522. *Complexes of Amines with Zinc Dialkyldithiocarbamates.*

By G. M. C. Higgins and B. Saville.

Conditions for the preparation of crystalline 1 : 1 complexes of several amines with zinc dialkyldithiocarbamates have been established. The ready formation of the complexes of primary and secondary aliphatic amines and of pyridine, and the failure to isolate complexes of aniline, dibenzylamine, or triethylamine, point to the importance of basicity and steric requirements of the amine as factors governing the stability of these co-ordination compounds.

Piperidine has also been shown to give a 1 : 1 complex with zinc diethyldiselenocarbamate and with cadmium diethyldithiocarbamate, the latter probably being the first recorded example of 5-co-ordinate cadmium.

Infrared-spectroscopic and chemical-kinetic methods have been used to gain information on (i) the dissociation of certain complexes in solution, and (ii) perturbations in the electronic structure of the dialkyldithiocarbamate ligands caused by the co-ordination of the amine to the metallic centre.

THE purpose of this paper is to call attention to the existence of complexes of one molecule of an amine with one of a zinc dialkyldithiocarbamate, $Zn(S\cdot CS\cdot NR_2)_2$.

Certain derivatives of this class are very active accelerators of vulcanisation of rubber by sulphur [1-3] and are considered of importance in agricultural problems.[4] The literature records the preparation of a 1 : 1 complex of zinc dimethyldithiocarbamate (ZD_MC) with ammonia,[5] and patent references to its complexes with cyclohexylamine [1] and monoalkyl derivatives thereof.[2] The increased solubility of this dithiocarbamate in benzene containing amines has been ascribed [6] to the existence of soluble complexes.

These compounds are also interesting as apparently including novel penta-co-ordination of zinc. Also it is important, in connexion with the acceleration of vulcanisation, to know whether co-ordination of an amine to a metal changes the nucleophilic properties of a dialkyldithiocarbamate group.

1 : 1 Complexes of primary and secondary aliphatic or cycloaliphatic amines with zinc

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[1] B.P. 486,109/1938.

[2] U.S.P. 2,231,301/1943.

[3] U.S.P. 2,409,109/1946.

[4] Kenworthy, *Science*, 1947, **105**, 238 (*Chem. Abs.*, 1947, **41**, 2524); Siggers, *J. Forestry*, 1951, **49**, 350 (*Chem. Abs.*, 1951, **45**, 6333); Frans and Aldrich, *Proc. Northeast States Weed Control Conf.*, 1951, 165 (*Chem. Abs.*, 1951, **45**, 8184); Fitzwater, *Amer. Nurseryman*, 1956, **104**, 92 (*Chem. Abs.*, 1957, **51**, 1523).

[5] Bedford and Gray, *Ind. Eng. Chem.*, 1923, **15**, 720.

[6] Tsurugi and Nakabayaski, *J. Soc. Rubber Ind. Japan*, 1952, **25**, 267.

dimethyl- or diethyl-dithiocarbamate are conveniently prepared by adding the powdered salt to a slight excess of the amine in warm benzene. The complexes crystallise on cooling, evaporation, or on addition of light petroleum. They are usually white plates or needles whose analyses correspond to 1 : 1 complexes although, if left in the atmosphere for some hours, they lose amine. The compound of zinc dimethyldithiocarbamate with benzylamine, however, is stable *in vacuo* for several hours. In most cases the complexes are significantly more soluble in benzene, acetone, etc., than is the parent salt, but the cyclohexylamine complexes are rather insoluble. The melting points and ease of crystallisation are in a sequence to be expected from considerations of the degree of disorder in the corresponding amines.

Table 3 (p. 2816) describes complexes from eight amines. Dibenzylamine and triethylamine failed to yield isolable complexes, although they are moderately strong bases, and aniline gave no complex whereas pyridine did; thus it appears that, whilst both steric requirements and basicity of the amines are factors in determining the stability of these complexes, the former is perhaps the more important.

