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RELATIONSHIPS BETWEEN THE CARBON—OXYGEN STRETCHING FREQUENCIES OF CARBOXYLATO COMPLEXES AND THE TYPE OF CARBOXYLATE COORDINATION

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A. INTRODUCTION

Because of the low symmetry of carboxylate ions, RCO_2^-, the differing types of carboxylate coordination cannot be distinguished on the basis of the number of infrared or Raman active vibrations [1]. Instead, attempts have been made to relate values of the carbon—oxygen stretching frequencies to the nature of the carboxylate coordination [1—3]. In many cases (section C), the proposed correlations or critical comments on them are based on a relatively small number of complexes, the structures of which have often not been determined crystallographically, hence a more definitive evaluation is needed. Infrared spectra are available for a wide range of acetato complexes

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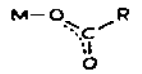
and a useful number of trifluoroacetato complexes of known structure. In this review, we use these data to assess critically the value of carbon—oxygen stretching frequencies in diagnosing the nature of carboxylate coordination.

B. THE NATURE OF CARBOXYLATE COORDINATION

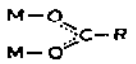
A carboxylate ion, RCO_2^-, can coordinate to metals in a number of ways, viz. as a unidentate ligand (I), as a chelating ligand (II), as a bridging bidentate ligand in a *syn—syn* (IIIa), *syn—anti* (IIIb) or *anti—anti* (IIIc) configuration, or as a monatomic bridging ligand, either alone (IVa), with additional bridging (e.g. IVb), or in arrangements involving chelation and bridging (e.g. IVc, IVd). Examples of the various arrangements are given with the figures.

I. 

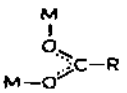
e.g. $Ph_3Sb(O_2CMe)_2$ [4]

II. 

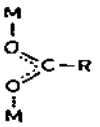
e.g. $Zn(O_2CMe)_2(H_2O)_2$ [5]
$Sn(O_2CMe)_4$ [6]

IIIa 

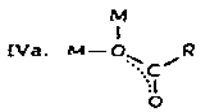
e.g. $\{Os(O_2CMe)(CO)_3\}_2$ [7]
$\{Rh(O_2CMe)_2py\}_2$ [8]

IIIb. 

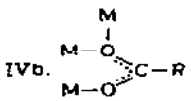
e.g. $Cu(O_2CH)_2$ [9]
$Me_3Sn(O_2CMe)$ [10]

IIIc. 

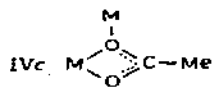
e.g. $Mn(O_2CMe)_2(H_2O)_4$ [11]
$Mn(O_2CMe)$(salen) [12]
[H_2salen = *N,N'*-ethylenedi(salicylaldimine)]

IVa. 

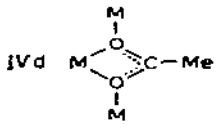
e.g. $Hg(O_2CMe)_2[(C_6H_{11})_3P]$ [13]

IVb. 

e.g. $Cu(O_2CMe)$ [14]

IVc 

e.g. $Cd(O_2CMe)_2(H_2O)_2$ [15]

IVd 

e.g. $Me_2Tl(O_2CMe)$ [16]

In addition to coordination derivatives, ionic metal carboxylates are also well established by crystallography, e.g. $[Co(imidazole)_6](O_2CMe)_2H_2O$ [17], $[Tl(SC(NH_2)_2)_4]O_2CPh$ [18] and $K(O_2CMe)MeCO_2H$ (contains acetic acid of solvation) [19], and are of importance in the following discussion.

C. SOME REPORTED CORRELATIONS BETWEEN THE NATURE OF CARBOXYLATE COORDINATION AND CARBON–OXYGEN STRETCHING FREQUENCIES

Unidentate coordination (I) removes the equivalence of the two oxygen atoms [2]. If the carbon–oxygen bond orders are appreciably affected, a pseudo-ester configuration M—O(C=O)R is obtained. This should increase

V.

$\nu_{asym}(CO_2)$, decrease $\nu_{sym}(CO_2)$ and increase the separation (Δ) between the $\nu(CO_2)$ frequencies relative to values for the free carboxylate ion [2], usually taken as those of the sodium or potassium salts. * Chelation or symmetrical bridging should not alter the bond orders, and it has been suggested that bidentate coordination should give separations similar to ionic values [3]. It also has been suggested that symmetrical bridging [2] or chelation [3] shifts both $\nu(CO_2)$ frequencies in the same direction. Several other correlations between $\nu(CO_2)$ frequencies and chelating or bridging bidentate carboxylate coordination have been proposed. Thus, separations significantly less than ionic values are considered indicative of chelating or bridging carboxylate groups [26]. This proposal has recently been revived and strongly supported by consideration of a wide range of compounds of known structure [27], and is consistent with data for many Group 8 carboxylates without crystallographically established structures [28 and refs. therein]. The converse of this correlation does not hold, i.e. not all chelating or bridging bidentate carboxylate groups have low Δ values [27]. From studies of metal haloacetates, several authors have claimed that an increase in $\nu_{asym}(CO_2)$ relative to the sodium salt is indicative of bridging whereas a decrease in $\nu_{asym}(CO_2)$ is indicative of chelation [29–31]. In a closely related proposal, it has been suggested that Δ (chelating) < Δ (bridging) for acetates [21,32]. Some quite contentious claims have been put forward. For example, the suggestion that Δ (unidentate) < Δ (bidentate) for lanthanoid acetates [33] is wrong [34], and the proposal that Δ is increased for chelating carboxylates relative to ionic [35] has been contradicted by the same authors [29].

