Crystal Structures of the Isomorphous Tris(hexafluoroacetylacetonato)-copper(II) and Tris(hexafluoroacetylacetonato)magnesium Salts of Mono-protonated 1,8-bis(dimethylamino)naphthalene

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Three-dimensional *X*-ray crystal structure analyses have been carried out on the compounds $[C_{14}H_{19}N_2]^+[(CF_3\cdot CO\cdot CH\cdot CO\cdot CF_3)_3M]^-$ (M = Mg or Cu). Both have $Z = 4$ in a monoclinic unit cell with space group $P2_1/n$ and dimensions: (M = Mg) $a = 12{\cdot}775$, $b = 21{\cdot}268$, $c = 13{\cdot}594$ Å, $\beta = 99°\ 10'$; (M = Cu) $a = 12{\cdot}878$, $b = 21{\cdot}00$, $c = 13{\cdot}620$ Å, $\beta = 98°\ 44'$. A full-matrix refinement gave R values of 0·095 for 1998 observations (Mg) and 0·108 for 2478 observations (Cu).

In the cation the proton lies in the plane of the naphthalene ring between the two nitrogen atoms which are slightly displaced on opposite sides of the ring, and are 2·60(1) (Mg) and 2·65(2) (Cu) Å apart; the proton appears closer to one nitrogen in the magnesium and the other nitrogen in the copper complex. With a standard deviation of 0·15 Å it is not possible to distinguish between a proton in a double potential well and a proton equidistant from the nitrogen atoms.

In the anions all six chelate rings show delocalisation. The magnesium ion is octahedrally co-ordinated by oxygen atoms, mean Mg–O 2·06(2) Å. For copper there appears to be a tetragonal distortion, four short bonds, mean Cu–O 2·01(2) Å, and two long ones at 2·16(3) and 2·20(3) Å. The evidence for accepting the significance of this is discussed.

A CONSEQUENCE of the ' remarkable basicity ' of 1,8-bis-(dimethylamino)naphthalene[1] is that an attempt to make its adduct with bis(1,1,1,5,5,5-hexafluoropentan-2,4-dionato)copper, $(hfac)_2Cu$, led to protonation of the base giving the 1,8-bis(dimethylammonium)naphthalene cation, (IH^+), and the $(hfac)_3Cu^-$ anion.[2] A higher yield was obtained from a 1 : 1 : 1 mixture of (**I**), hfacH, and $Cu(hfac)_2(H_2O)$ in benzene. Other divalent metals form similar complexes, those of magnesium,[2] manganese, and nickel are all isomorphous[3] with the copper compound. A preliminary account of the synthesis and crystal structures of the copper and magnesium complexes has been published.[2] We now report the complete results of crystal-structure analysis; the features of particular interest are the location of the protonic hydrogen atom, a comparison of the M^{2+}–O bond lengths for a d^9 and d^0 electronic configuration, and any consequent effect on the bond lengths in the chelate ligands.

Preliminary *X*-ray photographs had shown that the compounds were isomorphous being monoclinic with the space group $P2_1/n$. With $Z = 4$ no symmetry was

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[1] R. W. Alder, P. S. Bowman, W. R. S. Steele, and D. R. Winterman, *Chem. Comm.*, 1968, 723.

[2] D. E. Fenton, M. R. Truter, and B. L. Vickery, *Chem. Comm.*, 1971, 93.

[3] D. E. Fenton and C. Nave, 1971, personal communication.

required. Observations were collected on the automatic diffractometer for both compounds, and the structure of the copper compound was solved by direct methods. Refinement by full-matrix methods was carried out first on the copper compound, then, with the copper parameters as a starting point, on the magnesium compound. It was necessary to allow for anisotropic vibration of the metal atoms and of the CF_3 groups. All the hydrogen atoms were located but only for the protonic one, designated H(18), were the parameters refined.

The final parameters for the copper compound are given in Table 1 and for the magnesium compound in Table 2. For both compounds the same designations of the atoms were used and these are explained in Figures 1 and 2.

TABLE 1

(*a*) Fractional atomic co-ordinates for the copper compound and isotropic vibration parameters. Here, and throughout the paper, figures in parentheses are the standard deviations in the least significant digits

	x	y	z	B/Å^2
Cu	0·0149(1)	0·2392(1)	0·5165(1)	*
C(11)	0·3473(13)	0·1882(12)	0·5251(12)	*
C(12)	0·2362(10)	0·1871(6)	0·5474(10)	4·61(31)
C(13)	0·2109(10)	0·1380(6)	0·6066(9)	4·41(29)
C(14)	0·1063(10)	0·1285(6)	0·6256(9)	4·37(30)
C(15)	0·0911(19)	0·0693(10)	0·6831(18)	*
O(12)	0·1784(7)	0·2292(4)	0·5016(6)	5·66(22)
O(14)	0·0262(7)	0·1604(4)	0·5973(6)	5·53(22)
F(111)	0·4145(8)	0·1849(6)	0·6084(9)	*
F(112)	0·3784(8)	0·2397(6)	0·4886(8)	*
F(113)	0·3713(9)	0·1411(7)	0·4737(12)	*
F(151)	0·0289(12)	0·0788(6)	0·7494(11)	*
F(152)	0·1718(9)	0·0409(6)	0·7263(11)	*
F(153)	0·0394(12)	0·0264(6)	0·6257(11)	*
C(21)	−0·3195(17)	0·2828(17)	0·4533(20)	*
C(22)	−0·2210(10)	0·2515(6)	0·4397(10)	4·97(31)
C(23)	−0·2065(10)	0·2271(6)	0·3452(10)	5·03(31)
C(24)	−0·1156(10)	0·1963(6)	0·3296(9)	4·44(30)
C(25)	−0·1170(15)	0·1628(9)	0·2311(14)	*
O(22)	−0·1549(7)	0·2501(5)	0·5182(7)	6·71(24)
O(24)	−0·0302(7)	0·1888(4)	0·3901(7)	5·50(22)
F(211)	−0·3100(11)	0·3366(8)	0·4920(15)	*
F(212)	−0·3756(11)	0·2467(10)	0·5034(12)	*
F(213)	−0·3849(9)	0·2886(6)	0·3689(10)	*
F(251)	−0·1127(9)	0·1011(5)	0·2450(8)	*
F(252)	−0·1971(8)	0·1772(5)	0·1643(7)	*
F(253)	−0·0305(9)	0·1773(6)	0·1921(7)	*
C(31)	−0·0639(17)	0·4182(11)	0·3885(12)	*
C(32)	−0·0271(10)	0·3709(6)	0·4664(10)	4·80(31)
C(33)	−0·0255(10)	0·3894(6)	0·5639(10)	5·03(32)
C(34)	0·0092(11)	0·3503(7)	0·6419(10)	5·29(33)
C(35)	0·0134(21)	0·3775(12)	0·7445(14)	*
O(32)	0·0017(7)	0·3188(4)	0·4346(7)	5·79(23)
O(34)	0·0413(7)	0·2936(4)	0·6413(7)	5·87(23)
F(311)	−0·1113(10)	0·4671(6)	0·4113(8)	*
F(312)	0·0189(12)	0·4416(7)	0·3505(11)	*
F(313)	−0·1164(15)	0·3937(6)	0·3124(10)	*
F(351)	−0·0390(13)	0·4274(7)	0·7546(8)	*
F(352)	0·1081(15)	0·3983(10)	0·7781(12)	*
F(353)	−0·0003(20)	0·3412(7)	0·8108(11)	*
C(1)	0·2606(10)	0·3946(7)	0·3132(10)	5·02(32)
C(2)	0·2652(13)	0·3825(8)	0·4118(13)	7·61(43)
C(3)	0·2919(14)	0·4344(9)	0·4774(13)	9·15(51)
C(4)	0·3187(14)	0·4946(9)	0·4454(14)	8·70(48)
C(5)	0·3404(13)	0·5671(8)	0·3077(13)	7·78(44)
C(6)	0·3305(13)	0·5786(8)	0·2046(13)	7·78(44)
C(7)	0·2920(12)	0·5306(8)	0·1357(11)	6·47(38)
C(8)	0·2653(11)	0·4716(7)	0·1689(10)	4·99(32)
C(9)	0·2780(10)	0·4541(6)	0·2710(10)	4·57(31)
C(10)	0·3110(12)	0·5050(8)	0·3390(12)	6·61(39)
N(1)	0·2457(9)	0·3406(6)	0·2428(9)	5·71(28)
C(11N)	0·1474(12)	0·3009(7)	0·2540(11)	7·09(41)
C(12N)	0·3437(11)	0·3000(7)	0·2486(11)	6·34(38)
N(8)	0·2231(9)	0·4246(5)	0·0955(9)	5·16(26)
C(81N)	0·1072(13)	0·4380(8)	0·0644(12)	7·70(44)
C(82N)	0·2766(11)	0·4172(7)	0·0070(11)	6·29(37)
H(18)	0·2067(115)	0·3747(75)	0·1681(119)	11·95(497)

