

Complexes of alkali metals? (*)

MARY R. TRUTER

Agricultural Research Council, Unit of Structural Chemistry, London, Great Britain.

To explain the background to our work I am starting with a few words about my employer, the Agricultural Research Council. The Council spends about £ 12m per annum, in support of research of immediate or long-term benefit to agriculture, on three kinds of project. The largest is the maintenance of institutes, situated in the country, having fields and animals. Another is making grants for pieces of equipment or assistants to individual university teachers. The third is to encourage relevant fundamental research by provision of additional facilities for a university professor's department. The Unit of Structural Chemistry is such a facility; it was set up for Professor Sir Ronald Nyholm in October 1966, and is part of the Chemistry Department of University College.

Although the Unit has a wide brief to study chemistry relevant to agriculture, we decided to concentrate on one field, alkali metal chemistry. This has not been investigated as extensively as transition metal chemistry in recent years, probably because absence of magnetic moments and of characteristic electronic transitions limit the physical techniques available for studying alkali metals.

Alkali metals are of practical importance, there is, for example, the problem of de-salination. A compound which would remove sodium chloride from the sea, or even from flooded land, would bring tremendous benefits. We are not investigating this problem directly but the knowledge required to design such a compound could result from our work. Elements which to chemists seem very similar show remarkable differences in biological systems. Potassium is a major nutrient of plants, although its exact function is not known. It is taken up from solutions containing as little as one part

(*) Lecture held at the Istituto Superiore di Sanità on May 5, 1969. The author is grateful to the Consiglio Nazionale delle Ricerche and the British Council for their collaboration in making arrangements for this visit.

per million at a rate greater than can be accounted for by the rate at which water containing the potassium and other salts is drawn in by transpiration. Over a long period, plants will remove from the soil nearly all the potassium but over the shorter period it is difficult for potassium, as for many other elements, to find a method of chemical analysis which correlates with the amount taken up by the plant. The simplest hypothesis is that hydrated cations are taken up and transported through plants, but there is evidence against this, for example, iron EDTA is taken up complete, both iron and EDTA being found in the plant.

On the micro scale potassium is concentrated within plant and other cells and sodium is ejected against an electrochemical potential of 100mv. Possibly the activity coefficient of the alkali metal is affected by complex formation with ligands which discriminate between one metal and another. What properties would such ligands require? The first problem is to define what is meant by a complex; $[\text{Co}(\text{NH}_3)_6]^{3+}$ is generally accepted as a complex, is $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ also a complex, why not $[\text{Na}(\text{H}_2\text{O})_6]^+$? The criterion is partly a function of the method of investigation.

The first compounds described as complexes were made by Brewer and Sidgwick⁽¹⁾ in 1925. Salicylaldehyde and β -diketones were used as ligands. If these compounds are designated, HL, having an ionisable hydrogen, the compounds formed were first salts ML then complexes ML.HL or ML.2HL. One criterion for complex formation was that the adducts were soluble in toluene, while ML was not. The other criterion was a stoichiometric composition, that is 1:1 or 1:2. These compounds are based on a large, potentially chelating, anion.

Solvates of salts with simple anions have long been known. Sodium halides, MX, plus ammonia give definite compounds with the curious stoichiometry $5\frac{1}{7}$ NH_3 per NaX. The crystal structure⁽²⁾ shows the cation octahedrally surrounded by NH_3 , analogous to a $[\text{Co}(\text{NH}_3)_6]^{3+}$ salt. Similarly, the NaI.3 acetone compound⁽³⁾ contains Na^+ surrounded by six oxygen atoms. However, each oxygen is shared by two sodium ions. Although transition metals form well-established complexes containing shared or μ oxygens, sharing to give high coordination is characteristic of electrostatic compounds. To prove that an alkali metal is really complexed we might apply the criterion that it must be co-ordinated by ligand atoms, not shared by other alkali metal ions. Lithium is surrounded⁽⁴⁾ by four such oxygens in LiI. $(\text{OPPh}_3)_4$; this compound is also unusual in being stable in water⁽⁵⁾. A major difficulty is to find complexing agents more powerful than water for these metals. Some dramatic changes in solubility have been reported, for example, p,p'-diamino-2,3-diphenylbutane precipitates⁽⁶⁾ from an aqueous solution, a compound containing three molecules of amine to one of sodium chloride. Although the authors described this as complex forma-

tion, it may merely be the result of increase in lattice energy with the NaCl having a space-filling function.

