Comparison of Complex Formation by Thallium(I) and Potassium Salts of Potentially Chelating Anions

By **N. S. Poonia** and **Mary R. Truter,*** A.R.C. Unit of Structural Chemistry (University College London), Inveresk House, 346 Strand, London WC2R 0HG

Potassium and thallium salts, K(L) and Tl(L), have been prepared from the following acids H(L) where (L) is a potentially bidentate ligand: 8-hydroxyquinoline, H(1), isonitrosoacetophenone, H(2), 1-nitroso-2-naphthol, H(3), 2-nitrophenol, H(4), 2-aminobenzoic acid, H(5), 2,4-dinitrophenol, H(6), 2-hydroxybenzoic acid, H(7), and 2-nitrobenzoic acid, H(8). The thallium compounds, except Tl(6) have low conductivities in *N*-methylpyrrolidone. Addition of acids H(L') to the potassium salts K(L) gave the following new adducts K(6).H(7), K(3).2H(1), K(5).2H(1), K(6).2H(3), and K(8).2H(3). No corresponding thallium adducts Tl(L).H(L') could be obtained.

With 2,2'-bipyridyl a 1:1 adduct was obtained only with Tl(6). On addition to the corresponding metal salts 1,10-phenanthroline,phen, yielded Tl(4).phen, Tl(5).phen, Tl(6).phen, Tl(7).phen, Tl(8).phen, and K(7).2phen,-2H_2O. 2,9-Dimethyl-1,10-phenanthroline,dmphen, on addition to the metal salts, gave Tl(5).dmphen, Tl(6).-dmphen, Tl(7).dmphen, Tl(8).dmphen, K(5).dmphen, and K(7).dmphen.

Williams[1] has suggested that thallium(I) is a good probe for investigating the behaviour of potassium in biological systems. In practice thallium(I) appears to be more active than potassium. We have explored the comparative behaviour of the two cations with the compounds of Table 1.

The salts themselves were made from equimolar mixtures of metal hydroxide or carbonate and HL in ethanol. For thallium, anhydrous ML was isolated for all the acids (1)—(8). Four salts, KL, were obtained anhydrous. K(4) and K(6) Crystallise as hemihydrates and K(5) as a monohydrate, and K(1) (*i.e.* potassium oxinate) could not be isolated from ethanol.

Adducts with Chelating Acids.—As in previous investigations on alkali-metal compounds[2-4] the method for making an adduct was to suspend or dissolve the salt ML in ethanol and add HL or HL'. The criteria for adduct formation were (*i*) elemental analysis, (*ii*) an i.r.

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[1] R. J. P. Williams, *Quart. Rev.*, 1970, **24**, 331.

[2] A. K. Banerjee, A. J. Layton, R. S. Nyholm, and M. R. Truter, *J. Chem. Soc.* (*A*), 1969, 2536.

[3] A. K. Banerjee, A. J. Layton, R. S. Nyholm, and M. R. Truter, *J. Chem. Soc.* (*A*), 1970, 292.

[4] A. J. Layton, R. S. Nyholm, A. K. Banerjee, D. E. Fenton, C. N. Lestas, and M. R. Truter, *J. Chem. Soc.* (*A*), 1970, 1894.

spectrum different from that of a mixture of the components, (*iii*) a melting or transition point higher than the melting point of HL or HL′, and (*iv*) where possible, identification of a new phase by *X*-ray diffraction. We also measured the conductivity in solution and the u.v. and visible spectra.

TABLE 1

Ligands studied

Protonated ligands, H(L) or H(L′)		p*K*	M.p.
8-Hydroxyquinoline	H(1)	9·51	73—75°
Isonitrosoacetophenone	H(2)	8·50	112—116
1-Nitroso-2-naphthol	H(3)	7·70	105—106
2-Nitrophenol	H(4)	7·17	45—47
2-Aminobenzoic acid	H(5)	6·97	144—146
2,4-Dinitrophenol	H(6)	3·96	112—115
2-Hydroxybenzoic acid	H(7)	2·97	159—161
2-Nitrobenzoic acid	H(8)	2·16	144—148
Nitrogenous ligands			
1,10-Phenanthroline	phen		98°
2,9-Dimethyl-1,10-phenanthroline	dmphen		161—163
2,2′-Bipyridyl	bipy		69—71

