

The Association of Alkali Metal *N,N*-Dialkyldithiocarbamates in Solution

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A large number of hydrated and non-hydrated alkali metal *N,N*-dialkyldithiocarbamates have been prepared. The hydrated compounds are completely dissociated in aqueous solution. The non-hydrated compounds are in general much more soluble in inert organic solvents such as benzene, chloroform, and petroleum ether than the corresponding hydrated forms, and were found in general to be low-polymeric in these solvents. Thus, the non-hydrated lithium complexes behave as hexamers and tetramers in solution. Gel chromatography showed at least two different molecular sizes.

In solution, the non-hydrated sodium complexes with straight carbon chains behave like dodecamers. The isopentyl homologue behaves as an octamer, while the isopropyl and isobutyl homologues are quite insoluble in inert organic solvents and are assumed to be high polymers.

The non-hydrated potassium complexes with straight carbon chains are hexameric, and only one molecular species is indicated by gel chromatography. The isopropyl and isobutyl homologues are insoluble in inert organic solvents and are probably high polymers.

The rubidium complexes show degrees of association from 4 to 9. It has been shown that the complexes consist of at least two molecular sizes, the distribution of which seems to be dependent on the temperature.

The cesium complexes are found to be tetrameric and existing as a single molecular species in solution.

In a series of investigations, one of the authors¹ has studied the behaviour of organic sulphur containing complexes of group I b elements in solution, especially dithiocarbamates, thiocarbamates, and thiolates of copper, silver, and gold. Most of these complexes were found to exist as discrete small aggregates, for example, dimers, tetramers, hexamers, octamers, and dodecamers in inert solvents such as benzene, chloroform, and carbon disulphide. Several of the complexes have been the subject of structural studies in the solid state, and in many instances unique bonding relationships were found.²

In order to throw further light upon the polymer formation, the investigation has been expanded to include organic sulphur containing complexes of

group I a. The aim of the present investigation was to find out if certain alkali metal compounds, which normally form bonds having considerable ionic character, are under certain circumstances able to associate to small aggregates in solution.

In a preliminary communication, the authors³ reported that some alkali metal dibutyldithiocarbamates actually do form small aggregates in chloroform solution. The present paper gives a more detailed description of these investigations, and a method of investigating the homogeneity of the complexes is presented.

RESULTS

Hydrated alkali metal *N,N*-dialkyldithiocarbamates

The sodium- and potassium dialkyldithiocarbamates in particular have found practical application. They are described in the monograph on dithiocarbamates and related compounds by Thorn and Ludwig.⁴ The inhibiting effect of sodium dithiocarbamates on the photosynthesis in green algae and submersed plants has been studied by Lindahl and one of the authors.⁵⁻⁹

The alkali metal *N,N*-dialkyldithiocarbamates have been prepared according to Delépine¹⁰ by reacting the appropriate dialkylamine with carbon disulphide and an alkali metal hydroxide. The products are in general recrystallized from benzene and chloroform containing a small quantity of water. The lithium, sodium, and potassium compounds crystallize with three molecules of water, whereas the rubidium and the cesium compounds crystallize with two or less.

Solubility, dissociation and stability. The solubility of the hydrated compounds in inert organic solvents such as benzene or chloroform increases with increasing length of the alkyl chains. Thus, Lindahl and Åkerström⁵ have shown that it is possible to extract sodium dialkyldithiocarbamates from aqueous solution with chloroform, and that the apparent distribution coefficient of the compounds increases as the length of the alkyl chains increases.

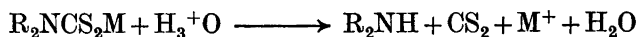
Osmometric molecular weight determination at 37°C has shown that the compounds are completely dissociated in aqueous solution (Table 1).

The dialkyldithiocarbamic acids are very unstable. Their alkali metal compounds are also unstable, although more stable than the free acids. The

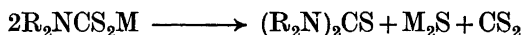
Table 1. Osmometric determination of the degree of dissociation in water solution.

Compound	Calc. conc. mmol/1000 g	Found conc. mmol/1000 g	Degree of dissociation α
(iso-C ₄ H ₉) ₂ NCS ₂ Li	117.9	248.0	1.05
(n-C ₅ H ₁₁) ₂ NCS ₂ Na	84.1	167.6	0.99
(n-C ₅ H ₁₁) ₂ NCS ₂ K	68.5	130.4	1.06
(n-C ₅ H ₁₁) ₂ NCS ₂ Rb	24.7	52.8	1.06
(n-C ₅ H ₁₁) ₂ NCS ₂ Cs	42.5	81.6	0.96

stability of the metal compounds increases from lithium to cesium, and their stability is of course very pH-dependent.¹¹ At low pH, the compounds decompose in solution:



Even in the solid state, a slow decomposition takes place, the rate of which increases with the temperature. Thus, the rate of decomposition increases by a factor of 8 between 7°C and 30°C¹¹ and seems to proceed as shown below:¹²



Non-hydrated alkali metal *N,N*-dialkyldithiocarbamates

1. *Preparation and properties.* The water of hydration of the alkali metal dialkyldithiocarbamates was removed as follows. The cesium and rubidium compounds were dried *in vacuo* over phosphorus(V) oxide. The potassium compounds, when dried in a similar way, still contained small quantities of water. The sodium and the lithium compounds were boiled in chloroform or benzene solution, and the water of hydration was removed azeotropically. However, the rate of decomposition increased appreciably during this procedure. Thus, when the water of hydration of the lithium compounds was removed, a white precipitate of lithium hydroxide was obtained, indicating a different path of decomposition from that mentioned previously.

All alkali metal dialkyldithiocarbamates are hygroscopic, and this property becomes more marked from cesium to lithium. Thus, crystals of the non-hydrated lithium and sodium compounds are rapidly transformed to a colourless liquid, thereafter recrystallizing as the hydrated forms. All operations with the non-hydrated dithiocarbamates must therefore be performed under a dry nitrogen atmosphere.

In general, the non-hydrated forms were much more soluble in inert organic solvents than the corresponding hydrated forms. However, the isopropyl and isobutyl homologues of sodium and potassium became insoluble in these solvents when the water of hydration was removed, recovering their solubility when some water, alcohol, or some other coordinating ligand was added.

The IR-spectra of the hydrated and the non-hydrated compounds were identical except for the two peaks at 3400 cm⁻¹ and 1610 cm⁻¹ in the hydrated compounds associated with the water of hydration. The water of hydration could be more easily removed from the isopropyl and isobutyl homologues of potassium by drying *in vacuo* or by gentle heating than the other homologues. By this drying procedure, the crystals lost their optical properties, but retained their outer form. On the other hand, the crystals of the other potassium compounds and the cesium and rubidium compounds retained their outer shapes as well as their optical properties after the dehydration procedure.

