Anionic Hexafluoroacetylacetonato Complexes of Alkali and other Metals and the Crystal Structure of Dirubidium Tris(hexafluoroacetylacetonato)-sodate

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Anionic alkali-metal complexes of the types M(hfac)$_2$$^-$ and M(hfac)$_3$$^{2-}$ are reported (hfac = CF_3·CO·CH·CO·CF_3). The counter ions present are mono-protonated, 1,8-bis(dimethylamino)naphthalene, $[C_{14}H_{19}N_2]^+$, or alkali metals. The preparations of the complexes $[C_{14}H_{19}N_2]^+$[M(hfac)$_3$]$^-$ (M = Cu, Mg, Ni, or Mn) and $[C_{14}H_{19}N_2]^+$-[Tl(hfac)$_2$]$^-$ are also reported.

The crystal structure of dirubidium tris(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)sodate has been determined by Patterson and Fourier methods from 1127 observed reflections measured on a diffractometer. *Z* = 4 in an orthorhombic cell, having *a* = 15·603(3), *b* = 15·809(3), *c* = 10·321(2), space group $P2_12_12_1$. Full-matrix refinement has led to *R* 0·096. Sodium is surrounded by a trigonal prism of oxygen atoms (Na–O 2·20—2·47 Å), the chelate β-diketonates forming the prism sides. Each trigonal face is shared with a rubidium ion which is also in contact with fluorine atoms (some of which are disordered) in the same and in other complex anions, one rubidium cation is also co-ordinated by the oxygen atoms of one β-diketone in another anion.

DIVALENT ions of transition metals usually have a co-ordination number towards oxygen greater than four. Neutral β-diketonates of these metals may therefore behave as Lewis acids and achieve co-ordinative saturation through addition of Lewis bases.[1] The bases may be unidentate ligands, such as ammonia, water, or pyridine, neutral chelates, or the enolate ion itself. Saturation may also be achieved through self-association as in the polymeric nickel(II) [2] and cobalt(II) acetylacetonates.[3] It has further been shown that progressive trifluoromethylation of the β-diketone facilitates co-ordinative saturation [4-6] as the Lewis acidity of the metal is affected by the relative electron-withdrawing power of the β-diketone.[4,7]

The neutral alkali-metal hexafluoroacetylacetonates (hfac),[8] if non-associated, can be considered as two-co-ordinate Lewis acids and therefore capable of undergoing addition reactions. It has been shown [9] that Li(hfac) will add *NNN'N'*-tetramethylethylenediamine (tmed) to form Li(hfac)(tmed) which is monomeric, presumably containing four-co-ordinate lithium, at low dilution in benzene. We have observed that the propensity for forming such complexes diminishes from lithium to caesium in reactions open to the atmosphere, and that complexes are readily formed with *o*-phenanthroline.[10]

We are interested in alkali-metal complexes which

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should yield information on preferred co-ordination numbers and geometries,[11] and now describe experiments designed to yield anionic complexes of these metals by methods we have established for some transition metals and magnesium.[12,13] A preliminary account has appeared.[14]

During investigations of the co-ordinative saturation of copper(II) [5] and magnesium(II) β-diketonates [6] we used the potential ligand 1,8-bis(dimethylamino)naphthalene (tmnd).[15] The reaction of tmnd with $Cu(hfac)_2(H_2O)$ in ethanol gave two products, $[Cu(hfac)(OEt)]_2$ and a crystalline species identified as $[tmndH^+][Cu(hfac)_3^-]$.[12] The crystal structure of this complex [13] unequivocally established its identity and confirmed that co-ordinative saturation was achieved through enolate addition. The reaction products are the result of a base hydrolysis facilitated by the remarkable basicity of the ligand; [15]

$$2Cu(hfac)_2(H_2O) + 2EtOH \xrightarrow{\text{base}} [(hfac)Cu(OEt)]_2 + 2hfacH + 2H_2O$$

$$hfacH + tmnd \longrightarrow [tmndH^+][hfac^-]$$

$$[tmndH^+][hfac^-] + Cu(hfac)_2(H_2O) \longrightarrow [Cu(hfac)_3^-][tmndH^+] + H_2O$$

The cleavage stage of this sequence is similar to the reaction of bis(acetylacetonato)copper(II), $Cu(acac)_2$, with methanol in the presence of a base such as potassium hydroxide, where $[Cu(acac)(OMe)]_2$ is formed.[16]

Excellent yields of the $[tmndH^+][Cu(hfac)_3^-]$ species were obtained by a different procedure. The tmnd reacted with hexafluoroacetylacetone to give $[tmndH^+][hfac^-]$, this salt on treatment with $Cu(hfac)_2$ in benzene or toluene gave the product. With magnesium, manganese and nickel, an isomorphous series of $[tmndH^+][M(hfac)_3^-]$ complexes were obtained.[14] The preparation of $[tmndH^+][Mg(hfac)_3^-]$, fully characterised by crystal-structure determination,[13] and the previous reports of $NaMg(acac)_3$ [17,18] suggested that alkali metals might also form anionic complexes.