The metal salts of ligands H(1)—H(8) are denoted by M(1), M(2), *etc.*

For potassium in the ML,*n*HL system previous work[2] was confirmed, particularly the finding that a 1 : 1 ratio gives K(1),H(1) while a 1 : 3 excess of H(1) gives K(1),2H(1); exceptions were that we failed to isolate K(5),H(5) but succeeded in isolating K(8),H(8) from the ethanol solution, this compound having previously been made from water.[5] For the mixed systems, all combinations were tried, that is, KL was made and HL′ added in various proportions. For each ligand of Table 1, seven other ligands were tried, and the product or products were characterised; five classes of reaction were found (*a*)—(*e*), as summarised in Table 2.

TABLE 2

Results of reaction between K(L) and H(L) or H(L′)

L in K(L) L′ in added HL′	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
(1)	*a′* $n = 1,2$	*e*	***a*** $n = 2$	*a*	***a*** $n = 2$	*c*	*d*	*c*
(2)	*e*	*a′*	*e*	*a*	*e*	*c*	*a*	*c*
(3)	***a*** $n = 0{\cdot}5$	*c′*	*a′*	*c′*	*e*	***a*** $n = 2$	*a*	***a*** $n = 2$
(4)	*a*	*a*	*e*	*a′* $n = 2$	*e*	*c*	*a*	*c*
(5)	***a*** $n = 0{\cdot}5$	*d*	*e*	*d*	–	*c*	*d*	*c*
(6)	*c′*	*c′*	***a*** $n = 0{\cdot}5$	*c′*	*c′*	–	***a***	*c′*
(7)	*b*	*a*	*a*	*a*	*d*	***a***	*a′*	*d*
(8)	*b*	*e*	***a*** $n = 0{\cdot}5$	*e*	*e*	*c*	*d*	*a′*

a, An adduct, $KL(HL')_n$, was obtained with $n = 1$ unless otherwise stated; $n = 0{\cdot}5$ indicates that a small yield of $KL'(HL)_2$ can be obtained. For new compounds ***a*** is shown in bold; *a′*, an adduct, $KL(HL)_n$, was obtained; –, no $KL,(HL)_n$ was obtained; *b*, H(1),HL′ was obtained; *c′*, KL′ was obtained; *c*, KL was recovered; *d*, mixtures of K-containing products were obtained; *e*, $KL(HL)_n$ and/or $KL'(HL')_n$ was obtained.

(*a*) An adduct can be isolated of formula KL,*n*HL′. In all the compounds obtained previously *n* was one and we report one more in this series K(6),H(7). In a new series $n = 2$, there are K(3),2H(1), K(5),2H(1), K(8),2H(3), and K(6),2H(3). Chemical analyses and physical properties of new compounds are shown in Table 3.

(*b*) The first crop of bright yellow crystals are devoid of potassium and have stoicheiometry HL,HL′. This is observed for the reaction of K(1),H(1) with 2-hydroxybenzoic acid or 2-nitrobenzoic acid. Chemical analysis and molecular weight determination by *X*-ray methods are consistent with the ionic formulation $H_2(1)^+,(7)^-$ or $H_2(1)^+,(8)^-$ or with molecular complexes of the charge transfer type. 8-Hydroxyquinolinium salicylate is known as a fungicide.[6]

(*c*) One potassium salt is recovered, either the starting material, KL or (c′) the exchange product, KL′, as in most systems involving H(6).

(*d*) A mixture is obtained, in some cases crystals of different compounds can be seen and separated under the microscope, then identified by chemical analysis and comparison with known compounds. This corresponds to a distribution of potassium between two different ligands, more than one of KL,HL′, KL,HL, and KL′HL′ being identified. For example, K(2),H(2) and K(1),H(1) are produced from K(2) and H(1) or K(1) and H(2) in ethanol. This illustrates the effect of the solvent, use of benzene for this system[3] gave K(2),H(1); benzene could not be used as the medium if the p*K* values of the ligands were very different, because it dissolves the undissociated molecule with the higher p*K* and leaves a precipitate of the potassium salt of the other component.