Quite apart from contradictions in the foregoing proposals, wrong structures have been predicted for $Er(O_2CMe)_3(H_2O)_4$ [33,34], $[Cu(O_2CMe)NH((CH_2)_3NH_2)_2]ClO_4$ [36,37], $[Mo(O_2CMe)_2]_2$ [38,39] and $[Co(O_2CMe)(NH_3)_5]^{2+}$ [40,41] on the basis of $\nu(CO_2)$ frequencies. Because of these difficulties, a number of authors have rejected various correlations as unreliable [25,42,43]. Others have accepted that large separations are indicative of uni-

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* The variation of $\nu(CO_2)$ frequencies with change in cation is quite small, e.g. for sodium, potassium and rubidium acetate, the antisymmetric mode is at 1578–1571 cm^{-1} and the symmetric at 1414–1402 cm^{-1} [20–22], and the respective separations are 164, 171 and 164 cm^{-1}. Similarly, the separations for sodium [23,24] and potassium [25] trifluoroacetate are 223 and 241 cm^{-1} respectively. Insensitivity to change of cation is consistent with an ionic formulation.

dentate coordination, but consider the converse to be untrue, reducing the value of the criterion [44,45].

One reason for the general lack of agreement is that many claims have been made on the basis of a few compounds or a closely related series of compounds. For example, the suggestion that Δ (chelating) < Δ (bridging) was based on six compounds [32], and it was subsequently rejected because of a single exception [44]. Other proposals (e.g. [29—31,35]) lack unambiguous structural support and hence have low credibility.

D. THE DATA BASE FOR THE PRESENT STUDY

From the foregoing discussion, assessment of the relationship between the $\nu(CO_2)$ frequencies and the nature of the carboxylate coordination should be based on consideration of infrared data for a wide range of complexes of known structure. A suitable data base is provided by acetato and trifluoro-

TABLE 1

Infrared and structural data for compounds with unidentate acetate groups

Compound	$\nu_{asym}(CO_2)$ [a] (cm^{-1})	$\nu_{sym}(CO_2)$ [a] (cm^{-1})	Δ [b] (cm^{-1})	Ref.
$[Co(O_2CMe)(NH_3)_5](Cl)ClO_4$ [d]	1600	e		40
	e	e	223	44
$Hg(O_2CMe)_2$	1600, 1566	1368	215	46
	e	e	270	47
$PhHg(O_2CMe)$ [g]	1615, 1590	1379, 1363	232	49
$[Me_3CC(O)]_2CHHg(O_2CMe)$	1618, 1580	1309	290	51
$Na[H(O_2CMe)_2]$ [g,h]	1710	1400	310	53
$Ph_3Sb(O_2CMe)_2$	1633	1320	313	54
$Si(O_2CMe)_4$	1760	1270	490	32
	1765	1200	565	55
(*cyclo*-C_6H_{11})$_3$Sn(O_2CMe)	1645	e		57
$Ni(O_2CMe)_2(H_2O)_4$	1550	1425	125	43
	1520	1413	107	36
$Ni(O_2CMe)_2(H_2O)_2py_2$ [g]	1550	1412	138	59
$Zn(O_2CMe)_2(SC(NH_2)_2)_2$	1577	1425	152	36
$Na(O_2CMe)$ [j]	1578	1414	164	20

[a] Shoulders not listed.
[b] Calculated using average $\nu(CO_2)$ values where necessary.
[c] M · · O refers to the second shortest metal—oxygen bond and is essentially non-bonding.
[d] Infrared values refer to $\{Co(O_2CMe)(NH_3)_5\}(ClO_4)_2$ [44] or $\{Co(O_2CMe)(NH_3)_5\}^{++}$ (anion unspecified) [40].
[e] Not given.

acetato complexes, for which over one hundred and ninety crystal structures have been carried out. Infrared spectra have been located for eighty-four of these complexes (70 acetates, 14 trifluoroacetates), and the $\nu(CO_2)$ frequencies and pertinent structural data are listed in Tables 1—5. For compounds with more than one similar carboxylate ligand, either average structural parameters or values for a single ligand are given. Several carboxylates are isostructural with the listed compounds, but have not been included unless the detailed structures have been determined. Compounds in which the acetate group is present solely as lattice or coordinated acetic acid, e.g. $[Ni(MeCO_2H)_6](BF_4)_2$ [148], have been excluded.

In general, the nature of the carboxylate coordination is readily evident from the X-ray data. For example, the M—O bond distance for each compound in Table 1 is considerably shorter than the next shortest M···O contact, consistent with interpretation of the coordination as unidentate. However, the mercury complexes (Table 1) require further comment. Mercury shows

∠ O—C—O (°)	C—O[1] (Å)	C—O[2] (Å)	M—O[1] (Å)	(M · · O)[c] (Å)	Ref.
e	1.30	1.23	e	e	41
119	1.28	1.26	2.09	(2.73)[f]	48
122	1.29	1.31	2.11	(2.85)[f]	50
123	1.32	1.24	2.10	(2.72)[f]	52
121.7	1.295	1.243	1.22[i]	e	53
121.6	1.298	1.214	2.13	(2.78)	4
119.3	1.374	1.196	1.63	(2.93)	56
e	1.39	1.25	2.12	(2.95)	57
122.5	1.272	1.255	2.067	e	58
126.4	1.260	1.247	2.050	e	60
121.2	1.252	1.228	1.95	(2.89)	61
123.3	1.275	1.215	1.97	(3.00)	

[f] Mercury—oxygen contacts of 2.72—2.85 Å in these molecules represent weak coordination, but are of a completely different type from Hg—O[1] (see text).
[g] Infrared values assigned in this work.
[h] A very strong O—H—O bond exists in this compound.
[i] Refers to O—H bond; see [h].
[j] Assumed ionic, included for comparison of infrared data.

