*Thermochemistry of Organo-boron compounds. Part V.**
Ethoxychloroborines.

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Values are reported for the heats of hydrolysis of ethoxydichloroborine and diethoxychloroborine, from which the heats of formation ($\Delta Hf°$) in the liquid state are derived, *viz.*:

$$\Delta Hf°[\mathrm{B(OEt)Cl_2}, \text{liq.}] = -158{\cdot}3 \pm 1{\cdot}2 \text{ kcal./mole}$$
$$\Delta Hf°[\mathrm{B(OEt)_2Cl}, \text{liq.}] = -206{\cdot}3 \pm 1{\cdot}2 \text{ kcal./mole.}$$

The bond-energy term values of the B–Cl and B–OEt links in the group $B(OEt)_nCl_{3-n}$ ($n = 0, 1, 2, 3$), for which thermal data are now complete, are not constant throughout the group. The molecule $B(OEt)Cl_2$ is more stable by 4·8, and $B(OEt)_2Cl$ by 4·0 kcal./mole, than would be the case if the bonds should have the same energies as B–Cl in BCl_3 and as B–OEt in $B(OEt)_3$.

The enhancement in bond energy in the " mixed " molecules is attributed to variations in the extent of back-co-ordination in this group of molecules. The observed bond-energy variations—and the similar, but more marked, variations in the group $B(NMe_2)_nCl_{3-n}$ (cf. Part IV)—may be quantitatively reproduced by a molecular-orbital treatment of back-co-ordination, from which it appears that back-co-ordination to the boron atom is more effective from nitrogen (NMe_2) than from oxygen (OEt), and that both these atoms are appreciably more effective in this respect than is the chlorine atom.

Wiberg and Sütterlin (*Z. anorg. chem.*, 1931, **202**, 1, 22) have described the preparation and properties of the compounds $B(OEt)_nCl_{3-n}$ ($n = 1, 2, 3$), each of which is readily hydrolysed at room temperature, giving boric acid as one of the products. The heat of hydrolysis of one of these compounds (triethyl borate) was reported recently by Charnley, Skinner, and Smith (*J.*, 1952, 2288), and in this paper we deal with the heats of hydrolysis of the two remaining compounds of the group, diethoxychloroborine, $B(OEt)_2Cl$, and ethoxydichloroborine, $B(OEt)Cl_2$. The study follows closely the pattern of a previous study on the compounds $B(NMe_2)_nCl_{3-n}$, in which we observed that the bond-energy terms of the B–Cl and B–NMe_2 linkages are not additive throughout the group. The present results lead to a similar conclusion in respect of the B–Cl and B–OEt bond-energy terms in the group $B(OEt)_nCl_{3-n}$ ($n = 0, 1, 2, 3$).

EXPERIMENTAL

Preparation of Compounds.—Ethoxydichloroborine was prepared by slowly adding equivalent quantites of ethanol in dry pentane to boron trichloride in the same solvent, with efficient stirring and cooling. The bulk of the solvent was then removed by low-pressure distillation at −50°. The product was fractionated in an apparatus similar to that described by Wiberg and Sütterlin (*loc. cit.*), and the fraction, v. p. 26 mm. at 0°, was retained. This was stored at −78°. We have observed that ethoxydichloroborine deteriorates at room temperature, and decomposes rapidly at 60—70°.

Diethoxychloroborine was prepared by adding two equivalents of ethanol to one of boron trichloride, both in pentane. The solvent was removed at atmospheric pressure, and the product distilled under reduced pressure, through a 6″ gauze-packed column. The sample, b. p. 45·5—46°/60 mm., was retained.

Calorimeter.—The calorimeter has been previously described (Skinner and Smith, *Trans. Faraday Soc.*, 1953, **49**, 601). Hydrolysis was carried out by breaking thin glass ampoules, containing known weights of reactant, under the surface of water (500 g.) in the Dewar vessel. The temperature changes were followed through the change in resistance of a shielded thermistor element immersed in the solution. The experiments were carried out at 25°.

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* Part IV, *J.*, 1954, 2324.

Units.—The calorimeter was calibrated electrically by the substitution method. Heat quantities are given in thermochemical calories, 1 calorie = 4·1840 abs. joule.

