

1095. *Co-ordination Compounds having Carboxylic Esters as Ligands. Part III.*¹ *The Thermochemistry of the Complexes of Ethyl Acetate with Group III Halides*

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The condensed-phase heats of formation (*i.e.*, heats of formation of the complexes in their standard states, from acceptor and donor in their standard states) of the 1 : 1 and 2 : 1 complexes of ethyl acetate with some Group III halides have been determined calorimetrically (Table 2). For the 2 : 1 complexes ($\text{MX}_3, 2\text{L}$; M = Al or Ga, X = Cl or Br), the first mole of ligand liberates more heat than does the second, and, furthermore, the heat of addition of the second mole of ligand is greater for the bromides than for the corresponding chlorides. For the 1 : 1 complexes, condensed-phase heats of formation for halides of individual elements increase as follows: $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3$; $\text{AlCl}_3 < \text{AlBr}_3$; $\text{GaCl}_3 < \text{GaBr}_3$; but $\text{InBr}_3 < \text{InCl}_3$. The Group trend for both chlorides and bromides is $\text{In} < \text{Ga} < \text{Al} < \text{B}$. The results are discussed, particularly in relation to spectroscopic data reported in Part II.

The latent heats of fusion of crystalline $\text{AlBr}_3, \text{MeCO}_2\text{Et}$ and $\text{GaBr}_3, \text{MeCO}_2\text{Et}$ are 2.4 ± 0.3 and 1.3 ± 0.3 kcal. mole⁻¹, respectively.

EXPERIMENTAL AND RESULTS

General Procedures.—Ethyl acetate was stored over granulated calcium chloride and distilled immediately before use, the fraction of b. p. 78° being taken. Indium(III) bromide was prepared by passing bromine in a stream of nitrogen over metallic indium at 400°. The product was purified by sublimation in a vacuum, as were the halides AlCl_3 , AlBr_3 , GaCl_3 , GaBr_3 , and InCl_3 . Boron tribromide and trichloride were purified by vacuum-distillation.

Preparation of Complexes.—The 1 : 1 complexes were prepared as previously described.¹

Aluminium(III) chloride bis(ethyl acetate) (Found: Cl, 34.3. $\text{C}_8\text{H}_{16}\text{AlCl}_3\text{O}_4$ requires Cl, 34.4%), *aluminium(III) bromide bis(ethyl acetate)* (Found: Br, 54.0. $\text{C}_8\text{H}_{16}\text{AlBr}_3\text{O}_4$ requires Br, 54.2%), *gallium(III) chloride bis(ethyl acetate)* (Found: Cl, 30.2. $\text{C}_8\text{H}_{16}\text{Cl}_3\text{GaO}_4$ requires Cl, 30.2%), and *gallium(III) bromide bis(ethyl acetate)* (Found: Br, 49.4. $\text{C}_8\text{H}_{16}\text{Br}_3\text{GaO}_4$ requires Br, 49.4%) were prepared by mixing, in stoichiometric amounts, ethyl acetate and the appropriate 1 : 1 complex at 0°. Evolution of heat accompanied the formation of the compounds, which were either white, low-melting, waxy solids ($\text{AlX}_3, 2\text{MeCO}_2\text{Et}$), or colourless, viscous liquids ($\text{GaX}_3, 2\text{MeCO}_2\text{Et}$).

Calorimetry.—The calorimetric apparatus used was that devised by Greenwood and Perkins.² All results refer to 25°C.

The heats of reaction or of solution of the Group III trihalides and their ethyl acetate complexes in either excess of ethyl acetate or excess of aqueous 5% hydrochloric acid are given in equations 1—22. Equation 23 shows the heat of solution of ethyl acetate in excess of aqueous 5% hydrochloric acid. These results are based on the thermochemical data given in Table 1. From equations 1—23, the condensed-phase heats of formation shown in Table 2 were calculated.

Equation 1 $\text{BCl}_3(\text{l.}) + \text{excess MeCO}_2\text{Et}(\text{l.}) = \text{BCl}_3, \text{MeCO}_2\text{Et}$ (in soln.)

Equation 2 $\text{BCl}_3, \text{MeCO}_2\text{Et}(\text{c.}) + \text{excess MeCO}_2\text{Et}(\text{l.}) = \text{BCl}_3, \text{MeCO}_2\text{Et}$ (in soln.)

