Diagnosis of the Nature of Carboxylate Coordination from the Direction of Shifts of Carbon–Oxygen Stretching Frequencies

G. B. DEACON*, F. HUBER

Lehrstuhl II für Anorganische Chemie, Universität Dortmund, D-4600 Dortmund 50, F.R.G.

and R. J. PHILLIPS

St. Vincent's Hospital, Fitzroy, Vic. 3065, Australia

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Abstract

Recent proposed correlations between the direction of shifts of carbon–oxygen stretching frequencies of acetato and trifluoroacetato complexes and the type of carboxylate coordination [1] are generally invalid or, in the case of unidentate binding, a restatement of an established criterion.

Introduction

Relationships between carbon–oxygen stretching frequencies and the nature of carboxylate coordination have been the subject of numerous papers and reviews, *e.g.* [2] and references therein. From consideration of essentially all acetato and trifluoroacetato complexes for which infrared spectra and reliable crystallographic data were available, it was concluded that use of $\nu(CO_2)$ frequencies in structural diagnosis is limited to (i) recognition of complexes with unidentate carboxylate coordination [$\Delta_{unidentate} > \Delta_{ionic}$; Δ is the separation between $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$] and (ii) identification of some complexes with chelating or (and) bridging bidentate carboxylate groups [$\Delta_{bridging\ or\ (and)\ chelating}$ often $< \Delta_{ionic}$] [2]. No other general conclusions could be drawn from the data. However, it has recently been claimed that the direction of shifts of $\nu(CO_2)$ frequencies provides a structural diagnosis 'applicable to all main types of carboxylate binding' and 'capable of making finer distinctions between the main types' [1]. The widespread possible application of the new criteria (Table I) and the markedly different conclusions from those of Deacon and Phillips [2] have led us to examine the claims and their basis in depth. We now report that they are based on a selective, incomplete, and often incorrect appraisal of the literature data and are of little value except in the case of unidentate coordination where the proposal (Table I) is a restatement of the established criterion [2].

Discussion

The Data Base

'The superiority and validity' of the new criterion were claimed to be due to study of 'a very large

TABLE I. Proposed Criterion [1] for relating Movements of $\nu(CO_2)$ Frequencies from Ionic Values to the Type of Carboxylate Coordination.

Carboxylate Binding	Shift of $\nu_{as}(CO_2)^a$	Shift of $\nu_s(CO_2)^a$
Unidentate	higher	lower
Unsymmetrical bridging bidentate	higher	virtually none
Symmetrical bridging bidentate	higher	higher
Unsymmetrical chelating	virtually none	higher
Symmetrical chelating	lower	higher

[a] From ionic values. Commonly accepted *e.g.* [1, 2] values for the acetate and trifluoroacetate ions are NaO_2CMe [3]: $\nu_{as}(CO_2)$ 1578, $\nu_s(CO_2)$ 1414, Δ 164 cm^{-1}. NaO_2CCF_3 [4]: $\nu_{as}(CO_2)$ 1680, $\nu_s(CO_2)$ 1457, Δ 223 cm^{-1}. KO_2CCF_3 [5]: $\nu_{as}(CO_2)$ 1678, $\nu_s(CO_2)$ 1437, Δ 241 cm^{-1}.

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*Present address: Chemistry Department, Monash University, Clayton, Vic. 3168, Australia.

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TABLE II. Reported $\nu(CO_2)$ Frequencies and Associated References for some Acetato Complexes Compared with Values and References Listed by Manhas and Trikha [1] for the same Compounds.

Compound	Actual Literature Data				Values and References of Manhas and Trikha [1]			
	$\nu_{as}(CO_2)$ (cm^{-1})	$\nu_s(CO_2)$ (cm^{-1})	Δ[a] (cm^{-1})	Ref.	$\nu_{as}(CO_2)$ (cm^{-1})	$\nu_s(CO_2)$ (cm^{-1})	Δ (cm^{-1})	Ref.
$[Co(O_2CMe)(NH_3)_5]^{2+}$[b]	1600	[c]	[c]	[6]				
$[Co(O_2CMe)(NH_3)_5](ClO_4)_2$	[c]	[c]	223	[7]	1603	1380	223	[6]
$Hg(O_2CMc)_2$	1600, 1566	1368	215	[10]	1600	1368	232	[10]
	[c]	[c]	270	[11]				
$(PhCH_2)_3Sn(O_2CMe)$	1618	1319	299	[13]	1618	1319	299	[13]
	1565	[c]	[c]	[14]				
$[Cu(O_2CMe)_2H_2O]_2$	1600	1425	175	[17]	1600	1425	175	[17]
	1610	1410	200	[18]				
$Sb_2(O_2CMe)Cl_6O(OH)$	1480	1435	45	[19]	1580	1435	145	[19]
$[Mo(O_2CMe)_2]_2$	1512, 1494	1409	94	[21]	1585	1440	145	[20]
	1515, 1495	1440, 1412	79	[17]				
	1585	1415	170	[18]				
$Sn(O_2CMe)_4$	1568[d]	1415[d]	153	[31]	1575	1440	135	[32,33]
	1635, 1575	1400, 1315	175, 320	[32]				
	1704, 1560	1440, 1262	120, 440	[33]				
$Cu(O_2CMe)(PPh_3)_2$	1552	1421	131	[34]	1565	1421	141	[34,35]
	1565	1405	160	[35]				