RESULTS

Ethoxydichloroborine.—This compound reacts violently with water, and the reactant was diluted with carbon tetrachloride. The observed heats of hydrolysis, $\Delta H_{\text{obs.}}$, refer to the reaction :

$$\mathrm{B(OEt)Cl_2(liq./CCl_4)} + (n + 3)\mathrm{H_2O(liq.)} \longrightarrow \mathrm{(H_3BO_3 + 2HCl + EtOH)},n\mathrm{H_2O} \quad . \quad (1)$$

$\Delta H_{\text{obs.}}$ is related to the heat of formation of liquid * ethoxydichloroborine by the thermochemical equation :

$$\Delta Hf^{\circ}[\mathrm{B(OEt)Cl_2,\ liq.}] = \Delta Hf^{\circ}\{\mathrm{H_3BO_3 + 2HCl + EtOH}\},n\mathrm{H_2O} - 3\Delta Hf^{\circ}(\mathrm{H_2O,\ liq.}) - \Delta H_{\text{obs.}} \quad (2)$$

In using eqn. (2), thermal data from the following sources were accepted : $\Delta Hf^{\circ}(\mathrm{HCl},n\mathrm{H_2O})$ from "Selected Values of Chemical Thermodynamic Properties," Nat. Bur. Standards, Washington, Circular 500; $\Delta Hf^{\circ}(\mathrm{H_2O,\ liq.}) = -68{\cdot}317$ kcal./mole (Circular 500); $\Delta Hf^{\circ}(\mathrm{EtOH},n\mathrm{H_2O}) = -68{\cdot}706$ kcal./mole [from $\Delta Hf^{\circ}(\mathrm{EtOH,\ liq.}) = -66{\cdot}356$, and the heat of solution (−2·35 kcal./mole) measured by Bose (*Z. physikal. Chem.*, 1907, **58**, 585)†]; and $\Delta Hf^{\circ}(\mathrm{H_3BO_3},n\mathrm{H_2O}) = -257{\cdot}33 \pm 0{\cdot}4$ kcal./mole (from Prosen, Johnson, and Pergiel, Nat. Bur. Standards, Report No. 1552, 1953). Table 1 contains a representative selection from our results. The mols. of reactant used in each experiment were determined by analysis of the $\mathrm{Cl^-}$ ion content of aliquot samples from the hydrolysed solution.

TABLE 1. *Heat of hydrolysis of* $\mathrm{B(OEt)Cl_2}$.

Expt.	$\mathrm{B(OEt)Cl_2}$ (mole)	n	$-\Delta H_{\text{obs.}}$ (kcal.)	$\Delta Hf^{\circ}[\mathrm{B(OEt)Cl_2}]$ (kcal./mole)	Mean values (kcal./mole)
1	0·00736	3770	42·87	−158·1	
2	0·006165	4501	42·61	−158·4	$-\Delta H_{\text{obs.}} = 42{\cdot}5$
3	0·007214	3847	42·45	−158·5	$\Delta Hf^{\circ} = -158{\cdot}5$
4	0·004342	6391	42·00	−159·0	

The possible error in $\Delta H_{\text{obs.}}$, after allowance for errors of analysis and of calorimetry, is estimated at *ca.* ±0·8 kcal./mole.

Diethoxychloroborine.—Hydrolysis of this compound takes place sharply, but is less violent than that of ethoxydichloroborine, so that it was unnecessary to dilute the reactant for hydrolysis studies. According to Wiberg and Sütterlin (*loc. cit.*) diethoxychloroborine can be distilled without decomposition, and can be kept indefinitely. Our findings do not contradict these, but we noted slight contamination of the product by triethyl borate when it was prepared by the method described. Because of the similar volatilities of the two compounds, it is not easy to purify diethoxychloroborine completely. Our samples contained from 5 to 10% of triethyl borate, and correction on this account was necessary in the thermal studies.‡

The observed heats of hydrolysis, $\Delta H_{\text{obs.}}$, refer to the reaction :

$$\mathrm{B(OEt)_2Cl(liq.)} + (n + 3)\mathrm{H_2O(liq.)} \longrightarrow \{\mathrm{H_3BO_3 + HCl + 2EtOH}\},n\mathrm{H_2O} \quad . \quad . \quad . \quad (3)$$

and the ΔHf° values are derived from the equation :

$$\Delta Hf^{\circ}[\mathrm{B(OEt)_2Cl,\ liq.}] = \Delta Hf^{\circ}\{\mathrm{H_3BO_3 + HCl + 2EtOH}\},n\mathrm{H_2O} - 3\Delta Hf^{\circ}(\mathrm{H_2O,\ liq.}) - \Delta H_{\text{obs.}} \quad (4)$$