Equation 3 $\text{BBr}_3(\text{l.}) + \text{excess MeCO}_2\text{Et}(\text{l.}) = \text{BBr}_3, \text{MeCO}_2\text{Et}$ (in soln.)

Equation 4 $\text{BBr}_3, \text{MeCO}_2\text{Et}(\text{c.}) + \text{excess MeCO}_2\text{Et}(\text{l.}) = \text{BBr}_3, \text{MeCO}_2\text{Et}$ (in soln.)

Equation 5 $\text{AlCl}_3(\text{c.}) + \text{excess MeCO}_2\text{Et}(\text{l.}) = \text{AlCl}_3, 2\text{MeCO}_2\text{Et}$ (in soln.)

Equation 6 $\text{AlCl}_3, \text{MeCO}_2\text{Et}(\text{l.}) + \text{excess MeCO}_2\text{Et}(\text{l.}) = \text{AlCl}_3, 2\text{MeCO}_2\text{Et}$ (in soln.)

Equation 7 $\text{AlCl}_3, 2\text{MeCO}_2\text{Et}(\text{c.}) + \text{excess MeCO}_2\text{Et}(\text{l.}) = \text{AlCl}_3, 2\text{MeCO}_2\text{Et}$ (in soln.)

Equation 8 $\text{AlBr}_3(\text{c.}) + \text{excess MeCO}_2\text{Et}(\text{l.}) = \text{AlBr}_3, 2\text{MeCO}_2\text{Et}$ (in soln.)

Equation 9 $\text{AlBr}_3, \text{MeCO}_2\text{Et}(\text{c.}) + \text{excess MeCO}_2\text{Et}(\text{l.}) = \text{AlBr}_3, 2\text{MeCO}_2\text{Et}$ (in soln.)

Equation 10 $\text{AlBr}_3, \text{MeCO}_2\text{Et}(\text{l.}) + \text{excess MeCO}_2\text{Et}(\text{l.}) = \text{AlBr}_3, 2\text{MeCO}_2\text{Et}$ (in soln.)

Equation 11 $\text{AlBr}_3, 2\text{MeCO}_2\text{Et}(\text{c.}) + \text{excess MeCO}_2\text{Et}(\text{l.}) = \text{AlBr}_3, 2\text{MeCO}_2\text{Et}$ (in soln.)

Equation 12 $\text{GaCl}_3(\text{c.}) + \text{excess MeCO}_2\text{Et}(\text{l.}) = \text{GaCl}_3, 2\text{MeCO}_2\text{Et}$ (in soln.)

¹ Part II, M. F. Lappert, *J.*, 1962, 542.

² N. N. Greenwood and P. G. Perkins, *J. Inorg. Nuclear Chem.*, 1957, 4, 291.

Equation 13 $\text{GaCl}_3, \text{MeCO}_2\text{Et}(l) + \text{excess MeCO}_2\text{Et}(l) = \text{GaCl}_3, 2\text{MeCO}_2\text{Et}$ (in soln.)Equation 14 $\text{GaCl}_3, 2\text{MeCO}_2\text{Et}(l.) + \text{excess MeCO}_2\text{Et}(l.) = \text{GaCl}_3, 2\text{MeCO}_2\text{Et}$ (in soln.)Equation 15 $\text{GaBr}_3(c.) + \text{excess MeCO}_2\text{Et}(l.) = \text{GaBr}_3, 2\text{MeCO}_2\text{Et}$ (in soln.)Equation 16 $\text{GaBr}_3, \text{MeCO}_2\text{Et}(c.) + \text{excess MeCO}_2\text{Et}(l.) = \text{GaBr}_3, 2\text{MeCO}_2\text{Et}$ (in soln.)Equation 17 $\text{GaBr}_3, \text{MeCO}_2\text{Et}(l.) + \text{excess MeCO}_2\text{Et}(l.) = \text{GaBr}_3, 2\text{MeCO}_2\text{Et}$ (in soln.)Equation 18 $\text{GaBr}_3, 2\text{MeCO}_2\text{Et}(l.) + \text{excess MeCO}_2\text{Et}(l.) = \text{GaBr}_3, 2\text{MeCO}_2\text{Et}$ (in soln.)Equation 19 $\text{InCl}_3(c.) + \text{excess aqueous 5\% HCl} = \text{InCl}_3$ (in soln.)Equation 20 $\text{InCl}_3, \text{MeCO}_2\text{Et}(l.) + \text{excess aq. 5\% HCl} = \text{InCl}_3$ (in soln.) + MeCO_2Et (in soln.)Equation 21 $\text{InBr}_3(c.) + \text{excess aq. 5\% HCl} = \text{InBr}_3$ (in soln.)Equation 22 $\text{InBr}_3, \text{MeCO}_2\text{Et}(l.) + \text{excess aq. 5\% HCl} = \text{InBr}_3$ (in soln.) + MeCO_2Et (in soln.)Equation 23 $\text{MeCO}_2\text{Et}(l.) + \text{excess aq. 5\% HCl} = \text{MeCO}_2\text{Et}$ (in soln.)

