Nickel(II) Fluoride Complexes of Diamines and Diimines

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Abstract

The reaction of nickel(II) fluoride hydrate, $NiF_2 \cdot 4H_2O$ with nitrogen donor ligands in methanol solution leads to $[NiL_3]F_2$, (L = ethylenediamine, 1,2- and 1,3-diaminopropane, 2,2′-bipyridyl, 1,10-phenanthroline), $[Ni(diethylenetriamine)_2]F_2$, and $[Ni(1,4,8,11\text{-tetraazacyclotetradecane})F_2]$. Further reaction of $[NiL_3]F_2$ with $NiF_2 \cdot 4H_2O$ in methanol produces NiL_2F_2, which are formulated $[L_2Ni(\mu\text{-}F)_2NiL_2]F_2$. The complexes were characterised by elemental analysis, IR and electronic spectroscopy, magnetic measurements and conductance studies. Attempts to oxidise them to higher valent nickel complexes have failed.

Introduction

In previous studies we have shown that oxidation of nickel(II) chloride or bromide complexes of various group VB ligands produces nickel(III) complexes [1, 2], whilst for certain diamines mixed-valence Ni(II)–(IV) compounds result [3, 4]. However only nickel(II) polyiodides are obtained on attempted oxidation of nickel(II) iodocomplexes [5]. The present work has initiated with the aim of examining the formation of higher valent nickel complexes with fluoride as co-ligands. With the exception of the anions $NiF_n^{(n-2)-}$, few nickel(II) fluorocomplexes have been reported [6], and in most cases these have been produced indirectly by decomposition of the fluoroborates [7–10].

Results and Discussion

Copper(II) fluoride hydrate $CuF_2 \cdot 4H_2O$, reacts directly with nitrogen donor ligands to give copper(II) fluorocomplexes [11], whilst phosphines bring about rapid reduction to Cu(I) [12]. We now report that a suspension of nickel(II) fluoride hydrate $NiF_2 \cdot 4H_2O$, in methanol reacts with excess diamines (L) [1,2-diaminoethane (en), 1,2-diaminopropane (pn), 1,3-diaminopropane (tn)] under reflux to give $[NiL_3]F_2$ complexes. Anhydrous nickel(II) fluoride reacts very slowly and incompletely to give the same products. Similarly diimines (L′) [L′ = 2,2-bipyridyl, 1,10-phenanthroline] react on prolonged reflux in methanol with $NiF_2 \cdot 4H_2O$ to give pink $[NiL'_3]F_2$, which are best isolated by precipitation with 2-propanol; evaporation often produces the green NiL'_2F_2 (below). Tris(ligand) complexes are also readily produced in aqueous solution, but are obtained heavily hydrated on evaporation, and complete removal of the water has not been achieved.

Upon heating the $[NiL_3]F_2$ with $NiF_2 \cdot 4H_2O$ in methanol, preferably with 2,2-dimethoxypropane as a dehydrating agent, blue solutions are produced, and after removal of excess $NiF_2 \cdot 4H_2O$ by filtration, precipitation with acetone or 2-propanol gives blue materials of empirical formula NiL_2L_2. The diimine complexes NiL'_2F_2 can be prepared similarly, and are also obtainable directly from $NiF_2 \cdot 4H_2O$ and a deficit of L′ in methanol. Attempts to produce 1:1 $[NiLF_2]$ complexes by further redistribution between NiL_2F_2 and $NiF_2 \cdot 4H_2O$ in a variety of solvents failed. However, the more sterically demanding $Me_2NCH_2CH_2NMe_2$ readily yields $[Ni(Me_2NCH_2CH_2NMe_2)F_2]$ when heated with $NiF_2 \cdot 4H_2O$ in 2-propanol.

Various primary and secondary amines ($MeNH_2$, Me_2NH, $EtNH_2$ etc.) failed to produce more than trace amounts of uncharacterised pink or bluish solids when heated with $NiF_2 \cdot 4H_2O$ in alcohols or water. Use of multidentate ligands was more successful, and the reaction of hydrated nickel(II) fluoride in methanol with diethylenetriamine (dien) and 1,4,8,11-tetraazacyclotetradecane(14-ane N_4) readily produced $[Ni(dien)_2]F_2$ and $[Ni(14\text{-ane }N_4)F_2]$.