The reaction of $[tmndH^+][hfac^-]$ with M(hfac), (M = Li, Na), in benzene–ethanol gave, on removal of the solvent, crystalline samples of $[tmndH^+][M(hfac)_2^-]$. The sodium salt was monohydrated. K(hfac) and $[tmndH^+][hfac^-]$ gave a crystalline complex of stoicheiometry 2[K(hfac)][tmndH][hfac]. The conductivity of this complex in nitromethane is compatible with its being a 2 : 1 electrolyte [19] and so the complex may be formulated as $[tmndH^+][K^+][K(hfac)_3^{2-}]$. For comparison with the alkali-metal complexes we also used Tl(hfac) and obtained $[tmndH^+][Tl(hfac)^{2-}]$. Analytical results and, where available, conductivities in nitromethane and molecular weights by *X*-ray methods are given for all compounds in Table 1. The conductivity of the Na, Li, and Tl complexes suggest 1 : 1 electrolytes. The i.r. spectra of the complexes (Table 2) are different from those of each component, and from physical mixtures of the components. *X*-Ray powder photographs show that the complexes are new crystalline phases, and not physical mixtures of the components. The broad

TABLE 1

	M.p. (°C)	Found (%)			Calc. (%)				*M*	
(*a*) Quaternary cation complexes		C	H	N	C	H	N	Λ [a]	*X*-ray	Calc.
$(tmndH)^+(hfac)^-$	135—136	53·6	4·6	6·2	54·0	4·8	6·6	81·4	422	422
$(tmndH)^+Cu(hfac)_3^-$	110—112	38·9	2·7	3·1	38·7	2·4	3·1	46·7	905	900
$(tmndH)^+Mg(hfac)_3^-$	117—118	40·4	2·6	3·2	40·5	2·6	3·3	52·8	878	860
$(tmndH)^+Ni(hfac)_3^-$	133—143	39·4	2·4	2·6	38·9	2·5	3·1		893	895
$(tmndH)^+Mn(hfac)_3^-$	112—114	40·0	2·9	3·2	39·1	2·5	3·1		894	891
$[Cu(hfac)(OEt)]_2$		26·2	1·8		26·6	1·9				631
$(tmndH)^+Li(hfac)_2^-$	141—143	45·1	3·4	4·2	45·3	3·3	4·4	71·4	656	636
$(tmndH)^+Na(hfac)_2^-(H_2O)$	103—105	43·1	3·3	4·4	43·0	3·5	4·2	80·1	661	670
$(tmndH)^+K_2(hfac)_3^-$		38·2	2·5	3·1	38·1	2·4	3·1	111·4	932	914
$(tmndH)^+Tl(hfac)_2^-$	114—117	34·7	2·5	3·2	34·6	2·5	3·4	63·6	808	833
(*b*) Mixed alkali-metal complexes										
$KLi(hfac)_2(H_2O)$		25·2	1·0		25·1	0·8		85·2	479	478
$RbLi(hfac)_2(H_2O)$		22·9	0·8		22·2	0·5			536	524
$CsLi(hfac)_2(H_2O)$		20·9	0·9		21·0	0·6		80·2	594	572
$KNa(hfac)_2(H_2O)$		24·3	0·8		24·3	0·8		59·5	482	494
$K_2Na(hfac)_3(H_2O)$		24·4	0·8		24·5	0·7			728	740
$Rb_2Na(hfac)_3$		21·6	0·6		22·1	0·4		110·1	814	815
$Cs_2Na(hfac)_3$		19·6	0·4		19·8	0·3			913	910
$RbK(hfac)_2$		21·6	0·5		22·3	0·4			526	538
$CsK(hfac)_2$		20·3	0·8		20·5	0·3		116·9	615	586
$CsRb(hfac)_2$		18·6	0·4		19·0	0·3			634	632

[a] In 10^{-4} m^2 S mol^{-1} measured for 10^{-3}M-solution in nitromethane. Calibration values [19] are: zero electrolytes. 0—20, 1 : 1 electrolytes 80—90, and 2 : 1 electrolytes 130—180.

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band centred at 2100 cm^{-1} attributed to the N $\cdots$ H $\cdots$ N bond in the cation,[15] also appears in the complexes. This suggests that the quaternary cation is retained in these species.

Studies of the mass spectra of volatile alkali-metal β-diketonates [20-22] had shown that peaks at *m*/*e* values greater than the (ML^+) peaks existed, and peaks attributable to $M_2L_2^+$ occurred. Similarly, such higher molecular-weight fragments occurred in the mass spectra of alkaline-earth metal β-diketonates.[23,24] For the alkali metals it was suggested that such peaks were due to polymeric ions arising from species produced by reactions occurring during evaporation.[22] Metal exchange between chelates in the ion source of the spectrometer was suggested to explain the existence of $MM'L_2^+$ type peaks which were also observed.[21] A mixture of calcium and strontium β-diketonates is not separable by gas chromatographic techniques,[24] and its mass spectrum contains high *m*/*e* peaks attributed to mixed-metal species. The heteronuclear polymers are accounted for by a reaction such as: *

TABLE 2

I.r. spectra [a]

