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Coordination Chemistry of Sodium and Potassium. 1,10-Phenanthroline as a Ligand; Role of Counter Organic Anions and Foreign Protonated Species During Complexation

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The in vitro *chemistry of sodium and potassium ions (M) has been investigated using 1,10-phenanthroline (PHEN), water, and organic anion (L) as ligands with the ultimate aim of following these cations* in vivo. *For L = benzoate (Benz), 2-hydroxybenzoate (Sal), 2-aminobenzoate (Anth), the acid anion of 8-hydroxyquinoline (Quin, QuinH), 1-nitroso-2-naphtholate (1N2N), 2-nitrophenolate (2-NP), 3-nitrophenolate (3-NP), 4-nitrophenolate (4-NP), 2,4-dinitrophenolate (Dnp) and 2,4,6-trinitrophenolate (Pic), hydrated as well as dehydrated complexes of stoichiometries ML(PHEN), ML(PHEN)$_2$, M(L, HL)(PHEN), and M(L, HL)(PHEN)$_2$ were isolated; the latter two are new classes of alkali metal complexes and are isolated when ML–PHEN interaction is carried out in the presence of HL and/or water. The stoichiometries of the complexes can be deliberately controlled which is, therefore, governed not by the coordinative characteristics of M but by the complexing environments.*

The counter anion, L, hinders M–PHEN interaction in accordance with its basicity and ion-associating ability with M; for the most self-stabilized HO-Sal, M–PHEN bonds appear distinctly covalent and the M(HO-Sal)(PHEN)$_2$ complexes have been synthesised from pure water. Foreign protonated molecules – water and/or HL – in the reaction mixture favour M–PHEN interaction, for they can stabilize L through conjugation. The conditions favouring conjugation are in turn influenced by structural aspects of L, the presence of water in the reaction medium, and the degree of stabilization of the counter cation.

Introduction

The interest in investigating the coordination chemistry of alkali metals, of sodium and potassium in particular, arises because of their biochemical implications [1, 2]. Instances are noted in the literature where covalent interactions of alkali metal ions with ligands such as β-diketonates, salicylaldehyde, dioxane, amides, pyridine, diverse amino compounds, triphenylphosphine, thiourea, sugars, peptides, cyclic polyethers, and naturally occurring macrocyclic antibiotics are suspected or detected. This topic is briefly reviewed [3, 4].

No particular ligand, however, has been studied extensively, particularly in aqueous medium, with a view to understand the factors which basically control complexation of alkali metal ions in aqueous media – a knowledge which is essential to follow sodium and potassium in natural system [1, 2]. Recently, again, the reports concerning the use of some pyridine 1-oxides [5], sulpholane, propylene carbonate, *sym*-tetramethylurea, and *sym*-tetramethylguanidine [6] and dioxane [7] deal with a few selected alkali metal systems. Complexation study of 5-phenacyl-2-hydroxymethyl-4-pyran-one (phenacylkojate) [8] with MX (M = Li through Cs and NH$_4$; X = Cl, Br, I, and NCS) is detailed but the stoichiometries of the isolated complexes could not be explained from the consideration of various physicochemical properties of M, X and MX. This difficulty of understanding the systems should obviously be attributed to the lack of fundamental information about the coordination of alkali metals in the literature.

We examined [9–11] in detail complexation of MX and ML salts with some cyclic polyethers. However, a polyether can be considered as a polarisable 'physical screen' which approaches a metal ion with a particular set of equivalent oxygens all of which interact. The M/polyether ratio in products with these ligands is usually invariant. Furthermore, during the complexation of a cation with a macrocyclic ligand a strong effect – macrocyclic effect [12, 13] – is incorporated which prevents recognition of the other factors which influence M–ligand interaction.

To provide answers to problems such as those mentioned above, 1,10-phenanthroline (PHEN) has extensively been studied for complexation of sodium and potassium in the present work. PHEN is a potential bidentate ligand due to a rich delocalised electronic system and to as high a charge as –0.377 on the donor nitrogens [14]. Also, unlike for the polyethers, the M/PHEN ratio in the complex can be varied and factors which influence the same can be studied.

