275. *The Parachors of Some Metal Carbonyl Compounds.*

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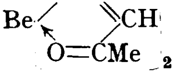
ANOMALIES in the parachor of co-ordination compounds were observed by Sugden ("Parachor and Valency," London, 1930, 145), who found that beryllium in, *e.g.*, the basic propionate $Be_4O(C_2H_5{\cdot}CO_2)_6$ and the acetylacetonate (inset) appeared to have a variable negative parachor. The same kind of parachor deficit is shown by co-ordination compounds of thallium and aluminium, and Sugden sought to obviate the anomaly by a singlet-link theory of co-ordination. More recently, Mann and Purdie (J., 1935, 1549) have made an exhaustive study of the effect as exhibited by homologous series of palladous halide arsine and sulphine derivatives, *e.g.*, $PdCl_2,2R_2S$ and $PdCl_2,2R_3As$. From their work emerges the striking fact that the anomaly increases as a homologous series is ascended; for instance, the apparent parachor of palladium decreases from 36 in $(Me_2S)_2,PdCl_2$ to -7 in the corresponding *n*-amyl compound, and from $+12$ in $(Et_3As)_2,PdCl_2$ to -27 in the triamylarsine compound. It follows necessarily from these results that the deficit cannot be accounted for by substituting a singlet linkage for the co-ordinate linkage, but must be regarded as a real effect, the magnitude of which varies with the size of the co-ordinated groups. Mann and Purdie suggested that this effect might be explained, in part at least, as a function of the shape of the molecule, since the *trans*-planar arrangement of groups about the palladium confers a molecular shape which might well be associated with anomalous packing effects.



Mann and Purdie's explanation may account in part for the trend of the parachor in the homologous series considered, but cannot be regarded as complete, since the same effect is exhibited by compact non-planar molecules. In this connection, results are now reported for the parachor of nickel carbonyl, $Ni(CO)_4$, tricarbonylnitrosylcobalt, $Co(CO)_3NO$, dicarbonyldinitrosyliron, $Fe(CO)_2(NO)_2$, and iron pentacarbonyl, $Fe(CO)_5$. The first three compounds are isosteric, as is shown by consideration of their chemical properties (Anderson, *Z. anorg. Chem.*, 1932, **208**, 238; Hieber and Anderson, *ibid.*, 1933, **211**, 132) and their structure as interpreted in terms of the electronic theory of valency (Sidgwick and Bailey, *Proc. Roy. Soc.*, 1934, *A*, **144**, 521). Nickel carbonyl has been assigned a tetrahedral configuration on the basis of its Raman spectrum (cf. Anderson, *Nature*, 1932, **130**, 1002), and this view has been recently confirmed by Brockway and Cross (*J. Chem. Physics*, 1935, **3**, 828) by the electron-diffraction method. The tetrahedral structure is to be expected, moreover, on the basis of Pauling's theory, since the co-ordination of the carbon-monoxide must be effected by the sp^3 eigenfunctions of a nickel atom with a completed 3*d* shell; the resulting structure is isoelectronic, further, with the $[Zn(CN)_4]''$ ion, which has been shown by *X*-ray methods to be tetrahedral. The nitrosocarbonyls are formed, according to Sidgwick and Bailey, by the co-ordination of the isosteric (CO) and (NO)$^\cdot$ groups to " pseudo-nickel " atoms, so that the same considerations apply here also. The configuration of iron pentacarbonyl, and indeed of compounds generally of the type AB_5, has not yet been determined, but two possibilities arise. (*a*) A tetragonal pyramid, in which the apical carbon monoxide molecule is further removed from (*i.e.*, less strongly attached to) the central atom than the other four; such a structure has been advocated by Graffunder and Heymann (*Z. physikal. Chem.*, 1932, *B*, **15**, **373**) to explain the small observed dipole moment. (*b*) A trigonal bipyramid. This is more symmetrical and appears more probable. It affords an explanation of the ready formation of $Fe_2(CO)_9$, as formulated by Sidgwick and Bailey, and provides the closest packing possible in a 5-co-ordinate arrangement. It is believed that the parachor definitely points to the latter. It will be observed that the parachor of nickel carbonyl, which undoubtedly has a close-packed structure, is a few units greater than four times the observed parachor of carbon monoxide; *i.e.*, if the carbon–oxygen bond of carbon monoxide is not considerably modified by co-ordination (an assumption supported by the evidence of the Raman spectrum), the nickel contributes little to the total parachor. For iron pentacarbonyl the observed total parachor is less than five times that of carbon monoxide, and would suggest that, in addition to the undoubted contraction occurring on co-ordination, the whole structure must be based upon the closest possible packing.