[a] Using averaged $\nu(CO_2)$ values where necessary. [b] Anion unspecified. [c] Not given. [d] From discussion section of [31]. In experimental Section 1568 cm^{-1} is wrongly assigned to the symmetric mode and 1415 is omitted.

number of compounds' [1]. In fact, thirtyseven acetato and five trifluoroacetato complexes were considered [1], compared with seventy acetato complexes and fourteen trifluoroacetato complexes in an earlier comprehensive review [2]. The examples cited by Manhas and Trikha [1] are essentially a selection from the Tables in [2], and no relevant and correct new data are presented.

Unidentate Carboxylate Coordination

The criterion [1] for unidentate carboxylate coordination (Table I) is simply an alternative statement of the established criterion, $\Delta_{unidentate} > \Delta_{ionic}$, because the $\nu(CO_2)$ shifts are the source of the change in Δ. However, the supporting data provided by Manhas and Trikha [1] contain some major errors. For convenience, some of their listed infrared data and associated references are compared in Table II with the correct reported data.

(a) The $\nu_{as}(CO_2)$, $\nu_s(CO_2)$, and Δ values listed for $[Co(O_2CMe)(NH_3)_5](ClO_4)_2$ by Manhas and Trikha [1] (Table II) are not in the cited reference [6], which gives only $\nu_{as}(CO_2)$ for the $[Co(O_2CMe)(NH_3)_5]^{2+}$ ion. The anion was not specified. The cited [1] Δ value is actually from reference [7], but this does not contain the associated $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$ given in [1] (Table II). In addition, the related crystal structure was determined for $[Co(O_2CMe)(NH_3)_5]Cl(ClO_4)$ [8] and not for the diperchlorate as stated in [1].

(b) The complex $Ni(teta)(O_2CMe)_2$ (teta = C-Meso-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) was included amongst examples with crystallographically established unidentate acetate ligands [1], but the cited [1] crystallography reference [9] does not contain the crystal structure, nor has the structure been subsequently determined.

(c) The $\nu(CO_2)$ frequencies listed [1] for mercuric acetate omit a second $\nu_{as}(CO_2)$ from the cited reference [10] (Table II), as well as data from another source [11].

(d) The compound $(PhCH_2)_3Sn(O_2CMe)$, described [1] as having unidentate acetates, has in fact asymmetrically-bridging acetate coordination [12]. Moreover, a $\nu_{as}(CO_2)$ value which does not agree with the proposed criterion (Table I) was omitted from the infrared compilation [1] (see Table II).

Asymmetrical Bridging Bidentate Coordination

The criterion (Table I) cannot be sustained since the authors themselves [1] list several exceptions and only one supporting compound, $CaCu(O_2CMe)_4(H_2O)_6$. In this the acetate ligands are, in fact, asymmetrically chelating as well as bridging [15]. Moreover, $[Cu(O_2CMe)_2H_2O]_2$, which has symmetrically bridging acetates [16], may be consid-

TABLE III. $\nu(CO_2)$ Frequencies and Acetate Coordination in some Acetato Complexes.

Compound	$\nu_{as}(CO_2)$ (cm^{-1})	$\nu_s(CO_2)$ (cm^{-1})	Δ (cm^{-1})	Ref.	Bonding	Ref.
$Me_2In(O_2CMe)$	1530	1445	85	37	Chelating and bridging[a]	38
$Et_2In(O_2CMe)$	1525	1465	60	39	Chelating and bridging[a]	39
$Tl(O_2CMe)_3$	1550 1500	1422	103	2	Chelating Chelating and bridging[b]	40
$UO_2(O_2CMe)_2(H_2O)_2$	1500	1500	<50	41	Chelating[c] Bridging[d]	42
$UO_2(O_2CMe)_2(Ph_3PO)$	1533 1524	1456 1425	88	43	Chelating[c] Bridging[e]	44

[a] Each acetate ligand is both chelating and bridging. [b] One chelating acetate group, two chelating and bridging acetate groups. [c] Two different acetate groups. [d] Anti-anti. [e] Syn.-syn.

ered to belong to the higher $\nu_{as}(CO_2)$, essentially unchanged $\nu_s(CO_2)$ category if both sets of reported infrared data are considered (Table II) [*cf.* listing of Manhas and Trikha [1] (Table II)].

Symmetrically Bridging Carboxylate Groups

Of thirteen examples considered by Manhas and Trikha, eight were claimed to support the criterion (Table I) and five were exceptions [1]. However, there are in fact eight exceptions and only five supporting if the literature data are correctly appraised.

(a) For $Sb_2(O_2CMe)Cl_6O(OH)$, $\nu_{as}(CO_2)$ is at 1480 cm^{-1} [19] not 1580 cm^{-1} as listed [1] making the compound a clear exception to the proposed criterion.

