Complexes of Thallium(I), Lead(II), and Calcium Hexafluoroacetylacetonates with Nitrogen Containing Ligands

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Complexes of thallium(I), lead(II), and calcium(II) hexafluoroacetylacetonates with 1,10-phenanthroline, 2,2′-bipyridyl, and *NNN′N′*-tetramethylethylenediamine have been prepared and their spectra (i.r. and n.m.r.) compared with their lithium and magnesium analogues. Anionic hexafluoroacetylacetonates of the same metals have been prepared and investigated.

INTEREST in the co-ordination chemistry of the alkali and alkaline earth metals has led to a search for suitable probes for these metals. Thallium(I) has been shown to replace potassium in pyruvate kinase and vitamin B_{12}-dependant diol dehydratase,[1] but comparative studies of complex formation by thallium(I) and the alkali metals have shown that, for systems involving potentially chelating anions such as 2-nitrophenol and 2-nitroso-1-naphthol, a similarity between thallium(I) and lithium rather than potassium is apparent.[2,3] The preferred co-ordination number of thallium(I) appears to be lower than that of potassium.[3]

We have investigated complexes of the hexafluoroacetylacetonates (hfac) of lithium, magnesium, calcium, thallium(I), and lead(II), M(hfac)$_n$, with the nitrogen containing ligands 1,10-phenanthroline (phen), 2,2′-bipyridyl (bipy), and *NNN′N′*-tetramethylethylenediamine (tmed), in an attempt to discern patterns of comparison. Anionic complexes, where the enolate anion, hfac$^-$, acts as the Lewis base, have also been investigated. The complexes isolated, together with their chemical analyses, are listed in Table 1.

TABLE 1
Analyses

	Found %			Calculated %		
	C	H	N	C	H	N
(tmed)Tl(hfac)	25·0	3·0	5·3	25·1	3·2	5·3
(phen)Tl(hfac)	34·5	1·6	4·8	34·5	1·5	4·7
(bipy)Tl(hfac)	31·6	1·4	4·7	31·8	1·6	4·9
(tmndH$^+$)[Tl(hfac)$_2$]$^-$	34·7	2·5	3·2	34·6	2·5	3·4
(tmed)Pb(hfac)$_2$	25·8	3·2	5·1	26·1	2·4	3·8
(phen)Pb(hfac)$_2$	32·8	1·4	3·7	32·9	1·2	3·5
(bipy)Pb(hfac)$_2$	30·9	1·5	3·3	30·9	1·3	3·6
(tmndH$^+$)$_2$[Pb(hfac)$_4$]$^{2-}$ (yellow)	39·4	2·9	4·0	39·6	2·9	3·8
(tmndH$^+$)$_2$[Pb(hfac)$_4$]$^{2-}$ (white)	39·5	3·2	3·8	39·6	2·9	3·8
(phen)Ca(hfac)$_2$,H_2O	40·5	1·8	4·3	40·6	2·3	4·1
(bipy)Ca(hfac)$_2$	39·3	1·7	4·5	39·7	2·1	4·3
(tmndH$^+$)[Ca(hfac)$_3$]$^-$-2H_2O	37·9	2·7	3·0	38·1	2·8	3·1
(tmndH$^+$)$_2$[Ca(hfac)$_4$]$^{2-}$	44·4	3·3	4·3	44·3	3·5	4·5
(phen)Li(hfac)	51·7	2·5	7·2	51·6	2·8	7·1
(tmndH$^+$)[Li(hfac)$_2$]$^-$	45·1	3·4	4·2	45·3	3·3	4·4
(tmed)Li(hfac),H_2O	37·3	5·1	7·6	37·9	5·4	8·0
(tmed)Li(hfac),2H_2O	35·6	5·3	7·9	36·1	5·7	7·7
(phen)Na(hfac),H_2O	48·2	2·6	6·7	47·7	2·6	6·6

RESULTS AND DISCUSSION

Under aerial conditions the ease of forming isolable crystalline complexes of tmed with the alkali metals decreases down the group. The complexes may be prepared in a direct reaction of the salt with the ligand but the potassium, rubidium, and caesium species all form atmosphere sensitive species. The lithium complex, previously reported as a 1 : 1 complex,[4] readily picks up water to form mono- and di-hydrates. This same pattern is observed for magnesium and calcium. A recent investigation into the formation of bis(dimethylformamido)bis(1,3-diphenylpropane-1,3-dionato)magnesium has shown that crystals of the complex were stable under low humidity conditions but otherwise decomposed slowly suggesting replacement of the addend by water.[5]