TABLE I

Heats of solution or reaction of acceptors and complexes in excess of either ethyl acetate or aqueous 5% hydrochloric acid

The weights of reactants together with their molar ratio are given. The temperature rise, ΔT , accompanying the reaction is expressed in microvolts, and is related to the number of calories evolved by means of the electrical calibration which was carried out during each experiment. The molar heat of solution is given in the final column.

Eqn.	Ligand (g.)	Acceptor or complex (g.)	Molar ratio	ΔT (μV)	Calibration (cal. per μV)	$-\Delta H$ (kcal. mole ⁻¹)	
							Mean
1	120	0.3770	424 : 1	726	0.1337	30.2	30.4 \pm 0.1
	120	0.3288	486 : 1	643	0.1335	30.6	
2	120	0.1126	2484 : 1	-7	0.1350	-1.72	-2.0 \pm 0.3
	120	0.1104	2534 : 1	-9	0.1352	-2.26	
3	120	0.1900	1795 : 1	190	0.1332	33.4	33.4
	120	0.5140	664 : 1	520	0.1318	33.4	
4	120	0.1260	3660 : 1	-11	0.1307	-3.86	-3.5 \pm 0.4
	120	0.1124	4105 : 1	-8	0.1303	-3.14	
5	120	0.1080	1683 : 1	136	0.1418	23.8	24.1 \pm 0.3
	120	0.3767	482 : 1	458	0.1506	24.4	
6	120	0.4806	628 : 1	83	0.1604	6.1	6.0 \pm 0.2
	120	0.3730	809 : 1	72	0.1358	5.8	
7	120	0.3137	1344 : 1	-9	0.1615	-1.4	-1.5 \pm 0.1
	120	0.3101	1360 : 1	-10	0.1613	-1.6	
8	120	0.6137	592 : 1	501	0.1392	30.3	30.4 \pm 0.1
	120	0.6393	568 : 1	599	0.1218	30.4	
9	120	0.2741	1763 : 1	27	0.1480	5.2	5.0 \pm 0.2
	120	0.3373	1433 : 1	29	0.1575	4.8	
10	120	0.4674	1034 : 1	61	0.1613	7.5	7.4 \pm 0.1
	120	0.3406	1419 : 1	44	0.1613	7.4	
11	120	0.2681	2250 : 1	-8	0.1460	-1.9	-1.6 \pm 0.3
	120	0.2414	2500 : 1	-5	0.1436	-1.3	
12	120	0.2963	810 : 1	236	0.1421	19.9	20.0 \pm 0.1
	120	0.2100	1143 : 1	172	0.1394	20.1	
13	120	0.2605	1382 : 1	19	0.1392	2.7	2.6 \pm 0.1
	120	0.6020	598 : 1	41	0.1392	2.5	
14	120	0.4210	1140 : 1	0	—	—	—
	120	0.3216	1492 : 1	0	—	—	
15	120	0.1861	2266 : 1	105	0.1421	24.8	24.9 \pm 0.1
	120	0.2014	2094 : 1	115	0.1409	24.9	
16	120	0.4694	1154 : 1	50	0.1458	6.1	6.0 \pm 0.1
	120	0.5120	1058 : 1	53	0.1442	5.9	
17	120	0.1847	2933 : 1	23	0.1441	7.1	7.3 \pm 0.2
	120	0.2016	2686 : 1	26	0.1440	7.4	
18	120	0.5132	1289 : 1	0	—	—	—
	120	0.4742	1394 : 1	0	—	—	
19	120 (H_2O)	0.4798	3072 : 1	130	0.3381	20.3	20.4 \pm 0.1
	120 (H_2O)	0.4143	3558 : 1	109	0.3516	20.5	
20	120 (H_2O)	0.3176	12,980 : 1	37	0.3322	12.0	12.4 \pm 0.4
	120 (H_2O)	0.2990	6894 : 1	37	0.3314	12.7	
21	120 (H_2O)	0.3193	7401 : 1	56	0.2726	17.0	17.0
	120 (H_2O)	0.2992	7897 : 1	54	0.2652	17.0	
22	120 (H_2O)	0.3052	9667 : 1	35	0.2576	13.5	13.2 \pm 0.9
	120 (H_2O)	0.3891	7583 : 1	44	0.2557	12.8	
23	120 (H_2O)	1.802 (MeCO_2Et)	326 : 1	86	0.2702	1.1	1.2 \pm 0.1
	120 (H_2O)	1.802 (MeCO_2Et)	326 : 1	87	0.2693	1.2	