(*e*) Any one of KL,*n*HL or KL′,*n*HL′ appears, *e.g.* K(2),H(2) from reaction of K(5) and H(2).

Probably many species are present in solution, the first crop of crystals may be different from the second. Adduct formation, class (*a*), appears not to be a function of p*K*, as is clearly shown in Table 2. If the p*K* values of the potential ligands are very different they may react together as in class (*b*). Low solubility of any species leads to its isolation as in (*c*) or (*c′*) so that, depending upon the starting material, there either appears to be no reaction or a metathetical reaction.

The proportion of reactants can have a marked effect on the product. For systems with low KL solubility excess of HL′ favours adduct formation, as for K(6) with H(7) when at least a 1 : 5 ratio is required to give K(6),H(7). Excess of HL′ may favour formation of KL′,HL′ so that, to obtain the adduct K(2),H(7), H(7) is added to K(2) in a 1 : 1 ratio not more. In Table 2 class (*d*), mixtures of products, has been assigned only to those systems in which no set of conditions yielded a pure product.

The i.r. spectra of the new compounds K(6),H(7) and KL,2H(L′) are similar to those found previously[3] for KL,H(L′) in having no recognisable hydroxy stretching frequency above 3000 cm^{-1}. Broad bands at 1950 cm^{-1}

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[5] R. C. Farmer, *J. Chem. Soc.*, 1903, 1440.

[6] D. Woodcock, *Chem. in Brit.*, 1971, **7**, 415.

for K(6),H(7) at 1870 cm^{-1} for K(6),2H(3) and two bands at 2600 and at 1800—1900 cm^{-1} for K(3),2H(1),K(5),2H(1), and K(8),2H(3) are probably due to hydrogen bonded hydroxy groups.[7] For H(1), however, it is difficult to distinguish this from the i.r. spectrum given by a hydrogen bonded NH^{+} (bands at 2650 and 2100 cm^{-1}) as found[8] in the adduct $UO_2(1)_2$,H(1). Evidence of 'anomalous' absorption characteristic[9] of very strong, possibly symmetrical hydrogen bonding, was shown only by K(6),2H(3).

The compounds of known crystal structure K(2),H(2),[10] K(4),H(2),[11] K(8),H(8),[12] are acid salts with short hydrogen bonds between the two parts of the [LHL′]$^{-}$ (L may = L′) anion, and their i.r. spectra indicate that all the hydroxy groups are hydrogen bonded.

TABLE 3

Description, behaviour on heating, conductivity, chemical analysis and, where available, molecular weight by *X*-ray methods