TABLE 2

Infrared and structural data for compounds with chelating acetate groups

Compound	$\nu_{asym}(CO_2)$ (cm^{-1})	$\nu_{sym}(CO_2)$ (cm^{-1})	Δ (cm^{-1})	Ref.
$Cu(O_2CMe)(Ph_3P)_2$	1552	1421	131	62
	1565	1405	160	63
$Hg(O_2CMe)_2(Bu_3P)$	1575	1403	172	65
$Mn(O_2CMe)(CO)_2(Ph_3P)_2$ [b]	1520	1437	83	66
$Ni(O_2CMe)(tet)ClO_4$ [c]	1550	1448	102	36
$Re(O_2CMe)(CO)_2(Ph_3P)_2$	1515	d		68
$Ru(O_2CMe)H(Ph_3P)_2$	1526	1451	75	69
$Ru(O_2CMe)R(CO)(Ph_3P)_2$ [e]	1527	1451	76	71
$Sn(O_2CMe)_4$	1568	1415	153	73
	1635, 1575	1400, 1315	175, 320	32
	1704, 1560	1440, 1262	120, 440 [f]	74
$NaUO_2(O_2CMe)_3$	1537	1472	65	75
$Zn(O_2CMe)_2(H_2O)_2$	1550	1456	94	21
	1550	1405	145	43
$Na(O_2CMe)$ [h]	1578	1414	164	20

[a] The difference between the $M-O^1$ and $M-O^2$ bonds is much less than for the mercury compounds in Table 1.
[b] Infrared values assigned (this work) by comparison with $Re(O_2CMe)(CO)_2(Ph_3P)_2$ [68].
[c] tet = *C-rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane.
[d] Not given.

TABLE 3

Infrared and structural data for compounds with bridging acetate groups [a]

Compound	$\nu_{asym}(CO_2)$ (cm^{-1})	$\nu_{sym}(CO_2)$ (cm^{-1})	Δ [b] (cm^{-1})	Ref.
$Be_4(O_2CMe)_6O$	1639	1483	156	21
	1603	1447	156	77
$[Co_2(O_2CMe)(OH)L](H_2O)EtOH$ [c]	1565	1410	155	79
$[Cr(O_2CMe)_2(H_2O)]_2$	1575	1420	155	77
	1573	1450	123	81
$[Cr_3(O_2CMe)_6O(H_2O)_3]Cl \cdot 6\,H_2O$	1595	d		83
$CrMo(O_2CMe)_4$ [f]	1552, 1525, 1500	1459, 1416, 1355 [g]	88	85
$[Cu(O_2CMe)NH((CH_2)_3NH_2)_2]ClO_4$	1550	1400	150	36
$[Cu(O_2CMe)_2(H_2O)]_2$	1600	1425	175	81
	1610	1410	200	43

∠O—C—O (°)	C—O¹ (Å)	C—O² (Å)	M—O¹ (Å)	M—O² (Å)	Ref.
121.8	1.247	1.261	2.257	2.162	64
120.9	1.24	1.24	2.58	2.27 [a]	65
123.5	1.23	1.27	2.66	2.25	
115.8	1.235	1.265	2.069	2.066	66
121.6	1.25	1.25	2.103	2.116	67
120	1.28	1.25	2.23	2.20	68
114.9	1.255	1.263	2.210	2.198	70
115.4	1.29	1.30	2.279	2.173	72
118.3	av. 1.264		2.13—2.29		6
121	1.26	1.28	2.47	2.51	76
111 [g]	1.30 [g]	1.38 [g]	2.18	2.17	5

[e] R = *p*-MeC$_6$H$_4$N=CH—.
[f] Data incorrect, see [73].
[g] Data inaccurate.
[h] Assumed ionic, included for comparison of infrared data.

∠O—C—O (°)	C—O¹ (Å)	C—O² (Å)	M¹—O¹ (Å)	M²—O² (Å)	Ref.
123.4	1.264	1.264	1.624	1.624	78
125.6	1.312	1.22	1.90	2.01	80
122.7	1.263	1.268	2.030	2.030	82
e	1.22—1.31		1.94—2.01		84
122.0	1.262	1.270	2.065	2.053	85
120.4	1.27	1.27	2.02	2.29 [h]	37
124.4	1.257	1.261	1.990	1.992	86

TABLE 3 (Continued)

Compound	$\nu_{asym}(CO_2)$ (cm^{-1})	$\nu_{sym}(CO_2)$ (cm^{-1})	Δ [b] (cm^{-1})	Ref.
$(Me_4N)_2[Cu(O_2CMe)_2(NCS)]_2$	1610	1425	185	87
$[Fe_3(O_2CMe)_6O(H_2O)_3]Y$ [i]	1595	1450	145	89
	1573 [j]			83
$Li(O_2CMe)(H_2O)_2$	1597	1435	162	91
$Mn(O_2CMe)(salen)$ [l]	1550	k		93
$[Mo(O_2CMe)_2]_2$ [f]	1512, 1494	1409	94	38
	1515, 1495	1440, 1412	79	81
	1585	1415	170 [m]	43
$[Os(O_2CMe)(CO)_3]_2$	1575, 1565	1465, 1430	123	94
$Me_3Pb(O_2CMe)$	1555	1410	145	95
$[Pd(O_2CMe)(C_3H_5)]_2$	1575 [n]	1425 [n]	150	97
$[Pd(O_2CMe)(Cl)(Me_2PhP)]_2$	1575	1418	157	99
$[Pd(O_2CMe)CO]_4(MeCO_2H)_2$	1555, 1518	1420 [j]	116	101
$[Pd_3(O_2CMe)_6]\frac{1}{2}H_2O$	1600	1427	173	102
$Re_2(O_2CMe)_2Me_2Cl_2(OSMe_2)$ [f]	1465 [j]	p	<100	104
$[Rh(O_2CMe)_2(H_2O)]_2$	1580	1430	150	102
$[Rh(O_2CMe)_2py]_2$	1590 [j]	1430 [j]	160	8
$[Rh(O_2CMe)_2(Et_2NH)]_2$	1595 [j]	1428 [j]	167	106
$[Rh_3(O_2CMe)_6O(H_2O)_3]ClO_4$	1598	1425	173	107
$[Ru(O_2CMe)(CO)_2py]_2$	1570 [j]	1440 [j]	130	94
$Ru_3(O_2CMe)_6O(Ph_3P)_3$	1540 [j]	1415 [j]	125	108
$Sb_2(O_2CMe)Cl_6O(OH)$	1480	1435	45	109
$Me_3Sn(O_2CMe)$	1558	1418	140	110
$(PhCH_2)_3Sn(O_2CMe)$	1618	1319 [q]	299 [q]	111
	1565	k		57
$[Ph_2Sn(O_2CMe)]_2$	1530	1405	125	113
$Zn_4(O_2CMe)_6O$	1600	1441	159	21
	1639	1489	150	77
$Na(O_2CMe)$ [r]	1578	1414	164	20

