1045. *Complexes of Amines with Zinc Dialkyldithiocarbamates. Part II.*[1] *A Study of the Influence of Amine Structure on the Stability of Complexes of Zinc Dimethyldithiocarbamate*

By E. Coates, B. Rigg, B. Saville, and D. Skelton

Amines add to zinc dialkyldithiocarbamates to provide 5-co-ordinate 1 : 1 complexes the solubilities of which in organic solvents are much higher than those of the parent dialkyldithiocarbamates. This behaviour has been utilised in developing a method, involving precise solubility measurements, for determining the dissociation constants of the complexes of zinc dimethyldithiocarbamate in solvent toluene. In this way the relative affinities of various amines for the zinc centre can be compared quantitatively, and it is found that although a broad relation exists between amine basicity and amine–zinc affinity, the latter is clearly subject to the steric requirements of the amine in the co-ordination shell. These steric effects, however, are of lower magnitude than those which obtain for the co-ordination of amines with trimethylboron. It is also found that sterically unhindered pyridines possess abnormally high co-ordinative affinities for the zinc centre.

We have recently reported[1] the isolation of 1 : 1 addition complexes of amines with zinc dialkyldithiocarbamates, compounds which are of interest with regard to the theory of action of accelerators of sulphur-vulcanisation of unsaturated elastomers. The complexes also appear to be further examples of pentaco-ordinated zinc(II), and in recent *X*-ray-crystallographic molecular-structure determinations on pyridine–zinc dimethyldithiocarbamate Mr. K. Fraser and Dr. Marjorie M. Harding * have shown that the four sulphur atoms of the two dimethyldithiocarbamate groups and the pyridine nitrogen atom form a distorted trigonal bipyramid around the zinc atom. Whilst this work will be reported soon, we have in our laboratories been interested in the effect of the structure of the amine on the strength of the Zn–N co-ordinate bond as indicated by the equilibrium constants of the solution processes:

$$\underset{\text{(1 : 1 addition complex)}}{\text{(Amine)Zn(S}_2\text{CNMe}_2)_2} \rightleftharpoons \underset{\text{(parent dimethyldithiocarbamate)}}{\text{Zn(S}_2\text{CNMe}_2)_2} + \text{Amine}$$

The method used to determine the dissociation constants was based on the observation that whereas zinc dimethyldithiocarbamate (ZD_MC) has a low solubility in various organic solvents, *e.g.*, toluene (*ca.* 0·004M at room temperature), the solubilities of the 1 : 1 amine complexes of ZD_MC are generally higher by at least an order of magnitude. Consider a set of solutions of an amine in the solvent, saturated with ZD_MC under isothermal conditions. If the amines were to associate completely with ZD_MC to provide a soluble 1 : 1 complex then the measured solubility of ZD_MC would rise from an initial value, S_Z, referring to pure solvent, in direct equivalence to the initial concentrations of the amine solutions according to Figure 1, curve 1.

This is because extra ZD_MC molecules would be taken into solution to combine with every molecule of amine present. On the other hand, if the amine did not give a complex at all with the ZD_MC then the measured solubility of ZD_MC would remain in all solutions at the same value, S_Z, as obtains for the pure solvent, giving a relationship such as that shown in Figure 1, curve 2. Between these two extremes of behaviour for complete association and dissociation, respectively, there will obviously exist a general increase of effective ZD_MC solubility which must relate to the degree of dissociation of the 1 : 1 complex in solution. This relation is discovered as follows.

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* Private communication.

[1] Part I, G. M. C. Higgins and B. Saville, *J.*, 1963, 2812.

At equilibrium, for the dissociation process,

$$\mathrm{ZA} \rightleftharpoons \mathrm{Z} + \mathrm{A}$$

the mass-action condition (activities set equal to concentrations) is

$$[\mathrm{Z}][\mathrm{A}]/[\mathrm{ZA}] = K_\mathrm{d} \qquad (1)$$

where ZA, Z, and A refer to the dissolved species (1 : 1 complex, free $\mathrm{ZD_MC}$, and amine, respectively), square brackets denote concentrations of the species enclosed, and K_d is the dissociation constant. Now, three quantities can be measured. They are

(*a*) the solubility of $\mathrm{ZD_MC}$ in the pure solvent $= S_\mathrm{Z}$,

(*b*) the total concentration, S_T, of dissolved zinc species, *i.e.*, [Z] + [ZA] in any solution originally containing amine,

and (*c*) the initial concentration of amine, $[\mathrm{A_0}]$, before the solution was saturated with $\mathrm{ZD_MC}$.