The non-hydrated forms of the sodium and lithium compounds crystallize as long fibrous threads, occupying the whole crystallization vessel. The corresponding hydrated forms crystallized as short lustrous needles.

2. *Molecular weight determination.* The degree of association of the non-hydrated alkali metal dialkyldithiocarbamates in benzene and in certain

cases ethanol-free chloroform has been investigated by ebullioscopic, cryoscopic, and osmometric methods. On account of their instability and temperature dependence of the molecular weight, the degree of association of these compounds, especially the most hygroscopic members, was found to fluctuate.

In order to understand more fully their behaviour in solution, it was important to study the degree of association at different temperatures. Thus, besides the ebullioscopic method, some compounds were investigated cryoscopically in benzene. However, owing to the low solubility for most compounds at 5°C, this method was limited to the higher homologues of the rubidium compounds. The osmometric method performed at 37°C was more suitable, since most compounds were sufficiently soluble at this temperature.

2a. *The lithium dialkyldithiocarbamates.* Only the molecular weights of the butyl and isobutyl compounds have been determined. The other homologues were too unstable and not readily crystallized. As shown in Table 2, both of the compounds investigated seem to exist as tetrameric and hexameric compounds in benzene solution.

2b. *The sodium dialkyldithiocarbamates.* These compounds are also very hygroscopic, but are somewhat more stable than the corresponding lithium compounds. The homologues with straight carbon chains have a degree of association of twelve. The sodium compounds with the isopropyl or isobutyl chains are insoluble in benzene or chloroform, and are probably high polymers. The isopentyl compound, however, is soluble in benzene and shows a degree of association of eight (Table 3).

The higher homologues containing straight carbon chains are very soluble in benzene and chloroform at room temperature. If the temperature of the solution is gradually decreased to 15–10°C, the compounds precipitate almost quantitatively. This marked difference in solubility may indicate a structural change, perhaps to a polymeric structure.

2c. *The potassium dialkyldithiocarbamates.* All homologues investigated show a degree of association of six (Table 4). The solubility in benzene at 5°C is not sufficient to perform a molecular weight determination. The isopropyl and isobutyl homologues are insoluble in all inert solvents (compare the corresponding sodium compounds) and are presumably high polymers.

2d. *The rubidium dialkyldithiocarbamates.* The higher homologues in the rubidium dialkyldithiocarbamate series generally have good solubility in benzene and chloroform. Molecular weight determinations have therefore been carried out at three different temperatures (Table 5). Thus, rubidium dipentylthiocarbamate shows a degree of association of five at 80°C, six at 37°C, and nine at 5°C. The molecular weight determinations at 80°C indicate that the rubidium compounds with straight carbon chains generally behave as pentamers and the branched compounds as tetramers. The rubidium dibutylthiocarbamate investigated by Aava and Hesse¹³ by X-ray crystallography is polymeric in the solid state, and the unit cell contains four formula units.

2e. *The cesium dialkyldithiocarbamates.* All the compounds investigated are tetrameric in inert organic solvents (Table 6). Their solubility is less than that of the rubidium compounds and not sufficient for cryoscopic investigations. An X-ray examination of cesium dibutylthiocarbamate by Aava and Hesse shows that the compound has a polymeric structure, composed of dimeric units.¹⁴

Table 2. Lithium *N,N*-dialkyldithiocarbamates, R_2NCS_2Li .

R	M.p. °C		Molecular weight ^a			Degree of association ^b		
	Anhydrous	Hydrated	$C_6H_6^{80}$	$C_6H_6^{37}$	$C_6H_6^5$	$C_6H_6^{80}$	$C_6H_6^{37}$	$C_6H_6^5$
Methyl	—	223—225 d.	—	—	—	—	—	—
Ethyl	106—108	94—95	—	—	—	—	—	—
Propyl	oil	64—65	—	—	—	—	—	—
Butyl	44—46	77—79	—	—	896	—	—	3.1—6.0 (11)
Isopropyl	139—140	70—71 d.	—	—	—	—	—	—
Isobutyl	97—99	67—68	880	1220	1261	4.0—4.3 (3)	6.3 (1)	5.9—6.2 (3)
Isopentyl	7—8	51—52	—	—	—	—	—	—

^a $C_6H_6^{80}$, $C_6H_6^5$, and $C_6H_6^{37}$ means that the determination of the molecular weights were performed ebullioscopically, cryoscopically and osmometrically at the temperatures 80°, 5°, and 37°C, respectively.

^b The figures within parentheses represent the number of experiments performed.

Table 3. Sodium *N,N*-dialkyldithiocarbamates, R_2NCS_2Na .

R	M.p. °C		Molecular weight ^a			Degree of association ^b		
	Anhydrous	Hydrated	$C_6H_6^{80}$	$C_6H_6^{37}$	$CHCl_3^{61}$	$C_6H_6^{80}$	$C_6H_6^{37}$	$CHCl_3^{61}$
Methyl	—	—	—	—	—	—	—	—
Ethyl	—	92—95	—	—	—	—	—	—
Propyl	128—129	53—54	—	—	2349	—	—	11.1—12.0 (3)
Butyl	123—125	39—40	2623	—	—	11.5—11.6 (3)	—	—
Pentyl	121—123	—	2565	2049	—	8.5—10.3 (3)	8.0 (1)	—
Isopropyl	147—149	—	high polymer			—	—	—
Isobutyl	198.5—	—	high polymer			—	—	—
	199.5	47—48	high polymer			—	—	—
Isopentyl	183—184	—	—	—	1839	—	—	7.2 (2)

^a $C_6H_6^{80}$, $CHCl_3^{61}$, and $C_6H_6^{37}$ means that the determination of the molecular weights were performed ebullioscopically and osmometrically at the temperatures 80°, 61°, and 37°C, respectively.

^b The figures within parentheses represent the number of experiments performed.

Table 4. Potassium *N,N*-dialkyldithiocarbamates, R_2NCS_2K .

R	M.p. °C		Molecular weight ^a			Degree of association ^b		
	Anhydrous	Hydrated	$C_6H_6^{80}$	$C_6H_6^{37}$	$CHCl_3^{61}$	$C_6H_6^{80}$	$C_6H_6^{37}$	$CHCl_3^{61}$
Methyl	>350	—	—	—	—	—	—	—
Ethyl	—	—	—	—	—	—	—	—
Propyl	185—187	—	—	—	—	—	—	—
Butyl	148—150	—	—	—	1429	—	—	5.8—6.0 (3)
Pentyl	162—164	—	1612	1841	—	5.7—6.1 (3)	6.7—6.9 (3)	—
Isopropyl	180—182 d	—	high polymer			—	—	—
Isobutyl	225—226	115—117	high polymer			—	—	—
Isopentyl	139—140	—	1533	—	—	5.3—6.0 (3)	—	—

^{a,b} Cf. notes to Table 3.