	ν(C=O)	Ring def.	δ(CF_3)
(*a*) Metal hfac complexes			
Li(hfac)	1660	670	595
Na(hfac)	1675, 1655	665	585
K(hfac)	1673	660	580
Rb(hfac)	1665bd	660	580
Cs(hfac)	1663bd	660	578
$Cu(hfac)_2(H_2O)$	1640	680	600
$Mg(hfac)_2(H_2O)_2$	1659	665	578
$Ni(hfac)_2(H_2O)_2$	1650	678	596
$Mn(hfac)_2(H_2O)_2$	1648	667	592
Tl(hfac)	1635, 1652	660	580
(*b*) Quaternary cation complexes			
$(tmndH)^+(hfac)^-$	1665	658	572
$(tmndH)^+Cu(hfac)_3^-$	1645	680	590
$(tmndH)^+Mg(hfac)_3^-$	1656	665	588
$(tmndH)^+Ni(hfac)_3^-$	1645	672	590
$(tmndH)^+Mn(hfac)_3^-$	1643	664	586
$(tmndH)^+Li(hfac)_2^-$	1655	663	580
$(tmndH)^+Na(hfac)_2^-(H_2O)$	1671	663	580
$(tmndH)^+K_2(hfac)_3^-$	1670	660	575
$(tmndH)^+Tl(hfac)_2^-$	1660	657	575
(*c*) Mixed alkali–metal complexes			
$KLi(hfac)_2(H_2O)$	1665bd	665	590
$RbLi(hfac)_2(H_2O)$	1655	660	582
$CsLi(hfac)_2(H_2O)$	1655bd	660	580
$KNa(hfac)_2(H_2O)$	1668bd	660	580
$K_2Na(hfac)_3(H_2O)$	1670, 1650sh	660	580
$Rb_2Na(hfac)_3$	1670, 1650sh	660	580
$Cs_2Na(hfac)$	1670, 1650sh	663	583
$RbK(hfac)_2$	1670bd	662	581
$CsK(hfac)_2$			
$CsRb(hfac)_2$	1662	659	580

[a] Assignments from ref. 9.

$$[Ca(thd)_2]_2 + [Sr(thd)_2]_2 \rightleftharpoons 2CaSr(thd)_4.$$

The complex $NaMg(acac)_3$ was prepared [18] by the reaction of magnesium acetate and Na(acac) in methanol. The reaction of K(hfac) and $Cu(hfac)_2(H_2O)$, or $Mg(hfac)_2(H_2O)_2$, gave $KM(hfac)_3$ [10] and an extension from magnesium to the alkali metals seemed feasible.

The reaction of M(hfac) with M′(hfac) where M and M′ are different alkali metals gave rise to the species $M'M(hfac)_2$ and $M'_2M(hfac)_3$ (Table 1). We have formulated the complexes with the lighter and potentially ligated metal as the anionic species. This is in accord with the quaternary cation complexes, and with the crystal structure of $Rb_2Na(hfac)_3$. The lower apparent co-ordination of the heavier metals, *i.e.* $CsRb(hfac)_2$, has been observed in complexes such as temf,CsNCS † (ref. 25) and phenacylkojate, CsNCS.[26] In these complexes polymerisation and sharing of the donor species boosts the co-ordination number of the metal, and gives it an optimised electron-rich environment. A low co-ordination number for thallium, however, probably results from the stereochemically active lone-pair of electrons.[27]

The i.r. spectra (Table 2) show that the species are not mixtures of the starting materials, although caution must be exercised as the formation of artefacts is possible,[28] and as the hydration of the cationic alkali-metal present may be facilitated. The ν(OH) band in the hydrated species is broad in all cases (3450—3480 cm^{-1}). The ring deformation and δ(CF_3) bands are all very sharp, the higher CF_3 regions (1300—1000 cm^{-1}) are similar for each stoicheiometric group of complexes and are not shown in Table 2. The carbonyl stretching bands are generally broad and this may be ascribed to the fact that all metals present may interact with both the donor oxygen atoms and the fluorine atoms from the trifluoromethyl group.[29,30] For the 2 : 1 species two ν(C=O) bands are observed, possibly the result of the dissimilar environments of the oxygen atoms. For example, four oxygen atoms make contacts with two cations and the other two with three cations in $Rb_2Na(hfac)_3$ (see later).

The conductivities of M(hfac) in nitromethane suggest an increased dissociation from Li to Cs [Λ values in nitromethane are: Li(hfac) 8·3, Na(hfac) 14·7, K(hfac) 33·7, Rb(hfac) 56·1, and Cs(hfac) 75·6 10^{-4} m^2 Siemens mol^{-1}], and the possibility of polymeric species with the smaller cations.

Conductivities of the complexes must be interpreted with caution because the hydrates may dissociate by

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* Where thd is 2,2,6,6-tetramethyl-3,5-heptanedione.

† Where temf is 6,7*R*,9*R*,10,17,18*S*,20*S*,21-octahydro-7,9,18,20-tetramethyldibenzo[*b*,*k*][1,4,10,13,16]hexaoxacyclooctadecin.

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more than one pathway. The value of the conductivity may be that of a 1 : 1 electrolyte [*e.g.* KLi(hfac)$_2$(H$_2$O)], a 2 : 1 electrolyte [*e.g.* Rb$_2$Na(hfac)$_3$], or the sum of the conductivities of the components, *e.g.* 72·8 10^{-4} m^2 Siemens mol^{-1} for an equimolar mixture of Na(hfac) and Rb(hfac). Both CsLi(hfac)$_2$(H$_2$O) and CsK(hfac)$_2$ also give results consistent with their being sums of components, the stoicheiometry of the latter compound does not suggest it to be a 2 : 1 electrolyte.

