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Metal Complex Formation in Non-hydroxylic Solvents. IV.[1] Thermodynamics of the Interaction between Primary, Secondary and Tertiary Alkylamines and Diacetyl-bisbenzoylhydrazino-nickel(II) in Benzene[2]

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Thermodynamic data on the equilibria between dialkylamines and the acceptor diacetyl-bisbenzoylhydrazino-nickel(II) in benzene were determined spectrophotometrically. These data are correlated with the sum of the inductive substituent constants σ^* and discussed together with results previously obtained for primary and tertiary alkylamines. Each class of normal amines lies on a different straight line. On the basis of the deviation of the ΔH values for secondary, tertiary and branched primary alkylamines from the corresponding values for the *n*-primary ones, the steric strain in the adducts NiDBH·2 amine were evaluated. Since solvation between solvent and the "heads" of the amines is not important in these systems, the behavior of the amines is ascribed to structural and electronic factors characteristic of each series of amine.

There are many thermodynamic data on acid-base equilibria of alkylamines in water, aqueous-mixed solvents and organic hydroxylic solvents. The interpretation of the results of these studies, however, is complicated by solvation effects. Thus the dissociation constants of primary, secondary and tertiary alkylamines are not directly comparable.[3]

To explain this behavior Trotman-Dickenson assumed that hydrogen bonds are formed between water or hydroxylic solvents on one hand, and N^+-H groups in the amine molecules or their cations on the other. This would lead to a different stabilization of ammonium ions, which differs for primary or secondary or tertiary amines.[4] Moreover, the order of basic strength of mono-, di- and trialkylamines is influenced also by the nature of the hydroxylic solvents used.[5]

For this reason several investigators have tried to obtain data on the acid-base function of amines in non-hydroxylic solvents.[6] Such data are scarce and incomplete, and few measurements have been made in non-polar solvents. Also in the measurements of the base strength of amines with respect to the hydrogen ion in non-proteolytic solvents, ideal conditions were not achieved owing to the presence of hydroxylic diluents of the acids and to the use of polar solvents.[7]

It therefore appeared desirable to obtain thermodynamic data on the acid-base function of primary, secondary and tertiary alkylamines in non-hydroxylic, non-polar solvents in which solvation effects are not believed to be important. In previous papers thermodynamic data on the equilibria involving primary and tertiary amines and the reference acceptor diacetyl-bisbenzoylhydrazino-nickel(II), NiDBH, in benzene were reported.[1,8]

This paper reports the results of a study of the equilibria between secondary alkylamines and NiDBH, *viz.*

$$\text{NiDBH} + 2\text{Dialkylamine} \rightleftarrows \text{NiDBH}\cdot 2\text{Dialkylamine}$$

Likewise a comprehensive discussion of all of the equilibria between such reference acceptor and primary, secondary and tertiary alkylamines in benzene is given.

Experimental

Materials.—The tertiary alkylamines and the benzene were purified by standard methods until their physical constants agreed with the values in the literature. Only dimethylamine was used without purification.

Measurements and Calculations.—The titration of amines in benzene solution, the spectrophotometric measurements and the calculations of thermodynamic functions were carried out as previously reported.[1]

The accuracy of the values of the thermodynamic quantities is ΔF, ± 0.06 kcal./mole; ΔH, ± 0.3 kcal./mole; ΔS, ± 0.7 e.u.

Results

Tables I and II list the thermodynamic data for dialkylamines. The trend of the $-\Delta F$, $-\Delta H$ and $-\Delta S$ values with a lengthening of the alkyl chains is analogous to that for trialkylamines[1] and opposite to that for monoalkylamines.[8] The values of $-\Delta F$ and $-\Delta H$ indeed decrease in going from dimethyl- to dibutylamine, but the slope decreases with a lengthening of the alkyl chain. The $-\Delta S$ values increase with decreasing slope up to dibutylamine.

