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Transition Metal Tetrafluoroborate Interactions with 2,6-lutidine N-oxide

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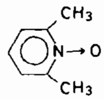
The interactions of transition metal tetrafluoroborates with 2,6-lutidine N-oxide(L) in organic solvents were studied, under various conditions. A number of adducts of the types $[CrL_6](BF_4)_3$, $[ML_4](BF_4)_2$ *(M = Fe, Cu, Zn, Cd),* $[CoL_4(FBF_3)](BF_4)\cdot H_2O$ *and* $[L_3NiL_2NiL_3](BF_4)_4$ *were isolated and characterized. In most cases, these compounds are similar to the corresponding metal perchlorate complexes (including the square-planar* Fe^{2+} *complex, which is partially spin-paired (*$S = 1$; $\mu_{eff} = 3.55\ \mu B$*)). The only differences are that the new* Co^{2+} *complex involves coordinated* FBF_3*, while the 4:1* $Co(ClO_4)_2$ *analog contains exclusively ionic* ClO_4*, and that, whereas the diamagnetic, square-planar* $[NiL_4](ClO_4)_2$ *complex remains unchanged for a long time before dimerizing to the paramagnetic* $[L_3NiL_2NiL_3](ClO_4)_4$*, with the* $[NiL_4](BF_4)_2$ *analog the monomeric species is unstable, dimerizing within a few hours. These differences were attributed to the significantly smaller steric hindrance exerted by* BF_4 *relative to* ClO_4*. In addition to the preceding adducts, a number of products of the types* $[L_3CoF_2CoL_3](BF_4)_2$, $[(F_2BF_2)L(ROH)MF_2M(ROH)L(F_2BF_2)]$ *(R =* CH_3 *for M = Mn; R =* C_2H_5 *for M = Ni) and* $MnLF(BF_4)\cdot 4MnF_2$ *were isolated. Formation of* $MF(BF_4)$ *or* MF_2 *is accompanied by elimination of* $BF_3\cdot L$ *from the initially formed adducts. This reaction seems to be favored when the initial adduct of L with* $M(BF_4)_2$ *involves cooordinated tetrafluoroborato ligands [1].*

Introduction

The two methyl substituents in 2,6-lutidine N-oxide (I; N-lutO; 2,6-dimethylpyridine N-oxide) exert considerable steric hindrance during complex formation with this ligand. Thus, for instance, N-lutO reportedly forms transition metal complexes of the $[MnL_4(OClO_3)](ClO_4)$, $[ML_4](ClO_4)_2$ (M = Fe, Co, Ni, Cu, Zn) [2–4], $[CoL_3(O_2ClO_2)](ClO_4)$, $[CoL_5](ClO_4)_2$ [4–6], $[NiL_5](ClO_4)_2$ (only in solution) [7], $[ML_2(ONO_2)(O_2NO)]$ (M = Mn, Co, Ni, Zn) and $[CuL_2(ONO_2)_2]$ [8] types. This is in contrast to the trends observed with non-sterically hindered pyridine N-oxides, which easily yield 6:1 complexes with 3d metal perchlorates [9–12], tetrafluoroborates [13] and nitrates [14]. N-lutO forms, of course, 6:1 cationic complexes with Cr^{3+} and Fe^{3+} [2, 5], but this is consistent with the general trend of tripositive 3d metal ions to form complexes with high ligand to metal ratios even with sterically hindered ligands [2, 5, 15].



(I)

During attempts at the syntheses of N-lutO complexes with 3d metal tetrafluoroborates, Reedijk *et al.* reported that the HBF_4 salt of the ligand, *i.e.*, $(N\text{-lutO-H-N-lutO})^+(BF_4)^-$, contaminated with minor amounts of authentic metal complex, is precipitated instead [16]. In the same paper it was mentioned that, under different synthetic conditions, $M(BF_4)_n$ ($n = 2$ or 3) adducts with N-lutO could be obtained in pure form [16], but these studies have not been reported so far. On the other hand, it is now well established that reactions of the type

$$M(BF_4)_2 + nL \rightarrow MF(BF_4)L_{n-1} + BF_3L \text{ or}$$

$$(M(BF_4)_2 + mL \rightarrow MF_2L_{m-2} + 2BF_3L \qquad (1)$$

are especially facile in the presence of ligands containing bulky substituents near the donor site [17–25]. Particularly suitable ligands for reaction (1) are

TABLE I. Analyses of Complexes Formed by Interaction of N-lutO(L) with Metal Tetrafluoroborates.

