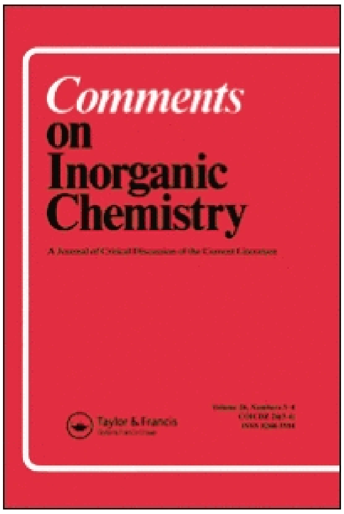

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Formation of Fluoride-Containing Coordination Compounds by Decomposition of Transition-Metal Tetrafluoroborates

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Formation of Fluoride-Containing Coordination Compounds by Decomposition of Transition-Metal Tetrafluoroborates

Transition-metal tetrafluoroborates are useful starting materials for the synthesis of fluoride-containing coordination compounds. In the presence of certain ligands first-row transition metals yield compounds of stoichiometry ML_4F_2 (monomers), M_2F_2 (ligand)$_n$ (anion)$_2$ (dimers), M_4F_4 (ligand)$_{12}$ (anion)$_4$ (tetramers), M_2F_3 (ligand)$_m$ (anion) (polymers), and MF_2 (ligand)$_2$ (polymers), depending upon the metal used, the particular ligand, and the solvent system.

INTRODUCTION

In coordination chemistry large counterions, such as ClO_4^-, PF_6^-, BF_4^- and $B(C_6H_5)_4^-$, are frequently used to stabilize large, complex cations.[1-3] As a result, species containing the maximum number of ligands per metal ion can often be obtained. Examples of such compounds are $[Ni(CH_3CN)_6](ClO_4)_2$, $[Cu(C_6H_5NO)_6](BF_4)_2$ and $[Co(hmpa)_4]$ $[B(C_6H_5)_4]_2$: (hmpa = hexamethylphosphortriamide). For the preparation of coordination compounds with PF_6^- or $B(C_6H_5)_4^-$, these anions have to be added as their alkali metal salts, because transition-metal salts of these anions are not stable, not even as their hydrates or alcoholates. Using ClO_4^- or BF_4^- has the advantage that transition-metal hydrates of these anions are easily prepared and are quite stable. Therefore, the number of transition-metal compounds containing these anions is great. However, the use of the perchlorate salts has a serious disadvantage, related

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to the thermal instability of certain perchlorate salts. This has occasionally resulted in heavy explosions,[4–6] especially with ligands unable to form hydrogen bonds towards the oxygen atoms, or with ligands that easily form radical species. The tetrafluoroborate anion seemed to be an almost ideal counterion for many coordination compounds, both in aqueous and nonaqueous solution. During the last five years, however, there have been a number of reports showing that the BF_4^- ion is not that stable, and that reaction with the ligand and the metal ion may occur, usually resulting in fluoride-containing compounds. The present Comment describes the known decomposition reactions and discusses how such reactions can be used in the preparation of new, otherwise inaccessible metal–fluoride compounds.

DECOMPOSITION OF TETRAFLUOROBORATES

It has been known for some time that heating of hydrated metal (II) tetrafluoroborates may result in metal (II) fluorides. Musgrave and Lin[7] were the first to observe that such a decomposition could be induced by the addition of certain ligands, resulting in a decomposition at room temperature. The reaction studied by these authors was

$$M(H_2O)_6(BF_4)_2 + qn \rightarrow MF_2 + BF_3(qn). \qquad (1)$$

In these reactions M = Co(II), Ni(II) and qn = quinuclidine. Unfortunately, ligands were not coordinated to the MF_2 salts and the system was not studied further.

