Acetates and Acetato-complexes. Part 2.[1] Spectroscopic Studies

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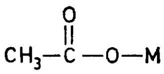
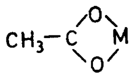
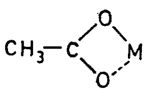
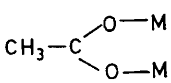
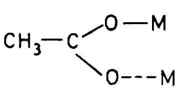
The effect of different modes of co-ordination on the i.r. spectrum of the acetate ion is reviewed. Infrared and ^1H n.m.r. spectra of a series of metal acetates and acetato-complexes are reported, and the type of co-ordination identified: $B_2O(O_2CMe)_4$ and $Na[B_2O(O_2CMe)_5]$ contain both bridging and unidentate acetate; $Al(O_2CMe)_3$ probably contains bridging acetate only; $Si(O_2CMe)_4$, $Ge(O_2CMe)_4$, $K_2[Si(O_2CMe)_6]$, and $K_2[Ge(O_2CMe)_6]$ contain only unidentate acetate; $Zr(O_2CMe)_4$ and $Pb(O_2CMe)_4$ contain only chelating acetate; $K_2[Sn(O_2CMe)_6]$, $K_2[Pb(O_2CMe)_6]$, and $[NMe_4][Sn(OMe)_5]$ contain both chelating and unidentate acetate; and $Sn(O_2CMe)_4$ contains symmetrical and unsymmetrical chelating acetate.

OUR aim in this work has been to examine the i.r. spectra (and to a lesser extent the ^1H n.m.r. spectra) of the series of acetates and acetato-complexes prepared in Part 1.[1] We have studied both the nature of the spectrum of acetate ion in different environments, and the possibility of identifying metal environments from the spectra.

Acetates and acetato-complexes can be divided into six groups according to the type of M–O_2CMe interaction (Table 1); the examples cited are all confirmed by crystal-structure analysis (except for type 1). The two unsymmetrical types (4 and 6) clearly cannot be uniquely characterised, but could exist in a continuous range between the unidentate type and the symmetrical chelating or bridging types. As one might expect, these unsymmetrical types are very rare, occurring only when special circumstances prevent the formation of one of the symmetrical types. This is very similar to the classification of co-ordinated nitrate groups,[2] except that the unsymmetrical bridge type has not been identified; unsymmetrical bidentate nitrate groups are also very rare.

TABLE 1

Acetate co-ordination types

Type	Co-ordination	Examples	Ref.
1	Unco-ordinated	$Na[O_2CMe]$	4
2	Unidentate	$B_2O(O_2CMe)_4$	11
	 $CH_3-\overset{\overset{O}{\|}}{C}-O-M$		
3	Bidentate, chelating, symmetrical	$Zn(O_2CMe)_2\cdot 2H_2O$	7
		$Na[UO_2(O_2CMe)_3]$	8
			
4	Bidentate, chelating, unsymmetrical	See text	
			
5	Bidentate, bridging, symmetrical	$[Zn_4O(O_2CMe)_6]$	9
		$[Be_4O(O_2CMe)_6]$	10
		$B_2O(O_2CMe)_4$	11
			
6	Bidentate, bridging, unsymmetrical	$[Sn(CH_2Ph)_3(O_2CMe)]$	14
			

Although no satisfactory crystal-structure determinations have been made for simple ionic acetates,† it seems from the identity of the solution and solid-state spectra of sodium acetate that there is little cation–anion interaction. These spectra have been examined by Itoh and Bernstein[4] and Nakamura,[5] whose assignments are in excellent agreement (Table 2); all but one of the 15 modes have been identified. C_{2v} Symmetry was assumed, implying free rotation of the CH_3 group around the C–C axis.