Piperidine gives similar 1 : 1 complexes with zinc diethyldiselenocarbamate * and with cadmium diethyldithiocarbamate. The latter result may represent the first example of penta co-ordinate cadmium.

Association of Piperidine with Zinc Dialkyldithiocarbamates in Solution.—In order to investigate the formation and dissociation of one of the above complexes in solution the infrared spectra of zinc dibutyldithiocarbamate (ZD_BC) in carbon tetrachloride solution in the presence of various proportions of piperidine were examined.

An absorption band at 3245 cm.$^{-1}$ in the spectra of these solutions has been provisionally assigned to the ν(N–H) vibration of the complexed amine, indicating a shift of -97 cm.$^{-1}$ on complex-formation. The intensity of this band was proportional to piperidine concentration when $[ZD_BC] > [\text{Piperidine}]$ but became independent of piperidine concentration when $[\text{Piperidine}] > [ZD_BC]$. This confirms the existence of a 1 : 1 complex in solution as well as in the solid state.

The apparent extinction coefficient of the band at 3245 cm.$^{-1}$ was obtained from the linear relation between intensity and dithiocarbamate concentration in the presence of a considerable excess of amine. A similar value was obtained from the converse experiment.

By using this value to determine the concentration of complex at various dilutions of a system containing equimolar concentrations of amine and zinc dibutyldithiocarbamate in carbon tetrachloride, and assuming the dissociation equilibrium

$$PZ \rightleftharpoons P + Z \qquad \text{(i)}$$

(where PZ, P, and Z represent respectively the undissociated complex, piperidine, and the dithiocarbamate), it was shown that the dissociation constant, K, for reaction (i), *i.e.*, $[P][Z]/[PZ]$, is about 10^{-3} mole l.$^{-1}$ at ambient temperature.

A value of K for dissociation of piperidine–zinc diethyldithiocarbamate in chloroform was determined by an alternative method. This rests on reaction of the complex with 1-chloro-2,4-dinitrobenzene (RX) to give only 1-(2,4-dinitrophenyl)piperidine, showing that the only effective nucleophil in the reaction is free piperidine. Zinc diethyldithiocarbamate reacts at a measurable rate with 1-chloro-2,4-dinitrobenzene in chloroform only at elevated temperatures. Hence, by measuring the first-order rate constants for decomposition of the chlorodinitrobenzene in various dilutions of piperidine–zinc diethyldithiocarbamate in chloroform under conditions where $([PZ] + [P] + [Z]) \gg [RX]$, the dissociation constant K can be calculated by use of the following argument.

Let the observed rate constant for decomposition of the chloronitrobenzene be k_0 and

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* On the basis of positions of N–H stretching bands in the infrared spectra of dithio- and diseleno-analogues it is concluded that the amine is bound more firmly to this compound than it is to zinc diethyldithiocarbamate.

the second-order rate constant for its bimolecular reaction with piperidine be k_2, then, from simple theory,

$$k_0 = k_2[\mathrm{P}]; \text{ or } [\mathrm{P}] = k_0/k_2 \qquad \text{(ii)}$$

Substitution of the value of [P] from eqn. (ii) into (i), written as (iii)

$$[\mathrm{P}]^2/(C - [\mathrm{P}]) = K, \qquad \text{(iii)}$$

where C is the *prepared* concentration of the complex, gives

$$k_0{}^2/k_2{}^2(C - k_0/k_2) = K. \qquad \text{(iv)}$$

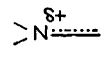
Rearrangement gives

$$k_0 = k_2{}^2K(C/k_0) - k_2K, \qquad \text{(iva)}$$

according to which a plot of k_0 against C/k_0 should be linear with a negative intercept. From the slope and the intercept, k_2 and K can be calculated; the value of k_2 derived can be confirmed by a normal determination. Table 1 records rate measurements for application to this analysis from which K is calculated to be $0{\cdot}91 \times 10^{-3}$ mole l.$^{-1}$. The value of k_2 also derived is 3·2 l. mole^{-1} min.$^{-1}$, compared with a conventionally determined value of 3·75.