PHEN was used long ago [15] for complexation of alkali metals. Recently, the complexes of PHEN with $MClO_4$ (M = Li or Na [16]) and ML (L = an organic anion such as a nitrophenolate; M = Li through Cs [17, 18]) have been isolated. Presently, detailed experimentation has been carried out using comparatively complicated reaction mixtures to allow a detailed analysis of the factors controlling M–PHEN complexation. $ML(PHEN)_n$ complexes have been isolated using ML–PHEN reaction mixtures where M = Na or K; and L is benzoate (Benz), 2-hydroxybenzoate (Sal), 2,6-dihydroxybenzoate (HO-Sal), 2-aminobenzoate (Anth), the acid anion of 8-hydroxyquinoline (Quin, QuinH), 1-nitroso-2-naphtholate (1N2N), 2-nitrophenolate (2-NP), 3-nitrophenolate (3-NP), 4-nitrophenolate (4-NP),2,4-dinitrophenolate (Dnp), or 2,4,6-trinitrophenolate(Pic). Water and/or the parent acid of L, HL, have also been added to the ML–PHEN reaction mixtures to observe the effect of foreign neutral molecules on the M–PHEN interaction and to investigate the role played by L in M–PHEN complexation, the latter because the anion can be stabilised by conjugation with water as well as HL.

Experimental

Synthesis of ML and PHEN Complexes

The starting material, ML, was obtained by a 1:1 reaction of the corresponding HL and the concerned caustic alkali using about 0.05*M* concentration of each reactant in water. ML was crystallised after necessary concentration. Recrystallisation was carried out using 95 percent aq–ethanol. To obtain PHEN complexes, the reactants in desired proportion (as indicated in Table I) were dissolved in absolute ethanol (EtOH, from which no effort was made to remove moisture absorbed from atmosphere) or 90 percent aqueous ethanol (EtOH–aq) and the solution was chilled in the refrigerator. Reaction mixtures in EtOH were sealed during crystallisation. The compound was filtered and its homogeneity was ascertained under a microscope. Mechanical separation was carried out when two or more complexes constituted the crop of crystals. After the removal of the first crop, the filtrate was again subjected to cooling or evaporation to dryness at room temperature. Solutions which failed to produce the first crop on cooling overnight in the refrigerator, were slowly evaporated at room temperature to obtain the product(s). The latter were mechanically picked up from the reactants and/or the byproduct (PHEN, HL), under a microscope. Variation of temperature of the reaction solution during crystallisation affected only the yield and never the stoichiometry of the products.

For metal benzoates, the isolation of the complexes was also attempted using ML_1–HL_2–PHEN type of reaction mixtures following the same procedure as above. For the same salts, except M(Anth), isolation of the complexes was attempted from water medium using ML–PHEN (1:2) reaction mixtures. Using 2,2′-bipyridyl, 2,2′-biquinoline, and 4,7-diphenyl-PHEN as ligands, isolation of complexes of M(Dnp) and M(Sal) was also attempted as for PHEN.

Characterisation of Complexes

The complexes were characterised employing techniques usually used for such systems [4, 8, 9, 19]. For Na(Anth, AnthH)(PHEN) and Na(HO-Sal)$(PHEN)_2$, unit cell volume and the molecular weight was determined by X-ray Weissenberg and precession photography. Coordination of PHEN in a complex was revealed by (i) the higher melting point of the product compared to that of free PHEN (115–17 °C), and (ii) the following infrared characteristics of the compound: (a) The absence of a characteristic broad band due to the stretching of –OH at 3320 to 3400 cm^{-1} which is shown by the original sample of PHEN hemihydrate. (b) The presence of sharp intense peaks at 840 to 850 and 730 to 735 cm^{-1} which are attributed to δC–H of 2 and 3 adjacent aromatic hydrogens, respectively [16], of the complexed PHEN. (c) The presence of a sharp peak around 1420 cm^{-1}, which due to its absence in the infrared spectra of phenanthrene and 9,10-phenanthrone, is attributed to the stretching of delocalised $C\overset{\cdot\cdot}{=}N$ bonds in PHEN.

Features (a) and (b) of the spectra are the same as noted for PHEN–transition metal coordinated compounds [16]. Since in the present work similar complexes are involved, mutual comparison of the infrared spectra can be made. The intensity of the peaks at 730–35, 840–50, and around 1420 cm^{-1}, which are always unobscured, can be used to know the M/PHEN ratio in the complex.

At this juncture it must be emphasised that the complexes Na(2-NP)$(PHEN)_2$ and Rb(2-NP)$(PHEN)_2$, which show characteristic infrared features (a) to (c), have been the subject of X-ray structural analysis [20]. The Na complex is monomeric and the cation is 6-coordinated (Na–N, 2.49 and 2.51, 2.45 and 2.56 Å; $Na–O^-$, 2.28 Å; Na–O, 2.42 Å). The Rb complex, which is isomorphous with the analogous K complex, is dimeric and the cation is 7-coordinated (Rb–N, 3.06 and 3.08, 3.05 and 3.07 Å; $Rb–O^-$, 2.84 Å; Rb–O, 2.95 and 3.19 Å). In both the complexes M–N distances conform to bonding distances.