It is to be noted that the complexes $\text{AlBr}_3\cdot\text{MeCO}_2\text{Et}$ (m. p. 38°) and $\text{GaBr}_3\cdot\text{MeCO}_2\text{Et}$ (m. p. 29°) are crystalline at room temperature (unlike the corresponding chlorides), and that because of their low melting points it was found possible to measure heats of solution for the crystalline and molten forms of each compound, severally in excess ethyl acetate. The results (equations 9, 10, 16, and 17) lead to latent heats of fusion of 2.4 ± 0.3 kcal. mole⁻¹ for $\text{AlBr}_3\cdot\text{MeCO}_2\text{Et}$ (compare 2.6 kcal. mole⁻¹ for $\text{AlCl}_3\cdot\text{NH}_3$) and 1.3 ± 0.3 kcal. mole⁻¹ for $\text{GaBr}_3\cdot\text{MeCO}_2\text{Et}$.

TABLE 2

Condensed-phase heats of formation of ethyl acetate complexes ($-\Delta H$ in kcal. mole⁻¹)
(Numbers in parentheses refer to the equations used in the calculations)

Halide in the complex	Heats of formation							
	1 : 1 Complex (liquid)	1 : 1 Complex (cryst.)	1 : 2 Complex (liquid)	1 : 2 Complex (cryst.)	1 : 2 Complex (liquid) from the 1 : 1 complex (liquid)	1 : 2 Complex (liquid) from the 1 : 1 complex (cryst.)	1 : 2 Complex (cryst.) from the 1 : 1 complex (liquid)	1 : 2 Complex (cryst.) from the 1 : 1 complex (cryst.)
BF_3		24.2 ± 0.2 (ref. 4)						
BCl_3		32.4 ± 0.5 (1, 2)						
BBr_3		36.9 ± 0.8 (3, 4)						
AlCl_3	18.1 ± 0.5 (5, 6)			25.6 ± 0.4 (5-7)			7.5 ± 0.3 (6, 7)	
AlBr_3	23.0 ± 0.2 (8-10)	25.4 ± 0.3 (8, 9)		32.0 ± 0.4 (8-11)			9.0 ± 0.4 (10, 11)	6.6 ± 0.5 (9-11)
GaCl_3	17.4 ± 0.2 (12, 13)		20.0 ± 0.1 (12-14)		2.6 ± 0.1 (13, 14)			
GaBr_3	17.6 ± 0.3 (15-17)	18.9 ± 0.2 (15, 16)	24.9 ± 0.1 (15-18)		7.3 ± 0.2 (17, 18)	6.0 ± 0.1 (16-18)		
InCl_3	9.2 ± 0.6 (19, 20, 23)							
InBr_3	5.0 ± 0.5 (21, 22, 23)							

DISCUSSION

This work was carried out in part to see if there is any correlation between the enthalpies of formation of the 1 : 1 complexes and the relative acceptor strength sequences for the Group III trihalides previously suggested by us, on the basis of infrared spectroscopic results.¹ The argument which we then used was that the shift ($\Delta\nu$) in carbonyl stretching frequency as between the free ligand and the complex affords a relative measure of the strength of the donor-acceptor bond, provided that related series of complexes are being examined. We recognised that this interpretation involved the considerable assumption that the carbonyl shift is related to the donor-acceptor bond stretching force constant,¹ and this proposition would be invalidated if there is a significant degree of mixing of vibrational modes, involving C=O stretching. References were cited in Part I,⁵ however, to show that various molecular properties are directly related to $\nu(\text{C}=\text{O})$ in carbonyl compounds. For example, in molecules of the form $\text{XYC}=\text{O}$, there is a linear correlation between the sum of the electronegativities of X and Y and the carbonyl stretching frequency.⁶

The infrared spectroscopic technique for measuring relative donor-acceptor bond strengths, which we proposed for carboxylic esters as ligands, has been extended by others to ethyleneurea⁷ and to triphenylphosphine oxide.⁸ As a general method, this

³ W. Klemm, E. Clausen, and H. Jacobi, *Z. anorg. Chem.*, 1931, **200**, 367.

