174. *Co-ordination Compounds having Carboxylic Esters as Ligands. Part I. Stoicheiometry, Structure, and Stereochemistry.**

By M. F. LAPPERT.

1 : 1 Addition compounds of ethyl acetate with some Group III and Group IV (2 : 1 for SnX_4) halides, iron(III) chloride (2 : 1), and a number of organoboron halides have been prepared. The infrared carbonyl stretching vibrations are lowered in frequency but increased in intensity, and the C_{Acyl}–O and CH stretching frequencies are increased, relatively to those in ethyl acetate. These data require structure (I) for the complexes, *i.e.*, acyl-oxygen is the donor atom. The relative donor strengths of carboxylic esters are discussed, as is the stereochemistry of the complexes. Nuclear magnetic resonance spectra of aluminium bromide–ethyl acetate and of acetone–boron trifluoride are described.

THE existence of complexes between carboxylic esters and inorganic electron-deficient halides has been known since Demarçay's preparation in 1873 of the 1 : 1 adduct of titanium(IV) chloride and ethyl acetate.[1] Complexes of the following Group III and IV halides have been reported: boron trifluoride [2-5] and trichloride,[6] tin(IV) chloride [7-12] and bromide,[7,12] titanium(IV) chloride,[1,8,13,14] and zirconium(IV) chloride,[15-17] bromide,[18] and iodide.[19] These were all 1 : 1 complexes except the tin and zirconium compounds which preferentially formed with 2 mols. of ester. Iron(III) chloride formed a 1 : 1 adduct with ethyl cinnamate.[7]

Physicochemical investigations have been concerned with measurements of electrical conductance,[2,12,13] viscosity,[3b,12,13] dipole moment, [8,16-19] surface tension and parachor,[4]

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* For preliminary results see Internat. Conference on Co-ordination Chemistry, London, 1959, *Chem. Soc. Spec. Publ.*, No. 13, p. 179.

[1] Demarçay, *Bull. Soc. chim. France*, 1873, **20**, 127.

[2] Greenwood and R. L. Martin, *J.*, 1953, 751.

[3] Greenwood and R. L. Martin, (*a*) *J.*, 1953, 1427; (*b*) *J.*, 1951, 1795; (*c*) *Proc. Roy. Soc.*, 1952, *A*, **215**, 46.

[4] Sugden and Waloff, *J.*, 1932, 1492.

[5] Greenwood and R. L. Martin, *Quart. Rev.*, 1954, **8**, 1; Morgan and Taylor, *J. Soc. Chem. Ind.*, 1931, **50**, 869; *J.*, 1932, 1497; Bowlus and Nieuwland, *J. Amer. Chem. Soc.*, 1931, **53**, 3835.

[6] Frazer and Gerrard, *J.*, 1955, 2959; Gerrard and Wheelans, *J.*, 1956, 4296.

[7] Rosenheim and Levy, *Ber.*, 1904, **37**, 3662; Pfeiffer, *Annalen*, 1910, **376**, 285; Pfeiffer and Halperin, *Z. anorg. Chem.*, 1914, **87**, 335.

[8] Osipov, *Zhur. obshchei Khim.*, 1956, **26**, 322.

[9] Khimov, Usanovich, and Sumarokova, *Izvest. Akad. Nauk Kazakh. S.S.R.*, *Ser. Khim.*, 1957, **2**, 3.

[10] Vol'nov, *Zhur. fiz. Khim.*, 1957, **31**, 2312.

[11] Ulich, Hertel, and Nespital, *Z. phys. Chem.*, 1932, **17**, *B*, 21.

[12] Kurnakov and Shternin, *Bull. Acad. Sci. U.R.S.S.*, *Classe sci. math. nat.*, *Ser. Khim.*, 1936, 467.

[13] Osipov and Suchkov, *Zhur. obshchei Khim.*, 1952, **22**, 1132; Osipov, Lysenko, and Akopov, *ibid.*, 1955, **25**, 249.