Complex	Color	Analysis, Found (Calc) %					
		C%	H%	N%	Metal%	B%	F%
$CrL_6(BF_4)_3$	Light green	48.16 (47.98)	5.49 (5.18)	8.24 (7.99)	5.32 (4.95)	2.80 (3.09)	22.06 (21.69)
$MnLF(BF_4)\cdot CH_3OH$	Off-white	29.97 (30.32)	4.22 (4.14)	4.26 (4.42)	17.87 (17.34)	3.65 (3.41)	30.24 (29.98)
$MnLF(BF_4)\cdot 4MnF_2$	Pinkish white	13.37 (12.82)	1.41 (1.38)	2.25 (2.14)	41.76 (41.90)	1.70 (1.69)	38.44 (37.67)
$FeL_4(BF_4)_2$	Light brown	46.16 (46.58)	4.78 (5.03)	7.80 (7.76)	7.51 (7.73)	3.15 (2.99)	20.69 (21.05)
$CoL_4(BF_4)_2\cdot H_2O$	Blue-purple	44.57 (45.25)	5.35 (5.15)	7.54 (7.72)	8.17 (7.93)	2.73 (2.91)	20.33 (20.45)
$CoL_3F(BF_4)$	Brown	47.51 (47.22)	4.80 (5.09)	7.63 (7.86)	10.56 (11.03)	2.12 (2.02)	18.24 (17.78)
$NiL_4(BF_4)_2$	Light green	46.44 (46.39)	4.76 (5.01)	7.55 (7.73)	8.32 (8.10)	3.24 (2.98)	21.43 (20.97)
$NiLF(BF_4)\cdot C_2H_5OH$	Bright light green	32.54 (32.31)	4.28 (4.52)	4.24 (4.19)	17.80 (17.54)	3.45 (3.23)	28.77 (28.39)
$CuL_4(BF_4)_2$	Turquoise	45.73 (46.09)	5.11 (4.97)	7.45 (7.68)	8.74 (8.71)	2.70 (2.96)	21.21 (20.83)
$ZnL_4(BF_4)_2$	White	45.65 (45.97)	4.63 (4.96)	7.72 (7.66)	9.31 (8.94)	3.41 (2.96)	20.59 (20.78)
$CdL_4(BF_4)_2$	White	42.96 (43.19)	4.84 (4.66)	7.37 (7.20)	13.98 (14.44)	2.42 (2.78)	19.93 (19.52)

several substituted amines, namely triethylenediamine, quinuclidine [17], 3,5-dimethylpyrazole [18, 20, 21] and substituted derivatives [23], N-ethylimidazole [22] and 3-hydroxypyridine [19]. The only other type of ligand that reportedly gives reactions of type (1), at least with $Co(BF_4)_2$, is N-lutO [24, 25]. It was of interest to us to investigate the interactions between transition metal tetrafluoroborates and N-lutO, especially in view of the difficulties previously encountered during attempts at the precipitation of authentic $M(BF_4)_n$ adducts with this ligand [16, 24, 25]. Accordingly, work in this direction was undertaken, and our findings are reported in the present paper.

Experimental

Chemicals

N-lutO (Baker grade) was utilized as received. Reagent grade transition metal tetrafluoroborates (in the form of the solid hydrated salt for M = Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} or its aqueous solution for M = Cr^{3+}, Mn^{2+}, Fe^{2+}, Cd^{2+}), triethyl orthoformate (tcof) and organic solvents were generally used.

Preparation Methods

Procedure A: This was essentially the same method we used for the isolation of 3d metal perchlorate complexes with N-lutO [2], *viz.*: The metal salt is dissolved in excess teof, a dehydrating agent [26]; a few drops of acetone are added for salts not completely soluble in teof (*CAUTION*: The amount of acetone added should be restricted to the exact minimum required for complete dissolution of the salt, because in the presence of excess acetone reactions leading to the precipitation of $[(N\text{-lutO})_2H](BF_4)$ are favored. When the reaction has taken the latter direction, the solution turns purple before the precipitation of the pale violet crude $[(N\text{-lutO})_2H](BF_4)$, in a manner similar to that described by Reedijk *et al.* for reactions of $Co(BF_4)_2$ with N-lutO in ethanol–teof (5:3 v/v) solution [16]. It was found during this work that if the metal salt is dissolved in alcohol and the stoichiometric amount of teof is then added for dehydration, no reactions leading to formation of the HBF_4 salt of N-lutO are observed upon interaction of the metal salt solution with the ligand). The metal salt solution is stirred at 50 °C for 2 hr, and an excess of N-lutO (ligand to salt molar ratio 8:1 for Cr^{3+} and 6:1 for M^{2+}) is then added. The following crystalline adducts precipitate immediately, under these conditions: $Cr(N\text{-lutO})_6(BF_4)_3$, $Co(N\text{-lutO})_4(BF_4)_2\cdot H_2O$ and $M(N\text{-lutO})_4(BF_4)_2$ (M = Ni, Cu, Zn, Cd). The Ni^{2+} complex is initially obtained in the form of a violet powder, which is presumably a monomeric, square-planar and diamagnetic species of the $[Ni(N\text{-lutO})_4](BF_4)_2$ type (2, 3, 5). This product, unlike its $[Ni(N\text{-lutO})_4](ClO_4)_2$ analog, which is fairly stable [2, 3, 5], is partially converted on the filter to the light green paramagnetic isomer [2, 3, 5] as soon as separated by filtration (either in the air or under N_2); the conversion of the violet to the green isomeric species becomes complete after a few hours of desiccation of the solid *in vacuo.* Attempts at the elimination of water from the new Co^{2+} complex, by heating to 60–70 °C, under reduced pressure, were unsuccessful, owing to the tendency of this compound to collapse to a viscous liquid upon such treatment. The preceding new complexes were separated by filtration, washed with teof and stored in an evacuated desiccator over P_4O_{10}. The dry solid complexes are stable in the atmosphere and soluble in various polar organic solvents, including nitromethane. Under the above synthetic conditions, Mn^{2+} and Fe^{2+} tetrafluoroborates yield solid precipitates, consisting of products of reactions of type (1). In fact, both these precipitates contain more than 40% Mn or Fe; the analysis of the Mn^{2+} product suggests that it is of the Mn(N-lutO)F(BF_4)·4MnF_2 type (Table I); however, the analysis of the Fe^{2+} precipitate could not be correlated with any reasonable empirical formula.

