FACTORS AFFECTING THE DEGREE OF ASSOCIATION OF ALKYL- AND HYDRIDO-ZINC COMPOUNDS *

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Summary

A tendency to complete the coordination shell of the zinc atoms provides a strong driving force for association of alkyl- and hydrido-zinc compounds, but the extent and manner of such association is largely controlled by steric effects.

Introduction

In presenting this review the authors wish to acknowledge the leadership, stimulation, generous encouragement and advice afforded by Geoffrey Coates during their research studies at Durham. By way of tribute this presentation surveys the diverse range of structures of organozinc compounds of the type RZnX. This unique study was initiated and promulgated as a direct result of Coates' perception of those factors which determine the remarkable range of association of these compounds.

The class of compound RZnX in which zinc is covalently bound to one alkyl group or hydrogen (R) and to one electronegative atom or group (X) leaves the metal atom coordinatively unsaturated. This deficiency provides a strong driving force for the fundamental molecule to associate in such a way that coordinate links are formed between the atoms of the electro-negative group, and the metal. Professor Coates and his group during the 1960's prepared examples of such molecules exhibiting degrees of association of 2, 3, 4, 5, 6, 8 and ∞ by the reaction of R_2Zn with a donor molecule containing an acidic hydrogen atom [1–3].

Several factors are likely to influence the manner in which the monomer units polymerise, and even when the degree of association is known it is not always

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* Dedicated to Professor G.E. Coates on the occasion of his 70th birthday.

possible to predict the structure of the product successfully [1,4]. This survey of the crystal structures [4–10] of a group of zinc-containing molecules indicates the order of importance in which the various factors exert their influence.

Influence on the degree of association

Seven factors considered likely to affect the degree of association and the ultimate shape of organo-zinc molecules RZnX, are listed below. Four of them have been pointed out in a discussion of the association of organometallic compounds of a Group III acceptor bound to a Group V atom [11] but are applicable here also.

(i) Entropy. The greater the number of independent molecules the higher will be the entropy of the system. Entropy thus favours the smallest degree of association.

(ii) Coordination saturation. The driving force for association involves the incomplete outer electron shell of 2-coordinate zinc. Once the metal attains a coordination number of 4 the shell will be complete.

(iii) Valence angle deformation. Atoms involved in the coordination bonds formed during association, are likely to be sp^3-hybridised and thus suffer valence angle deformation if constrained to take part in four-membered rings. Valence angle distortion is tolerated more readily by heavier elements than by those of the first period [12].

(iv) Steric influence of bulky substituents. Bulky substituent groups in X are forced together less around small than around large rings and will thus tend to favour lower degrees of association.

(v) Nature of the donor atom. Atoms from Group VI have 2 lone pairs of electrons and hence, in some circumstances, take part in 2-coordinate links to zinc whereas atoms from Group V have only 1 lone pair to contribute.

(vi) Inner core repulsions of bulky atoms. An unfavourable radius ratio involving large atoms will tend to discourage the formation of 4-membered rings.

(vii) The nature of intermediate species. The outcome of the association process may be influenced by the type of any intermediate species which is formed during the reaction. Such an influence is likely to be most significant in the case of X groups containing more than one donor atom.

The above list is one entry shorter than it might be for compounds of other Group II elements such as beryllium and magnesium since none of the zinc compounds examined so far exhibits electron-deficient bridging alkyl bonds.
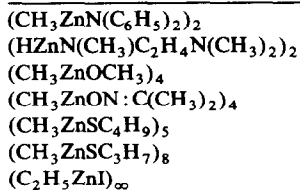
The list may not be exhaustive but it includes several factors which appear to be important in determining molecular shape among zinc compounds, as shown below.

The molecular structure

The group of zinc structures available for consideration (Table 1) includes examples of the metal bonded to nitrogen, oxygen, sulphur and halogen. The molecular structures adopted are shown in figs. 1–7 and although a few other structures of analogous molecules are known, e.g. [EtZn(Et)(Bu^t)NC(H)=C(Me)O]$_2$ [13] these fit the pattern in the range of structures described herein.

Methyl(diphenylamino)zinc (Fig. 1) is dimeric both in benzene solution [2] and in the crystal [5]. The molecule has a four-membered ring in which the zinc atom achieves a coordination of 3. Further association (e.g. to form larger rings with

TABLE 1

ASSOCIATED ALKYL AND HYDRIDO ZINC COMPOUNDS OF TYPE RZnX

$(CH_3ZnN(C_6H_5)_2)_2$
$(HZnN(CH_3)C_2H_4N(CH_3)_2)_2$
$(CH_3ZnOCH_3)_4$
$(CH_3ZnON:C(CH_3)_2)_4$
$(CH_3ZnSC_4H_9)_5$
$(CH_3ZnSC_3H_7)_8$
$(C_2H_5ZnI)_\infty$

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lower valence angle deformation) is prevented by the presence of the bulky diphenylamino groups, by consideration of entropy or both. It is not possible for the zinc atom to achieve a coordination of four in a simple way when the group X contains only a single nitrogen atom as the donor atom. When X contains two nitrogen atoms however as in hydridotrimethylethylenediamino zinc (Fig. 2) then a dimer may be formed [6] in which the second nitrogen atom contributes its lone pair to complete the metal coordination. In both these examples, bond angles in the ring are near to 90°. Substantial valence angle deformation is tolerated in preference to more associated forms.

