_2)Fe(pdc)\cdot H_2O$	(C)	26.94	1.26	3.49	26.51	13.92	yellowish-brown	darkens above 200
	$C_9H_5NCl_3O_7Fe$	(F)	26.61	1.32	3.50	26.77	14.08		
6	(acac)Fe(pdc)·urea	(C)	41.08	3.71	11.05	–	14.69	brown	darkens above 240
	$C_{13}H_{14}N_3O_7Fe$	(F)	41.10	3.76	11.31	–	14.34		
7	$(acac)_2Fe(pc)$	(C)	51.09	4.82	3.72	–	14.84	brownish-red	m.s. at 245
	$C_{16}H_{18}NO_6Fe$	(F)	51.36	4.75	3.81	–	15.06		
8	$(dbzac)_2Fe(pc)$	(C)	68.01	4.36	2.33	–	9.30	brownish-red	m.s. at 128
	$C_{34}H_{26}NO_6Fe$	(F)	68.33	4.41	2.40	–	9.35		
9	$(acac)_2Fe(CO_2CCl_3)\cdot H_2O$	(C)	33.18	3.71	–	24.48	12.85	red	darkens at 80 m.s. at 110
	$C_{12}H_{16}Cl_6O_7Fe$	(F)	33.29	3.52	–	24.39	13.04		
10	$(acac)_2Fe(CO_2CHCl_2)$	(C)	37.83	3.97	–	18.61	14.66	red	m.s. at 136
	$C_{12}H_{15}Cl_2O_6Fe$	(F)	38.02	4.03	–	18.90	14.35		
11	$(acac)_2Fe(CO_2CH_2Cl)\cdot H_2O$	(C)	39.43	4.96	–	9.70	15.27	brownish-red	m.s. at 145
	$C_{12}H_{18}ClO_7Fe$	(F)	39.71	5.05	–	9.85	15.30		
12	$(acac)Fe(CO_2CCl_3)(R_B)\cdot H_2O$	(C)	23.33	2.18	–	38.26	12.05	brownish-red	m.s. at 170
	$R_B = CHCl_2CO_2^-$	(F)	23.06	2.20	–	38.51	12.03		
	$C_9H_{10}Cl_5O_7Fe$								
13	$(acac)Fe(CO_2CCl_3)(R_A)\cdot H_2O$	(C)	25.21	2.59	–	33.07	13.02	brownish-red	m.s. at 150
	$R_A = CH_2ClCO_2^-$	(F)	25.09	2.64	–	33.29	13.19		
	$C_9H_{11}Cl_4O_7Fe$								

TABLE II. Infrared Spectra (cm^{-1}) of Metal Complexes (Nujol Mulls).

Complex	Assignment						
	Pyridine-acid OCO^{a}		Diketonate^{b}		Haloacetate OCO^{c}		Metal–Ligand Vibrations
	ν_{as}	ν_{s}	$\nu C\overset{\cdots}{-}O$	$\nu C\overset{\cdots}{-}C$	ν_{as}	ν_{s}	
1	1663(s) 1630(s)	1410(s)	1565(s)	1530(s)	–	–	660(w), 562(m), 536(m), 442(s), 298(m) Fe–O(acac)^{d}
2	1675(s) 1650(s)	1410(s)	1587(m)	1525(s)	–	–	665(m), 565(w), 550(w), 438(s), 292(m) Fe–O(bzac)^{d}
3	1680(s)	1412(s)	1578(m)	1518(s)	–	–	668(w), 568(m) 547(m), 439(m), 293(m) Fe–O(dbzac)^{d}
4	1670(s) 1645(s)	1410(s)	–	–	–	–	330(s), 382(m) νFe–O(Ox), 265(m) νFe–N(Ox)^{e}
5	1660(s) 1637(s)	1415(m)	–	–	1650(s)	1385(s)	^{f}
6	1660(s) 1640(s)	1415(s)	1565(s)	1528(m)	–	–	652(w), 565(m), 550(s), 438(s), 287(s) Fe–O(acac)^{d}
7	1674(s)	1380(m)	1570(m)	1520(m)	–	–	653(w), 560(m), 552(m), 442(s), 305(m) Fe–O(acac)^{d}
8	1675(s)	1392(m)	1577(s)	1518(s)	–	–	650(m), 556(m), 538(m), 452(m), 284(m) Fe–O(dbzac)^{d}
9	–	–	1572(s)	1528(s)	1680(s)	1360(m)	648(m), 560(m), 547(m), 452(s), 282(m) Fe–O(acac)^{d,f}
10	–	–	1575(s)	1519(s)	1656(m)	1394(m)	652(s), 562(m), 550(m), 435(s), 280(m) Fe–O(acac)^{d}
11	–	–	1568(s)	1514(m)	1615(s)	1405(m)	654(w), 560(m), 550(m), 440(s), 265(m) Fe–O(acac)^{d,f}
12	–	–	1570(s)	1520(m)	1665(s) 1640(s)	1380(m) R_C 1400(m) R_B	655(w), 565(m), 552(m), 440(s), 280(w) Fe–O(acac)^{d,f}
13	–	–	1565(s)	1522(m)	1655(m) 1612(s)	1380(s) R_C 1412(m) R_A	652(m), 565(m), 548(m), 443(s), 277(m) Fe–O(acac)^{d,f}

w = weak, m = medium, s = strong.

