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Some results and problems in inorganic, especially fluorine, chemistry

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The author's research activities over the past 50 years, particularly in fluorine chemistry, are outlined. The account is divided into three parts: (i) results prior to and during fluorine research; (ii) results in fluorine chemistry; and (iii) results obtained subsequently.

1. Results prior to and during fluorine research

Research started in 1939 with comprehensive studies on oxides, hydroxides and oxide hydroxides. Of these, the most notable is the synthesis of γ -MnO₂ [1] for application in primary cells. Investigations of the higher Ni hydroxides followed later [2]. These compounds play an important role as positive electrodes in Ni/Cd accumulators. Gaseous hydroxides such as MO₂(OH)₂ (M=Cr, Mo, W) are interesting variants of these hydroxides [3].

The largest isopolymetallate ion [Mo₃₆O₁₁₂(H₂O)₁₆]⁸⁻ may be formed by acidifying solutions containing [MoO₄]²⁻ ions [4]. Spirals and threads of Si₃N₄, which are of high technical interest these days, were first prepared by us in 1962 [5]. A technical synthesis of CCl₄ from COCl₂ (2COCl₂ → CO₂ + CCl₄) was developed [6]. In addition, the production of SiH₄ or B₂H₆ by reaction of SiCl₄ and H₂ in a melt of LiCl/KCl was developed [7]. Subsequently, separations of Zr/Hf [8] and reactions of electrons with inorganic solids [9] were investigated.

2. Results in fluorine chemistry

The syntheses and characterization of compounds containing fluorine have been of major interest during the past 40 years.

2.1. Boron–nitrogen fluorides

In liquid HF, BN reacts to give NH₄BF₄ [10]. Borazoles such as [–BF–NC₆F₅]₃ and [–B(C₆F₅)–N(C₆F₅)–]₃ are formed from C₆F₅NH₂ and BCl₃ followed by reaction with NaF or C₆F₅MgI [11].

2.2. Nitrogen fluorides

N₂F₂ produced from NaN₃ and F₂ is of particular interest. By reaction with MF₅ (M=As, Sb), [N₂F]⁺[MF₆]⁻ is obtained [12]. The reaction of NF₃ with elementary sulfur, giving NSF and S=SF₂ is very interesting [13]. Cyanides such as NaCN and ClCN give (CN)₂ and F₃C–N=N–CF₃ [14], the latter being better obtained from CNCl and AgF [15]. PS compounds react to give SPF₃, PF₃, PF₅ and mainly (NPF₂)_n (n=3–9). Ca₃P₂ exhibits similar behaviour to give PF₃, PF₅ and (NPF₂)_n (n=3–6) [16].

2.3. Pentafluorophenyl derivatives of Group V compounds

The discovery of pentafluorophenylmagnesium halides opened the door to perfluorinated aromatic compounds and their derivatives. Thus, for example: C₆F₅MgBr + ECl₃ → E(C₆F₅) (E=As, Sb) [17] or C₆F₅PCl₂ + C₆F₅PH₂ → (C₆F₅)₄P₄ [18]. Alkylaminopentafluorophosphazines are obtained by the reaction of (NPF₂)₃ with amines [19]. Chlorodifluorocarbonylnickel complexes are formed from Ni(CO)₄ and PF₂Cl and have the structure Ni(CO)₃PF₂Cl ··· Ni(PF₂Cl)₄ [20].

2.4. Halogen fluorides

Irradiation of ClF₅ + OF₂ gives ClOF₃ and ClOF₅. In addition, [ClOF₄]⁻ was detected [21].

2.5. Metal fluorides

Fluorination of Cr metal powder under pressure with manganese metal powder as catalyst leads to lemon-yellow CrF_6 which decomposes at -80 to 100°C to give fire red CrF_5 [22]. Using a fluidized bed, Mn, Pb, Bi and Re were fluorinated at 600°C to give MnF_4 , PbF_4 , BiF_5 and ReF_4 [23].

2.6. Sulfur–nitrogen–fluorine compounds [24]

S–N–F compounds form acyclic and cyclic derivatives with remarkable chemical properties and interesting structural and bonding relationships. The small molecules NSF and NSF_3 are key substances; nearly all S–N–F compounds can be derived from them.