Procedure B: Fe(N-lutO)$_4$(BF_4)$_2$ was prepared by a method similar to that used by de Bolster *et al.* for the preparation of metal tetrafluoroborate complexes with triphenylphosphine oxide [27], *i.e.*: Fe(BF_4)$_2$ is dissolved in methanol and the stoichiometric amount of teof is added for dehydration. A methanolic solution of N-lutO is then added (at a 4:1 N-lutO to Fe ratio), and the mixture is allowed to stand at room temperature overnight. The crystals of the new complex are then separated by filtration, washed with anhydrous diethyl ether and stored *in vacuo* over P_4O_{10}. Procedure B can be also used for the preparation of all the complexes obtained by procedure A: Co(BF_4)$_2$ yields the same monohydrate complex as above, while the rest of the metal tetrafluoroborates form the anhydrous 6:1 (M = Cr^{3+}) or 4:1 (M = Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}) complexes. However, Mn(BF_4)$_2$ undergoes reactions of type (1) even under the conditions of procedure B, affording a solid analyzing as Mn(N-lutO)F(BF_4)·CH_3OH in small yield. This product is soluble in nitromethane and other polar organic solvents, in contrast to Mn(N-lutO)F(BF_4)·4MnF_2, which is only sparingly soluble in these media.

Preparation of other MF(BF$_4$) complexes with N-lutO

Since [M(N-lutO)$_5$]$^{2+}$ (M = Co, Ni) cationic species are known to exist in solution [2, 6, 7] and the solid [Co(N-lutO)$_5$](ClO_4)$_2$ complex was recently isolated [5], we made several attempts at the precipitation of solid 5:1 N-lutO complexes with Co^{2+} and Ni^{2+} tetrafluoroborates. With Co(BF_4)$_2$, during a preparation made by procedure A and by using a 6:1 ligand to Co ratio, instead of filtering off the blue-purple 4:1 complex initially formed we allowed it to remain in suspension in the mother liquor and heated this mixture to 70–80 °C, under stirring. Within a few minutes the color of the precipitate changed to brown; this product analyzes as Co(N-lutO)$_3$F(BF_4), as already reported [25]. In the case of Ni(BF_4)$_2$, the salt was dissolved in ethanol, the stoichiometric amount of teof was added for dehydration and then excess ligand (6:1 N-lutO to Ni molar ratio). Under these conditions, a bright light green solid, analyzing as Ni(N-lutO)F(BF_4)·C_2H_5OH was slowly precipitated in low yield. The new CoF(BF_4) and NiF(BF_4) complexes are soluble in various polar organic solvents.

Characterization Studies

Analytical data (Schwarzkopf Microanalytical Laboratories, Woodside, N.Y.) are given in Table I. Infrared (Table II) and solid-state (Nujol mull) electronic (Table III) spectra, magnetic susceptibility and molar conductivity (Table III) measurements were obtained by methods described elsewhere [2, 3, 28]. It should be mentioned that attempts at recrystallizing the new complexes from organic solvents were generally unsuccessful.

Discussion

Infrared Evidence

Most of the complexes formed by simple addition of N-lutO to M(BF_4)$_n$ show IR spectra (Table II) very similar to those of the transition metal perchlorate analogs [2, 3]. Thus, Cr(N-lutO)$_6$(BF_4)$_3$ and M(N-lutO)$_4$(BF_4)$_2$ (M = Fe, Ni, Cu, Zn, Cd) obviously involve cationic species with a single type of ligand (*i.e.*, N-lutO) and exclusively ionic BF_4. In fact, the ν_3 and ν_4 fundamental vibrational modes of ionic (T_d) BF_4 appear as single bands [25, 27, 29, 30]; no bands attributable to ν_2(BF_4) are observed, whilst the presence of ν_1(BF_4) can not be detected with any degree of confidence, as strong ligand absorption (γ_{CH}) characterizes the 810–750 cm^{-1} region in the spectra of N-lutO metal complexes [31]. Coordination of N-lutO is manifested by ν_{N-O} shifts to lower wavenumbers, relative to the position of this mode (1245 cm^{-1}) in uncomplexed N-lutO [32, 33]; similar negative ν_{N-O} frequency shifts are observed in the spectra of the new MF(BF_4) (M = Mn, Co, Ni) complexes. Unlike the rest of the M(BF_4)$_n$ complexes, Co(N-lutO)$_4$(BF_4)$_2$·H_2O shows clearcut evidence in favor of both ionic and coordinated BF_4, *viz.*: each of the ν_3 and ν_4(BF_4) modes are triply split, while ν_1 and ν_2(BF_4) are IR-active [25, 27, 29, 30, 34–36]. This complex seems to contain lattice water, as suggested by the presence of a medium intensity, very broad ν_{OH} absorption, covering the whole 3650–3200 cm^{-1} region (37) (none of

TABLE II. Pertinent Infrared Data for N-lutO Complexes with Metal Tetrafluoroborates (cm^{-1}).