[14] Bradley, Hancock, and Wardlaw, *J.*, 1952, 2773; Scagliarini and Tartarini, *Atti Accad. naz. Lincei, Rend. Classe Sci. fiz. mat. nat.*, 1926, **4**, 318; Hertel and Demmer, *Annalen*, 1932, **499**, 134.

[15] Bradley, Abd-El Halim, and Wardlaw, *J.*, 1950, 3450; Rosenheim and Hertzmann, *Ber.*, 1907, **40**, 810.

[16] Osipov and Kletenik, *Zhur. obshchei Khim.*, 1957, **27**, 2921.

[17] Osipov and Kletenik, *Zhur. obshchei Khim.*, 1959, **29**, 1375.

[18] Kletenik and Osipov, *Zhur. obshchei Khim.*, 1959, **29**, 1423.

[19] Osipov and Kletenik, *Zhur. obshchei Khim.*, 1959, **29**, 2119.

density,[3c,10,13] dielectric permeability,[17] specific heat,[12] heat of mixing,[11,17] and transport of ions during electrolysis.[3a,9] Little work has been done on the chemical behaviour of the ester complexes, except with those of boron trichloride,[6] which were shown to decompose either by acyl–oxygen (if R in $R'{\cdot}CO_2R$ was a primary alkyl or an aryl group) or alkyl–oxygen fission.

The original suggestion about the structure of the complexes was that acyl-oxygen was the donor atom in tin(IV) chloride derivatives, because these, like ketone and aldehyde but unlike ether adducts, were of 1 : 2 stoicheiometry.[7] Alkyl–oxygen donation was proposed for boron trifluoride–ethyl acetate, because its stability appeared to be comparable with that of ether–trifluoride complexes (but different from that of aldehyde and ketone adducts).[20] Ionic self-dissociation for the same molten compound was interpreted in terms of $Et^+[BF_3,Me{\cdot}CO_2]^-$,[21] but this was excluded by the results of electrolysis and structures $H^+[BF_3,Me{\cdot}CO_2C_2H_4]^-$ and $[CH_3{\cdot}CO]^+[BF_3{\cdot}OEt]^-$ were instead proposed.[3a]

Donor properties of the alkoxycarbonyl group in metal chelates have long been recognised, *e.g.*, in derivatives of ethyl acetoacetate and methyl salicylate, and in some cases, *e.g.*, $R_2B{\cdot}O{\cdot}CMe{:}CH{\cdot}CO_2Et$,[22] it has been shown that acyl-oxygen is the donor atom.

Hydrogen-bonding with carboxylic esters has also been studied. In the enol form of ethyl acetoacetate, it is acyl-oxygen which is the donor atom.[23] This was also believed to be the case in ethanolic ethyl acetate; the evidence was a small (9 $cm.^{-1}$) decrease in the carbonyl stretching frequency, as between the ester in ethanol and the free ester,[24] and a high value for the association constant (as in ethanolic acetic anhydride).[25] On the other hand, in certain steroid hydroxy-esters, alkyl-oxygen was the donor atom.[26] In discussion of mechanism for fission of certain carboxylic esters the formation of adducts with the alkyl-oxygen atom as donor has been postulated (*i.e.*, $R'{\cdot}CO_2R,H^+$ in acid-catalysed hydrolyses and transesterifications,[27] $Ar{\cdot}CO_2R,AlCl_3$ in the Fries rearrangement,[28] and $R'{\cdot}CO_2R,BH_3$ in the diborane–ester reaction [20]).

Our work had the following objects: (i) to determine the range of compounds which co-ordinate with carboxylic esters and to establish the stoicheiometry of the adducts; (ii) to obtain at least a qualitative indication of the donor strengths of carboxylic esters relative to other common ligands (particularly those in which an oxygen atom is the donor); (iii) to establish the structure and stereochemistry of the adducts; (iv) to measure spectroscopically the relative acceptor strengths of Lewis acids (with an ester as reference base) and the transmission of electronic effects through atoms other than carbon in electron-deficient compounds; and (v) to apply the results [particularly of (iii)] to the mechanism of reactions of carboxylic esters. The present paper deals with matters (i)—(iii); the others will be considered in later Parts.