⁴ M. F. Lappert and J. K. Smith, *J.*, 1965, in the press.

⁵ M. F. Lappert, *J.*, 1961, 817.

⁶ R. E. Karagise, *J. Amer. Chem. Soc.*, 1955, **77**, 1377.

⁷ R. J. Berni, R. R. Benerito, W. M. Ayres, and H. B. Jonassen, *J. Inorg. Nuclear Chem.*, 1963, **25**, 807.

⁸ M. J. Frazer, W. Gerrard, and W. Twaits, *J. Inorg. Nuclear Chem.*, 1963, **25**, 637.

TABLE 3

Carbonyl shifts for $\text{MX}_3, \text{MeCO}_2\text{Et}$ complexes

Acceptor	BF_3	BCl_3	AlCl_3	GaCl_3	InCl_3	BBr_3	AlBr_3	GaBr_3^*	InBr_3
$\Delta\nu$	119	176	117	141	113	191	138	150	107

* Present work; the other results are from ref. 1.

must clearly be applied with considerable caution, as has been emphasised by Beattie and Gilson.⁹ They carried out normal co-ordinate analysis of the complexes MeCN, BX_3 and found that the "CN stretching frequency" was remarkably insensitive to variations in BN force constant.

It would be most meaningful for purpose of discussion of relative acceptor strengths of the Group III halides to have available not just the condensed-phase heats of formation of the complexes, but their gas-phase enthalpies of formation (see ref. 10). However, such data are not available, since the complexes are not sufficiently stable in the gas-phase to permit their latent heats of vaporisation or sublimation to be measured. In this connection, $\text{BCl}_3, \text{MeCO}_2\text{Et}$ decomposes irreversibly at 82° .¹¹ Conversion into gas-phase data, as far as is possible, is indicated in Table 4, where ΔH_f = the latent heat of fusion, and ΔH_v = the latent heat of vaporisation, for a complex. The following data were used: $\text{MeCO}_2\text{Et}(l.) = \text{MeCO}_2\text{Et}(g.)$, $\Delta H = 8.7$ kcal. mole⁻¹ (ref. 12); $\text{BCl}_3(l.) = \text{BCl}_3(g.)$, $\Delta H = 5.5$ kcal. mole⁻¹ (ref. 13); $\text{BBr}_3(l.) = \text{BBr}_3(g.)$, $\Delta H = 8.2$ kcal. mole⁻¹ (ref. 14); $\frac{1}{2}\text{Al}_2\text{Cl}_6(c.) = \frac{1}{2}\text{Al}_2\text{Cl}_6(g.)$, $\Delta H = 13.5$ kcal. mole⁻¹ (ref. 15); $\frac{1}{2}\text{Al}_2\text{Cl}_6(g.) = \text{AlCl}_3(g.)$, $\Delta H = 14.5$ kcal. mole⁻¹ (ref. 15); $\frac{1}{2}\text{Al}_2\text{Br}_6(c.) = \frac{1}{2}\text{Al}_2\text{Br}_6(g.)$, $\Delta H = 9.7$ kcal. mole⁻¹ (ref. 15); $\frac{1}{2}\text{Al}_2\text{Br}_6(g.) = \text{AlBr}_3(g.)$, $\Delta H = 13.3$ kcal. mole⁻¹ (ref. 15); $\frac{1}{2}\text{Ga}_2\text{Cl}_6(c.) = \frac{1}{2}\text{Ga}_2\text{Cl}_6(g.)$, $\Delta H = 8.5$ kcal. mole⁻¹ (ref. 16); $\frac{1}{2}\text{Ga}_2\text{Cl}_6(g.) = \text{GaCl}_3(g.)$, $\Delta H = 10.5$ kcal. mole⁻¹ (ref. 17); $\frac{1}{2}\text{Ga}_2\text{Br}_6(c.) = \frac{1}{2}\text{Ga}_2\text{Br}_6(g.)$, $\Delta H = 9.8$ kcal. mole⁻¹ (ref. 18); $\frac{1}{2}\text{Ga}_2\text{Br}_6(g.) = \text{GaBr}_3(g.)$, $\Delta H = 9.3$ kcal. mole⁻¹ (ref. 17).