EXPERIMENTAL.

Surface tensions were determined throughout by the capillary-rise method, two capillaries being used as described by Sugden. The difference in capillary rise was measured with a measuring microscope. The liquids were introduced into the measuring apparatus by distillation in a high vacuum between room temperature and liquid air. Surface tensions were thus measured in each case for the interface liquid–saturated vapour, in the absence of foreign gas.

Nickel carbonyl was rigorously purified as already described (Anderson, J., 1930, 1653). The densities were taken from Mond and Nasini's data (*Z. physikal. Chem.*, 1891, **8**, 150); d' was calculated from the author's vapour-pressure measurements (*loc. cit.*).

t	$-10{\cdot}9°$	$-6{\cdot}9°$	$-3{\cdot}4°$	$+1{\cdot}2°$	$3{\cdot}5°$	$6{\cdot}85°$
γ, dynes/cm.	18·28	17·85	17·50	17·02	16·72	16·27
P	254·4	254·9	255·1	255·6	255·5	255·2
t	10·3°	13·1°	17·1°	21·4°	26·2°	30·0°
γ, dynes/cm.	15·79	15·48	15·09	14·52	14·16	13·80
P	255·1	255·0	255·4	255·2	255·9	256·1

Mean $D_0 = 1{\cdot}807_4$; T_c, calc. = 171° (Dewar and Jones found 190—200°).

Cobalt nitrosocarbonyl. The density of cobalt nitrosocarbonyl was redetermined dilatometrically between 0° and 63·9° to supplement the one recorded value of Mond and Wallis (J., 1922, **121**, 32), which falls well on the density–temperature curve now found. The material used for this purpose was prepared by the successive absorption of carbon monoxide and nitric oxide in alkaline cobalt cyanide suspension. That used for surface-tension measurements was prepared by the action of nitric oxide on cobalt tetracarbonyl at 40°. Both samples were purified by fractionation in a vacuum.

t	0·05°	4·35°	10·2°	12·4°	14·3°	23·5°	32·0°	39·2°	49·7°	56·3°	61·3°	63·9°
$d^{t°}_{4°}$	1·507	1·498	1·487	1·482	1·479	1·460	1·442	1·428	1·404	1·391	1·381	1·375

The variation of density with temperature over the range of measurement is excellently reproduced by the expression $d^{t°}_{4°} = 1{\cdot}507(1—0{\cdot}00208t)$, from which the values required for parachor calculations were interpolated. Vapour pressures were extrapolated with sufficient accuracy from the measurements of Blanchard, Rafter, and Adams (*J. Amer. Chem. Soc.*, **1934**, **56**, 16).

t	1·0°	5·5°	11·8°	19·8°	29·6°	38·9°	50·8°	59·3°	69·4°
γ	22·32	21·62	21·15	20·26	19·44	18·06	17·16	15·78	14·80
P	248·7	248·9	249·9	250·1	250·9	249·8	251·2	249·3	249·3
D_0	1·9005	1·8990	1·8971	1·8957	1·8967	1·8957	1·8971	1·9000	1·9011

Mean $D_0 = 1{\cdot}898_1$; T_c, calc. = 235°.

Iron nitrosocarbonyl. The same sample was used as was employed for vapour-pressure and density measurements (Anderson, *Z. anorg. Chem.*, 1932, **208**, 238). Densities were calculated from the smoothed expression $d^{t°}_{4°} = 1·555_6—0·001792\ (t - 20)$.

....	29·6°	39·0°	50·8°	59·2°	68·3°
γ	26·07	24·48	23·51	22·46	20·70
P	252·6	251·5	252·5	252·2	249·9
D_0	1·9615	1·9615	1·965	1·961	1·9575

Mean D_0 = 1·961 ; T_c, calc. = 274°.

Iron pentacarbonyl. This was purified by vacuum fractionation, and distilled into the apparatus in artificial light. The tube was kept in the dark until measurements were actually made. Densities were taken from the values of Dewar and Jones (*Proc. Roy. Soc.*, 1905, *A*, **76**, 558), the obviously erroneous value of 1·4330 at 40° being omitted; the remaining values fall on a straight line.

t	1·0°	11·6°	20·4°	32·1°	45·4°	60·4°	76·4°
γ	27·78	26·47	25·14	23·86	21·81	20·06	18·07
P	301·1	301·5	301·1	301·7	300·0	300·0	298·9

Mean D_0 = 1·842 ; T_c, calc. = 268°.

