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Metal benzoylpivaloylmethanates. Part 4. Aluminium(III) chelates

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Abstract

Tris(benzoylpivaloylmethanato)aluminium(III) and its ring-substituted derivatives, Al(*p*X-BPM) (*p* means the para position in the phenyl ring; X is H, F, Cl, NO_2, MeO, Me) have been synthesized and the forms less soluble in an ethanol–benzene mixture have been examined by means of elemental analysis, HPLC, ^{1}H NMR, IR and Raman spectroscopy, and thermogravimetry. ^{1}H NMR spectra show that these forms adopt mer configuration. The chelates where X is H, F, Cl are volatile, but those where X is Me, MeO, NO_2 decompose in the 350–450°C temperature range. IR data suggest inequivalence of the two CO bonds in each of the coordinated ligands. The four bands were assigned to Al–O vibration on the basis of the metal effect.

INTRODUCTION

The great interest in the study of metal β-diketonates has been stimulated in the past by their potential application in areas such as separation techniques (extraction, gas chromatography), NMR spectroscopy (shift reagents), laser technology (laser chelates), chemical catalysis and the polymer industry (catalysts), and medicine (anti-inflammatory and anti-fungal agents) [1–4]. Although the coordination chemistry associated with symmetric β-diketones is extremely well developed, certain analogous areas of the chemistry of unsymmetric β-diketones are far less advanced. Some years ago [5–7], we prepared and characterized by different techniques new compounds of this type, namely copper(II), iron(III) and manganese(III) complexes with derivatives of benzoylpivaloylmethane. Their interesting spectroscopic, structural and chemical properties prompted us to extend our investigations to complexes of other metals. This paper deals with the preparation and isolation of the most stable

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geometric isomers, and reports on the volatility, thermal stability, and ^{1}H NMR, IR and Raman spectra of new aluminium(III) complexes comprising monoanions of benzoylpivaloylmethane or its ring-substituted derivatives.

EXPERIMENTAL

Aluminium(III) trichloride hexahydrate, sodium acetate and all the solvents were of reagent grade purity.

Ligands

Benzolypivaloylmethane (H(HBPM)), *p*-fluorobenzoylpivaloylmethane (H(*p*F-BPM)), *p*-chlorobenzoylpivaloylmethane (H(*p*Cl-BPM)), *p*-nitrobenzoylpivaloylmethane (H(*p*NO_2-BPM)), *p*-methoxybenzoylpivaloylmethane (H(*p*Me-OBPM)), *p*-methylbenzoylpivaolylmethane (H(*p*Me-BPM)) and monodeuterated benzoylpivaloylmethane were obtained as reported [5].

Complexes

Aluminium complexes were prepared by a general procedure [8, 9], adapted as follows. To a stirred solution of aluminium(III) trichloride hexahydrate (0.7243 g; 0.003 mol) and anhydrous sodium acetate (1.00 g; 0.012 mol) in water (20 cm^3) was added the solution of the appropriate (0.009 mol) β-diketone in methanol (50 cm^3). The resulting mixture was stirred for 1 h at ambient temperature. The solid products were filtered off, washed with a water–methanol mixture (1:1), recrystallized 3 times from ethanol containing a little benzene, and dried in vacuo at 100°C to give the following products:

Tris(benzoylpivaloylmethanato)aluminium(III), Al(BPM)$_3$, m.p. 213°C. Found: C, 73.3; H, 7.2; calculated for $C_{39}H_{45}O_6Al$: C, 73.6; H, 7.1.

Tris(*p*-flurobenzoylpivaloylmethanato)aluminium(III), Al(*p*F-BPM)$_3$, m.p. 256°C. Found: C, 67.8; H, 6.1; calculated for $C_{39}F_3H_{42}O_6Al$: C, 67.8; H, 6.1.

Tris(*p*-chlorobenzoylpivaolylmethanato)aluminium(III), Al(*p*Cl-BPM)$_3$, m.p. 244°C. Found: C, 63.3; H, 5.7; calculated for $C_{39}Cl_3H_{42}O_6Al$: C, 63.3; H, 5.7.