Table 5. Rubidium *N,N*-dialkyldithiocarbamates, R_2NCS_2Rb .

R	M.p. °C	Molecular weight ^a				Degree of association ^b			
	Anhydrous	$C_6H_6^{80}$	$C_6H_6^{37}$	$C_6H_6^5$	$CHCl_3^{61}$	$C_6H_6^{80}$	$C_6H_6^{37}$	$C_6H_6^5$	$CHCl_3^{61}$
Butyl	148–150	—	—	—	1388	—	—	—	4.8–4.9 (3)
Pentyl	94–96	1412	1915	2665	—	4.4–4.5 (3)	6.0 (1)	8.4 (2)	—
Hexyl	111–113	1588	1275	3017	—	4.5–4.7 (2)	3.7 (1)	8.4–9.4 (3)	—
Isobutyl	209–210	—	—	—	1204	—	—	—	3.7–4.3 (5)
Isopentyl	143–145	—	—	—	1298	—	—	—	3.9–4.4 (3)

^a $C_6H_6^{80}$, $CHCl_3^{61}$, $C_6H_6^5$, and $C_6H_6^{37}$ means that the determination of the molecular weights were performed bullioscopically, cryoscopically and osmometrically at the temperatures 80°, 61°, 5°, and 37°C, respectively.

^b The figures within parentheses represent the number of experiments performed.

Table 6. Cesium *N,N*-dialkyldithiocarbamates, R_2NCS_2Cs .

R	M.p. °C	Molecular weight ^a			Degree of association ^b		
	Anhydrous	$C_6H_6^{80}$	$C_6H_6^{37}$	$CHCl_3^{61}$	$C_6H_6^{80}$	$C_6H_6^{37}$	$CHCl_3^{61}$
Butyl	158–159	—	—	1209	—	—	3.5–3.7 (2)
Pentyl	104–105.5	1318	1409	—	3.6 (2)	3.9 (1)	—
Isobutyl	185–186 d	1269	—	1312	3.7 (1)	—	3.9 (1)
Isopentyl	163–165	1330	—	—	3.9–4.0 (2)	—	—

^{a,b} Cf. notes to Table 3.

3. *Gel chromatography.* The molecular weights determined by the methods mentioned are means of the different molecular sizes present in the solution. If the distribution between two or more molecular species of different sizes changes, e.g. by change in temperature, the experimental molecular weight will also be changed. To determine whether the alkali metal *N,N*-dialkyldithiocarbamates exist as one or more molecular species in inert organic solvents, we have studied the compounds by means of gel chromatography. To study the effect of temperature on the distribution of the molecular species, gel chromatography has been performed at two different temperatures.

3a. *Method.* Gel chromatography was performed in thermostated columns at 30°C and 10°C. A hydrophobic gel without adsorbing properties was required and a cross-linked polystyrene polymer was chosen using benzene as eluent. A recording refractometer was used for detection.

To establish the chromatographic characteristics of the column, a number of stable copper, silver, and gold thio- and dithiocarbamates, which were well characterized in solutions of organic inert solvents¹ and in the solid state,^{2,15,14,16} were used. These examinations showed that the compounds were homogeneous and that the column allowed molecules to be separated on basis of their molecular weights and forms (Fig. 1).

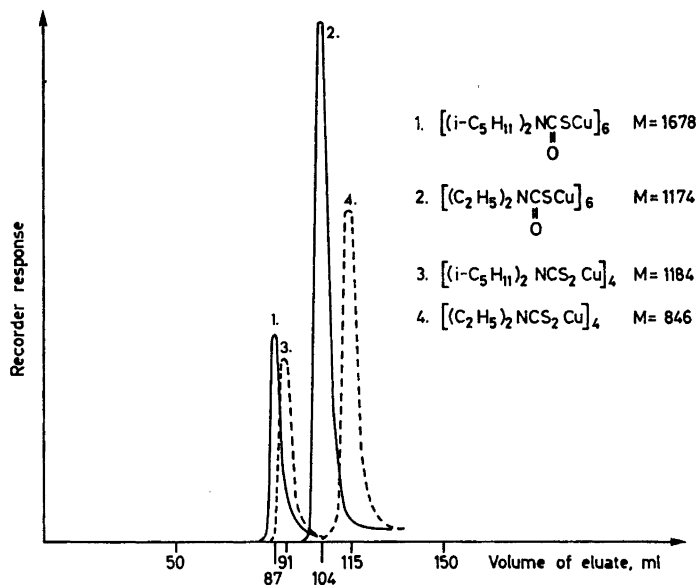


Fig. 1. Gel chromatography at 30°C on Bio-Beads S-X2 of copper(I) diisopentylthiocarbamate, copper(I) diethylthiocarbamate, copper(I) diisopentylthiocarbamate, and copper(I) diethylthiocarbamate.

3b. *Gel chromatography at 30°C.* Benzene solutions of sodium, potassium, rubidium, and cesium dipentylthiocarbamates and lithium diisobutylthiocarbamate were examined at 30°C. The elution patterns from the gel chromatography permitted the following observations to be made.

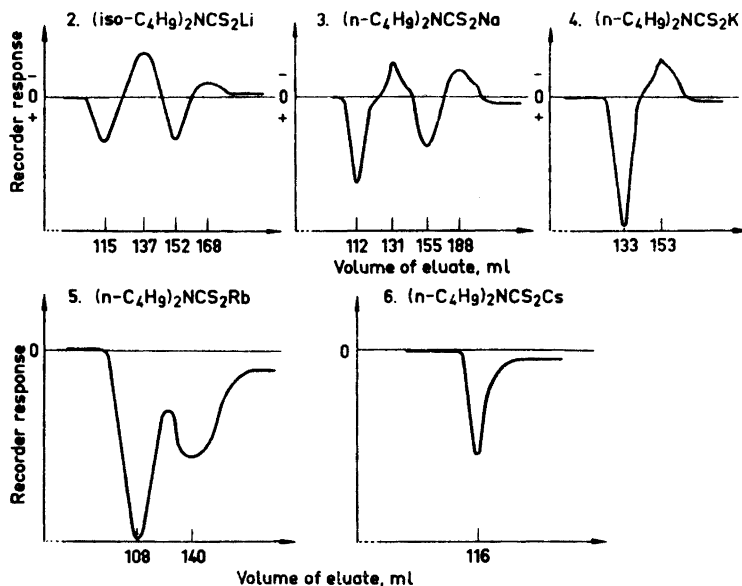
The lithium and sodium compounds were separated into four components (Figs. 2 and 3), two of which had a lower refractive index than benzene and two a higher refractive index.