Complex		Fundamental BF_4 Vibrations					
	ν_{N-O}[a]	ν_3	ν_1[b]	ν_4	ν_2	ν_{M-O}[c]	ν_{M-F}[c]
$CrL_6(BF_4)_3$	1210sh, 1180s	1065vs,b	762m,sh	528s	–	478vs	–
$MnLF(BF_4)\cdot CH_3OH$	1209ms	1124vs,vb, 1063vs,b, 1027vs	758s,sh	549s,sh, 531s, 520s	353s,sh	347sh[d] 330s, 319s	380s
$MnLF(BF_4)\cdot 4MnF_2$	1202mw	1066m,b	755m,sh	543m	–	322s,b	385vs,b
$FeL_4(BF_4)_2$	1209s	1060s,b	770m,sh	527s	–	400m, 380m	–
$CoL_4(BF_4)_2\cdot H_2O$	1209s	1110vs, 1055vs,b, 1029vs	760ms	537m, 521m	356m,sh	393s, 384s	[e]
$CoL_3F(BF_4)$	1205s	1052vs,b	770w,sh	528m	–	379s	420ms,b
$NiL_4(BF_4)_2$	1183s	1061vs,b	772mw,sh	523ms	–	399s, 379s	–
$NiLF(BF_4)\cdot C_2H_5OH$	1211m,sh, 1182s	1145vs, 1062vs,b, 1030vs,sh	767ms	546ms, 533m,sh, 522m,b	357mw,sh	362m[d], 352m	402ms
$CuL_4(BF_4)_2$	1219s,sh, 1200s	1059vs,b	775m,sh	527s	–	437s	–
$ZnL_4(BF_4)_2$	1188m,sh	1050vs,b	770m,sh	531m	–	382s,sh, 365s,b	–
$CdL_4(BF_4)_2$	1204m, 1177m,sh	1049vs,b	772mw,sh	528m	–	341vs, 320vs,b	–

[a] Free N-lutO shows ν_{N-O} at 1245 cm^{-1} (neat or Nujol mull) [2, 3, 25]. [b] $\nu_1(BF_4)$ overlaps with γ_{CH} (N-lutO) [31]. [c] IR maxima at 550–200 cm^{-1} for free N-lutO: 550ms, 538w, 469m, 449m, 336m,b, 280m, 243m. [d] Bands assigned as ν_{M-O} (alcohol). [e] Not identified.

the rest of the new complexes shows IR bands attributable to the presence of water). On the basis of the preceding evidence and the fact that the $Co(BF_4)_2$ complex appears to be pentacoordinated (*vide infra*), this compound may be formulated as $[Co(N\text{-}lutO)_4(FBF_3)](BF_4)\cdot H_2O$, with one ionic BF_4^- group and one unidentate coordinated $-FBF_3$ (C_{3v} symmetry) ligand. Nevertheless, an alternative interpretation of the $\nu(BF_4)$ splittings in the spectrum of the preceding complex would be BF_4 interaction with H_2O rather than Co_2^{+} [38]. This would also explain why the water is not eliminated in the presence of teof [27, 38], but in such a case the presence of one aqua ligand would be required for completion of coordination number five, *i.e.*, $[Co(N\text{-}lutO)_4(OH_2)](BF_4)_2$; this possibility can be ruled out on the basis of the absence of any ir bands attributable to ν_{Co-O}(aqua) at 460–420 cm^{-1} [39] in the spectrum of the complex (the broad ν_{OH} character might be, of course attributed to the water–tetrafluoroborate interaction, if such was the case). Regarding the new $MF(BF_4)$ complexes, $Co(N\text{-}lutO)_3F(BF_4)$ and $Mn(N\text{-}lutO)F(BF_4)\cdot 4MnF_2$ contain exclusively ionic BF_4, whilst $Mn(N\text{-}lutO)F(BF_4)\cdot CH_3OH$ and $Ni(N\text{-}lutO)F(BF_4)\cdot C_2H_5OH$ obviously comprise coordinated tetrafluoroborato ligands. The IR spectra of the latter two complexes might be taken as indicative of the presence of either both ionic BF_4 groups and unidentate $-FBF_3$ ligands or exclusively coordinated bidentate chelating $=F_2BF_2$ (C_{2v} symmetry) ligands. The fact that these compounds contain only one BF_4 group per metal ion, combined with significantly larger splittings of the ν_3 and ν_4 fundamentals, relative to those observed for $Co(N\text{-}lutO)_4(BF_4)_2\cdot H_2O$, favors the presence of bidentate chelating $=F_2BF_2$ ligands in these complexes [27, 29, 30, 34–36, 40]. The ν_{OH}(alcohol) mode in the spectra of these compounds occurs at 3420 in $Mn(N\text{-}lutO)F(BF_4)\cdot CH_3OH$ and at 3445 cm^{-1} in $Ni(N\text{-}lutO)F(BF_4)\cdot C_2H_5OH$; both these maxima are relatively sharp [41, 42].

Tentative metal–ligand band assignments (Table II) were based on previous ν_{M-L} assignments for transition metal complexes with N-lutO and other aromatic amine N-oxides [3, 5, 8, 43–45], fluoro ligands [18, 19, 23, 46] and alcohols (45, 47]. These assignments are suggestive of the following coordination numbers: six for the Cr^{3+}, the two Mn^{2+} and the $NiF(BF_4)$ complexes [43–47]; five for the two Co^{2+} and the $Ni(BF_4)_2$ complexes [3, 5, 7, 45]; and four for the Fe^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} complexes [3, 7]. As far as the ν_{M-F} assigned bands are concerned, they apparently correspond to the metal–fluoride ion bond [18, 19, 23, 27, 46]. No bands

TABLE III. Solid-state (Nujol mull) Electronic Spectra, Magnetic Properties (300 K) and Molar Conductivities (10^{-3} M nitromethane solutions, 25 °C) of N-lutO(L) Complexes with Metal Tetrafluoroborates.