The presence of an acid anion, L, HL, for most carboxy acids is shown by a broad band or a peak between 1650 and 1700 cm^{-1}. The position of

TABLE I. Showing the Index of Results (Isolated Products) from PHEN–ML and PHEN–Ml–HL Reaction Mixtures in Ethanol (EtOH) and Aqueous Ethanol (1:9) (aq–EtOH).

Anion, L$^-$ (symbol)	Crop No.	Products Isolated					
		Sodium			Potassium		
		PHEN–ML (2:1)	PHEN–ML–HL (2:1:1)		PHEN–ML (2:1)	PHEN–Ml–HL (2:1:1)	
		EtOH or aq–EtOH	EtOH	aq–EtOH	EtOH or aq–EtOH	EtOH	aq–EtOH
Benz$^-$(1)	C$_1$	Na(1) and Na(1)(PHEN)$_2$·2aq^a	Na(1, H1)(PHEN)	(PHEN, H1) and Na(1, H1)(PHEN)	K(1) and K(1)(PHEN)$_2$·2aq^a	K(1)	K(1) and K(1, H1)(PHEN)
	C$_2$	–	–	as above	as above	K(1) and K(1, H1)(PHEN)	*
Sal$^-$(2)	C$_1$	Na(2)(PHEN)$_2$	Na(2)(PHEN)$_2$	Na(2)(PHEN)$_2$	K(2)(PHEN)$_2$·2aq	K(2, H2)(PHEN)$_2$·2aq^b	K(2, H2)(PHEN)$_2$·2aq
	C$_2$	as above	as above	Na(2, H2)(PHEN)$_2$·2aq	as above	as above	as above
HO-Sal$^-$(3)	C$_1$	Na(3)(PHEN)$_2$	Na(3)(PHEN)$_2$ and Na(3, H3)(PHEN)$_2$^{c} and Na(3, H3)(PHEN)$_2$·2aq	Na(3, H3)(PHEN)$_2$^{c}	K(3)(PHEN)$_2$	K(3, H3)(PHEN)$_2$^{d}	K(3, H3)(PHEN)$_2$^{c}
	C$_2$	as above	Na(3, H3)(PHEN)$_2$·2aq	as above	as above	as above	K(3, H3)(PHEN)$_2$^{d}
	C$_3$	–	as above	Na(3, H3)(PHEN)$_2$·2aq	*	K(3, H3)(PHEN)$_2$	K(3, H3)(PHEN)$_2$
Anth$^-$(4)	C$_1$	Na(4)(PHEN)$_2$·2aq^f	Na(4, H4)(PHEN) and Na(4, H4)(PHEN)$_2$·2aq	Na(4, H4)(PHEN)$_2$·2aq and Na(4, H4)(PHEN)	K(4)(PHEN)$_2$·2aq^f	K(4, H4)(PHEN) and K(4, H4)(PHEN)$_2$·2aq	K(4, H4)(PHEN)$_2$·2aq and K(4, H4)(PHEN)
	C$_2$	as above	*	*	as above	*	*
(Quin, HQuin)$^-$ (5, H5)	C$_1$	not possible^e	Na(5, H5)(PHEN)	Na(5, H5)(PHEN)	not possible^e	K(5, H5)(PHEN) and K(5, H5)	K(5, H5)(PHEN)
1N2N$^-$(6)	C$_1$ (C$_2$)	Na(6)(PHEN)^g	Na(6)(PHEN)	Na(6)(PHEN)	K(6)(PHEN)	K(6, H6)	K(6, H6)
2-NP$^-$(7)	C$_1$	Na(7)(PHEN)$_2$	Na(7)(PHEN)	Na(7)(PHEN)$_2$	K(7)(PHEN)·aq	K(7, H7)(PHEN)	K(7)(PHEN)$_2$
	C$_2$	as above	Na(7)(PHEN)$_2$ and Na(7, H7)(PHEN)$_2$	as above	as above and K(7)(PHEN)$_2$	K(7)(PHEN)·aq and K(7)(PHEN)$_2$	K(7, H7)(PHEN)$_2$
Dnp$^-$(8)	C$_1$ (C$_2$)	Na(8)(PHEN)	(PHEN, H8) and Na(8)(PHEN)	(PHEN, H8) and Na(8)(PHEN)	K(8)(PHEN)	(PHEN, H8) and K(8)(PHEN)	(PHEN, H8) and K(8)(PHEN)
Pic$^-$(9)	C$_1$ (C$_2$)	Na(9)(PHEN)	(PHEN, H)9 and Na(9)(PHEN)	(PHEN, H)9 and Na(9)(PHEN)	K(9)(PHEN)	(PHEN, H)9 and K(9)(PHEN)	(PHEN, H)9 and K(9)(PHEN)

