Novel Transition Metal Complexes in Liquid Sulphur Dioxide

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Summary In liquid SO_2 very weak *N*- and *O*- donors [*e.g.*, NSF_3, OPX_3 (X = F, NCO)] form transition metal complexes.

FROM SO_2-stabilised Lewis acids such as F_5SbOSO,[1] $[(CO)_5MSO_2]^+$ (M = Mn, Re),[2] and $MeOSO^+$ [3] the SO_2 ligand can be easily replaced by very weak nucleophiles (*e.g.* NSF_3).[4] This behaviour can be extended to SO_2 complexes of transition metals,[5] and thus a novel transition metal complex chemistry with weakly basic and/or unstable ligands becomes possible in liquid SO_2.

Tetrakis(thiazyl trifluoride) complexes can be formed quantitatively from the corresponding AsF_6^- salts, see equation (1). An increase in wavenumber for ν_{SN} and

$$\underset{\mathbf{(1)}}{[M(SO_2)_x]^{2+}\,(AsF_6)_2^-} + \text{excess}\ \underset{\mathbf{(2)}}{NSF_3} \xrightarrow{SO_2} \underset{\mathbf{(3)}}{[M(NSF_3)_4]\,(AsF_6)_2} \qquad (1)$$

Complex†	M	ν_{SN}/cm^{-1}	ν_{SF}/cm^{-1}	Colour
(3a)	Mn	1580	880,836	Colourless
(3b)	Fe	1590	883,837·5	Ochre
(3c)	Co	1598	885,840	Lilac
(3d)	Ni	1610	885,840	Faint green
(3e)	Cu	1621	898,849	Faint blue
NSF_3 (gas)		1515	811,775	Ref. 6

ν_{SF} is observed on complex formation, as with addition of other Lewis acids to the N atom of (**2**). This increase parallels the decrease in metal atom radius (and hence the increase in its Lewis acid strength).

Reaction (1) is not confined to metals with stable SO_2 complexes, see equation (2). With excess of (**2**) the

$$\begin{tikzcd}
AgAsF_6 + \text{excess}\ \mathbf{(2)} \arrow[r] & \underset{\mathbf{(4)}}{[Ag(NSF_3)_2]\,(AsF_6)} \arrow[d, "\text{high vacuum}"', "\text{room temp.}"] \\
\underset{\mathbf{(6)}}{[(O_2S)Ag(NSF_3)](AsF_6)} & \underset{\mathbf{(5)}}{[Ag(NSF_3)](AsF_6)} \arrow[l, "SO_2"']
\end{tikzcd} \qquad (2)$$

bis(thiazyl trifluoride) complex (**4**) is formed, which easily loses a mole of (**2**) to give the stable compound (**5**). There is a sharp decrease in ν_{SN} from 1551 cm^{-1} in (**4**) to 1507 cm^{-1} in (**5**). The Raman spectrum of (**5**) in SO_2 shows ν_{SN} at 1555 cm^{-1}, implying that in liquid SO_2 the free co-ordination site is occupied by the solvent.

Complexes of very weakly basic or unstable phosphoryl derivatives OPX_3 (*e.g.* X = F, NCO) have never been reported. However, complexes $[ML_x][AsF_6]_2$ (x = 2 or 4, depending on the stoicheiometry) may be prepared in liquid SO_2, see reaction (3). In complexes (**7**) and (**8**)

$$[Ni(SO_2)_2](AsF_6)_2 + 2\,OP(NCO)_3 \longrightarrow \underset{\mathbf{(7)}}{\{Ni[OP(NCO)_3]_2\}(AsF_6)_2}$$

$$\mathbf{(1)} + \text{excess}\ OPF_3 \longrightarrow \underset{\mathbf{(8)}}{[M(OPF_3)_4]\,(AsF_6)_2} \qquad (3)$$

a, M = Mn
b, M = Ni

co-ordination is through the O-atoms, as in other phosphoryl complexes [ν_{PO} in (**7**) 1218 cm^{-1}]. OPF_3 is isoelectronic with NSF_3; however ν_{PO} is shifted to lower wavenumber in (**8**) while ν_{PF} increases (Table). This may be explained if the M–O–P group is bent (in contrast to the M–N–S group[7]). The addition to Lewis acids confers more single bond character to the P–O bond and partial positive charge to the P atom.

TABLE

	$\nu_{P=O}$/cm^{-1}	ν_{PF}/cm^{-1}
$O{=}PF_3$ (liquid)[a]	1395	982,875
(**8a**)	1360	1032,910
(**8b**)	1364	1037,913
$F_5Sb{-}OPF_3$	1302	1073,933

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