[a] Bonding as in III(a)—(e). [b] Using average $\nu(CO_2)$ values where necessary.
[c] H_3L = 4-hydroxy-3,5-bis[*N*-(2'-hydroxyphenyl)formimidoyl]toluene.
[d] Only strong bands are reported [83]. $\nu_{asym}(CO_2)$ assigned this work. The assignment of $\nu_{sym}(CO_2)$ at 1515 cm^{-1} [44] is implausible. [e] 120—131°.
[f] Contains a very short metal—metal bond. [g] Assigned to both $\nu_{sym}(CO_2)$ and δ(Me)

∠O—C—O (°)	C—O[1] (Å)	C—O[2] (Å)	M[1]—O[1] (Å)	M[2]—O[2] (Å)	Ref.
126.2	1.24	1.24	2.03	2.03	88
k	1.24	1.24	2.02	2.02	90
125.7	1.245	1.245	1.895	1.895	92
121.3	1.259	1.259	2.201	2.201	12
121.8	1.279	1.272	2.110	2.107	39
125	1.284	1.286	2.10	2.07	7
125	1.330	1.229	2.08	2.06	
121.5	1.232	1.214	2.327	2.555	96
k	1.20	1.28	2.10	2.12	98
125.6	1.28	1.21	2.03	2.12	100
127	1.25	1.27	2.11	2.12	101
127 (av)	k	k	1.97—2.01		103
121.8	1.259	1.256	2.040	2.035	105
119.7	1.256	1.284	2.025	2.021	
124.6	1.265	1.273	2.047	2.042	82
125.6	1.266	1.269	2.042	2.040	8
127.8	1.255	1.259	2.031	2.046	106
124—128	1.24—1.30		1.99—2.05		107
k	k		k		7
124—128	1.22—1.30		2.03—2.09		108
124.2	1.294	1.261	2.103	2.103	109
122.6	1.269	1.240	2.205	2.391	10
k	1.31	1.21	2.14	2.65	112
125.6	1.20	1.31	2.25	2.25	114
125	1.24	1.24	1.96	1.98	115

[85]. If 1355 cm^{-1} is attributed to δ(Me), then $\Delta \simeq 88$ cm^{-1} (using average $\nu(CO_2)$ values). [h] Value of $M^2—O^2$ in Table 4 of [37] (2.74 Å) is assumed incorrect. [i] Y = Cl or ClO_4. [j] Assigned this work. [k] Not given. [l] H_2salen = *N,N'*-ethylenedi(salicylaldimine). [m] Probably wrong. [n] Approximate values. [p] Assignment uncertain. [q] Assignment of $\nu_{sym}(CO_2)$ is probably incorrect. [r] Assumed ionic, included for infrared comparison.

TABLE 4

Infrared data and acetate coordination modes of compounds with more than one type of acetate coordination or with acetate groups that are monatomically bridging

Compound	$\nu_{asym}(CO_2)$ (cm^{-1})	$\nu_{sym}(CO_2)$ (cm^{-1})	Δ [a] (cm^{-1})	Ref.	Bonding mode [b]	Ref.
$B_2(O_2CMe)_4O$	1725, 1615	1480, 1418	135, 307	32	I, III(a)	116
$Cd(O_2CMe)_2(H_2O)_2$	1555	1409	146	21	II, IV(c)	15
$Ce(O_2CMe)_3(H_2O)_x$ [c]	1565 1557	1415 1443, 1396	150 138	43 22	III(a), IV(c)	117
$Cu(O_2CMe)$	1525 [d]	1414 [d]	111	118	IV(b)	14
$CaCu(O_2CMe)_4(H_2O)_6$	1590	1410	180	36	IV(c)	119
$Er(O_2CMe)_3(H_2O)_4$	1538	1458, 1412	103	22	II, IV(c)	34
$MeGa(O_2CMe)_2$	1670, 1575, 1543	1477, 1460, 1403, 1305	ca. 120, 365	120	I, III(b)	120
$Hg(O_2CMe)(S(CH_2)_2Me)$	1528	1400	128	121	IV(b)	121
$Hg(O_2CMe)(S(CH_2)_3Me)$	1526	1408	118	121	IV(b)	121
$Me_2In(O_2CMe)$	1530	1445	85	122	IV(d)	123
$Et_2In(O_2CMe)$	1525	1465	60	124	IV(d)	124

$K(O_2CMe)MeCO_2H$	1715, 1675, 1620	1430, 1315	190, 380	125	Ionic [e]	19
$Mn(O_2CMe)_2(H_2O)_4$	1570	1400	170	43	III(a), IV(b)	11
$MeRe(O_2CMe)_2$	1555, 1450	f		104	II, III(a)	105
$(Me_4N)Sn(O_2CMe)_5$	1635, 1570	1430, 1310	140, 325	32	I, II	126
$Tl(O_2CMe)_3$	1550, 1500	1422	103	g	II, IV(c)	127
$Me_2Tl(O_2CMe)$	1541	1418	123	128	IV(d)	16
$UO_2(O_2CMe)_2(H_2O)_2$	h	h	<100	129	II, III(c)	130
$UO_2(O_2CMe)_2(Ph_3PO)$	1533, 1524	1456, 1425	88	42	II, III(a)	131
$U(O_2CMe)_4$	1560, 1510	1402	133	132	III(a), IV(c)	133
$Na(O_2CMe)$ [i]	1578	1414	164	20		

[a] Calculated using average $\nu(CO_2)$ values where appropriate. For compounds that have one high $\nu_{asym}(CO_2)$ band and one low $\nu_{sym}(CO_2)$ band, these absorptions have been treated as a separate pair. [b] Numbers refer to I (unidentate), II (chelating), III(a)–(c) (bridging bidentate) and IV(a)–(d) (monatomic bridging modes) – (Section B). [c] For infrared data, $x = 1.5$; for structure, $x = 0.7$. [d] Values from Supp. Publication for ref. 118. [e] Also contains acetic acid. [f] Not assigned. [g] Infrared data (this work) from Nujol and hexachlorobutadiene mulls between silver chloride plates: $\nu_{sym}(CO_2)$ may also contribute to absorptions at 1385 and 1370 cm^{-1}. [h] A broad absorption centred on 1500 cm^{-1} has been assigned to $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ [129]. [i] Assumed ionic, included for comparison of infrared data.