Compound	λ_{max}, nm (kK)	$10^6\ \chi_M^{cor}$, cgsu	μ_{eff}, μ_B	Λ_M, Ω^{-1} cm^2 mol^{-1}
N-lutO	219(45.7)s,sh, 275(36.4)vs,b, 297(33.7)vs,sh, 319(31.3)svs,sh			
$CrL_6(BF_4)_3$	223(44.8)vs, 269(37.2)vs,b, 397(25.2)sh, 600(16.7)m,vb	5702	3.71	244
$MnLF(BF_4)\cdot CH_3OH$	209(47.8)vvs, 261(38.3)vvs, 393(25.4)m	13,861	5.79	29[a]
$MnLF(BF_4)\cdot 4MnF_2$	208(48.1)vvs, 253(39.5)vvs, 264(37.9)vvs,sh, 384(26.0)m	11,656	5.31	[b]
$FeL_4(BF_4)_2$	214(46.7)vvs, 224(44.6)vvs,sh, 263(38.0)vs,vb, 342(29.2)vs,sh, 357(28.0)vs, 568(17.6)m,sh, 975(10.3)m,b	5194	3.55	181
$CoL_4(BF_4)_2\cdot H_2O$	216(46.3)vs, 223(44.8)vs, 264(37.9)vvs,sh, 272(36.8)vvs, 354(28.2)s, 510(19.6)m,sh, 555(18.0)m,b, 770(13.0)mw,sh, 815(12.3)mw,b, 1140(8.8)w, 1900(5.3)wm	8250	4.47	47
$CoL_3F(BF_4)$	221(45.2)vs,sh, 268(37.3)vvs,vb, 294(34.0)vs,sh, 365(27.4)s,sh, 403(24.8)s, 512(19.5)m,sh, 535(18.7)m,sh, 751(13.3)mw, 780(12.8)mw, 1169(8.6)mw, 1300(7.8)mw,b, 1850(5.4)w,sh	8219	4.46	63[a]
$NiL_4(BF_4)_2$	214(46.7)vvs, 259(38.6)vvs,b, 433(23.0)s,sh, 510(19.6)m,sh, 690(14.5)mw, 755(13.2)mw,sh, 1120(8.2)wvw,b	3793	3.05	194[a]
$NiLF(BF_4)\cdot C_2H_5OH$	218(45.9)vvs, 225(44.4)vvs,sh, 256(39.1)vs,vb, 267(37.5)vs,sh, 357(28.0)m,sh, 409(24.4)m, 695(14.4)w,sh, 740(13.5)w, 1220(8.2)wvw,b	4662	3.36	33[a]
$CuL_4(BF_4)_2$	216(46.3)s,sh, 231(43.3)s,sh, 268(37.3)vs, 286(35.0)vs,sh, 382(26.2)vs,b, 647(15.5)s,vb	1655	2.00	197
$ZnL_4(BF_4)_2$	214(46.7)vs, 222(45.0)vs,sh, 261(38.3)vs,sh, 284(35.2)s,sh	Diamagnetic		190
$CdL_4(BF_4)_2$	222(45.0)vvs,b, 229(43.7)vvs,sh, 254(39.4)vs,sh, 299(33.4)s,sh	Diamagnetic		178

[a] Calculated by assuming that these compounds are binuclear, as proposed. [b] Insufficiently soluble in polar organic solvents.

attributable to ν_{M-F} (tetrafluoroborato) modes could be distinguished with reasonable certainty; most probably the weak absorptions corresponding to this vibrational mode are masked by the rich spectrum of the ligand at 450–240 cm^{-1} (Table II), in the spectra of the new complexes involving coordinated $-FBF_3$ or $=F_2BF_2$ ligands. Regarding the ν_{M-F} band assignments, it should be noted that for M = Mn, Ni they must be considered as very tentative, at best [38].

Molar Conductivities and Magnetic Susceptibilities

The conductance data (Table III) for $Cr(N\text{-}lutO)_6(BF_4)_3$, $M(N\text{-}lutO)_4(BF_4)_2$ (M = Fe, Ni, Cu, Zn, Cd) and $Co(N\text{-}lutO)_3F(BF_4)$ are in agreement with the IR evidence, *i.e.*, in favor of the exclusive presence of ionic BF_4^-. Thus, the Cr^{3+} complex behaves as a 1:3 electrolyte, the above $M(BF_4)_2$ complexes as 1:2 (or 2:4) electrolytes and the $CoF(BF_4)$ complex as a 2:2 electrolyte [48]. $Co(N\text{-}lutO)_4(BF_4)_2 \cdot H_2O$ shows a slightly low Λ_M value for a 1:1 electrolyte (47 Ω^{-1} cm^2 mol^{-1}); it is, nevertheless, quite clear that one of the BF_4 groups is ionic, as suggested by the IR evidence, and the relatively low Λ_M may be due to partial displacement of N-lutO ligands in solution by BF_4 groups that are ionic in the solid state [49]. Finally, the two complexes appearing to contain exclusively coordinated bidentate tetrafluoroborato ligands ($Mn(N\text{-}lutO)F(BF_4) \cdot CH_3OH$ and $Ni(N\text{-}lutO)F(BF_4) \cdot C_2H_5OH$) show Λ_M values intermediate between those corresponding to 2:2 and 'non'-electrolytes [48]. These data indicate that BF_4 is indeed coordinated in the preceding two solid complexes, and that partial dissociation of these compounds occurs in solution [2, 9].