For a particular crop the products are shown in the order of their yield. *The nature of the isolated product is uncertain. [a]Poor yield particularly for the potassium compound from ethanol. [b]The compound K(2, H2)(PHEN) is isolated when the proportion of the reactants is 2:1:2. [c]The shining but translucent crystals of the product M(3, H3)(PHEN)$_2$ crystallize as a solid solution with (PHEN, H)3, analysing nearly for the reported stoichiometry, containing variable (low) metallic contents and giving ir spectra related to that of (PHEN, H)3. [d]Contaminated with (PHEN, H)3. [e]It is not possible to synthesise M(Quin) even by the 1:1 reaction of HQuin and the caustic alkali irrespective of the media of synthesis; work had to be performed with the acid salt, M(Quin, HQuin). [f]The compound M(4)(PHEN) isolates when acetone is used for the media of synthesis; the analysis of potassium compound is poor. [g]Crystallizable only from aq–EtOH.

absorption is in between the one due to C=O in monomeric (about 1720 cm^{-1}) and the one in dimeric (about 1650 cm^{-1}, *eg*, benzoic acid in nujol) carboxy group For most compounds containing only one PHEN molecule, broad bands at 1900 and 2500 cm^{-1} are the usual indications of the acid anion in the complex although the same become weak in high molecular weight compounds containing two molecules of PHEN For some compounds containing L, HL there is an ill defined spectrum in the fingerprint region which has also been attributed earlier to a 1 1 conjugation between L and HL [21]

Summing up, the very infrared spectra of the compounds can give an idea about the composition of the products and can help classifying the latter in groups (i) to (iv) described below Analysis of the metal and nitrogen is sufficient to confirm the composition In conjunction with the analysis of nitrogen and hydrogen the analysis of carbon serves to strengthen the same and to determine the number of water molecules in the complex as and when indicated by the infrared spectrum

1 10-Phenanthroline hemihydrate, 4,7-diphenyl-1,10-phenanthroline, 2,2′-bipyridyl and 2,2′-biquinoline were British Drug House products Infrared spectra were taken employing Perkin–Elmer spectrophotometer Model 377 Microelemental analysis was performed using a GDR (German) microanalyser Determinations of sodium and potassium were made flame photometrically employing Toshniwal flame photometer Code RL-01 Conductivity measurements were made using systronics conductivity bridge Model 301-1 Melting point study of the complexes was made using a 360° hot stage microscope

Results and Discussion

Regardless of the water molecules present in the complexes, the latter constitute four classes of compounds

ML(PHEN)	ML(PHEN)$_2$
(i)	(ii)
M(L,HL)(PHEN)	M(L, HL)(PHEN)$_2$
(iii)	(iv)

Complexes of the types (i) and (ii) were isolated from any of the ML–PHEN or ML–HL–PHEN reaction mixtures dissolved in EtOH or EtOH–aq The compounds of the types (iii) and (iv), which constitute the new classes of alkali metal complexes, were isolated only when HL was used in the reaction mixture All the results, for the purpose of comparison, are indexed in Table I Description of the new compounds is provided in Table II From ML–PHEN reaction mixtures in EtOH–aq, some old compounds of the types (i) and (ii) were isolated as from EtOH [17] Such compounds find a mention in Table I and not in II Compounds containing L as well as L, HL were isolated for most ML salts However, for IN2NH, the homoconjugate (1N2N, 1N2NH)$^-$ could never be isolated whereas in the QuinH derivatives the charge neutraliser was invariably the homoconjugate (Quin, QuinH)$^-$