TABLE 5

Infrared and structural data for trifluoroacetates

Compound	$\nu_{asym}(CO_2)$ [a] (cm^{-1})	$\nu_{sym}(CO_2)$ [a] (cm^{-1})	Δ (cm^{-1})	Ref.	Bonding mode	Ref.
$K[H(O_2CCF_3)_2]$ [b]	1792	1420	372	134	Unidentate	135
$Cs[H(O_2CCF_3)_2]$ [b]	1790	1408	382	134	Unidentate	136
$K[D(O_2CCF_3)_2]$ [b]	1745	1418	327	134	Unidentate	135
$Mo(O_2CCF_3)(CO)_2(C_3H_5)L$ [c]	1725	1400	325	137	Unidentate	137
$W(O_2CCF_3)(CO)_2(C_3H_5)L$ [c]	1712	1397	315	137	Unidentate	137
$Sn(O_2CCF_3)_2(CH{=}CH_2)_2bpy$	1713	d		138	Unidentate	138
$[Co(O_2CCF_3)_4](Ph_4As)_2$	1692	1421	271	25	Unidentate	139
$Hg(O_2CCF_3)_2$	1680	1416	264	46	Unidentate	140
$NH_4(O_2CCF_3)$	1667	1465	202	25	Ionic [e]	141
$[V(O_2CCF_3)_2C_5H_5]_2$ [f]	1720	1475	245	142	Bridging	142
$Me_3Sn(O_2CCF_3)$	1652	1340 [g]	312 [g]	110	Bridging	10
$[Ag(O_2CCF_3)]_2$	1623	1454	169	46	Bridging	143
$[Mo(O_2CCF_3)_2py]_2$ [f]	1615, 1605	1455	155	144	Bridging	144
$[Mo(O_2CCF_3)_2]_2$ [f]	1592, 1572	1459	133	145	Bridging	145
$\{[Sn(O_2CCF_3)(CH{=}CH_2)_2]_2O\}_2$	1700, 1660	d		146	Unidentate, bridging	146
$[Pr(O_2CCF_3)_3(H_2O)_3]_2$ [f]	1710, 1660, 1620	d		147	Unidentate, bridging	147
$K(O_2CCF_3)$ [h]	1678	1437	241	25		
$Na(O_2CCF_3)$ [h]	1680	1457	223	23		

[a] Shoulders not listed

[b] Two trifluoroacetate groups are strongly coordinated to the pseudo-metals H or D.

[c] L = 1,2-dimethoxyethane.

[d] Not assigned.

[e] Pseudo-bridging owing to hydrogen-bonding with the cation.

[f] Assigned (this work) from the reported spectrum.

[g] The assignment of $\nu_{sym}(CO_2)$ for this compound is inconsistent with the assignment of this mode in other trifluoroacetates.

[h] Assumed ionic, included for comparison of infrared data.

dual coordination behaviour, so called *characteristic coordination* where the metal—ligand bonds are very short and *effective coordination* where the mercury—ligand distances are very long, but just within the sum of the mercury and donor atom Van der Waals radii [149,150]. The longer Hg···O contacts (Table 1) represent effective coordination interactions (sum of Van der Waals radii of mercury and oxygen, 2.9—3.1 Å [149] or even ~3.4 Å [151]), but have been disregarded in classifying the acetate coordination as unidentate because they are considerably longer than the shortest Hg—O distances. As can be seen from the examples in Table 1, the same criteria have been used for mercury derivatives as for complexes of antimony and tin.

E. PROBLEMS IN INTERPRETATION OF THE INFRARED SPECTRA

Several problems with reported infrared data need to be recognized.

(i) Anion exchange

Examination of carboxylate complexes in solution, or as mulls between alkali halide plates, or in potassium halide discs can result in anion exchange, though many authors overlook this.

$$MO_2CR + M'X \rightarrow MX + M'O_2CR \qquad (1)$$

(M' = Na or K; X = Cl or Br)

The possibility of exchange is enhanced in obtaining high resolution spectra, since the longer scan times provide increased opportunity for reaction. Complete exchange has been reported to occur in a KCl disc of dimethylthallium(III) acetate [152]. There are several reports of exchange between Nujol mulls of carboxylate complexes and KBr or NaCl plates [153—155], and exchange between solutions and plates has also been observed [152]. Two independent studies have given $\nu_{asym}(CO_2)$ of silver pentafluorobenzoate as 1610 cm^{-1} [156,157], the same value as that of the sodium salt [156]. However, reexamination of the spectrum using a Nujol mull on silver chloride plates reveals $\nu_{asym}(CO_2)$ at 1565 cm^{-1} [158] and there is no significant absorption at 1610 cm^{-1}. Thus complete anion exchange must have occurred during the earlier studies.

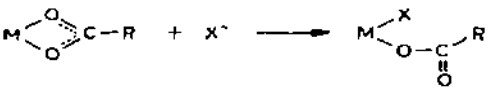
Many authors give no details of the method used to obtain the infrared spectra, so that it is not possible to determine whether some unusual or inconsistent values could result from exchange with plates. Certainly, doubts must attach to all cases where the $\nu(CO_2)$ frequencies are similar to those of the sodium or potassium carboxylates unless the spectra were recorded on inert plates (AgCl, Irtran). * Splitting of $\nu_{asym}(CO_2)$ absorptions has been

* Covering alkali metal halide plates with polystyrene film offers satisfactory protection against exchange with Nujol mulls, but hexachlorobutadiene is likely to attack the coating [152,159].