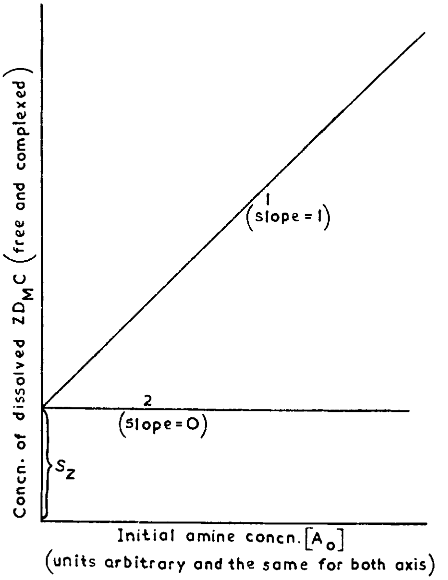

FIGURE 1. Extremes of solubility behaviour based on 1 : 1 complex formation for the systems $\mathrm{ZD_MC}$ (solid)/$\mathrm{ZD_MC}$ (dissolved), amine, solvent

Therefore, assuming that the presence of small concentrations of uncomplexed amine and of the 1 : 1 complex do not alter the solubility of $\mathrm{ZD_MC}$ *per se* in the presence of solid $\mathrm{ZD_MC}$, we can define [ZA], [Z], and [A] in terms of the measured quantities; thus $[\mathrm{Z}] = S_\mathrm{Z}$, $[\mathrm{ZA}] = S_\mathrm{T} - S_\mathrm{Z}$, and $[\mathrm{A}] = [\mathrm{A_0}] - [\mathrm{ZA}] = [\mathrm{A_0}] - (S_\mathrm{T} - S_\mathrm{Z})$, so that equation (1) becomes

$$\frac{S_\mathrm{Z}\{[A_0] - (S_\mathrm{T} - S_\mathrm{Z})\}}{S_\mathrm{T} - S_\mathrm{Z}} = K_\mathrm{d} \qquad (2)$$

or

$$S_\mathrm{T} = \left(\frac{S_\mathrm{Z}}{K_\mathrm{d} + S_\mathrm{Z}}\right)[A_0] + S_\mathrm{Z} \qquad (3)$$

From equation (3) it is seen that if the concentration of soluble zinc species (S_T) be plotted, against the corresponding initial amine concentration ($[A_0]$) one should obtain a straight line of slope equal to $S_\mathrm{Z}/(K_\mathrm{d} + S_\mathrm{Z})$. Since S_Z is also known K_d can be calculated.

Application of this method to the determination of dissociation constants of various amine complexes requires precise solubility data. In the Experimental section is described a method for the determination of solubilities under isothermal conditions to an accuracy of about ±0·5%, consideration of which leads to the conclusion that the useful limits of K_d which can be determined by the present technique are given approximately by the condition $20\ S_\mathrm{Z} > K_\mathrm{d} > 0{\cdot}05\ S_\mathrm{Z}$. If K_d is less than $0{\cdot}05\ S_\mathrm{Z}$ then the slope of the solubility *vs.* [A] plot approaches unity too closely, whereas if K_d is greater than $20\ S_\mathrm{Z}$ inordinately high initial amine concentrations are required to bring about appreciable increases in the solubility of $\mathrm{ZD_MC}$.

EXPERIMENTAL

Materials.—AnalaR toluene was dried over sodium and redistilled. Zinc dimethyldithiocarbamate, prepared from AnalaR zinc sulphate and sodium dimethyldithiocarbamate, was recrystallised twice from toluene and was finely powdered. It had m. p. 253—254°. 4-Methylpyridine (γ-picoline) was an extremely pure (99·97%) specimen supplied by the National Chemical Laboratory, Teddington, and 2,4,6-trimethylpyridine (*sym*-collidine) which could not be obtained adequately pure from commercial sources was an unambiguously synthesised sample kindly made available by Dr. P. F. G. Praill (Queen Elizabeth College, London). It was dried over 5A molecular sieves. All other amines from commercial sources were carefully fractionated. Solutions of ethylenediaminetetra-acetic acid (EDTA) (0·01M) were prepared from the AnalaR disodium salt and standardised against pure zinc oxide using titration conditions specified previously.[1]