Our experiments were with complexes of ethyl acetate and the following: boron trifluoride, trichloride, and tribromide, aluminium chloride and bromide, tin(IV) chloride and bromide, gallium(III), indium(III), titanium(IV), iron(III), and some organoboron chlorides. These were all 1 : 1 complexes, except for the tin and iron compounds which had 2 mol. of ligand. Most of them were prepared by interaction of equimolar proportions in pentane, the complex being precipitated [this method failed for the tin bromide and di-n-butylboron chloride complexes (see below) and was inapplicable to others (complexes

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[20] Brown, Schlesinger, and Burg, *J. Amer. Chem. Soc.*, 1939, **61**, 673.

[21] Booth and D. R. Martin, " Boron Trifluoride and its Derivatives," J. Wiley and Sons, New York, 1949, p. 200.

[22] Duncanson, Gerrard, Lappert, Pyszora, and Shafferman, *J.*, 1958, 3652; Gerrard, Lappert, and Shafferman, *Chem. and Ind.*, 1958, 722.

[23] Rasmussen and Brattain, *J. Amer. Chem. Soc.*, 1949, **71**, 1073.

[24] Searles, Tamres, and Barrow, *J. Amer. Chem. Soc.*, 1953, **75**, 71.

[25] Grunwald and Coburn, *J. Amer. Chem. Soc.*, 1958, **80**, 1322.

[26] Henbest and Lovell, *J.*, 1957, 1965.

[27] Ingold, " Structure and Mechanism in Organic Chemistry," G. Bell and Sons, London, 1953, pp. 770, 776.

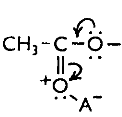
[28] Baltzly, Ide, and Phillips, *J. Amer. Chem. Soc.*, 1955, **77**, 2522.

of AlX_3, $GaCl_3$, $InCl_3$, and $FeCl_3$)]. The remaining compounds were prepared in absence of solvent and invariably (except $InCl_3$) mixing was exothermal. The indium chloride adduct was prepared by heating the chloride with an excess of ethyl acetate and evaporation of solvent from the supernatant liquor. The aluminium chloride complex was also prepared by metathesis between the diethyl ether complex and ethyl acetate. All the complexes were low-melting white solids, except for the titanium (yellow) and iron (rust-coloured) chloride adducts.

Silicon(IV) and germanium(IV) chloride did not react with ethyl acetate: there was no heat of mixing and spectroscopic examination (see Part II) showed only slight association, even at −180°.

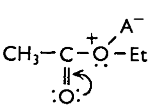
Ethyl acetate and tin bromide were miscible in pentane and spectroscopic examination showed slight association between them; di-n-butylboron chloride behaved similarly. Thus the tin bromide and di-n-butylboron chloride complexes are the least stable of those described. The next in order of instability appears to be that of diphenylboron chloride, because its dissociation vapour pressure at 20° was sufficiently large for ethyl acetate to be slowly removed at 0·1 mm.

Infrared Spectra and Structure of the Complexes.—In the light of previous suggestions, three structures (I—III) require consideration (A denotes the acceptor molecule).



$CH_3{-}C({=}\overset{+}{O}{-}A^-){-}\ddot{O}{-}Et$

(I)



$CH_3{-}C({=}O){-}\overset{+}{O}(A^-){-}Et$

(II)

$[CH_3{\cdot}CO]^+[EtOA]^-$

(III)