TABLE 1 (*Continued*)

(*b*) Hydrogen atoms in assumed positions

	x	y	z	B/Å^2
H(13)	0·2658	0·1088	0·6353	5·00
H(23)	−0·2631	0·2320	0·2895	5·00
H(33)	−0·0492	0·4318	0·5770	5·00
H(2)	0·2528	0·3421	0·4373	6·50
H(3)	0·2923	0·4297	0·5487	6·50
H(4)	0·3433	0·5291	0·4899	6·50
H(5)	0·3657	0·5995	0·3559	6·50
H(6)	0·3493	0·6204	0·1818	6·50
H(7)	0·2857	0·5390	0·0652	6·50
H(111)	0·1000	0·3040	0·2370	7·00
H(112)	0·1900	0·3040	0·3190	7·00
H(113)	0·1600	0·2660	0·2030	7·00
H(121)	0·3900	0·3100	0·2370	7·00
H(122)	0·3600	0·2850	0·3190	7·00
H(123)	0·3100	0·2660	0·2030	7·00
H(811)	0·0500	0·3900	0·0290	7·00
H(812)	0·1000	0·4750	0·0200	7·00
H(813)	0·0700	0·4370	0·1420	7·00
H(821)	0·3533	0·4098	0·0332	7·00
H(822)	0·2400	0·3670	−0·0360	7·00
H(823)	0·2652	0·4536	−0·0337	7·00

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	62(1)	54(2)	56(1)	5(1)	10(1)	2(1)
C(11)	47(11)	171(22)	41(10)	−8(13)	11(9)	26(13)
F(111)	71(7)	240(16)	152(11)	−4(8)	21(8)	48(12)
F(112)	87(8)	184(11)	153(10)	1(8)	52(7)	85(10)
F(113)	117(11)	217(16)	322(20)	−48(9)	141(12)	−173(16)
C(15)	118(20)	78(16)	106(18)	−15(15)	−5(16)	18(14)
F(151)	229(16)	150(11)	177(14)	25(11)	112(13)	78(12)
F(152)	84(8)	165(11)	268(16)	19(8)	2(10)	151(12)
F(153)	194(15)	119(11)	188(15)	−38(9)	34(11)	20(10)
C(21)	71(16)	274(37)	131(20)	−25(20)	39(16)	−145(25)
F(211)	153(13)	237(18)	342(22)	37(12)	−3(14)	−221(19)
F(212)	116(11)	359(27)	200(16)	6(13)	94(11)	1(17)
F(213)	107(10)	178(11)	169(13)	39(8)	28(10)	−35(10)
C(25)	73(14)	91(16)	87(15)	−21(12)	25(12)	−15(12)
F(251)	217(13)	58(7)	116(9)	−5(8)	15(8)	−20(7)
F(252)	87(7)	160(11)	84(7)	24(7)	−7(6)	−29(7)
F(253)	118(9)	170(11)	96(8)	15(8)	30(7)	−14(7)
C(31)	96(16)	131(20)	42(11)	22(15)	6(11)	−4(12)
F(311)	190(13)	131(9)	110(9)	94(9)	34(9)	25(7)
F(312)	196(14)	179(13)	214(16)	74(12)	119(14)	115(13)
F(313)	396(25)	105(9)	113(10)	6(12)	−121(14)	15(9)
C(35)	138(20)	107(18)	66(14)	−7(16)	25(14)	−16(13)
F(351)	278(20)	181(13)	85(8)	116(13)	34(10)	−32(9)
F(352)	229(19)	343(27)	145(15)	0(19)	−39(13)	−128(17)
F(353)	600(40)	117(11)	117(11)	−10(16)	190(17)	11(10)

* Anisotropic vibration parameters (10^3U/Å^2) in the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{13}hla^*c^* + 2U_{23}klb^*c^* + 2U_{12}hka^*b^*)]$.

The structure as a whole is shown in Figure 3. It consists of sheets parallel to the (101) planes in which each ion has four neighbours of the opposite charge. These sheets are stacked in the direction of the [101] axis so that ions of the same charge are in contact. This may account for the low melting points (110—112 °C for the copper and 117—118 °C for the magnesium compound) but not for the crystal habits; the needle axis is c for both compounds.

Interionic distances <4·0 Å were calculated excluding all hydrogen atoms except H(18). None were found between cations but many between anions and also between cations and anions. Contacts <3·5 Å in either compound are shown in Table 3. It can be seen that the anion–anion contacts are shorter than the anion–cation contacts on the whole, and there are no particularly short contacts to that part of the cation where the positive charge might be expected. The first group of cation–anion contacts are those in the sheet parallel to (101), the first anion–anion contacts [to (IV) and (V)] are along the [101] direction.

The Cation.—Bond lengths and angles in the cation in both structures are given in Table 4, with the corresponding distances in naphthalene.[4] With our larger standard deviations there are no significant differences between the different kinds of bonds. The C(sp^2)–N distances (1·48, 1·48, 1·45, and 1·48 Å) are close to standard values[5] for carbon to four-covalent nitrogen, but the C(Me)–N distances average 1·52(1) Å which is longer than usual. The planes through the carbon atoms of the naphthalene rings were computed [planes (A) and (B) of Table 5]. The nitrogen atoms are on opposite sides of the naphthalene ring, making the distance between them greater than if they were coplanar. The hydrogen atom is not significantly out of the plane; it is on the same side as the nearer nitrogen atom. As the hydrogen appears closer to N(1) in the copper compound and closer to N(8) in the magnesium compound we may say that there is a double potential well or that the position found is not significantly different from that for a symmetrical hydrogen bond