From nine experiments (in which n varied from 2200 to 3200), the mean $\Delta H_{\text{obs.}}$ was −23·5 (±0·3) kcal./mole, and the mean value of ΔHf° was −206·3 kcal./mole. Because of the unsatisfactory feature contained in the need for impurity corrections, we feel we ought to allot an error limit of ±0·7 kcal./mole to $\Delta H_{\text{obs.}}$, although the observed spread was less than half this.

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* The heat of mixing of $\mathrm{B(OEt)Cl_2}$ (liq.) with $\mathrm{CCl_4}$ (liq.) was assumed to be negligible.

† Circular 500 gives a slightly larger heat of solution; but we do not use it here since we made use of Bose's value in determining $\Delta Hf^{\circ}(\mathrm{Et_3BO_3})$.

‡ By using the heat of hydrolysis of ethyl borate measured by Charnley, Skinner, and Smith (*loc. cit.*). This correction was small, not more than 0·7 kcal./mole.

DISCUSSION

In Table 2, we list the values obtained for the heats of formation of each member of the group $B(OEt)_nCl_{3-n}$, together with the latent heats of vaporisation, $\Delta H_{vap.}$, calculated from Wiberg and Sütterlin's vapour-pressure measurements (*loc. cit.*). The final column gives the heats of hydrolysis, $\Delta H_{hyd.}$, of the compounds in the gaseous state.

TABLE 2.

Compound	$\Delta Hf°$(liq.)	$\Delta H_{vap.}$	$\Delta Hf°$(gas)	$\Delta H_{hyd.}$
BCl_3	$-103·0 \pm 1$	5·5	$-97·5 \pm 1$	$-74·7 \pm 0·3$
$BCl_2·OEt$	$-158·3 \pm 1·2$	$8·4 \pm 0·2$	$-149·9 \pm 1·4$	$-50·9 \pm 1·0$
$BCl(OEt)_2$	$-206·3 \pm 1·2$	$9·3 \pm 0·2$	$-197·0 \pm 1·4$	$-32·8 \pm 0·9$
$B(OEt)_3$	$-251·3 \pm 1$	$10·5 \pm 0·2$	$-240·8 \pm 1·2$	$-17·8 \pm 0·3$

The variation in $\Delta H_{hyd.}$ from BCl_3 through the series to $B(OEt)_3$ is non-linear in relation to the number of chlorine atoms, from which it follows that the redistribution reactions between BCl_3 and $B(OEt)_3$ are not thermoneutral, and that the mean bond dissociation energies $\bar{D}$(B–Cl) and $\bar{D}$(B–OEt) are not constant in the group $B(OEt)_nCl_{3-n}$. From the values of $\Delta H_{hyd.}$ in Table 2 [or of ΔHf (gas)], we derive the heats of redistribution, ΔH_r, of the two redistribution reactions (5) and (6):

$$\tfrac{2}{3}BCl_3(g.) + \tfrac{1}{3}B(OEt)_3(g.) \longrightarrow BCl_2OEt(g.). \quad \Delta H_r = -4·8\ (\pm 0·7)\ \text{kcal./mole} \quad . \quad (5)$$

$$\tfrac{1}{3}BCl_3(g.) + \tfrac{2}{3}B(OEt)_3(g.) \longrightarrow BCl(OEt)_2(g.). \quad \Delta H_r = -4·0\ (\pm 0·7)\ \text{kcal./mole} \quad . \quad (6)$$

These ΔH_r are smaller (by a factor >2) than the heats of redistribution of the corresponding reactions between BCl_3 and $B(NMe_2)_3$ (cf. Part IV).

