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DIARYLTHALLIUM(III) SELENOCYANATES

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SUMMARY

Four diarylthallium(III) selenocyanates (aryl = phenyl, *o*-, *m*- or *p*-tolyl) have been synthesised by the interaction of diarylthallium(III) chlorides with potassium selenocyanate. The compounds have been characterised, and the spectral data indicate the presence of selenium–thallium bonds.

INTRODUCTION

Aynsley and co-workers[1] recently described the synthesis of some organometallic selenocyanates of lead, tin and thallium. On the basis of IR spectral studies they concluded that diphenyltin diselenocyanate possesses an iso structure while the corresponding compounds of thallium and lead exist in the normal form. They failed to obtain diphenylthallium(III) selenocyanate by metathesis between diphenylthallium(III) halides and potassium selenocyanate, which is contrary to our observations. Thus we have obtained four diarylthallium(III) selenocyanates (aryl = phenyl, *o*-, *m*- or *p*-tolyl) by the interaction of diarylthallium(III) chloride with potassium selenocyanate. We suggest that the selenocyanate group in these compounds is selenium-bonded to the metal atom.

EXPERIMENTAL

Diarylthallium(III) chlorides were synthesised by treatment of tetrahydrated thallium(III) chloride with diaryltin dichlorides[2-4]. Potassium selenocyanate was freshly prepared by the published method[5]. Diarylthallium(III) selenocyanates were synthesised by treatment of diarylthallium(III) chlorides with potassium selenocyanate.

In a typical reaction, 1 mmole of diarylthallium(III) chloride in 50 ml of pyridine was mixed with a saturated solution of potassium selenocyanate in acetonitrile. The reaction mixture was heated on water-bath for 1 h after which it was treated with water and the desired compound was precipitated. It was washed with water, alcohol, ether and dried at 90°. The experimental data are summarised in Table 1.

The compounds are thermally stable at room temperature but decompose at their melting points. They are insensitive to moisture and atmospheric oxygen. They

TABLE 1

EXPERIMENTAL DATA OF DIARYLTHALLIUM(III) SELENOCYANATES

Aryl	M.p. (°C)	Analysis found (calcd.) (%)			
		Tl	C	H	N
Phenyl	212–214 dec.	44.5 (44.0)	33.5 (33.4)	2.2 (2.1)	3.0 (3.0)
o-Tolyl	182 dec.	41.9 (41.5)	36.4 (36.6)	3.1 (2.8)	2.9 (2.8)
m-Tolyl	178 dec.	41.2 (41.5)	36.5 (36.6)	3.2 (2.8)	2.9 (2.8)
p-Tolyl	194–196 dec.	42.0 (41.5)	36.5 (36.6)	3.1 (2.8)	2.8 (2.8)

TABLE 2

CHARACTERISTIC ABSORPTION FREQUENCIES (cm^{-1}) OF $SeCN^-$ GROUP IN DIARYLTHALLIUM(III) SELENOCYANATES

Aryl	ν_{asym}(SeCN)	ν_{sym}(SeCN)	SeCN deform.	Tl–SeCN bend
Phenyl	2090 vs	571 vw	402 vw	348 vw
o-Tolyl	2098 vs	575 vw	398 vw	352 vw
m-Tolyl	2120 vs	572 vw	396 vw	349 vw
p-Tolyl	2142 vs	575 w	408 vw	350 vw

are insoluble in water and organic solvents such as benzene, carbon tetrachloride, petroleum ether.

The IR spectra of the compounds in nujol were recorded in the range 4000–200 cm^{-1} using Perkin–Elmer model 421 spectrophotometer and the absorption frequencies associated with the various modes of vibration of the selenocyanate group are collected in Table 2.

Aynsley *et al.*[1] have shown that organolead selenocyanates have a sharp single C≡N stretch at 2100 cm^{-1}, indicating that the selenocyanate group is selenium bonded to the lead atom. On the other hand the corresponding tin compounds show a broad band at 2108 cm^{-1}, which in chloroform solution resolves into a weak band at 2144 cm^{-1}, and a broad band of strong intensity at 2055 cm^{-1} suggesting an iso structure of the compound.

In the IR spectra of all the four diarylthallium(III) selenocyanates there is a sharp band of strong intensity at 2120 ± 20 cm^{-1}, which does not show any sign of splitting when the spectrum is recorded in chloroform. This may be taken as an evidence that the compounds have the normal structure. The three absorptions of weak intensity located at 573 ± 2, 402 ± 6 and 350 ± 2 cm^{-1} can be assigned to the SeCN symmetric stretching, Se–CN deformation and Tl–SeCN bending modes respectively, in agreement with the assignments of Thayer and Strommen[6] for organometallic thiocyanates of Group IV elements.

The absorptions associated with aromatic group in the molecule (not listed in the table) are observed at the expected positions.

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REFERENCES

1 E. E. Aynsley, N. N. Greenwood, G. Hunter and M. J. Sprague, *J. Chem. Soc. A*, (1966) 1344.
2 R. Kh. Freidlina, A. K. Kochetkov and A. N. Nesmeyanov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (1948) 445, [*Chem. Abstr.*, 44 (1950) 10569e].
3 A. K. Kochetkov and R. Kh. Freidlina, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (1950) 203, [*Chem. Abstr.*, 44 (1950) 9342].
4 A. K. Kochetkov and R. Kh. Freidlina, *Org. Khim.*, 7 (1950) 144, [*Chem. Abstr.*, 50 (1956) 7728f].
5 W. Conard Fernelius, *Inorganic Syntheses*, Vol. II, 1st Ed., 1946, p. 186.
6 J. S. Thayer and D. P. Strommen, *J. Organometal. Chem.*, 5 (1966) 383.