Solubility Measurements.—The apparatus, in which an amine solution was saturated with ZD$_{M}$C, and in which the supernatant liquid was filtered off under isothermal conditions and weighed prior to chemical analysis for dissolved zinc species, was constructed of Pyrex and is indicated in Figure 2. It consisted essentially of a 2-necked 30-ml. flask (A) incorporating a No. 2 porosity sintered-glass disc (S) and capillary bypass-tube (C) of 2-mm. internal diameter connected to an inverted flask (B) *via* a B14 joint. In operation the powdered ZD$_{M}$C (0·3 g.) and the solution of the amine in toluene (25 ml.) were placed in the lower flask (A), *via* the entry (E), and the apparatus reassembled with a spring attached to the hooks (D) and placed in a thermostat bath using a device which allowed the apparatus to be oscillated gently through ±30° about an axis through (X) perpendicular to the plane of the diagram. After being agitated in this way for 24 hours to achieve equilibrium conditions the apparatus, whilst still totally immersed in the thermostat, was turned through an angle of 180° in the direction shown about the axis of oscillation bringing (A) above (B). The supernatant saturated solution in (A) could then flow under gravity *via* the sinter into (B) displacing the vapour in (B) *via* (C). When filtration was complete the flask (B) was removed, cooled, and the weight of the saturated solution contained therein determined. The total zinc content of the filtrate was then determined by transferring quantitatively the whole of the contents of the flask (B) (using more solvent) to an evaporation flask, removing the solvent and treating the residue at 100° for 5 minutes with concentrated hydrochloric acid (1 ml.), then for 5 minutes with water (2 ml.), and finally with cold water (100 ml.). Ammonia solution (3·5M, 5 ml.) was added to the zinc solution which was titrated with 0·01M-EDTA using Eriochrome Black T as indicator. From the value of the titre, and knowledge of the weight of solution taken for analysis, the equilibrium concentration of total soluble zinc species (moles per 1000 g. of solution) could be calculated.

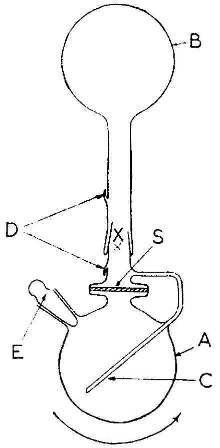

FIGURE 2. Solubility apparatus

Results.—Before selecting toluene as a convenient solvent for this work the solubility of ZD$_{M}$C in various solvents at room temperature was first roughly assessed by simply saturating the solvent, quickly filtering the solution, and analysing for zinc in the filtrate. In this way the data shown in Table 1 were obtained.

Precision measurements, using the apparatus described above, of the solubility of ZD_MC in pure toluene were then carried out using 24 hours for equilibration as shown to be adequate by independent experiments. These data (Table 2) are essential to the calculation of the dissociation constants. Proceeding then to the determination and interpretation of the solubilities of ZD_MC in several solutions of various amines at a variety of temperatures it was found in every case that a satisfactory linear relationship as predicted by theory [see equation (3)] was obtained. Presentation of the complete solubility data would be beyond scope of this Paper, but as example some of the results for the pyridine systems are shown in Table 3 and the linearity of the solubility *vs.* amine concentration plots is illustrated in Figure 3.

TABLE 1

Approximate solubilities (at 18—20°) of zinc dimethyldithiocarbamate in organic solvents

Solvent	Concentration (moles/litre × 10^4) of ZD_MC in saturated solution
n-Heptane, light petroleum (b. p. 30—40°), or diethyl ether	<0·8
Ethanol	4·5
Methanol	4·8
Carbon tetrachloride	12
Acetonitrile	41
Toluene	42
Acetone	76
Benzene	80
Tetrahydrofuran	163
Chloroform	336

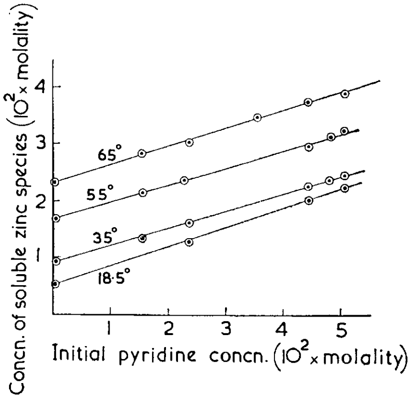

FIGURE 3. Solubility of zinc dimethyldithiocarbamate in solutions of pyridine in toluene