DISCUSSION.

The results are collected below :

	P.	Apparent P of metal.	V_0.	V_0 of CO or NO (mean).	P/V_0.
$Ni(CO)_4$	255·3	+ 8·9	94·4	21·4	2·68
$Co(CO)_3NO$	249·8	− 8·9	91·1	20·6	2·73
$Fe(CO)_2(NO)_2$	252·5	−18·5	87·6	19·9	2·87
$Fe(CO)_5$	300·6	− 7·4	106·3	19·7	2·83
CO	61·6	—	—	26·3	—

The parachor of carbon monoxide (61·6) shows it to be intermediate between the limiting forms $\mathrm{C}\overset{\leftarrow}{=}\mathrm{O}$ and $\mathrm{C}{=}\mathrm{O}$ (calc. 48·0 and 69·6 respectively). In the carbonyls, the available evidence indicates that the carbon–oxygen linkage differs little from that in carbon monoxide, so that the assumption that the parachor of co-ordinated CO is the same as that of free carbon monoxide should give an approximate value for the parachor of the metal atom. In the nitrosocarbonyls, NO must be closely related in structure to CO. It is therefore reasonable to calculate the parachor on the assumption that $P_{NO} - P_{CO} = P_N - P_C$. Although this procedure is admittedly arbitrary, it is justified in that the molecules are isosteric in their co-ordination compounds (Sidgwick and Bailey, *loc. cit.*; see also deductions from the zero-point volumes, below). Calculation shows that, even if the value so obtained for the parachor of NO be considerably too high, the main conclusion is in no way invalidated. The parachor of the central metal atom calculated in this way is given in col. 3. From the trend of Sugden's atomic number–parachor curve, iron, cobalt, and nickel should have nearly equal atomic parachors of about 50 (Cr=54·3, Cu=46). It is plain that all four substances show a large deficit, just as do the co-ordination compounds of beryllium or palladium.

In col. 4 of the table are given the zero-point volumes of the substances, for comparison with those of solid carbonyl compounds (cf. Hieber, Ries, and Bader, *Z. anorg. Chem.*, 1930, **190**, 215). The zero-point densities were calculated from Sugden's relation (J., 1927, 1780), $D - d = D_0(1 - T/T_c)^{3/10}$, and are given in the experimental results. On calculating the mean zero-point volume of CO and NO (col. 5) in $Fe(CO)_2(NO)_2$, it is seen to be very close to that of CO in $Fe(CO)_5$, whereas the mean value for $Co(CO)_3(NO)$ falls midway between the volumes occupied by CO in $Fe(CO)_5$ and $Ni(CO)_4$. Hence the NO and the CO group are truly isosteric.

From the figures of col. 3, it appears that the substitution of NO for CO, which is known to elevate the Trouton constant perceptibly, increases the parachor anomaly. In no case, however, is the latent heat of vaporisation (calculated from the vapour-pressure data) high enough to correspond to an abnormally high internal pressure, such as should be found on the basis of the effect suggested by Mann and Purdie. The dimensions of the parachor are $\gamma^{1/4}V$, so that the parachor anomaly may be due either to a real volume contraction, or to abnormality in the surface-tension term, which takes account of intermolecular interactions. In col. 6 of the table are recorded the values of P/V_0, which are seen to be perfectly normal (Sugden's figures, J., 1927, 1783, give $P/V_0 = 2{\cdot}87$ for normal liquids). Calculation of P/V_0 for bis(triamylarsine)palladous chloride, Mann and Purdie's density data being used, gives the value 2·65; this, however, involves a long extrapolation, so that little weight can be attached to the perceptibly low figure. Accordingly, it seems probable from the normal ratio of P to V_0, which has the dimensions of the intermolecular interaction term of the parachor, that the negative anomaly represents a real volume effect.

SUMMARY.

The surface tensions and parachors of $Ni(CO)_4$, $Co(CO)_3(NO)$, $Fe(NO)_2(CO)_2$, and $Fe(CO)_5$ have been determined. The apparent parachor of the central atom shows that in all these compounds there is a large anomaly, such as has been found with other co-ordination compounds. It is concluded that no adequate explanation of this anomaly has yet been advanced.

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