TABLE 2

(*a*) Fractional atomic co-ordinates for the magnesium compound and isotropic vibration parameters

	x	y	z	B/Å^2
Mg	0·0163(3)	0·2391(2)	0·5198(3)	*
C(11)	0·3439(12)	0·1854(8)	0·5268(12)	*
C(12)	0·2357(9)	0·1834(5)	0·5486(9)	4·03(27)
C(13)	0·2135(10)	0·1350(6)	0·6082(9)	4·97(29)
C(14)	0·1138(10)	0·1239(6)	0·6304(9)	4·69(29)
C(15)	0·1009(12)	0·0664(8)	0·6906(13)	*
O(12)	0·1742(6)	0·2260(3)	0·5091(5)	4·24(18)
O(14)	0·0328(6)	0·1596(4)	0·6053(6)	4·89(19)
F(111)	0·4174(7)	0·1852(5)	0·6071(9)	*
F(112)	0·3738(6)	0·2385(5)	0·4892(8)	*
F(113)	0·3710(8)	0·1400(6)	0·4763(11)	*
F(151)	0·0419(11)	0·0762(5)	0·7541(9)	*
F(152)	0·1778(7)	0·0368(5)	0·7272(10)	*
F(153)	0·0390(9)	0·0259(5)	0·6337(10)	*
C(21)	−0·3177(11)	0·2777(8)	0·4612(12)	*
C(22)	−0·2161(10)	0·2487(6)	0·4415(10)	5·12(30)
C(23)	−0·2075(10)	0·2274(6)	0·3500(9)	4·78(29)
C(24)	−0·1153(10)	0·1954(5)	0·3297(9)	4·62(28)
C(25)	−0·1241(11)	0·1640(7)	0·2326(10)	*
O(22)	−0·1465(6)	0·2476(3)	0·5200(6)	4·82(18)
O(24)	−0·0303(6)	0·1911(4)	0·3885(6)	4·81(19)
F(211)	−0·3066(7)	0·3320(6)	0·5006(10)	*
F(212)	−0·3681(7)	0·2381(6)	0·5116(8)	*
F(213)	−0·3880(7)	0·2857(5)	0·3781(7)	*
F(251)	−0·1165(8)	0·1022(4)	0·2446(7)	*
F(252)	−0·2001(7)	0·1779(4)	0·1637(6)	*
F(253)	−0·0326(7)	0·1765(4)	0·1919(6)	*
C(31)	−0·0650(13)	0·4188(7)	0·3862(11)	*
C(32)	−0·0261(10)	0·3729(6)	0·4700(10)	4·95(30)
C(33)	−0·0261(9)	0·3896(6)	0·5641(10)	5·06(30)
C(34)	0·0110(9)	0·3502(6)	0·6453(10)	4·91(30)
C(35)	0·0058(16)	0·3779(8)	0·7450(12)	*
O(32)	0·0074(6)	0·3213(4)	0·4410(6)	4·93(19)
O(34)	0·0402(6)	0·2959(4)	0·6429(6)	4·57(18)
F(311)	−0·1113(7)	0·4680(4)	0·4106(7)	*
F(312)	0·0227(10)	0·4442(5)	0·3574(8)	*
F(313)	−0·1139(11)	0·3948(5)	0·3124(8)	*
F(351)	−0·0436(10)	0·4274(5)	0·7547(7)	*
F(352)	0·1037(12)	0·3977(8)	0·7809(9)	*
F(353)	−0·0049(16)	0·3399(6)	0·8136(8)	*
C(1)	0·2661(10)	0·3984(6)	0·3153(10)	5·35(31)
C(2)	0·2707(11)	0·3854(7)	0·4173(12)	7·67(40)
C(3)	0·2967(13)	0·4382(9)	0·4781(13)	9·03(46)
C(4)	0·3248(13)	0·4970(8)	0·4456(14)	8·86(45)
C(5)	0·3422(11)	0·5659(7)	0·3074(12)	6·80(37)
C(6)	0·3319(11)	0·5774(6)	0·2101(12)	6·40(35)
C(7)	0·2969(10)	0·5308(6)	0·1417(10)	5·41(31)
C(8)	0·2710(9)	0·4731(6)	0·1717(9)	4·05(27)
C(9)	0·2826(9)	0·4578(6)	0·2762(9)	4·45(28)
C(10)	0·3172(11)	0·5079(7)	0·3441(11)	6·08(34)
N(1)	0·2481(8)	0·3456(5)	0·2479(8)	5·60(25)
C(11N)	0·1560(12)	0·3032(7)	0·2618(11)	8·00(41)
C(12N)	0·3416(10)	0·3025(6)	0·2480(10)	5·88(33)
N(8)	0·2248(8)	0·4263(5)	0·1024(8)	4·82(23)
C(81N)	0·1024(12)	0·4388(7)	0·0693(12)	8·38(42)
C(82N)	0·2730(11)	0·4178(7)	0·0116(11)	7·01(37)
H(18)	0·2470(78)	0·3737(51)	0·1405(79)	6·56(304)

TABLE 2 (*Continued*)

(*b*) Hydrogen atoms in assumed positions

Atom	x	y	z	B
H(13)	0·2731	0·1063	0·6376	5·00
H(23)	−0·2680	0·2353	0·2941	5·00
H(33)	−0·0532	0·4321	0·5772	5·00
H(2)	0·2597	0·3429	0·4434	7·00
H(3)	0·2921	0·4333	0·5515	7·00
H(4)	0·3442	0·5324	0·4952	7·00
H(5)	0·3696	0·6003	0·3554	7·00
H(6)	0·3489	0·6202	0·1857	7·00
H(7)	0·2922	0·5399	0·0688	7·00
H(111)	0·1900	0·3040	0·3200	7·00
H(112)	0·1000	0·3230	0·2900	7·00
H(113)	0·1250	0·2900	0·2100	7·00
H(121)	0·4000	0·3230	0·2610	7·00
H(122)	0·3200	0·2750	0·1950	7·00
H(123)	0·3800	0·2950	0·3190	7·00
H(811)	0·0800	0·4370	0·1250	7·00
H(812)	0·1000	0·4650	0·0250	7·00
H(813)	0·0700	0·4100	0·0000	7·00
H(821)	0·3300	0·4100	0·0270	7·00
H(822)	0·2900	0·3670	−0·0300	7·00
H(823)	0·2700	0·4500	−0·0250	7·00

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mg	42(2)	55(2)	62(3)	7(3)	11(3)	0(3)
C(11)	64(13)	141(18)	87(14)	−42(12)	13(11)	24(14)
F(111)	57(7)	248(14)	185(12)	−7(8)	48(8)	56(11)
F(112)	64(6)	185(11)	196(12)	0(7)	55(7)	78(10)
F(113)	127(10)	232(14)	331(20)	−66(10)	152(12)	−183(14)
C(15)	70(14)	104(16)	111(16)	−28(12)	6(13)	35(14)
F(151)	304(18)	113(9)	187(14)	40(11)	158(14)	77(10)
F(152)	86(8)	161(11)	303(17)	36(8)	13(10)	166(11)
F(153)	165(12)	106(9)	245(15)	−28(8)	− 1(13)	56(10)
C(21)	47(12)	132(18)	105(15)	49(12)	6(13)	−25(14)
F(211)	83(8)	214(14)	337(19)	62(8)	13(10)	−183(14)
F(212)	78(8)	301(18)	161(12)	28(9)	69(8)	49(11)
F(213)	76(7)	175(9)	141(9)	48(7)	4(7)	−15(9)
C(25)	58(11)	110(16)	61(11)	2(11)	16(10)	−1(11)
F(251)	195(11)	66(7)	114(8)	1(7)	2(7)	−22(6)
F(252)	91(6)	171(9)	73(6)	27(7)	−11(6)	−23(7)
F(253)	127(8)	129(9)	81(6)	35(7)	30(6)	−11(6)
C(31)	118(17)	94(16)	59(13)	0(14)	25(12)	16(11)
F(311)	157(10)	95(7)	124(9)	64(7)	32(7)	16(7)
F(312)	228(14)	161(11)	167(12)	78(10)	110(11)	98(10)
F(313)	330(19)	99(9)	112(9)	23(10)	−126(11)	−2(7)
C(35)	202(25)	80(16)	60(15)	6(15)	31(16)	−36(11)
F(351)	244(16)	166(7)	101(8)	106(11)	21(9)	−50(9)
F(352)	238(18)	340(25)	135(14)	−13(6)	−29(12)	−135(16)
F(353)	591(36)	130(11)	99(10)	16(15)	177(16)	1(9)

* Anisotropic vibration parameters, 10^3U/Å^2.

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[4] D. W. J. Cruickshank, *Acta Cryst.*, 1957, **10**, 504.