The properties of the $[Ni(bidentate)_3]F_2$ (bidentate = en, tn, pn, bipy phen) and $[Ni(dien)_2]F_2$ (Tables I and II), in particular the electronic spectra, which are very similar to those of $[Ni(bidentate)_3]Y_2$ (Y = Cl, $0.5SO_4$, BF_4, etc.) [13–15] clearly show that NiN_6^{2+} chromophores are present. The magnetic moments are in agreement with expectations for pseudooctahedral d^8 Ni(II). The similarity of the

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TABLE I. Analytical Data

	Color	Analysis (found (calc.))				
		C	H	N	Ni	F
$[Ni(en)_3]F_2$	light blue–pink	26.0(26.0)	8.5(8.7)	30.1(30.5)	21.9(21.2)	–
$[Ni_2(en)_4F_2]F_2$	light blue	21.8(22.2)	7.6(7.4)	26.0(25.9)	28.0(27.1)	17.0(17.1)
$[Ni(pn)_3]F_2$	light pink	34.1(33.9)	9.6(9.6)	26.1(26.5)	18.8(18.4)	11.0(11.9)
$[Ni_2(pn)_4F_2]F_2$	light blue	29.2(29.4)	8.3(8.2)	22.8(23.0)	24.3(24.0)	–
$[Ni(tn)_3]F_2$	light blue	33.8(33.9)	9.6(9.6)	26.6(26.5)	–	–
$[Ni_2(tn)_4F_2]F_2$	light blue	29.5(29.4)	8.2(8.2)	23.1(23.0)	–	–
$[Ni(bipy)_3]F_2$	pink	64.6(63.7)	4.2(4.3)	15.0(14.9)	–	–
$[Ni_2(bipy)_4F_2]F_2$	green	59.0(58.7)	3.9(3.9)	13.6(13.8)	14.7(14.3)	9.6(9.3)
$[Ni(phen)_3]F_2$	pink	68.6(67.8)	3.7(3.8)	13.1(13.2)	10.3(9.9)	–
$[Ni_2(phen)_4F_2]F_2$	green	62.8(63.0)	3.3(3.5)	12.4(12.3)	12.8(12.9)	–
$[Ni(tmen)F_2]_n$	green	33.3(33.8)	7.3(7.6)	13.0(13.2)	–	18.2(17.9)
$[Ni(14\text{-}aneN_4)F_2]$	blue	40.6(40.4)	8.0(8.0)	18.9(18.8)	20.1(19.8)	–
$[Ni(dien)_2]F_2$	light blue	31.7(31.6)	8.4(8.6)	27.8(27.7)		

TABLE II. Spectroscopic and Physical Data

	E_{max} (10^3 cm^{-1}) ϵ_{mol} (dm^3 cm^{-1} mol^{-1})[a]	μ_{eff} (BM)[b]	Λ_M (cm^2 mol^{-1} ohm^{-1})[c]
$[Ni(en)_3]F_2$	11.7(6), 18.5(10), 29.6(20) 11.4, 18.2, 29.2 dr	2.80	185
$[Ni_2(en)_4F_2]F_2$	11.0(8), 19.2(11), 26.3(9), 32.7(20) 8.47(sh), 11.0, 18.0, 28.6 dr	3.16	180
$[Ni(pn)_3]F_2$	11.6(8), 18.3(5), 29.4(16) 12.4, 19.0, 24.9(sh), 30.3 dr	2.85	210
$[Ni_2(pn)_4F_2]F_2$	10.2(6), 17.0(8), 27.6(12) 8.5(sh), 10.9, 17.8, 28.4 dr	2.98	172
$[Ni(tn)_3]F_2$	10.2(3), 17.1(10), 27.6(16) 9.0(sh), 12.5, 17.8, 28.5 dr	2.98	190
$[Ni_2(tn)_4F_2]F_2$	9.7(6), 10.7(6), 17.0(16), 27.6(24) 8.2(sh), 9.6, 11.8, 17.9, 28.6 dr	2.94	165
$[Ni(bipy)_3]F_2$	12.8(9), 19.2(20), 30.0(1500) 12.7, 18.9, 25.1(sh), 32.1 dr	2.87	175
$[Ni_2(bipy)_4F_2]F_2$	10.8(14), 13.1(sh), 17.5(12), 34.0(18200) 11.3, 13.2, 17.0, 23.7, 28.6 dr	2.85	190
$[Ni_2(phen)_4F_2]F_2$	10.9(14), 12.3(sh), 18.0(12) 11.7, 13.3, 16.9, 29.0 dr	2.80	174
$[Ni(phen)_3]F_2$	12.3(4), 19.1(9), 29.2(1220) 12.8, 19.2, 25.1(sh), 30.5 dr	2.88	192
$[Ni(Me_2NCH_2CH_2NMe_2)F_2]_n$	10.0(4), 13.3(sh), 14.8(7), 25.8(14), 29.4(49) 13.2, 14.8, 21.3, 25.6 dr	3.37	–
$[Ni(dien)_2]F_2$	11.7(11), 18.6(6), 29.0(10) ~12.0, 18.2, 27.9	2.90	185
$[Ni(14\text{-}aneN_4)F_2]$	22.2(30) 9.8, 14.9, 18.9, 28.3	–	200