TABLE I

FORMATION CONSTANTS OF NiDBH ADDUCTS WITH SECONDARY ALKYLAMINES IN BENZENE SOLUTION

Amine, R_2NH, R-	log K_{10}	log K_{15}	log K_{20}	log K_{25}	log K_{40}	pK_a	
Methyl	7.04	6.80	6.60	6.47		10.71[a]	10.78
Ethyl	4.25	4.05		3.72	3.10	10.98	10.96
n-Propyl	3.85	3.68		3.36	2.72	10.91	11.00
i-Propyl	2.28			1.80	1.21	11.05	
n-Butyl	3.51			3.03	2.40	11.31	11.25
i-Butyl	2.21			1.70	1.09	11.50	
s-Butyl	1.04	0.85		0.56	−0.04	11.01	

[a] N. F. Hall and M. R. Sprinkle, THIS JOURNAL, **54**, 3469 (1932). [b] H. C. Brown, H. Bartholomay, Jr., and M. D. Taylor, *ibid.*, 66, 435 (1944).

Figure 1 shows that the values of $-\Delta F$, $-\Delta H$ and $-\Delta S$ change, respectively, when the three series of amines are plotted against the sum of the values of the inductive substituent constant.

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[1] Paper III, L. Sacconi, G. Lombardo and P. Paoletti, THIS JOURNAL, **82**, 4185 (1960).

[2] This research was supported in part by the U. S. Department of the Army through its European Research Office, under Contract No. DA-91-508-EUC-304.

[3] R. P. Bell and J. W. Bayles, *J. Chem. Soc.*, 1518 (1952); J. W. Bayles and A. Chetwyn, *ibid.*, 2328 (1958).

[4] A. F. Trotman-Dickenson, *ibid.*, 1293 (1949).

[5] P. Rumpf, G. Giraoult-Vexlearschi and R. Schaal, *Bull. soc. chim. France*, 554 (1955).

[6] *Cf.* V. K. La Mer and H. C. Downes, THIS JOURNAL, **53**, 888 (1931); D. C. Griffiths, *J. Chem. Soc.*, 818 (1938); R. G. Pearson and F. V. Williams, THIS JOURNAL, **76**, 258 (1954); R. G. Pearson and D. C. Vogelsong, *ibid.*, **80**, 1038 (1958).

[7] H. K. Hall, Jr., *J. Phys. Chem.*, **60**, 63 (1956).

[8] L. Sacconi, G. Lombardo and L. Ciofalo, THIS JOURNAL, **82**, 4182 (1960).

TABLE II

THERMODYNAMIC FUNCTIONS FOR THE REACTION NiDBH + 2 AMINE ⇄ NiDBH·2 AMINE AT 25° IN BENZENE SOLUTION

Amine, R_2NH, R-	$-\Delta F$ (kcal./mole)	$-\Delta H$ (kcal./mole)	$-\Delta S$ (e.u.)	$-\Sigma\sigma^*$
Methyl	8.82	14.4	19.1	−0.49
Ethyl	5.07	13.5	28.4	− .29
n-Propyl	4.58	13.3	29.3	− .25
i-Propyl	2.45	12.6	34.5	− .11
n-Butyl	4.13	13.1	30.0	− .23
i-Butyl	2.31	13.2	36.6	− .23
s-Butyl	0.76	12.6	39.7	− .08

Discussion

The values of $-\Delta F$ as well as of $-\Delta H$ plotted against $-\Sigma\sigma^*$ lie roughly on three straight lines corresponding to the primary, secondary and tertiary amines, respectively. The primary amines fall on one straight line with positive slope, whereas the lines for di- and trialkylamines have a negative slope. This must be ascribed to the presence of steric factors which become increasingly important as the amines becomes more bulky. It is opposite to the effect of inductive effect.

It may be remembered, in this connection, that no regularities appear in the plot of pK_a *vs.* $-\Sigma\sigma^*$, in water, for the primary, secondary and tertiary *n*-alkylamines here used. The linearity between pK_a and $-\Sigma\sigma^*$ for the three classes of amines holds in a rough manner only if a larger number of amines is considered.[9]

The amount of steric effect in these equilibria with NiDBH can be evaluated from the plot in Fig. 1. In fact the equation for the straight line given by the primary amines for which no steric factor is assumed is

$$-\Delta H = -7.69\Sigma\sigma^* + 23.45 \qquad (1)$$

The branched primary amines as well as the normal secondary and tertiary ones exhibit $-\Delta H$ values smaller than those predicted from equation 1. In agreement with Taft[10] one can assume that the deviation from this straight line for all the amines is a measure of the steric compression or strain in the addition compounds. The values of this deviation, $\Delta(\Delta H)$, are given in Table III. The steric hindrance increases from di- to the trialkylamines, the $\Delta(\Delta H)$ values for normal secondary and tertiary alkylamines being in the range of 5.3–8.6 and 9.5–13.3 kcal./mole, respectively. The branched alkylamines are more hindered than the normal ones. The $\Delta(\Delta H)$ values for primary, *s*-butyl- and *t*-butylamine indeed are 1.2 and 2 kcal., respectively, whereas those for branched secondary amines are 10–10.2 kcal.

