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Preliminary communication

DIORGANOTELLURIUM DIISOCYANATES

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Summary

Diaryltellurium diisothiocyanates are reported. The solid state structures and solution properties vary within the series $R_2Te(NCS)_2$ (R = Ph, p-$MeOC_6H_4$, p-$EtOC_6H_4$).

The recently reported synthesis of a range of triphenyltellurium pseudohalides [1], together with crystallographic data [2] and the crystal and molecular structures of $(Ph_3Te)(NCO)\cdot½CHCl_3$ [3] and $(Ph_3Te)(NCS)$ [4], prompts us to report some results for the new compounds $R_2Te(NCS)_2$ where R = Ph, p-$CH_3OC_6H_4$ and p-$C_2H_5OC_6H_4$.

Three new compounds which, to our knowledge, are the first examples of diorganotellurium dipseudohalides are conveniently prepared from the reaction of thiocyanogen [5] with the appropriate telluride. Alternatively, the compounds may be prepared by the reaction of ammonium thiocyanate and the diorganotellurium dichloride in methanolic solution. Some physical data are reported in Table 1.

The diphenyl and di-p-methoxytelluride products are pale yellow whereas that obtained using di-p-ethoxytelluride is white. Furthermore substantial differences are noted in the solid state IR spectra. Thus, for R = Ph and p-$CH_3OC_6H_4$, ν(CN) is a doublet with both components above 2000 cm^{-1}, which may imply a nonlinear SCN—Te—NCS system with relatively weak tellurium—nitrogen bonds; or which may arise from factor group splitting. By contrast, for $(p\text{-}C_2H_5OC_6H_4)_2$-$Te(NCS)]^+ (NCS)^-$. However the possibility of weak association between 2053 cm^{-1}) and the other is extremely broad ($\Gamma_{½}$ 100 cm^{-1}) and centred on 1980 cm^{-1}. The width and position of the latter band suggest a covalently bound isothiocyanato group [6] and a solid state structure $[(p\text{-}C_2H_5OC_6H_4)_2$-$Te(NCS)]^+(NCS)^-$. However the possibility of weak association between the ionic units in the crystal cannot be eliminated, a point emphasised by the oligomeric structure of $[Ph_3Te](NCS)$ [4].

TABLE 1

Compound	Colour	M.p. (°C)	Infrared data ν(CN) (cm^{-1})	Λ_m (10^{-3} M/$MeNO_2$)
$Ph_2Te(NCS)_2$	pale yellow	140	2060 s (sharp), 2050 s (sharp)	Insoluble
$(p\text{-}CH_3OC_6H_4)_2Te(NCS)_2$	pale yellow	110	2060 s (sh), 2040 s	61
$(p\text{-}C_2H_5OC_6H_4)_2Te(NCS)_2$	white	100	2040 s (sharp), 1980 s (v.br)	106

The structures of the phenyl and *p*-methoxyphenyl derivatives are believed to be similar, and most probably based on a very distorted six coordinate arrangement around tellurium. Thus we envisage diorganotellurium diisothiocyanato units (which, if the s^2 electrons are stereochemically active, may be considered trigonal bipyramids with axial isothiocyanato groups) linked to other units by long Te—S bonds. This tellurium—sulphur association probably accounts for the pale yellow colour of the solids.

The solution behaviour of these materials is also of interest. $Ph_2Te(NCS)_2$ is insoluble in solvents suitable for conductivity measurements, but both the *p*-methoxy and *p*-ethoxyphenyl derivatives dissolve in nitromethane to give colourless, conducting solutions (Table 1). Investigation of the conductivity over a range of concentration for both compounds gives non linear plots of Λ against (concentration)$^{1/2}$, hence we are probably dealing with the following equilibria:

$$R_2Te(NCS)_2 \rightleftharpoons R_2Te(NCS)^+ + NCS^-$$

$$R_2Te(NCS)^+ \rightleftharpoons R_2Te^{2+} + NCS^-$$

We believe that the interesting variation of solid state and solution properties is determined more by the effect of the increasing size of the *p*-substituent in the phenyl ring on the balance between the energies of various possible lattices and solvation energies, than it is by the electronic influence of the substituent.

The compounds gave satisfactory analyses and the full details of their synthesis together with more detailed and extensive physical properties will be given in due course.

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