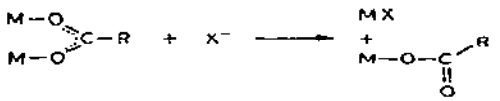
attributed to many causes, e.g. two coordination modes [32,38,160], polymer—dimer equilibria [161], coupling between neighbouring carboxylate groups [162,163], or 'solid state effects' [38,162,164]. However, unless partial anion exchange has been conclusively ruled out, these other explanations must be viewed with suspicion.

(ii) Pressure-induced changes

Formation of potassium halide discs may result in pressure-induced changes of spectra. For example, $\nu_{asym}(CO_2)$ of potassium formate is at 1581 cm^{-1} in Nujol [165,166] but can shift to 1630 cm^{-1} in a KBr disc. The shift of $\nu_{asym}(CO_2)$ of copper(II) acetate [167] may have a similar origin. Obviously pressure can enhance anion exchange between the complex and the disc material (E(i)), but other effects are possible. For example, pressure could promote hydrolysis of $M(O_2CR)$ groups by coordinated water or by traces of moisture in the disc material. In addition, pressure-induced coordination of halide ions could change the nature of the carboxylate coordination, apart from conversion into ionic carboxylate caused by exchange. Thus, changes from chelating or bridging to unidentate carboxylate groups are readily conceived.



(2)



(3)

(iii) Contradictory spectroscopic data or wrong assignments

There are many inconsistencies in reported $\nu(CO_2)$ frequencies, e.g. $\nu_{asym}(CO_2)$ of $Zn_4(O_2CMe)_6O$ has been given as 1600 [21] or 1639 [77] cm^{-1}, $\nu_{asym}(CO_2)$ of $Be_4(O_2CMe)_6O$ as 1603 [77] or 1639 [21] cm^{-1}, $\nu_{asym}(CO_2)$ of $(PhCH_2)_3SnO_2CMe$ as 1565 [57] or 1618 [111] cm^{-1} and Δ for $[Mo(O_2CMe)_2]_2$ as ca. 90 [38,81] or 170 [43] cm^{-1}. These differences originate in the observed spectra, not in disagreements over assignments. In some cases, they may arise from factors such as anion exchange or pressure-induced changes discussed above.

Where similar spectra have been obtained, there may be differences in assignments, particularly of $\nu_{sym}(CO_2)$. Thus, this mode has been given as 1405 [43], 1430 [36] and 1456 [21] cm^{-1} for $Zn(O_2CMe)_2(H_2O)_2$, as 1420 [77] and 1450 [81] cm^{-1} for $Cr(O_2CMe)_2H_2O$, and as 1200 [55] and 1270 [32] cm^{-1} for $Si(O_2CMe)_4$. Because of uncertainties in locating $\nu_{sym}(CO_2)$, some authors prefer not to assign it at all [168], or to assign a group of absorptions to $\nu_{sym}(CO_2)$ and $\delta(Me)$ [85].

F. DEVELOPMENT OF CORRELATIONS BETWEEN CARBON—OXYGEN STRETCHING FREQUENCIES AND THE TYPE OF CARBOXYLATE COORDINATION

In this section, relationships between $\nu(CO_2)$ frequencies and carboxylate coordination are established from the data in Tables 1—5.

(i) Compounds for which Δ is large

Virtually all acetato complexes which have $\Delta \geqslant 200$ cm^{-1} (cf. 164 cm^{-1} for ionic acetates — section C) have unidentate coordination for some or all acetate groups, viz. $Co(O_2CMe)(NH_3)_5^{2+}$, $Hg(O_2CMe)_2$, $PhHg(O_2CMe)$, $(Me_3CC(=O))CHHg(O_2CMe)$, $NaH(O_2CMe)_2$, * $Ph_3Sb(O_2CMe)_2$, $Si(O_2CMe)_4$, (*cyclo*-$C_6H_{11})_3Sn(O_2CMe)$ ** (Table 1), together with $B_2(O_2CMe)_4O$, $MeGa(O_2CMe)_2$ and $Me_4N[Sn(O_2CMe)_5]$ (Table 4). Large Δ values have also been reported for $(PhCH_2)_3Sn(O_2CMe)$ (Table 3), which has unsymmetrical bridging bidentate carboxylate ligands [112] and $Sn(O_2CMe)_4$ (Table 2), which has chelating acetates [6]. However, there are problems with the infrared spectra in each case. Conflicting values have been given for $\nu_{asym}(CO_2)$ of $(PhCH_2)_3Sn(O_2CMe)$ (Table 3) and the assignment of $\nu_{sym}(CO_2)$ at 1319 cm^{-1} is implausible. It is possible that the higher value of $\nu_{asym}(CO_2)$ is correct and that Δ still exceeds 200 cm^{-1}, since the lower $\nu_{asym}(CO_2)$ frequency could result from anion exchange. If this is the case, it may be correlated with the highly unsymmetrical bridging (Table 3), which can be viewed as approaching a unidentate arrangement (see the interpretation of the acetate coordination in the mercury complexes of Table 1 — section D). For $Sn(O_2CMe)_4$, several authors have reported two $\nu_{asym}(CO_2)$ absorptions, one near 1570 cm^{-1} and one much higher [32,74,169]. A possible explanation, viz. that chelation of one acetate group is very unsymmetrical [32] is not convincingly supported by the crystal structure [6]. Furthermore, it has been shown that the higher $\nu_{asym}(CO_2)$ and the lower $\nu_{sym}(CO_2)$ values result from partial hydrolysis of the compound [73], and it is not clear whether anion exchange has been ruled out in the case of the other frequencies.