TABLE 4

Gas-phase heats of formation of $\text{MX}_3, \text{MeCO}_2\text{Et}$ ($-\Delta H$ in kcal. mole⁻¹)

M in MX_3	Halogen in MX_3		
	F	Cl	Br
B	32.9 - $(\Delta H_f + \Delta H_v)$	46.6 - $(\Delta H_f + \Delta H_v)$	53.8 - $(\Delta H_f + \Delta H_v)$
Al		54.8 - ΔH_v	54.7 - ΔH_v
Ga		45.1 - ΔH_v	45.4 - ΔH_v

In earlier thermochemical studies, arguments were put forward to support the assumption that, for related series of complexes, their heats of sublimation are likely to be very close to one another.¹⁸ Similarly, with the MX_3 -ester complexes, if the ΔH_f and ΔH_v values are severally similar, then the gas-phase enthalpies of formation show agreement with the infrared data. Thus, the trends (a) $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3$, and (b) $\text{GaCl}_3 < \text{GaBr}_3$ are valid from both infrared and thermochemical data, and (c) $\text{AlBr}_3 > \text{AlCl}_3$ from infrared results, but $\text{AlBr}_3 = \text{AlCl}_3$ from thermochemical work. The latent heats of sublimation of the indium(III) halides are not known; consequently, speculation as to the gas-phase heats of formation of their ethyl acetate adducts is not appropriate. However, the condensed-phase heats of formation of the complexes follow the order of their carbonyl stretching frequency shifts ($\text{InCl}_3 > \text{InBr}_3$).

⁹ I. R. Beattie and T. Gilson, *J.*, 1964, 2292.¹⁰ F. G. A. Stone, *Chem. Rev.*, 1958, 58, 101.¹¹ W. Gerrard and M. A. Wheelans, *J.*, 1956, 4296.¹² Calculated using the data of J. Wade and R. W. Merriman, *J.*, 1912, 101, 2438.¹³ Nat. Bur. Stand., Circular 500, Washington, 1952.¹⁴ *U.S. Bur. Mines Bull.*, 1935, No. 383.¹⁵ W. Fischer and O. Rahlfs, *Z. anorg. Chem.*, 1932, 205, 1.¹⁶ A. W. Laubengayer and F. B. Schirmer, *J. Amer. Chem. Soc.*, 1940, 62, 1578.¹⁷ W. Fischer and O. Jübermann, *Z. anorg. Chem.*, 1936, 227, 227.¹⁸ N. N. Greenwood and P. G. Perkins, *J.*, 1960, 1141, 1145.

Group trends suggested by the computed gas-phase heats of formation of the complexes ($\text{Al} > \text{B} = \text{Ga}$ for chlorides, $\text{Al} = \text{B} > \text{Ga}$ for bromides) do not follow the same order as do their carbonyl stretching frequency shifts ($\text{B} > \text{Ga} > \text{Al} > \text{In}$ for both chlorides and bromides). However, the sequence $\text{Al} > \text{B} = \text{Ga}$ for the chlorides is in agreement with the order $\text{AlCl}_3 > \text{GaCl}_3$ which is established for the computed gas-phase heats of (1:1) complex formation of these halides with ammonia,¹⁹ and the order $\text{AlCl}_3 > \text{BCl}_3 > \text{GaCl}_3$ when pyridine is donor.¹⁸

It is doubtful whether very close agreement between the thermochemical and infrared work was in fact to be expected. Assuming localisation of vibrations, the carbonyl stretching frequency shifts as between free ethyl acetate and its complexes can be considered to reflect the relative strengths of the donor-acceptor bonds in the complexes themselves. The enthalpy of formation of a complex in the gas phase, however, includes not only the heat of formation of the donor-acceptor bond, but also the energy of reorganisation of the donor and acceptor moieties.

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¹⁹ H. L. Friedman and H. Taube, *J. Amer. Chem. Soc.*, 1950, **72**, 2236.
