

Relationships Between the Direction of Shifts in the Carbon-oxygen Stretching Frequencies of Carboxylate Complexes and the Type of Carboxylate Coordination

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On the basis of the directions of the shifts in the ir frequencies of $\nu_{\text{asym}} \text{OCO}$ and $\nu_{\text{sym}} \text{OCO}$ from those for ionic carboxylate, the various modes of carboxylate binding—unidentate, chelating bidentate (unsymmetrical and symmetrical) and bridging bidentate (unsymmetrical and symmetrical)—are distinguished. This criterion is superior to the previously better-known ir spectral criterion because of its uniform applicability and its capability of making even finer distinctions between symmetrical and unsymmetrical types within the chelating and bridging bidentate modes. This finding is based on the analysis of ir spectral data of a very large number of acetato— and trifluoroacetato compounds with known crystal structures.

ACETATE ion can coordinate a metal ion in a variety of ways; as a simple unidentate ligand, as a chelating bidentate group (unsymmetrical or symmetrical) and as a bridging bidentate group (unsymmetrical or symmetrical). Acetate ion is of such a low symmetry (C_{2v}) that all the fifteen vibrational modes are ir active even in the free ion and further lowering of symmetry upon coordination is not expected to increase the number of ir bands due to acetate group. However, of the fifteen fundamental vibrational modes for the acetate the modes due to COO^- part namely antisymmetric OCO stretch ($\nu_{\text{asym}} \text{OCO}$), symmetric OCO stretch ($\nu_{\text{sym}} \text{OCO}$) and OCO bend are expected to be more sensitive to coordination and the frequencies due to them could be shifted on complexation. The shifts in the first two have indeed been observed and the magnitude of separation (Δ) between the frequencies due to $\nu_{\text{asym}} \text{OCO}$ and $\nu_{\text{sym}} \text{OCO}$ in different compounds has been found to be affected by several factors¹⁻³. Curtis⁴, Grigor'ev⁵, Deacon⁶, Deacon and Phillips⁷ and Alcock *et al.*⁸ made more systematic studies of the relationship between the magnitude of Δ and the mode of coordination of the acetate group and thus developed the Δ criterion for distinguishing the main types of acetate binding—unidentate, chelating bidentate and bridging bidentate. Their conclusions, though not in complete agreement with each other, may be broadly summarized as: the compounds which have unidentate acetate groups have Δ values of the very high order while those with chelating and/or bridging bidentate type have Δ values significantly less than the value in ionic acetate.

As has been recently demonstrated^{6,10}, the Δ criterion, though helpful in identifying some modes of acetate coordination, is incapable of distinguishing all the main types of acetate binding. Moreover, the Δ value may frequently be similar for two different types or different for two similar types of

coordination (see Table 1). In view of the absence of a clear-cut differentiation on this basis it is not a good criterion. Its earlier success and apparent validity⁴⁻⁸ were based mainly on the fact that it was developed from the analysis of, and subsequently tested on, a very few cases of known molecular structure¹⁰. It has no theoretical sanction either to enforce its use in the face of its gross limitation; although originally it appeared to have a basis in the fundamentals of bonding¹⁻³ ultimately it proved to be largely empirical¹⁰.

We have examined the ir spectral data of 46 acetato- and trifluoroacetato complexes whose crystal structures had been determined by various earlier workers. From the analysis of the values of $\nu_{\text{asym}} \text{OCO}$ and $\nu_{\text{sym}} \text{OCO}$ in these compounds it has been observed that in compounds with unidentate carboxylate groups the directions of the shifts in the frequencies due to $\nu_{\text{asym}} \text{OCO}$ and $\nu_{\text{sym}} \text{OCO}$ are higher and lower respectively relative to those for ionic carboxylate. Unidentate coordination removes the equivalence of two oxygen atoms and two C—O bond orders are appreciably affected giving a pseudo ester type configuration. In the case of chelating and bridging bidentate carboxylates there is little change in the C—O bond orders and the movement of frequencies is less in comparison to those for the unidentate coordination; here the directions of the shifts in the positions of $\nu_{\text{asym}} \text{OCO}$ and $\nu_{\text{sym}} \text{OCO}$ relative to those in ionic carboxylates are as unsymmetrical bridging bidentate: higher, almost the same; symmetrical bridging bidentate: higher, higher; unsymmetrical chelating bidentate: almost the same, higher; and symmetrical chelating bidentate: lower, higher.