With two exceptions ($Fe(N\text{-}lutO)_4(BF_4)_2$ and $Mn(N\text{-}lutO)F(BF_4) \cdot 4MnF_2$), the new metal complexes exhibit normal ambient temperature magnetic moments (Table III) for high-spin $3d^3$ and $3d^5$–$3d^8$ compounds or the $3d^9$ configuration [50]. The magnetic moments of the two Co^{2+} complexes are within the range of values predicted and observed for pentacoordinated cobaltous compounds [51]. The moment of the pentacoordinated $Ni(N\text{-}lutO_4)(BF_4)_2$ complex is also within the range of values observed for $Ni(ClO_4)_2$ analogs with N-lutO (2.83 μB) [52] and 2-picoline N-oxide (N-picO) (3.16 μB) [49], whereas that of the hexacoordinated $Ni(N\text{-}lutO)F(BF_4) \cdot C_2H_5OH$ compound (3.35 μB) is slightly higher than the upper limit of the 'octahedral' region for Ni^{2+} (2.83–3.30 μB); several hexacoordinated Ni^{2+} complexes with aromatic amine N-oxides show μ_{eff} values slightly exceeding 3.30 μB [53]. The Fe^{2+} complex is characterized by a μ_{eff} (3.55 μB) suggestive of a S = 1 spin configuration (half-quenched spin), as was also the case with the $Fe(ClO_4)_2$ analog [2]. As regards $Mn(N\text{-}lutO)F(BF_4) \cdot 4MnF_2$, the low room temperature μ_{eff} observed (5.31 μB) was not unexpected, since MnF_2, which has a rutile-type structure [54], is reportedly antiferromagnetic and exhibits a μ_{eff} of 5.10 μB at 300 K [55]. The new product is probably a mixture of Mn^{2+} salt(s) and a N-lutO complex (*i.e.*, MnF_2 and $Mn(N\text{-}lutO)F(BF_4)$ or $MnF_2\text{-}MnF(BF_4)$ and $Mn(N\text{-}lutO)F_2$); N-lutO is apparently coordinated to hexacoordinated Mn^{2+} ions, as suggested by the occurrence of ν_{Mn-O} at 322 cm^{-1} [43, 44].

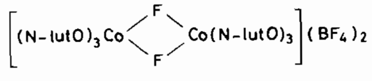
Electronic Spectra

The UV spectrum of the ligand shows the usual shifts of the main $\pi \rightarrow \pi^*$ transition band (275 nm) [56] to higher energies upon metal complex formation (Table III) [45]. The $n \rightarrow \pi^*$ transition band of N-lutO (319 nm) is not observed in the spectra of the metal complexes, as is commonly the case with aromatic amine N-oxide metal complexes [45, 57, 58]. The spectra of the paramagnetic metal complexes are characterized by strong metal-to-ligand charge-transfer bands, originating in the UV and trailing off into the visible, as expected [58]. The d–d transition spectra of the Cr^{3+} and the $Ni(N\text{-}lutO)F(BF_4) \cdot C_2H_5OH$ complexes are compatible with low-symmetry hexacoordinated configurations [53]; band assignments, nm: Cr^{3+}: $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ 397; $\rightarrow {}^4T_{2g}(F)$ 600; Ni^{2+}: $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ 459; $\rightarrow {}^3T_{1g}(F)$ 695, 740; $\rightarrow {}^3T_{2g}(F)$ 1220. Approximate Dq values: Cr^{3+} 1667 cm^{-1}; Ni^{2+} 820 cm^{-1}. With respect to the Dq value of N-lutO towards octahedral Cr^{3+}, it should be noted that these laboratories have previously calculated it to be 1686 cm^{-1} from the spectrum of $[Cr(N\text{-}lutO)_6](ClO_4)_3$ [2], while Nathan reports a Dq of 1570 cm^{-1} for the same cationic complex [59]; in addition, Schmauss and Specker [52] observed the $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ transition at 595 nm (corresponding to a Dq of 1680 cm^{-1}) in the spectrum of a product which was presumably [16] a mixture of $[Cr(N\text{-}lutO)_6](ClO_4)_3$ with $[(N\text{-}lutO)_2H](ClO_4)$. The calculation of Dq at 1667 cm^{-1} for the new $Cr(BF_4)_3$ complex seems to settle the uncertainty created by the preceding conflicting results; hence, N-lutO (Dq = 1667–1686 cm^{-1}) functions as a significantly stronger ligand than other aromatic amine N-oxides (*e.g.*, pyridine N-oxide; Dq = 1587 [12] or 1539 [60] cm^{-1}; quinoline N-oxide; Dq = 1610 cm^{-1} [61]) in its $[CrL_6]^{3+}$ cationic complex. The unusually high Dq value observed for $[Cr(N\text{-}lutO)_6]^{3+}$ compounds may be very well due to the significantly lower symmetry imposed by the accommodation of six sterically hindered N-lutO ligands about the Cr^{3+} ion, relative to the symmetries of $[CrL_6]^{3+}$ cationic complexes with non-sterically hindered aromatic amine N-oxides [38].

