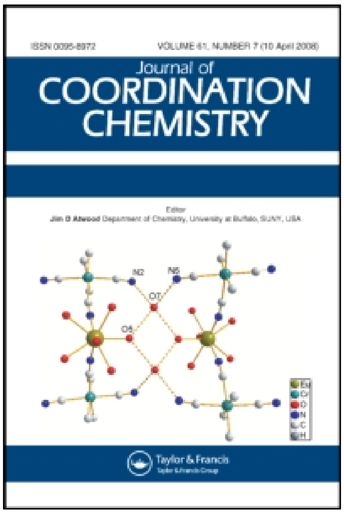

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SHORT COMMUNICATION

The Decomposition of Transition Metal Tetrafluoroborates by some strong Base Ligands

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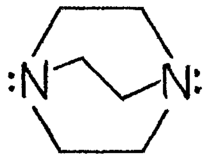
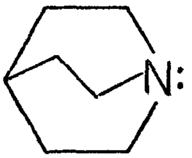
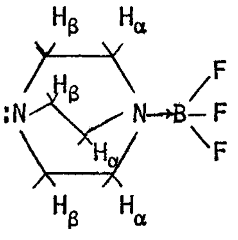
Some transition metal complexes of triethylenediamine (TED, I) and quinuclidine (Q, II) have been reported.[1-5] Recently we treated I and II with metal bistetrafluoroborates (M = Co^{2+}, Ni^{2+}, and Cu^{2+}) which have not been studied yet, and postulated that pure coordination complexes might be obtained. However, evidence for the existence of 1:1 adducts such as $C_6H_{12}N_2$:BF_3 (III) and $C_7H_{13}N$:BF_2 (IV) in treatment of I and II with metal bistetrafluoroborates has now been found. We wish to describe our results concerning formation of these two new 1:1 adducts in this letter.



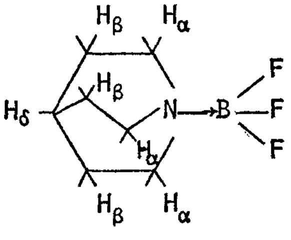
(I)



(II)



(III)



(IV)

The white 1:1 adducts were collected from the filtrate solutions obtained by refluxing hydrated metal bistetrafluoroborates and I and II respectively in the media of tetrahydrofuran dimethoxypropane azeotrope for 24 hours. They were washed with ether and dried in a vacuum desiccator over CaH_2 at room temperature. Analysis, chosen from the adduct of $Ni(BF_4)_2$ and I and II, for III, Calcd: F = 31.67, Found: F = 30.92; for IV, Calcd: F = 31.85, Found: F = 30.77. All six adducts made were identical as proved from infrared and NMR spectra. The spectra were identical with adducts which were obtained from reactions of BF_3 gas and each ligand in the THF-DMP azeotrope.

It is known that transition metal bistetrafluoroborates are easily decomposed with heat[6] or slowly at room temperature,[7] and also that TED and Q are strong bases, pK_a's = 8.60[8] and 10.65[8] respectively. The reaction which we have observed occurs during refluxing and tetrafluoroborate salts can be decomposed to form 1:1 adducts with these two ligands.

$$M(BF_4)_2 + 2\,L \xrightarrow{\Delta} MF_2 + 2\,L:BF_3$$

Here L = TED and Q.

The bis-adduct of III, $C_6H_{12}N_2:(BF_3)_2$, has not been found. The basicity of monoprotonated or monomethylated TED species (pK_a = 2.90–2.75) is dramatically lower than that of TED itself,[8] and the donation of electrons from the second nitrogen becomes weaker. By analogy, it seems that TED: BF_3 is the only product formed.

All the bands assigned in the infrared spectra of III and IV are identical to those obtained for the products of the reaction of BF_3 gas with the ligands. The characteristic absorption peaks[9] were shown in cm^{-1}:1110 (w, sh, BN str.), 1050 (s, br, CN str. + BF str.), 897 (w, sym BF str.) for III; and

1085 (w, sh, BN str.), 1053 (s, br, CN str. + BF str.), 890 (w, sym BF str.) for IV. Assignments for 1050 cm^{-1} and 1053 cm^{-1} are strong and broad in which skeletal C–N stretching of TED and Q are strongly overlapped by B–F absorption. There is an extra medium infrared absorption band at 800 cm^{-1} which is assigned as a vibration of the uncoordinated second nitrogen of TED in III. Most CH_2 bands in TED and Q are shifted to higher frequencies compared to the free ligands.

The found values of fluorine for III and IV analysis were markedly less than the calculated values, doubtless because of an impurity in the adducts. The impurity might be boric acid. The formation of boric acid could occur in the reaction solution.

$$M(BF_4)_2 \times H_2O \xrightarrow{\Delta} MF_2 + 2\,BF_3 + \times H_2O$$

$$4\,BF_3 + 3\,H_2O \longrightarrow HBF_4 + B(OH)_3{}^{12}$$

Both TED and Q are very hygroscopic so that they may yield some boric acids too as they react with BF_3 gas. The frequencies assigned for boric acid, OH stretching, BO stretching, BOH bonding, and BO_3 bending appear in the infrared spectra of III and IV, and are consistent with data from the literature.[13]

From the data presented here it seems clear that while attempting sytheses of transition metal complexes of TED and Q, the principal products were the 1:1 BF_3 adducts. Considering the increasing use of metal tetrafluoroborate salts for syntheses of coordination compounds we felt our findings should be made available to other investigators.

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