TABLE 3

(*a*) Atomic co-ordinates (× 10^4) and isotropic vibration parameters (× 10^3) with estimated standard deviations in parentheses. A prime in the atom labelling indicates an alternative position for a disordered fluorine atom

	x/a	y/b	z/c	U/Å^2
Rb(1)	−2710(3)	−0086(4)	4522(5)	
Rb(2)	0899(3)	−0714(4)	−0113(5)	
Na	−0873(12)	−0421(12)	2223(15)	45(5)
C(1)	−2946(34)	−2355(35)	3037(53)	61(16)
C(2)	−2176(24)	−1931(24)	2151(33)	17(11)
C(3)	−1692(35)	−2549(32)	1509(48)	74(16)
C(4)	−1043(33)	−2128(34)	0804(46)	75(17)
C(5)	−0460(—)	−2653(—)	0020(—)	219(42)
O(1)	−2068(18)	−1150(19)	2337(27)	59(10)
O(2)	−0696(16)	−1457(19)	0549(26)	50(9)
F(1)	−3530(38)	−1746(38)	3333(58)	78(20)
F(2)	−2699(44)	−2794(46)	3991(66)	105(23)
F(3)	−3363(29)	−3006(29)	2108(46)	35(14)
F(1′)	−2909(30)	−3237(28)	2972(48)	40(14)
F(2′)	−3687(40)	−2069(41)	2338(66)	88(22)
F(3′)	−2744(45)	−2128(49)	4149(64)	112(25)
F(4)	−0966(23)	−3278(21)	−0888(32)	136(13)
F(5)	0060(26)	−2485(26)	−0873(42)	174(19)
F(6)	−0145(27)	−3316(28)	0467(48)	187(18)
C(6)	0178	1731	1001	228(41)
C(7)	−0439(34)	1138(39)	0753(56)	91(20)
C(8)	−0732(30)	1840(29)	1565(43)	53(14)
C(9)	−1476(34)	1439(34)	2080(51)	71(17)
C(10)	−1862	1988	3050	282(60)
O(3)	−0468(18)	0467(22)	0349(33)	72(11)
O(4)	−1833(17)	0731(19)	2269(24)	45(9)
F(7)	0568(20)	2390(23)	0428(36)	135(13)
F(8)	1093(22)	1334(22)	0445(39)	153(14)
F(9)	0484(27)	1609(29)	−1021(44)	179(19)
F(10)	−1543(27)	2701(23)	3432(35)	137(14)
F(11)	−2102(26)	1762(26)	4170(38)	169(16)
F(12)	−2655(30)	2336(28)	2673(39)	185(20)
C(11)	2102(50)	−0376(59)	3637(78)	138(28)
C(12)	0959(34)	−0503(30)	3646(51)	72(15)
C(13)	0722(30)	−0413(27)	4908(47)	64(15)
C(14)	−0193(29)	−0432(26)	5155(46)	60(15)
C(15)	−0373(99)	−0623(96)	6919(132)	249(54)
O(5)	0635(19)	−0398(24)	2589(30)	69(11)
O(6)	−0795(18)	−0385(17)	4436(24)	44(8)
F(13)	2343(29)	−1067(31)	3898(46)	190(18)
F(14)	2214(22)	−0402(19)	2286(33)	119(12)
F(15)	2261(27)	0298(30)	4072(41)	171(19)
F(16)	−1243(28)	−0286(31)	6881(41)	34(15)
F(17)	−0033(50)	−1139(50)	7194(71)	117(27)
F(18)	−0202(83)	0132(78)	6970(103)	162(39)
F(16′)	0297(38)	−0311(47)	7431(53)	72(21)
F(17′)	−0769(65)	0397(58)	6789(78)	158(35)
F(18′)	−0930(64)	−1083(65)	6842(90)	162(35)

(*b*) Anisotropic vibrations parameters (× 10^3) for the rubidium ions in the form $\exp[-2\pi(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + U_{23}klb^*c^* + 2U_{31}lhc^*a^* + 2U_{12}hka^*b^*)]$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rb(1)	60(3)	93(4)	55(3)	−10(4)	20(3)	3(4)
Rb(2)	55(3)	112(5)	57(4)	10(4)	15(4)	13(4)

In the solid state all may be associated. The *X*-ray powder photographs of the mixed-metal complexes show that they are new crystalline phases and not physical mixtures.

Crystal Structure of Rb$_2$Na(hfac)$_3$.—To elucidate the nature of the complexes isolated we determined the crystal structure of Rb$_2$Na(hfac)$_3$ which is isomorphous with Cs$_2$Na(hfac)$_3$. There are four formula units in an orthohombic unit cell having the space group $P2_12_12_1$ so that all the atoms of one chemical formula, 2Rb, Na, 18F, 15C, and 6 O had to be located, the three hydrogen atoms being neglected. While the other atoms were located satisfactorily there was persistent evidence for disorder of the CF$_3$ groups, for two of which two sets of positions were found.

Atomic co-ordinates and vibration parameters are given in Table 3, and the more important of the bond distances and angles in Table 4. Because of the disorder, the distances and angles involving the CF$_3$ groups are generally meaningless and are not given.

TABLE 4

(*a*) Interatomic distances (Å)

O(1)–C(2)	1·26(5)	Na–O(3)	2·47(4)
O(2)–C(4)	1·22(6)	Na–O(4)	2·36(4)
C(2)–C(3)	1·40(6)	Rb(1)–O(4)	2·99(3)
C(3)–C(4)	1·41(7)	Rb(2)–O(3)	2·87(4)
O(1)–O(2)	2·87(4)	Rb(1)–O(3^{I})	3·03(4)
Na–O(1)	2·20(4)	Rb(1)–O(4^{I})	3·10(3)
Na–O(2)	2·40(4)	O(5)–C(12)	1·21(6)
Rb(1)–O(1)	2·90(4)	O(6)–C(14)	1·20(5)
Rb(2)–O(2)	2·84(3)	C(12)–C(13)	1·36(7)
Rb(1)–O(1^{I})	3·52(4)	C(13)–C(14)	1·45(6)
Rb(1)–O(2^{I})	3·64(3)	O(5)–O(6)	2·94(4)
O(3)–C(7)	1·14(7)	Na–O(5)	2·38(4)
O(4)–C(9)	1·26(6)	Na–O(6)	2·29(4)
C(7)–C(8)	1·46(7)	Rb(1)–O(6)	3·03(3)
C(8)–C(9)	1·43(7)	Rb(2)–O(5)	2·86(4)
O(3)–O(4)	2·94(5)		