In summary, Δ values > 200 cm^{-1} for acetato complexes appear generally associated with unidentate coordination, a possible exception involving highly unsymmetrical bridging, i.e. "pseudo-unidentate" coordination. This

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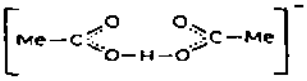
* The hydrogen (as a pseudo-metal) bridges two acetate ions,



giving two unidentate acetate groups.

** Only $\nu_{asym}(CO_2)$ has been reported but this value is so high that Δ must exceed 200 cm^{-1}.

correlation is also consistent with observation of much higher Δ values for many $R_3M(O_2CR')$ (M = Sn or Pb) complexes in solution than in the solid state [e.g. 95,110,170—172]. This increase has widely been interpreted as being due to a change from a polymeric five coordinate solid state structure with bridging bidentate carboxylate groups to a monomeric four or five (solvent coordinated) solution species with unidentate carboxylate groups. In many cases, these proposals have quite convincing support from molecular weight and spectroscopic data.

The correlation between high Δ values and unidentate carboxylate coordination can be extended to trifluoroacetates (Table 5). All complexes with $\Delta > 260$ cm^{-1} (cf. 223 for NaO_2CCF_3 [23]) have unidentate trifluoroacetate ligands, except $Me_3Sn(O_2CCF_3)$ (bridging bidentate carboxylate groups [10]) for which Δ has been given as 312 cm^{-1}. However, the assignment of $\nu_{sym}(CO_2)$ to a band at 1340 cm^{-1} is almost certainly wrong, being inconsistent with values for other trifluoroacetato complexes (Table 5). The antisymmetric frequency (1652 cm^{-1}) is much lower than those of unidentate trifluoroacetates (1792—1680 cm^{-1}), and, given a "normal" $\nu_{sym}(CO_2)$ value, Δ would be ca. 210 cm^{-1}. The symmetric carboxylate frequency has not been assigned for three compounds with unidentate carboxylate groups, but the relatively high values of $\nu_{asym}(CO_2)$ (Table 5) suggest that $\Delta > 260$ cm^{-1}.

One recent exception to the high Δ/unidentate coordination correlation should be mentioned, even though it involves a carboxylate ligand ($Me_3CCO_2^-$) not being considered in this review (owing to lack of sufficient examples of known structure). Although the complex $(\eta\text{-}C_5H_5)_2Nb(O_2CCMe_3)$ has a symmetrical chelating carboxylate group [173], a Δ value of 347 cm^{-1} has been reported [174] (cf. 138 cm^{-1} [175] for NaO_2CCMe_3). However, the spectrum was recorded as a KBr disc, and pressure-induced changes, e.g. a conversion from chelating to unidentate trimethylacetate induced by halide coordination [see reaction (2), section E(ii)] or partial hydrolysis, must be considered plausible. Thus, reinvestigation of the spectrum is highly desirable, preferably for a mull of the compound between inert plates.

(ii) Unidentate carboxylates without large Δ values

Three complexes with unidentate acetate ligands, $Zn(O_2CMe)_2(SC(NH_2)_2)_2$, $Ni(O_2CMe)_2(H_2O)_4$ and $Ni(O_2CMe)_2(H_2O)_2(py)_2$, have been assigned Δ values less than 200 cm^{-1} (Table 1). In each case, the acetate oxygen not coordinated to the metal is hydrogen bonded to other ligands (thiourea or water), giving what may be regarded as a "pseudo-bridging" arrangement. In addition, the $\nu(CO_2)$ frequencies of the zinc complex [36] are sufficiently close to those of alkali metal acetates to raise the possibility of anion exchange. At this stage, there appears to be no unequivocal example of a unidentate acetato complex with $\Delta < 200$ cm^{-1}.

(iii) Compounds with very low Δ values

Inspection of the examples in Tables 2 and 4 suggests a relationship between Δ values < 105 cm^{-1} [cf. 164 cm^{-1} for $Na(O_2CMe)$] and chelating acetate groups. Thus, six complexes [possibly seven — see conflicting data for $Zn(O_2CMe)_2(H_2O)_2$ (Table 2)] which have only chelating acetate groups (Table 2), four complexes with chelating as well as other carboxylate groups (Table 4), and two in which the carboxylate groups are both chelating and bridging (structure IVd; Table 4) have Δ < 105 cm^{-1}. The connection between low separations and chelation appears weakened by observation of low Δ values for three or four * complexes which only have bridging bidentate acetate ligands (Table 3). However, all of these except $Sb_2(O_2CMe)Cl_6O(OH)$ may be regarded as special cases, since the acetate groups bridge two metals linked by very short metal—metal bonds [39,85,105]. Where acetate spans longer metal—metal bonds, as in $[Cr(O_2CMe)_2(H_2O)]_2$ [82] or $[Ph_2Sn(O_2CMe)]_2$ [114], the separation is significantly larger (Table 3). The complex $Sb_2(O_2CMe)Cl_6O(OH)$ is exceptional, having a low Δ value and a bridging acetate group, but no Sb—Sb bond. Thus, a very small Δ value for an acetato complex is generally indicative of chelating acetate groups or of acetate groups which are both chelating and bridging unless a short metal—metal bond is present. ** However the absence of a very small separation does not rule out chelation (Tables 2 and 4).

The applicability of this criterion to trifluoroacetato complexes cannot be tested, as only one complex with chelating trifluoroacetate groups has been characterized crystallographically, viz. $Ru(O_2CCF_3)CO(PPh_3)_2(C_4HPh_2)$ [176], and no infrared data were reported. It is of some interest that the two trifluoroacetato complexes with the smallest separations (Table 5), viz. $[Mo(O_2CCF_3)_2]_2$ and $[Mo(O_2CCF_3)_2py]_2$, have very short metal—metal bonds bridged by trifluoroacetate groups [144,145], thereby paralleling the behaviour of acetato complexes.