The effect of acyl–oxygen donation (I) would be to lengthen the C=O bond and shorten the contiguous acyl C–O bond (the O–alkyl-C bond would probably be slightly lengthened). The effect of alkyl-oxygen donation (II) would be the reverse. The acetylium ion in (III) would have considerable triple bond character ($CH_3{\cdot}C^+{=}O \longleftrightarrow CH_3{\cdot}C{\equiv}O^+$) and thus the carbonyl bond would be much shortened. These bond-length changes refer to the situation in the free ester as standard. It is to be expected, from simple Hooke's law considerations, that these bond-length changes would be reflected in the appropriate bond vibration stretching frequencies (*i.e.* bond lengthening by decrease in the stretching frequency, and conversely). That this assessment is correct, at any rate for the carbonyl group, is evident since the bond length of a carbonyl group increases with polarity,[29] the vibration stretching frequency is a direct function of the bond length,[30] and in molecules XYC=O there is a linear relation between the sum of the electronegativities of X and Y and the carbonyl stretching frequency.[31] Moreover, in esters $R'{\cdot}CO_2R$ (where R and R′ are alkyl groups) the carbonyl stretching frequency generally lies at about 1740 cm.$^{-1}$ and this value is increased or decreased, depending on whether the groups R and R′ are electron-attracting or releasing.[32] Finally, in co-ordination compounds of carbonyl compounds, such as aldehydes and ketones, where there is no ambiguity regarding the carbonyl-oxygen's being the donor atom, a substantial decrease (50—150 cm.$^{-1}$) in the carbonyl stretching frequency in the complex relative to that in the free ligand has been observed.[33]

The suggestion that bond-length changes would be reflected in the observed vibration frequencies ignores the kinematic coupling effects between the two oscillators C–O and O–A. Thus, in structure (I) for example, this effect would give rise to a slight rise in the carbonyl stretching frequency, but a precise estimate would require knowledge of the

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[29] Walsh, *Trans. Faraday Soc.*, 1946, **42**, 561.

[30] Margoshes, Filtwalk, Fassel, and Rundle, *J. Chem. Phys.*, 1954, **22**, 381.

[31] Karagise, *J. Amer. Chem. Soc.*, 1955, **77**, 1377.

[32] Thompson and Torkington, *J.*, 1945, 640; Rappaport, Hampton, and Newell, *Analyt. Chem.*, 1949, **21**, 914.

[33] Cassimatis and Susz, *Helv. Chim. Acta*, 1960, **43**, 852, and previous papers by Susz.

C–O and O–A stretching force constants (such an estimate has been made for the P=O vibration frequency in phosphine oxide complexes [34]).

The infrared spectra of all the complexes were investigated. The principal changes, compared with the spectrum of ethyl acetate,[35] were: (i) the carbonyl stretching frequency decreased from 1741 in ethyl acetate to between 1656 ($FeCl_3$, the highest value) and 1548 cm.$^{-1}$ (BBr_3, the lowest value); (ii) the stretching frequency of the C–O group contiguous to the carbonyl group increased from 1240 in the ester to between 1300 ($FeCl_3$, the lowest value) and 1350 cm.$^{-1}$ (BBr_3, the highest value); (iii) the stretching frequency of the C–O group contiguous to the ethyl group decreased from 1047 in the ester by 5—20 cm.$^{-1}$; (iv) the CH stretching frequencies at 2940 and 2896 cm.$^{-1}$ in ethyl acetate increased by 20—40 cm.$^{-1}$; (v) changes appeared in the CH deformation frequencies; (vi) the intensities of the carbonyl stretching frequency and of the CH deformation frequencies considerably increased in the complexes. Observations (i)—(iii) are precisely those predicted for structure (I) which is also consistent with (vi); thus carbonyl intensities increase also in solvents of high polarity.[36] As all the complexes qualitatively showed the same changes, the comparisons with ethyl acetate of only two are detailed in the Table and in the Figure. Quantitative aspects will be considered in Part II.