(*b*) Bond angles (°) in the ligands

O(1)–C(2)–C(3)	133(4)	C(8)–C(9)–O(4)	144(5)
C(2)–C(3)–C(4)	107(4)	O(5)–C(12)–C(13)	137(5)
C(3)–C(4)–O(2)	147(5)	C(12)–C(13)–C(14)	116(5)
O(3)–C(7)–C(8)	154(6)	C(13)–C(14)–O(6)	131(4)
C(7)–C(8)–C(9)	98(4)		

(*c*) Bond angles (°) O(*n*)–Na–O(*m*)

	O(6)	O(5)	O(4)	O(3)	O(2)
O(1)	90(1)	147(1)	82(1)	124(1)	77(1)
O(2)	137(1)	91(1)	128(1)	78(1)	
O(3)	139(1)	82(1)	75(1)		
O(4)	90(1)	128(1)			
O(5)	78(1)				

The structure, with atomic designations, is shown in Figures 1 and 2. The sodium is surrounded by a trigonal prism of oxygen atoms from the three β-diketonates and has no other atomic contact. The compound can therefore be considered as an anionic complex of sodium, Na(hfac)$_3^{2-}$. The same co-ordination geometry has been found before in a neutral complex of sodium [31] where the metal is surrounded by a trigonal prism of oxygen atoms from the ligand bis(diphenylphosphinyl)methane. Trigonal prismatic co-ordination has been found for rubidium in its acid salt with 5-bromo-3-hydroxy-6-methyluracil.[32]

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[31] W. H. Hewertson, B. T. Kilbourn, and R. H. B. Mais, *Chem. Comm.*, 1970, 952.

[32] M. R. Truter and B. L. Vickery, *J. Chem. Soc.* (*A*), 1971, 2077.

The rubidium ions are situated above and below the triangular faces of the trigonal prism and approximately *on its* three-fold axis. They have different environments, Rb(1) also being co-ordinated to $O(3^I)$ and $O(4^I)$ of a symmetry-related hfac and having a longer contact to $O(1^I)$ and $O(2^I)$. Each rubidium ion forms three five-membered rings with the F–C–C–O groups of the ligands, *e.g.* Rb(1) with F(1) [or F(3′)], C(1), C(2), and O(1). Rb(1) makes one additional contact to fluorine, F(16), in another molecule while Rb(2) makes contact with four fluorine atoms in other molecules, a disordered pair counting as one contact. All contacts to fluorine (2·80—3·35 Å) are probably fairly weak, as the fluorine atoms are disordered with high temperature factors, so their rotation is not hindered by a strong Rb–F interaction.

The compound is comparable with anionic tetrakis(hexafluoroacetylacetonato)-complexes of the lanthanides with caesium as the cation.[29] In these the lanthanide is only bonded to the oxygen atoms of the surrounding hfac while the caesium has contacts to the oxygen and fluorine atoms of the ligand.

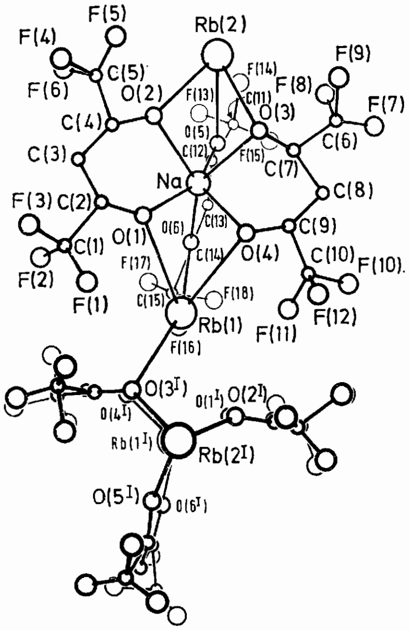

FIGURE 1 Two asymmetric units projected onto the plane $O(1^I)$, $O(4^I)$, $O(6^I)$. The atoms of the crystal chemical unit are designated without a Roman numeral, those with a superscript I are related by a screw axis $-\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z$ which is at *ca.* 45° to the direction of view and approximately passes through Rb(1) and $Rb(1^I)$. For F(1)—(3), F(16)—(18) only one set of the disordered positions are shown

The distances of the metal ions from the mean plane of the chelate ring differ for each hfac ligand, probably owing to the approach of the symmetry-related rubidium ion to two of the hfac ligands (see Table 5). The sodium–oxygen, and rubidium–oxygen distances are similar to those found for other compounds of these metals.[33,34]

The distances between the oxygen atoms of each chelate (2·87—2·94 Å) are larger than has been found for previous hfac complexes (2·69—2·81 Å)[13,29] and much larger than the bite in hexafluoroacetylacetone (2·55 Å) as found by electron diffraction.[35] The bond distances and angles in the hfac ligands do not differ significantly from those found previously apart from the O–C–C angles, which are increased to accommodate the larger sodium ion. It has been suggested,[36] from consideration

