Bis(fluorosulphuryl)imide derivatives of zinc(II), cadmium(II), mercury(II) and their coordination complexes with oxygen and nitrogen donors

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Bis(fluorosulphuryl)imides of zinc(II) and cadmium(II), [M{N(SO$_2$F)$_2$}$_2$], have been prepared in > 90% yield by reacting the metal trifluoroacetates with excess bis(fluorosulphuryl)imide in trifluoroacetic acid medium. These compounds and [Hg{N(SO$_2$F)$_2$}$_2$], which has been prepared by a known method, have been characterized by their elemental analyses and infrared spectral data. These are found to be thermally stable up to 200°C and are insoluble in non-coordinating solvents and HN(SO$_2$F)$_2$. These form coordination complexes of the type [M(L)$_x$ {N(SO$_2$F)$_2$}$_2$] where M = Zn(II), Cd(II) and Hg(II); x = 4, L = pyridine, acetonitrile and triphenylphosphine oxide; x = 2, L = 2,2'-bipyridyl.

The high electronegativity of the N(SO$_2$F)$_2$ group attracted a lot of attention from the workers in the field of noble gas chemistry, which led to the discovery of xenon-nitrogen bond[1-4]. Some organotransition derivatives[5,6] of the types M(CO)$_5$N(SO$_2$F)$_2$ (M = Mn or Re) and C$_5$H$_5$Cr(NO)$_2$N(SO$_2$F)$_2$ are also known, which form adducts with acetonitrile and triphenylphosphine by displacing the weakly coordinating N(SO$_2$F)$_2$ anion. [Hg{N(SO$_2$F)$_2$}$_2$], which was used for the preparation of Br-N(SO$_2$F)$_2$, is the only reported simple binary metal-bis salt containing N(SO$_2$F)$_2$ ligand[7]. In continuation of our earlier work[8-12] on the chemistry of HN(SO$_2$F)$_2$, we report herein the preparation and characterization of zinc(II) and cadmium(II) derivatives of bis(fluorosulphuryl)imide and their coordination complexes with pyridine (Py), acetonitrile (MeCN), triphenylphosphine oxide (TPPO) and 2,2'-bipyridyl (Bipy).

Materials and Methods

Bis(fluorosulphuryl)imide, HN(SO$_2$F)$_2$, was prepared and purified by the reported method[13]. Trifluoroacetic acid (Aldrich) was distilled before use. Zinc(II) and cadmium(II) trifluoroacetates were prepared as reported[14,15]. [Hg{N(SO$_2$F)$_2$}$_2$] was prepared by a known method[7]. Pyridine, acetonitrile and other solvents were purified by standard techniques[16]. 2,2'-Bipyridyl (AR, BDH) and triphenylphosphine oxide (E. Merck) were used as such.

The analytical data of the complexes are given in Table 1. Sulphur and fluorine were determined as described earlier[17] after fusing the compound with a Na$_2$O$_2$-Na$_2$CO$_3$ mixture in 1:2 ratio for 36 h in a nickel crucible. Metal contents were determined by standard techniques[18]. Carbon, hydrogen and nitrogen were determined microanalytically.

The IR spectra of the compounds were recorded on a Perkin Elmer-1430 spectrophotometer as neat solids and nujol/hexachlorobutadiene mulls between silver chloride/potassium bromide plates. All manipulations were carried out under dry nitrogen.

Preparation of metal bis{ bis(fluorosulphuryl)imide}

In a typical preparation, excess of HN(SO$_2$F)$_2$ [14.5 g, 80 mmol] was added to 5.83g (20 mmol) of Zn(O$_2$CCF$_3$)$_2$ taken in 15 ml of trifluoroacetic acid. The contents were refluxed for ~ 16 h. The white solid so formed was filtered, repeatedly washed with trifluoroacetic acid and finally with dichloromethane. Removal of all volatiles *in vacuo* at 80°C gave the desired product, Zn[{N(SO$_2$F)$_2$}$_2$] (7.83g, 18.4 mmol) in 92% yield.
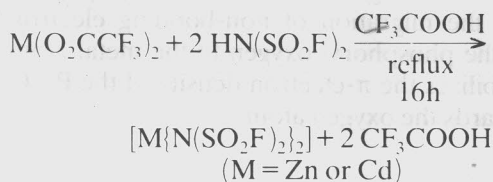
Cadmium(II) bis (fluorosulphuryl) imide, Cd{N(SO$_2$F)$_2$}$_2$, was prepared similarly in > 90% yield.

Preparation of Py, MeCN, TPPO and Bipy complexes

The complexes [ML$_x${N(SO$_2$F)$_2$}$_2$] where M = Zn(II), Cd(II) and Hg(II); x = 4, L = Py, MeCN, TPPO; x = 2, L = Bipy were prepared by stirring a suspension of M{N(SO$_2$F)$_2$}$_2$ in an appropriate solvent (dichloromethane for Py/MeCN and benzene for Bipy/TPPO) with the ligand in the required stoichiometry for 48 h at 30°C. The adducts formed were filtered under a positive pressure of dry nitrogen, washed several times with the respective solvents and finally dried *in vacuo*.