TABLE 2

Assignment of frequencies in the i.r. spectrum of $Na[O_2CMe]$

Type of vibration	Assignment	Bands (cm^{-1}) Itoh and Bernstein[4]	Bands (cm^{-1}) Nakamura[5]
A_1 ν_1	CH_3 Sym. str.	2 936	2 924
A_1 ν_2	CH_3 Sym. def.	1 344	1 339
A_1 ν_3	C–O Sym. str.	1 414	1 425
A_1 ν_4	C–C Str.	924	923
A_1 ν_5	CO_2 Sym. def.	646	6 47
A_2 ν_6	Torsion		
B_1 ν_7	C–H Antisym. str.	2 989 or 3 010	2 985
B_1 ν_8	C–O Antisym. str.	1 578	1 582
B_1 ν_9	CH_3 Def.	1 430	1 440
B_1 ν_{10}	CH_3 Rock	1 009	1 007
B_1 ν_{11}	CO_2 Rock	460	670
B_2 ν_{12}	CH Asym. str.	3 010 or 2 989	2 985
B_2 ν_{13}	CH_3 Def.	1 443	1 484
B_2 ν_{14}	CH_3 Rock	1 042	1 045
B_2 ν_{15}	CO_2 Out of plane	615	616

The main effect of co-ordination of the acetate ion will clearly be on the C–O frequencies ν_3, ν_5, ν_8, ν_{11}, and ν_{15}; it seems also that ν_4, the C–C stretch, is often shifted. M–O Frequencies will also appear, and there is also a possibility (depending on the molecular symmetry) in molecules containing more than one acetate that absorptions may be split, even if the acetate ions have

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† In $Li[O_2CMe]\cdot 2H_2O$ the hydrogen bonding must clearly influence the spectroscopic properties.[3]

[1] Part 1, N. W. Alcock, V. M. Tracy, and T. C. Waddington, preceding paper.

[2] C. C. Anderson, N. Logan, S. C. Wallwork, and C. D. Garner, *Quart. Rev.*, 1971, **25**, 289.

[3] J. L. Galigné, M. Mouvet, and T. Falgueirettes, *Acta Cryst.*, 1970, **B26**, 368.

[4] K. Itoh and H. J. Bernstein, *Canad. J. Chem.*, 1956, **34**, 170.

[5] K. Nakamura, *J. Chem. Soc. Japan*, 1958, **79**, 1411, 1420.

identical environments. In this work, however, no such splitting has been identified.

For analysis in more detail, the major difference is between co-ordination type 2, possibly with 4 and 6 in some cases, and the remainder, *i.e.* between compounds in which the oxygen atoms of the acetate group are clearly distinct and those in which they are nearly or completely identical. As would be expected, the spectra of unidentate acetate groups show a large increase in ν_8, and a similar decrease in ν_3, these frequencies corresponding approximately to C=O and C–O. The best evidence comes from Group 4 (Table 3).

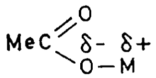
TABLE 3

Unidentate acetate groups (wavenumbers in cm^{-1})

Compound	ν_8	ν_3	$\nu_8 - \nu_3$	Ref.
$MeCO_2Me$	1 771	1 248	523	*a*
$SiMe_3(O_2CMe)$	1 725	1 267	458	*b*
$GeMe_3(O_2CMe)$	1 698	1 267	431	13
$SnEt_3(O_2CMe)$ (sol.)	1 655	1 302	353	13
$PbPh_3(O_2CMe)$ (sol.)	1 623	1 311	312	13

[a] K. Wilmshurst, *J. Mol. Spectroscopy*, 1957, **1**, 201. [b] R. Okawara, D. E. Webster, and E. G. Rochow, *J. Amer. Chem. Soc.*, 1960, **82**, 3287.

The decrease in ($\nu_8 - \nu_3$) as the Group is descended may be due to increased polarity in the O–M bond, leading to a bonding situation which is closer to that in the free acetate ion:



Alternatively it may indicate that with increasing size of M a weak interaction with the second oxygen atom becomes possible, and the compounds move from type 2 to 4.

The most useful analysis of the bidentate acetates is that of Grigor'ev.[6] He started from the premise that in chelating acetates the O–C–O angle will be smaller than in bridging acetates. This is very reasonable, because we can expect a decrease in the first case because of interligand repulsions, but in bridging acetates an increase above 120° is likely because few pairs of metal atoms will be only 2.2 Å apart, the separation of the oxygen atoms. This is confirmed by the structural evidence, chelating acetate angles [7,8] being 111 and 121°, bridging angles [9-11] 125, 123, and 124°.* Grigor'ev calculated the effect of changing the O–C–O angle without changing the force constant; he found that increasing this angle should decrease ν_3 and increase ν_8, and hence increase $\Delta\nu = \nu_8 - \nu_3$. He also showed that changing the force constant had much less effect on $\Delta\nu$, although it altered the frequencies significantly. His figures are not very close to those of a more sophisticated calculation by Nakamura;[5] this suggests that Grigor'ev's calculation can be taken as a guide to the trends but that the specific frequencies may not be reliable.