In methylzincmethoxide (Fig. 3), where the donor atom is from Group VI both the lone pairs of electrons are used in coordination to zinc and a cubane-like tetramer results [7]. This arrangement represents the lowest degree of association in which a zinc compound containing a single donor atom in the fundamental molecule may achieve four coordination for the metal. Evidently, the presence of bulky substituents at R and X may preclude the possible adoption of this economic structure since, in solution at least, t-butylzinc t-butoxide is only dimeric [14].

The structure of methylzinc methoxide, while appearing an efficient means of achieving four coordination for the metal, imposes substantial valence angle strain on all the atoms involved in the central cube. The acetoximate derivative of methyl zinc (Fig. 4) has nitrogen as well as oxygen in the donor group and this provides a means of achieving a complete coordination shell for the zinc within a tetrameric
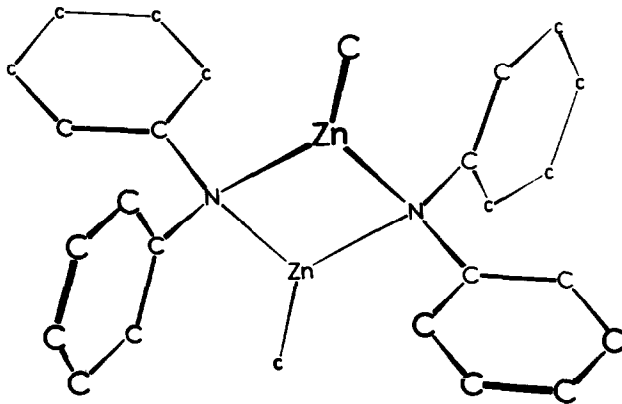

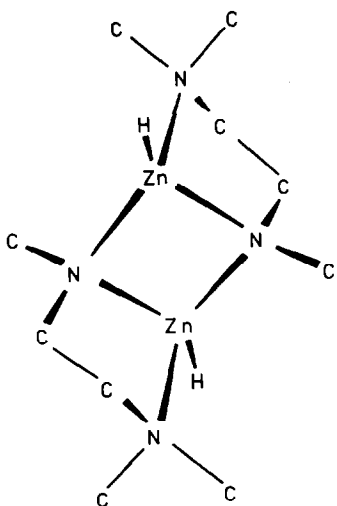Fig. 1. Molecular structure of $(CH_3ZnN(C_6H_5)_2)_2$. Hydrogen atoms not shown [5].

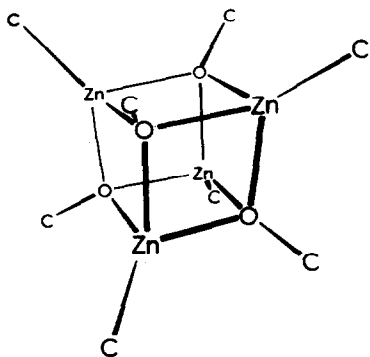Fig. 2. Molecular structure of $(HZnN(CH_3)C_2H_4N(CH_3)_2)_2$. Non-hydride hydrogen atoms not shown [6].

Fig. 3. Molecular structure of $(CH_3ZnOCH_3)_4$. Hydrogen atoms not shown [7].

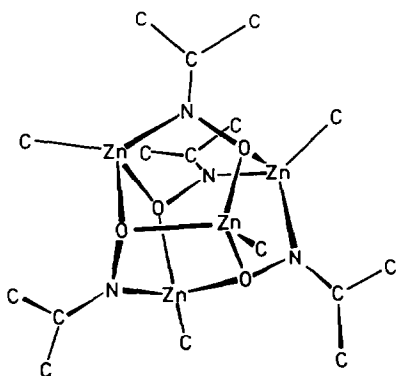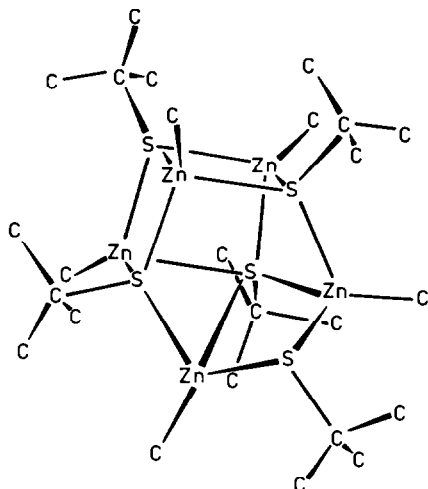Fig. 4. Molecular structure of $(CH_3ZnON:C(CH_3)_2)_4$. Hydrogen atoms not shown [4].