The potassium compound separated into two components with a higher and a lower refractive index than benzene (Fig. 4).

The rubidium compound separated into two components, the refractive indices of which were both larger than that of benzene (Fig. 5).

The cesium compound was homogeneous and gave only one peak with a refractive index larger than that of benzene (Fig. 6).

The IR-spectra of the sample solutions were recorded immediately after the gel chromatography and they showed that the lithium, sodium, and potassium compounds were hydrated. A trace of water then was added to the sample solutions of the sodium and potassium compounds before gel chromatography. The peaks representing compounds with lower refractive indices than benzene now increased markedly, while those with larger refractive indices decreased. This suggests that the peaks with a smaller refractive index than benzene represent the hydrated forms. It was possible, later on, to prepare an anhydrous sample of the potassium compound and analyze it



Figs. 2–6. Gel chromatography at 30°C on Bio-Beads S-X2 of 2 lithium diisobutyldithiocarbamate; 3 sodium dibutyldithiocarbamate; 4 potassium dibutyldithiocarbamate; 5 rubidium dibutyldithiocarbamate; 6 cesium dibutyldithiocarbamate.

by gel chromatography. This compound gave only one peak with a refractive index which was larger than that of benzene.

3c. *Gel chromatography at 10°C.* During the molecular weight determinations of the rubidium and, to some extent, the sodium compound, a tendency for the association to vary with temperature was noticed. Gel chromatography of the rubidium and sodium compounds at 30°C revealed that they consist of at least two anhydrous molecular species. The proportion of the two molecular species was also examined at 10°C using gel chromatography.

The sodium compound showed a marked change in solubility when the temperature was lowered below room temperature becoming completely insoluble in benzene at 10°C. It was thus not possible to examine it by gel chromatography at that temperature.

The rubidium compound was still very soluble in benzene at 10°C. A solution of the sample was kept at room temperature and then examined at 10°C. The elution pattern showed two incompletely separated components (Fig. 7 B). If the solution then was kept at 10°C for 30 h before gel chromatography was performed, the faster component almost disappeared and the slow one now became preponderant (Fig. 7 C). However, on keeping the solution at 30°C for 24 h, and thereafter examining at the same temperature, the original elution pattern with the two components was restored (Fig. 7 A).

The mass spectra of rubidium and cesium di-butyldithiocarbamates. Mass spectrometric studies of ethyllithium,¹⁷ lithium *t*-butoxide, and lithiomethyl-

trimethylsilane¹⁸ have shown these compounds to be associated in the vapor phase with the same degree of association as that observed in solution. The association of two alkali metal *N,N*-dialkyldithiocarbamates, the rubidium

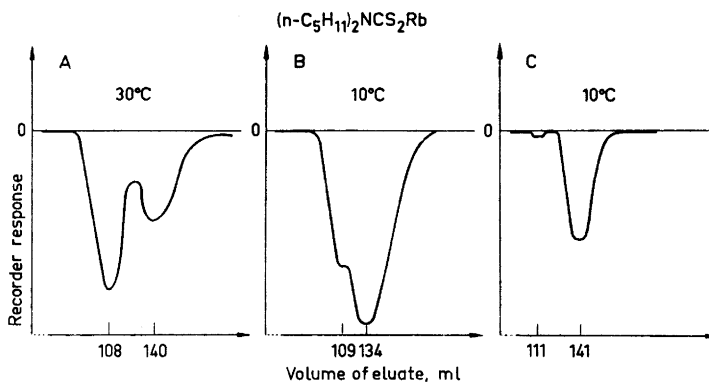


Fig. 7A. Gel chromatography at 30°C on Bio-Beads S-X2 of rubidium dipentylthiocarbamate. The sample was kept at 30°C for 24 h before gel chromatography was performed. *B.* Gel chromatography at 10°C on Bio-Beads S-X2 of rubidium dipentylthiocarbamate. The sample was kept at room temperature a few hours before gel chromatography was performed. *C.* Gel chromatography at 10°C on Bio-Beads S-X2 of rubidium dipentylthiocarbamate. The sample was kept at 10°C for 30 h before gel chromatography was performed.

and cesium *N,N*-dibutylthiocarbamates in the vapor phase, was examined by mass spectrometry. The resulting mass spectra revealed peaks at $m/e = 375$ and $m/e = 570$, respectively, corresponding to fragments consisting of the monomer with an extra metal atom. Attempts were made to observe still heavier polymeric fragments, but no such signals were observed. The experiments were performed at electron energies of 70 and 25 V and at a temperature of 240°C. Most of the unstable dithiocarbamate molecules gave fragments with m/e below the monomeric molecular ion. These mass spectrometric examinations suggest that the dithiocarbamates may exist as dimers in the vapor phase.

DISCUSSION

Each element strives to attain its characteristic co-ordination number in its complexes by co-ordinating suitable available ligands. This is determined mainly by a combination of electronic and steric factors. Sometimes the solvent, used for the preparation of the compound, may function as the co-ordinating ligand. If such is not available or if the co-ordinating solvent is removed, the compound may be forced to aggregate in order to attain co-ordination saturation. This results either in small discrete aggregates or high-polymers¹ as typified by the alkali metal dialkyldithiocarbamates.

Owing to the experimental difficulties caused by the hygroscopic and unstable nature of the non-hydrated alkali metal dialkyldithiocarbamates,

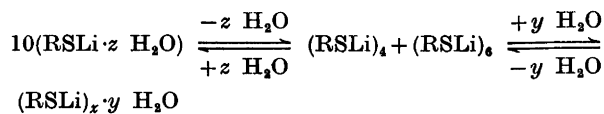
it has not always been possible to draw definite conclusions about several of the complexes. However, it can be concluded that all alkali metal dialkyldithiocarbamates are polymeric, some of them high-polymeric. Thus, the sodium and potassium diisopropyldithiocarbamates and the sodium and potassium diisobutyldithiocarbamates were found to be quite insoluble in inert organic solvents. Water of crystallization was especially easily removed from the former complexes. These insoluble polymers were readily solubilised by treating them with co-ordinating ligands such as water, alcohols, *etc.* From the above facts, and the general solubility properties of the sodium- and potassium dialkyldithiocarbamates, these complexes would appear to be high-polymeric. The sodium dialkyldithiocarbamates with straight chains are very soluble in, *e.g.*, benzene at 23°C but when the temperature is decreased to 15–10°C, there is an abrupt decrease in solubility, indicating a transition to the polymeric state.