The experimental evidence (Table 4) for compounds of known crystal structure containing only one type of acetate group supports Grigor'ev's conclusions, showing substantially smaller $\Delta\nu$ for chelating than bridging acetates. Interestingly, copper(II) and chromium(III) acetate both have large $\Delta\nu$, even though their O–C–O angles are only 112°.[12] Unfortunately it is less simple to distinguish free acetate from bridging acetate as both have similar $\Delta\nu$; it is possible that ν_8 (Tables 2 and 4) is lower for free acetate, but there is not enough experimental evidence to confirm this. Similarly, unsymmetrically bound acetate groups (types 4 and 6) cannot be identified without *X*-ray structural data, and there seem to be no examples where the structure and the spectrum have both been reported. The trialkyl-tin and -lead acetates, which are unidentate in solution (Table 3), are acetate bridged from their spectra in the solid state,[13] and these bridges may well be unsymmetrical as tribenzyltin acetate is found [14] to have Sn–O distances of 2.14 and 2.65 Å. The range of frequencies are ν_8 1 565—1 570 and 1 555—1 560, ν_3 1 408—1 412 and 1 406—1 410, and $\Delta\nu$ 153—162 and 145—154 cm^{-1} for Sn and Pb respectively, and it is possibly significant that these ν_8 values are all low, although the $\Delta\nu$ values correspond to bridging geometry. This is certainly the reason why for a long time these acetates were believed to be ionic.[14]

TABLE 4

Bidentate acetate groups (wavenumbers in cm^{-1})

Compound	ν_8	ν_3	$\Delta\nu$ $\nu_8 - \nu_3$	ν_5	ν_4	Ref.
(*a*) Bridging						
$[Zn_4O(O_2CMe)_6]$	1 600	1 441	155	695	942	6
$[Be_4O(O_2CMe)_6]$	1 639	1 483	156	657	980	6
$[Cu_2(O_2CMe)_4]\cdot 2H_2O$	1 603	1 418	185			12
$[Cr_2(O_2CMe)_4]\cdot 2H_2O$	1 591	1 420	171		958	15
(*b*) Chelating						
$Zn(O_2CMe)_2\cdot 2H_2O$	1 550	1 456	94	695	955	6
$Na[UO_2(O_2CMe)_3]$	1 537	1 472	65		948	9

RESULTS AND DISCUSSION

The i.r. and ^{1}H n.m.r. spectra are recorded in Tables 5 and 6. For $B_2O(O_2CMe)_4$ and $Na[B_2O(O_2CMe)_5]$ the spectra are very similar to those previously recorded;[15] the C–O stretching regions of each is complex, with ν_8 of both at 1 720—1 725 and 1 615—1 675 cm^{-1}, indicating

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* It should however be noted that for the nitrate group [2] the evidence is that the O–N–O angle is reduced from 120° in chelating and bridging geometry.

[6] A. I. Grigor'ev, *Russ. J. Inorg. Chem.*, 1963, **8**, 409.

[7] J. H. Talbot, *Acta Cryst.*, 1953, **6**, 720.

[8] W. H. Zachariasen and H. A. Plettinger, *Acta Cryst.*, 1959, **12**, 526.

[9] H. Koyama and Y. Saito, *Bull. Chem. Soc. Japan*, 1954, **127**, 113.

[10] W. H. Bragg and G. T. Morgan, *Proc. Roy. Soc.*, 1923, **A104**, 437.

[11] A. Dal Negro, L. Ungaretti, and A. Perotto, *J.C.S. Dalton*, 1972, 1639.

[12] J. N. van Niekerk and F. R. L. Schoening, *Acta Cryst.*, 1953, **6**, 101, 227.

[13] M. J. Janssen, J. G. A. Luitjten, and G. J. M. van der Kerk, *Rec. Trav. chim.*, 1963, **82**, 90.

[14] N. W. Alcock and R. E. Timms, *J. Chem. Soc. (A)*, 1968, 1873.

