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Coordination Complexes of Copper(II) Fluoride

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Very few complexes of the 3d transition metal fluorides are known in sharp contrast to the many hundreds formed by the corresponding chlorides, bromides and iodides [1]. In the case of copper(II) fluoride the only well established examples are $CuF_2 \cdot 2H_2O$ [2], and the fluorocuprate(II) ions CuF_3^-, CuF_4^{2-} and CuF_6^{4-} [1]. There is also an old report [3] of the formation of $Cu(NH_3)_xF_2$ (x = 2, 4, 5), and a $Cu(quinoline)_2F(BF_4)$ has been obtained indirectly by decomposition of the bis(fluoroborate) [4]. Here we report the synthesis and properties of some copper(II) fluoride complexes with N-donor ligands.

Results and Discussion

Anhydrous copper(II) fluoride was found to be unreactive towards most ligands. The blue hydrate $CuF_2 \cdot 2H_2O$ was much more reactive and a range of complexes with aliphatic diamines and nitrogen heterocycles (Table I) were isolated by refluxing a suspension of $CuF_2 \cdot 2H_2O$ with the ligand in methanol. No reaction occurred between hydrated copper(II) fluoride and $Ph_3P{=}O$, $Ph_3P{=}S$, $PhS(CH_2)_2SPh$, $MeNH_2$, Et_3N, $Me_2S{=}O$ and $(MeO)_3P{=}O$. Triphenylphosphine [5], PMe_2Ph and $Ph_2P(CH_2)_2PPh_2$ [6] bring about reduction to copper(I), but surprisingly no reaction occurred with $AsPh_3$. The isolated complexes were fairly soluble in methanol and ethanol, but insoluble in most other common organic solvents. The $Cu(dien)F_2 \cdot H_2O$ (dien = diethylenetriamine) was very deliquescent, but the other complexes were not affected by exposure to moist air for a short time.

The $Cu(diamine)_2F_2$ (diamine = 1,2-diaminoethane, 1,2-diaminopropane and 1,3-diaminopropane) are clearly members of the $Cu(diamine)_2Y_2$ (Y = Cl, Br, I, CNS, NO_3, ClO_4, BF_4, ½SO_4 *etc.*) series [7, 8] which have distorted octahedral structures (4 + 2 coord). All the far IR spectral absorbtions can be assigned as 'ν(Cu–N)' or internal ligand modes [8–10], no bands assignable to ν(Cu–F) were observed (or expected in view of the weak axial interaction). The properties of $Cu(dien)F_2 \cdot H_2O$ compared with those of $Cu(dien)Cl_2$ [10] suggest a planar N_3F donor set with weaker axial interaction. The reaction of 1,2-bis(dimethylamino)ethane (N,N,N′,N′-tetramethylethylenediamine) with $CuF_2 \cdot 2H_2O$ in a 2:1 mol ratio gave only an intractable blue oil, but on washing with diethyl ether this gave the blue $Cu(Me_2NCH_2CH_2NMe_2)F_2 \cdot 2H_2O$. Pale blue or green complexes were formed with the nitrogen heterocycles, 2,2′-bipyridyl, 1,10-phenanthroline and 2,2′,2″-terpyridyl. The terpyridyl complex may well be 5-coordinate (*cf.* $Cu(terpy)Cl_2 \cdot 2H_2O$) [11] but the structures of the others are unclear.

The magnetic moments for all the complexes are 'normal' for d^9 copper(II), showing that no appreciable intermolecular interaction is present ($CuF_2 \cdot 2H_2O$ is also magnetically dilute [2]). The complexes dissolve in methanol with varying amounts of solvolysis as shown by changes in the electronic spectra (Table I). In 10^{-3} $M_{(MeOH)}$ solution the $Cu(diamine)_2F_2$ are 1:2 electrolytes [12] and the $Cu(dien)F_2 \cdot H_2O$ a 1:1 electrolyte. The other com-

TABLE I. Physical Data.

	Colour	μ(BM)[a]	Electronic Spectra		Δ_M[d]
			Solid[b]	Solution[c]	
$Cu(H_2NCH_2CH_2NH_2)_2F_2$	Violet	1.75	17.8, 14.25h	18.0(54)	196
$Cu(H_2N(CH_2)_3NH_2)_2F_2$	Violet	1.75	17.1, 14.25h	27.7(232), 17.8(68)	182
$Cu(H_2NCH_2CH(NH_2)CH_3)_2F_2$	Blue-violet	1.84	17.5, 14.3sh	29.7(46), 18.0(48)	189
$Cu(Me_2NCH_2CH_2NMe_2)F_2 \cdot 2H_2O$	Blue	1.95	14.8, 12.2sh	15.4(87)	67
$Cu(bipyridyl)F_2 \cdot 2H_2O$	Pale blue	1.78	14.6	14.9(27)	69
$Cu(phenanthroline)F_2$	Pale green	1.77	25.0sh, 16.0	29.0(310), 14.7(19), 10.0sh	54
$Cu(terpyridyl)F_2 \cdot 2H_2O$	Green	1.91	28.5, 24.5sh, 16.0	24.0(98), 14.6(72)	72
$Cu[H_2N(CH_2)_2NH(CH_2)_2NH_2]F_2 \cdot H_2O$	Blue	1.92	16.3	16.3(63), 10.9(15)	102