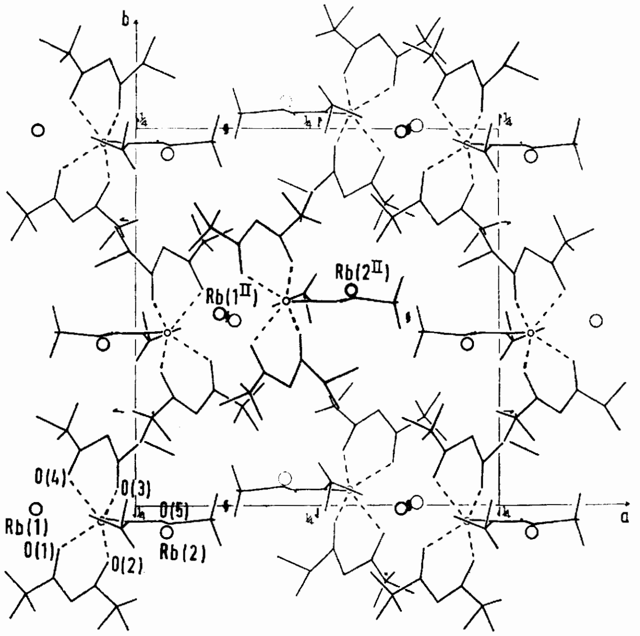

FIGURE 2 The structure projected down the *c* axis. Atoms with a superscript II are related to the asymmetric unit by the screw axis $\frac{1}{2} + x, \frac{1}{2} - y, z$. The environment of the $Rb(1^{II})$ and $Rb(2^{II})$ ions can be seen. The Rb(1) ions are linked by oxygen atoms to form columns down the *c* axis

TABLE 5

Planes through the hfac ligands. Distances of atoms from the plane (Å) are given in square brackets for atoms used to define the plane

Plane (*A*): $0{\cdot}618x - 0{\cdot}148y - 0{\cdot}772z + 0{\cdot}955 = 0$
[C(2) 0·05, C(3) −0·05, C(4) −0·02, O(1) −0·02, O(2) 0·01]
Rb(1) −0·89, Rb(2) −0·83, Na −0·91, $Rb(1^I)$ 2·73
Plane (*B*): $0{\cdot}615x - 0{\cdot}286y - 0{\cdot}735z + 0{\cdot}622 = 0$
[C(7) −0·02, C(8) −0·04, C(9) 0·10, O(3) 0·01, O(4) −0·02]
Rb(1) −1·25, Rb(2) −1·49, Na −1·42, $Rb(1^I)$ 2·21
Plane (*C*): $0{\cdot}40x + 0{\cdot}999y - 0{\cdot}024z - 0{\cdot}358 = 0$
[C(12) 0·10, C(13) −0·06, C(14) 0·02, O(5) −0·02, O(6) 0·00]
Rb(1) −0·35, Rb(2) 0·53, Na 0·12

Angles (deg.) between normals to planes

(*A*)–(*B*)	(*A*)–(*C*)	(*B*)–(*C*)
8	96	104

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[33] BIDICS, *e.g.* Na–O distances in BIDICS for 1969 and 1970 by I. D. Brown and C. P. Weiss, Institute for Materials Research, McMaster University, Hamilton, Ontario, Canada, 2nd edn., 1972.

[34] See *e.g.* L. Golic and J. C. Speakman, *J. Chem. Soc.*, 1965, 2521; M. Cotrait, *Acta Cryst.*, 1970, *B*, **26**, 1152; D. Bright and M. R. Truter, *J. Chem. Soc.* (*B*), 1970, 1544; ref. 32.

[35] A. L. Andreassen, D. Zebelman, and S. H. Bauer, *J. Amer. Chem. Soc.*, 1972, **93**, 1148.

[36] O. L. Kepert, *Inorg. Chem.*, 1972, **11**, 1561.

of the repulsions between co-ordinating atoms in different chelates, that the ratio of the bite to metal–ligand bond lengths (b/a) determines whether tris-bidentate complexes form trigonal prisms, trigonal antiprisms, or have intermediate geometry with a twist angle, ϕ, between the triangular faces from 0° (trigonal prism) to 60° (trigonal antiprism). It was observed that maleonitriledithiolates $[M(S_2C_2R_2)_3]^{x+}$ (b/a 1·31) did not conform to this analysis but no explanation was given for the discrepancy between the observed twist angles ($\phi = 0°$) and the predicted ($\phi = 50°$). Valence-bond theory does lead to the conclusion that bonding in a trigonal prism should be strongest when the prism has square sides corresponding to a b/a ratio of 1·31.[37]

The value of b/a for our compound is 1·2 which gives a predicted ϕ of *ca.* 40° according to the curves given in ref. 36. While the interaction of the oxygen atoms with the rubidium ions is likely to affect the geometry of the compound, no such explanation can be applied for the tris[bis(diphenylphosphinyl)methane]sodium[31] cation in which b/a is also 1·2 and trigonal prismatic co-ordination is present. It would seem that the criteria used for predicting the stereochemistry of tris-bidentate chelate complexes does not hold when trigonal prismatic co-ordination is in fact present, and some other explanation is required, possibly involving the directional properties of the lone pairs on the co-ordinating atoms. For cations with d^0 configurations there is no preferred six-co-ordinate stereochemistry on the basis of ligand-field stabilisation.[38] For values of $b/a < 1·1$, seven- or eight-co-ordination usually occurs through dimerisation or solvent or ligand addition.[39]

We suggest that in the anionic complexes formed, the lighter metal atom is present in the anion, the greater ease of bonding to the smaller cation being taken as the necessary factor in forming the anion. The cation of the heavier metal is in an approximately spherical surrounding of electron density derived from shared oxygen atoms and fluorine atoms.