The strain given from the values of $\Delta(\Delta H)$ must be ascribed mainly to the interference between the planar molecule of NiDBH and the CH_3 groups which protrude beyond the nitrogen atom (F-strain).[11]

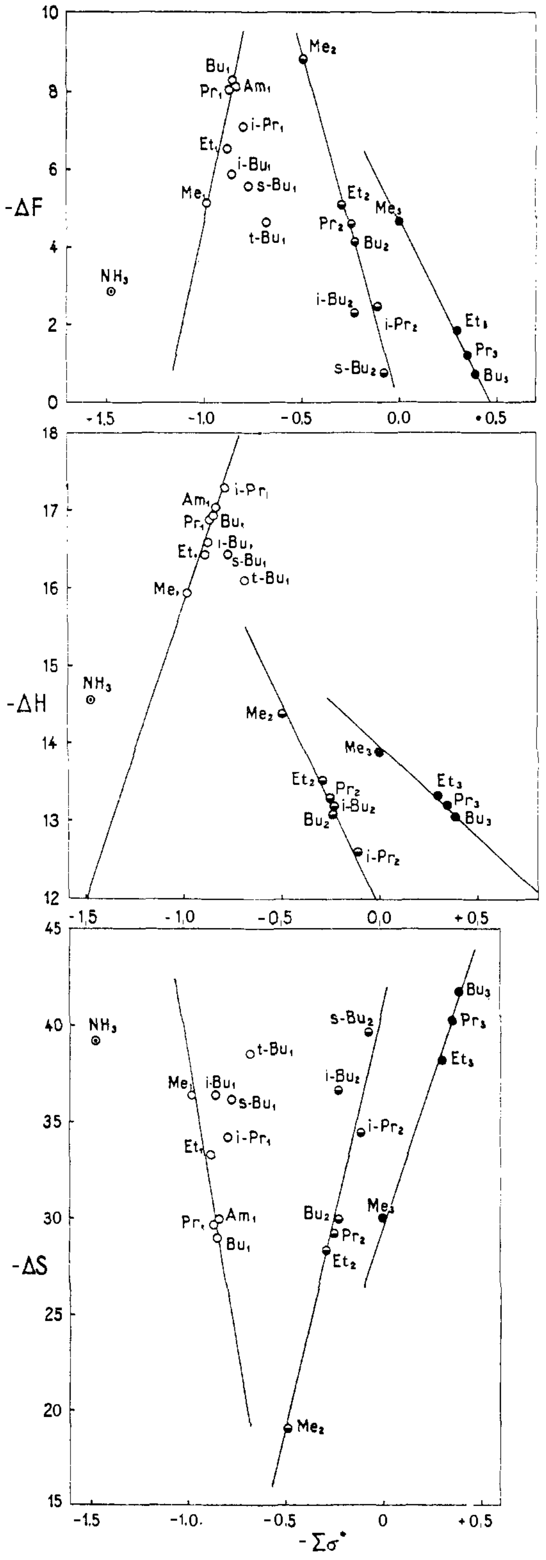

Fig. 1.—Free energy, enthalpy and entropy changes values for NiDBH·2 amine adducts plotted against the inductive substituent constant: ○, monoalkylamines; ⊖, dialkylamines; ●, trialkylamines.

The highest increase in the $\Delta(\Delta H)$ values for each series of amines occurs on passing from the methyl- to the ethylamines. Beyond this point for members of each of the series, the $\Delta(\Delta H)$ values increase very slowly and tend to telescope. This would indicate that, starting with the secondary and tertiary ethylamines, other steric factors,

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[9] H. K. Hall, Jr., THIS JOURNAL, **79**, 5441 (1957).