The occurrence of complexation in the hfac systems may be shown by investigation of the i.r. spectra (Table 2) in the regions 900—1100 and 2700—3000 cm^{-1} compared to the free ligand.[6-8] The reaction of Tl(hfac) and Pb(hfac)$_2$ with tmed gave novel 1 : 1 complexes. For thallium(I) salts ethylenediamine complexes have been proposed in solution but not isolated;[9] the use of trifluoromethylation to increase the acceptor ability of metal β-diketonates is well established,[10] and presumably facilitates complexation here. The i.r. spectra of these complexes as Nujol mulls showed absence of free ligand and resembled those of Mg(hfac)$_2$(tmed) [10] and Cu(hfac)$_2$(tmed) [11] where it was proposed that chelation had occurred. The spectrum of Mg(hfac)$_2$(tmed) in $CDCl_3$ or benzene is similar to that in the solid state and to that reported for Li(hfac)(tmed) in benzene.[4] The spectra for the Tl and Pb complexes however differed from these two suggesting a difference between the solid and solution

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states. The molecular weights of the Tl and Pb complexes (by osmometry in benzene) did not follow the associative trends displayed by Li(hfac)(tmed)[4] and were consistently low, suggesting dissociation.

TABLE 2

Infrared spectra of the tmed complexes

	Solvent	
Li(hfac)(tmed)	$CDCl_3$	1020m, 1038m, 1066w, 1658s, 2780w, 2820m, 2850w, 2940m
	benzene	944m, 1020m, 1066w, 1660s, 2780w, 2820m, 2940m
	Nujol	946m, 1023ms, 1039m, 1072w, 1660s
$Mg(hfac)_2(tmed)$	$CDCl_3$	956m, 1018w, 1028m, 1062w, 1660s, 2790w, 2840m, 2860m, 2950w
	benzene	956m, 1018w, 1060w, 1660s, 2800w, 2840m, 2860m, 2950w
	Nujol	936w, 955m, 1012w, 1048w, 1060w, 1664s
Tl(hfac)(tmed)	$CDCl_3$	1028m, 1080m, 1660s, 2780w, 2820m, 2850w, 2950m
	benzene	948m, 1078m, 1658s, 2780w, 2820m, 2850w, 2930m
	Nujol	940w, 952ms, 1024m, 1039ms, 1668s
$Pb(hfac)_2(tmed)$	$CDCl_3$	1028m, 1084m, 1645s, 1658sh, 2760m, 2810m, 2850sh, 2950
	benzene	946m, 1082m, 1645s, 1660sh, 2760m, 2800m, bd, 2940m
	Nujol	920w, 939w, 958ms, 1015m, 1028ms, 1080w, 1643s, 1653sh
$Ca(hfac)_2(tmed)$	Nujol	924w, 954ms, 1020m, 1035ms, 1078w, 1662s, 1680sh
tmed	neat	938w, 1034s, 1040sh, 1100w, 2780s, 2820sh, 2860s, 2950s

The regions reported are those ascribed to the carbonyl stretching frequency,[6] the bands due to the $>$N–Me groups (2700—2950 cm^{-1})[9] and the region between 900 and 1100 cm^{-1} where changes due to differences in ligand conformation are observed.[10]

1 : 1 Complexes were also isolated for Tl(hfac) and $Pb(hfac)_2$ with phen and bipy. In these species as with those containing Li, Mg, and Ca, the i.r. spectra showed shifts and splittings of the bands at 854 and 738 cm^{-1} for phen and at 758 cm^{-1} for bipy. These changes have been used as criteria for complexation by these ligands.[12] The complex of $Ca(hfac)_2$ with phen and that of Na(hfac) with phen analysed as monohydrates.