(iv) Compounds with Δ significantly less than ionic values

The earlier correlation that Δ values significantly less than ionic are indicative of chelating and/or bridging carboxylate groups [26,27] is clearly validated by the data of Tables 1—5. Virtually all acetato complexes with Δ < 150 cm^{-1} (ionic, 164—171 cm^{-1}) and trifluoroacetato complexes with Δ < 200 cm^{-1} (ionic, 223—240 cm^{-1}) have these types of carboxylate ligands. The

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* Three bands of $CrMo(O_2CMe)_4$ have been assigned to $\nu_{sym}(CO_2) + \delta(Me)$ [85]. If the lowest energy absorption is assigned to $\delta(Me)$, as seems reasonable by comparing the reported spectrum [85] with that of sodium acetate [20], and the others to $\nu_{sym}(CO_2)$, then the separation based on average $\nu(CO_2)$ frequencies is less than 100 cm^{-1}.

** This correlation could be viewed as a more accurate definition of an earlier proposal that Δ chelating < Δ bridging [21,32].

only acetato complexes with $\Delta < 150$ cm^{-1} that are not in this category are two "pseudo-bridging" complexes (section F(ii)) where one oxygen of the acetate is coordinated to the metal and the other is hydrogen bonded to another ligand.

(v) Other complexes

The remaining group of complexes to be considered are those with Δ values from just below ionic to just above. From the previous discussion (sections F(i)—(iv), this group includes acetato complexes with separations of 150—200 cm^{-1}, and there are a considerable number in this category. Complexes with Δ values of 155—175 cm^{-1} must include several where the observed bands arise from anion exchange and where reinvestigation of the spectra is needed. Setting this problem aside, virtually all complexes with Δ in the range 150—200 cm^{-1} have chelating and/or bridging acetate groups. However, this cannot form the basis of a straightforward correlation, since there are a number of examples where ionic acetate could not be ruled out on the basis of spectra alone, e.g. $Hg(O_2CMe)_2PBu_3$ (Table 2) and $Pd(O_2CMe)Cl(PMe_2Ph)$ (Table 3).

(vi) Conclusions for acetato and trifluoroacetato complexes

Three useful correlations between $\nu(CO_2)$ frequencies and carboxylate coordination can be justified for acetato and trifluoroacetato complexes (sections F(i)—(v)), viz. (a) separations between $\nu(CO_2)$ frequencies (Δ) substantially greater than ionic are indicative of unidentate carboxylate coordination; (b) separations significantly less than ionic values are indicative of chelating and/or bridging carboxylate groups; (c) (for acetates only at this stage) very low separations generally indicate chelation or a combination of chelation and bridging if short metal—metal bonds are not present.

The converse of (a) viz. that the absence of large separations rules out unidentate carboxylates appears true at present, apart from the hydrogen-bonded "pseudo-bridging" derivatives (section F(ii)). However, chelating and/or bridging carboxylates cannot be excluded by the absence of the appropriate Δ values given in (b) and (c). It is obviously difficult to draw structural conclusions when Δ is near ionic values.

In reaching the above conclusions, we have attempted to make allowance for uncertainties in the spectroscopic data, most of which arise from the possibility of anion exchange with plates and in discs. It should be stressed again that it is intrinsically unsatisfactory to examine carboxylato complexes in alkali metal halide discs, and that the possibility of exchange between mulls or solutions and plates should always be checked.

(vii) Extensions to other carboxylates

There appear to be no substantial reasons why the conclusions (a)–(c)

(section F(vi)) should not also apply to coordination of other simple carboxylate ions, RCO_2^- (R = alkyl or aryl), at least in general terms. However, the applications must necessarily be less precise than for acetato complexes, where the availability of spectroscopic data for so many compounds of known structure has enabled fairly clear definition of the various ranges of Δ values to be made. In other cases a more conservative approach (i.e. larger differences from ionic values before drawing structural conclusions) is needed. However, it would be unwise to extrapolate to more complex carboxylates, amino acids, other carboxylates with donor atoms adjacent to the carboxyl function, dicarboxylates etc., especially since the present correlations are essentially empirical (section G).

G. THE BASIS OF THE PRESENT CORRELATIONS

It is frequently assumed that the increase in $\nu_{asym}(CO_2)$ and Δ accompanying the change from ionic to unidentate carboxylate is due to a change from equivalent to inequivalent carbon—oxygen bonds [e.g. 2,26,28,102,177], i.e. bonding in the complex approaches the pseudo-ester arrangement V. Indeed, silicon tetraacetate has this structure (see Table 1 for bond distances) and a very large $\nu_{asym}(CO_2)$ frequency and Δ value. However, this interpretation is not generally satisfactory, since plotting the difference between the carbon—oxygen bond lengths against $\nu_{asym}(CO_2)$ or Δ for either all acetato complexes in Tables 1—3 or those with unidentate acetate ligands (Table 1) alone reveals no clear relationship between these parameters [155]. Accordingly structure I is generally a more satisfactory representation of unidentate carboxylate groups than V, and the correlation between high Δ and unidentate carboxylate coordination appears to be an empirical one. The correlations (b) and (c) (section F(vi)) also appear to be empirical, especially since the converse of each does not apply.

An oversimplified correlation, Δ chelating < Δ bridging [21,32] (section F(iii)) was based on the assumption that the O—C—O angle is smaller in chelating than in bridging acetates, and on calculations [21] showing that decreasing the O—C—O angle decreases Δ. Comparison of structural data in Tables 2 and 3 shows that on average O—C—O angles are smaller for chelating than bridging acetates, but that low Δ values are not necessarily associated with small angles. Thus, $Na[UO_2(O_2CMe)_3]$ has the smallest separation of the chelating acetato complexes (Table 2), but one of the largest O—C—O angles. Likewise, for complexes with bridging acetates (Table 3), $Sb_2(O_2CMe)Cl_6O(OH)$ has the smallest Δ yet an average bond angle.

It is evident that factors affecting the separations between the carbon—oxygen stretching frequencies are more complex than differences between carbon—oxygen bond lengths or the size of the O—C—O angles alone.

ACKNOWLEDGEMENT

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