Compound		Temp./°C	Conductivity [c]	Found					Calculated				
				Metal	C	H	N	*M*	Metal	C	H	N	*M*
K(6),H(7)	Bright yellow needles	195—197 [m]	37	11·0	44·0	2·8	7·5		10·9	43·5	2·5	7·8	
K(3),2H(1)	Dark brown crystals	120,[d] 230 [m]	17—18	7·7	67·0	4·3	8·2		7·8	67·2	4·0	8·4	
K(5),2H(1)	Rust-coloured crystals	165 [t]	17—18	8·1	64·8	4·4	9·1	481	8·4	64·5	4·4	9·0	466
K(6),2H(3)	Yellow-brown powder	160—165 [m]	40	6·6	55·9	3·2	9·4		6·8	55·0	3·0	9·8	
K(8),2H(3)	Dark brown crystals	140—145 [m]	27	7·7	59·0	3·5	7·6	575	7·1	58·8	3·3	7·6	552
Tl(1) [a]	Green-yellow needles	210—215 [m]	2	58·2	30·8	1·8	4·0		58·7	31·0	1·7	4·0	
Tl(2)	Dark grey flakes	230 [m]	2 (18) [b]	57·0	27·0	1·7	3·9		58·0	27·2	1·7	4·0	
Tl(3)	Dark brown powder	240—245 [m]	2 (18)	54·0	31·0	1·5	3·5		54·4	31·9	1·6	3·7	
Tl(4) [a]	Purple crystals	205 [m]	9 (20)	60·0	21·2	1·1	4·4	343	59·7	21·0	1·2	4·1	342
Tl(5) [a]	Off-white crystals	155,[t] 190—195 [m]	2 (18)	59·1	24·7	1·8	4·5	347	60·1	24·7	1·8	4·1	340
Tl(6) [a]	Orange-yellow crystals	235—240 [m]	32 (35)	52·5	18·7	0·8	7·2	395	48·7	17·2	0·7	6·7	419
Tl(7)	Pale pink crystals	200—205 [m]	14 (33)	59·7	24·7	1·5			60·0	24·6	1·5		
Tl(8) [a]	Off-white flakes	140—145 [m]	4 (25)	55·0	24·5	1·8	4·0	368	55·1	22·8	1·1	3·8	370
K(7),2phen,2H_2O	Colourless crystals	80,[d] 167 [m]	34	7·2	65·0	4·6	9·7	577	6·8	65·0	4·4	9·8	572
K(5)dmphen	Pale brown needles	135 [t]	19	10·0	64·7	5·0	10·8		10·2	65·8	4·7	11·0	
K(7)dmphen	Colourless crystals	200 [m]	32	10·7	65·6	4·6	7·4		10·2	65·6	4·4	7·3	
Tl(4),phen	Orange-yellow needles	155 [m]	8	38·9	41·2	2·5	8·2		39·0	41·4	2·3	8·0	
Tl(5),phen	Off-white crystals	245 [m]	2	39·4	43·3	2·9	7·9		39·2	43·7	2·7	8·1	
Tl(6),phen	Orange-yellow laths	232—234 [m]	32	36·2	38·1	2·0	9·5		36·0	37·0	1·9	9·9	
Tl(7),phen	Colourless crystals	200 [m]	14	39·1	43·8	2·6	5·5	528	39·2	43·7	2·5	5·4	521
Tl(8),phen	Small colourless crystals	170—172 [m]	4	36·7	41·8	2·4	7·9		37·2	41·5	2·2	7·6	
Tl(5),dmphen	Fine off-white needles	220 [m]	2	37·0	45·7	3·2	8·1		37·2	45·9	3·3	7·7	
Tl(6),dmphen	Bright yellow needles	195 [m]	31	34·2	41·0	2·6	9·5		34·3	40·3	2·5	9·4	
Tl(7),dmphen	Colourless crystals	210 [m]	14	37·0	46·1	3·1	5·1	550	37·1	45·9	3·1	5·1	549
Tl(8),dmphen	Pale orange powder	200—205 [m]	4	35·0	44·0	3·0	7·1		35·3	43·6	2·8	7·3	
Tl(6),bipy	Bright yellow crystals	145 [m]	31—32	38·2	35·2	1·9	10·1		37·5	35·4	2·0	10·3	
H(1)H(8),H_2O	Yellow crystals	80 [m]	2		57·8	4·2	8·4	330		58·3	4·3	8·5	329

[a] Previously reported in ref. 4. [b] Values in parentheses are for the potassium salt from ref. 2. except for K(6) to K(8). [c] In Ω^{1} cm^{2} mol^{-1}. [m] Melting point. [d] Colour change (darkening). [t] Transition.

The equivalent conductivities in solution in *N*-methylpyrrolidone are shown in Table 3; the values of KL,*n*HL′ are the same as those for KL. These values compare with 35—40 Ω^{-1} cm^{2} mol^{-1} for 1 : 1 electrolytes and suggest that, although KL and KL′ ion pairs may be present in solution, the conductivity corresponds to that of the more dissociated species.

The appearance of several compounds KL,2(HL′) led us to try to make adducts with three different ligands KL(HL′)(HL″) but without success.

No adducts were obtained for thallium whatever the ratio of reactants, in agreement with the findings of Lee.[13]

The analyses and conductivities of the thallium salts are shown in Table 3, with the conductivities for the corresponding potassium salts in parentheses. The conductivity for thallium is much lower, implying at least a stronger Tl^{+}L^{-} ion-pairing, except for 2,4-dinitrophenol,H(6). Tl(6) Also had much the highest conductivity in methanol and acetone.[13]

Adducts with Chelating Bases.—Three chelating bases containing aromatic nitrogen atoms and no acidic or hydrogen bond forming hydrogen atoms were each added to ethanolic solutions of K(1) · · · (8) and Tl(1) · · · (8).