If thallium(I) can isomorphously replace potassium in its complexes it may act as an n.m.r. probe for the alkali metals. The ^1H n.m.r. spectrum of the complex formed between the macroheterobicyclic diamine, 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane, (cryptate 2,2,2), and TlCl shows, at 7°, splittings of all the $-CH_2$ proton signals due to the interaction of the $^{203,205}Tl$ nuclei with these protons.[13] This has been attributed to the probability of some covalent character in the Tl–N bonds.[14] No discernible splittings were observed by us either at ambient temperature or at lower temperatures for the Tl and Pb tmed complexes. The ^1H n.m.r. spectra of $Mg(hfac)_2(tmed)$ and Li(hfac)(tmed) in benzene show signals at 1·83 and 1·78 p.p.m., and at 1·79 and 1·76 p.p.m. respectively, in integral ratio 3 : 1. These results are consistent with Noltes' proposition that in complexes where tmed acts as a chelate the CH_3–N singlet is observed at lower field than the CH_2–N singlet when benzene is the solvent.[15] In contrast the Tl and Pb complexes show the CH_3–N signal at higher field in each case. The chemical shifts are 1·80 and 1·93 p.p.m. for the Tl complex and 2·09 and 2·17 p.p.m. for the Pb complex, in 3 : 1 integral ratio. The free ligand signals are at 2·16 (CH_3–N) at 2·32 (CH_2–N) p.p.m. These results suggest that either the criterion for chelation is not applicable or that a non-chelated species is present in solution. The latter seems more likely as the evidence from the i.r. spectra and the molecular weights also indicates differences from solid to solution.

A second comparison was made using a series of anionic hexafluoroacetylacetonates. The reaction of 1,8-bis(dimethylamino)naphthalene, tmnd, with hfacH gives the salt $tmndH^+hfac^-$.[16] The reaction of this salt with alkali and alkaline earth metal hfacs was shown to give a series of anionic complexes, *e.g.*, $tmndH^+[Li(hfac)_2]^-$, $tmndH^+[K_2(hfac)_3]^-$,[17] and $tmndH^+[Mg(hfac)_3]^-$.[16] The crystal structure of the latter showed the presence of discrete $[Mg(hfac)_3]^-$ ions,[18] and that of $Rb_2[Na(hfac)_3]^{2-}$ showed the presence of $[Na(hfac)_3]^{2-}$.[19] The reaction of $tmndH^+hfac^-$ with Tl(hfac) and $Pb(hfac)_2$ in varying stoicheiometries yielded only $tmndH^+[Tl(hfac)_2]^-$ and $(tmndH^+)_2[Pb(hfac)_4]^{2-}$. The latter was isolated as either a white amorphous powder or as yellow crystals.*

In both the Tl and Pb complexes the i.r. spectra showed retention of the broad band centred on 2600 cm^{-1} and attributed to the quaternary $\geqslant N \cdots H \cdots N \leqslant$ stretch.[20] The spectra show single carbonyl stretches and comparison with the starting materials indicates new phases. Conductivity measurements in nitromethane show that $tmndH^+[Tl(hfac)_2]^-$ is a 1 : 1 electrolyte ($\Delta = 63{\cdot}6\ \Omega^{-1}\ cm^2\ mol^{-1}$) and that $[Pb(hfac)_4]^{2-}(tmndH^+)_2$ is a 1 : 2 electrolyte ($\Delta = 126{\cdot}1\ \Omega^{-1}\ cm^2\ mol^{-1}$).[21] The reaction of $Ca(hfac)_2$ with $tmndH^+hfac^-$ gave two isolable species, $tmndH^+[Ca(hfac)_3]^-,2H_2O$ and $(tmndH^+)_2[Ca(hfac)_4]^{2-}$.

The ^1H n.m.r. spectra of these complexes in $CDCl_3$ have

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* The molecular weights of these compounds and of Tl(hfac)(tmed), Tl(hfac)(phen), and $Pb(hfac)_2(phen)$ as determined by *X*-ray techniques are compatible with their formulations. The complexes are also new crystalline phases and not mixtures of the starting materials. (C. Nave and M. R. Truter, personal communication, 1973.)

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proved interesting. Although the spectrum of the Mg complex shows, at ambient temperature, a doublet for the $>$N–Me signal (*J ca.* 2 Hz), those of the parent tmndH$^+$hfac$^-$ and the Li, Tl, and Pb complexes show single lines (Table 3). A preliminary low temperature study shows that at -30 to $-40°$ doublets with *J ca.* 2 Hz evolve and that the coalescence temperature in the case of tmndH$^+$hfac$^-$ is $+6°$. The addition of water to the Mg complex leads to a collapse of the doublet and the addition of D_2O gives a broad triplet. This suggests that an exchange of the quaternary proton takes place *via* removal of the proton from the system. In the quaternary cryptate 4,10,15-trioxa-1,6-diazabicyclo-[5.5.5]heptadecane dihydrochloride, a coupling of *J ca.* 5 Hz is observed from the slowly exchanging ammonium proton to the bridging $-CH_2-$ groups,[22] and in the spectrum of tmed run in CF_3CO_2H a coupling of *J ca.* 4·5 Hz is observed for the N-Me protons. The spectra of tmnd recorded in CF_3CO_2H [20] and in neat hfacH both showed doublets for the N-Me signal (*J ca.* 2 Hz).