EXPERIMENTAL

I.r. spectra were measured on a Perkin-Elmer 457 spectrophotometer as Nujol mulls or KBr discs. Conductivities were measured using a Philips bridge PR 9500 and a specially constructed cell. Microanalyses are included in Table 1.

Preparations.—The alkali-metal hexafluoroacetylacetonates were prepared by the methods of ref. 8. The metal(II) hexafluoroacetylacetonates were prepared by literature methods (Mg,[6] Cu,[40] Mn,[41] and Ni,[41]). Thallium hexafluoroacetylacetonate, prepared by the method of ref. 42, had m.p. 130—131 °C although literature values are 148—150 and 119 °C.[42,43]

(*a*) *Monoprotonated* 1,8-*bis*(*dimethylamino*)*naphthalene hexafluoroacetylacetonate.* 1,8-Bis(dimethylamino)naphthalene (0·1 mol) and hexafluoroacetylacetone (0·1 mol) were warmed gently in benzene–ethanol. Addition of pentane precipitated a white compound. Concentration of the pentane wash gave crystals, m.p. 135—136 °C, and subsequent recrystallisation of these crystals, or the white compound, gave *crystals* of monoprotonated 1,8-bis(dimethylamino)naphthalene hexafluoroacetylacetone.

(*b*) *Copper compounds.* The reaction of aquobis(hexafluoroacetylacetonato)copper(II) and 1,8-bis(dimethylamino)naphthalene in 1 : 1 stoicheiometric ratio in ethanol gave a dark green solution. Emerald green *crystals*, m.p. 165—166° were obtained on slow evaporation, and identified as di-μ-ethoxo-bis(hexafluoroacetylacetonato)dicopper(II). Pale yellow *needles*, m.p. 110—112 °C, were recovered from the level of the meniscus in the beaker and were subsequently shown to be the tris(hexafluoroacetylacetonato)-copper(II) salt of monoprotonated 1,8-bis(dimethylamino)-naphthalene.

(*c*) *Quaternary cation salts of anionic metal* hfac *complexes.* The reaction of monoprotonated 1,8-bis(dimethylamino)-naphthalene hexafluoroacetylacetonate with the bis(hexafluoroacetylacetonates) of divalent metals (Mg, Cu, Ni, or Mn) in 1 : 1 stoicheiometric ratio in benzene or toluene, gave on slow evaporation *crystals* of the corresponding tris(hexafluoroacetylacetonato)metal(II) salt of monoprotonated 1,8-bis(dimethylamino)naphthalene. The complexes of thallium and of alkali-metal hexafluoroacetylacetonates with this cation were prepared similarly, with benzene or benzene–ethanol as solvent.

(*d*) *Dirubidium tris*(*hexafluoroacetylacetonato*)*sodate.* The reaction of rubidium hexafluoroacetylacetonate and sodium hexafluoroacetylacetonate in 2 : 1 stoicheiometric ratio in ethanol gave *crystals* of the complex on slow evaporation.

(*e*) *Other mixed alkali-metal hexafluoroacetylacetonates.* These were prepared by similar procedures to (*d*), although variation of the solvent from ethanol to ethanol–methanol, methanol, or butanol sometimes gave better crystalline species. The mixed potassium and sodium salts gave a 1 : 1 compound as the major product and a 2 : 1 compound as the minor product, irrespective of the initial stoicheiometries. Both could be isolated from the mixture as single crystals for *X*-ray examination. No consistent results could be obtained for the mixed sodium and lithium salts, the powder photographs of the products showing a mixture of new phase.

Characterisation by X-*ray Methods.*—*X*-Ray single-crystal photographs of all the alkali-metal hfac salts and anionic complexes were taken, and the density of a single crystal of each was measured in order to determine the molecular weight. Where possible, the powder photograph, obtained by use of a Guinier camera, was indexed from the cell dimensions obtained from the single-crystal photographs in order to show that the bulk sample was one phase. For some triclinic compounds sufficiently good crystals could not be found for determination of the complete unit cell in order to index the powder photographs; however, the patterns showed no trace of the starting materials. None of the alkali-metal hfac salts are isomorphous so there was no formation of solid solutions.

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[42] C. Z. Moore and W. H. Nelson, *Inorg. Chem.*, 1969, **8**, 143.

[43] F. A. Hartman, M. Kilner, and A. Wojcicki, *Inorg. Chem.*, 1967, **6**, 34.

Crystal Structure Determination of Dirubidium Tris(hexafluoroacetylacetonato)sodate

Preliminary *X*-ray photographs were taken by use of Weissenberg and precession cameras to determine the space group. Cell dimensions were refined from 42 measured lines on an *X*-ray powder photograph taken with a Guinier camera.

Crystal Data.—$C_{15}H_3F_{18}NaO_6Rb_2$, $M = 815$, Orthorhombic, $a = 15{\cdot}603(3)$, $b = 15{\cdot}809(3)$, $c = 10{\cdot}321(2)$ Å, $U = 2546(1)$ Å^3, $D_c = 2{\cdot}125$, $Z = 4$, $D_m = 2{\cdot}12$, $F(000) = 1552$. Cell dimensions with Cu-$K_{\alpha 1}$ (crystal monochromator) radiation, $\lambda = 1{\cdot}5405$ Å (1 Å $= 10^{-10}$ m). Space group $P2_12_12_1$ from systematic absences. $\mu = 43{\cdot}5$ cm^{-1} for Mo-$K_{\alpha 1}$ radiation, $\lambda = 0{\cdot}70926$ Å.

