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Conversion of $Co(BF_4)_2$ to $CoF(BF_4)$ in the Presence of 2,6-Lutidine N-Oxide

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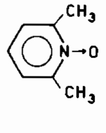
Divalent 3d metal tetrafluoroborates have been found to yield complexes of the corresponding MF_2 or $MF(BF_4)$ salts, upon interaction with several nitrogen ligands [1–6] (*e.g.*, triethylenediamine, quinuclidine [1], 3,5-dimethylpyrazole [2, 4, 5] and alkylated derivatives [6], 3-hydroxypyridine [3]). The by-product of these reactions is the BF_3 adduct of the ligand (L), *viz.*:

$$M(BF_4)_2 + xL \rightarrow MF_2L_{x-2} + 2BF_3{\cdot}L \text{ or } MF(BF_4)L_{x-1} + BF_3{\cdot}L \qquad (1)$$

Reaction 1 appears to be especially facile in the presence of ligands containing bulky substituents near the donor site [1, 2, 6].

In the case of interaction with aromatic amine N-oxides, 3d metal(II) tetrafluoroborates usually form $ML_n(BF_4)_2$ complexes (*e.g.*, L = pyridine N-oxide) [7, 8]. However, the sterically hindered 2,6-lutidine N-oxide (N-lutO; I) can reportedly undergo an unusual reaction in the presence of $M(BF_4)_m$ (m = 2 or 3), yielding mainly the HBF_4 salt, *i.e.*, $(N\text{-lutO-H-N-lutO})^+(BF_4)^-$, contaminated with small amounts of the $M(BF_4)_m$–N-lutO complex [6, 9]. Under different synthetic conditions, $M(BF_4)_m$–N-lutO complexes may be obtained, as indicated by Reedijk [9], and later reported by these laboratories [10].



During our recent studies [10], we found that interaction of N-lutO with divalent 3d metal tetrafluoroborates at elevated temperatures may lead to the formation of $MF(BF_4)$ complexes [11]. The present letter deals with the preparation and characterization of $Co(BF_4)_2(N\text{-lutO})_4{\cdot}H_2O$ and $CoF(BF_4)(N\text{-lutO})_3$ complexes.

By employing the synthetic procedure used for 3d metal perchlorate complexes with N-lutO [12], we have been able to isolate the complex $Co(BF_4)_2(N\text{-lutO})_4{\cdot}H_2O$. The preparation involved treatment (in a dry-box; N_2 atmosphere) of the hydrated Co^{2+} salt with triethyl orthoformate, a dehydrating agent [13], containing a few drops of acetone (for complete dissolution of the salt), at 50–60 °C, under stirring for 1 hr, and subsequent addition of the ligand (6 mol N-lutO per mol Co^{2+} salt) into the stirred solution. Precipitation of the blue–purple $Co(BF_4)_2(N\text{-lutO})_4{\cdot}H_2O$ (analysis: found(calc.)%: C 44.57(45.25); H 5.35 (5.15); N 7.72 (7.54); B 2.73 (2.91); F 20.33 (20.45); Co 8.17 (7.93)) was immediate. This complex was filtered, washed with triethyl orthoformate and stored in an evacuated desiccator over P_2O_5. During an identical experiment, the preceding complex was allowed to remain suspended in the mother liquor, and this suspension was heated to 70–80 °C; under these conditions the blue–purple solid was replaced, within a few minutes, by a brown solid, analyzing as $CoBF_5(N\text{-lutO})_3$ (found(calc.)%: C 47.51 (47.22); H 4.80 (5.09); N 7.63 (7.86); B 2.12 (2.02); F 18.24 (17.78); Co 10.56 (11.03)), which was filtered, washed and dried in the same manner as above. Characterization of the new complexes was based on ir and electronic spectral, magnetic susceptibility and conductance measurements, obtained by methods described elsewhere [12].

Table I shows pertinent characterization data for the two complexes. The UV spectrum of the ligand [14] undergoes the expected shifts of the $\pi \rightarrow \pi^*$ transition (275 nm band) to higher energies, upon complexation [15]. The d–d transition spectra of the two complexes exhibit similarities, and are compatible with pentacoordinated configurations, favored by the presence of absorption bands at 750–815 and 1850–1900 nm [16, 17]. The ir spectra of the new complexes show the anticipated negative ν_{N-O} frequency shifts [7]. The brown $CoF(BF_4)$ complex exhibits single ν_3 and $\nu_4(BF_4)$ bands and a weak absorption in the ν_1 region and apparently involves ionic BF_4^- [18, 19]. Whereas, the blue–purple $Co(BF_4)_2$ complex shows split ν_3 and ν_4 and clearly ir-active ν_1 and $\nu_2(BF_4)$ bands, suggestive of the presence of both coordinated and ionic BF_4 groups [18, 19]. Tentative ν_{Co-O} band assignments are compatible with coordination number five for both complexes [12]. The brown complex exhibits also a band at 420 cm^{-1}, which is assigned as the ν_{Co-F} (fluoro) mode [2, 3, 6, 20]. No band attributable to $\nu_{Co-F}(BF_4)$ was observed in the spectrum of the blue–purple complex; perhaps, the weak absorption corresponding to this vibrational mode is masked by ligand bands (free N-lutO shows the following maxima at 550–200 cm^{-1}: 550m–s, 538w, 469m, 449m, 336m,b, 280m, 243m)