This set of relationships between the modes of carboxylate binding and the directions of the shifts in the frequencies of $\nu_{\text{asym}} \text{OCO}$ and $\nu_{\text{sym}} \text{OCO}$ may be used as an ir spectral criterion for the mode of carboxylate binding. This criterion, based on the

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TABLE I—INFRARED AND STRUCTURAL DATA FOR ACETATO AND TRIFLUOROACETATO COMPOUNDS

Sl. No.	Compound	ν_{asymOCO}	ν_{symOCO}	$\Delta(\text{IR})$ Ref.	Directions of the shift in comparison to those in ionic carboxylates		Mode of binding	Ref. (Cryst. Struct.)
					ν_{asymOCO}	ν_{symOCO}		
1.	$\text{Co}(\text{NH}_3)_4(\text{OOCCH}_3)_2(\text{ClO}_4)_2$	1603	1380	228(11)	Higher	Lower	Unidentate	(48)
2.	$\text{Ni}(\text{tetra})(\text{OOCCH}_3)_2^{\text{a}}$	1583	1405	178(4)	Higher	Lower	Unidentate	(4)
3.	$\text{Hg}(\text{OOCCH}_3)_2$	1600	1368	232(12)	Higher	Lower	Unidentate	(49)
4.	$\text{PhHg}(\text{OOCCH}_3)$	1615 ^d	1379 ^d	232(13)	Higher	Lower	Unidentate	(50)
5.	$[\text{Me}_2\text{CC}(\text{O})_2]\text{OHg}(\text{OOCCH}_3)$	1590	1363					(51)
		1618 ^d	1309	290(14)	Higher	Lower	Unidentate	
6.	$\text{Na}[\text{H}(\text{OOCCH}_3)_2]$	1710	1410	310(15)	Higher	Lower	Unidentate	(15)
7.	$\text{Ph}_2\text{Sb}(\text{OOCCH}_3)_2$	1633	1320	313(16)	Higher	Lower	Unidentate	(52)
8.	$(\text{Cyclo-C}_6\text{H}_4)_2\text{Sn}(\text{OOCCH}_3)_2$	1645	— ^e	— ^e (17)	Higher	—	Unidentate	(17)
9.	$\text{K}[\text{H}(\text{OOCCH}_3)_2]$	1792	1420	372(18)	Higher	Lower	Unidentate	(53)
10.	$\text{Cs}[\text{H}(\text{OOCCH}_3)_2]$	1790	1408	382(18)	Higher	Lower	Unidentate	(54)
11.	$\text{Hg}(\text{OOCCH}_3)_2$	1690	1416	274(12)	Higher	Lower	Unidentate	(55)
12.	$(\text{PhCH}_2)_2\text{Sn}(\text{OOCCH}_3)_2$	1618	1319	299(19)	Higher	Lower	Unidentate	(56)
13.	$[\text{Co}(\text{OOCCH}_3)_2](\text{Ph}_3\text{As})_2$	1692	1421	271(20)	Higher	Lower	Unidentate	(57)
14.	$\text{CaCu}(\text{OOCCH}_3)_4 \cdot 6\text{H}_2\text{O}$	1590	1410	180(4)	Higher	Almost the same	Unsym. Bridging Bidentate	(58)
15.	$[\text{Cu}(\text{OOCCH}_3)_2(\text{H}_2\text{O})_2]$	1600	1425	175(21)	Higher	Higher	Sym. Bridging Bidentate	(59)