Infrared spectra frequencies (cm.$^{-1}$) *of ethyl acetate and two complexes.**

$CH_3{\cdot}CO_2Et$ (liquid)	$(CH_3{\cdot}CO_2Et)_2,SnCl_4$ (liquid)	$CH_3CO_2Et,AlCl_3$	Assignment †
2940 (1)	2967 (1)	2976 (1)	νCH_3
2896 (2)	2930 (2)	2941 (2)	νCH_2
1741 (3)	1613 (3)	1622 (3)	$\nu C{=}O$
1475 (4)	1470 (4)	1475 (4)	
1464 (5)	1422 (5)	1439 (5)	
1450 (6)	1383 (6)	1389 (6)	
1396 (7)			
1374 (8)			
1300 (9)			
1268 (10)	1285 (8)	1250 (8)	
1240 (11)	1319 (7)	1332 (7)	ν(CO–O)
1112 (12)	1111 (9)	1156 (9)	
		1114 (10)	
1096 (13)	1098 (10)	1098 (11)	
1047 (14)	1040 (11)	1042 (12)	νC–O(–Et)
1004 (15)	1004 (12)	1004 (13)	
937 (16)	850 (13)	983 (14)	
917 (17)		852 (15)	
847 (18)		806 (16)	

* Numbers in parentheses refer to the Figure.

† Assignments based on ref. 35 and Wilmshurst, *J. Mol. Spectroscopy*, 1957, **1**, 201.

Structure (III) would require the presence of the carbonyl stretching frequency at ~2190 cm.$^{-1}$ (this has been shown to be characteristic for the acetylium ion in $[CH_3{\cdot}CO]^+[BF_4]^-$ [37]) and may therefore be discounted.

The Donor Strength of Ethyl Acetate.—That the ester displaced diethyl ether from its complex with aluminium chloride indicates that it is the stronger donor. Among carbonyl compounds, on the assumption that esters donate through the acyl-oxygen atom, it would be predicted that donor strengths would decrease in the series Me·CO·OEt > Me·CO·R > Me·CO·H, because of the possibility of mesomeric and inductive effects in the first two cases. Data are not available for such a series, but the shifts in carbonyl stretching frequency of some ketone–boron trifluoride complexes (acetone 70 cm.$^{-1}$; acetophenone 107 cm.$^{-1}$; benzophenone 112 cm.$^{-1}$) may be compared with that (119 cm.$^{-1}$) for ethyl acetate–boron trifluoride: such a comparison appears reasonable because kinematic coupling is

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[34] Cotton, Barnes, and Bannister, *J.*, 1960, 2199.

[35] Nolin and Jones, *Canad. J. Chem.*, 1956, **34**, 1392.

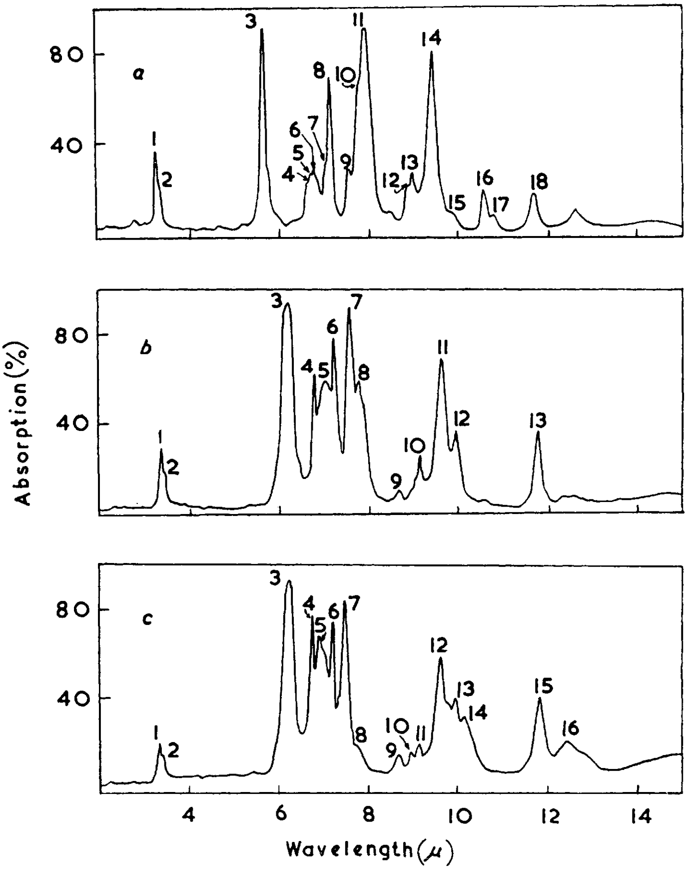
[36] Archibald and Pullin, *Spectrochim. Acta*, 1958, **12**, 34.