2.6.1. Properties of NSF

NSF forms the cyclic trimer $(\text{NSF})_3$ at room temperature and BF_3 and MF_5 ($\text{M}=\text{As}, \text{Sb}$) give thiazyl salts, for example $[\text{NS}]^+[\text{BF}_4]^-$. Transition metal cations form complexes such as $[\text{M}(\text{NSF}_3)_6]^+$ ($\text{M}=\text{Co}, \text{Ni}$). In these complexes, the SN as well as the SF distances are short compared with the starting material. NSF reacts with perfluoroalkenes in the presence of CsF to give disulfides and linear sulfur diimides. Nucleophilic substitution occurs during hydrolysis of NSF to HNSO and subsequently to $[\text{S}_3\text{O}_6]^{2-}$ and $[\text{S}_6\text{O}_6]^{2-}$ ions. An increase in coordination number occurs on nucleophilic addition with F_2 in the presence of CsF to yield CINSF_2 , an example of RNSF_2 species of which many are known.

Halogen derivatives ($\text{X}=\text{F}, \text{Cl}, \text{Br}, \text{I}$) are best synthesized from $\text{Hg}(\text{NSF}_2)_2$ and X. Many RNSF_2 species are obtained by reacting halogen compounds with SF_4 . Of practical interest are the aminosulfur trifluorides R_2NSF_3 ; the product with $\text{R}=\text{C}_2\text{H}_5$ is called DAST and serves as a fluorinating agent. Higher coordinated species are formed from RNSF_2 and F_2 . For example, $\text{C}_2\text{F}_5\text{NSF}_2$ leads to $\text{C}_2\text{F}_5\text{N}-\text{SF}_4$ and thereafter to $\text{C}_2\text{F}_5\text{N}-\text{SF}_5$.

2.6.2. Properties of NSF_3

In contrast to NSF, NSF_3 does not polymerize. Lewis acids only yield addition products such as $\text{A}\cdot\text{NSF}_3$ ($\text{A}=\text{BF}_3, \text{AsF}_5, \text{SbF}_5$). In a similar manner to NSF, NSF_3 forms transition metal complexes, for example $[\text{Mn}(\text{NSF}_3)_4]^{2+}[\text{AsF}_6]_2^{2-}$; ($\text{M}=\text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$). NSF_3 adds ClF to $\text{F}_3\text{S}-\text{NCl}_2$ and to the four-membered ring $(\text{ClN}-\text{SF}_4)_2$. The nucleophilic attack of BCl_3 on the S atom is noteworthy with $[\text{N}(\text{SCl})_2]^+[\text{BCl}_4]^-$ being formed. Another type of nucleophilic attack (by OH^- ions) occurs during hydrolysis of NSF_3 to give HNSOF₂ and, in addition, $\text{H}_2\text{NSO}_2\text{F}$ and $\text{H}_2\text{NSO}_3\text{H}$. HNSOF₂ is the parent compound of the RNSOF_2 series. Derivatives are halogen species ($\text{R}=\text{F}, \text{Cl}, \text{Pr}, \text{I}$), non-metallic derivatives such as $\text{B}(\text{NSOF}_2)_3\text{OP}(\text{NSOF}_2)_3$ or

$\text{SP}(\text{NSOF}_2)_3$, as well as transition metal complexes, for example, $\text{R}(\text{CO})_5\text{NSOF}_2$ or $[\text{Mn}(\text{CO})_4\text{NSOF}_2]_2$. Use of $\text{LiN}(\text{SiMe}_3)\text{R}$ ($\text{R}=\text{SiMe}_3, \text{CMe}_3$) enables a combined electrophilic and nucleophilic attack on NSF_3 , leading to $\text{Me}_2\text{SiN}-\text{SF}_2-\text{NSiMe}_3$ and $\text{S}(\text{NR})_3$. The latter compound, which is isoelectronic with SO_2 , is a derivative of the hitherto unknown sulfur triimide $\text{S}(\text{NH})_3$. The ‘Ypsilon trien’ structure has been deduced for $\text{R}=\text{SiMe}_3, \text{CMe}_3, \text{SF}_4$ or SOF_4 . The latter react with $\text{Me}_3\text{SiN}=\text{SF}_2=\text{NSiMe}_3$ to give $\text{N}=\text{SF}_2-\text{N}=\text{SF}_2$ or $\text{N}=\text{SF}_2-\text{N}=\text{SOF}_2\cdot 2\text{SF}_4$ which, in turn, is converted to $\text{F}_2\text{SN}-\text{SF}_4-\text{NSF}_2$, a fluoride existing in a *cis* and *trans* form.

