

Novel Transition Metal Complexes in Liquid Sulphur Dioxide

By RÜDIGER MEWS

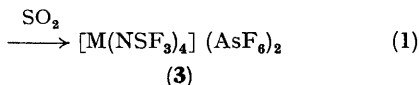
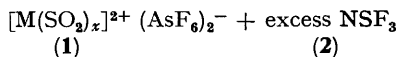
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Summary In liquid SO_2 very weak *N*- and *O*- donors [*e.g.*, NSF_3 , OPX_3 ($\text{X} = \text{F}$, NCO)] form transition metal complexes.

FROM SO_2 -stabilised Lewis acids such as F_5SbOSO ,¹ $[(\text{CO})_5\text{MSO}_2]^+$ ($\text{M} = \text{Mn}$, 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 .

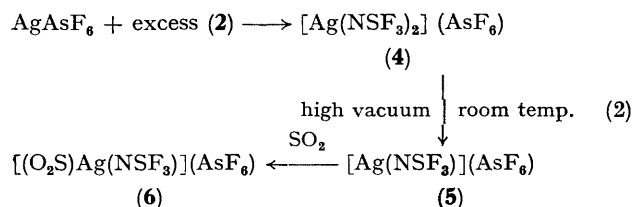
Tetrakis(thiazyl trifluoride) complexes can be formed quantitatively from the corresponding AsF_6^- salts, see equation (1). An increase in wavenumber for ν_{SN} and



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).

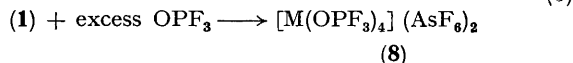
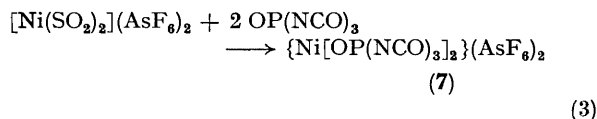
Reaction (1) is not confined to metals with stable SO_2 complexes, see equation (2). With excess of (2) the



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 stoichiometry) may be prepared in liquid SO_2 , see reaction (3). In complexes (7) and (8)



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 group⁷). The addition to Lewis acids confers more single bond character to the P-O bond and partial positive charge to the P atom.

TABLE

	$\nu_{P=O}/\text{cm}^{-1}$	ν_{PF}/cm^{-1}
O=PF ₃ (liquid) ^a	1395	982,875
(8a)	1360	1032,910
(8b)	1364	1037,913
F ₅ Sb-OPF ₃	1302	1073,933

^a M. L. Delwaulle and F. Francois, *J. Chim. phys.*, 1949, **46**, 87; H. S. Gutowsky and A. D. Liehr, *J. Phys. Chem.*, 1952, **20**, 1652. ^b H. Selig and N. Aminadav, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 595; R. Mews, to be published.

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† All compounds [except (6)] were characterised by complete elemental analyses and vibrational spectroscopy.

¹ E. E. Aynsley, R. D. Peacock, and P. L. Robinson, *Chem. and Ind.*, 1951, 1117; J. W. Moore, H. W. Baird, and H. B. Miller, *J. Amer. Chem. Soc.*, 1968, **90**, 1359.

² R. Mews, *Angew. Chem.*, 1975, **87**, 669.

³ P. E. Petersen, R. Brockington, and D. W. Vidrine, *J. Amer. Chem. Soc.*, 1976, **98**, 2660; G. A. Olah, D. J. Donovan, and H. C. Liu, *ibid.*, 2661; R. J. Gillespie, F. G. Riddell, and D. R. Slim, *ibid.*, 8069.

⁴ R. Mews and O. Glemser, *Angew. Chem.*, 1975, **87**, 208; *Angew. Chem. Internat. Edn.*, 1975, **14**, 186; R. Mews, *Angew. Chem.*, 1978, **90**, 561; *Angew. Chem. Internat. Edn.*, 1978, **17**, 530.

⁵ P. A. W. Dean, *J. Fluorine Chem.*, 1975, **5**, 499; C. D. Desjardins and J. Passmore, *ibid.*, 1975, **6**, 379.

⁶ H. Richert and O. Glemser, *Z. anorg. Chem.*, 1961, **307**, 328.

⁷ B. Buss, M. Noltemeyer, R. Mews, and O. Glemser, to be published.