16.	$\text{Li}(\text{OOCCH}_3)(\text{H}_2\text{O})_2$	1597	1435	162(22)	Higher	Higher	Sym. Bridging Bidentate	(60)
17.	$[\text{Mo}(\text{OOCCH}_3)_2]_2$	1585	1440	145(23)	Higher	Higher	Sym. Bridging Bidentate	(61)
18.	$[\text{Pd}(\text{OOCCH}_3)_2]_2 \cdot 0.5\text{H}_2\text{O}$	1600	1427	173(24)	Higher	Higher	Sym. Bridging Bidentate	(62)
19.	$[\text{Rh}(\text{OOCCH}_3)_2\text{Py}]_2^{\text{b}}$	1590	1430	160(25)	Higher	Higher	Sym. Bridging Bidentate	(25)
20.	$\text{Sb}_2(\text{OOCCH}_3)_2\text{Cl}_2\text{O}(\text{OH})$	1580	1435	145(26)	Higher	Higher	Sym. Bridging Bidentate	(26)
21.	$\text{Zn}_4(\text{OOCCH}_3)_2\text{O}$	1639	1489	150(3)	Higher	Higher	Sym. Bridging Bidentate	(63)
22.	$[\text{V}(\text{OOCCH}_3)_2\text{C}_6\text{H}_5]_2$	1720	1475	245(27)	Higher	Higher	Sym. Bridging Bidentate	(27)
23.	$\text{Zn}(\text{OOCCH}_3)_2 \cdot \text{tu}_2^{\text{c}}$	1577	1425	152(4)	Almost the same	Higher	Unsym. Chelating Bidentate	(64)
24.	$\text{Cu}(\text{OOCCH}_3)(\text{Ph}_2\text{P})_2$	1565	1421	141(28,29)	Almost the same	Higher	Unsym. Chelating Bidentate	(65)
25.	$\text{Sn}(\text{OOCCH}_3)_4$	1575	1440	135(8,30)	Almost the same	Higher	Unsym. Chelating Bidentate	(66)
26.	$\text{Na}_2\text{UO}_2(\text{OOCCH}_3)_2$	1537	1472	65 (31)	Lower	Higher	Sym. Chelating Bidentate	(67)
27.	$\text{Mn}(\text{OOCCH}_3)(\text{CO})_2(\text{Ph}_2\text{P})_2$	1520	1437	83 (32)	Lower	Higher	Sym. Chelating Bidentate	(32)
28.	$\text{Zn}(\text{OOCCH}_3)_2 \cdot 2\text{H}_2\text{O}$	1550	1456	94 (5)	Lower	Higher	Sym. Chelating Bidentate	(68)
29.	$\text{Re}_2(\text{CH}_3)_2(\text{OOCCH}_3)_2$	1555	1450	105(33)	Lower	Higher	Sym. Chelating Bidentate	(33)
Only one compound, $\text{Ru}[\text{OOCCH}_2(\text{CO})\text{Ph}_2\text{P}]_2[\text{C}_6\text{H}_5\text{Ph}_2]$, has been crystallographically shown to contain chelating trifluoroacetato group but no ir data have been reported ³⁴ .								
30.	$\text{Na}(\text{OOCCH}_3)_2^{\text{f}}$	1578	1414	164(35)	—	—	Ionic	
31.	$\text{Na}(\text{OOCCH}_3)_2^{\text{f}}$	1680	1457	223(36)	—	—	Ionic	
32.	$\text{K}(\text{OOCCH}_3)_2^{\text{f}}$	1678	1437	241(20)	—	—	Ionic	