Using the ligand 3,5-dimethylpyrazole, Guichelaar *et al.*[8] were able to isolate compounds of formula $MF_2(L)_2$ (L = 3,5-dimethylpyrazole), for which a difluoro-bridged linear chain structure was proposed based on the magnetic properties and the analogous chloride compounds. A subsequent investigation of this system, using variations of solvent and temperature, showed that this decomposition reaction takes place in two steps:[9–11]

$$M(H_2O)_6(BF_4)_2 + nL \xrightarrow{\text{solvent}} MF(L)_3(BF_4) + BF_3(L); \qquad (2)$$

$$MF(L)_3(BF_4) \xrightarrow{\text{solvent}} MF_2(L)_2 + BF_3(L). \qquad (3)$$

The products of the first step [Eq. (2)] were isolated as solid compounds for several pyrazole ligands[10] and were characterized spectroscopically and magnetically. A subsequent x-ray crystal structure determination for M = Co(II)[10] and Cu(II)[12] indicated that these compounds are dimeric with a structure $(L)_3MF_2M(L)_3(BF_4)_2$ (see Figure 1).

In the meantime some other workers have also shown that fluoride-containing products can be obtained from a variety of metals and ligands. These results will be briefly summarized. Smit and Groeneveld have reported[13] that compounds with formula $M(pyoH)_4F_2$ (M = Co,Ni; pyoH = 3-hydroxypyridine) readily form from the metal(II) tetrafluoroborates and 3-hydroxypyridine in ethanol solution. Uchida and co-workers[14] found a coordinated fluoride ion in $Mo(N_2H_2)(dppe)_2F(BF_4)$ when aqueous HBF_4 was reacted with $Mo(N_2)_2(dppe)_2$. Enemark *et al.*[15] similarly found $Mo(CO)_2(dppe)F(PF_6)$ (dppe = diphenylphosphine ethylene). Carroll *et al.*[16] reported that when $IrH(CO)(PPh_3)_3$ was reacted with phenyldiazonium tetrafluoroborate, a product characterized as $Ir(NH\text{-}NC_6H_4)F(CO)(PPh_3)_2(BF_4)$ precipitated. With 2,6-dimethylpyridine-*N*-oxide as a ligand, transition-metal tetrafluoroborates were found to yield compounds such as $CoF(L)_3(BF_4)$, but the structures of the products could not be determined.[17,18] With the ligand $N(CH_2\text{-}3,5\text{-dimethylpyrazole})_3$, Mani *et al.*[19] obtained a proposed dimeric product analyzing as $Ni(L)F(BPh_4)\cdot$acetone. These authors[20] found that when Cr(II) is reacted with 3(5)-methylpyra-

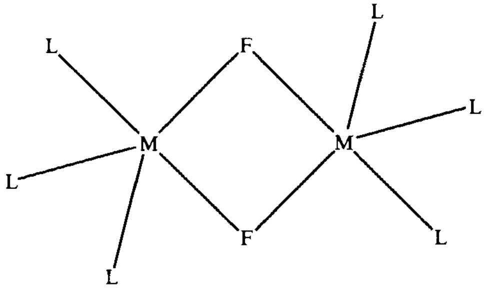

FIGURE 1 Schematic representation of the structure of the dimeric species $M_2F_2(L)_6^{2+}$. M = Co(II) and Cu(II). M–M distances are 3.09 Å [Co(II) and L = DMPz][10] and 3.14 Å [Cu(II) and L = DMPz/5MPz].[12] The coordination geometry is trigonal bipyramidal (Co) or square pyramidal (Cu).

zole in the presence of BF_4^-, a Cr(III) product is formed, which was found to be *trans*-$CrF_2(L)_4$-(BF_4). These decompositions are in fact related to the thermal decomposition reaction found by Nuttall *et al.*[21] for $Cu(quin)_2(BF_4)_2$; heating this compound and the corresponding Co(II) and Ni(II) compounds (quin = quinoline) resulted in products analyzing as $M(quin)_2F(BF_4)$.

Our contributions to this research involved dimeric species of formula $[(LL)_2MF_2(LL)_2](BF_4)_2$, with LL = bis(3,5-dimethylpyrazolyl)methane,[22] tetrameric species of the cubane type with formula $[M_4F_4(L)_{12}](BF_4)_4$, (L = *N*-alkyl imidazoles, 5-methylpyrazole, *N*-vinylimidazole).[23,24] The syntheses of these and other new products will be described below.