[5] Interatomic Distances, *Chem. Soc. Special Publ.*, No. 18, London, 1965.

with both N-H at 1·4 Å. This ambiguous result is commonly found in structures with strong, possibly symmetrical, hydrogen bonds. For the hydrobromide an anomalous i.r. spectrum was noted[1] with a weak absorption from 3000—800 cm^{-1} but no recognisable N-H stretching frequency, taken as indicative of strong hydrogen bonding. The angles round the nitrogen are approximately tetrahedral, that subtended at H(18) is consistent with hydrogen bonding. The geometry of this hydrogen bond, *i.e.* formation of a six-membered ring, is similar to that of a β-diketone in the enol form. Unfortunately, in the electron diffraction study of hexafluoroacetylacetone,[6] the hydrogen atom could not be located precisely but it appeared approximately midway between the oxygen atoms [O · · · O 2·55(3) Å] giving an O · · · H · · · O angle of 176(2)°.

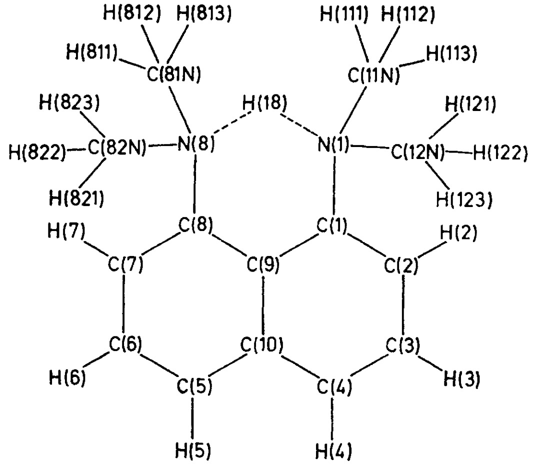

FIGURE 1 The designations of the atoms in the 1,8-bis(dimethylammonium)naphthalene cation, IH$^+$. Except for the methyl carbon atoms C(*n*N) and the hydrogen atoms in these groups, all atoms are approximately coplanar

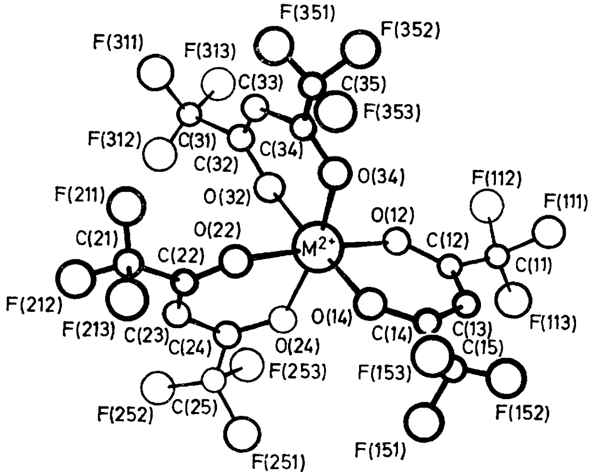

FIGURE 2 The anion [(hfac)$_3$-M^{2+}]$^-$ showing the designations of the atoms. The view is along the normal to the plane through O(12), O(24), and O(32). In the hfac groups each atom has two numbers, the first, 1, 2, or 3 being that of the chelate ring. There are two anions with this configuration and two with its mirror image in the unit cell

There is no reason to suppose that the cation is really different in the compounds with the different anions, particularly as cation–anion contacts are relatively long. We shall use differences between the measured dimensions to estimate the error in comparing the structures and particularly to fix a level of statistical significance which must be achieved before chemical significance can be claimed. Apart from dimensions involving H(18) the largest difference in the bond lengths is for N(8)-C(81N) which is 2·68 times the corresponding statistical standard deviation (non-rounded figures were used for this calculation, not the rounded ones in Table 4). A more serious discrepancy is found in the angles, *e.g.* for the Cu compound it appears that C(8)-C(9)-C(1) (129°) is significantly greater than C(4)-C(10)-C(5) (117°) the difference being 5·8σ, whereas for the magnesium compound the difference is only 1·9σ and not significant. The corresponding angles do not differ significantly between the two compounds so we think the effect in the copper compound is not of chemical significance.

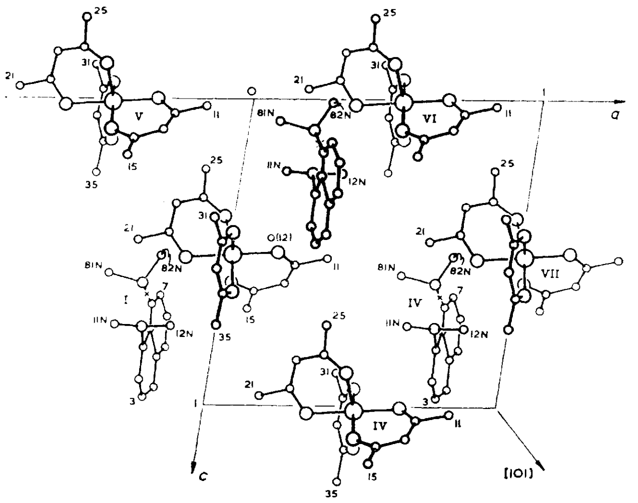

FIGURE 3 The structure in projection down the *b* axis showing ions which lie approximately between $y = 0$ and $y = \frac{1}{2}$. For clarity the fluorine atoms have been omitted from the anions. The smallest circles represent carbon atoms, some with their designations, the crosses represent H(18), and the largest circles represent the metal atoms. The ions corresponding to the co-ordinates of Tables 1 and 2 are shown without Roman numerals, the others are obtained by the operations defined in Table 3. In a complete projection each ion of one kind would be covered by another of the same kind, the anions being related by centres of symmetry and the cations by screw axes. Thus cation (II) is above cation (I) (which is shown) while anion (II) is beneath and anion (VIII) is above the original anion

Dimensions of Chelate Ligands.—The bond lengths and angles in the ligands are shown in Table 6. All six ligands have the same dimensions for the corresponding bonds and there is no indication of alternation in any of the ligands attached to copper. In hfacH itself the bond lengths are: C-F 1·337(2), C(CF$_3$)-C 1·546(3), C-C

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[6] A. L. Andreassen, D. Zebelman, and S. H. Bauer, *J. Amer. Chem. Soc.*, 1971, **93**, 1148.

TABLE 3

Interionic distances <3·5 Å. Standard deviations are *ca.* 0·06 Å except for those including H(18), 0·2 Å