Since the pK value of (PHEN, H)$^+$ is 4 96 [22] the (PHEN, HL) byproducts were invariably isolated from ML–HL–PHEN reaction mixtures whenever the pK of HL was below 5 Although enough acidic, OnpH did not transfer its proton to PHEN perhaps due to its intramolecular bonding To understand the nature of the various (PHEN, HL) species and to become familiar with the conditions favouring their formation in the ML–HL–PHEN reactions, control experimentation with HL–PHEN systems in EtOH and EtOH–aq was carried out The presence of water for the crystallisation (and presumably also for their formation) was found necessary for the products of BenzH, SalH, and AnthH whereas absence of water favoured the isolation of the HO–SalH product (here and elsewhere presence or absence of water in the medium of synthesis denotes whether or not 10 percent water has been added to EtOH) For nitrophenols, the nature of the medium was immaterial Molar conductivities of PHEN–BenzH, –SalH, –HO-SalH, –AnthH, –4-NPH, –DnpH, and –PicH in acetone at 22 ± 1 °C were 0 50, 1 9, 51 3, 0 67, 1 5, 4 47, and 65 5, respectively On this basis only (PHEN, PicH) and (PHEN, HO–SalH) have been formulated as (PHEN, H)$^+$L$^-$ whereas all the rest as (PHEN, H$^{+\delta}$ L$^{-\delta}$)

Isolation studies using the reaction mixtures of the type ML$_1$–HL$_2$–PHEN in EtOH or EtOH–aq have shown that HL$_2$ with pK higher than that of HL$_1$ exercise no effect on the normal reaction between ML$_1$ and PHEN However, for more acidic HL$_2$, distribution of the metal into ML$_1$ and ML$_2$ takes place and each salt produces the respective complex containing a homoconjugated acid anion Such results show that the process of homoconjugation is preferred over that of heteroconjugation even when HL$_1$ and HL$_2$ are structurally similar such as SalH and HO-SalH

Out of the PHEN complexes of metal benzoates attempted from pure water, only those of M(HO-Sal) crystallised immediately, those of M(Sal) isolated slowly in small yield whereas of M(Benz) did not crystallise at all For M(Sal) and more so for M(Benz) unreacted PHEN recrystallised Since required amount of PHEN did not recrystallise a degree of M–PHEN interaction in solution is indicated even for these salts Interestingly, the yield of M(HO-Sal)(PHEN)$_2$ (80 percent for Na and 60 percent for K) complexes was about 20 percent higher compared to those from corresponding reaction mixtures in EtOH

TABLE II. New Complexes. Physical State, Behaviour on Heating and Analysis.