TABLE 2

Variation of the solubility of zinc dimethyldithiocarbamate in toluene with temperature

Temp.	18·5°	25·0°	35·0°	46·0°	55·0°	60·0°	65·0°
Solubility (10^4 × molality)	49·1	63·3	88·5	129·6	171·2	202·3	233·9

Heat of solution derived from log (solubility) *vs.* $1/T$ plot = 6·5 kcal./mole

The values of the dissociation constant, K_d, were then derived from the slope, obtained by the method of least squares, of straight lines, such as those shown in Figure 3, making use of equation (3). It should be noted that equation (3) is dependent on the assumption that only a 1 : 1 amine–ZD_MC complex is formed. If a 2 : 1 complex is formed then deviations from linearity of the S_T *vs.* $[A_0]$ plot should occur, but this deviation could lie within experimental error for significant amounts of ZA_2 for some amines. Detailed calculation shows that, for pyridine, the presence of up to 25% of the zinc as ZA_2 would not be detected by significant deviations from linearity. However, for the much stronger complexing amines, *e.g.*, piperidine, no more than approximately 3% of ZA_2 could be present. It follows that the dissociation constant for ZA_2 (K_{D2}) must be greater than $60K_D$ for piperidine. Since the ratios of successive formation (or dissociation) constants are approximately constant for a series of similar ligands with a given central atom or ion, it is probable that $K_{D2} > 60K_D$ for the weaker complexing amines also. Consequently, for pyridine, the concentration of ZA_2 is not likely to be more than 1% of the total

TABLE 3

Solubilities of zinc dimethyldithiocarbamate in some solutions of pyridine in toluene at various temperatures

Concentration of pyridine	Concentration ($10^4 \times$ molality) of soluble zinc species in ZD_MC-saturated solution at			
($10^4 \times$ molality)	18·5°	35°	55°	65°
0	49·1	88·5	171	234
153	—	135	218	283
236	132	164	240	302
447	208	232	301	367
487	—	246	321	—
506	231	253	330	378

TABLE 4

Dissociation constants (K_d) and thermodynamic data (free energies, ΔF, heats, ΔH, and entropies, ΔS, of dissociation) of 1 : 1 complexes of amines with zinc dimethyldithiocarbamate in solvent toluene

Amine (A)	Temp.	10^4K_d (moles/1000 g. solution)	ΔF (25°) (kcal.)	ΔH (kcal.)	ΔS (e.u.)	pK_d *	pK_a (AH^+) †
Aniline	25°	9200	0·05	—	—	0·04	4·58 [a]
Pyridine	18·5	89·2	2·60	7·6	17	1·91	5·23 [a]
	25·0	122					
	35·0	186					
	46·0	288					
	55·0	386					
	65·0	560					
4-Methylpyridine	25·0	45·4	3·19	9·6	21	2·34	6·05 [b]
	46·0	126					
2-Methylpyridine	25·0	890	1·43	(7)	(17)	1·05	5·96 [b]
	46·0	1860					
2,4,6-Trimethylpyridine	25·0	19,000	−0·39	(7)	(26)	−0·28	7·45 [b]
	46·0	44,000					
n-Butylamine	18·5	5·0	4·31	7·5	11	3·16	10·61 [c]
	25·0	6·9					
	35·0	10·3					
	55·0	23·0					
	65·0	30·2					
t-Butylamine	18·5	17·8	3·52	9·8	21	2·58	10·45 [c]
	25·0	26·3					
	35·0	43·2					
	46·0	69·6					
	55·0	118					
	65·0	194					
Ethylamine	25·0	3·9	4·65	—	—	3·41	10·72 [c]
Di-n-butylamine	18·5	22·2	3·36	8·9	19	2·47	11·31 [c]
	25·0	34·1					
	35·0	56·9					
	46·0	87·7					
	55·0	134					
	65·0	198					
Pyrrolidine	25·0	4	4·6	—	—	3·4	11·32 [c]
Piperidine	25·0	3	4·8	—	—	3·5	11·23 [c]
Morpholine	25·0	7·7	4·23	—	—	3·11	8·36 [c]

* $-\log_{10}$ [dissociation constant, K_d at 25°]. † $-\log_{10}$ [dissociation constant of corresponding ammonium ion in water at 25°].