TABLE 3

^{1}H N.m.r. spectra of the anionic complexes

	Solvent	δ(CH_3)/ p.p.m.	Signal	δ(CH)/ p.p.m.
tmnd	$CDCl_3$	2·83	singlet	
	hfacH	3·29	*J ca.* 2 Hz	
	CF_3CO_2H *	3·21	*J ca.* 2 Hz	
tmndH$^+$hfac$^-$	$CDCl_3$	3·22	singlet	5·63
tmndH$^+$[Mg(hfac)$_3$]$^-$	$CDCl_3$	3·05	*J ca.* 2 Hz	5·92
tmndH$^+$[Li(hfac)$_2$]$^-$	$CDCl_3$	3·05	singlet	5·84
tmndH$^+$[Tl(hfac)$_2$]$^-$	$CDCl_3$	3·19	singlet	5·61
(tmndH$^+$)$_2$[Pb(hfac)$_4$]$^{2-}$	$CDCl_3$	3·18	singlet	5·73
(tmndH$^+$)$_2$[Ca(hfac)$_4$]$^{2-}$	$CDCl_3$	3·23	*J ca.* 2 Hz	5·94
tmed	$CDCl_3$	2·27		
	CF_3CO_2H	3·21	*J ca.* 4 Hz	
hfacH	$CDCl_3$			6·42

* Ref. 20.

The apparent similarity between thallium(I) and lithium is reinforced here in the observed behaviour patterns, and is probably due to the greater potential for covalent character relative to the other alkali metals. For lead(II) as with calcium it is suggested that the ionic contribution is dominant and that this, together with the increased ion size leads to the higher co-ordination numbers reached in the anionic series.

EXPERIMENTAL

I.r. spectra were recorded using a Perkin-Elmer 137 Infracord and n.m.r. spectra were recorded on a Perkin Elmer R 12B spectrometer. Microanalyses were carried out by the University College, London and the University of Sheffield Microanalytical Laboratories.

Li(hfac),[23] Mg(hfac)$_2$,2H_2O,[10] and Tl(hfac) [24] were prepared by literature methods. Ca(hfac)$_2$,2H_2O was prepared by refluxing $CaCO_3$ and hfacH, in the required ratio, in diethyl ether. The colourless solution slowly turned pink and a pink crystalline material was recovered. The pink colouration persisted on washing with benzene or recrystallisation. A metathetical reaction between $CaCl_2$ and Tl(hfac) gave a white product having the same i.r. spectrum as the pink product. This colouration has also been observed in preparations of Mg(hfac)$_2$,2H_2O from basic magnesium carbonate and hfacH. Pale yellow crystals of Pb(hfac)$_2$ were recovered from the reaction of basic lead carbonate and hfacH in CH_3Cl under reflux. The reaction of lead acetate and hfacH in water gave a pale yellow powder which analysed as 'basic lead hexafluoroacetylacetonate'.

Analyses.—Ca(hfac)$_2$,2H_2O (Found: C, 24·9; H, 1·3. $C_{10}CaF_{12}H_6O_6$ requires C, 24·5; H, 1·2%). Pb(hfac)$_2$ (Found: C, 19·4; H, 0·8. $C_{10}F_{12}H_2O_4Pb$ requires C, 19·3; H, 0·3%). 2Pb(hfac)$_2$,Pb(OH)$_2$,2H_2O (Found: C, 15·8; H, 0·8. $C_{20}F_{24}H_{10}O_{12}Pb_3$ requires C, 15·8; H, 0·6%).

The neutral complexes were prepared by stoicheiometric reaction of the components in benzene, toluene, or ethanol. The anionic complexes were prepared by reaction of tmndH$^+$hfac$^-$ with the corresponding M(hfac)$_n$ in benzene or toluene.

We thank Professor M. R. Truter and Mr. C. Nave for *X*-ray crystallographic information and for helpful discussions.

[3/2079 *Received, 10th October,* 1973]

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