In this connection it is worth-while to point out the insolubility of one of the forms of silver(I) diisopropyldithiocarbamate.¹

As has been mentioned earlier, considerable difficulties were caused by the hygroscopicity and instability of the *lithium dialkyldithiocarbamates* especially. These complexes apparently exist as low-polymers. The degree of association of the butyl homologue at 5°C in benzene varied between 3 and 6, and the isobutyl homologue between 4 and 6 in benzene at 80°C, 37°C, and 5°C (Table 2). Lithium diisobutyldithiocarbamate in benzene solution consists of at least two different molecular sizes (Fig. 2), the proportions of which seem to be temperature dependent. It is interesting to note that the degree of association of ethyllithium is 4.5–6.9 in benzene at 5°C,^{19,20} and 5.7–6.4 in cyclohexane.²¹ IR, NMR, and a molecular weight determination indicated that ethyllithium is a hexamer. Structures for both the tetramer and the hexamer have been proposed.²² In the gas phase *in vacuo* at 80–95°C mainly hexameric and tetrameric fragments are found.¹⁷ In the solid phase, however, the complex is tetrameric. The four Li atoms are situated at the corners of a regular tetrahedron.²³ In benzene and hexane, *t*-butyllithium exists as a tetramer.²⁴ Likewise, lithium-methyltrimethylsilane and *sec.* butyllithium form tetramers in 2-methylpentane, cyclohexane and benzene.^{25,26,18,27} The former complex was also tetrameric in gas phase.¹⁸ Butyllithium, on the other hand, was reported hexameric in benzene and cyclohexane²¹ and a structure based on IR, Raman spectra, and NMR presented.²⁸ It is worthy of note that in ether, butyllithium has been assigned a dimeric structure (BuLi)₂·OEt₂.²⁹ Alkyl lithium compounds generally co-ordinate ligands (B) as (RLi)₂·B.^{30,31}

On gel chromatography, lithium, diisobutyldithiocarbamate gave two components with a lower refractive index than pure benzene. These two peaks may represent (RSLi)^{*}_x·y H₂O, where *x* may be 4 and 2, and *y* = 1, respectively.

The polymerisation of the lithium dialkyldithiocarbamates can be formulated as follows:



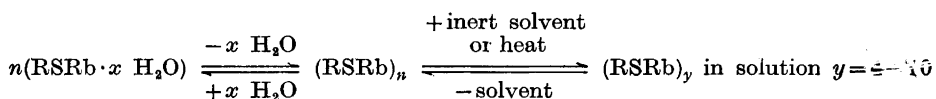
where *z* = 2–3, *x* = 4 or 2, *y* = 1, and RS = R₂NCS₂.

Except for the diisopropyl- and diisobutyl dithiocarbamates of sodium, the other homologues behave as low-polymers in solutions of inert organic solvents. The degree of association varies from 7 to 12. These complexes are more stable than the corresponding lithium complexes. Gel chromatographic studies indicated that they existed as at least two aggregates in solution (Fig. 3), possibly dodecamers and octamers. The peaks with a lower refractive index than benzene represent the hydrated forms of the complexes.

Apart from the diisopropyl and diisobutyl homologues, the dialkyldithiocarbamates of potassium behave as hexamers in solution. The degree of association varied from 5.3 to 6.9 (Table 4). Gel chromatographic studies showed that the complexes were homogeneous in solution (Fig. 4). Thus, these complexes seem to be composed entirely of hexameric aggregates.

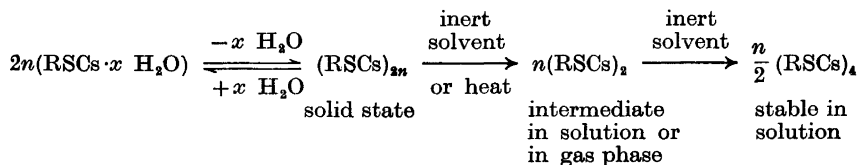
Molecular weight determinations at different temperatures indicate that the rubidium dialkyldithiocarbamates consist of different molecular species, the sizes of which seem temperature dependent (Table 5). The degree of association varied from 3.7 at 80°C to 9.4 at 5°C in benzene.

Gel chromatographic studies indicated that the complexes were composed of at least two molecular sizes (Fig. 5); the relation between the two however, is temperature dependent (Fig. 7, A-C). Mass spectrometric investigations suggest that the complexes may consist of dimers in the gas phase, and X-ray studies by Aava¹³ have shown the rubidium dibutyldithiocarbamate to be a high-polymer in the solid state. Thus, the rubidium complexes, which are completely dissociated in aqueous solution, polymerize after removing the water of crystallization:



Inert solvents or heat then split the high polymer into smaller aggregates. In the solution, an equilibrium exists between at least two molecular species, the proportions of which are temperature dependent.

The cesium dialkyldithiocarbamates were found to be entirely tetrameric in solution (Table 6 and Fig. 6). Mass spectrometric studies showed the compounds to be at least dimeric in the gas phase. X-Ray investigations by Aava and Hesse¹⁴ indicated the cesium dibutyldithiocarbamate to be high-polymeric in the solid state. The basic units of the crystal lattice were dimers. The cesium dialkyldithiocarbamates crystallized with 1 or 2 water molecules ($x=1$ or 2) and are completely dissociated in aqueous solution:



When the water of crystallization is removed, the compounds polymerize. Addition of an inert solvent disrupts the molecule forming dimeric units. These are unstable intermediates in solution and in the gas phase. The reuniting of two dimeric units to give the more stable tetrameric aggregate may be understood on geometric and kinetic grounds.

EXPERIMENTAL

General. The melting points were determined with a Kofler hot stage microscope, using a rate of heating of two degrees per minute. For most of the hygroscopic compounds, the melting points were determined in a sealed glass capillary. All melting points are uncorrected. IR-spectra were recorded with a Perkin-Elmer model 157.

Mass spectra were recorded with an LKB A 9000 mass spectrometer. The temperature of the ionization chamber was 240°C, and the energy of the ion beam was 70 eV (25 eV). The molecular weights were determined ebullioscopically in benzene ($M_{C_6H_6}^{80}$) chloroform ($M_{CHCl_3}^{81}$), cryoscopically in benzene ($M_{C_6H_6}^5$) and osmotically in benzene ($M_{C_6H_6}^{87}$). The figures for the molecular weights are averages and based on several independent determinations. Solvents used were A.R. benzene, *p.a.* freshly distilled chloroform freed from ethanol stabilizer according to Vogel.³⁸ The light petroleum used for recrystallization was dried over metallic sodium and had the boiling range of 40–60°C.

Ebullioscopic measurements. A differential ebulliometer, built by AB Bofors, Sweden, was used. The differential thermometer was made up of two platinum wires, which were continuously washed with the boiling solvent resp. the boiling solution. The difference in resistance between the two wires was then measured by a Wheatstone bridge. Measurements were made at various concentrations in benzene and in chloroform, and the molecular weights estimated with the aid of calibration curves, which were constructed from *p*-dichlorobenzene and diphenyl. None or very little decomposition was observed after 5 min refluxing in either of the solvents used.