Results and Discussion

Excess $HN(SO_2F)_2$ reacts with metal trifluoroacetates in trifluoroacetic acid, at reflux, to form $[M\{N(SO_2F)_2\}_2]$.

$$M(O_2CCF_3)_2 + 2\,HN(SO_2F)_2 \xrightarrow[\substack{reflux \\ 16h}]{CF_3COOH}$$

$$[M\{N(SO_2F)_2\}_2] + 2\,CF_3COOH$$
$$(M = Zn \text{ or } Cd)$$

The reaction between $Hg(O_2CCF_3)_2$ and $HN(SO_2F)_2$ was quite exothermic and proceeded to completion at room temperature. The reactions took longer time to complete if stoichiometric amounts of $HN(SO_2F)_2$ were used. Anhydrous metal acetates reacted very exothermically with $HN(SO_2F)_2$. However, the final product contained varying amounts of CH_3COOH. The salts $[M\{N(SO_2F)_2\}_2]$ are exceptionally moisture-sensitive but are thermally stable up to 200°C in a dry atmosphere. These are insoluble in common non-coordinating solvents and $HN(SO_2F)_2$. Their lack of volatility, thermal stability and insolubility in $HN(SO_2F)_2$ probably reflects their polymeric nature.

The infrared spectra of $[M\{N(SO_2F)_2\}_2]$ give sufficient evidence that the $N(SO_2F)_2$ group is covalently bonded to the metal ion. The $\nu_{as}SO_2$ band has been found to be most effective in differentiating between ionic and covalent $N(SO_2F)_2$ groups. Dispersal of charge from nitrogen in covalent compounds probably favours $p_\pi - d_\pi$ bonding between oxygen and sulphur. Thus, $\nu_{as}SO_2$ appears at ~ 1480 cm^{-1} in covalent compounds[19,20], i.e. ~ 100 cm^{-1} higher than those in ionic compounds[20,21] viz., ~ 1380 cm^{-1}, where the negative charge is localized on nitrogen. A band appearing at 1445 cm^{-1} in $M\{[N(SO_2F)_2]_2$ [M = Zn(II), Cd(II) and Hg(II)], comparable to the bands at 1456-1477 cm^{-1} (Raman) in $Xe[N(SO_2F)_2]_2^2$, and at $1425 - 1454$ cm^{-1} (Raman) in $FXe[N(SO_2F)_2]_2^2$, is assigned to $\nu_{as}SO_2$. The IR bands at 1252, 1250 and 1222 cm^{-1} in zinc, cadmi-

Table 1—Analytical data of compounds

Compound	Found (calc.) %					
	M	S	F	C	H	N
$[Zn\{N(SO_2F)_2\}_2]$	14.82 (15.37)	29.80 (30.09)	17.62 (17.87)	—	—	6.44 (6.58)
$[Cd\{N(SO_2F)_2\}_2]$	22.91 (23.79)	26.92 (27.10)	15.89 (16.09)	—	—	5.67 (5.93)
$[Hg\{N(SO_2F)_2\}_2]$	35.00 (35.77)	23.04 (22.84)	13.11 (13.56)	—	—	4.85 (5.00)
$[Zn(Py)_4\{N(SO_2F)_2\}_2]$	8.65 (8.82)	17.03 (17.27)	9.86 (10.25)	31.90 (32.37)	2.58 (2.69)	11.16 (11.33)
$[Cd(Py)_4\{N(SO_2F)_2\}_2]$	14.14 (14.26)	15.98 (16.24)	9.42 (9.64)	30.21 (30.44)	2.50 (2.54)	10.59 (10.66)
$[Hg(Py)_4\{N(SO_2F)_2\}_2]$	22.17 (22.88)	14.81 (14.60)	8.20 (8.67)	26.97 (27.38)	2.15 (2.28)	9.43 (9.58)
$[Zn(Bipy)_2\{N(SO_2F)_2\}_2]$	9.21 (9.54)	18.42 (18.68)	10.85 (11.09)	27.65 (28.01)	1.68 (1.75)	12.09 (12.26)
$[Cd(Bipy)_2\{N(SO_2F)_2\}_2]$	15.20 (15.35)	17.19 (17.48)	9.87 (10.38)	25.86 (26.22)	1.59 (1.64)	11.26 (11.47)
$[Hg(Bipy)_2\{N(SO_2F)_2\}_2]$	23.87 (24.44)	15.81 (15.60)	8.93 (9.26)	23.31 (23.40)	1.40 (1.46)	9.98 (10.24)
$[Zn(MeCN)_4\{N(SO_2F)_2\}_2]$	10.65 (11.09)	21.55 (21.72)	12.80 (12.90)	16.01 (16.29)	1.97 (2.04)	13.90 (14.25)
$[Cd(MeCN)_4\{N(SO_2F)_2\}_2]$	17.25 (17.66)	19.87 (20.11)	11.33 (11.94)	14.78 (15.09)	1.84 (1.89)	13.02 (13.20)
$[Hg(MeCN)_4\{N(SO_2F)_2\}_2]$	26.93 (27.67)	17.84 (17.67)	10.05 (10.49)	12.95 (13.25)	1.64 (1.66)	11.47 (11.59)
$[Zn(TPPO)_4\{N(SO_2F)_2\}_2]$	3.91 (4.25)	8.19 (8.33)	4.73 (4.94)	55.71 (56.20)	3.77 (3.90)	1.80 (1.82)
$[Cd(TPPO)_4\{N(SO_2F)_2\}_2]$	6.56 (7.09)	7.86 (8.08)	4.58 (4.80)	54.20 (54.53)	3.64 (3.79)	1.73 (1.77)
$[Hg(TPPO)_4\{N(SO_2F)_2\}_2]$	11.14 (11.99)	7.85 (7.65)	4.32 (4.54)	50.79 (51.66)	3.47 (3.59)	1.65 (1.67)