Tris(*p*-methoxybenzoylpivaloylmethanato)aluminium(III), Al(*p*MeO-BPM)$_3$, m.p. 150°C. Found: C, 69.5; H, 7.1; calculated for $C_{42}H_{51}O_9Al$: C, 69.4; H, 7.1.

Tris(*p*-methylbenzoylpivaloylmethanato)aluminium(III), Al(*p*Me-BPM)$_3$, m.p. 208°C. Found: C, 74.4; H, 7.6; calculated for $C_{42}H_{51}O_6Al$: C, 74.3; H, 7.6.

Tris(*p*-nitrobenzoylpivaloylmethanato)aluminium(III), Al(*p*NO_2-BMPM)$_3$, m.p. 234°C. Found: C, 60.4; H, 5.5; N, 5.7: calculated for $C_{39}H_{42}N_3O_{12}Al$: C, 60.7; H, 5.5; N, 5.5.

Apparatus and measurements

Elemental analyses of the chelates were made on a Carlo Erba elemental analyser MOD 1106.

Thermogravimetric and DTA curves were obtained on a Paulik–Paulik type OD-103 derivatograph using Al_2O_3 as a reference.

The 100 MHz ^1H NMR spectra were recorded using a Tesla BS 567A spectrometer. All samples were run in CCl_4 with TMS used as an internal reference.

The chromatographic analysis was performed using a Hewlett-Packard liquid chromatograph type 1090A equipped with a diode array detector and a Hypersil Si 100-5, $200 \times 4.6\,mm^2$ column or a Nucleosil ODS 100-5, $100 \times 4.6\,mm^2$ column. A mixture of THF + *n*-hexane (0.5 + 99.5) or H_2O + MeOH (5 + 95) at a flow rate $0.3\,cm^3\,min^{-1}$ were used as the mobile phases for the NP or RP analyses, respectively.

IR spectra of chelates on Nujol and C_2Cl_6 mulls were recorded on a Perkin-Elmer 457 in the region $4000–250\,cm^{-1}$.

The Raman spectra were recorded in the range $4000–0\,cm^{-1}$ by means of a Cary 83 spectrophotometer after argon laser excitation at $\lambda = 488\,nm$.

The IR and Raman spectra were measured at room temperature. The frequencies of the spectra were read with an accuracy of $1\,cm^{-1}$.

RESULTS AND DISCUSSION

Elemental analyses and thermogravimetric studies (Fig. 1) indicate that benzoylpivaloylmethane and its derivatives react with Al(III) to give unsolvated Al(*p*X-BPM)$_3$ chelates. The complex compound in which the metal ion is bound to three unsymmetrical bidentate ligands may exist in two geometric isomers: mer (possessing no symmetry) and fac (with a threefold rotation axis) [10].

Repeated recrystallization of the Al(*p*X-BPM)$_3$ chelates from ethanol with 10% benzene produced less soluble isomers, samples of which when dissolved in THF, showed single peaks in the HPLC chromatograms. Moreover, samples of the recrystallized compounds gave ^1H NMR spectra with fine structures consistent with the non-equivalence of three *tert*-butyl or methine groups, as expected for the mer isomer. No additional single peaks due to *tert*-butyl or methine protons for the fac isomer, possessing equivalent protons in each functional group by C_3 rotation axis, were observed. Table 1 lists the ^1H NMR data for all the complexes.

The thermal behaviour of the Al(*p*X-BPM)$_3$ chelates was investigated by thermogravimetry and differential thermal analysis up to 500°C. The