Cryoscopic measurements. Because of the extreme sensitivity to humidity of the substances, the sample solutions were prepared in a glove-box in a dried nitrogen atmosphere. Measurements were made at various concentrations in benzene. The freezing point depression was measured by a Beckmann thermometer, and the sample freezing points were duplicated and reproduced to $\pm 0.01^\circ\text{C}$. The molal freezing-point constant for benzene was estimated with *p*-dichlorobenzene and diphenyl.

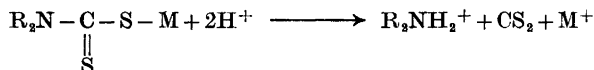
Osmometric measurements. A Mechrolab model 301 A thermoelectric osmometer was used. The molecular weight determinations were made at various concentrations in benzene at 37°C. Calibration curves were made for benzene and water at 37°C with diphenyl and glucose, respectively.

Gel chromatography. Gel chromatography was performed on Bio-Beads S-X2, (Bio-Rad Laboratories, USA) a cross-linked non-ionic polystyrene polymer. The particle size of the dry material was 200–400 mesh, and the approximate exclusion limit was 2700. Before packing, the gel was suspended in excess of benzene and allowed to swell overnight at room temperature. Redistilled and absolutely anhydrous benzene was used as eluent. The column used was a 45 cm long water-jacketed glass column with a diameter of 2.5 cm (Pharmacia Fine Chemicals K 45/25). Gel chromatography was performed with the column thermostated at 10°C and 30°C. An upward flow adaptor was used and the effluent was passed through a Waters differential refractometer Model R 4. The variations in the refractive index were automatically recorded. The fractions were not collected. The bead volume of the column was 85 ml. The flow was maintained by gravity, and the flow-rate was 0.32 ml/min at 30°C, and 0.27 ml/min at 10°C. Operating pressure was 15 cm benzene. Sample volumes varied between 0.3–0.5 ml of 0.2–0.5 % benzene solutions.

Synthesis of the alkali metal *N,N*-dialkyldithiocarbamates

General procedure. 0.12 mol of the appropriate alkali metal hydroxide dissolved in 3–5 ml of water, and 0.12 mol of CS₂ dissolved in 25 ml of benzene were added to a three-necked flask, fitted with a reflux condenser and a stirrer. 0.1 mol of the appropriate dialkylamine was then added dropwise with stirring. A vigorous exothermic reaction resulted, and the reaction vessel had to be cooled. When all the amine solution had been added, the reaction mixture was stirred for 1 h. During that time, crystals began to precipitate. The crystallization was completed by addition of petroleum ether, and the crystals were filtered off. The yields were 80–95 %. The compounds prepared according to this method were hydrated, and were shown by NMR spectrum and analysis to contain up to 3 mol of water. The hydrated compounds were made anhydrous, either by drying *in vacuo* over P₂O₅ at 50°C, or by distilling azeotropically a benzene or chloroform solution of the compound. Repeated recrystallization of the anhydrous product was required to obtain a pure sample. The anhydrous compounds of particularly the light alkali metals were very hygroscopic, and to preserve them in an anhydrous state, all work had to be performed in a glove-box in a dry nitrogen atmosphere. The nitrogen used was dried by passing it through a tube, which was chilled with liquid nitrogen. The dried nitrogen was then allowed to stream through the glove-box for 2 h, and after that the valves were closed and a vessel with P₂O₅ was placed in the box to remove traces of humidity.

Analyses. The dithiocarbamate content has been analysed according to the acid method of Shankaranarayana and Patel.³³ The sample was dissolved in excess of HClO₄ and then placed on a boiling water bath for 1 ½ h. After that time, the solution was evaporated to half its volume, chilled, and the excess of HClO₄ titrated potentiometrically with NaOH. The amount of dithiocarbamate was then estimated from the reaction formula:



Lithium N,N-dialkyldithiocarbamates. These compounds were prepared according to the general method given above and the hydrated compound crystallized as lustrous colourless needles. The compounds were converted to the anhydrous state by azeotropic distillation of a benzene or chloroform solution. During this procedure, most of the homologues, however, were extensively decomposed and the anhydrous residue was very unstable.

Lithium N,N-dimethyldithiocarbamate. As the dimethylamine was supplied as an aqueous solution, the reaction was conducted in water. The product was isolated by evaporation *in vacuo* to dryness. The solid residue was quite insoluble in solvents such as benzene, chloroform, or carbon disulphide, and very soluble in ethanol, acetone, or water. When crystallized from acetone-petroleum ether, small colourless needles were obtained, m.p. 223–225°C (dec.). Infrared spectrum of the compound showed it to be hydrated. After the compound had been dried *in vacuo* over P₂O₅ for 48 h, it was analysed. The product contained 80 % dithiocarbamate.

Lithium N,N-diethyldithiocarbamate. Recrystallization from chloroform afforded the hydrated compound (2.2 mol H₂O) as colourless needles, m.p. 94–95°C. A chloroform solution of the compound was distilled to remove the water azeotropically. During this operation, a white crystalline compound was precipitated. Infrared spectrum showed the compound to be lithium hydroxide by comparison with an authentic sample. The residual solution was then concentrated, and when anhydrous petroleum ether was added, a small quantity of colourless needles was obtained. When recrystallized from benzene-petroleum ether, white, very hygroscopic and unstable needles were obtained, m.p. 106–108°C. Due to the very rapid decomposition it was not possible to carry out an analysis. The infrared spectrum of the compound, however, did correspond to that of the hydrated compound, with exception of the peaks due to hydration (3400, 1610 cm⁻¹).

Lithium N,N-dipropyldithiocarbamate. When recrystallized from benzene, the hydrated compound (3 mol H₂O) was obtained as lustrous colourless needles, m.p. 64–65°C. To obtain the anhydrous form, a benzene solution was distilled azeotropically. The residual

solution was then evaporated *in vacuo* to give a yellow oil, the infrared spectrum of which corresponded to that of the hydrated compound minus the hydration peaks. All attempts to crystallize the oil were unsuccessful.

Lithium N,N-dibutylidithiocarbamate. On recrystallization from benzene, the hydrated compound (24 mol H₂O) was obtained as lustrous, colourless needles, m.p. 77–79°C. The water was then removed by azeotropic distillation in benzene, the residual solution was evaporated *in vacuo* to an oil from which crystals were precipitated by addition of anhydrous petroleum ether. Recrystallization from anhydrous petroleum ether gave colourless needles, m.p. 44–46°C. The infrared spectrum of the anhydrous compound corresponded to that of the hydrated compound minus the hydration peaks.