These results, though limited, suggested that affinity of zinc dialkyldithiocarbamates for a representative amine is fairly high.

In order to gain insight into the structure of the complexes it seemed desirable to study the spectroscopic consequences of amine association with dithiocarbamates. Preliminary results may be summarised as follows: (*a*) The infrared spectrum of methyl dimethyldithiocarbamate is unaffected by addition of a mol. of piperidine in carbon tetrachloride solution. (*b*) The complexes, solid or in solution, are characterised by bands in the N–H stretching region, these being considerably more intense than bands in the corresponding amines (cf. amine complexes of platinum and palladium [7]). The frequency of the band is lowered as the strength of the nitrogen–metal bond is increased, for example, by increasing the base-strength of the amine or by changing sulphur for selenium in the carbamate ligands. (*c*) In some cases the complexes, irrespective of the nature of the dithiocarbamate, exhibit new absorption bands characteristic of the amine ligand; *e.g.*, piperidine complexes show a band at 870 cm.$^{-1}$ and cyclohexylamine complexes at 1050 cm.$^{-1}$. These bands are absent from the spectra of the corresponding amines and their intensities are unaffected by the presence of an excess of the amine. (*d*) The positions of many bands in the spectra of zinc dialkyldithiocarbamates are shifted in the presence of amines. The most significant shift occurs with respect to those bands which have been assigned to the stretching (A) of the dithiocarbamate ligands.[8] These bands, occurring at ~1500 cm.$^{-1}$, move to lower frequencies in the amine complexes; there are, however unassigned bands, *e.g.*, at ~1420 cm.$^{-1}$ for all zinc diethyldithiocarbamate complexes, which also show frequency shifts in the same direction on complex formation.


(A)

Observation (*a*) indicates the importance of the metal for existence of complexes in solution, and proves that amine-addition to a thiocarbamyl group cannot be important.

TABLE 1.

First-order rate constants at 25° for the decomposition of 1-chloro-2,4-dinitrobenzene (initially 0·0005M) in chloroform solutions of piperidine–zinc diethyldithiocarbamate (initially C moles l.$^{-1}$).

10^2C	0·909	1·82	3·64	5·45	9·09
10^2k_0 (min.$^{-1}$)	0·905	1·30	1·97	2·46	3·28
C/k_0 (mole l.$^{-1}$ min.)	1·01	1·41	1·77	2·23	2·67

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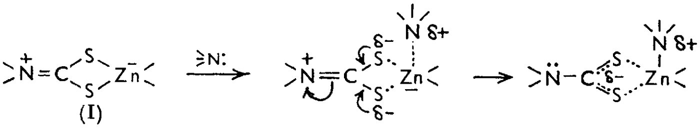
[7] Chatt *et al.*, *J.*, 1955, 4461; 1956, 2712; 1958, 3203.
[8] Chatt, Duncanson, and Venanzi, *Nature*, 1956, **177**, 1042; *Suomen Kem.*, 1956, **29**, *B*, 75.

Evidence (*b*) requires little comment since it is consistent with use by the nitrogen of its 2*p*-electron pair for bond formation with a suitable vacant orbital, presumably available on the metal atom. The new bands described under (*c*) are also consistent with the nitrogen's being rendered positive in the complex and having a secondary effect on the contiguous structure.