[a] Data of ref. 2; [b] data of ref. 3, broadly confirmed by refs. 4 and 5; [c] data of ref. 6.

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[2] "Handbook of Chemistry and Physics," 44th edn., Chemical Rubber Publishing Company, Cleveland, Ohio, U.S.A., p. 1749.

[3] A. Gero and J. J. Markham, *J. Org. Chem.*, 1951, **16**, 1835.

[4] N. Ikekawa, Y. Sato, and T. Maeda, *Pharm. Bull.* (*Japan*), 1954, **2**, 205.

[5] R. J. Bruehlmann and F. H. Verhoek, *J. Amer. Chem. Soc.*, 1948, **70**, 1401.

[6] H. K. Hall, *J. Phys. Chem.*, 1956, **60**, 63.

zinc concentration. Hence, 2 : 1 complexes need not be considered further. From the variations of K_d with temperature, determined for most amine systems, it was possible using the familiar relationships: $\Delta F = -\boldsymbol{R}T \ln K_d$, $\Delta H = -R\partial(\ln K_d)/\partial(1/T)$, and $\Delta S = (\Delta H - \Delta F)/T$, to arrive at the free energies (25°), heats, and entropies of dissociation of the amine complexes.

Table 4 presents these data together with pK_d and pK_a values as convenient measures, respectively, of amine–ZD_MC affinities and aqueous amine-proton affinities in anticipation of the following Discussion.

A consideration of the probable errors involved in the determinations of the K_d values leads to the conclusion that for pyridine at 25° the error in K_d is approximately 2·5%, and the errors in ΔH and ΔS are 5 and 10%, respectively. For the amine complexes of very high or very low stability the errors are likely to be much greater and in these cases the values have been recorded in parentheses in the Table.

DISCUSSION

The main outcome of this and earlier [1] work is that zinc dimethyldithiocarbamate (ZD_MC) can be regarded as a weak Lewis acid-type acceptor molecule. For a range of amines the affinities of which for the aqueous proton vary by seven powers of ten as indicated by the K_a values, the affinities, indicated by K_d, towards ZD_MC cover a range of four powers of ten. In contrast with the simple correlation between the basicities of amines and the affinities of amines for sterically uncomplicated acceptors, in aqueous solutions, *e.g.*, Ag^+,[5] the affinities of various amines for ZD_MC are only broadly related to aqueous basicities. This is illustrated in Figure 4 where we have compared pK_d and pK_a values as defined by the equations

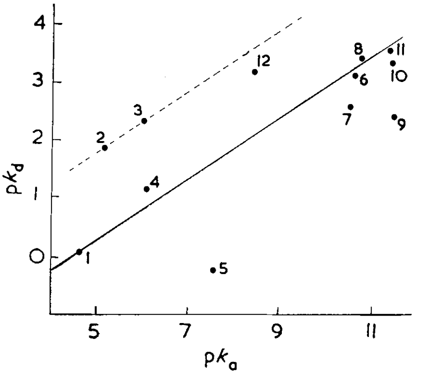

FIGURE 4. Relationship between amine–proton and amine–zinc affinities. Numbers refer to data on (1) aniline, (2) pyridine, (3) 4-methylpyridine, (4) 2-methylpyridine, (5) 2,4,6-trimethylpyridine, (6) n-butylamine, (7) t-butylamine, (8) ethylamine, (9) di-n-butylamine, (10) pyrrolidine, (11) piperidine, and (12) morpholine

$$[ZD_MC][\text{Amine}]/[1:1 \text{ complex}] = K_d; \; pK_d = -\log_{10}K_d \qquad (4)$$

$$[H^+][\text{Amine}]/[\text{Protonated amine}] = K_a; \; pK_a = -\log_{10}K_a \qquad (5)$$

The solid line is drawn, with some reservations, in an attempt to indicate the general importance of basicity on the affinity of simple primary amines for the zinc centre. Its value for the present discussion is that points in the diagram which fall above or below the line must represent the special incursion of additional " extra-basicity " factors, the magnitude and nature of which can then be considered.