Anion	Cation	Cu compound	Mg compound
F(253) ···	C(11N)	3·48	3·64
O(32) ···	C(11N)	3·33	3·34
F(112) ···	C(12N)	3·47	3·51
F(312) ···	C(1)	3·38	3·39
F(112) ···	C(2)	3·43	3·47
F(312) ···	C(2)	3·39	3·38
F(212) ···	C(11N$^{\mathrm{I}}$)	3·53	3·48
O(14) ···	C(12N$^{\mathrm{I}}$)	3·45	3·45
F(151) ···	C(12N$^{\mathrm{I}}$)	3·49	3·63
O(22) ···	C(12N$^{\mathrm{I}}$)	3·31	3·30
O(22) ···	H(18$^{\mathrm{I}}$)	3·91	3·45
F(212) ···	H(18$^{\mathrm{I}}$)	3·45	3·17
F(153) ···	C(7$^{\mathrm{I}}$)	3·43	3·34
F(151) ···	C(9$^{\mathrm{I}}$)	3·36	3·45
F(211) ···	C(5$^{\mathrm{II}}$)	3·47	3·48
F(113) ···	C(7$^{\mathrm{III}}$)	3·33	3·39
F(253) ···	C(5$^{\mathrm{III}}$)	3·37	3·38
F(253) ···	C(6$^{\mathrm{III}}$)	3·44	3·42
Anion	Anion		
O(12) ···	F(252$^{\mathrm{IV}}$)	3·20	3·18
C(12) ···	F(252$^{\mathrm{IV}}$)	3·31	3·38
C(13) ···	F(313$^{\mathrm{IV}}$)	3·37	3·12
F(111) ···	F(252$^{\mathrm{IV}}$)	3·37	3·42
F(111) ···	F(253$^{\mathrm{IV}}$)	3·15	3·19
F(111) ···	F(313$^{\mathrm{IV}}$)	3·31	3·35
F(112) ···	F(252$^{\mathrm{IV}}$)	3·23	3·22
F(112) ···	(F253$^{\mathrm{IV}}$)	3·33	3·35
F(151) ···	F(213$^{\mathrm{IV}}$)	3·33	3·45
F(152) ···	F(311$^{\mathrm{IV}}$)	3·47	3·37
F(152) ···	F(313$^{\mathrm{IV}}$)	3·12	3·09
F(212) ···	F(353$^{\mathrm{V}}$)	3·40	3·40
F(213) ···	F(353$^{\mathrm{V}}$)	3·15	3·12
F(252) ···	O(34$^{\mathrm{V}}$)	3·39	3·33
F(112) ···	F(353$^{\mathrm{V}}$)	3·51	3·47
F(113) ···	F(353$^{\mathrm{V}}$)	2·98	2·95
F(152) ···	F(251$^{\mathrm{VIII}}$)	3·12	3·10
F(153) ···	F(251$^{\mathrm{VIII}}$)	3·26	3·26
C(33) ···	F(311$^{\mathrm{II}}$)	3·48	3·49
F(312) ···	F(351$^{\mathrm{II}}$)	3·13	3·16

Roman numeral superscripts relate the ions to those of Tables 1 and 2 at x, y, z by the following operations:

I $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$
II $-x, -y + 1, -z + 1$
III $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$
IV $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$
V $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$
VI $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$
VII $x + 1, y, z$
VIII $-x, -y, 1 - z$

TABLE 4

Bond lengths (Å) and bond angles (°) in the cation

(*a*) Distances

	Cu	Mg
C(1)–C(2) ^{a}	1·36(2)	1·41(2)
C(2)–C(3) ^{b}	1·42(2)	1·40(2)
C(3)–C(4) ^{a}	1·40(2)	1·39(2)
C(4)–C(10) ^{c}	1·45(2)	1·39(2)
C(5)–C(10) ^{c}	1·44(2)	1·39(2)
C(5)–C(6) ^{a}	1·41(2)	1·33(2)
C(6)–C(7) ^{b}	1·41(2)	1·38(2)
C(7)–C(8) ^{a}	1·38(2)	1·35(2)
C(8)–C(9) ^{c}	1·42(2)	1·44(1)
C(9)–C(1) ^{c}	1·41(2)	1·40(2)
C(9)–C(10) ^{d}	1·44(2)	1·43(2)
C(1)–N(1)	1·48(2)	1·45(1)
N(1)–C(11N)	1·54(2)	1·52(2)
N(1)–C(12N)	1·51(2)	1·51(1)
C(8)–N(8)	1·45(2)	1·43(1)
N(8)–C(81N)	1·51(2)	1·58(2)
N(8)–C(82N)	1·48(2)	1·48(2)
N(1)–H(18)	1·27(17)	1·58(11)
N(8)–H(18)	1·49(16)	1·25(11)
N(1) ··· N(8)	2·65(2)	2·60(1)

In naphthalene [4] the bond lengths of types *a*, *b*, *c*, and *d*, average 1·361(4), 1·421(3), 1·425(6), and 1·410(6).

TABLE 4 (*Continued*)

(*b*) Angles

	Cu	Mg
C(1)–C(2)–C(3)	117(2)	113(2)
C(2)–C(3)–C(4)	123(2)	126(2)
C(3)–C(4)–C(10)	118(2)	119(2)
C(4)–C(10)–C(9)	120(2)	119(1)
C(4)–C(10)–C(5)	117(2)	122(2)
C(10)–C(5)–C(6)	117(2)	122(1)
C(5)–C(10)–C(9)	123(2)	120(1)
C(5)–C(6)–C(7)	121(1)	120(1)
C(6)–C(7)–C(8)	120(1)	121(1)
C(7)–C(8)–C(9)	124(1)	121(1)
C(7)–C(8)–N(8)	118(1)	122(1)
C(8)–C(9)–C(1)	129(1)	125(1)
C(8)–C(9)–C(10)	115(1)	116(1)
C(9)–C(8)–N(8)	118(1)	117(1)
C(9)–C(1)–C(2)	126(1)	125(1)
C(9)–C(1)–N(1)	115(1)	114(1)
C(1)–C(9)–C(10)	117(1)	118(1)
C(2)–C(1)–N(1)	119(1)	117(1)
C(1)–N(1)–C(11N)	112(1)	116(1)
C(1)–N(1)–C(12N)	112(1)	115(1)
C(1)–N(1)–H(18)	95(6)	106(4)
C(11N)–N(1)–C(12N)	112(1)	106(1)
C(11N)–N(1)–H(18)	99(7)	117(4)
C(12N)–N(1)–H(18)	126(7)	97(4)
C(8)–N(8)–C(81N)	108(1)	111(1)
C(8)–N(8)–H(18)	96(6)	108(5)
C(8)–N(8)–C(82N)	117(1)	117(1)
C(81N)–N(8)–C(82N)	111(1)	108(1)
C(81N)–N(8)–H(18)	95(6)	115(5)
C(82N)–N(8)–N(18)	127(6)	98(5)
N(1)–H(18)–N(8)	148(12)	134(8)

TABLE 5

Planes through various groups of atoms. The equations refer to an orthogonal system of axes parallel to the crystallographic *a*, *b*, and *c** axes. Deviations of the atoms from these planes are shown in square brackets; atoms designated in italics were used to define the plane

Plane (A, Mg): $-0{\cdot}961X + 0{\cdot}274Y - 0{\cdot}026Z + 0{\cdot}328 = 0$
[*C(1) −0·07, C(2) −0·02, C(3) 0·07, C(4) 0·01, C(5) −0·04, C(6) −0·02, C(7) 0·02, C(8) 0·06, C(9) 0·01, C(10) −0·01,* N(1) −0·27, N(8) 0·23, C(11N) 0·64, C(12N) −1·67, C(81N) 1·75, C(82N) −0·57, H(18) −0·28]

Plane (B, Cu): $-0{\cdot}959X + 0{\cdot}282Y - 0{\cdot}018Z + 0{\cdot}262 = 0$
[*C(1) −0·07, C(2) −0·03, C(3) 0·06, C(4) 0·03, (C5) −0·05, C(6) −0·04, C(7) 0·03, C(8) 0·07, C(9) −0·01, C(10) 0·00,* N(1) −0·33, N(8) 0·19, C(11N) 0·67, C(12N) −1·77, C(81) 1·64, C(82) −0·67, H(18) 0·22]

Plane (C, Cu): $-0{\cdot}100X - 0{\cdot}561Y - 0{\cdot}822Z + 8{\cdot}409 = 0$

Plane (D, Cu): $0{\cdot}393X + 0{\cdot}870Y - 0{\cdot}297Z - 1{\cdot}370 = 0$

Plane (E, Cu): $-0{\cdot}944X - 0{\cdot}330Y - 0{\cdot}015Z + 1{\cdot}433 = 0$

Plane (F, Mg): $-0{\cdot}130X - 0{\cdot}547Y - 0{\cdot}827Z + 8{\cdot}448 = 0$

Plane (G, Mg): $0{\cdot}362X + 0{\cdot}878Y - 0{\cdot}312Z - 1{\cdot}442 = 0$

Plane (H, Mg): $-0{\cdot}934X - 0{\cdot}355Y - 0{\cdot}047Z + 1{\cdot}853 = 0$

For planes (C)–(H) the ligands are designated hfac(*n*) and the (*n*) has been omitted from the designations of the atoms