Some complexes of transition metals can be sublimed unchanged. Volatile derivatives of alkali metals are also known, particularly for perfluoro β -diketone compounds, for example, Cs $[Y(CF_3COCHCOCF_3)_4]$ in the mass spectrograph gives caesium-containing fragments (7). The crystal structure (8) of this shows the Cs in an environment of fluorine atoms so that the sublimation is that of ion pairs.

Measurements of electrical conductivity in solution may indicate ion pairing or complex formation, both of which result in a lower value than that for a completely dissociated electrolyte. The distinction between an ion pair and a complex is that the former has no stereochemical implications.

Compounds formed by alkali metal halides and sugars, e.g. glucose, can be studied by electrophoresis (9); the sugar accompanies the cation, indicating metal-sugar interaction. Complexes with sugars can also be studied with a polarimeter (9), addition of metal salt to an aqueous solution of the sugar changes the optical activity. Nuclear magnetic resonance can be used to study either the effect on a protonated solvent (10) or addition of alkali metal or the effect on the alkali metal nucleus of various additions (11). The conclusion from the first type is that there is some interaction with oxygen-containing solvents such as tetrahydrofuran. A diminution in reactivity (12) of an alkali metal in the presence of a potential ligand is further evidence for interaction. These studies of interactions in solution showed that saturated diethers with two CH_2 groups between the oxygens had the greatest effect.

Cyclic polyethers of this kind have been synthesised by Pedersen (13), a typical one is shown in Fig. 1. These render some alkali metal salts so-

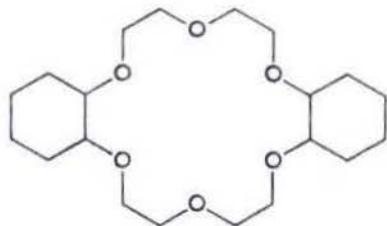


Fig. 1. — A cyclic polyether (13), the 6-membered rings may be cyclohexyl or phenyl.

luble in benzene, e.g. KNCS is solubilized but K_2CO_3 is not; presumably the lattice energy of the salt must not be too high. The cyclic ethers form similar compounds with a range of metal salts, M^{2+} and M^{3+} . In the first compounds the stoichiometry was $1M^{n+} : 1L$, but recently 1 : 2 and 2 : 3 compounds have been made. No structures have yet been determined; the

fascinating question is whether the metal is held in a cage in the ring or whether some oxygens interact with a metal essentially outside the ring as suggested⁽¹⁴⁾ for the cobalt compound on the basis of spectroscopic and magnetic evidence. There is some discrimination between alkali metals; potassium can be separated from caesium by means of the 6-oxygen compound of Fig. 1. Lithium reacts with a 4-oxygen ring and sodium with a 5-oxygen ring. Pedersen also found that no complexes were formed if an oxygen was replaced by a CH_2 group. The complexes can be extracted from aqueous solution, show changes in the U.V. spectrum of the ligand, and seem to indicate that the formation of a 5-membered chelate ring with the metal is an essential feature.

However, a naturally-occurring and highly discriminatory ligand was discovered, more or less by accident, and it does not have this feature. Organic chemists isolated and characterised a fungal metabolite, nonactin, and showed it to be a cyclic macrotetrolid⁽¹⁵⁾ (Fig. 2). This proved to be a

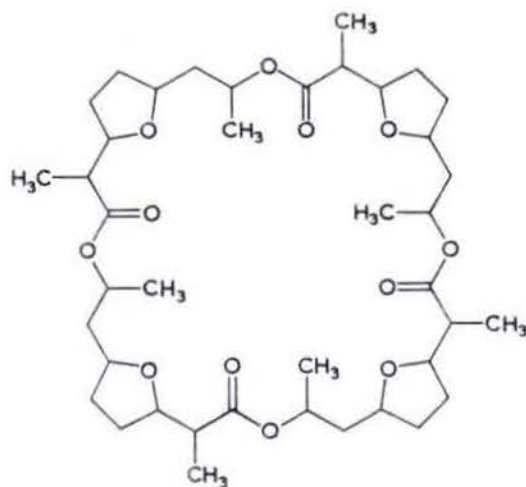


Fig. 2. — Nonactin⁽¹⁵⁾.

discriminatory ligand for potassium versus sodium; the stability constant of the $\text{MNCS} : \text{ligand} (1 : 1)$ compound is 28 times as great for $\text{M} = \text{K}$ as for $\text{M} = \text{Na}$. The crystal structure⁽¹⁶⁾ shows that the cyclic ligand is wound like the seam of a tennis ball round the cation. Co-ordination is by the furan oxygens and carbonyl oxygens, so that there are alternately 6- and 8-membered rings including the potassium. Other naturally-occurring cyclic compounds have been found⁽¹⁷⁾ selectively to affect the permeability of artificial membranes to alkali metals, for example, enniatins, antibiotic depsipeptides.