[10] R. W. Taft, Jr., *ibid.*, **74**, 3120 (1952); **75**, 4231 (1953).

[11] *Cf.* M. Aroney and R. J. W. LeFèvre, *J. Chem. Soc.*, 3002 (1958).

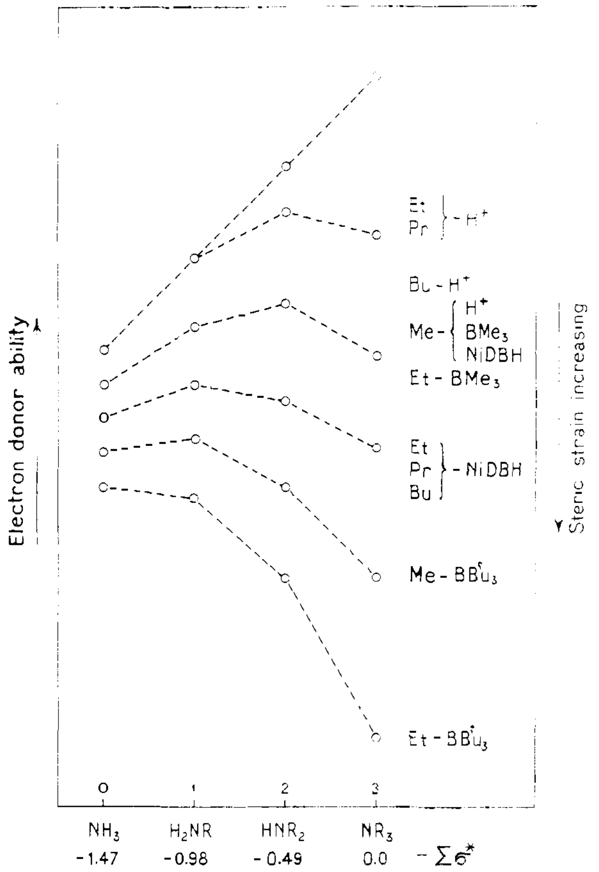

Fig. 2.—Relative strength of ammonia and alkylamines toward different reference acceptors.

TABLE III

STRAIN ENERGIES FOR THE FORMATION OF NiDBH·2 AMINE ADDUCTS

Amine	$-\Delta H_{(\text{exptl.})}$	$-\Delta H_{(\text{calcd.})}$ (kcal./mole)	Steric strain
H_2NMe	15.9	15.9	0
H_2NEt	16.5	16.6	0
$H_2N(n\text{-Pr})$	16.9	16.8	0
$H_2N(i\text{-Pr})$	17.3	17.4	0
$H_2N(n\text{-Bu})$	16.9	16.9	0
$H_2N(i\text{-Bu})$	16.6	16.6	0
$H_2N(s\text{-Bu})$	16.5	17.5	1.0
$H_2N(t\text{-Bu})$	16.1	18.2	2.1
$H_2N(n\text{-Am})$	17.1	17.0	0
$HNMe_2$	14.4	19.7	5.3
$HNEt_2$	13.5	21.1	7.7
$HN(n\text{-Pr})_2$	13.3	21.5	8.2
$HN(i\text{-Pr})_2$	12.6	22.6	10.0
$HN(n\text{-Bu})_2$	13.1	21.7	8.6
$HN(i\text{-Bu})_2$	13.2	21.7	8.5
$HN(s\text{-Bu})_2$	12.6	22.8	10.2
NMe_3	13.9	23.4	9.5
NEt_3	13.3	25.7	12.4
$N(n\text{-Pr})_3$	13.2	26.1	12.9
$N(n\text{-Bu})_3$	13.1	26.4	13.3

namely B-strain, begin to operate, as suggested by Spitzer and Pitzer.[12]

However, it should be pointed out that in these systems it is difficult to distinguish between B-strain and F-strain. Since the long alkyl chains must remain above or below the NiDBH plane, it is apparent that these chains are forced to coil back away from the front of the amine. Because of crowding at the front (F-strain), there results in turn crowding at the back (B-strain). This type of B-strain is not visualized as resulting from a change in the tetrahedral angle around nitrogen. Instead the strain is caused by the coiling of the alkyl chains in a backward position.