um and mercury derivatives, respectively, may be assigned to $\nu_s SO_2$. The peaks observed at ~ 885 cm^{-1} (Zn and Cd) and at ~ 900 cm^{-1} (Hg) derivatives are assigned to $\nu_{as} SNS$ mode.

The peak attributable to ν_{S-F} is observed at ~ 858 cm^{-1} in these derivatives. The Xe-N bond in $FXeN(SO_2F)_2$ and $F[Xe\{N(SO_2F)_2\}_2]^+ AsF_6^-$ appears at 422 and 423 cm^{-1} (Raman), respectively[4]. The band appearing at 420 cm^{-1} in $[M\{N(SO_2F)_2\}_2]$ may thus be tentatively assigned to the M — N bond.

$[M\{N(SO_2F)_2\}_2]$ forms coordination complexes with Py, MeCN, TPPO and Bipy to give $[M(bipy)_2\{N(SO_2F)_2\}_2]$ and $[ML_4\{N(SO_2F)_2\}_2]$; L = Py, MeCN and TPPO. Their stoichiometry is based on elemental analyses (Table 1). These are hygroscopic and insoluble in non-coordinating solvents like chloroform, dichloromethane, carbon tetrachloride, etc.

In all the above complexes, appearance of bands at 1437-1454 cm^{-1}, attributable to $\nu_{as} SO_2$, indicates coordinated nature of the anion. Bands at 880-898 cm^{-1} in these complexes may be assigned to $\nu_{as} SNS$. The broad strong band at ~ 830 cm^{-1} in the pyridine complexes of Zn(II) and Hg(II) may be due to the overlapping of ν_{S-F} and ν_{SNS} modes.

In the pyridine complexes, appearance of weak bands at 1228-1232 cm^{-1} and the upward shift of bands at 1578 (out-of-plane ring deformation), 601, 403 cm^{-1} (in-plane ring deformation) in pure pyridine to 1605, 635 and 426 cm^{-1} respectively indicates the coordination of pyridine to metal[22].

Appearance of IR bands at 412, 1015 and 1320 cm^{-1} in bipyridyl complexes indicate the coordination of bipyridyl to metal[23,24]. The bands appearing at 2296, 2280 and 2266 cm^{-1} in $[M(MeCN)_4\{N(SO_2F)_2\}_2]$ where M = Zn(II), Cd(II) and Hg(II), respectively, show an upward trend in $C \equiv N$ stretching frequency (free acetonitrile, 2252 cm^{-1}). This increase in frequency upon coordination is explained on the basis of kinenmatic coupling (coupling of the C — N and M — N stretching frequency) and ionic contribution to the C — N bond[25]. The magnitude of shift in ν_{C-N}, may be correlated to the bonding ability of the metal ion to the ligand. The values for $\Delta\nu$ $C \equiv N$ for the $M(MeCN)_4[N(SO_2F)_2]_2$ complexes are found to be 44, 28 and 14 cm^{-1} respectively, which reflect the bonding ability or electronegativity of these metal ions in the order Zn(II) > Cd(II) > Hg(II).

The lowering of $\nu P = O$ from 1190 cm^{-1} in free base to 1120 cm^{-1} in the present triphenylphos-

phine oxide complexes reveals coordination through phosphoryl oxygen[26]. As a result of coordination, $\nu P - C$, observed at 1440 cm^{-1} in pure TPPO, shifts upwards to 1480 cm^{-1} in these complexes. The lowering of $\nu P = O$ has been explained as due to the migration of non-bonding electron cloud on the phosphoryl oxygen to the metal atom which mobilizes the π-electron density of the P = O group towards the oxygen atom.

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