[a–e] These are assigned according to Refs. [13], [12], [17], [23] and [16] respectively. The νFe–O of the carboxylates cannot be assigned with certainity owing to the complexity of the systems. [f] Broad band at 3500–3200 cm^{-1} of the νO–H of the lattice or coordinated water molecule in these complexes (hydrogen bonding). R_C, R_B and R_A in complexes 12 and 13 refer to trichloro-, dichloro-, and monochloroacetates respectively.

anion (through the nitrogen atom and an oxygen atom from each carboxylate) produced metal complexes 1–3 which are formulated as shown in Table I. These formulations are compatible with the analytical data and with the spectral measurements. Thus, the $C\overset{\cdots}{-}O$ and $C\overset{\cdots}{-}C$ stretching bands of the diketonate indicate bidentate coordination of the ligands [12] (see Table II). Two stretching vibrations for the carboxylates of (pdc) were observed from complexes 1 and 2 while only the higher frequency band could be detected from complex 3. It is assumed that in the latter complex both carboxylates are monodentate [13] which is not the case for former complexes where the possible coordination of a ketonic oxygen atom to the adjacent iron atom of another molecule cannot be ruled out. Two stretching vibrations should be expected from the two types of carboxylates in complexes 1 and 2 with the higher frequency vibration to be associated with the monodentate carboxylate and the lower frequency band to be responsible for the bridging carboxylate (see Fig. 1). Similar cases of chelated and bridging carboxylate of the (pdc) ligand in a metal complex were recently reported [13, 14].

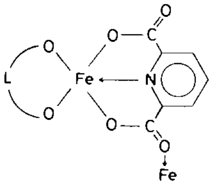


Fig. 1. Suggested molecular formulation for complexes 1, 2 and 4–6, L refers to the bidentate ligands in these metal complexes.

The magnetic moment of complex 1 (with relatively the least steric effect of two methyl groups compared with complexes 2 and 3) was found to be 5.98 B.M. which is indicative of a spin-free iron(III) complex. Bridging of the carboxylate will be therefore more likely through the ketonic oxygen and not through the chelated oxygen atoms of the carboxylate which could allow a higher probability for metal–metal interaction (Fig. 1).

That the acetylacetonate in complex 1 could be replaced by other ligands is shown by the reaction of this complex with either oxine or trichloroacetic acid to produce the mixed ligand complexes 4 and 5 respectively. Bidentate coordination of the oxinate in this complex is based on vibrational bands (1108(s) νC–O [15], 498(w) in-plane C–O bending, 404(m) chelate ring deformation [16] and the metal–ligand stretching bands in Table II) which characterize this type of coordination to iron(III). Similar coordination for the trichloroacetate in complex 5 is suggested owing to the similarity of ν_{as} and ν_s with those of known bidentate haloacetates [17]. The appearance of two stretching vibrations for the carboxylates of (pdc) implies that complexes 4 and 5 have the same polymeric structure suggested for complexes 1 and 2. This formulation, shown in Fig. 1, seems to be a structural feature for the (pdc) complexes of transition metal ions [18].

The suggested coordinative unsaturation of the iron atom in complex 1 is substantiated by its reaction with urea to give rise to complex 6. The coordination of urea to the iron(III) atom through oxygen in the latter complex (which is usually the case for the iron(III)–urea complexes) is explained [19] by the shift of the νC=O of urea from 1683 to 1552 cm^{-1}, while those of the $\nu \mathrm{NH}_2$ bands persisted at 3400, 3315, and 3200 cm^{-1}. Moreover, the shift of ν_{as} of the carboxylate to higher frequency (Table II) on increasing the size of the diketonate from (acac) to (dbzac), complexes 1 to 3, could be associated with a weaker Fe–O bond in the chelate ring and a stronger Fe–O bond in the bridge.