NEWLY CHARACTERIZED PRODUCTS

As noted above, the decomposition of the tetrafluoroborate anion in the presence of suitable ligands and metal ions may lead to several new products. These products can at present be divided into monomeric species, dimeric species, cubane-type tetramers and polymeric compounds. The several types are summarized in Table I, together with some synthetic and structural information. The monomeric species are in fact the most simple ones, and several compounds of this type can also be prepared by simple metathesis reactions in aqueous solution. Reviews of this group of compounds are available.[25] Crystal structure determinations have clearly shown that hydrogen bonding between N-H groups of the ligands and the coordinated F^- ion are important in the stabilization of the structure of these compounds,[26] especially for the divalent metal ions. The relevance of hydrogen bonding in the formation and stabilization of the other compounds will be discussed below in further detail.

The structures of the compounds mentioned in Table I are all known from x-ray single-crystal studies and from isomorphism within a group, except for the monomeric species for which only spectral and magnetic information is available,[27] and the unusual type $M_2F_3(L)_6(BF_4)$, for which no structure has been proposed so far. From the synthetic methods mentioned in Table I, only method B (reaction of the metal tetrafluoroborates with the ligand under

TABLE I

New fluoro-bridged transition-metal coordination compounds, with BF_4^- as the source of F^-

Composition	Metal	Ligand	Structure	Synthesis	Reference
CuL_4F_2	Cu	IzH[a]	D_{4h} monomer	A[b]	27
$CuL_4F(BF_4)$	Cu	IzH	C_{4v} monomer	A	27
$CoL_3F(BF_4)$	Co	DMPz RPz	Co_2F_2 dimer	B	10
$CuL_3F(BF_4)$	Cu	DMPz TMPz	Cu_2F_2 dimer	C	28
$CuLL'_2F(BF_4)$	Cu	DMPz 5MPz(L')	Cu_2F_2 dimer	A	12
$M(L)_2F(BF_4)$	Mn,Fe,Co,Ni	BDPM	M_2F_2 dimer	B	22
$Cu(L)_2F(BF_4)$	Cu	BDPM	Cu_2F_2 dimer	C	28
$ML_3F(BF_4)$	Mn,Co,Cd	Etiz	M_4F_4 tetramer	B	23
$CoL_3F(BF_4)$	Co	Priz, viz	M_4F_4 tetramer	B	23,27
$ML_3F(BF_4)$	Mn,Co,Ni,Cd	5MPz	M_4F_4 tetramer	C	24
ML_2F_2	Mn,Co,Cd	DMPz	MF_2 chain	B	8
ML_2F_2	Ni,Cu	DMPz	MF_2 chain	C	27
$M_2F_3L_6(BF_4)$	Cu,Zn	DMPz TMPz	Unknown	C	27

[a] IzH = imidazole; DMPz = 3,5-dimethylpyrazole; RPz = 4-substituted 3,5-dimethylpyrazole; 5MPz = 5-methylpyrazole; BDPM = *bis*(3,5-dimethylpyrazolyl) methane; Etiz = *N*-ethylimidazole; Priz = *N*-propylimidazole; viz = *N*-vinylimidazole; TMPz = 3,4,5-trimethylpyrazole.

[b] Method A: Ligand exchange, starting from $Cu_2F_2(DMPz)_6(BF_4)_2$;
Method B: $M(BF_4)_2$ + ligand + solvent at room temperature;
Method C: $M(BF_4)_2$ + ligand + solvent at elevated temperatures (30–60°C).

ambient conditions) has been fully exploited. A slight increase of the temperature (method C) has allowed us to prepare many Cu(II) and Ni(II) compounds that could not be prepared otherwise. The most promising synthetic method, however, appears to be method A, in which a stable fluoro-bridged cluster is used as a starting product for other clusters with ligand exchange reactions.