[15] H. A. Lehmann, G. Kessler, P. Denecke, and G. Nickl, *Z. anorg. Chem.*, 1965, **340**, 16.

unidentate and bridging acetate. This is fully consistent with the structures determined by *X*-ray analysis for the first (I),[11] and proposed[15] for the second (II). Similarly, for aluminium acetate, the present spectrum agrees with the previous report,[16] and with the interpretation in terms of three bridging acetate groups; chelating acetates are less likely, but perhaps should not be excluded by comparison with $[NMe_4][Sn(O_2CMe)_5]$ (below). For both the boron and aluminium compounds, the ^1H n.m.r. spectra show the expected number of distinct acetate groups.

TABLE 5

Assignments for metal acetates and acetato-complexes. Peak positions are in cm^{-1}. Recorded in the present work, unless otherwise noted

Compound	ν_1, ν_7 ν_{12}	ν_8	ν_3	ν_{10} ν_{14}	ν_4	ν_5	$\Delta\nu = \nu_8 - \nu_3$
$B_2O(O_2CMe)_4$	2 990	1 725, 1 615	1 480, 1 418		990, 935 910	690, 675	307, 135
(Ref. 15)	3 018 2 996, 2 943	1 726, 1 608	1 488 1 421		995		306, 128
$Na[B_2O(O_2CMe)_5]$	2 950 (sh) 2 925m	1 720 1 675	1 500 1 420				
(Ref. 15)	3 015 2 950	1 726 1 685	1 510 1 430—1 436				
$Al(O_2CMe)_3$	3 020	1 590	1 465, 1 430 (sh)		985	680, 660	128
(Ref. 16)		1 595	1 472 1 417 (sh)		989	645	123
$Zr(O_2CMe)_4$	2 930	1 540	1 455		945	690, 650	85
$Si(O_2CMe)_4$	2 970	1 760	1 270		950	650	490
$K_2[Si(O_2CMe)_6]$	3 100	1 770	1 270		970	670, 635	500
$Ge(O_2CMe)_4$	2 930	1 710	1 280		930	680	430
$K_2[Ge(O_2CMe)_6]$	3 000	1 710	1 240		912	680, 630	470
$Sn(O_2CMe)_4$	3 000, 2 955	1 635, 1 575	1 400, 1 315		970, 922	652, 630	320, 175
$K_2[Sn(O_2CMe)_6]$	3 010	1 675, 1 650, 1 640, 1 540	1 430 1 400, 1 300		925, 915	648	375, 340 100
$[NMe_4][Sn(O_2CMe)_5]$		1 635, 1 570	1 430, 1 365, 1 310				325, 140
$Pb(O_2CMe)_4$	3 000, 2 940	1 540	1 430		960	695	110
$K_2[Pb(O_2CMe)_6]$	2 950	1 710, 1 545	1 460, 1 315		960, 930	695, 660	395, 85

TABLE 6

Proton magnetic spectra of metal acetates and acetato-complexes

Compound	$B_2O(O_2CMe)_4$	$Na[B_2O(O_2CMe)_5]$	$Al(O_2CMe)_3$	$Zr(O_2CMe)_3$	$Si(O_2CMe)_4$
τ	7.87, 7.93	7.74, 8.10	7.93	7.97	7.82
Compound	$K_2[Si(O_2CMe)_6]$	$Ge(O_2CMe)_4$	$K_2[Ge(O_2CMe)_6]$	$Sn(O_2CMe)_4$	$K_2[Sn(O_2CMe)_6]$
τ	7.90	7.75	7.78	7.95	7.82, 7.95
Compound	$Pb(O_2CMe)_4$	$K_2[Pb(O_2CMe)_6]$			
τ	7.82	7.82, 7.85			

The i.r. spectra of $Si(O_2CMe)_4$ and $Ge(O_2CMe)_4$ are quite similar, and the high values of ν_8 and $\Delta\nu$ clearly indicate unidentate acetate; there are no marked changes on co-ordination of further acetate ions to give the $[M(O_2CMe)_6]^{2-}$ ions, and these must also contain unidentate acetate, with six-co-ordinate Si and Ge. The ^1H n.m.r. spectra again show one type of acetate only. The compounds $Zr(O_2CMe)_4$ and $Pb(O_2CMe)_4$ show corresponding spectra, with much lower ν_8 and $\Delta\nu$ of only 85 cm^{-1}. These clearly contain only bidentate acetate groups with eight-co-ordinate Zr and Pb.*

