Potassium Thiazate KNSO

By D. A. ('Fred') Armitage* and John C. Brand

(*Department of Chemistry, Queen Elizabeth College, Campden Hill, London* W8 7AH)

Summary The preparation and characterisation of the title compound and its complex with 18-crown-6 are described, and the use of these compounds as synthetic intermediates in the preparation of organo-silicon, -germanium, and -tin isothiazates is briefly explored.

THREE of the triatomic combinations of the elements carbon, nitrogen, oxygen, and sulphur are known. While carbon oxysulphide is a monomeric gas, the others occur in variously bonded permutations of the component atoms as the pseudohalides cyanate $^{-}$OCN, isocyanate $^{-}$NCO, fulminate $^{-}$CNO, thiocyanate $^{-}$SCN, and isothiocyanate $^{-}$NCS. All these pseudohalides form covalent derivatives with metallic and non-metallic elements, while cyanate and thiocyanate also form ionic compounds with electropositive metals.

The fourth triatomic combination of the above elements is the sulphinylamine group $^{-}$NSO. Although it has been known in the form of organic sulphinylamines for more than a century,[1] covalent derivatives of other elements have been synthesised only relatively recently.[2]

We report here for the first time the unequivocal generation of compounds containing the NSO anion. By analogy with other pseudohalides, we suggest that it be called the thiazate ion.[3]

Potassium t-butoxide and sulphinylaminotrimethylsilane (isothiazatotrimethylsilane) slowly reacted in THF to give potassium thiazate as an insoluble cream solid in good yield [reaction (1)]. t-Butoxytrimethylsilane was characterised from the filtrate.

$$\mathrm{KOBu^t + Me_3SiNSO \rightarrow KNSO + Me_3SiOBu^t} \qquad (1)$$

Potassium thiazate darkens on heating at about 135 °C, and melts at 190 °C to a bubbling orange liquid, explodes on ignition, and ignites on contact with water. It exhibits peaks in its i.r. spectrum characteristic of the symmetric (990 cm^{-1}) and antisymmetric (1270 cm^{-1}) stretches and bend (515 cm^{-1}) of the thiazate group, and analyses well for potassium, sulphur, and nitrogen. This exchange reaction has also been used to prepare potassium thiocyanate in excellent yield using isothiocyanatotrimethylsilane.

Like many potassium salts, the thiazate is soluble in a benzene solution of 18-crown-6. Evaporating the solution gives the crown complex in good yield as a white crystalline solid, m.p. 150—153 °C (decomp.) which analyses well for C, H, N, K, and S.

Potassium thiazate reacts with Me_3SiCl, Me_2SiCl_2, and Et_3GeCl to give the appropriate isothiazate in low yield [reaction (2)]. With trimethyltin chloride, however, heating under reflux for 6 h in THF gave trimethyltin isothiazate in good yield.

$$\mathrm{R_3MCl + KNSO \rightarrow R_3MNSO + KCl} \qquad (2)$$
$$\mathrm{(M = Si,\ Ge,\ Sn)}$$

The addition of *ca.* 0·2 g of 18-crown-6 in the case of Me_3SiCl and Et_3GeCl increased the yield of the isothiazate formed considerably, in line with its success in catalysing the pseudohalogenation of $Bu^t{}_3SiCl$.[4]

The authors would like to thank the Department and College for financial support.

(*Received, 16th August* 1979; *Com.* 879.)

---

[1] C. Bottinger, *Ber.*, 1878, **11**, 1407.

[2] P. W. Schenk, *Ber.*, 1942, **75**, 94 (hydrogen); W. Verbeek and W. Sundermeyer, *Angew. Chem. Internat. Edn.*, 1969, **8**, 376 (mercury); O. J. Scherer and P. Hornig, *ibid.*, 1966, **5**, 729 (silicon); D. A. Armitage and M. J. Clark, *J. Organometallic Chem.*, 1970, **24**, 629 (germanium); D. A. Armitage and A. W. Sinden, *ibid.*, 1972, **44**, C43 (tin); W. Lidy and W. Sundermeyer, *Z. Naturforsch.*, 1974, **29b**, 276 (*Chem. Abs.*, 1974, **81**, 63712b) (oxygen); M. Becke-Goehring and J. Heinke, *Z. anorg. Chem.*, 1953, **272**, 297 (sulphur); W. Verbeek and W. Sundermeyer, *Angew. Chem. Internat. Edn.*, 1969, **8**, 376 (halogens).

[3] Other permutations of the atoms of this group are known. HOSN is only briefly stable at room temperature. It readily polymerises and forms red-violet derivatives LiOSN and NaOSN, but no structural properties were reported (M. Becke-Goehring, R. Schwarz, and W. Spiess, *Z. anorg. Chem.*, 1957, **293**, 294). A few derivatives of the thionitrite group –SNO have also been characterised [*e.g.* H. Rheinboldt, F. Mott, and E. Motzkus, *J. prakt. Chem.*, 1932, **134**, 257 (*Chem. Abs.*, 1932, **26**, 5544)].

[4] M. Weidenbruch and H. Pesel, *Z. Naturforsch.*, 1978, **33b**, 1465 (*Chem. Abs.*, 1979, **90**, 87566u).