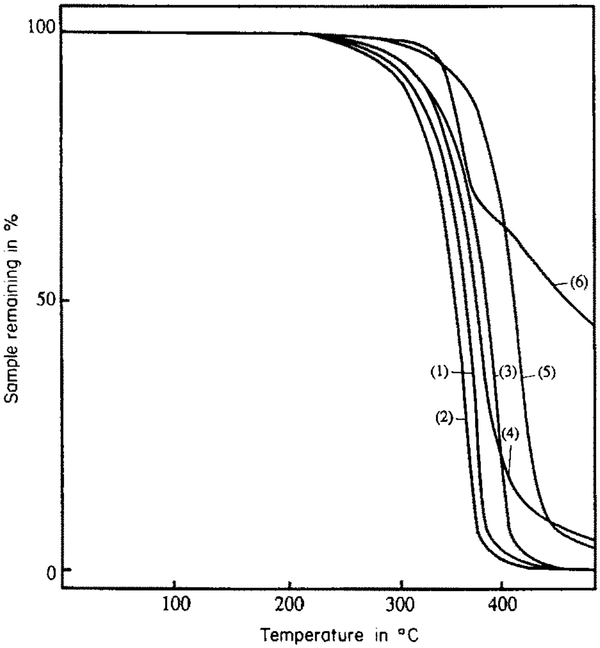

Fig. 1. Thermogravimetric curves for: (1) Al(BPM)$_3$; (2) Al(*p*F-BPM)$_3$ (3); Al(*p*Cl-BPM)$_3$; (4) Al(*p*Me-BPM)$_3$; (5) Al(*p*MeO-BPM)$_3$; (6) Al(*p*NO$_2$-BPM)$_3$.

thermal properties of the related compounds tris(dipivaloylmethano)-aluminium(III) (Al(DPM)$_3$) and tris(dibenzoylmethanato)aluminium(III) (Al(DBM)$_3$) were reported earlier by Utsunomiya [11] who showed that while Al(DPM)$_3$ sublimed at approx. 200°C to give a smooth TG curve, the Al(DBM)$_3$ complex started to decompose at this temperature. The Al(BPM)$_3$ complex, which contains both benzoyl and pivaloyl fragments, and also its derivatives, differ notably in thermal behaviour from Al(DPM)$_3$ and Al(DBM)$_3$. Some of the Al(*p*X-BPM)$_3$ chelates (where *X* is H, F, Cl)

TABLE 1

100 MHz ^{1}H NMR chemical shifts for Al(*p*X-BPM)$_3$ complexes in CCl$_4$ solutions (TMS internal standard)

Compound	Chemical shifts (ppm) of protons of the following groups				
	t-Butyl	Methyl	Methine	Phenyl [a]	
Al(BPM)$_3$	1.13: 1.16: 1.18	–	6.22; 6.24; 6.26	7.31	7.82
Al(*p*Me-BPM)$_3$	1.12: 1.13; 1.17	2.32	6.21; 6.22; 6.23	7.10	7.76
Al(*p*MeO-BPM)$_3$	1.11; 1.13; 1.16	3.73	6.15; 6.19; 6.21	6.76	7.78
Al(*p*Cl-BPM)$_3$	1.12; 1.16; 1.18	–	6.22; 6.23; 6.24	7.29	7.78
Al(*p*F-BPM)$_3$	1.11; 1.13; 1.15	–	6.20; 6.22; 6.24	6.98	7.82
Al(*p*NO$_2$-BPM)$_3$	1.19; 1.22; 1.24	–	6.33; 6.36; 6.38	7.98	8.18

[a] The position of the most intense band in the multiplet.

are volatile but very high temperatures, 350–450°C, are required to induce volatilization (Fig. 1). Al(pNO$_2$-BPM)$_3$ decomposes in this temperature range giving an exothermic peak on the DTA curve. A partial decomposition of Al(pMe-BPM)$_3$ and Al(pMeO-BPM)$_3$ is also observed; the weight of the residue at 500°C for both compounds is approx. 5% of the sample weight. Ring substitution has some effect on the volatility of the complexes. The following trend in volatility is apparent from the positions of the TG curves on the temperature scale: Al(pCl-BPM)$_3$ < Al(pF-BPM)$_3$ < Al(BPM)$_3$.