[a] ±0.05 BM. [b] Nujol mull E × 10^{-3} cm^{-1}. [c] Methanol solution E × 10^{-3} cm^{-1} (ε mol). [d] Ohm^{-1} cm^2 M^{-1} in 10^{-3} M methanol.

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plexes appear to be considerably solvolysed but have conductivities less than those expected for 1:1 electrolytes. Unfortunately insolubility prevented measurements being made in other solvents where solvolysis should be a smaller problem.

These results show that copper(II) fluoride complexes of hard N-donor bidentate ligands can be prepared easily. Our failure to prepare complexes with softer phosphine sulphide or thioether donors does not necessarily mean that these complexes could not be made by another route. Successful syntheses using a *suspension* of $CuF_2 \cdot 2H_2O$ require ligands which can produce dissolution of the copper fluoride.

Experimental

Physical measurements were made as described previously [13]. Copper was determined by atomic absorbtion, and fluoride spectrophotometrically by the alizarin fluorine-blue reagent [14] after destruction of the complex by fusion with NaOH. Hydrated copper(II) fluoride (ALFA) was used as received. The complexes were prepared by the same general method, one example of which is described.

Difluorobis(1,2-diaminoethane)copper(II)

Hydrated copper(II) fluoride (0.55 g, 4 mmol) was suspended in methanol (50 cm^3), 1,2-diaminoethane (0.48 g, 8 mmol) added and the mixture refluxed for 3 hours. The deep blue solution was filtered to remove unreacted metal fluoride, and evaporated. The blue-violet powder was rinsed thoroughly with diethylether (4 X 50 cm^3) and vacuum dried. *Ca.* 65%, Fd C = 20.7%, H = 7.0%, N = 25.4%, F = 17.9%, $C_4H_{16}N_4CuF_2$ req C = 21.7%, H = 7.2%, N = 25.3%, F = 17.2%.

Difluorobis(1,2-diaminopropane)copper(II)

Fd C = 28.6%, H = 8.0%, N = 22.25%, F = 15.2%, Cu = 23.0%, $C_6H_{20}N_4CuF_2$ req C = 28.85%, H = 8.0%, N = 22.4%, F = 15.2%, Cu = 25.5%.

Difluorobis(1,3-diaminopropane)copper(II)

Fd C = 28.8%, H = 8.2%, N = 21.9%.

Difluoro(1,2-bis(dimethylamino)ethanecopper(II)·2-hydrate)

Fd C = 28.6%, H = 8.2%, N = 11.4%, F = 15.3%, Cu = 25.1%, $C_6H_{20}N_2CuF_2O_2$ req C = 28.4%, H = 7.9%, N = 11.1%, F = 15.0%, Cu = 25.1%.

Difluoro(2,2'-bipyridyl)copper(II)-2hydrate

Fd C = 44.2%, H = 3.5%, N = 9.4%, F = 13.0%, Cu = 21.6%, $C_{10}H_{12}N_2CuF_2O_2$ req C = 43.6%, H = 3.6%, N = 10.1%, F = 13.0%, Cu = 21.6%.

Difluoro(1,10-phenanthroline)copper(II)

Fd C = 50.2%, H = 2.9%, N = 9.9%, $C_{12}H_8N_2CuF_2$ req C = 51.1%, H = 2.8%, N = 9.9%.

Difluoro(2,2',2''-terpyridyl)copper(II)-2hydrate

Fd C = 47.2%, H = 3.8%, N = 10.8%, F = 11.1%, Cu = 16.3%, $C_{15}H_{15}N_3CuF_2O_2$ req C = 48.5%, H = 4.0%, N = 11.3%, F = 10.2%, Cu = 17.1%.

Difluoro(diethylenetriamine)copper(II)-hydrate

Fd C = 21.5%, H = 6.3%, N = 17.9%, F = 16.0%, $C_4H_{15}N_3CuF_2O$ req C = 21.6%, H = 5.9%, N = 18.8%, F = 15.6%.

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