Our work since the Unit was formed has included the synthesis and investigation of about 100 compounds. A. K. Banerjee⁽¹⁸⁾ has made three classes of compound, having the general formulae

ML.nHL

ML.HL' (i.e. two different potential ligands)

ML.nS S is a ligand without ionisable hydrogen atoms or ones suitable for H-bonding.

He used as ligands, the five compounds shown in Fig. 3 as (1), 8-hydroxyquinoline, (2) isonitrosoacetophenone, (3) 1-nitroso-2-naphthol, (4) *o*-nitrophenol, (5) salicylic acid, and also 2,4-dinitrophenol, *o*-aminobenzoic acid, *o*-nitrobenzoic acid, and 1,10-phenanthroline. All contain « hard » ligand atoms and can chelate.

The method of preparation is to make a concentrated solution or suspension of ML in ethanol, benzene or acetone and add HL, HL' or S. Isonitrosoacetophenone gives the most spectacular results, the salt KL is deep red, addition of more ligand gives a yellow solution from which beautiful crystals are obtained. Many of the compounds are crystalline and have been characterised by preliminary X-ray work. This is one of the pieces of evidence which shows that they are not mixtures; the other evidence is the stoichiometric composition, the melting point which is higher than that of HL, HL' or S and the I.R. spectrum which is different from that of a mixture. Other measurements made on the compounds include conductivity, and visible and U.V. spectra.

The compounds obtained of formulae ML.nHL are shown in Table 1, those of ML.HL' in Fig. 3, and those of ML.nS in Table 2. Potassium forms

TABLE 1.

Compounds of formula ML.nHL

Compound	Number	pK	Values of n in ML.nHL				
			M = Li	Na	K	Rb	Cs
8-hydroxyquinoline	(1)	9.51	1	1	1,2	2	2
isonitrosoacetophenone.	(2)	8.5	0	0	0,1	0,1	1
1-nitroso-2-naphthol	(3)	7.7	0	0	0,1	0,1	0,1
<i>o</i> -nitrophenol	(4)	7.17	0	0	0,2	0,2	0,1
<i>o</i> -aminobenzoic acid (anthranilic acid)		6.97	0	0	0,1	0,1	0,1
2,4-dinitrophenol		3.69	0	0	0	0	0,2
<i>o</i> -nitrobenzoic acid		2.16		0	0,1	0,1	0,1