(b) The $\nu(CO_2)$ frequencies given for $[Mo(O_2CMe)_2]_2$ [1] (see Table II) are not in the cited reference [20], which deals with magnetism of copper carboxylates and does not mention infrared spectroscopy. Three sets of $\nu(CO_2)$ frequencies have been reported for this compound [17, 18, 21] and none support the proposed criterion (Table II). Only two of the nine reported $\nu(CO_2)$ bands, each from a separate reference, could be combined in support of the new criterion and these correspond to the values given by Manhas and Trikha [1] (see Table II).

(c) Only one of two sets of $\nu(CO_2)$ frequencies reported [17, 18] for $[Cu(O_2CMe)_2(H_2O)]_2$ was cited [1]. The alternative values [18] and the averaged $\nu(CO_2)$ frequencies are inconsistent with the criterion (Table II).

Some caution must also be exercised with regard to the five compounds apparently conforming to the criterion. Two of the compounds, $[Rh(O_2CMe)_2py]_2$ [22] and $[V(O_2CCF_3)_2C_5H_5]_2$ [23], have only been examined as KBr discs. This can lead to anion exchange or to changes in coordination owing to pressure and/or bromide complexation [2]. For $Zn_4(O_2CMe)_6O$, which conforms to the criterion [1], the $\nu(CO_2)$ values (KBr disc), 1639, 1489 cm^{-1} [24] differ markedly from those, 1600, 1441 cm^{-1} for mulls [25]. There are also reproducibility problems with KBr discs. Thus, for sodium acetate in this medium, $\nu_s(CO_2)$ varies over 1405 cm^{-1} [26], 1440, 1410 cm^{-1} [27], and 1425 cm^{-1} [28]. The shifts (10–27 cm^{-1}) of $\nu(CO_2)$ from ionic values for $Zn_4(O_2CMe)_6O$ [25] (above), $Li(O_2CMe)(H_2O)_2$ [$\nu(CO_2)$, 1597, 1435 cm^{-1}] [29], $Pd_3(O_2CMe)_6(H_2O)_{0.5}$ [$\nu(CO_2)$, 1600, 1427 cm^{-1}] [30], and $[Rh(O_2CMe)_2py]_2$ [$\nu(CO_2)$, 1590, 1430 cm^{-1}] [22] are quite small and hence of marginal significance, considering the broadness of $\nu(CO_2)$ absorptions.

Asymmetrically Chelating Carboxylates

The criterion for asymmetrical chelation [1] (Table I) can be totally rejected. Of the three cited supporting examples [1], inclusion of $Sn(O_2CMe)_4$ and $Cu(O_2CMe)(PPh_3)_2$ cannot be sustained since the listed conforming infrared frequencies [1] are a misrepresentation of the reported data (Table II). Moreover, to list a 13 cm^{-1} shift of $\nu_{as}(CO_2)$ from ionic as 'almost the same' and a 7 cm^{-1} shift of $\nu_s(CO_2)$ from ionic as 'displaced higher' as done [1] for $Cu(O_2CMe)(PPh_3)_2$ is indefensible. In the remaining compound cited [1], *viz.* $Zn(O_2CMe)_2[SC(NH_2)_2]_2$, the longer Zn–O bonds [2.891(9), 2.996(5)] Å are viewed as secondary coordination [36], and these distances are certainly longer than those overlooked by Manhas and Trikha [1] in classifying the acetate coordination in $(PhCH_2)_3Sn(O_2CMe)$ and $CaCu(O_2CMe)_4(H_2O)_6$ as unidentate and asymmetrically bridging respectively. We have preferred to view the acetate coordination as unidentate and to attribute the unusual (for unidentate) $\nu(CO_2)$ frequencies to the hydrogen bonding [36] between thiourea and the acetate oxygens [2].

Symmetrically Chelating Carboxylates

The number of exceptions to the proposed new criterion (Table I) is considerable. Besides those given by Manhas and Trikha [1], we mention a further five compounds (Table III) with low Δ values and either two types of acetate group or acetates that are both chelating and bridging. In addition, the compound $Re_2Me_2(O_2CMe)_4$, listed as $Re_2Me_2O_2CMe$ in [1] as an example with symmetrically chelating acetates, has in fact both symmetrically bridging and asymmetrically chelating acetate ligands [45], and the low $\nu_{as}(CO_2)$ value (1555 cm^{-1}) has been specifically assigned to the asymmetrically chelating group [46].

Conclusions

Thus, the new proposed correlations (Table I) are generally invalid except in the case of unidentate coordination, where an established criterion, *e.g.* [2], is restated. More detailed examination may establish that some complexes with symmetrically bridged carboxylates have both $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$ at higher frequencies than the corresponding ionic values. However, this behaviour is not observed for the majority of complexes with symmetrical acetate bridging. The value of the higher $\nu_{as}(CO_2)$, $\nu_s(CO_2)$ correlation would at best be similar to that [2] which states that very small Δ values usually indicate the presence of chelating carboxylate groups, if short metal–metal bonds are not present.

Application of infrared spectroscopy to the diagnosis of carboxylate coordination is limited. No amount of wishful thinking based on the convenience of the technique can change this.

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