The IR and Raman spectroscopic data are listed in Table 2. All the chelates show an intense Raman band at approx. 1600 cm^{-1} assigned to the C=C stretching vibrations in the aromatic ring. In addition, the Al(BPM)$_3$ complex (but not its derivatives) exhibits a 1002 cm^{-1} Raman band characteristic for the presence of a mono-substituted benzene ring [12]. An interesting feature of the IR spectra of the complexes is a surprisingly high number (4–5) of resolved bands in the 1610–1500 cm^{-1} region, as compared to complexes with symmetric β-diketonates (usually 1–3 bands). It is generally accepted that bands in this region may be due to C=O and C=C stretching, and to C–H out-of-plane bending vibrations. Several bands in the region of carbonyl stretching vibrations and the reported differences in C–O bond lengths in *trans*-Cu(BAM)$_2$ [13] and *trans*-Pd(BAM)$_2$ [14] (BAM means the anion of benzoylacetylmethane) of 0.038 Å and 0.074 Å respectively, suggest the presence of two inequivalent CO bonds in each of the coordinated pX-BPM ligands, which may give rise to two ν(CO) vibrations. This inequivalence derives from the fact that the CO group adjacent to the *tert*-butyl group has comparatively more double bond character than that adjacent to the *para*-substituted or unsubstituted phenyl ring. As pointed out by Nakamoto et al. [15], the presence of a phenyl substituent on the β-diketone framework leads to a contribution of the quinoid form of this substituent to the resonance hybrid, which, in consequence, would weaken the double bond character of the CO bond. Thus the bands in Al(pX-BPM)$_3$ chelates at approx. 1590 cm^{-1} were assigned to the stretching vibrations of the CO group adjacent to the *tert*-butyl group by reference to ν(C–O) in Al(DPM)$_3$ (1582 cm^{-1}) [16], while the other band occurring at approx. 1560 cm^{-1} was assigned to the CO group adjacent to the aromatic ring for the reasons given above and by reference to ν(CO) in Al(DBM)$_3$ (1569 cm^{-1}) [16]. The bands at 1530 cm^{-1} are sensitive to the replacement of the methine protons (γ-protons of the β-diketone moiety) by deuterium, as we have already shown for bis(benzoylpivaloylmethanato)copper(II) [5]. These bands may be combination bands to which the C–H out-of-plane vibrations contribute strongly, as suggested earlier by Mikami et al. [17] for the 1550 cm^{-1} band of bis(acetylacetonato)copper(II).

Comparing the IR spectra of Al(pX-BPM)$_3$ chelates with those of

TABLE 2

Vibration frequencies in the range 1650–200 cm^{-1} determined from the IR and Raman spectra of the aluminium(III) benzoylpivaloylmethanates and their interpretation

Al(BPM)$_3$		Al(pMe-BPM)$_3$		Al(pMeO-BPM)$_3$		Al(pCl-BPM)$_3$		Al(pF-BPM)$_3$		Al(pNO$_2$-BPM)$_3$		Type of vibrations
RS	IR	RS	IR	RS	IR	RS	IR	RS	IR	RS	IR	
218 s	–	218 s	–	218 s	–	223 s	–	218 s	–	223 s	–	
–	–	–	–	–	–	294 w	–	–	–	–	–	δ(C–Cl)
316 w	–	306 w	–	314 w	–	316 w	–	317 w	–	303 w	–	Def. chelate ring
–	372	379 w	380 w	382 w	377 m	383 w	392 vw	382 w	–	370 w	–	
409 w	402 m	407 m	405 w	414 m	402 m	413 m	407 vw	419 w	400 w	413 m	400 w	ν(Al–O)
–	–	–	–	–	–	–	–	424 w	–	–	–	δ(C–F)
439 w	441 m	439 w	440 w	435 sh	430 m	433 sh	445 sh	–	437 w	–	440 sh	ν(Al–O) and def. chelate ring
–	455 m	–	–	–	465 m	–	467 vw	–	–	–	465 vw	
–	–	–	477 m	–	480 s	–	490 m	489 w	485 m	–	–	
497 m	492 s	494 w	495 m	502 w	492 s	500 m	507 vw	514 vw	510 w	503 w	497 w	ν(AL–O) and def. chelate ring
–	555 m	–	540 m	–	550 m	–	550 vw	–	540 w	–	560 vw	Out-of-plane
619 m	620 m	634 sh	640 sh	637 w	630 sh	633 m	620 vw	638 w	645 m	632 m	620 m	Def. chelate ring
–	–	642 m	650 m	657 w	650 s	–	–	–	–	–	–	
674 m	670 s	690 w	685 vw	692 w	685 m	684 m	680 w	682 w	685 w	677 w	690 w	ν(Al–O) and def. chelate ring
–	–	–	–	–	–	–	–	–	–	697 m	695 sh	δ(NO$_2$)
712 w	697 s	700 vw	705 sh	–	715 sh	707 m	–	722 vw	715 w	717 w	710 m	
–	–	739 m	732 m	749 m	735 m	744 m	735 vw	749 m	740 m	–	–	
777 m	762 s	784 w	785 s	–	785 vs	782 w	772 vw	792 w	790 s	767 m	760 m	
812 m	807 m	800 m	–	807 m	802 m	797 w	785 m	817 w	812 w	802 w	795 m	
–	–	–	–	–	–	–	–	–	–	844 m	840 s	
–	–	837 m	–	–	–	834 m	–	–	–	–	–	