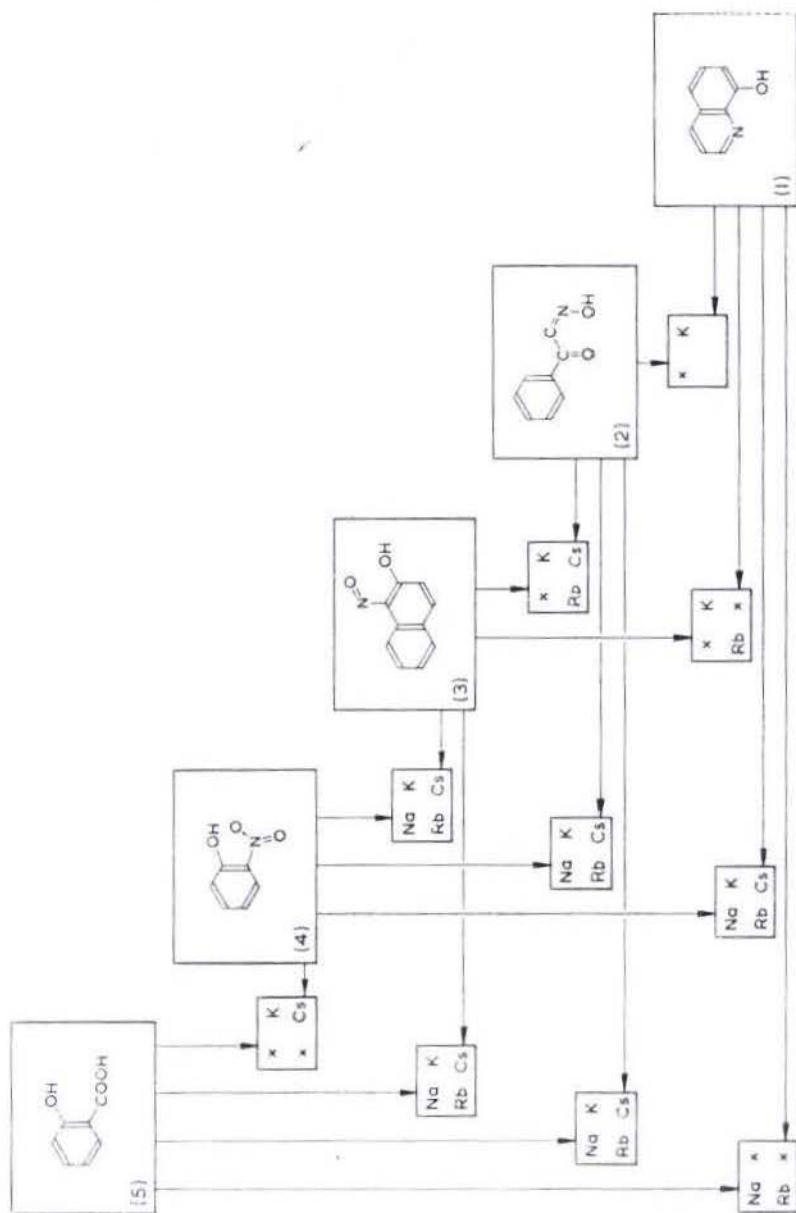


Fig. 3. — The four corners of the boxes are allocated to the alkali metals Na, K, Rb, and Cs. Where the symbol appears the compound $ML_2 \cdot HI$ has been made, HI being connected to the box by a vertical arrow and HL by a horizontal arrow. Crosses indicate that the corresponding compounds could not be synthesised.

two adducts with 8-hydroxyquinoline, $n = 1$ if the preparation is rapid, $n = 2$ if the reaction mixture is warmed overnight. All the compounds are decomposed by water and most organic solvent, however, they are soluble in *N*-methylpyrrolidone.

TABLE 2.

Compounds of formula $ML_n(1,10\text{-phenanthroline})$

Compound HL	Values of n in $ML_n(1,10\text{-phenanthroline})$				
	M - Li	Na	K	Rb	Cs
8-hydroxyquinoline	1	1	1		
1-nitroso-2-naphthol		1	1		
<i>o</i> -nitrophenol	1	2	1	2	1.5
2,4-dinitrophenol		1	2	1	1
2,6-dinitrophenol	1	1	1	1	1
<i>o</i> -nitrobenzoic acid		1	1		

Compounds ML_nHL with $HL = 8\text{-hydroxyquinoline}$, isonitroso-acetophenone or 1-nitroso-2-naphthol appeared to persist in this solution as judged by conductivity measurements and the visible spectrum. By the same criteria the other compounds were completely dissociated, *N*-methylpyrrolidone being a solvent for both components.

The formula $ML.HL$ can represent three arrangements :

(i) A true complex with both entities exclusively co-ordinated to the metal, as authenticated in the compound with $M = Ag$ and $HL = 8\text{-hydroxyquinoline}$ ⁽¹⁹⁾.

(ii) An addition compound, the metal being surrounded by anions L^- which are hydrogen-bonded to the molecules HL . Such compounds, type B acid salts, are formed with *o*-nitrobenzoic acid ; in the crystal structure ⁽²⁰⁾ of the rubidium compound the anion and acid could be distinguished by their bond lengths.

(iii) An acid salt of type A, MHL_2^- , in which the L anions share a hydrogen.

All three types can be distinguished by the I.R. spectrum. (i) has no recognisable OH stretching band, (ii) does have one shifted by H-bonding, (iii) gives an anomalous spectrum ⁽²¹⁾ with a broad overall absorption between 1500 and 600 cm^{-1} . The I.R. spectrum indicated that only for the ML_nHL compounds with the three ligands of highest pK was the complex of type (i).

Most of the ML.HL' compounds showed I.R. bands at 1800-1900 cm^{-1} , possibly due to hydrogen bonding. However, the presence of these was not correlated with the melting point, so it seemed unlikely that adduct formation was solely due to hydrogen bonding. This was confirmed by our success in forming adducts with 1,10-phenanthroline. The shifts in the I.R. spectrum of the 1,10-phenanthroline were similar to those observed in transition metal complexes of this ligand.