a—Teta=C—Meso—5,7,7,12,14,14 hexamethyl-1,4,8,11-tetraazacyclotetradecane

b—Py=Pyridine.

c—tu=Thiourea.

d—Using average values of $\nu(\text{COO})$ where necessary.

e—Not given.

f—Assumed ionic for infrared comparison.

directions of the shifts in ν_{asymOCO} and ν_{symOCO} frequencies, is superior to the previously better-known ir criterion (Δ criterion) because in addition

to its being applicable to all main types of carboxylate binding, it is also capable of making finer distinctions within the main types. The superiority

TABLE 2—INFRARED AND STRUCTURAL DATA FOR THE COMPOUNDS WHICH DO NOT FIT IN THE PRESENT
 CRITERION WITH POSSIBLE EXPLANATIONS

Sl. No.	Compound	ν_{asymOCO}	ν_{symOCO}	$\Delta(\text{IR})$	Ref.	Directions of the shift in comparison to those in ionic acetate ν_{asymOCO} ν_{symOCO}	Mode of binding	Ref. (Cryst. Struct.)	Explanations
1.	$[\text{Co}_2(\text{OOCCH}_2)(\text{OH})\text{L}](\text{H}_2\text{O})(\text{EtOH})^a$	1565	1410	155	(37)	Lower	Unsym. Bridging bidentate	(69)	Hydrogen bonding, two types of Co atoms are present
2.	$\text{Ni}(\text{OOCCH}_2)_2(\text{H}_2\text{O})_2(\text{Py})_2^b$	1550	1412	138	(38)	Lower	Unidentate	(70)	Hydrogen bonding
3.	$\text{Me}_2\text{Pb}(\text{OOCCH}_2)_2$	1550	1410	140	(39)	Lower	Unsym. Bridging bidentate	(71)	—
4.	$\text{Me}_2\text{Sn}(\text{OOCCH}_2)_2$	1558	1418	140	(40)	Lower	Unsym. Bridging bidentate	(72)	—
5.	$[\text{Pb}_2\text{Sn}(\text{OOCCH}_2)_2]_2$	1530	1405	125	(41)	Lower	Sym. Bridging bidentate	(73)	Short M - M bond
6.	$[\text{Cu}(\text{OOCCH}_2)\text{NH}(\text{OH})_2(\text{NH}_2)_2]\text{ClO}_4$	1550	1400	150	(4)	Lower	Syn.-Anti geometry	(74)	Acetate acts as a chelate as well as a bridge
7.	$[\text{Pd}(\text{OOCCH}_2)(\text{Cl})(\text{Me}_2\text{PhP})]_2$	1575	1418	157	(42)	Almost the same	Unsym. Bridging bidentate	(75)	Short M - M bond.
8.	$[\text{Cr}(\text{OOCCH}_2)_2(\text{H}_2\text{O})]_2$	1575	1420	155	(3)	Almost the same	Sym. Bridging bidentate	(76)	Hydrogen bonding
9.	$\text{Os}_2(\text{OOCCH}_2)_4(\text{CO})_2$	1575	1465	110	(43)	Almost the same	Cisoid bridging	(77)	CO groups distort the geometry
10.	$[\text{Pd}(\text{OOCCH}_2)_2\text{C}_2\text{H}_5]_2$	1575	1425	150	(44)	Almost the same	Unsym. Bridging bidentate	(78)	Short M - M bond
11.	$\text{CrMo}(\text{OOCCH}_2)_4$	1552	1459	93	(45)	Lower	Cisoid bridging	(45)	Short M - M bond
12.	$[\text{Pd}_4(\text{CO})_4(\text{OOCCH}_2)_4](\text{AcOH})$	1555	1420	135	(46)	Lower	Sym. Bridging bidentate	(46)	Hydrogen bonding
13.	$\text{Ni}(\text{OOCCH}_2)_4\text{H}_2\text{O}$	1550	1425	125	(47)	Lower	Unidentate	(79)	Hydrogen bonding

^a - H₂L = 4-Hydroxy-3,5-bis[N-(2'-hydroxyphenyl)formimidoyl]toluene, b - Py = Pyridine

and validity of this criterion are further established by its having been derived from the study of, and hence applicability to, a very large number of compounds which do not belong to just one particular series or group.

The compounds listed in Table 2, however, do not observe the preceding relationships. For this there may be several reasons; pressure induced changes in KBr discs while taking the ir spectra, anion exchange while taking the high resolution spectra due to larger scanning time, hydrogen bonding effects, existence of polynuclear structures and short metal-metal bonds in the compounds are some of them. In seven of these compounds (1-7 in Table 2) the observed directions of the shifts in the frequencies of ν_{OCO} are of different types than observed in the relationships forming the basis of the present criterion; so even though the present criterion does not help in predicting or supporting their actual structure the shifts do not contradict the criterion. The remaining six compounds (8-13 in Table 2) have acetate binding different than would be suggested by the present criterion; their case is, therefore, problematic. However, closer examination indicates that five of them fall under one or the other category of possible explanations indicated above and are either dinuclear or polynuclear and the sixth one (13 in Table 2) need not be examined by any technique since the unidentate nature of the acetate binding is obvious from its composition.

This minor limitation, though cautions us, does not contra-indicate the proposed criterion. X-Ray diffraction crystallography, generally the most definitive source of information about the structural parameters for, and hence the nature of linkages in, chemical species, would of course be the most desirable technique to employ. Although it is becoming a routine analytical technique, it is still time and resource consuming. It is, therefore, best even in well-endowed laboratories to exhaust other, more conventional and easily accessible, approaches. The only conventional approach of wider applicability for the mode of carboxylate binding is ir spectroscopy and as is evident from the preceding discussion out of the ir criteria proposed so far, the present one has clearly an edge over the others.

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