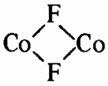
TABLE I. Spectral, Magnetic (304 °K) and Conductance (10^{-3} *M* CH_3NO_2 solutions, 25 °C) Data[a]

	$CoF(BF_4)(N\text{-}lutO)_3$	$Co(BF_4)_2(N\text{-}lutO)_4 \cdot H_2O$
Electronic spectra (Nujol mulls), λ_{max}, nm:	221vs,sh, 268vvs,vb, 294vs,sh 365s,sh, 403s, 512m,sh, 535m,sh 751m–w, 780m–w, 1160m–w, 1300m–w,b 1850w,sh	216vs, 223vs, 264vvs,sh, 272vvs, 354s, 510m,sh, 555m,b, 770m–w,sh, 815m–w,b, 1140w, 1900w–m
Infrared spectra, cm^{-1}		
ν_{OH}		3650–3200m,vvb
ν_{N-O}	1205s	1209s
BF_4 modes ν_3	1052vs,b	1110vs, 1055vs,b, 1029vs
ν_1	770w,sh	760m–s
ν_4	528m	537m, 521m
ν_2	–	356m,sh
ν_{Co-O}	379s	393s, 384s
ν_{Co-F}(fluoro)	420m–s,b	–
μ_{eff}, μB:	4.46	4.47
Λ_M, Ω^{-1} cm^2 mol^{-1}:	63	47

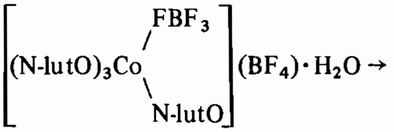
Abbreviations: s, strong; m, medium; w, weak v, very; b, broad; sh, shoulder.

[a] N-lutO exhibits the ν_{N-O} mode at 1245(vs) cm^{-1} (neat or Nujol mull); its electronic spectrum (Nujol mull) is as follows (nm): 219s,sh, 275vs,b, 297vs,b, 319s–vs,sh.

[12, 15]. Regarding the water in the $Co(BF_4)_2$ complex, a very broad continuous absorption in the ν_{OH} region (3650–3200 cm^{-1}) suggests that lattice rather than coordinated H_2O is present [21]. Both new complexes behave as 1:1 electrolytes in nitromethane [22], in agreement with the ir evidence (*i.e.* one ionic BF_4 group per Co^{2+} ion). The magnetic moments of the complexes are within the range of values (4.20–4.60 μB) predicted for pentacoordinated Co^{2+} compounds [23].

On the basis of the overall evidence, reasonable formulations for the new complexes are: blue–purple $[Co(N\text{-}lutO)_4(FBF_3)](BF_4)\cdot H_2O$; brown $[(N\text{-}lutO)_3CoF_2Co(N\text{-}lutO)_3](BF_4)_2$. The proposal of a dimeric structure, involving  $Co\overset{F}{\underset{F}{\diamond}}Co$ bridges for the $CoF(BF_4)$ complex, is in agreement with previous assignments for analogous complexes with N-ligands [3–6]. On the other hand the $Co(BF_4)_2$ complex is monomeric, cationic, characterized by a CoO_4F chromophore; a similar complex previously reported is $[Mn(N\text{-}lutO)_4(OClO_3)](ClO_4)$ [12].

An interesting aspect of this work is the fact that, in addition to a $CoF(BF_4)$ complex, the normal adduct of $Co(BF_4)_2$ with N-lutO, an intermediate of reaction 1, can be obtained. Comparison of the structural types of the two new complexes suggests that the elimination of the $BF_3(N\text{-}lutO)$ adduct proceeds by interaction between coordinated tetrafluoroborato and N-lutO ligands. In fact, the brown complex presumably results by elimination of one N-lutO and the BF_3 moiety of the tetrafluoroborato ligand from the blue–purple complex, *viz.*:

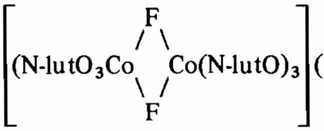


$$\left[(N\text{-}lutO)_3Co\begin{matrix}/FBF_3\\ \backslash N\text{-}lutO\end{matrix}\right](BF_4)\cdot H_2O \rightarrow$$

$$[(N\text{-}lutO)_3CoF](BF_4) + BF_3(N\text{-}lutO) + H_2O \qquad (2)$$

The fluoro-bridged binuclear cationic species is then formed by combination of two coordinatively unsaturated $[(N\text{-}lutO)_3CoF]^+$ complex cations, *i.e.*,

$$2[(N\text{-}lutO)_3CoF](BF_4) \rightarrow$$



$$\left[(N\text{-}lutO_3Co\overset{F}{\underset{F}{\diamond}}Co(N\text{-}lutO)_3\right](BF_4)_2 \qquad (3)$$

Further work aimed at the isolation of N-lutO complexes with MF_2 or $MF(BF_4)$ salts, and a better understanding of the mechanism of reaction 1, as well as the steric features of the ligands favoring these reactions, is currently in progress.

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11 Prof. J. Reedijk indicated during discussions with one of us (NMK) that he has also observed reactions of this type between N-lutO and $M(BF_4)_2$.

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