The compounds ML.nHL in Table I show trends indicating that adduct formation is favoured by a high pK value for HL and increase in radius of M^+ (possibly because of some change in a property correlated with increase in atomic number of M^+). Compounds ML.HL' (Fig. 3) show no regular variation among the alkali metals, nor do the phenanthroline derivatives. One feature of all systems is that the anion L^- must be capable of chelation to form a 5- or 6-membered ring. Although *m*-nitrophenol has a high pK (8.18) no adduct was formed by an alkali metal salt of this with excess of the *m*-nitrophenol, nor with 1,10-phenanthroline, nor with 8-hydroxyquinoline or isonitrosoacetophenone. With the last two the corresponding alkali metal salt was formed and *m*-nitrophenol liberated. While the adducts between the planar ligand and 1,10-phenanthroline may be of the molecular type like naphthalene/picric acid, we consider that the phenanthroline is chelated to the metal. The evidence is partly the I.R. spectrum and partly the observation that it was possible in some cases to make compounds containing more than one 1,10-phenanthroline per metal, but it was not possible to make such compounds with the sterically hindered 2,9-dimethyl-1,10-phenanthroline.

As the compounds exist in the solid state they can be studied by X-ray crystal structure analysis. This is now being undertaken and will, we hope, lead to greater understanding of the preferred environment of alkali metals.

REFERENCES

- (1) BREWER, F. M. & N. V. SIDGWICK. *J. Chem. Soc.*, **127**, 2379 (1925).
- (2) OLOVSSON, I. *Acta Cryst.*, **19**, 379 (1965).
- (3) PIRET, P., Y. GOBILLON & M. VAN MEERSSCHE. *Bull. Soc. Chim. France*, **1963**, 205.
- (4) YASIN, Y. M. G., O. J. R. HODDER & H. M. POWELL. *Chem. Commun.*, **1966**, 705.
- (5) HANDS, A. R. & A. J. H. MERCER. *J. Chem. Soc. (A)*, **1968**, 449.
- (6) NARULLO, N. P. & R. A. LLOYD. *J. Am. Chem. Soc.*, **88**, 1076 (1966).
- (7) LIPPARD, S. J. *J. Am. Chem. Soc.*, **88**, 4300 (1966).
- (8) BENNETT, M. J., F. A. COTTON, P. LEGZDINS & S. J. LIPPARD. *Inorg. Chem.*, **7**, 1770 (1968).
- (9) RENDLEMAN, J. A. *Advan. Carbohydrate Chem.*, **21**, 209 (1966).
- (10) SCHRASCHEL, E. & M. C. DAY. *J. Am. Chem. Soc.*, **90**, 503 (1968).
- (11) BURGESS, J. & M. C. R. SYMONS. *Quart. Rev.*, **22**, 276 (1968).
- (12) e.g. SHATENSHEIN, A. I. & E. S. PETROV. *Usp. Khim.*, **36**, 269 (1967).

- (13) PEDERSEN, C. J. *J. Am. Chem. Soc.*, **89**, 7017 (1967).
- (14) SU, A. C. L. & J. F. WEIBER. *Inorg. Chem.*, **7**, 176 (1968).
- (15) BECK, J., H. GERLACH, V. PRELOG & W. VOSER. *Helv. Chim. Acta*, **45**, 621 (1962).
- (16) KILBOURN, B. T., J. D. DUNITZ, L. A. R. PIODA & W. SIMON. *J. Mol. Biol.*, **30**, 559 (1967).
- (17) WIPF, H. K., L. A. R. PIODA, Z. STEFANAC & W. SIMON. *Helv. Chim. Acta*, **51**, 377 (1968).
- (18) BANERJEE, A. K., A. J. LAYTON, R. S. NYHOLM & M. R. TRUTER. *Nature*, **217**, 1147 (1968) and unpublished work.
- (19) FLEMING, J. E. & H. LYNTON. *Can. J. Chem.*, **46**, 471 (1968).
- (20) SHRIVASTAVA, H. N. & J. C. SPEAKMAN. *J. Chem. Soc.*, **1961**, 1151.
- (21) BLINC, R., D. HADZI & A. NOVAK. *Z. Elektrochem.*, **64**, 567 (1960).