Fig. 5. Molecular structure of $(CH_3ZnSBu^t)_5$. Hydrogen atoms not shown [8].

unit and at the same time avoiding four-membered rings [4]. Only five- and six-membered rings are formed and in these the valence angle deformation is much less. The avoidance of four-membered rings is only achieved by using a single lone pair from oxygen and nitrogen rather than both lone pairs from oxygen. It is worth noting that the dimeric structure of hydridotrimethylethylenediamino zinc is not available to the acetoximate because the 2 donor atoms in the latter are too close together and would result in the formation of 3-membered rings.

With the derivatives of thiols the pattern is more complicated and unexpected degrees of association have been found. There are rather subtle influences exerted by small changes in the alkyl groups in X.

Methyl zinc methyl sulphide is insoluble in benzene and is believed to have a polymeric structure rather than the tetrameric form of methylzinc methoxide [2]. This finding might be counted as a surprise since the larger sulphur atom might be expected to tolerate participation in four-membered rings more readily than oxygen – not less. Indeed the structure of methyl zinc t-butyl sulphide (Fig. 5) is a highly irregular cage but exhibits six four-membered (and one six-membered) Zn–S rings in a pentameric unit [8]. All the zinc atoms are four coordinate and it is clear that four-membered rings are not avoided. Seven of the atoms (three zinc and four sulphur) lie near the corners of a cube and there appears to be no steric reason why a CH_3–Zn unit should not be incorporated at the remaining corner.

Substituting an isopropyl group for the t-butyl group in methylzinc t-butyl-sulphide causes an increase in the degree of association. In benzene solution methylzinc isopropyl sulphide is hexameric, but in the solid it is an octamer (Fig. 6). This molecule has a rather regular cage structure of Zn and S atoms, the surface of which is bounded by six four-membered and four six-membered rings [9]. All the zinc atoms are four-coordinate and once again four-membered rings are not avoided.

Changes in the nature of the alkyl groups are sufficient to alter the nature of the polymer formed by the sulphur compounds. A key factor seems to be the avoidance
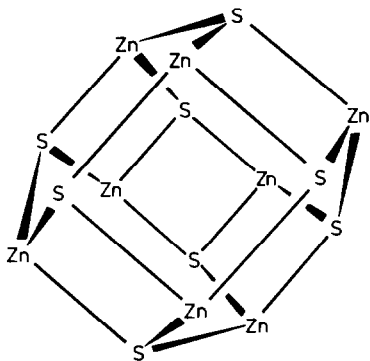
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Fig. 6. Molecular structure of $(CH_3ZnSPr^i)_8$. Alkyl groups not shown [9].

of a cubane-like tetramer. Although four-membered rings are allowed in molecules in conjunction with six-membered rings they are not tolerated as the only type of linkage. Potential inner core repulsions within the cubane-like structure may be responsible for this. In support of this concept we note that the octameric structure of methylzinc isopropyl sulphide can be derived from the cubane structure by opening out two cubes and fitting them together.

Finally, we consider the structures of ethylzinc halides. The chloride and bromide C_2H_5ZnCl and C_2H_5ZnBr are reported to be tetrameric in benzene solution [15] and are likely to have the cubane-like structure of $(CH_3ZnOCH_3)_4$ [7]. The iodide, on the other hand, is insoluble in benzene and in the solid state forms a coordination polymer [10] which is shown in Fig. 7. The positions of iodine and zinc atoms in the coordination polymer are such that only relatively small positional readjustments would be necessary to form the cubane-like structure presumed for the lower halides. That the polymeric structure, which contains only six-membered rings, is preferred, is probably due to the need to avoid inner core repulsions resulting from the size of the iodine atoms.
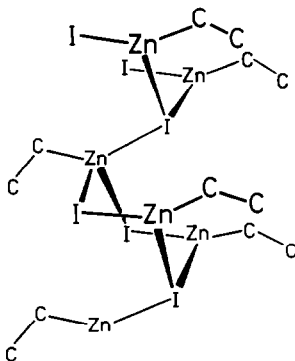

Fig. 7. Structure of the C_2H_5ZnI polymer. Hydrogen atoms not shown [10].

TABLE 2

TETRAHEDRAL COVALENT RADII (Å)

zinc	1.31
nitrogen	0.70
oxygen	0.66
sulphur	1.04
iodine	1.28

Conclusions

During the survey of the structures adopted by the zinc derivatives considered, most of the factors listed appeared at one stage or another.

The driving force towards coordination saturation for zinc is clearly demonstrated, and can only be resisted by the presence of bulky substituents. The effects of donor atoms from different groups allow the use of one or two lone pairs and a preference for avoiding the valence angle deformation dictated by four-membered rings where possible is also clear. Generally the molecules adopt the smallest, simplest unit allowed by other factors for entropy reasons and, finally, the importance of inner core repulsions appears to manifest itself in the avoidance of the cubane-like structure by those compounds in which zinc is bound to the largest electro-negative atoms, sulphur and iodine (see Table 2).

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