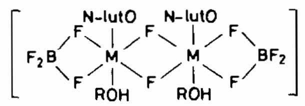
The d–d transition spectra of the two new Co^{2+} complexes are typical for pentacoordinated complexes of this metal ion with aromatic amine N-oxides, showing characteristic absorption maxima at 750–815 and 1850–1900 nm [5, 53, 62], as previously discussed [25]. $Ni(N\text{-}lutO)_4(BF_4)_2$ shows a spectrum very similar to that of the light green paramagnetic $Ni(ClO_4)_2$ analog, which shows maxima at 433, 513, 769 and 1111 nm [3]. These spectra, although not ruling out hexacoordinated configurations for Ni^{2+}, are compatible with coordination number five [63], which is also favored by the ν_{Ni-O} band assignment [3]. Finally, the new Fe^{2+} and Cu^{2+} complexes show very similar d–d transition maxima to those reported for the corresponding $[M(N\text{-}lutO)_4](ClO_4)_2$ complexes, which are square-planar (*i.e.*, Fe^{2+} perchlorate complex 962 nm, and Cu^{2+} perchlorate complex 644 nm) [2].

Conclusion

The present study establishes that adducts of N-lutO with transition metal tetrafluoroborates can be isolated in all but one ($M = Mn^{2+}$) of the cases investigated, if the appropriate synthetic conditions are developed. On the other hand, the steric features of N-lutO make also possible the occurrence of reactions of type (1), again under appropriate conditions of interaction of ligand and salt. $Co(N\text{-}lutO)_3F(BF_4)$ has a stoichiometry similar to that of several well characterized complexes, prepared by reaction of sterically hindered amines (3,5-dimethylpyrazole and substituted derivatives) with $Co(BF_4)_2$; these complexes involve binuclear, fluoro-bridged, pentacoordinated cationic species, with three terminal amine ligands per Co^{2+} ion [23]. A similar structure(II) seems most likely for the new $CoF(BF_4)$ complex. The $MF(BF_4)$ (M = Mn, Ni) complexes involve two neutral ligands per metal ion (one N-lutO and one alcohol ligand), and they are most probably dimers of type (III) ($R = CH_3$ for M = Mn; $R = C_2H_5$ for M = Ni) with $M\text{–}F_2\text{–}M$ bridges and bidentate chelating $=F_2BF_2$ ligands. A pentacoordinated structure of the $[M(N\text{-}lutO)(ROH)F(F_2BF_2)]$ (M = Mn, Ni) type for these complexes would be incompatible with the far-ir evidence, which is clearly in favor of coordination number six. It is worth noticing at this point that, in order to further substantiate the proposed structural types (II) and (III), studies of magnetic susceptibility variation with temperature would be very helpful [20–23, 38]; similar studies would be required for the apparently N-lutO-bridged $Ni(N\text{-}lutO)_4(BF_4)_2$ complex (*vide infra*). We plan to initiate work in this direction in the near future. In the case of isolation of $Mn(N\text{-}lutO)F(BF_4)\cdot 4MnF_2$, it is remarkable that the reaction of $Mn(BF_4)_2$ with N-lutO, under the conditions of synthetic procedure A, resulted in 80% conversion of the metal tetrafluoroborate to the corresponding difluoride. It is also somewhat surprising that the final product contains only one N-lutO ligand for every five Mn^{2+} ions present. The corresponding reactions of $M(BF_4)_2$ (M = Mn, Co, Ni, Cu, Zn or Cd) with amines reportedly lead to stoichiometric 1:1 (L = triethylenediamine, quinuclidine) [17], 2:1 (L = 3,5-dimethylpyrazole) [18] or even 4:1 (L = 3-hydroxypyridine) [19] adducts of ligand and MF_2. It appears that the initially formed adduct of N-lutO with MnF_2 is dissociated under our synthetic conditions.

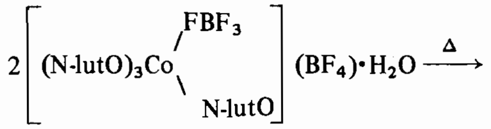


(II)



(III)

As far as the mechanism by which reaction (1) proceeds is concerned, it seems most likely that a prerequisite for its occurrence is the formation of an adduct involving coordinated BF_4 ligands, as an intermediate. This is obvious in the case of $Co(BF_4)_2$, which forms $[Co(N\text{-}lutO)_4(FBF_3)](BF_4)\cdot H_2O$ initially. When this adduct is allowed to remain in the mother liquor and heated to 70–80 °C, one of the N-lutO ligands reacts with the coordinated FBF_3 group, yielding the fluoro-bridged dimer (II), the 1:1 adduct of BF_3 with N-lutO and water [25]:



$$2\left[(N\text{-}lutO)_3Co\begin{matrix}\diagup FBF_3\\ \diagdown N\text{-}lutO\end{matrix}\right](BF_4)\cdot H_2O \xrightarrow{\Delta}$$

$$(II) + 2BF_3\cdot N\text{-}lutO + 2H_2O \quad (2)$$

With $Mn(BF_4)_2$ no adducts with N-lutO were isolated; however, it is likely that $[Mn(N\text{-}lutO)_4(FBF_3)](BF_4)$ is formed initially, especially since the corresponding perchlorate complex is of the $[Mn(N\text{-}lutO)_4(OClO_3)](ClO_4)$ type [2, 3]. On the other hand, $Ni(lutO)_4(BF_4)_2$, which does not show any evidence favoring the presence of coordinated tetrafluoroborate, was found to remain unchanged if heated in the mother liquor of its precipitation at 70–80 °C; the same behavior is observed with the rest of the adducts obtained by synthetic procedure A ($M = Cr^{3+}$, Cu^{2+}, Zn^{2+}, Cd^{2+}). The preceding implies that, during interaction of $Ni(BF_4)_2$ with N-lutO in ethanol solution, containing the stoichiometrically required amount of teof for dehydration, a different adduct, presumably comprising N-lutO, ethanol and tetrafluoroborato ligands, is formed initially, and then decomposed by a reaction similar to (2).