With reference to (*d*), if we accept that the 1500 cm.$^{-1}$ band is due to carbon–nitrogen partial-double-bond stretching, then the frequency shifts on complex-formation suggest that canonical structure (I) makes a more important contribution to the parent dithiocarbamate than it does to the complex. This conclusion supports the concept that with respect to co-ordinating an amine with the dithiocarbamate the zinc–sulphur bonds are rendered more ionic, as indicated in the annexed scheme:



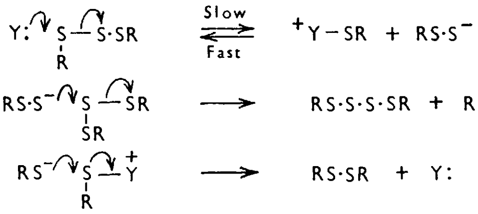
(I)

This interpretation is in agreement with Nyholm's general principle[9] that the larger the number of donor ligands around a metal the lower is the charge donated by each.

If, then, the sulphur atoms of the amine complexes carry higher negative charge-densities than do those of the parent dialkyldithiocarbamates one might expect corresponding differences in the rate of some chemical reaction specifically involving the 3*p*-electrons of the sulphur groups. Study of this would require a nucleophilic displacement by the dialkyldithiocarbamate ligands at an appropriate electrophilic centre. It is believed that the polar disproportionation of a dialkyl trisulphide provides a convenient system of the required kind.

Although diethyl trisulphide is stable in dry heptane in the dark at 100°, it disproportionates into diethyl disulphide and higher polysulphides, *e.g.*, $2Et_2S_3 \longrightarrow Et_2S_2 + Et_2S_4$, under the influence of a nucleophilic catalyst by a mechanism such as:

[Y: = nucleophilic sulphur centre, R = Et]



Hence, the initial rate of formation of diethyl disulphide indicates the nucleophilic power of the catalyst employed. Accordingly, we have found that, whereas zinc dialkyldithiocarbamates and piperidine are separately rather weak catalysts for disproportionation of diethyl trisulphide (see Table 2) they are together much more active.

This suggests strongly that the sulphur atoms of the amine complexes are considerably more nucleophilic than are those of the parent dithiocarbamates, supporting our contentions regarding electron-density perturbations due to complex-formation with amines.

Significantly, the catalytic activity of a zinc dialkyldithiocarbamate is increased considerably when the amine : dithiocarbamate ratio is raised to well above unity. This seems consistent with reaction of the 1 : 1 complex with a further amine molecule to produce a low equilibrium concentration of a 2 : 1 complex which should have a very high intrinsic catalytic activity by virtue of still higher negative charge-densities on its sulphur

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[9] **Nyholm, *Proc. Chem. Soc.*, 1961, 279.**

TABLE 2.

Formation of diethyl disulphide * from diethyl trisulphide (0·300M) in heptane at 100° in presence of dithiocarbamate catalysts.

Catalyst	Catalyst concn. (M)	Concn. (10^3M) of disulphide formed in 7 hr.	24 hr.	Catalyst	Catalyst concn. (M)	Concn. (10^3M) of disulphide formed in 7 hr.	24 hr.
$\mathrm{ZD_EC}$ ‡	0·03	4	6	$\mathrm{ZD_BC}$ †	0·03	8	20
Piperidine	0·03	3	6	$\mathrm{ZD_BC}$ †	0·03	33	82
,, ...	0·30	8	26	Piperidine ...	0·03		
$\mathrm{ZD_EC}$ ‡	0·03	22	54	$\mathrm{ZD_BC}$ †	0·03	58	113
Piperidine	0·03			Piperidine ...	0·09		
$\mathrm{ZD_EC}$ ‡	0·03	113	117	Aniline	0·03	—	2
Piperidine	0·30			$\mathrm{ZD_EC}$ ‡	0·03	—	7
$\mathrm{ZD_EC}$ ‡	0·30	24	70	Aniline	0·03		
Piperidine	0·03						

* Concentration of diethyl disulphide in uncatalysed reaction is less than 1 × 10^{-3}M in 14 days at 100°. † Zn dibutyldithiocarbamate. ‡ Zn diethyldithiocarbamate.

atoms. In contrast, aniline, which appears not to co-ordinate with zinc diethyldithiocarbamate, does not activate this salt as a catalyst for the disproportionation of diethyl trisulphide.