[a] Methanol solution 5000–32000 cm^{-1}, dr = diffuse reflectance. [b] Gouy measurement ±0.05 BM, 295 K. [c] 10^{-3} mol dm^{-3} MeOH. 1:1 electrolytes have Λ_M = ~80–115 ohm^{-1} cm^2 mol^{-1}, 2:1 ~160–220 ohm^{-1} cm^2 mol^{-1}.

solid state and solution electronic spectra, and the conductivity data* indicate that the $[Ni(bidentate)_3]^{2+}2F^-$ constitution is also present in solution in methanol.

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*Methanol has been criticised [17] as a solvent for conductivity measurements due to its strong solvolytic nature, but the poor solubility of these complexes in less polar solvents, necessitated its use in the present cases.

In the solid state the electronic spectrum of the blue [Ni(14-aneN_4)F_2] resembles that of other tetragonal nickel(II) complexes of this ligand [16], but on dissolution in methanol a yellow solution is formed consistent with the production [18] of planar [Ni(14-aneN_4)]$^{2+}$, also indicated by the high conductance. The X-ray structure of the analogue [Ni(*meso*-Me_6(14)aneN_4)F_2]$\cdot 5H_2O$ (*meso*-Me_6(14)aneN_4 = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) [19] revealed *trans* N_4F_2 coordination.

The structures of the NiL_2F_2 (L = diamine, diimine) are less immediately clear, and as attempts to grow crystals suitable for an X-ray study have so far failed, only a tentative assignment of structure based upon spectroscopic data is possible. The electronic spectra (Table II) are typical of nickel(II) complexes in a six-coordinate environment, but do not show the large splittings especially of the lowest energy band characteristic of a tetragonal *trans*-NiY_4X_2 (D_{4h}) [16]. Elimination of *trans* NiL_2F_2 structure leaves either a *cis* NiL_2F_2 or an oligomer structure. All the NiL_2F_2 complexes have significant conductances in 10^{-3} M solution in methanol and although solvolysis complicates these measurements they would appear to be inconsistent with a non-ionic structure. The structure of $Nien_2Cl_2$ has been established by X-ray studies [20, 21] to be [$en_2Ni(\mu\text{-}Cl)_2Nien_2$]$Cl_2$, and ($\mu$-F)$_2$-bridges are present in [Co_2(3,5-Me_2pyrazole)$_6F_2$]$(BF_4)_2$ [9] and [Cu_2(3,4,5-Me_3pyrazole)$_6F_2$]$(BF_4)_2$ [10] whilst μ_3-F bridges are present in the cubane [Co_4F_4(N-propylimidazole)$_{12}$]$(BF_4)_4$ [22].

From the structure of '$Nien_2Cl_2$' and with the precedent of M(μF)$_2$M bridges in the pyrazole complexes, we propose that the Ni(diamine)$_2F_2$ have a [(diamine)$_2$Ni(μ-F)$_2$(diamine)$_2$]F_2 structure. Based upon this formula the conductances (Table II) are consistent with 1:2 electrolytes, and a careful comparison of the far IR spectra of the corresponding [Ni(diamine)$_3$]F_2, Ni(diamine)$_2F_2$, and their chloride analogues reveals very broad bands in the Ni(diamine)$_2F_2$ at ~378 cm^{-1} (en), ~364 cm^{-1} (pn), and ~372 cm^{-1} (tn) which are absent in the other complexes and which can be tentatively assigned as ν(Ni–F$_{\text{bridge}}$), *cf.* refs. 7–10. The diimine complexes appear to be similar having ν(Ni–F) at ~358 cm^{-1} (phen) and ~360 cm^{-1} (bipy). (Both Ni(diimine)$_2X_2$ (X = Cl, Br) [23, 24] and [(bipy)$_2$Ni(μ-Cl)$_2$Ni(bipy)$_2$]$NiCl_4$ [25] are known). All the Ni(diamine)$_2F_2$ show broad ν(N–H) vibrations at ~3200–2800, ~2500 cm^{-1} indicative of strong N–H–F hydrogen bonding [7, 8].