It is first worth noting in Figure 4 that the data for pyridine and 4-methylpyridine, amines the steric requirements of which at the zinc centre should be closely similar, form a line above and almost parallel to our general line. The distance between the lines, *i.e.*, *ca.* 1·5 pK_d units, represents an added driving force of ~2 kcal. for the co-ordination of pyridine–nitrogen over and above that which obtains for co-ordination of primary-amine nitrogen at comparable basicities. This effect is even more marked with trimethylboron [7-9] for which the stabilities with ethylamine and 4-methylpyridine are approximately

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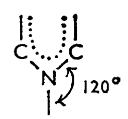
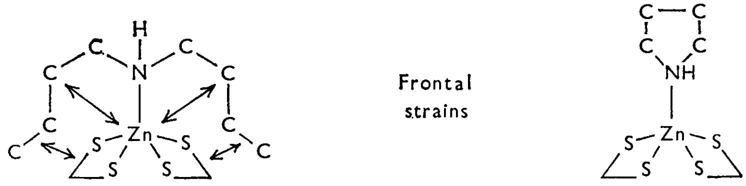
[7] H. C. Brown and G. K. Barbaras, *J. Amer. Chem. Soc.*, 1947, **69**, 1137.
[8] H. C. Brown and G. K. Barbaras, *J. Amer. Chem. Soc.*, 1953, **75**, 6.
[9] H. C. Brown, M. D. Taylor, and S. Sujishi, *J. Amer. Chem. Soc.*, 1951, **73**, 2464.

the same in spite of the large difference in basicity of the amines. This may be due to the lower steric requirements of pyridine–nitrogen in the complexes where atoms neighbouring nitrogen are mutually disposed at angles of 120°, whereas atoms neighbouring nitrogen in complexes of primary and other aliphatic amines would be interdisposed at nearer 109·5° assuming approximately tetrahedral hybridisations at nitrogen. Clearly, the sharper the angle the greater is the steric problem. On the other hand, for the amine complexes of Ag^{+}, in which steric requirements are likely to be much less severe, the $\mathrm{p}K_{\mathrm{d}}$ values vary linearly with the $\mathrm{p}K_{\mathrm{a}}$ values.[5]



Further reference to Figure 4 shows, however, that when methyl groups are introduced into the 2-, or 2- and 6-, positions of the pyridine ring the affinities for the zinc centre drop markedly. Thus, the position of 2-methylpyridine (4) is 1·23 $\mathrm{p}K_{\mathrm{d}}$ units (1·68 kcal.) below that of a hypothetical sterically unhindered pyridine of identical basicity * [see also 4-methylpyridine (3)], and for 2,4,6-trimethylpyridine (5) this difference is 3·32 $\mathrm{p}K_{\mathrm{d}}$ units (4·51 kcal.). Thus it is tempting to suggest that each 2- or 6-methyl group contributes *ca.* 2 kcal. of steric strain repulsion in the co-ordination of the pyridine to $\mathrm{ZD_{M}C}$. The magnitude of these strains, however, is relatively small compared with that discovered by Brown and Barbaras[7] for complexes of the pyridines with trimethylboron, although larger than the effects found by Graddon and Watton[10] for the complexes with copper(II) β-diketone chelates in organic solvents.

Considering now differences in affinities of different classes of aliphatic amines for $\mathrm{ZD_{M}C}$, ethylamine (8) and pyrrolidine (10) have identical affinities for the zinc centre in spite of pyrrolidine being the more basic by 0·6 $\mathrm{p}K_{\mathrm{a}}$ units. However, if a secondary amine of the open-chain kind, *e.g.*, di-n-butylamine (9) is considered we see that this has an affinity some 1·6 kcal. lower than that of a simple isobasic primary amine. Setting this beside the earlier result[1] that triethylamine has an extremely low affinity for $\mathrm{ZD_{M}C}$ it emerges that introduction of alkyl groups on nitrogen to beyond the primary amine stage is of no advantage in increasing the amine's affinity for $\mathrm{ZD_{M}C}$. Further comparisons of the secondary amines are of interest: piperidine (11) and pyrrolidine (10) ($\mathrm{p}K_{\mathrm{c}}$ values, 3·53 and 3·41) are considerably better donors towards $\mathrm{ZD_{M}C}$ than is di-n-butylamine (9) ($\mathrm{p}K_{\mathrm{d}} = 2{\cdot}60$) in spite of the three amines being nearly isobasic ($\mathrm{p}K_{\mathrm{a}}$ 11·23, 11·32, and 11·31). Because of the probable operation of considerable frontal strain in the di-n-butylamine complex as compared with the cyclic amine complexes as pictured below, the entropy of formation should be less favourable for the former.