Thus we consider this evidence to offer strong support for the operation of Nyholm's principle [9] with regard to amine complexes of zinc dialkyldithiocarbamates.

EXPERIMENTAL

Zinc dialkyldithiocarbamates were recrystallised several times from toluene or chloroform. Amines were commercial materials, except that piperidine was fractionated from the B.D.H. product (it had b. p. 105—106°). Other materials were of " AnalaR " grade.

Preparation of 1 : 1 *Amine–Zinc Dialkyldithiocarbamate Complexes.*—To a solution of the amine (*ca.* 0·03 mole) in benzene (20—40 ml.) at 50° was added, in portions, the powdered zinc dialkyldithiocarbamate (0·02 mole). On cooling of the resulting solution, or partial removal of the solvent, or addition of light petroleum (b. p. 40—60°; 100 ± 20 ml.), the products crystallised; they were collected, washed with light petroleum, and dried in air.

Details concerning these *complexes* appear in Table 3. Analyses for zinc were made by digesting a sample (*ca.* 80 mg.) of the complex in hot concentrated hydrochloric acid (1 ml.), adjusting the pH to ~9 with aqueous ammonia, and titrating equivalent Zn^{2+} with EDTA to an Eriochrome Black T end-point; the accuracy is considered to be very high.

TABLE 3.

1 : 1 Complexes of amines with zinc dialkyldithiocarbamates.

Amine	M. p.	Formula	Zinc (%) Reqd.	Zinc (%) Found
Dimethyldithiocarbamate				
n-Butylamine	132—133°	$C_{10}H_{23}N_3S_4Zn$	17·3	17·35
Cyclohexylamine	137	$C_{12}H_{25}N_3S_4Zn$	16·2	16·2
Benzylamine	117—118	$C_{13}H_{21}N_3S_4Zn$	15·85	15·8
Piperidine *	129—130	$C_{11}H_{23}N_3S_4Zn$	16·75	16·65
Pyridine	(High)	$C_{11}H_{17}N_3S_4Zn$	17·0	17·0
Diethyldithiocarbamate				
n-Butylamine	74·5°	$C_{14}H_{31}N_3S_4Zn$	15·1	15·1
Cyclohexylamine ‡	108—109	$C_{16}H_{33}N_3S_4Zn$	14·2	14·15
Dimethylamine	99·5—100·5	$C_{12}H_{27}N_3S_4Zn$	16·1	15·9
Diethylamine	87·5	$C_{14}H_{31}N_3S_4Zn$	15·1	15·2
Di-n-butylamine	51—52	$C_{18}H_{39}N_3S_4Zn$	13·3	13·25
Piperidine †	115—116	$C_{15}H_{31}N_3S_4Zn$	14·7	14·55

* Found: C, 33·6; H, 6·1; N, 10·6; S, 32·8. Required: C, 33·8; H, 5·9; N, 10·75; S, 32·8%. † Found: C, 40·5; H, 6·9. Required: C, 40·3; H, 2·0%. ‡ Found: C, 41·9; H, 7·2. Required: C, 41·8; H, 7·2%.

Zinc diethyldithiocarbamate was recovered unchanged from benzene solutions of triethylamine, dibenzylamine, and aniline.

Related Complexes.—Cadmium diethyldithiocarbamate was converted as above into its *complex* with piperidine; this product had m. p. 114—115° (Found: C, 36·2; H, 6·1; Cd, 22·8. $C_{15}H_{31}CdN_3S_4$ requires C, 36·5; H, 6·28; Cd, 22·8%). Also prepared was *piperidine–zinc diethyldiselenocarbamate*, orange-yellow, m. p. *ca.* 136° (decomp.) (Found: C, 28·8; H, 4·8; N, 6·5; Se, 48·8; Zn, 10·15. $C_{15}H_{31}N_3Se_4Zn$ requires C, 28·4; H, 4·95; N, 6·6; Se, 49·75; Zn, 10·3%).