Entropy Changes.—Entropy changes for the three classes of amines are always negative, in agreement with the conversion of translational to vibrational and rotational entropy. Therefore, the decrease in the stability of the adducts of secondary and tertiary amines is due both to a decrease in $-\Delta H$ and to an increase in $-\Delta S$.

The values of $-\Delta S$ for the three series of amines, plotted against $-\Sigma\sigma^*$, lie roughly on three straight lines with slopes opposite to that of the lines given by $-\Delta F$ and $-\Delta H$ (Fig. 1). The secondary and tertiary amines give values of $-\Delta S$ which increase with $-\Sigma\sigma^*$, *i.e.*, with the length of the alkyl chains as well as with the number of alkyl groups bonded to the same nitrogen atom. This is in accord with the hypothesis that F- and B-strains are in operation.

These results show that even in the absence of water or hydroxylic solvents, each class of amines behaves in a particular way. Since, in the present case, solvation of the "heads" of the amines through hydrogen bonding cannot be invoked, this must be ascribed to some property of the molecules themselves.

Comparison of Thermodynamic Data for the Three Series of Amines.—Substitution of hydrogen by alkyl groups in ammonia produces a regular increase in the polarity of the amines as shown by the values of $-\Sigma\sigma^*$. If this were the only factor determining the complexing power of the amines, evaluated in terms of stability constants, the order of donor capacity should be: $NH_3 < H_2NR < HNR_2 < NR_3$, irrespective of the acceptor used. Any discrepancy from this sequence would be ascribed to the operation of steric factors.

Toward hydrogen ion as an acceptor, the order of donor affinities is reported as $NH_3 < H_2NR < HNR_2 > NR_3$[13] (R = Me, Et). Instead, toward NiDBH this sequence is verified only in the case of the methylamines. For R from Et to *n*-Bu the order observed with NiDBH changes to $NH_3 < H_2NR > HNR_2 > NR_3$. This signifies that in the case of the methylamines the steric requirements of the alkyl groups are low. Therefore, although the steric requirements of NiDBH are much larger than those of proton or hydrated proton, the sequence of donor affinities does not change. However when the methyl groups are replaced by the larger ethyl-, propyl- and butyl- groups, the steric interactions with NiDBH prevail earlier and the sequence presents a maximum at monoalkylamines.

The sequence of Ni–N bond strengths for methyl-, ethyl-, propyl- and butylamines evaluated on the basis of the enthalpy values is $NH_3 < H_2NR >$

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[12] R. Spitzer and K. S. Pitzer, THIS JOURNAL, **70**, 1261 (1948).

[13] *Cf.* H. C. Brown and M. D. Taylor, *ibid.*, **69**, 1332 (1947).

$HNR_2 \geqslant NR_3$. For amines with more bulky alkyl groups (propyl and butyl), the maximum of steric strain occurs with the secondary amines and thereafter the $-\Delta H$ values do not decrease. This series of the bond strength is equal to that of acid-base equilibria of methylamines in aqueous solution.[14]

It is interesting to compare the $-\Delta F$ and $-\Delta H$ values for the homologous series methylamine, ethylamine, *i*-propylamine, *t*-butylamine which is derived from the successive substitution of a C–H hydrogen atom by a methyl group in methylamine. The values of $-\Delta F$ and $-\Delta H$ plotted against $-\Sigma\sigma^*$ show a maximum at *i*-propylamine. The sequence of increasing affinity ($-\Delta F$) and bond strength ($-\Delta H$) are

$$H_2NCH_3 < H_2NCH_2CH_3 < H_2NCH(CH_3)_2 > H_2NC(CH_3)_3$$

Here, too, there are opposing polar and steric factors. Beyond *i*-propylamine the steric effect predominates and the values of $-\Delta F$ and $-\Delta H$ decrease. Stuart models show that the bulky $C(CH_3)_3$ group prevents the nitrogen atom from sufficiently approaching the nickel atom in a direction suitable for the formation of a tetrahedral bond with respect to the nitrogen atom.

The free energy data reported here and those found for the equilibria with H^+ in water and the acceptors BEt_3 and $B(t\text{-}Bu)_3$ in the gas phase[15] permit a comparison of the relative donor properties of the alkylamines toward the different acceptors.