The structure of the tetrameric species in Table I is schematically drawn in Figure 2. The structure of the linear-chain type compounds is depicted in Figure 3. This latter structure is quite general among transition-metal compounds of formula MX_2L_2 (X = Cl,Br).[29,30] As yet, no detailed study has been reported about the boron-containing decomposition products in these reactions. It is assumed that these retain in solution as adducts BF_3L or BF_3S (S = solvent). Very recently we have found crystallographic evi-

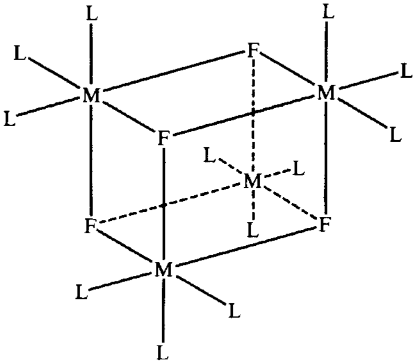

FIGURE 2 Schematic representation of the structure of the tetrameric species $M_4F_4(L)_{12}^{4+}$. The metals are Mn,Co,Ni,Cd [all M(II)]. The ligands are 5MPz, viz, Etiz, Priz (see Table I for abbreviations). The M–M distance has been determined to be 3.29 Å (M = Co, L = Etiz).

dence[31] that such products can indeed be formed. The counterion in the complex cation $Cu(EDTB)^{2+}$ appeared to be $BF_3(OC_2H_5)^-$ when $Cu(BF_4)_2$ was used as the starting salt and temperatures up to 30–50°C were used for recrystallization. In all other cases, the fluoride-containing products are the least soluble and precipitate, resulting in the compounds listed in Table I.

Apart from the fluoride- and the boron-containing products, one should also be aware of the formation of other compounds, as shown by the formation of $Co(viz)_4SiF_6$ when $Co(BF_4)_2$ is reacted with *N*-vinylimidazole (viz) in ethanol in glass equipment.[32] Apparently, the slowly released F^- ions can also react with silicon ions from glass. The driving force in this reaction is the insolubility of the SiF_6-containing product.

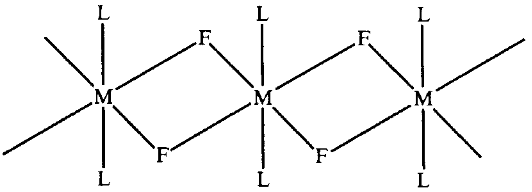

FIGURE 3 Schematic structure of the chain-type compounds with formula $MF_2(L)_2$. M = Mn,Ni,Cu,Cd(II). L = DMPz and 4-substituted derivatives.

INTERESTING PROPERTIES

The fluoride-containing coordination compounds of the types described above are of interest for spectroscopic and magnetic reasons. The spectroscopic interest in such compounds originates from the ionic character of the F^- ion. This ionic character and weak polarizability result in a tendency of the F^- ion to be surrounded by more than one acid group. Consequently, when a fluoride ion is coordinated monodentately to a divalent metal ion, the negative charge of the anion needs further compensation, which is found in hydrogen bonding with "acid" protons of the ligands. This hydrogen bonding is not only relatively strong (as is easily deduced from the IR spectra), but can also have unusual structures, such as the trifurcated structure[10] found in $Co_2F_2(DMPz)_6(BF_4)_2$ and the bifurcated structure in the corresponding copper compound.[12]

Infrared spectra of other monomeric and dimeric compounds show that several types of hydrogen bonding may occur.[10,24,27] When ligands without acidic protons are present, tetrameric structures of the type $M_4F_4L_{12}(BF_4)_4$ are formed, in which each F^- ion is bound to three metal ions. The magnetic interest in these compounds results from the presence of MF_2M groups (in dimers and chains) and M_4F_4 groups (in tetrameric clusters) through which metal-metal superexchange interactions occur. A systematic study[9,33] of such compounds (relation between structural parameters and magnetic exchange) may yield information about the details of the ferromagnetic and antiferromagnetic exchange interactions between transition-metal ions. The simple ligand F^- will also allow theoretical calculations of the magnetic exchange.