	(C) hfac(1)	(D) hfac(2)	(E) hfac(3)	(F) hfac(1)	(G) hfac(2)	(H) hfac(3)
C(1)	*0·05*	*0·00*	*−0·01*	*0·02*	*−0·02*	*0·01*
C(2)	*−0·04*	*−0·01*	*0·01*	*−0·01*	*0·01*	*0·01*
C(3)	*−0·07*	*0·08*	*0·03*	*−0·06*	*0·11*	*0·16*
C(4)	*−0·03*	*0·05*	*0·02*	*0·00*	*0·04*	*−0·16*
C(5)	*0·06*	−0·10	*−0·04*	*0·04*	*−0·11*	*−0·02*
O(2)	*0·03*	*−0·08*	*−0·03*	*0·02*	*−0·08*	*−0·04*
O(4)	*0·00*	*0·05*	*0·02*	*−0·01*	*0·05*	*0·04*
Cu	−0·03	0·59	0·50			
Mg				0·02	0·51	0·58

1·407(10), and C–O 1·259(6) Å as determined by electron diffraction [6] and are consistent with delocalisation in the enol ring, *i.e.* they should be comparable with those in metal complexes.

We find a large spread in the C–F distances; mean values are 1·30(4) Å for both complexes but this standard deviation from the spread about the mean value is twice that from ORFFE.* Although anisotropic vibration parameters were obtained we did not attempt to apply a correction for libration to the bond lengths. The apparent shortness probably results from this systematic error. As shown in Tables 1 and 2 the isotropic temperature factors of all the atoms are fairly high (if $B = 7{\cdot}2$ Å^2 the mean square amplitude of vibration is 0·09 Å^2 or root-mean-square amplitude 0·3 Å, which is large compared with the bond lengths). For fluorine the mean square amplitudes of vibration can be as much as 0·6 Å^2. These high values may be in part a result of disorder rather than actual motion.

For the other bond lengths the spread about the mean gives the same standard deviation as ORFFE, mean lengths are C(CF_3)–C, 1·49, C–C 1·39, and C–O 1·26 Å. All the bond lengths are the same as those found in π-C_5H_5(hfac)$_3$Zr [7] and CsM^{III}(hfac)$_4$ (M^{III} = Y,[8] Eu,[9] or Am [9]) even including the short C–F distances. Other comparable compounds are (hfac)$_2$(bipy)Cu^{II} (ref. 10) and (hfac)(Me$_2$en)$_2$Cu^{II} (ref. 11) (bipy = 2,2′-bipyridyl and Me$_2$en = *NN*-dimethylethylenediamine). In the latter compound the hfac is co-ordinated to the copper through one oxygen atom only but there are no significant differences between the two C–O bond lengths (mean 1·234 Å) or the C–C bond lengths in the ring (mean 1·390 Å); the C–CF_3 distance is 1·530(5) Å and the mean C–F bond lengths is 1·313(9) Å. Only for the bipyridyl

TABLE 6

(*a*) Bond lengths, (Å) and angles, (°) in the anions. The chelate rings are designated hfac(*n*) and *n* has been omitted in the designations of the atoms

(i) Bonds	hfac(1)	hfac(2)	hfac(3)
Cu–O(2)	2·156(9)	2·201(10)	2·002(9)
Cu–O(4)	1·981(9)	2·028(9)	2·035(9)
C(1)–C(2)	1·51(2)	1·47(2)	1·48(2)
C(2)–C(3)	1·38(2)	1·42(2)	1·38(2)
C(3)–C(4)	1·42(2)	1·38(2)	1·36(2)
C(4)–C(5)	1·50(2)	1·51(2)	1·50(2)
C(2)–O(2)	1·26(1)	1·26(1)	1·25(1)
C(4)–O(4)	1·24(1)	1·28(1)	1·26(1)
C(1)–F(11)	1·32(1)	1·24(2)	1·26(2)
C(1)–F(12)	1·28(2)	1·31(2)	1·35(2)
C(1)–F(13)	1·28(2)	1·32(2)	1·26(2)
C(5)–F(51)	1·31(2)	1·31(2)	1·27(2)
C(5)–F(52)	1·26(2)	1·30(2)	1·31(2)
C(5)–F(53)	1·31(2)	1·34(2)	1·21(2)
(ii) Angles			
O(2)–Cu–O(4)	88·9(4)	84·7(4)	89·2(4)
Cu–O(2)–C(2)	122(1)	122(1)	123(1)
Cu–O(4)–C(4)	128(1)	126(1)	122(1)
C(1)–C(2)–C(3)	116(1)	121(1)	117(1)
C(2)–C(3)–C(4)	122(1)	122(1)	122(1)
C(3)–C(4)–C(5)	114(1)	117(1)	117(1)
O(2)–C(2)–C(1)	113(1)	113(1)	115(1)
O(2)–C(2)–C(3)	130(1)	126(1)	128(1)
O(4)–C(4)–C(3)	129(1)	129(1)	129(1)
O(4)–C(4)–C(5)	116(1)	114(1)	113(1)
C(2)–C(1)–F(11)	110(1)	115(2)	119(1)
C(2)–C(1)–F(12)	117(1)	111(2)	110(1)
C(2)–C(1)–F(13)	115(1)	112(1)	113(2)
F(11)–C(1)–F(12)	101(1)	109(2)	108(2)
F(11)–C(1)–F(13)	104(2)	107(2)	108(2)
F(12)–C(1)–F(13)	109(1)	100(2)	101(1)
C(4)–C(5)–F(51)	112(2)	110(1)	118(2)
C(4)–C(5)–F(52)	118(2)	114(1)	111(2)
C(4)–C(5)–F(53)	111(1)	110(1)	118(2)
F(51)–C(5)–F(52)	107(2)	110(1)	100(2)
F(51)–C(5)–F(53)	102(2)	105(1)	107(2)
F(52)–C(5)–F(53)	105(2)	107(1)	100(2)

TABLE 6 (*Continued*)

(iii) Bonds			
Mg–O(2)	2·064(8)	2·088(9)	2·043(9)
Mg–O(4)	2·044(9)	2·059(9)	2·048(9)
C(1)–C(2)	1·46(2)	1·50(2)	1·52(2)
C(2)–C(3)	1·37(1)	1·35(2)	1·33(2)
C(3)–C(4)	1·38(2)	1·42(2)	1·41(2)
C(4)–C(5)	1·50(2)	1·47(2)	1·49(2)
C(2)–O(2)	1·26(1)	1·27(1)	1·26(1)
C(4)–O(4)	1·28(1)	1·25(1)	1·21(1)
C(1)–F(11)	1·32(2)	1·27(2)	1·27(2)
C(1)–F(12)	1·32(2)	1·32(2)	1·36(2)
C(1)–F(13)	1·26(2)	1·34(1)	1·21(1)
C(5)–F(51)	1·25(2)	1·33(1)	1·25(2)
C(5)–F(52)	1·21(1)	1·27(1)	1·34(2)
C(5)–F(53)	1·33(2)	1·40(1)	1·26(2)
(iv) Angles			
O(2)–Mg–O(4)	85·1(3)	83·9(3)	84·9(3)
Mg–O(2)–C(2)	128(1)	124(1)	125(1)
Mg–O(4)–C(4)	130(1)	128(1)	125(1)
C(1)–C(2)–C(3)	116(1)	120(1)	120(1)
C(2)–C(3)–C(4)	123(1)	122(1)	123(1)
C(3)–C(4)–C(5)	117(1)	116(1)	115(1)
O(2)–C(2)–C(1)	116(1)	111(1)	114(1)
O(2)–C(2)–C(3)	128(1)	128(1)	126(1)
O(4)–C(4)–C(3)	125(1)	125(1)	128(1)
O(4)–C(4)–C(5)	118(1)	119(1)	117(2)
C(2)–C(1)–F(11)	114(1)	114(1)	116(1)
C(2)–C(1)–F(12)	116(1)	110(1)	107(1)
C(2)–C(1)–F(13)	116(1)	113(1)	114(1)
F(11)–C(1)–F(12)	96(1)	113(1)	111(2)
F(11)–C(1)–F(13)	103(2)	105(1)	111(2)
F(12)–C(1)–F(13)	109(1)	102(1)	106(1)
C(4)–C(5)–F(51)	112(1)	110(1)	122(2)
C(4)–C(5)–F(52)	120(1)	120(1)	106(2)
C(4)–C(5)–F(53)	109(1)	109(1)	116(1)
F(51)–C(5)–F(52)	110(2)	111(1)	99(1)
F(51)–C(5)–F(53)	98(1)	101(1)	110(2)
F(52)–C(5)–F(53)	106(2)	105(1)	98(2)