We propose to discuss the present results in essentially similar manner to our earlier discussion in Part IV, *i.e.*, in terms of π-conjugation ("back-co-ordination"). The conjugation problem is regarded as one of six electrons, extending over the central B atom and the three atoms trigonally attached to it. The localized reference system is considered to have the $2p_z$ boron orbital vacant, and to have p_z^2 pairs localized on each oxygen and/or chlorine atom. We need to estimate the energy stabilization arising from delocalization of these three p_z^2 pairs. The procedure may be illustrated by the example of $BCl_2·OEt$, for which the secular equation is:

$$\begin{vmatrix} \alpha_B - \varepsilon & \gamma^* - S^*\varepsilon & \gamma - S\varepsilon & \gamma - S\varepsilon \\ \gamma^* - S^*\varepsilon & \alpha - \varepsilon_O & 0 & 0 \\ \gamma - S\varepsilon & 0 & \alpha_{Cl} - \varepsilon & 0 \\ \gamma - S\varepsilon & 0 & 0 & \alpha_{Cl} - \varepsilon \end{vmatrix} = 0 \quad . \quad . \quad . \quad (7)$$

In eqn. (7), α_B, α_O, and α_{Cl} are coulomb integrals, $\gamma^* = \gamma^*(B–O)$ and $\gamma = \gamma(B–Cl)$ are exchange integrals, and $S^* = S(B–O)$ and $S = S(B–Cl)$ are overlap integrals. The total π-electronic energy of the delocalized system is obtained by filling the three lowest-energy levels obtained on solution of (7). The energy stabilization (relative to the defined localized system) is symbolized $R_\pi(BOCl_2)$ and given by $2\left[\sum_{i=1}^{3} \varepsilon_i - 2\alpha_{Cl} - \alpha_O\right]$.

To assist the solution of (7) (and the similar equations relating to the systems BO_3, BO_2Cl, BCl_3), we have made the following substitutions:

$$\gamma - \frac{S}{2}(\alpha_O + \alpha_{Cl}) = \beta \qquad \gamma^* - \frac{S^*}{2}(\alpha_O + \alpha_{Cl}) = \beta^*$$

$$\beta = n\beta^*$$

$$(\alpha_{Cl} - \alpha_B) = m\beta^* \qquad (\alpha_O - \alpha_B) = 1·5\,m\beta^*$$

$$S = 0·206 \qquad S^* = 0·189$$

The overlap integrals were calculated from the formulæ of Mulliken, Ricke, Orloff, and Orloff (*J. Chem. Phys.*, 1949, **17**, 1248), the bond distances $r_{B–Cl} = 1·73$ Å and $r_{B–O} = 1·38$ Å being used. The assumption $(\alpha_O - \alpha_B) = 1·5(\alpha_{Cl} - \alpha_B)$ is made to comply with the relative electronegativities of O, Cl, and B (Pauling's scale gives O = 3·5, Cl = 3·0, B = 2·0). Calculated R_π values (in units of β^*) for a range of values of the unknown parameters m and n are given in Table 3. The solutions of the secular equations relating to the systems

$BOCl_2$ and BO_2Cl were obtained for us by Dr. F. H. Sumner, using the Manchester University electronic computing machine.

TABLE 3. R_π *values in units of* β^*.

	n =	1·5	1·3	0·7	0·5	0·4	0·3
m = 0·5	$R_\pi(BCl_3)$	3·5498	3·0426	1·5305	1·0355	0·7926	0·5559
	$R_\pi(BOCl_2)$	3·1536	2·7549	1·7210	1·4473	1·3362	1·2465
	$R_\pi(BO_2Cl)$	2·6752	2·4383	1·8962	1·7802	1·7383	1·7086
	$R_\pi(BO_3)$	2·0599	2·0599	2·0599	2·0599	2·0599	2·0599
m = 1·0	$R_\pi(BCl_3)$	3·3109	2·8120	1·3466	0·8830	0·6622	0·4541
	$R_\pi(BOCl_2)$	2·8729	2·4885	1·4482	1·1699	1·0529	0·9551
	$R_\pi(BO_2Cl)$	2·3204	2·1021	1·5473	1·4210	1·3729	1·3329
	$R_\pi(BO_3)$	1·6434	1·6464	1·6434	1·6434	1·6434	1·6434
m = 1·5	$R_\pi(BCl_3)$	3·1064	2·6192	1·2136	0·7824	0·5830	0·3989
	$R_\pi(BOCl_2)$	2·6393	2·2630	1·2507	0·9800	0·8650	0·7769
	$R_\pi(BO_2Cl)$	2·0699	1·8445	1·2896	1·1616	1·1113	1·0712
	$R_\pi(BO_3)$	1·3291	1·3291	1·3291	1·3291	1·3291	1·3291