These results also give some information on the steric requirements of the different acceptors. The diagram in Fig. 3 shows that the steric requirements of NiDBH are intermediate between those of BEt_3 and $B(t\text{-}Bu)_3$, the series of increasing steric requirements for different acceptor being: $H^+ < BMe_3 <$ NiDBH $< B(t\text{-}Bu)_3$. Since the four coordinated atoms and the nickel in the NiDBH are coplanar, this suggests that the hydrogen atoms of the *tert*-butyl groups in $B(t\text{-}Bu)_3$ extend beyond the plane which contain the boron atom.[16]

[14] D. H. Everett and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **35**, 1380 (1939).

[15] H. C. Brown, *J. Chem. Soc.*, 1248 (1956), and references quoted therein.

[16] It should be pointed out that the acceptor reported as $B(t\text{-}Bu)_3$ was in fact triisobutylboron (*cf.* G. F. Hennion, P. A. McCusker, E. C. Ashby and A. J. Rutkowski, THIS JOURNAL, **79**, 5190 (1957). However this in no way may change the discussion presented here.

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Hydrogen Bonding Studies.[1a] IV. Acidity and Basicity of Triphenylhydroxy Compounds of the Group IVB Elements and the Question of Pi-bonding from Oxygen to Metals[1b]

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The acidity[2] and basicity[2] as hydrogen bond donors and acceptors have been measured for the compounds Ph_3MOH, where M = C, Si, Ge, Sn and Pb. The trends in acidity and basicity in these compounds indicate that dative pi-bonding from oxygen to M is strong in Ph_3SiOH, weaker in Ph_3GeOH, and negligible in the other three compounds.

Dative pi-bonding to silicon is now fairly well established as a fact of organosilicon chemistry,[3] but the possibility of pi-bonding to the other group IVB metals has received less attention. The two previous comparative studies of pi-bonding to group IV metals deal with pi-bonding from aromatic rings to these elements. Chatt and Williams have measured the dissociation constants of aromatic acids substituted in the para position by a carbon, silicon, germanium or tin trialkyl group,[4] while Benkeser, DeBoer, Robinson and Sauve have determined the Hammett sigma constants for *para* triphenysilyl and triphenylgermanyl groups by reaction rate studies.[5a] Chatt and Williams found that *pK* values for the Si, Ge and Sn compounds were all slightly greater than for the carbon compound but differed little among themselves.[4] They explained these findings on the basis that dative pi-bonding from the aromatic ring to the metal atom takes place to about the same extent in the Si, Ge and Sn compounds. In agreement with this interpretation Benkeser concluded that the amount of pi-bonding to germanium and silicon is essentially identical.[5a] In the one theoretical paper which has appeared on the subject of $p\pi$–$d\pi$ bonding, the prediction is made that the strength of this type of bonding should not be strongly dependent upon the radius of the atom bearing the d-orbitals

[1] (a) Previous paper in this series: G. Hite, E. E. Smissman and R. West, THIS JOURNAL, **82**, 1207 (1960). (b) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. AF 49(638)-285. Reproduction in whole or part is permitted for any purpose of the United States Government.

[2] Henceforth, in this and succeeding papers in this series, unless otherwise specified the terms "acidity" and "basicity" will refer to Lewis acidity and Lewis basicity in hydrogen bonding reactions; that is, to relative proton donating power and proton attracting power, respectively, in hydrogen bond formation. This terminology may be questioned on the basis that the hydrogen bonding interaction is different from other types of Lewis acid-base interaction. This point is debatable, but the authors feel that the similarity between hydrogen bonding and other Lewis-acid-base reactions is great and that at present it is preferable to consider hydrogen bonding in terms of Lewis acid-base theory; *cf.* the terminology used in G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," Freeman and Co., San Francisco, 1960.

[3] F. G. A. Stone and D. Seyferth, *J. Inorg. Nuclear Chem.*, **1**, 112 (1955).

[4] J. Chatt and A. A. Williams, *J. Chem. Soc.*, 4403 (1954).

[5] (a) R. A. Benkeser, C. E. DeBoer, R. E. Robinson and D. M. Sauve, THIS JOURNAL, **78**, 682 (1956); (b) D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel and L. E. Sutton, *J. Chem. Soc.*, 332, 354 (1954).