(*b*) Angles O–Cu–O′ and, in parentheses, O–Mg–O′ (°). The estimated standard deviation in the difference between corresponding values is 0·5°

O O′	O(12)	O(14)	(O22)	O(24)	O(32)	O(34)
O(12)		88·9 (85·1)	175·3 (175·2)	91·6 (91·3)	91·7 (92·9)	95·2 (96·7)
O(14)			94·0 (94·8)	91·4 (94·1)	179·4 (176·2)	90·9 (92·0)
O(22)				84·7 (83·9)	85·3 (87·4)	88·5 (88·1)
O(24)					88·5 (89·2)	172·9 (170·3)
O(32)						89·2 (84·9)
O(34)						

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* ORFFE, the Busing–Levy programme with local modifications.

[7] M. Elder, *Inorg. Chem.*, 1969, **8**, 2103.

[8] M. J. Bennett, F. A. Cotton, P. Legzdins, and S. J. Lippard, *Inorg. Chem.*, 1968, **7**, 1770.

[9] J. H. Burns and M. D. Danford, *Inorg. Chem.*, 1969, **8**, 1780.

[10] M. V. Veidis, G. H. Schreiber, T. E. Gough, and G. J. Palenik, *J. Amer. Chem. Soc.*, 1969, **91**, 1859.

[11] M. A. Bush and D. E. Fenton, *J. Chem. Soc.* (*A*), 1971, 2446.

complex [10] is there evidence for incomplete delocalisation; estimated standard deviations are not quoted for the C–O bonds, 1·261 and 1·218 Å, or the C–C(ring) bonds, 1·433 and 1·385 Å, but comparison with those quoted for Cu–O and Cu–N suggests ±0·01 Å so that the differences would be *ca.* 3σ, the minimum which crystallographers now require before attributing chemical significance to differences. Of the six chelate hfac ligands reported here, only the third one of the magnesium (Table 6) shows differences of this kind and chemical significance is most improbable; we take it as yet another warning to be wary of estimates of statistical significance.

For each hfac ligand the plane through the five carbon and two oxygen atoms was calculated; there are no significant deviations from planarity (Table 4), each metal lying in the plane of one chelate ring and *ca.* 0·5 Å from those of the other two.

The Environment of the Metal.—No symmetry is required so that six independent metal–oxygen distances are obtained; the arrangement approximates to octahedral round magnesium and to a tetragonally distorted octahedron about copper. The bond lengths and chelate angles are shown in Table 6(*a*). All chelate angles are less than 90° those at magnesium being smaller than those at copper. Other angles subtended at the metal are shown in Table 6(*b*). Planes through the groups of four oxygen atoms were calculated and greater deviations from the ideal arrangement, coplanar oxygens with the three sets of planes orthogonal, were found for magnesium than for copper.

Only in two actual M–O bond lengths does the copper structure appear less regular than the magnesium. These differences in bond lengths must be treated with caution, since internal evidence suggests that chemical significance cannot be assigned to differences less than six times the corresponding statistical deviation in comparing the two structures. Further, for the copper compound there is the possibility that the calculated standard deviations in the Cu–O bonds are too small (such an explanation often being required for metal–ligand bond distances which vary by statistically significant amounts without any chemically convincing reason). For magnesium the six bonds are equal, mean 2·058(17) Å; for copper there are four short bonds, mean 2·012(25), and two long ones, mean 2·178(32) Å. Here the values in parentheses are obtained from the spread about the mean; for magnesium the value is twice that from the estimated standard deviation in the coordinates.

In another pair of isomorphous tris-chelated complexes of copper and magnesium, the octamethylphosphoramides,[12] crystallographic symmetry (corresponding to a true instead of a pseudo-three-fold axis in Figure 2), precludes tetragonal distortion and the mean Mg–O and Cu–O bond lengths are 2·061(2) and 2·065(2) Å. That for Mg–O is in good agreement with ours. It has been suggested that this and other tris-chelated copper complexes with three-fold symmetry involve a ' dynamic ' Jahn–Teller distortion with the ' long ' bonds spread equally.[13,14] No such restriction is found in this compound so that it makes an ideal example for checking on the reality of the Jahn–Teller distortion.

The ' long ' bonds are closely parallel to the *a* axis, the difference between the length of which in the copper and the magnesium compounds would account for only 0·02 Å in M–O bond length. The shorter of the ' long ' bonds [Cu–O(12) 2·156 Å] is 0·121 Å longer than the longest of the short bonds, so that in the most unfavourable case the difference is 9·5σ, while the difference between the mean long and mean short values at 0·156 Å is 3·8 times the standard deviation obtained from the spread. On balance we think that the distortion is probably significant.

EXPERIMENTAL

Copper Compound

A pale green acicular crystal 0·025 × 0·03 × 0·055 cm was mounted on a rigid support * on a Picker 4-circle automatic diffractometer.

Preliminary *X*-ray photographs had established the space group and approximate unit-cell dimensions. Accurate dimensions were obtained by careful centering of 16 reflections and refinement by the least-squares programme PICK3.[15]

Crystal Data.—$C_{29}H_{22}CuF_{18}N_2O_6$, $M = 900$, Monoclinic, $a = 12\cdot878(7)$, $b = 21\cdot00(1)$, $c = 13\cdot620(7)$ Å, $\beta = 98° 44'(2')$, $U = 3640(7)$ Å^3, D_m (flotation) = 1·66, $Z = 4$, $D_c = 1\cdot64$, $F(000) = 1796$. Space-group $P2_1/n$ (C^5_{2h}) uniquely determined. This is a non-standard setting of $P2_1/c$ and the equivalent positions are: x, y, z; $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; and $\bar{x}, \bar{y}, \bar{z}$. No molecular symmetry is required. Mo-K_α radiation, Zr-filtered; λ(Mo-K_α) = 0·70926 Å (1 Å ≡ 10^{-10}m). Single-crystal diffraction intensities measured by counter. μ(Mo-K_α) 7·70 cm^{-1}, no absorption correction applied.

Intensities were collected in shells of reciprocal space for the (*hkl*) and ($\bar{h}kl$) octants out to $2\theta = 45°$. Scanning was carried out at 1° min^{-1} from 0·4° below the Mo-$K_{\alpha,1}$ peak to 0·4° above the Mo-$K_{\alpha,2}$ peak and backgrounds were counted for 10 s at each end of the scan. Three standard reflections, (400), (006), and (060) were measured after every 50 reflections. 4739 unique reflections were measured, Lorentz and polarisation factors (*LP*) were applied and the standard deviation was calculated from the formula $\sigma^2{}_{(F)} = \sigma^2(I)/4.I.LP$ where $\sigma^2(I)$ = total count + (0·25 × background) × (scan time/background time) [2] with the programme PRED.[16]

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* Designed by R. H. B. Mais and P. G. Owston, Imperial Chemical Industries Ltd.