[37] Susz and Wuhrmann, *Helv. Chim. Acta*, 1957, **40**, 971.

likely to be similar in all cases. Qualitative comparisons of donor properties [with antimony(v) chloride as reference acid] between acetone and ethyl acetate, by differential thermochemistry, indicate that the latter is the stronger donor.[38]

Stereochemistry of the Complexes.—On the basis of structure (I), the carbonyl-oxygen atom may, in simplified terms, be considered as having sp^2-hybridised bond orbitals, with the remaining p_z-electrons involved in π-bonding. The angle $\angle$COA approximates to 120° and the possibility is that *cis*- and *trans*-isomers may exist owing to restricted rotation about a C=O bond. Accordingly, the proton nuclear magnetic resonance spectrum of the aluminium bromide complex was compared with that of ethyl acetate. In ethyl acetate, bands due to the protons of the acyl-methyl group (i) and the methylene group (ii) were at 0·76 and 2·88 p.p.m., respectively, both on the low-field side of band (iii) which arises from protons of the alkyl-methyl group. In the complex, examined as a solution in benzene, bands (i) and (ii) were separated by 0·99 and 2·37 p.p.m., respectively from band (iii). That on complex-formation there should be chemical shifts in opposite directions for the two sets of protons is surprising and no clear interpretation appears possible.

Infrared spectra of (a) *ethyl acetate* (*liquid*), (b) $(CH_3{\cdot}CO_2Et)_2,SnCl_4$ (*liquid*), *and* (c) $CH_3{\cdot}CO_2Et,AlCl_3$.



For the complex of acetone and boron trifluoride there should, on the above argument, be a chemical shift between the two sets of methyl-protons, as one methyl group would be *cis* and the other *trans* to the acceptor. However, even when the complex, dissolved

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[38] Linqvist and Zackrisson, *Acta Chem. Scand.*, 1960, **14**, 453.

in methylene dichloride, was cooled to −70°, the spectrum showed merely one sharp band, which was on the low-field side at 0·975 p.p.m., against cyclohexane as internal reference. This may be compared with a band on the low-field side at 0·655 p.p.m. for acetone; the shift to the lower field in the complex may be accounted for by the electron-demand made on the methyl groups in co-ordinated acetone. The failure to demonstrate a chemical shift between the two sets of protons in the complex is not necessarily due to angle COB's being 180° and indeed is more likely due to rapid exchange of boron trifluoride among donor molecules, as has been demonstrated for trifluoride–alcohol adducts.[39]

Experimental.—The complexes were prepared as already described. The ratio donor : acceptor was established gravimetrically and confirmed by analysis for halide ion (Volhard) on hydrolysed samples.

Infrared spectroscopic measurements were taken on a Grubb–Parsons S3A double-beam spectrometer with rock-salt optics and calibrated throughout its range by using water, ammonia, and carbon dioxide as standards. Samples were studied as pure materials or (BBr_3, $TiCl_4$, $FeCl_3$) as solid mulls in both liquid paraffin and hexachlorobutadiene. With tin(IV) bromide–ethyl acetate, the pentane solution was also examined in a low-temperature cell with a variable path length.

Nuclear magnetic resonance spectra were obtained at 40 Mc./sec. on a Varian Associates model 4300B spectrometer.

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[39] Diehl and Gränacher, *Helv. Phys. Acta*, 1958, **31**, 43.