857 m	850 s	852 m	850 m	857 w	847 s	854 m	842 m	857 w	850 sh	864 w	865 m	
937 w	925 sh	934 sh	940 sh	933 sh	932 sh	937 w	937 sh	942 w	934 sh	942 w	930 sh	ν(C–CH$_3$) and ν(C–O)
967 m	960 s	962 s	962 m	967 s	960 s	967 s	960 vw	967 m	960 m	967 m	960 m	ν[C–C(CH$_3$)$_3$]
1002 vs	–	–	–	–	–	–	–	–	–	–	–	
1029 w	1027 m	1017 w	1022 m	1029 w	1025 s	1017 w	1010 m	1024 w	1015 w	1017 m	1010 w	Def. chelate ring
1104 s	1097 s	1097 m	1095 m	1102 w	1100 s	1097 s	1087 m	1104 m	1100 s	–	1092 m	γ(C–C) and γ(C–H)
–	–	–	1117 m	–	1110 vs	–	1105 m	–	–	1112 s	1105 m	
–	–	–	–	–	–	–	1157 m	–	1152 s	–	–	
1164 s	1160 s	1167 m	1165 m	1174 vs	1170 s	1177 m	1175 m	1162 m	1165 s	1167 m	1160 m	δ(C–H)
1188 sh	1182 s	1187 s	1190 s	–	–	–	–	–	–	–	–	
–	1222 s	1209 m	1222 m	–	1225 sh	–	1220 m	–	1222 s	–	1222 m	ν(C–C)
1244 s	1240 s	1247 s	1242 m	1247 s	1240 vs	1247 m	1240 m	1247 m	1235 s	1244 s	1240 m	ν[C–C(CH$_3$)$_3$]
–	–	–	–	–	1255 vs	–	–	–	–	–	–	
–	1300 vs	1304 sh	1305 s	1304 sh	1297 vs	1304 sh	1295 sh	1304 sh	1290 m	–	1305 sh	
1314 vs	1315 vs	1319 vs	1317 s	1324 vs	1320 vs	1317 vs	1312 s	1317 vs	1317 s	1313 vs	1320 sh	
–	1357 vs	–	1360 vs	1362 w	1357 vs	1362 vw	1365 vs	–	1365 vs	1347 vs	1345 vs	δ(CH$_3$)
1397 M	–	1387 w	–	1392 w	1405 vs	–	–	1397 w	–	1387 w	–	
–	1420 vs	–	1430 vs	–	1420 vs	1412 m	1412 vs	1422 w	1420 s	–	1420 s	
–	–	–	–	–	–	1446 w	–	–	1440 vs	1435 w	–	
1457 m	–	1462 w	1462 vs	1467 vw	–	1472 w	–	–	1465 vs	–	–	
1497 m	1485 vs	–	–	1484 w	–	1489 w	1485 vs	1485 w	–	1482 w	–	
–	1505 vs	–	1500 vs	–	1500 vs	–	1505 sh	–	1500 vs	–	1505 s	ν(C–C) phenyl ring
1529 s	1525 s	1527 m	1527 vs	1532 vs	1520 vs	1519 vs	1535 vs	1527 s	1525 vs	1527 m	1530 s	γ(C–H) out-of-plane
–	1562 vs	–	1552 vs	–	1550 vs	–	1550 vs	–	1565 s	–	1560 s	ν(C–O) next to phenyl
–	1590 vs	–	1590 vs	–	1585 vs	–	1582 vs	–	1573 sh	–	1580 s	ν(C–O) next to *t*-butyl
1602 vs	1610 sh	1609 vs	1610 s	1607 vs	1602 vs	1592 vs	1590 vs	1604 vs	1602 vs	1602 s	1609 m	ν(C–C) pneyl ring