The replacement of one of the coordinated diketonate ligand from the iron(III) complex either the picolinate (complexes 7 and 8) or the chloroacetate (complexes 9–11) produced different types of mixed ligand complexes in which both ligands are bidentate. In such a case the regular octahedral structure of the iron(III)–diketonate complex is expected to be largely preserved. Bidentate coordination of the remaining two diketonate ligands in complexes 7–11 is evidenced by the stretching vibrations of $\mathrm{C}\overset{\cdots}{-}\mathrm{O}$ and $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$, while a similar type of coordination [17] for the chloroacetates is in accordance with the values of ν_{as} and ν_s listed in Table II. These bands are observed at comparable locations to those reported for bidentate haloacetates of transitions metal ions [17] with the usual sensitivity of the stretching vibrations to the number of electron withdrawing substituents in the acetate group [17]. A magnetic moment of complex 9 of 5.96 B.M. indicated that it is a spin-free d^5 complex.

The bidentate coordination of the picolinate anion in complexes 7 and 8 is acquired through the combined coordination of the nitrogen and the monodentate carboxylate. The stretching vibrations of the carboxylate in these complexes (Table II) suggest this type of coordination by comparison with picolinic acid complexes of some transition metals [20]. The appearance of a strong band at 1605 cm^{-1}, and weak bands at 1235 and 625 cm^{-1} is diagnostic for the coordination of the heterocyclic nitrogen [21, 22] to the metal ion in these complexes. Other bands at 1250 and 420 cm^{-1} are mixed with those of the diketonate. These bands are similarly observed from complexes 1–5 and have the same implication.

The formation of complex 1 from the reaction of the spin-free complex 9 with pyridine-2,6-dicarboxylic acid required the substitution of an acetylacetonate and a carboxylate by an anion of the dicarboxylic acid. It is concluded, therefore, that the Fe–O bond of the carboxylate chelate ring is weaker than the corresponding bond of the acetylacetonate one in the mixed ligand complex 9. If this were not the case then the replacement process would have involved the two acetylacetonates of complex 9.

Substitution of a second acetylacetonate by a carboxylate in the mixed acetylacetonate–trichloroacetate–iron(III) complex 9 was achieved by its reaction with either dichloro- or monochloroacetic acid to give complexes 12 and 13 respectively. Infrared evidence for the coordination of the bidentate acetylacetonate and carboxylates is similar to that discussed above for their precursor (Table II).

The Fe–O vibrations (oxygen of diketonate) of complexes 1–3 and 6–13, listed in Table II, show some shifts from their observed [23, 24] locations from Fe(acac)$_3$ particularly the 300 cm^{-1} band which produced the largest isotopic shift in Nakamoto's investigation [23]. It is interesting to note, in this connection, that the strength of the 436 cm^{-1} band, which was the strongest among the other νFe–O vibrations in complexes 1 and 7 (diketonate = acac) has decreased in complexes 3 and 8 (diketonate = dbzac). In fact it acquired the same strength like the 300, 551, and 562 cm^{-1} bands associated with νFe–O. This result appears to be compatible with the earlier suggestions [23, 24] that the 436 cm^{-1} band is a coupled vibration between the Fe–O and C–CH$_3$ stretching modes.

The electronic spectra of the metal complexes are summarized in Table III. In essence, the positions of the ultraviolet peak (π–π^* transition [25, 26]) as well as those of the visible region peaks (charge transfer or intraligand interactions [26]) related to the coordinated diketonate have suffered insignificant change. This observation supports the infrared assignments concerning the bidentate coordination of the diketonate. The decrease in the strength of the absorption peaks for the mixed chelates when compared with Fe(diketonate)$_3$ is ascribed to the lower number of diketonate anion in the former complexes. However, the electronic spectra of the complexes are compatible with the assumption that the energy difference between the d_ϵ (responsible [26] for the charge transfer) and d_γ electrons was not perturbed by the ligand substitution reactions.

TABLE III. Electronic Spectra (in Chloroform and in Some Cases as Nujol Mulls) and Magnetic Moments of Metal Complexes.

Complex	λ_{max} (nm); values in parenthesis are molar absorptivities in l mol^{-1} cm^{-1}
1	445, 357, 274^a; μ_{eff} = 5.98 B.M. 461 as nujol mull
2	455(1620), 385(2730), 299(21600), 251(14530)
3	500(1020), 417(3640), 328(18200), 278(10900), 258(13500)
4	450 br as nujol mull^b
5	263^a
6	445, 351, 271^a
7	445(1710), 351(1770), 272(19900)
8	500(2030), 417(5300), 345 sh (25000), 320 (30600), 274 sh (24400), 257(28100)
9	445(1520), 355(1990), 278(16300), μ_{eff} = 5.96 B.M.
10	445(1610), 345(2650), 274(16300)
11	445(1600), 345 sh (2390), 271(15760)
12	445, 345 sh, 271^a
13	445, 351, 274^a

^{a,b}Refer to partially and completely insoluble in chloroform (0.01 gm in 10 ml) respectively. br = broad, sh = shoulder.

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