The only 1:1 diamine complex Ni($Me_2NCH_2CH_2NMe_2$)F_2 isolated has a similar electronic spectrum to Ni($Me_2NCH_2CH_2NMe_2$)Cl_2, which is a pseudo-octahedral polymer [25], and a similar structure is likely. Various attempts to isolate complexes of diphosphine, diarsine, or diphosphine dioxide ligands with nickel(II) fluoride, using $NiF_2 \cdot 4H_2O$ in methanol, n-butanol or n-butanol/chlorobenzene, have been unsuccessful.

Attempted Oxidations

Apart from the well known NiF_6^{2-} and NiF_6^{3-} [27], the only report of a high valent nickel fluoride complex is by Larin *et al.* [28] who observed fluorine hyperfine coupling in the ESR spectrum of [Ni(en)$_2Cl_2$]$^+$ in 40% aqueous hydrofluoric acid, although no solid complex was isolated. We attempted oxidation of the nickel diamine and diimine complexes described above with Ce(IV) and $S_2O_8^{2-}$ (no evident reaction), concentrated nitric acid (hydrolytic decomposition), chlorine or bromine (decomposition and oxidation to Ni(III) chloro or bromo complexes). Finally in an attempt to overcome these ligand exchange reactions we used caesium fluoroxysulphate Cs[SO_3OF], which is soluble in acetonitrile and gives only SO_4^{2-} and F^- on reduction [29]. In fact Cs[SO_3OF] and Ni(diamine)$_2F_2$ in dry MeCN immediately gave greeen solids but these proved to be ESR silent, and had electronic spectra consistent with octahedral nickel(II) materials. The IR spectra suggested oxidation of the diamine ligands rather than the metal had occurred.

Experimental

Physical measurements were made as described previously [1, 5, 11]. Nickel fluoride hydrate (Alfa Inorganics), and the ligands (Aldrich or BDH Ltd) were used as received. Methanol was dried by distillation from magnesium methoxide. Preparations were conducted under a dry dinitrogen atmosphere.

[Ni(en)$_3$]F_2

A suspension of powdered $NiF_2 \cdot 4H_2O$ (1.7 g, 10 mmol) in methanol (25 cm^3) was stirred under reflux with 1,2-diaminoethane (2.0 g, 33 mmol). After about 4 h a deep purple solution had been produced and approximately 75% of the nickel(II) fluoride had dissolved. The solution was cooled, filtered, and the solvent removed on a rotary evaporator to yield a purple oil. The oil was stirred with a mixture of methanol–diethyl ether, 25 cm^3 (1:10 v/v) until a pale pink powder was produced. The latter was filtered off and dried *in vacuo*, 2.0 g, 72% (on $NiF_2 \cdot 4H_2O$). [Ni(tn)$_3$]F_2, [Ni(pn)$_3$]F_2, [Ni(dien)$_2$]F_2 and [Ni(14-aneN_4)F_2] were made similarly.

[Ni(bipy)$_3$]F_2

Was prepared in a similar manner by heating together $NiF_2 \cdot 4H_2O$ (10 mmol) and 2,2′-bipyridyl (5.5 g, 35 mmol) in methanol (25 cm^3) for 5 h. After removal of the unreacted $NiF_2 \cdot 4H_2O$, 2-propanol (*ca.* 30 cm^3) was added to the solution, which was cooled to –20 °C overnight. The pink powder was filtered off, rinsed with diethyl ether and dried. 1.7 g, 30%. $[Ni(phen)_3]F_2$ was made similarly.

$[Ni_2(en)_4F_4]F_2$

$[Ni(en)_3]F_2$ (1 g, 3.6 mmol) in methanol (20 cm^3) was refluxed for 4 h with $NiF_2 \cdot 4H_2O$ (1 g, 6 mmol) and 2,2-dimethoxypropane (1 cm^3). The blue solution was filtered, and the filtrate treated dropwise with diethyl ether with stirring to produce a blue powder. The latter was filtered off, rinsed with diethyl ether and dried *in vacuo, ca.* 1 g.

$[Ni_2(tn)_4F_2]F_2$, $[Ni_2(pn)_4F_2]F_2$, $[Ni_2(bipy)_4F_2]F_2$, $[Ni_2(phen)_4F_2]F_2$ were made in a similar manner. The diimine complexes could be made directly by heating $NiF_2 \cdot 4H_2O$, and the diimine (1:2 ratio) in methanol.

$[Ni(Me_2NCH_2CH_2NMe_2)F_2]$ was prepared by heating $NiF_2 \cdot 4H_2O$ with the ligand in a 1:2 mole ratio in 2-propanol.

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