Table 4 gives values of two quantities, Δ_1 and Δ_2, defined by :

$$\Delta_1 = R_\pi(BOCl_2) - \tfrac{2}{3}R_\pi(BCl_3) - \tfrac{1}{3}R_\pi(BO_3) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8a)$$

$$\Delta_2 = R_\pi(BO_2Cl) - \tfrac{1}{3}R_\pi(BCl_3) - \tfrac{2}{3}R_\pi(BO_3) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8b)$$

TABLE 4. Δ *values in units of* β^*.

		n = 1·5	1·3	0·5	0·4	0·3
m = 0·5	Δ_1	0·1004	0·0398	0·0703	0·1211	0·1892
	Δ_2	0·1186	0·0508	0·0617	0·1008	0·1500
m = 1·0	Δ_1	0·1179	0·0660	0·0335	0·0636	0·1046
	Δ_2	0·1212	0·0692	0·0311	0·0566	0·0860
m = 1·5	Δ_1	0·1253	0·0738	0·0153	0·0334	0·0679
	Δ_2	0·1480	0·0854	0·0147	0·0309	0·0522

Our suggestion is that the ΔH_r of eqns. (5) and (6) are to be identified with Δ_1 and Δ_2 respectively.

The negative ΔH_r of eqns. (5) and (6) imply that there is an *enhancement* of the bond-energy term values (of B–Cl, or B–OEt, or both) in the " mixed " molecules relative to their values in the " parent " molecules, BCl_3 and $B(OEt)_3$. Experimentally, the enhancement is found to be larger, by 0·8 kcal., in the $BOCl_2$ system (eqn. 5) than in the BO_2Cl system (eqn. 6). But the limits of error attached to the ΔH_r values are too large to allow us to say definitely that ΔH_r of eqn. (5) is more negative than ΔH_r of eqn. (6), and therefore that numerically, $|\Delta_1| > |\Delta_2|$. The presumption in this direction is, however, strengthened by our studies on the dimethylaminochloroborines, in which we found the enhancement to be larger in the $BNCl_2$ system than in BN_2Cl, and concluded that the corresponding Δ values follow $|\Delta_1| > |\Delta_2|$.

The calculated Δ values predict enhancement in the mixed molecules for a range of values of n greater or less than unity, but whereas for $n > 1$, $|\Delta_2| > |\Delta_1|$, for $n < 1$, $|\Delta_1| > |\Delta_2|$. For the remainder of this discussion, we accept (with due reservation) the strong presumption from experiment that the proper interpretation is $|\Delta_1| > |\Delta_2|$, and $n < 1$.

In the discussion of Part IV, we remarked that the Δ_1 and Δ_2 there reported are very satisfactorily reproduced by a particular choice of parameter values (*i.e.*, n, m), leading to β^*(B–N) = −43·5 kcal., $(\alpha_{Cl}-\alpha_B)$ = −21·75 kcal., and $R_\pi(BCl_3)$ = −21·6 kcal. It is useful, for comparison of the present study with the earlier one, to adopt fixed reference points (common to both) so that we retain for the moment the values for $(\alpha_{Cl}-\alpha_B)$ and $R_\pi(BCl_3)$ given above. With these restrictions, the parameter values leading to agreement with our present results are quite sharply defined, as may be seen from the calculated Δ values below :

n	m	β^*(B–O)	Δ_1 (calc.)	Δ_2 (calc.)
0·30	0·54	−40·1	−7·2	−5·7
0·33	0·60	−36·2	−5·3	−4·3
0·34	0·62	−35·1	−4·7	−3·9
0·35	0·64	−34·1	−4·2	−3·6
0·40	0·72	−30·1	−2·75	−2·35

Good agreement with the observed $\Delta_1 = -4{\cdot}8$, $\Delta_2 = -4{\cdot}0$, is given by $\beta^*(\text{B–O}) = -35{\cdot}1 \pm 1$ kcal. The important point is that the ratio $\beta^*(\text{B–N}) : \beta^*(\text{B–O})$ is found to greater than unity.