Kinetics of Decomposition of 1-*Chloro*-2,4-*dinitrobenzene in Chloroform Solutions of Piperidine–Zinc Diethyldithiocarbamate.*—The product of reaction of the halide (70 mg.) with piperidine–zinc diethyldithiocarbamate (1·2 g.) in chloroform (10 ml.) after 24 hr. at 25° was established by washing the mixture with water and passing it through an alumina column with chloroform as eluent. The yellow band was eluted from the column and found to be free from zinc diethyldithiocarbamate (negative test with Cu^{2+} ions) and chromatographically homogeneous. Removal of the solvent gave 1-(2,4-dinitrophenyl)piperidine, m. p. and mixed m. p. 91—92°, which contained no sulphur (sodium fusion). This freedom proved the absence of 2,4-dinitrophenyl diethyldithiocarbamate from the product.

Kinetics of this reaction were studied by mixing a 0·1—0·01M-solution of the complex in chloroform (50 ml.) with a 0·0055M-solution of 1-chloro-2,4-dinitrobenzene in chloroform (5 ml.) at 25° and measuring the increase in the intensity of the yellow colour of the solution, by means of a Spekker Absorptiometer with violet filters, as a function of time. Absorptiometer readings were referred to a smooth calibration curve relating 1-(2,4-dinitrophenyl)piperidine concentration in chloroform to colour intensities. First-order plots for disappearance of the halide were linear up to at least 90% total reaction.

Infrared Spectra.—Solutions of the complexes in carbon tetrachloride were examined in a Hilger H 800 spectrometer with a sodium chloride prism. Spectroscopic assessment of dissociation of piperidine–zinc dibutyldithiocarbamate in carbon tetrachloride solution was achieved as follows. The extinctions of 0·02—0·04M-solutions of piperidine at the perturbed N–H stretching frequency (3245 cm.$^{-1}$) in the presence of a considerable excess (0·1M) of zinc dibutyldithiocarbamate were measured and shown to refer to virtually complete formation of undissociated piperidine–zinc dibutyldithiocarbamate. Since free piperidine has a weak N–H stretching frequency at 3342 cm.$^{-1}$ there is no interference from the amine with the absorption band of the complex at 3245 cm.$^{-1}$. Free zinc dibutyldithiocarbamate is also transparent in this region. Hence by measuring extinctions of various dilutions of equimolar piperidine and zinc dibutyldithiocarbamate together in carbon tetrachloride at room temperature the corresponding concentrations of the 1 : 1 complex were calculated, and, through mass-balance considerations, those of its dissociation partners. When such values were substituted into the appropriate mass-action equation (i), K values were obtained which varied from 1·16 to $0{\cdot}62 \times 10^{-3}$ mole l.$^{-1}$ for initial [Piperidine] = [Zinc dibutyldithiocarbamate] varying from 0·500 to 0·005M.

Activity of Dithiocarbamates and Amines as Catalysts in the Disproportionation of Diethyl Trisulphide.—Diethyl trisulphide [10] was obtained by two distillations with a purity of $>99{\cdot}9\%$. Gas–liquid chromatography showed it to contain *ca.* 0·05% of diethyl disulphide. A stock solution (0·600M) of this material in pure dry heptane containing n-decane (0·200M) as internal standard was prepared and stored in the dark. Equal volumes of this stock solution and pure heptane, or heptane solutions of amines, were mixed to achieve desired initial concentrations and added where necessary to solid dithiocarbamates. These mixtures, sealed in dry tubes in a vacuum, were heated at 100° for 7 or 24 hr. in light-proof apparatus. The concentrations of diethyl disulphide formed were determined by gas–liquid chromatography on Celite containing 20% of squalane at 100°, with reference to n-decane as standard. Each figure given in Table 2 is the means of three determinations.

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[10] Milligan, Saville, and Swan, *J.*, 1961, 4850.