With 1,10-phenanthroline neither metal gave adducts for Tl(1) or M(2). For potassium the previous results[4] with K(3), K(4), and K(6) were confirmed and a new compound, K(7),2phen,2H_2O was characterised by chemical analysis and preliminary *X*-ray investigation;

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[7] D. Hadži, A. Novak, and J. E. Gordon, *J. Phys. Chem.*, 1963, **67**, 1118.

[8] A. Corsini, J. Abraham, and M. Thompson, *Chem. Comm.*, 1967, 1101.

[9] D. Hadži, *Pure Appl. Chem.*, 1965, **11**, 435.

[10] M. A. Bush, H. Luth, and M. R. Truter, *J. Chem. Soc.* (*A*), 1971, 740.

[11] M. A. Bush and M. R. Truter, *J. Chem. Soc.* (*A*), 1971, 745.

[12] H. N. Shrivastava and J. C. Speakman, *J. Chem. Soc.*, 1961, 1151.

[13] A. G. Lee, *J. Chem. Soc.* (*A*), 1971, 2007.

its i.r. spectrum differed from that of a mixture, *e.g.* two sharp peaks at 760 and 770 cm^{-1} and two small peaks at 812 and 822 cm^{-1} compared with one strong peak at 775 and another at 817 cm^{-1} in a mixture of K(7) and phen,H_2O.

Attempts to add phen to KL,(HL′) were not successful; K(4),H(2), K(7),H(2), and K(3),H(7) were recovered when phen was added to the corresponding solution. Addition of phen to K(7),H(4) gave some H(7),phen but mainly recovery of K(7),H(4) while K(6),H(7) gave a mixture of H(6),phen, K(6),phen, and H(7),phen. The H(L),phen for each of H(4) to H(8) were characterised by comparison of the i.r. spectra of 1 : 1 mixtures obtained by grinding and of the adduct crystallised from ethanol.

Adducts of formula Tl(L),phen were obtained for L = (4), (5), (6), (7), and (8); for L = (3) it was always contaminated with Tl(3) and is not included in Table 3. Lee[13] was unable to isolate Tl(4),phen from water or ethanol; we found an excess of phen (1 : 3) was necessary, no adduct being obtained with a 1 : 1 ratio. These adducts all melt at temperatures much higher than the melting point of phen, their conductivities in solution are the same as those of the Tl(L) salts, even including the high value for Tl(6), indicating that they, like the alkali metal adducts, dissociate in solution. A diagnostic feature of the i.r. spectra is the absence of hydroxy stretching frequencies above 3000 cm^{-1} in the adducts; the hydrate of phen was used for the reaction and its physical mixtures with Tl(L) give strong hydroxy bands. Neither Tl(7) nor Tl(7),phen shows a hydroxy stretching frequency, suggesting that the phenolic group is strongly hydrogen bonded, as in other 2-hydroxybenzoates.[14]

2,9-Dimethyl-1,10-phenanthroline,dmphen has the methyl groups in positions which may provide steric hindrance. Alkali metal 2-nitrophenolates, which formed M(4),2phen, gave only M(4),dmphen.[4] We have now made two more 1 : 1 potassium adducts K(5),-dmphen and K(7),dmphen. For thallium no adduct was formed with Tl(4) but Tl(5), Tl(6), Tl(7), and Tl(8) gave 1 : 1 adducts. These had the same conductivities as the corresponding salts.

No adduct was obtained with 2,2′-bipyridyl for any potassium salt and only one, Tl(6),bipy, from the eight thallium salts even in ratios up to 1 : 20. This ligand is *trans* in its crystalline form[15] and non-planar in the gas[16] but to form a *cis*-chelate, as it does with transition metals, it has to adopt an arrangement giving steric hindrance between the hydrogen atoms in the 3 and 3′ positions.