MECHANISM OF BF_4^- DECOMPOSITION

The decomposition products obtained so far from the several ligands and metal ions allow some speculation about the driving force for the BF_4^- decomposition reaction. When comparing the ligand systems that have been found to yield the decomposition products, it is observed that all ligands involved are heterocyclic ligands such as pyrazoles,[8,10–12,24] pyridines,[13,21] imidazoles,[23,27] pyridine-

N-oxides[17,18] or derivatives of these ligands,[19,22,27,28,31] except for the molybdenum and iridium compounds[14–16] mentioned above. It is further observed that all these heterocyclic ligands have bulky substituents near the donor site (except the *N*-alkylimidazoles). The decomposition products with *N*-alkylimidazoles, on the other hand, are only formed when an excess of the metal salt is used.[23] These observations point towards a possible intermediate in which the BF$_4^-$ ions are coordinated to the metal ion, and this intermediate may be the initiation of the decomposition. After its formation the species "M-F" may further react with the available ligands and metal ion and finally result in the precipitation of the monomeric, dimeric, tetrameric or polymeric products described above. Another factor contributing to the driving force of this reaction may be the stability of the adducts BF$_3$·L, although such adducts

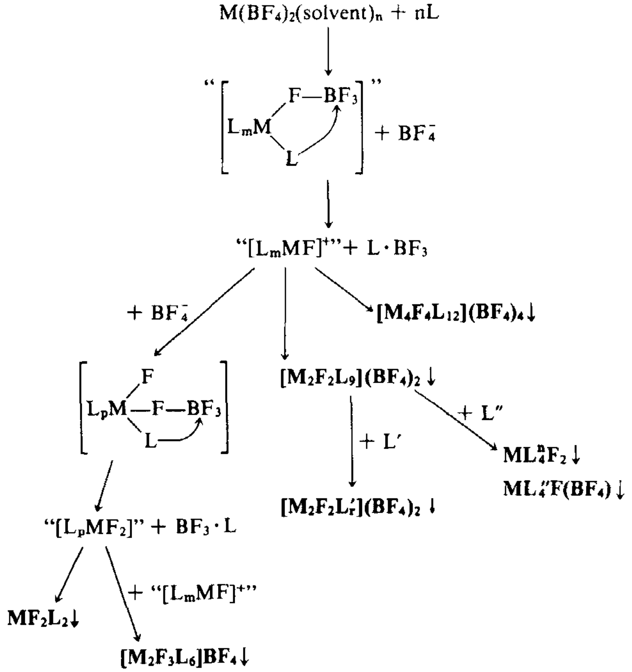

FIGURE 4 Observed reactions and proposed mechanism in the system M(II)-F-L-BF$_4$. The products between quotation marks are supposed intermediates. The isolated products are indicated by bold type. For ligands and coefficients, see Table I.

have not been isolated yet from the reaction mixtures. The only product found by x-ray structure analysis is the $BF_3(OC_2H_5)^-$ anion.[31] A scheme describing all the observed reactions is given in Figure 4.

FURTHER DEVELOPMENTS AND FURTHER APPLICATIONS

It will be clear from the results described above that many synthetic variations are open for further investigation. Simple heating of the solvent used up to now (mainly alcohols) has allowed the synthesis of the Ni(II) and the Cu(II) compounds,[24,28] at least for the pyrazole-type ligands. It is to be expected that the use of other solvents may stabilize other types of compounds and types different from the ones known so far are likely to be found. These other solvents may also allow the use of higher reaction temperatures, so that decomposition reactions may also be found with ligands that so far have not yielded fluoride-containing products.

The slow release of M-F species will allow special products to crystallize that otherwise would not have been formed from the insoluble anhydrous metal fluorides and the ligands.

A second important synthetic possibility comes from the use of ligand-exchange reactions, according to Reaction (4):

$$M_xF_y(L)_z(\text{anion})_p + L' \rightarrow M_xF_y(L')_q(\text{anion})_p. \quad (4)$$

This reaction has been shown to be possible, at least for Cu(II),[28] with several types of ligands. Even products containing mixed ligands have been found and crystallographically characterized.[12] Preliminary results also indicate that changes in the cluster M_xF_y may occur during these ligand-exchange reactions.[27] For M = Cu(II) this system is under investigation in our laboratory.[34]

CONCLUSIONS

1. Interesting new classes of fluoride-containing coordination compounds can be prepared via controlled decomposition reac-

tions of transition-metal tetrafluoroborates in the presence of certain organic ligands.

2. The structures of the resulting compounds are of great interest from the point of view of hydrogen bonding and magnetic exchange (especially dimers, clusters and chains).

3. Many new compounds can be expected upon extension of these investigations through solvent changes, temperature variation and ligand-exchange reactions.

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