2.6.3. Cyclic compounds

Cyclic SNF compounds exist as unsaturated or electron-rich species (thiazenes). $(\text{NSF})_4$ arises from S_4N_4 by reaction with AgF_2 . Polymerization of NSF leads to $(\text{NSF})_3$ and fluorination of $(\text{NSOCl})_3$ with SbF_3 gives $(\text{NSOF})_3$. $(\text{NSF})_4$ exhibits a puckered eight-membered ring with alternate SN bond lengths, two F atoms being axial and two equatorial. $(\text{NSF})_3$ has a chair configuration with all F atoms in *cis* positions. Three islands of delocalized SNS π -bonds exist in the ring molecule. These originate from three-centred two-electron π -bonds between an N atom and two S atoms. Experiments show that of the three ring systems $(\text{NSF})_4$, $(\text{NSF})_3$ and $(\text{NSOF})_3$, only the latter is suitable for substitution reactions with retention of the ring structure. An interesting chemical system was developed with the relatively stable $(\text{NSOF})_3$ molecule. The cyclic anion $[\text{N}_3\text{S}_3\text{O}_3\text{F}_2\text{O}]^-$ can be obtained from $(\text{NSOF})_3$ with methanol in the presence of trimethylamine. Ag_2CO_3 gives the silver salt, which on treatment with CH_3I gives $\text{MeN}_3\text{S}_3\text{O}_3\text{F}_2$. This compound possesses two asymmetrical S atoms.

3. Results obtained subsequently

3.1. Doped-cobalt and nickel hydroxides

$\beta\text{-Co}(\text{OH})_2$ and $\beta\text{-Ni}(\text{OH})_2$ [25] applied as electrodes in secondary cells act in a protonic manner. To improve their electrochemical properties, the hydroxides were doped with Al^{III} and Fe^{III} in the molar ratio $\text{M}^{\text{II}}/\text{M}^{\text{III}}=4:1$ ($\text{M}=\text{Al}^{\text{III}}, \text{Fe}^{\text{III}}$). The doped structures are of the pyroaurite type consisting of brucite-like cationic layers $[\text{M}^{\text{II}}_4\text{M}^{\text{III}}(\text{OH})_{10}]^+$ with disordered anion layers $[\text{X}\cdot n\text{H}_2\text{O}]$ ($\text{X}=\text{NO}_3^-, \text{CO}_3^{2-}, \text{SO}_4^{2-}, \text{PO}_4^{3-}$) between them. The influence of the dopands is as follows. (a) With nickel hydroxide, the addition of Al^{III} weakens the OH bond and hence increases the mobility of the protons. Charging gives Ni^{IV} as shown by Mössbauer spectra. Addition of Fe^{III} has a similar effect to Al^{III} leading to a siderophilic character. The existence

of Fe^{IV} in addition to Ni^{IV} has been demonstrated by Mössbauer spectra. (b) With cobalt hydroxide, Al^{III} stabilises the electrochemically inert character of the CoOOH formed.

3.2. Doped MnO₂ electrodes [26]

Doping with Ba²⁺ may be achieved according to $2\text{MnO}_4^- + 3\text{Mn}^{2+} + 2\text{H}_2\text{O} \rightarrow 5\text{MnO}_2 + 4\text{H}^+$ (Guyard 1862). This was the first real reversible MnO₂ electrode (1982). In addition, β-MnO₂ (pyrolusite) may be doped with Bi₂O₃ which exhibits a catalytic effect according to $2[\text{Mn}(\text{OH})_4(\text{H}_2\text{O})_2]^- \rightarrow \text{Mn}(\text{OH})_2 + \text{MnO}_2 + 2\text{OH}^- + 6\text{H}_2\text{O}$. An electrochemical redox reaction occurs between the two layer structures δ-MnO₂ and β-Mn(OH)₂.

3.3. Computer-controlled precipitation of MnO₂

The Guyard reaction has been used for the preparation of MnO₂ from Mn^{II} salts and KMnO₄ in acid solution. Precipitations were carried out at constant potential (electrographite electrode) and constant pH values. At pH=0 and pH=1, manganese dioxides of uniform particle size were formed.

3.4. Economical process for the preparation of silver(I, III) oxide AgO [27]

AgO can be prepared in up to 98% yield through oxidation of an aqueous, alkaline silver nitrate solution with mixtures of SO₂ and O₂ or air, or with mixtures of SO₃²⁻ solutions and O₂ or air. Both the pH, 10.5–10.6, of the solution and the redox potential (480–600 mV, referred to an Ag/AgCl electrode) must be kept constant at temperatures between 70 °C and 90 °C. The following reaction mechanism is assumed to occur: $[\text{O}_2\text{SOO}]^{2-} + 2\text{Ag}^+ + 2\text{OH}^- \rightarrow 2\text{AgO} + \text{SO}_3^{2-} + \text{H}_2\text{O}$.

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