We measured the electronic spectra of typical systems in ethanol solution to compare the metals and to discover whether addition of phen gave effects not attributable to mixtures of the components. In contrast to Lee's findings[13] for phenolates (which we confirmed) that the wave length of absorption was greater for M^+ = alkali metal than for H^+ or Tl^+ we found for the carboxylates (5) and (7) that, where there were differences, the wave lengths were $H^+ > Tl^+ > K^+$. For H(5), Tl(5), and K(5) absorption was found at 337, 322, and 317 nm respectively, and for all three at 246 and at 215 nm. In the salicylate system peaks are found for H(7), Tl(7), and K(7) at 304, 297, and 296 nm, respectively then a distinct one at 235 nm for H(7) and inflections at about 225 nm for K(7) and Tl(7). Addition of phen, which itself absorbs at 324, 308(sh), 265, and 228 nm, in 1 : 1 ratio gave the three absorptions characteristic of this molecule unshifted. These completely masked any other absorptions in the 2-hydroxybenzoate system and also the ones at 246 and 215 nm for the 2-aminobenzoic acid system but the higher wave length peak did show an effect; there was a very broad peak at 340—320 nm for H(5) and double maxima at 325 and 315 nm for Tl(5) and at 324 and 310 nm for K(5), so that for both metals there were shifts of 7 nm to higher energies, possibly indicative of stronger ion pairing by the phenanthroline-chelated metal.

There was no additional absorption in the $Tl^{(I)}$ compounds, as compared with the H^+ or K^+ compounds, attributable to the $Tl^{(I)}$ band.

DISCUSSION

There is a contrast between thallium and potassium in the possibility of isolating adducts from ethanol solution and in the low conductivity in *N*-methylpyrrolidone solution of Tl(L) for most systems.

The species present in the solution of K(L) + H(L′) are probably solvated forms of K^+, L^-, L'^-, H(L), H(L′), and $(LHL')^-$; the conductivities suggest some ion-pairing. For the two compounds of known crystal structure K(2),H(2)[10] and K(4),H(2)[11] the anion $(LHL')^-$ is held by a strong hydrogen bond and acts as a tetradentate ligand to potassium; sharing of ligand atoms increases the co-ordination number of potassium to seven (or eight) and results in polymeric structures.

Comparison of the u.v. spectra of 2-aminobenzoic acid and its potassium and thallium salts in ethanol suggests that for both metals (5) is present in solution as the anion; the molar conductivities in ethanol, 30·5 and 13·5 Ω^{-1} for potassium and thallium respectively, suggested stronger ion-pairing by the thallium ion. For the salicylates u.v. spectra for Tl(7) and K(7) again indicate a similar anion while the molar conductivities in ethanol, 26·0 and 33·5 Ω^{-1}, are consistent with stronger ion-pairing for thallium. Although the conductivities in ethanol are all greater than in *N*-methylpyrrolidone (Table 3) they follow the same trends qualitatively. This stronger ion-pairing is consistent with the higher stability constants found[17] for cation–anion interaction by thallium than by potassium. The lack of adduct formation with ' hard ' ligands may arise from repulsion

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[14] I. M. Koltoff and M. K. Chantooni, *J. Amer. Chem. Soc.*, 1971, **93**, 3843.

[15] L. L. Merritt and E. D. Shroeder, *Acta Cryst.*, 1956, **9**, 801.

[16] A. Almenningen and O. Bastiansen, *K. norske vidrnsk Selsk. Skr.*, 1958, No. 4.

[17] J. P. Manners, K. G. Morallu, and R. J. P. Williams, *Chem. Comm.*, 1970, 165.

by a stereochemically active lone-pair of electrons on the thallium ion, so that the thallium ion has a smaller co-ordination number than potassium.

Phen forms five-membered chelate rings with metals. The ligand (2) which might form five- or six-membered rings was found[10,11] to give five-membered ones, so preference for this geometry may explain the observation that adducts were obtained for both potassium and thallium with all the anions which would, if chelated, give six-membered or larger rings but not for those which themselves give five-membered rings, *i.e.* H(1) and H(2). For alkali-metal 2-nitrophenolates two molecules of phen could be added giving $M(4),phen_2$, but only one could be added to Tl(4); this again is consistent with a lower co-ordination number for thallium. The complex cation $(phen)_2Tl^+$ is formed with nitrate or perchlorate ions but there is no evidence for expansion of the co-ordination number beyond four.[18]

In biological systems there is a possibility that the complete environment of thallium is different from that of potassium even if the first cation–anion interaction is comparable. Not only does the preferred co-ordination number of thallium appear lower but much less symmetrical, for example crystal structure analysis has shown that in Tl(7)phen the thallium is at the apex of a distorted pentagonal pyramid.[19]