The anhydrous compound was found to contain 93.2 % dithiocarbamate. The molecular weight is given in Table 2.

Lithium N,N-diisopropylidithiocarbamate. The reaction was slow and no heat was evolved. After the reaction mixture had been stirred for 2 h, a voluminous precipitation of colourless needles occurred, m.p. 70–71°C (dec.). The compound was poorly soluble in benzene or chloroform, and the infrared spectrum showed it to be hydrated. The anhydrous form was obtained by distilling a chloroform solution. During this distillation, however, a large part of the salt decomposed, and lithium hydroxide was formed. When all the water had been azeotropically distilled, the residual solution was filtered and evaporated *in vacuo* to an oil from which colourless needles, m.p. 139–140°C, were obtained on addition of petroleum ether. The crystals were very soluble in benzene or chloroform, very hygroscopic and unstable. The infrared spectrum corresponded to that of the hydrated compound minus the hydration peaks. Owing to the rapid decomposition, no dithiocarbamate analysis could be performed.

Lithium N,N-diisobutylidithiocarbamate. On recrystallization from benzene, the hydrated compound (3 mol H₂O) was obtained as lustrous, colourless needles, m.p. 67–68°C. The anhydrous form was obtained by azeotropic distillation of a benzene solution. The residual solution was then evaporated *in vacuo* to an oil. The anhydrous compound was precipitated by addition of petroleum ether to the oil. Recrystallization from petroleum ether yielded colourless, unstable and very hygroscopic needles, m.p. 97–99°C. The compound was found to contain 102.8 % dithiocarbamate. The molecular weight is given in Table 2.

Lithium N,N-diisopentylidithiocarbamate. Recrystallization from benzene afforded the hydrated compound (3 mol H₂O) as lustrous, colourless needles, m.p. 51–52°C. The anhydrous form was obtained by azeotropic distillation of a benzene solution. The residual solution was then evaporated *in vacuo* to a yellow oil from which colourless needles were obtained in the cold, m.p. 7–8°C. The infrared spectrum of the oil corresponded to that of the hydrated compound minus the hydration peaks.

Sodium N,N-dialkylidithiocarbamates. These compounds were prepared by the general method, and the NMR-spectra of chloroform solutions of the hydrated compounds showed them to contain almost 3 mol of water. The water was removed by azeotropic distillation of a benzene or chloroform solution. The residual solution was then concentrated to an oil from which the anhydrous compound was precipitated by addition of petroleum ether. Repeated recrystallizations were required to obtain the pure compounds.

Sodium N,N-diethylidithiocarbamate. The reaction mixture was evaporated to dryness. The residue was insoluble in benzene or chloroform. Recrystallization from acetone afforded colourless needles, m.p. 92–95°C. The infrared spectrum of the dried compound showed it to be hydrated.

Sodium N,N-dipropylidithiocarbamate. Lustrous, colourless needles, m.p. 53–54°C, were obtained on recrystallizing the hydrated product from benzene. When the water was removed azeotropically from a benzene solution, the compound was considerably less soluble in benzene. The anhydrous compound was recrystallized from chloroform-petroleum ether, giving long, colourless, fibrous and very hygroscopic needles, which precipitated as a gel, m.p. 128–129°C. The compound was found to contain 99.7 % dithiocarbamate. The molecular weight is given in Table 3.

Sodium N,N-dibutylidithiocarbamate. Recrystallization from benzene yielded the hydrated product as colourless needles, m.p. 39–40°C. The anhydrous product recrystallized from chloroform-petroleum ether as colourless, fibrous and very hygroscopic needles, m.p. 123–125°C. The compound was found to contain 97.7 % dithiocarbamate. The molecular weight is given in Table 3.

Sodium N,N-dipentylidithiocarbamate. Recrystallization of the anhydrous product from petroleum ether gave colourless, fibrous and very hygroscopic needles, which precipitated as a gel. The product was dried *in vacuo* at 40°C for 2 h, m.p. 121–123°C. The compound was found to contain 99.8 % of dithiocarbamate. The molecular weight is given in Table 3.

Sodium N,N-diisopropylidithiocarbamate. The reaction rate was very slow. After 3 h of vigorous stirring, the hydrated compound began to precipitate. The hydrated product was very soluble in benzene or chloroform. When the water was azeotropically removed, the compound became completely insoluble in both benzene and chloroform. The anhydrous compound crystallized as colourless fibrous and hygroscopic needles, m.p. 147–149°C. The infrared spectrum of the anhydrous compound corresponded to that of the hydrated compound minus the hydration peaks. The anhydrous compound was found to contain 98.2 % dithiocarbamate.

Sodium N,N-diisobutylidithiocarbamate. The reaction was very slow. The hydrated product was obtained as lustrous, colourless needles, m.p. 47–48°C, which were soluble in benzene or chloroform. The water of hydration was readily removed by careful heating or *in vacuo*. The resulting anhydrous, non-lustrous needles, m.p. 198.5–199.5°C, were insoluble in benzene or chloroform. The solubility returned if a little water was added to the benzene or chloroform. IR spectrum of the anhydrous compound corresponded to that of the hydrated compound minus the hydration peaks. The dehydrated compound was found to contain 98.9 % dithiocarbamate.

Sodium N,N-diisopentylidithiocarbamate. The reaction proceeded rapidly with the evolution of much heat. Recrystallization of the hydrated compound from benzene gave lustrous, colourless needles. The anhydrous compound was recrystallized from benzene-petroleum ether to give long, colourless very hygroscopic needles, m.p. 183–184°C. The dehydrated compound was found to contain 99.7 % dithiocarbamate. The molecular weight is given in Table 3.

Potassium N,N-dialkyldithiocarbamates. These compounds were prepared according to the general procedure given above. The anhydrous product could be obtained by drying *in vacuo* (10 mmHg) over P₂O₅ at 40°C for 2 h.

Potassium N,N-dimethylidithiocarbamate. The reaction was carried out in water, and the product was isolated by evaporation to dryness. The solid residue, which was insoluble in benzene or chloroform, was recrystallized from acetone. Colourless needles, m.p. >350°C, were obtained and converted to the anhydrous form by drying *in vacuo*. The dehydrated compound was found to contain 93.7 % dithiocarbamate.

Potassium N,N-dipropylidithiocarbamate. The product was isolated by evaporation to an oil from which crystals were obtained by addition of petroleum ether. Recrystallization from chloroform and drying *in vacuo* gave small colourless needles, m.p. 185–187°C. The solubility in benzene or chloroform was insufficient for ebullioscopic studies. The anhydrous compound was found to contain 99.2 % dithiocarbamate.