[12] M. D. Joesten, M. Sakhawat, and P. G. Lenhert, *Inorg. Chem.*, 1970, **9**, 151.

[13] D. L. Cullen and E. C. Lingafelter, *Inorg. Chem.*, 1970, **9**, 1858.

[14] B. J. Hathaway, M. J. Bew, D. E. Billing, R. J. Dudley, and P. Nicholls, *J. Chem. Soc.* (*A*), 1969, 2312.

[15] Programmes PICK3, FORDAP, NUCLS4, ORFFE, from the Northwestern University; crystallographic systems, J. A. Ibers.

[16] B. L. Vickery, programmes MAMIE and PRED for the IBM 1130.

Structure Determination.—Attempts to determine the structure by Patterson and Fourier methods were unsuccessful. Both the Patterson synthesis and a difference Patterson synthesis with coefficients $(F_{\mathrm{Cu}}^2 - F_{\mathrm{Mg}}^2)$ showed that the copper was close to (1/4, 0, 1/4), (0, 1/4, 0), or (1/4, 1/4, 1/4). All positions gave R *ca.* 0·60 and no recognisable molecule could be obtained from Fourier syntheses. Apart from the false symmetry produced by having one atom in these positions, the copper contributes only *ca.* 20% of the total scattering power and so failure of the heavy-atom method is not surprising.

Direct methods were tried, the programmes SAP1 and SAP2[17] were used to calculate the overall scale and temperature factor ($B = 4{\cdot}0$ Å^2) and the E values. The 578 largest were used as input to the programme REL1[18] which calculated eight sets of signs. One set converged in eight cycles to leave only one reflection unsigned and was clearly the most promising. An E map was calculated using FORDAP[15] and revealed the copper (at 0·014, 0·255, 0·515), the cation, and an octahedron about the copper, two atoms of which were part of a clearly defined chelating hfac group. This group, the cation, and the copper were used to calculate structure factors having I greater than $3\sigma(I)$. A Fourier synthesis for the 1691 observations revealed the remaining two hfac ligands. Isotropic refinement was carried out by full-matrix least-squares with the programme MAMIE[16] which refined only 81 parameters at a time; this meant that the parameters had to be divided into 4 groups to be refined in successive cycles. R was reduced from 0·38 to 0·17 but some fluorine atoms had very high vibration parameters. A Fourier difference synthesis was computed and indicated anisotropic vibration for the copper and the fluorine atoms.

Final refinement was carried out with the full-matrix programme NUCLS4.[15] At first the copper atom only was allowed anisotropic vibration and all parameters refined together; R was reduced to 0·14. To allow anisotropic vibration for the CF_3 groups the number of parameters was increased to 350 $(56 \times 3 + 25 \times 6 + 31 \times 1 + 1)$ so that a large number of observations was required; those with $|F_o| > 3\sigma(F_o)$ were included, giving a total of 2561.

To prevent the computing time becoming prohibitive the parameters were refined alternately in two sets, one containing the copper and CF_3 groups, *i.e.* all the anisotropic atoms, and the scale factor, and the second, again containing the copper parameters and the scale factor, and also the remaining atoms with isotropic vibration parameters. The function minimised was $R' = \Sigma w(|F_o| - |F_c|)^2$ and the weighting function $w = 1/\sigma^2$ where ideally σ is that given by the counting statistics σ_{count} but in practice to give a uniform value of R' in ranges of $\sin\theta/\lambda$ and of $|F_o|$ a function $\sigma = \sigma_{\mathrm{count}} + 0{\cdot}01|F_o| + 0{\cdot}0003|F_o|^2$ was required. R was reduced to 0·121 and a difference synthesis revealed all twelve hydrogen atoms on the methyl groups and the proton between the nitrogen atoms. Positive regions appeared at the expected positions for the hydrogens round the naphthalene ring and on C(n3) of the hfac ligands. All the hydrogen atoms with isotropic temperature factors were included in the next structure-factor calculations. Only for the cationic proton were the parameters refined, making another four parameters in the second set. Scattering factors for hydrogen were taken from ref. 19, those for the other atoms from ref. 20; for copper the Cu^{2+} curve was used and allowance was made for the real and imaginary parts of the anomalous dispersion so that the calculated structure-factors became complex numbers.

Several cycles of refinement reduced R to 0·111. Eighty-three planes were found to have $|F_o|$ in the range 10—20 with $|F_c|$ close to zero. This phenomenon of very weak reflections being observed at too high a value is discussed elsewhere.[21] These planes were removed and refinement continued until the largest shift was $<0{\cdot}5\sigma$ when R was 0·108 for 2478 observed reflections.

In a final difference synthesis there were peaks of 0·7 eÅ^{-3} near CF_3 groups, probably an indication of disorder in these groups, as found[7] in other hfac complexes. No attempt was made to include this in the model.

The parameters are shown in Table 1.

Magnesium Compound

Only measurements which differ from those for the copper compound are described. A colourless acicular crystal $0{\cdot}02 \times 0{\cdot}04 \times 0{\cdot}08$ cm was mounted with the needle axis, c, approximately coincident with the ϕ-axis of the diffractometer. Accurate cell dimensions were obtained from 24 reflections.

Crystal Data.—$C_{29}H_{22}F_{18}MgN_2O_6$, $M = 860{\cdot}8$, Monoclinic, $a = 12{\cdot}775(5)$, $b = 21{\cdot}268(8)$, $c = 13{\cdot}594(6)$ Å, $\beta = 99° 10'(2')$, $U = 3646$ Å^3, $D_m = 1{\cdot}60$, $Z = 4$, $D_c = 1{\cdot}57$, $F(000) = 1728$. $\mu(\text{Mo-}K_\alpha) = 1{\cdot}99$ cm^{-1}, no absorption correction applied.

Intensities were collected for $2\theta = 3°$ to $2\theta = 40°$. The scanning range was 0·35° below and above the $K_{\alpha,1}$ and $K_{\alpha,2}$ peaks, respectively. The standard reflections were (060), (008), and (600). After 3895 observations had been recorded the crystal rapidly decomposed.

For refinement 1998 planes for which I was $>3\sigma(I)$ were used (*i.e.* corresponding to the 1691 planes of the copper compound) and the initial parameters were those which had given the minimum R value with these 1691 planes, except that the scattering factor for Mg^{2+} was used instead of that for Cu^{2+} and no allowance was made for anomalous dispersion. NUCLS4 was used with the same two sets of parameters, the weighting scheme was adjusted so that $\sigma = \sigma_{\mathrm{count}} + 0{\cdot}01|F_o| + 0{\cdot}0004|F_o|^2$ and the final R value was 0·095. The difference map again showed peaks of 0·7 eÅ^{-3} near the CF_3 groups. Parameters are listed in Table 2.

Both Compounds.—Observed and calculated structure amplitudes are listed in Supplementary Publication No. SUP 20255 (32 pp., 1 microfiche).*

Bond lengths and angles were calculated with the programme ORFFE.[15] This computes the standard deviations from the variance–covariance matrix; to obtain an appropriate matrix for each compound one cycle of refinement was carried out, having as parameters all the atomic co-ordinates, 171, but no vibration parameters. The results are in Tables 4 and 6.

Interionic distances were computed with the programme

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[17] Programmes SAP and MPLN adapted by B. L. V. for the IBM 1130 from N.R.C. programmes by F. R. Ahmed.

[18] Programme REL1 by R. E. Long, Ph.D. Thesis, University of California at Los Angeles, 1965.

[19] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[20] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[21] M. R. Truter and B. L. Vickery, *Acta Cryst.* (*B*), 1972, in the press.

BANGL [22] and planes through various groups of atoms with MPLN.[17] Computations were carried out on the Unit's IBM 1130 or the CDC 6600 in the University of London (FORDAP, NUCLS4, REL1, and ORFFE).

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[22] Programme BANGL by D. Bright for the IBM 1130.