EXPERIMENTAL

Potassium was estimated by flame photometry. Thallium was estimated gravimetrically by precipitation as the iodide, organic matter was removed by washing with ethanol–benzene (1 : 1) in 2—3 ml portions. Carbon, hydrogen, and nitrogen were determined by microanalysis in University College. I.r. spectra were measured in Nujol mulls with a Perkin-Elmer 137 spectrometer. Conductivities were measured using a Philips bridge PR9500 in *N*-methylpyrrolidone. Use of this solvent for conductivity measurements has been investigated in detail elsewhere,[20] we have used the same procedure and calibration as before,[2] *i.e.* 10^{-3}M concentrations at 25 °C. The same concentration was also used for ethanol. U.v. and visible spectra were measured on a Unicam SP 500 as ethanolic solutions at concentrations of about $0{\cdot}5 \times 10^{-3}$M for the 290—350 nm region, and $0{\cdot}5 \times 10^{-4}$M for the 200—290 nm region.

Preparations.—Metallic thallium was dissolved in hot water with constant passage of a stream of oxygen or air to give the hydroxide or carbonate respectively,[21] which crystallised out on evaporation.

Potassium Salts, K(L).—Potassium hydroxide was dissolved in ethanol and stoicheiometric amounts of H(L) added. K(L) Formed either instantaneously or was crystallised out from the solution.

Thallous Salts, Tl(L).—Thallous hydroxide (61 mg) was dissolved in ethanol (10—15 ml) by heating the mixture in a covered beaker, a small turbidity was obtained from formation of the carbonate. A slight excess over the equimolar amount of H(L) dissolved in 2—3 ml of ethanol was added and the mixture heated for about 10 min. For Tl(2) and Tl(3) the product crystallised on cooling, for the other, more soluble, salts reduction in volume to 5 ml was necessary before crystallisation. The more soluble salts can conveniently be made by suspending thallous carbonate in ethanol and adding a slight excess over a 1 : 1 ratio of H(L), heating, filtering off any unreacted carbonate, and concentrating the filtrate from which the product crystallises.

Adducts.—All adducts (Table 2) were prepared in ethanol. Reactants were heated on a steam bath until dissolved and the solution allowed to cool at room temperature until the product crystallised out. The adduct $K(L)(HL')_n$ could be prepared by starting from either of K(L) + HL′ and K(L′) + H(L) [where pK_a of H(L) is lower than that of H(L′)] but we describe below the methods starting from K(L). Various ratios of the reactants were tried but those giving the purest product are mentioned below.

Potassium(1-nitroso-2-naphtholate)(8-hydroxyquinoline)$_2$.—A K(3) : H(1) (1 : 2) reaction mixture was used. Some K(3) was deposited on cooling and was filtered off before the adduct was crystallised.

Potassium(2-aminobenzoate)(8-hydroxyquinoline)$_2$.— A K(5) : H(1) (1 : 2) reaction mixture was used. Variation of proportions affects the yield but not the nature of the product.

Potassium(2,4-dinitrophenolate)(1-nitroso-2-naphthol)$_2$.—A K(6) : H(3) (1 : at least 3) reaction mixture was used. The excess of H(3) prevents the partial recrystallisation of $K(6),\frac{1}{2}H_2O$.

Potassium(2-nitrobenzoate)(1-nitroso-2-naphthol)$_2$.— A ratio of H(3) : K(8) of at least 3 : 1 was required.

Potassium(2-hydroxybenzoate)(2,4-dinitrophenol).— A K(7) : H(6) : H(7) (1 : 1 : at least 4) reaction mixture was used. Excess of H(7) in this reaction mixture prevents the partial recrystallisation of $K(6),\frac{1}{2}H_2O$.

Thallium(2-nitrophenolate)(1,10-phenanthroline).— A Tl(4) : phen (1 : 3) ratio was used.

Thallium(2,4-dinitrophenolate)(2,2′-bipyridyl).—A Tl(6) : bipy (1 : at least 20) ratio was used.

For all the other ML (M = K or Tl) adducts with nitrogeneous ligands 1 : 1 reaction mixtures were employed.

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