Potassium N,N-dibutylidithiocarbamate. The hydrated compound was recrystallized from chloroform as lustrous needles. After drying *in vacuo*, the anhydrous compound was obtained as very hygroscopic colourless needles, m.p. 148–150°C. The anhydrous compound was found to contain 98.3 % dithiocarbamate. The molecular weight is given in Table 4.

Potassium N,N-dipentylidithiocarbamate. The product was isolated by evaporation of the reaction mixture to dryness, and the solid residue was recrystallized from petroleum ether. The colourless needles were dried *in vacuo*. The anhydrous product was very hygroscopic, m.p. 162–164°C. The solubility in benzene was insufficient for cryoscopic studies. The dried compound was found to contain 98.5 % dithiocarbamate. The molecular weight is given in Table 4.

Potassium N,N-diisopropylidithiocarbamate. The reaction was slow and no heat was evolved. When the reaction mixture had been stirred vigorously for 2 h, crystals started to separate, and after another 2 h the reaction mixture was evaporated to dryness. The solid residue was recrystallized from chloroform to give lustrous, colourless needles, m.p. 180–182°C (dec.). Water was released at 60°C. The hydrated compound, which was soluble in chloroform and benzene, was dried *in vacuo*. After removal of water, the compound became quite insoluble in chloroform and benzene. IR spectra of the hydrated and hydrous compounds were identical, except for the absence of the hydration peaks in

the anhydrous compound. The dried compound was hygroscopic and was found to contain 98.5 % dithiocarbamate.

Potassium N,N-diisobutylidithiocarbamate. The reaction was slow, and the product was isolated by evaporation to dryness. The solid residue was recrystallized from chloroform, and lustrous colourless needles, m.p. 115–117°C (water was evolved at 50°C), were obtained. The needles were very soluble in benzene or chloroform. The anhydrous compound, made by careful heating or *in vacuo*, was quite insoluble in chloroform or benzene. The anhydrous compound appeared as long, colourless, somewhat hygroscopic needles, m.p. 225–226°C. The IR spectrum of the anhydrous compound corresponded to that of the hydrated compound minus the hydration peaks. The dried compound was found to contain 99.2 % dithiocarbamate.

Potassium N,N-diisopentylidithiocarbamate. The reaction was rapid, and the product was isolated by evaporation to dryness. Recrystallization of the solid residue from benzene-petroleum ether gave colourless very hygroscopic needles, which after drying melted at 139–140°C. The solubility in benzene was insufficient for cryoscopic studies. The dried compound was found to contain 99.0 % dithiocarbamate. The molecular weight is given in Table 4.

Rubidium N,N-dialkylidithiocarbamates. These compounds were prepared according to the general method for the preparation of alkali metal *N,N*-dialkylidithiocarbamates. The reactions were rapid and strongly exothermic. The reaction product was isolated by evaporation to dryness, and the solid residue was repeatedly recrystallized. The anhydrous compound was obtained by drying *in vacuo* for 2 h at 50°C.

Rubidium N,N-dibutylidithiocarbamate. Recrystallization from chloroform-petroleum ether and drying *in vacuo* gave colourless very hygroscopic needles, m.p. 148–150°C. The solubility in benzene was insufficient for ebullioscopic studies. The compound was found to contain 99.2 % dithiocarbamate. The molecular weight is given in Table 5.

Rubidium N,N-dipentylidithiocarbamate. Recrystallization from petroleum ether and drying *in vacuo* gave colourless, long and very hygroscopic needles, m.p. 94–96°C. The anhydrous compound was very soluble in benzene, chloroform, and petroleum ether. The compound was found to contain 98.8 % dithiocarbamate. The molecular weight is given in Table 5.

Rubidium N,N-dihexylidithiocarbamate. Recrystallization from petroleum ether and drying *in vacuo* gave colourless, fibrous and very hygroscopic needles, m.p. 111–113°C. The compound was found to contain 98.1 % dithiocarbamate. The molecular weight is given in Table 5.

Rubidium N,N-diisobutylidithiocarbamate. Recrystallization from benzene and drying *in vacuo* gave hygroscopic, colourless needles, m.p. 209–210°C. The compound was found to contain 98.5 % dithiocarbamate. The molecular weight is given in Table 5. (Found: C 37.23; H 6.25; N 4.84; Rb. 29.53. Calc. for $(C_4H_9)_2NCS_2Rb$: C 37.30; H 6.26; N 5.17; Rb 29.14.)

Rubidium N,N-diisopentylidithiocarbamate. Recrystallization from petroleum ether and drying *in vacuo* gave fibrous, colourless and very hygroscopic needles, m.p. 143–145°C. The solubility in benzene was insufficient for ebullioscopic studies in that solvent. The compound was found to contain 99.0 % dithiocarbamate. The molecular weight is given in Table 5.

Cesium N,N-dialkylidithiocarbamates. The cesium compounds have been prepared according to the general method given for preparation of alkali metal *N,N*-dialkylidithiocarbamates. The reactions were rapid and strongly exothermic, and the product was isolated by evaporation *in vacuo* to an oil from which crystals were precipitated by addition of petroleum ether. The anhydrous product was obtained by drying *in vacuo* at 50°C for 2 h. The anhydrous compounds were hygroscopic and unstable, and the solubility in benzene was insufficient for cryoscopic studies.

Cesium N,N-dibutylidithiocarbamate. Recrystallization from benzene and drying *in vacuo* gave colourless, hygroscopic, hexagonal plates, m.p. 158–159°C. The compound was found to contain 98.8 % dithiocarbamate. The molecular weight is given in Table 6. (Found: C 32.25; H 5.37; N 4.03; Cs 39.33. Calc. for $(C_4H_9)_2NCS_2Cs$: 32.04; H 5.38; N 4.17; Cs 39.40.)

Cesium N,N-dipentylidithiocarbamate. The hydrated product crystallized as colourless needles, m.p. 95–97°C. Recrystallization from benzene-petroleum ether and drying *in vacuo* gave colourless, very hygroscopic needles, m.p. 104–105.5°C. The compound

was found to contain 98.1 % dithiocarbamate. The molecular weight is given in Table 6.

Cesium N,N-diisobutyldithiocarbamate. Recrystallization from benzene and drying *in vacuo* gave long, colourless and hygroscopic needles, m.p. 185–186°C (dec.). The compound was found to contain 94.3 % dithiocarbamate. The molecular weight is given in Table 6.

Cesium N,N-diisopentyldithiocarbamate. Recrystallization from benzene and drying *in vacuo* gave colourless, very hygroscopic needles, m.p. 163–165°C. The compound was found to contain 99.0 % dithiocarbamate. The molecular weight is given in Table 6. (Found: C 31.72; H 5.32; N 4.01; Cs 39.73. Calc. for $(C_4H_9)_2NCS_2Cs$: C 32.04; H 5.38; N 4.17; Cs 39.40.)

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