The complexes formed by addition of N-lutO to $M(BF_4)_n$ appear to be, in most cases, similar to the corresponding metal perchlorate complexes [2, 3, 5, 52], *i.e.*, $[Cr(N\text{-}lutO)_6](BF_4)_3$, $[M(N\text{-}lutO)_4](BF_4)_2$ (M = Fe, Cu, Zn, Cd) and $[(N\text{-}lutO)_3Ni(N\text{-}lutO)_2Ni(N\text{-}lutO)_3](BF_4)_4$. For the pentacoordinated Ni^{2+} complex, a dimeric N-lutO-bridged structure, similar to that proposed for the corresponding $Ni(ClO_4)_2$ complexes with N-lutO [2, 3, 5] and N-picO [49], is considered as most probable. $M–L_2–M$ bridging of this type is very common for Cu^{2+} complexes with aromatic amine N-oxides [64], and occasionally also occurs in complexes of other 3d metal ions, including Ni^{2+}, with N- [2, 3, 5, 65], P- (66, 67] or As- [68, 69] oxide ligands. $[Cu(N\text{-}lutO)_4](BF_4)_2$ is presumably square-planar, as is the case with all known $[CuL_4]X_2$ (X = ClO_4 or BF_4) complexes with aromatic amine N-oxides [2, 3, 5, 10–12, 53, 70], while $[Cr(N\text{-}lutO)_6](BF_4)_3$ is low-symmetry hexacoordinated [2, 3, 10–12, 53, 61, 71] and $[M(N\text{-}lutO)_4](BF_4)_2$ (M = Zn, Cd) are most probably tetrahedral [2, 3, 72]. For $[Fe(N\text{-}lutO)_4](BF_4)_2$, which is partially spin-paired (S = 1), as was also the case with the $Fe(ClO_4)_2$ analog [2, 3], a square-planar configuration is most likely. In fact, the presence of a d–d transition maximum at 975 nm rules out the possibility of a tetrahedral structure [73], while the position of $\nu_{Fe–O}$ favors coordination number four. Furthermore, it appears that the S = 1 spin configuration for Fe^{2+} is common in square-planar compounds [2, 3, 74, 75]. The only adduct differing from its metal perchlorate analog is $[Co(N\text{-}lutO)_4(FBF_3)](BF_4)\cdot H_2O$. The high-spin 4:1 N-lutO complex with $Co(ClO_4)_2$ is obviously not pentacoordinated, as demonstrated by its d–d transition spectrum, and has been considered as square-planar of the type $[Co(N\text{-}lutO)_4](ClO_4)_2$ (since it shows the $\nu_{Co–O}$ mode at 416 cm^{-1}) by these laboratories [2, 3, 5], whereas Herlocker proposed that it is octahedral, involving weakly coordinated perchlorate [4]. Other $Co(ClO_4)_2$ complexes with N-lutO, formed in the solid-state or in solution, are $[Co(N\text{-}lutO)_3(O_2ClO_2)](ClO_4)$ and $[Co(N\text{-}lutO)_5](ClO_4)_2$ [4–6]; both these compounds are pentacoordinated, exhibiting d–d transition spectra very similar to that of the new $Co(BF_4)_2$ complex; moreover, the IR spectrum of the 3:1 complex of $Co(ClO_4)_2$ shows clearcut evidence in favor of the presence of coordinated perchlorate [5]. A likely interpretation of the structural differences between the 4:1 adducts of N-lutO with $Co(ClO_4)_2$ and $Co(BF_4)_2$ is that the arrangement of the ligands in $[Co(N\text{-}lutO)_4]^{2+}$ may provide sufficient steric hindrance as to impede the coordination of a $–OClO_3$ group, but can allow the accommodation of a smaller anionic ligand, such as $–FBF_3$, in the first coordination sphere of the Co^{2+} ion. The importance of the size of the anionic groups is also manifested by the fact that, while the diamagnetic, monomeric, violet form of $Ni(N\text{-}lutO)_4(ClO_4)_2$ is stable for a long period of time (one year in the atmosphere and considerably longer *in vacuo*), the corresponding monomeric violet $Ni(BF_4)_2$ complex is converted completely to the paramagnetic light green dimer within a few hours (*vide supra*). The perchlorate anions, although not coordinated to Ni^{2+}, apparently shield this ion effectively from the approach of N-lutO ligands of a neighboring square-planar $[Ni(N\text{-}lutO)_4]^{2+}$ species, and the dimerization of the complex proceeds very slowly. The smaller tetrafluoroborate ions do not seem to exert a similar shielding effect, and the dimerization of the $Ni(BF_4)_2$ complex is quite rapid [5].

A final point that should be made is that, owing to the fact that all the synthetic work herein reported was carried out in the atmosphere, we have not been able to isolate and identify the $BF_3(N\text{-}lutO)$ by-product, when reactions of type (1) were occurring (*i.e.*, M = Mn, Co or Ni). This is probably due to the fact that BF_3 adducts with aromatic amine N-oxides are air-sensitive [76]. We plan to repeat these reactions under inert conditions in the future, in an attempt at isolating and identifying the above by-product.

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