Compound	Color of Crystals	Behaviour on Heating^{a}	Elemental Analysis							
			Found				Calc.			
			C	H	N	M	C	H	N	M
Na(Benz)(PHEN)$_2$·2aq	Colorless	110^{bl}, 215–25^{m}	68.0	4.4	10.5	4.1	68.7	4.6	10.4	4.3
K(Benz)(PHEN)$_2$·2aq	"	105^{bl}, 200–05^{m}	65.8	4.6	10.2	6.8	67.0	4.5	10.1	7.0
Na(Benz, BenzH)(PHEN)	"	138–42^{m}	69.1	4.3	6.3	5.0	70.0	4.2	6.3	5.2
K(Benz, BenzH)(PHEN)	"	130–33^{m}	67.0	3.8	6.2	8.2	67.5	4.0	6.1	8.5
Na(Sal)(PHEN)$_2$	"	208–12^{m}	70.9	4.2	10.7	4.4	71.6	4.1	10.8	4.4
Na(Sal, SalH)(PHEN)$_2$·2aq	"	100^{bl}, 170^{m}	65.0	4.5	7.8	3.3	65.5	4.4	8.1	3.4
K(Sal, SalH)(PHEN)$_2$·2aq	"	110^{bl}, 130^{m}	61.7	4.2	7.5	5.5	63.0	4.5	8.2	5.7
K(Sal, SalH)(PHEN)	"	210–15^{m}	64.3	4.1	5.7	7.7	63.2	3.8	5.7	7.9
Na(HO-Sal)(PHEN)$_2$^{b}	Off white	230–35^{m}	69.4	4.2	10.7	4.4	69.4	3.9	10.3	4.3
K(HO-Sal)(PHEN)$_2$	"	187–90^{m}	67.2	3.9	10.2	7.0	67.4	3.8	10.1	7.1
Na(HO-Sal, HO-SalH)(PHEN)$_2$·2aq	Colorless	150^{t}, 175–79^{m}	62.8	4.4	7.6	3.0	62.8	4.3	7.7	3.2
Na(HO-Sal, HO-SalH)(PHEN)$_2$	Yellowish	100^{bl}, 149^{m}	63.5	4.6	7.5	3.1	66.1	3.9	8.1	3.3
K(HO-Sal, HO-SalH)(PHEN)$_2$	"	110^{bl}, 150^{t}	62.1	4.6	7.3	5.3	64.6	3.8	7.9	5.5
Na(Anth)(PHEN)	Rusty	130^{t}, 235^{m}	67.2	4.3	12.4	6.8	67.2	4.1	12.4	6.8
Na(Anth)(PHEN)$_2$·2aq	"	110^{bl}, 200^{m}	67.2	4.8	12.8	3.9	67.0	4.5	12.6	4.1
K(Anth)(PHEN)$_2$·2aq	"	90^{bl}, 173–75^{m}	65.0	4.5	12.3	7.0	65.1	4.4	12.3	6.8
Na(Anth, AnthH)(PHEN)^{c}	"	180–90^{m}	65.1	4.5	11.9	4.7	65.5	4.4	11.8	4.8
K(Anth, AnthH)(PHEN)	"	150–52^{m}	63.4	4.4	11.8	8.0	63.4	4.3	11.4	7.9
Na(Anth, AnthH)(PHEN)$_2$·2aq	Colorless	155–65^{m}	65.6	4.9	12.0	–	65.9	4.8	12.1	3.3
K(Anth, AnthH)(PHEN)$_2$·2aq	"	144^{m}	64.5	4.8	12.1	5.6	66.4	4.7	11.9	5.5
Na(Quin, QuinH)(PHEN)	Yellow	200–05^{m}	73.9	4.6	11.3	4.6	73.3	4.1	11.4	4.7
K(Quin, QuinH)(PHEN)	"	180–85^{m}	71.5	4.4	11.1	7.5	70.9	4.1	11.0	7.7
Na(2-NP)(PHEN)	"	192–94^{m}	63.6	3.8	12.5	5.8	63.3	3.5	12.3	5.8
Na(2-NP, 2-NPH)(PHEN)$_2$	"	183–85^{m}	67.1	4.1	13.0	–	65.5	3.9	12.7	3.5
K(2-NP, 2-NPH)(PHEN)	"	176^{m}	57.8	3.5	11.3	7.9	58.1	3.4	11.3	7.8
K(Pic)(PHEN)	"	250^{m}	48.0	3.1	16.0	8.5	48.3	2.7	15.7	8.7
Na(Pic)(PHEN)	"	275^{m}	49.9	2.7	16.2	5.5	50.1	2.9	16.2	5.3

[a] bl, blackening; t, transition; m, melting. [b] Mol. Wt. as found by X-ray method, 472 (Calc. 476). [c] Mol. Wt. as found by X-ray method, 540 (Calc. 536).

Both from EtOH and EtOH–aq, 2,2′-bipyridyl, 2,2′-biquinoline, and 4,7-diphenyl-PHEN recrystallised unreacted alongwith ML.

The following are the specific points which have been found to influence the M–PHEN interaction as well as the composition of the resulting solid complexes.

The Role of Water

Water, which aids ionisation of ML in organic media and the stabilisation of M and L, serves as an useful intermediate ligand for M–PHEN complexation; Na(1N2N)(PHEN) complex, *e.g.*, fails to appear from EtOH until 5–10 percent water is added to the reaction solution. Previous work [17] was not carried out from this viewpoint and the effect of water was ignored. The reported isolation of this compound from acetone [17] should be attributed to the absorption of moisture by the reaction solution from the atmosphere, for dry acetone cannot even solubilise M(1N2N) salts in the presence of PHEN. The positive role played by water during M–PHEN interaction is also demonstrated by the fact that K(Quin, QuinH)(PHEN) crystallises free of K(Quin, QuinH) from EtOH–aq and not from EtOH (Table I).

When EtOH–aq is used as synthesis medium the PHEN/M ratio in the isolated compounds is usually high compared to those isolated from EtOH. See the results especially for M(2-NP) and M(Anth) salts in Table I. Water apparently stabilizes L through the formation of heteroconjugates and helps M–PHEN interaction. For M(Pic)$_2$–CROWN (where M is also a s-block cation – Ca^{2+} or Mg^{2+}) systems, a similar effect was noted [23]. From EtOH as medium of synthesis, 1:1 complexes were always isolated whereas on the addition of some water and/or PicH to the reaction mixture 1:2 complexes were only isolated, irrespective of the proportion of the reactants employed.