A single crystal of dimensions 0·048 × 0·094 × 0·164 mm was mounted inside a quartz glass capillary tube and set on a Picker four-circle automatic diffractometer * using the centred positions for 11 reflections to determine the orientation angles. 1917 reflections of the type *hkl* and $\bar{h}\bar{k}l$ from 2θ 2—35° were measured by 2θ scan from $2\theta_{\alpha 1} - 0{\cdot}5°$ to $2\theta_{\alpha 2}$ 0·5° by use of zirconium-filtered Mo-K_{α} radiation. Reflections were scaled using three standard reflections (002, 400, 020) every 50 observations and were rejected for $I \leqslant 2\sigma(I)$.[44] No significant decrease in intensity occurred during data collection. Reflections were corrected for Lorentz and polarisation effects and for absorption.[44] 1127 reflections were used for structure determination and refinement.

Computation was carried out on an IBM 1130 computer [44] at the Unit of Structural Chemistry and an IBM 360 at the University College Computer Centre.[45] The principal computer programmes used are listed in refs. 44 and 45.

The positions of the rubidium ions were obtained from a three-dimensional Patterson synthesis. As these were situated at approximately $z = 0$, electron-density maps produced using phases derived from the heavy-atom positions had false mirror-symmetry. A position for the sodium ion was obtained from the resultant map, but because of the disorder of the CF_3 groups, no ligand fragments were recognisable until a weighted Fourier synthesis [46] was used to determine positions for all non-fluorine atoms. A further electron-density map showed the disordered CF_3 groups, and for two of these two possible positions were found. Atomic co-ordinates, scale and thermal parameters were refined using full-matrix least-squares [44] with the rubidium ions anisotropic, and initially giving all the observations unit weight. Scattering factors for rubidium, sodium, carbon, fluorine, and oxygen were taken from ref. 47 and the anomalous scattering of rubidium ($\Delta f'$ $-0{\cdot}9$, $\Delta f''$ 3·2 at $\theta = 0$) was allowed for. The two possible configurations of the molecule in the non-centrosymmetric space group gave R values of 0·095 and 0·106 after completion of refinement and the configuration giving the lower R value was taken as correct. A weighting scheme $w = 1/\sigma^2 = 1/(88 - 1{\cdot}1|F_o| + 0{\cdot}0053|F_o|^2)$ was used, having been chosen to give reasonably constant values of $\Sigma w\Delta^2$ as a function of $|F_o|$ and sin θ. At the end of refinement the largest shift was 0·5 σ for the *y* co-ordinate of the carbon on a CF_3 group. The co-ordinates of the CF_3 groups did not in general refine well, giving high standard deviations and temperature factors and unreasonable bond lengths and angles. This has been found previously in a fluorinated β-diketonate complex when anisotropic refinement of the fluorines was not carried out.[48] For the two CF_3 groups for which disordered fluorine positions could be found, and for another with little disorder, as shown on an electron-density map, the C–CF_3 bond lengths were *ca.* 1·65 Å. For the remaining CF_3 groups, which seemed to have a higher degree of disorder, the C–CF_3 bond lengths refined to $>2{\cdot}00$ Å, presumably because the least squares compensated for the absence of disordered fluorine atoms in the calculation by shifting the carbon atom to which they were attached. As no model could be found to describe the disorder, these CF_3 carbon atoms were fixed in their positions determined from an electron-density difference map and refinement was completed with R 0·096 and wR (R') 0·095. No attempt was made to refine the occupancy factors of the fluorine atoms as these are highly correlated with the temperature factors. No significant peaks were found on a final electron-density difference map other than near the fluorine atoms.

The standard deviations in the bond lengths were calculated from those in the atomic co-ordinates (Table 3) with allowance for correlation between the parameters.[45] Because the formula used assumes all observations are unique (whereas we have *hkl* and $\bar{h}\bar{k}l$), σ for the atomic co-ordinates are 15% too low. The σ values of the bond lengths in Table 4 have been corrected for this. The observed and calculated structure factors for the 1127 observed reflections are listed in Supplementary Publication No. SUP 20812 (11 pp., 1 microfiche).†

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† For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

[44] *X*-RAY ARC: IBM 1130 Program System for Crystallography, compiled by B. L. Vickery, D. Bright, and P. R. Mallinson, including: least-squares program BLOK by B. L. Vickery; Fourier program FODAP by A. Zalkin and D. Bright; Picker setting program PICK3 by W. C. Hamilton and D. Bright; data-reduction program PRED by B. L. Vickery and P. R. Mallinson; mean planes program MPLN (NRC 22) by M. E. Pippy and F. R. Ahmed; intermolecular contacts program BANGL by D. Bright; and absorption correction program ABSEP by F. R. Ahmed and B. L. Vickery.

[45] IBM 360: Full-matrix least-squares program, NUCLS, by R. J. Doedens and J. A. Ibers; interatomic distances and errors, ORFFE, by W. R. Busing, K. O. Martin, and H. A. Levy.

[46] G. A. Sim, *Acta Cryst.*, 1960, **13**, 511.

[47] International Tables for *X*-Ray Crystallography, vol. III, Kynoch Press, Birmingham, 1962, pp. 202—211.

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