However, the choice $\beta^*(\text{B–N}) = -43{\cdot}5$ kcal. does not represent a unique solution to the problem discussed in Part IV, and a range of parameter values can be chosen to give agreement (within the limits of experimental error) with the observed Δ values. For example, the choice of parameters leading to $\beta^*(\text{B–N}) = -48$ kcal. and $(\alpha_{\text{Cl}}-\alpha_{\text{B}}) = -36$ kcal. is only slightly inferior to the one we have already used. If we now adopt $(\alpha_{\text{Cl}}-\alpha_{\text{B}}) = -36$ kcal. and $R_\pi(\text{BCl}_3) = -14{\cdot}8$ kcal. [determined by the value of $\beta^*(\text{B–N})$] as fixed points in the present problem, we obtain the Δ values :

n	m	$\beta^*(\text{B–O})$	Δ_1 (calc.)	Δ_2 (calc.)
0·25	0·90	−40·0	−5·6	−4·6
0·305	1·10	−32·7	−3·3	−2·6

from which it is clear that good agreement with experimental observation requires $\beta^*(\text{B–O})$ to be *less* negative than $\beta^*(\text{B–N}) = -48$ kcal., so that, again, the condition $\beta^*(\text{B–N})/\beta^*(\text{B–O}) > 1$ is found to hold.

From the equations defining the β^* (and relating them to the exchange integrals γ^*) it follows that :

$$\frac{\gamma^*(\text{B-N})}{\gamma^*(\text{B-O})} = \frac{\beta^*(\text{B-N}) + 0{\cdot}22\alpha_{\text{Cl}}}{\beta^*(\text{B-O})\{1 + 0{\cdot}04715m\} + 0{\cdot}189\alpha_{\text{Cl}}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and, since m is most unlikely to be a large number, and both the β^* and α_{Cl} are negative quantities, the condition $\beta^*(\text{B–N})/\beta^*(\text{B–O}) > 1$ leads to the more significant conclusion that the ratio $\gamma^*(\text{B–N})/\gamma^*(\text{B–O})$ is also larger than unity. Furthermore, the acceptable values of the parameter n (all of which are fractional) leave no doubt that $\beta^*(\text{B–O})/\beta(\text{B–Cl}) > 1$, and that $\gamma^*(\text{B–O})/\gamma(\text{B–Cl}) > 1$. The implications are that the N atom back-co-ordinates more powerfully to B than does the O atom, and that both N and O are appreciably more effective in this respect than is the Cl atom.

This order of effectiveness ($\text{N} > \text{O} \gg \text{Cl}$) in back-co-ordination to B is reflected in the strengths of the *co-ordinate* links formed by trimethylamine and diethyl ether with boron trifluoride [$D(\text{Me}_3\text{N}\rightarrow\text{BF}_3) \sim 28$ kcal./mole, $D(\text{EtO}\rightarrow\text{BF}_3) = 12{\cdot}5$ kcal./mole; cf. Skinner and Smith, *J.*, 4025, 1953], coupled with the fact the methyl chloride (and alkyl chlorides generally) does not form a complex with boron trifluoride at all. However, some factors which influence the strength of donor–acceptor bonding (*e.g.*, change of shape in the acceptor molecule, steric interactions) are not relevant to back-co-ordination, and we would not overstress the parallelism we have noted or suggest that it should hold generally.

The conclusions reached in this paper could be further tested by a thermochemical study on the dimethylaminoethoxyborines. Neither of the compounds $\text{B(OEt)}_2\text{NMe}_2$, $\text{B(NMe}_2)_2\text{OEt}$, appears to have been described and an attempt to prepare the former, by interaction of $\text{B(OEt)}_2\text{Cl}$ with excess of dimethylamine, gave a 2 : 1 mixture of triethyl borate and trisdimethylaminoborine. This suggests that $\text{B(OEt)}_2\text{NMe}_2$ (if formed at all) is disproportionated when heated, but further work is needed to establish this.

Finally, it should be emphasized that the explanation we have given of the heats of redistribution begins from the assumption that they are to be attributed *entirely* to back-co-ordination. This may be an oversimplification of the problem (cf. Skinner, *Rec. Trav. chim.*, in the press) in that other factors—of which steric interaction between the relatively bulky Cl atoms may be one of the more important—are neglected.

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