The Role of Anion, L

Since M–PHEN interactions are of the ion–dipole type, some degree of ionisation of ML salts should be a pre-requisite for their coming into existence. It explains why M–PHEN complexation appears facilitated for self-stabilised anions such as Pic, and HO-Sal and is difficult for ML (particularly NaL) salts derived from high pK HL such as 1N2NH. The yield and ease of crystallisation is markedly better for each series 3-NP, 4-NP, and 2-NP; 2-NP, DNP, and Pic; Benz, Sal, and HO-Sal, in this order although for the last two series the size of the anion increases in this order and the problems of lattice packing, if any, should become accordingly acute. Obviously, complexation of M with ligands such as PHEN is deterred by the charge neutralising anion in accordance with the basicity and ion-associating ability of the latter. Chelation of M with L is not the basic necessity for M–PHEN interaction as believed earlier [17] because infrared spectra of the undefined products of the M(3-NP)–PHEN reaction mixtures also indicate the presence of metal-coordinated PHEN. All important is obviously the charge delocalisation of L by its own substituents on the aromatic nucleus by electromeric effects or by intramolecular bonding so that L loosens its hold on M and the latter effectively polarises PHEN. This also explains the marked *ortho*-effect noted earlier [17].

The Role of HL

HL in the reaction plays the same role as water by stabilising L through homoconjugation. Complexation of M with PHEN and conjugation of L with HL apparently help each other in solution. Thus, the compound M(1N2N)(PHEN) can be isolated from EtOH using the reaction mixture Na(1N2N), 1N2NH, PHEN (1:1:1) but not when 1N2NH is eliminated from the reaction mixture. Also, using Na(Anth) and AnthH in EtOH or EtOH–aq, effective homoconjugation of Anth with AnthH cannot be carried out to favour the isolation of Na(Anth, AnthH) [19] but when PHEN is also added then the acid anion product Na(Anth, AnthH)(PHEN) can be easily isolated.

Although $ML(HL)_n$ types of acid adducts are well known [4, 19, 24, 25] the $M(PHEN)_n$ (LHL) complexes are of their own type where the charge neutralising anion for a complexed cation is an acid anion. In view of the present results the formation of such compounds is not spectacular. They did not exist because they were not deliberately synthesized; conjugation of L with HL in solution as well as in the solid state is infact a natural consequence of the stabilization of the counter M with a ligand. Starting from M(Quin) salts, Banerjee *et al.* [18] claim to have isolated Na(Quin)(PHEN) and K(Quin)(PHEN)·1/2-H_2O. However, in line with the foregoing conclusion the present author failed to prevent homoconjugation and obtained only M(Quin, QuinH)(PHEN) type of complexes.

Particularly for benzoic and substituted benzoic acids, crystallisation of the complexes containing an acid anion is aided by the presence of water in the synthesis medium. The complex Na(Sal, SalH)-$(PHEN)_2$·2aq, for instance, is crystallisable from EtOH–aq but not from ethanol, for water not only favors the stabilisation of M with PHEN but also aids depolymerisation of $(HL)_n$.

Lack of Characteristics of Coordination

There are results in Table I, especially those for M(Anth) and M(HO-Sal) salts, which indicate that the composition of the alkali metal complexes can be deliberately varied with relative ease. Obviously, a fixed coordination number and a rigid stereochemistry for the alkali metal cations becomes difficult to visualise. Although the coordination number usually shown by sodium and potassium is 6 and 8, respectively [3], yet some cases of reversal may be noticed in the present results. Compare, for instance, Na(2-NP, 2-NPH)$(PHEN)_2$ with K(2-NP, 2-NPH)(PHEN); X-ray structural work has shown a decrease in coordination number with the size of the alkali metal ion in ML, HL type of solid phases [26].

Hydration of the Complexes

Hydration of the solid phase is not a function of the presence of water in the synthesis medium. When necessary for the stabilisation of M or L, water is captured even from the atmosphere as for the formation of K(Sal)$(PHEN)_2$·2aq and K(Anth)$(PHEN)_2$·-2aq and, if not needed, dehydrated complexes isolate from pure water as the M(HO-Sal)$(PHEN)_2$ complexes. Interestingly, complexes carrying two PHEN molecules are more heavily hydrated compared to those with one PHEN (Table I). Apparently, water in the former is also anion-bonded, not only due to space limitations around the cation but also due to a greater stabilisation of M with PHEN and to the consequent greater destabilization of L. Peaks due to –OH stretching in complexes K(Benz)$(PHEN)_2$·2aq and K(Sal)$(PHEN)_2$·2aq, for instance, show up as broad around 3400 cm^{-1} which is not the characteristic of metal-coordinated water.