Key: ν, stretching vibrations; γ, out-of-plane bending; δ, in-plane bending; sh, shoulder; vs, very strong; s, strong; m, medium; w, weak: vw, very weak.

Fe(pX-BPM)$_3$ compounds obtained by us earlier [7], some bands in the 700–200 cm^{-1} region can be seen to be metal sensitive. The ν(M–O) values for the Al(III) chelates are expected to be higher than for Fe(III) compounds, due to the smaller ionic radius and lower mass of the Al(III) ion as compared to the Fe(III) ion in the high-spin state ($r_{\mathrm{Al}^{3+}} = 0.54$ Å; $r_{\mathrm{Fe}^{3+}(\text{high spin})} = 0.65$ Å [18]) and with no crystal field stabilization energy for d^0 and high-spin d^5 systems. An increase in wavenumbers observed for the following bands of Al(BPM)$_3$ relative to the corresponding bands of Fe(BPM)$_3$ (given in parentheses) seems to justify the assignment of these bands to Al–O vibrations: 670 (650), 492 (486), 441 (422) and 402 (380) cm^{-1}.

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REFERENCES

1 R.C. Mehrotra, R. Bohra and D.P. Gaur, Metal β-Diketonates and Allied Derivatives, Academic Press, London, 1978.
2 J.P. Fackler, Jr., Prog. Inorg. Chem., 7 (1966) 361.
3 S. Kawaguchi, Coord. Chem. Rev., 70 (1986) 51.
4 A. Komarov, Zh. Anal. Khim., 31 (1976) 366.
5 E. Kwiatkowski and Z. Pepliński, Transition Met. Chem., 3 (1978) 305.
6 E. Kwiatkowski, Z. Pepliński and J. Baranowski, Transition Met. Chem., 4 (1980) 337.
7 E. Kwiatkowski and W. Nowicki, Transition Met. Chem., 12 (1987) 546.
8 E.W. Berg and J.T. Truemper, J. Phys. Chem., 64 (1960) 487.
9 R.C. Young, Inorg. Synth., 2 (1946) 25.
10 R.C. Fay and T.S. Piper, J. Am. Chem. Soc., 84 (1962) 2303.
11 K. Utsunomiya, Bull. Chem. Soc. Jpn., 44 (1971) 2688.
12 B. Schrader, Angew. Chem. Int. Ed. Engl., 12 (1973) 884.
13 P.K. Hon, C.E. Pfluger and R.L. Belford, Inorg. Chem., 5 (1966) 516.
14 P.K. Hon, C.E. Pfluger and R.L. Belford, Inorg. Chem., 6 (1967) 730.
15 K. Nakamoto, Y. Morimoto and A.E. Martell, J. Phys. Chem., 66 (1962) 346.
16 D. Hancock and D.A. Thornton, J. Mol. Struct., 4 (1969) 377.
17 M. Mikami, I. Nagakawa and T. Shimanouchi, Spectrochim. Acta, Part A, 23 (1967) 1037.
18 R.D. Shannon and C.T. Prewitt, Acta Crystallogr. Sect. B, 26 (1970) 1046.