The most complicated i.r. spectra are those of $Sn(O_2CMe)_4$, and the acetato-ions of Sn and Pb, for which interpretation has been much aided by the crystal-structure determinations[18] of $Sn(O_2CMe)_4$ and $[NMe_4][Sn(O_2CMe)_5]$. In the second compound, the tin is seven-co-ordinate, from the oxygen atoms of two bi- and three uni-dentate acetate groups. This fits its spectrum reasonably well, with ν_8 at 1 635, ν_3 at 1 310, and $\Delta\nu$ 325 cm^{-1} corresponding to the unidentate acetate, and ν_8 at 1 570, ν_3 at 1 430, and $\Delta\nu$ 140 cm^{-1} corresponding to the bidentate acetate, although $\Delta\nu$ is somewhat larger than found so far for bidentate groups.

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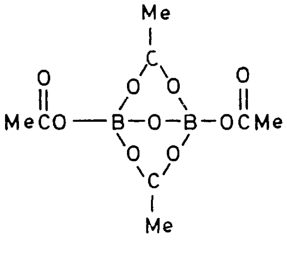
* This is consistent with a preliminary report[17a] of the structure of $Pb(O_2CMe)_4$, but as a later note[17b] gives this compound a different space group the structure clearly cannot be considered as firmly defined.

[16] A. I. Grigor'ev and V. Maksimov, *Russ. J. Inorg. Chem.*, 1964, **9**, 580.

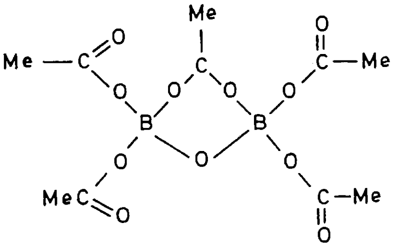
[17] (*a*) B. Kamenar, *Acta Cryst.*, 1963, **16** (Suppl), A34; (*b*) B. Kamenar and M. Bruvo, *ibid.*, 1972, **B28**, 321.

[18] Parts 3 and 4, in preparation.

The salts $K_2[Sn(O_2CMe)_6]$ and $K_2[Pb(O_2CMe)_6]$ are clearly similar; the latter compound may well be eight-co-ordinate in view of the larger size of Pb. Both these compounds show the expected two types of acetate groups in their ^1H n.m.r. spectra. The two tin compounds show some additional i.r. absorptions, and for $[NMe_4][Sn(O_2CMe)_5]$ this may be due to crystal-splitting effects because it contains two independent anions in its unit cell.



(I)



(II)

The i.r. spectrum of $Sn(O_2CMe)_4$ also clearly contains two types of acetate, and these appear to be similar to those in $[NMe_4][Sn(O_2CMe)_5]$; however, puzzlingly, the ^1H n.m.r. spectrum shows only one type of acetate group. The explanation comes from the crystal structure. This shows that $Sn(O_2CMe)_4$ is nearly eight-co-ordinate, but that there is not quite enough space around the tin for 8 ligand atoms with the result that one acetate group is asymmetrical, with one Sn–O distance normal, and the other significantly longer, *i.e.* it is an asymmetrical chelating group (type 4). This is clearly sufficient to transform the vibrations of one acetate group from the chelating pattern very nearly into the unidentate pattern. This also fits the n.m.r. result, because exchange between the acetate groups, leading to different groups becoming the odd one, could clearly be rapid enough to give only one n.m.r. signal.

It appears that the spectra of this class of acetates fit the general predictions rather well, but some ambiguities remain, particularly with the assignment of bridging or chelating groups where crystallographic information is important.

EXPERIMENTAL

Materials were prepared as in Part 1. Infrared spectra were recorded as mulls in Nujol or hexachlorobutadiene, between caesium iodide plates (protected by Polythene liners in the case of lead tetra-acetate), on a Perkin-Elmer 621 grating spectrophotometer. Comparison with the spectrum of polystyrene film showed the instrument to be accurate to ±1 cm^{-1}. Proton magnetic resonance spectra were recorded on a Perkin-Elmer R10 spectrometer at 60 MHz, using tetramethylsilane as internal standard for saturated solutions in $CDCl_3$. All the spectra were obtained at this machine's thermostatted temperature of 33 °C. When this work was carried out, ^{13}C facilities were not available to us.

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