As counter anions to a cation of a very low charge density, $[K(CROWN)_2]^+$, the heteroconjugation behaviour of Sal and HO-Sal with water has been studied [10]. Only Sal was noted to form (L, HOH). This is in agreement with the fact that K(Sal)$(PHEN)_2$ is dihydrated and K(HO-Sal)$(PHEN)_2$ is dehydrated and indicates the possibility of anion-bonded water in the former. In the crystal lattice of the adduct NH_4(Sal, SalH)·aq [25], Sal is found to bridge with water. For Na(HO-Sal, Ho-SalH)$(PHEN)_2$·2aq the possibility of anion-bonded as well as metal-coordinated water is, however, suggested by the wide differences in the position and sharpness of peaks due to the stretching of –OH which exist at 3570 and 3400 (broad) cm^{-1}.

Covalency in M–PHEN Bond

In view of the high charge on the donor atoms of PHEN, M–PHEN interaction in addition to being ion-dipole may also be considered as ion–ion. Both the forces can collectively give rise to a distinct covalency in the M–PHEN bond. For a given cation, the ion–dipole contribution and hence the degree of covalency in the bond should, obviously, be high as L behaves self-stabilized. The complexes M(HO-Sal)-$(PHEN)_2$, for example, can be considered distinctly covalent, for the same are not hydrolysed by water and are easily crystallised from this medium.

Apparently, M–ligand bond can be made water-stable, understandably appreciably covalent, as the influence of the charge neutralising anion is lifted from the complexing cation. The complexes Na[di(4-aminodiphenylmethane)$_3$] Cl [27] and Na(*p,p'*-diamino-2,3'-diphenylbutane)$_3$Cl [28], which are ion-separated systems and where X-ray analysis reveals a bridging of Cl^- with amino protons, are water-stable and are crystallized from this medium.

2,2'-bipyridyl and 2,2'-biquinoline exist preferably in the *trans* form [29, 30] due to coulombic repulsion between anionic nitrogens. However, transition cations [31, 32] and even thallous [19], which shows a potential for covalency in the Tl–N bond [33, 34], form stable complexes with these ligands. Present results, however, indicates that alkali cations fail to complex with these ligands although donor sites carried by these ligands are even more anionic than those of PHEN [14]. Obviously, the degree of covalency in M–N bond is low, as a consequence of which the *cis* form of these ligands is not stabilized against the destabilization caused by the steric hindrance due to 3,3'-hydrogens.

Basic Difference in the Chemistry of Sodium and Potassium

Sodium is distinctly harder than potassium and exhibits a higher 'anionphilicity' with anionic species [cf. 35]. With PHEN, the same is evidenced by the conductivity results [36] and by the constantly higher temperature needed for the thermal elimination of this ligand from sodium complexes compared to those from potassium analogues (see melting points in Table II; elimination of PHEN marks the melting point of complexes [17]). The anionphilicity of Na^+ towards L and PHEN and consequently its counteraction towards L•••HL interaction is particularly evidenced by the results of the M(1N2N)–1N2NH–PHEN (1:1:1) systems where for K^+ it is not the complex but only the acid anion salt K(1N-2N, 1N2NH) which isolates whereas for Na^+, it is not the acid anion salt but the complex Na(1N2N)-(PHEN) which isolates. This is in spite of the fact that Na(1N2N, 1N2NH) exists [19] and is even more insoluble than the analogous K product. Greater anionphilicity of Na^+ for PHEN compared to that of K^+ is also evident from the comparatively very high yields of Na(Quin, QuinH)(PHEN) complex from EtOH and EtOH–water systems (Table III). X-ray molecular structure analysis of the M(2-NP)$(PHEN)_2$ (M = Na or Rb) complexes has shown [20] a distortion of the benzene ring of 2-NP in the Na lattice only.

TABLE III. Percent Yield of the M(Quin, QuinH)(PHEN) Complexes from Ethanol–Water (E–W) Systems.

Metal	Medium of Synthesis			
	EtOH	E–W(9:1)	E–W(6:4)	E–W(2:8)
Sodium	85	70	35	15
Potassium	2	0.2	Crystals did not appear	

Stronger interaction of Na^+ with L^- and consequently its counteraction towards L•••HL interaction, in general, is evidenced by the fact that for Na^+ (Table I) there are fewer compounds containing the acid anion compared to K^+. This so-called "bridge breaking" property of Na^+ towards conjugation was also noted earlier [10, 19].

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