(Present) (Absent)

[Arrows suggest repulsions]

The above explanation may also be extended to cover the large observed difference (200-fold) in the solubility of $\mathrm{ZD_{M}C}$ in tetrahydrofuran compared with that in diethyl ether if it is assumed that oxygen co-ordination to zinc is involved in the process of solution. The position of morpholine in Figure 4 is clearly very interesting. The quite remarkable affinity in this case seems to be outside the scope of simple steric explanation, and we are inclined to suggest that it may be due to this amine functioning as a bidentate ligand;

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* We need a term in this Discussion to define amines of identical basicities and suggest the adjective " isobasic."

[10] D. P. Graddon and E. C. Watton, *J. Inorg. Nuclear Chem.*, 1961, **21**, 49.

with morpholine in the "boat" conformation the oxygen atom might occupy a 6th-co-ordination position around zinc.

Now to return to the magnitude of steric effects in the co-ordination of amines to ZD_MC, which as we have seen in the case of the substituted pyridines are not nearly as great as for similar co-ordination to trimethylboron, a further interesting quantitative comparison can be made from the present data concerning n- and t-butylamines, these amines being almost isobasic. Taking the thermodynamic data it is calculated that, at 100°, the differences between the free energies of dissociation of the n- and t-butylamine complexes is 1·43 kcal./mole corresponding to a K_d ratio of 8·2. In contrast, Brown *et al.*[8,9] find the dissociation constant for the gas-phase decomposition of t-butylamine–trimethylboron to be 200 times that of the n-butylamine analogue. Assuming that this comparison is not materially affected by the solvent factor it becomes clear, taking trimethylboron as a reference acceptor, that the methyl groups of *t*-butylamine are only weakly engaged with repulsive fields near the zinc atom.

It is considered that the generally lower importance of steric effects in co-ordination of amines to ZD_MC as compared with those obtained during co-ordination to trimethylboron can be attributed partly to the larger size of the zinc centre with correspondingly greater spaces between ligand atoms, and partly to the fact that the tighter (and shorter) bonds for the boron co-ordination would place further restrictions on the free volume near the central atom available to the ligand's substituents.

Viewing the present results broadly from a thermodynamical aspect one notes that for the range of amines studied one has a spread of ΔH values of 6·6—9·8 kcal., indicative incidentally of fairly weak Zn–N bonds, whereas the spread of ΔS values is ~8—26 entropy units. This means that, at ordinary temperature, differences in heats (3·2 kcal./mole) tend to contribute rather less than do entropy differences ($T\Delta S$ = 5·5 kcal./mole) to the general stability of 1 : 1 amine–ZD_MC complexes. Also it should be noted that, although the heats are favourable to complex formation, the entropies of formation are negative and unfavourable. This competition for stability is also apparent for the amine–trimethylboron complexes [7-9] in the gaseous state and for the amine–copper bisacetylacetonate [11] complexes in benzene. In all three series (Zn, B, and Cu) both the heat and entropy of formation become more negative going from pyridine to 4-methylpyridine and thus provide a relatively small change in stability. In the Zn series the heat of formation for 2-methylpyridine is less negative than for 4-methylpyridine and is the major factor contributing to the lower stability of the former and could be attributed to steric interference of the 2-methyl group producing a weaker Zn–N bond. The smaller entropy change for n-butylamine compared with di-n-butylamine is consistent with a greater loss of rotational freedom on complex formation for the latter. The corresponding figure for t-butylamine might suggest some preferred orientation by rotation about the N–C bond of the three methyl groups with respect to the zinc centre, thus preventing too much interference with the Zn–N bond but providing additional entropy loss on formation. Any comparison between the aliphatic and aromatic amines on an entropy basis is difficult in view of possible solvent effects.

This work has in part been admitted as an Industrial Training and 4th year Project requirement leading to the award to one of us (D. S.) of the Diploma of Technology. The valuable practical contribution of Mr. F. H. Devitt to the early part of this work is gratefully acknowledged.

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[11] W. R. May and M. M. Jones, *J. Inorg. Nuclear Chem.*, 1963, **25**, 507.