

Synthesis and characterization of new bis[2-(4,4-dimethyl-2-oxazoliny)phenyl] chalcogenides: crystal and molecular structure of bis[2-(4,4-dimethyl-2-oxazoliny)phenyl] telluride

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The synthesis and characterization of two new symmetric chalcogenides based on 4,4-dimethyl-2-phenyloxazoline substrate are described.

The chemistry of diorgano chalcogenide ligands is of current interest.¹ So far a number of unsymmetric as well as symmetric diaryl chalcogenide ligands have been reported. Minkin *et al.*² have studied a series of symmetric diaryl tellurides containing two imino nitrogens in the close proximity to the tellurium and found that only one of the nitrogen atoms interacts with the tellurium in the solid state. Our group has recently reported a series of diaryl dichalcogenides and their derivatives based on the phenyloxazoline substrate.³ In the derivatives of type R₂E₂ or REX, [(R = (4,4-dimethyl-2-oxazoliny)phenyl, (*R*)-(4-ethyl-2-oxazoliny)phenyl; E = Se, Te; X = Cl, Br, I, CH₂, Ph)] it was found that the strength of E⋯N interaction depended upon the nature of the substituent attached to the chalcogen. In view of this, it was thought worthwhile to prepare the corresponding selenide and telluride derivatives and probe the nature of E⋯N interaction. In addition, these chalcogenides can act as tridentate ligands and are potentially capable of forming six-membered rings upon chelation. Here we report the synthesis and characterization of two new diaryl chalcogenides (**3**) and (**4**) based on 4,4-dimethyl-2-phenyloxazoline substrate. In addition, we also describe the crystal structure of bis[2-(4,4-dimethyl-2-oxazoliny)phenyl] telluride.

Compounds **3** and **4** were synthesized by the *ortho*-lithiation route (Scheme 1). *Ortho*-lithiation of **1** in hexane by *n*-BuLi gave a white slurry of the aryllithium compound (**2**). The reaction of **2** with TeI₂ in ether afforded **3** in low yield. Alternatively, when Te(dtc)₂ (dte=diethyldithiocarbamate) in benzene was used as the Te(II) source, the reaction afforded **3** in a better yield. The corresponding selenide (**4**) was synthesized by treating **2** with Se(dtc)₂ in benzene. The reaction proceeded smoothly and afforded the desired compound as a white crystalline solid. However, the reaction of Se(dtc)₂ with **2** in a more polar solvent such as ether led to decomposition and no formation of the product was observed. Both the

compounds (**3**) and (**4**) are highly soluble in all common organic solvents but insoluble in hexane at room temperature. Compounds **3** and **4** are crystalline solids which could be further purified by recrystallization from dichloromethane : hexane (1:3) mixture. In mass spectra, the compounds show the corresponding molecular ion peaks in low intensity. The peaks observed for the main fragment in these compounds correspond to the loss of one phenyloxazoline unit to give RE⁺ (E = Se/Te) peak.

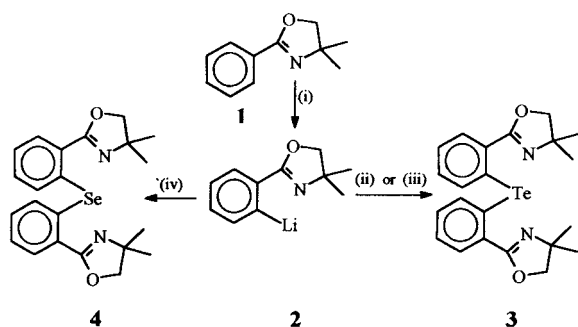
The ¹H-NMR spectra of **3** and **4** were recorded in CDCl₃. The signals due to the methyl and methylene protons for these compounds are not much shifted as compared with that of the starting material **1**. However, the signals due to the aromatic protons are relatively well resolved due to the *ortho*-substitution on the benzene ring. The ¹²⁵Te-NMR of **3** shows a sharp singlet at 492.5 ppm. This value is shifted upfield by 52.1 ppm as compared with that of bis[(*N,N*-dimethylamino)benzyl] telluride (544.6 ppm).^{1e} The ⁷⁷Se-NMR of **4** shows a sharp singlet at 440.3 ppm which is shifted downfield by 99.5 ppm as compared with that of bis[(*N,N*-dimethylamino)benzyl] selenide (340.8 ppm).^{1g}

The diffraction measurements for compound **3** were performed at room temperature (293 K) on a Siemens R3m/V diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.7107 Å). The data for **3** were corrected for Lorentz,

Table 1 Crystal data and structure refinement for **3**

	Compound 3
Empirical formula	C ₂₂ H ₂₄ N ₂ O ₂ Te
Formula weight	476.03
Crystal system	Triclinic
Space group	P1
Unit cell dimensions	
a(Å)	11.4837 (19)
b(Å)	11.9237 (16)
c(Å)	16.879 (3)
α(°)	76.124 (10)
β(°)	76.985 (12)
γ(°)	85.312 (11)
V(Å ³)	2185.2 (6)
Z	4
D _{calc.} (Mg m ⁻³)	1.447
Temperature (K)	293 (2)
λ (Å)	0.71073
Absorption coeff. (mm ⁻¹)	1.379
Observed reflections	9970
Final R(F) [I > 2σ(I)] ^a	0.0370
wR(F ²) indices [I > 2σ(I)]	0.0924
Data/restraints/parameters	9970/0/544
Goodness-of-fit on F ²	1.034

^aDefinitions: $R(F_0) = \sum ||F_0 - |F_c|| / \sum |F_0|$ and $wR(F_0^2) = \{ \sum [w(F_0^2 - F_c^2)^2] / \sum [w(F_c^2)^2] \}^{1/2}$. Additional crystallographic details are given in the supporting information.



Scheme 1 Reagents and conditions. (i) *n*-BuLi, hexane (ii) TeI₂, ether, r.t. (iii) Te(dtc)₂, benzene, r.t. (iv) Se(Dtc)₂, benzene, r.t.

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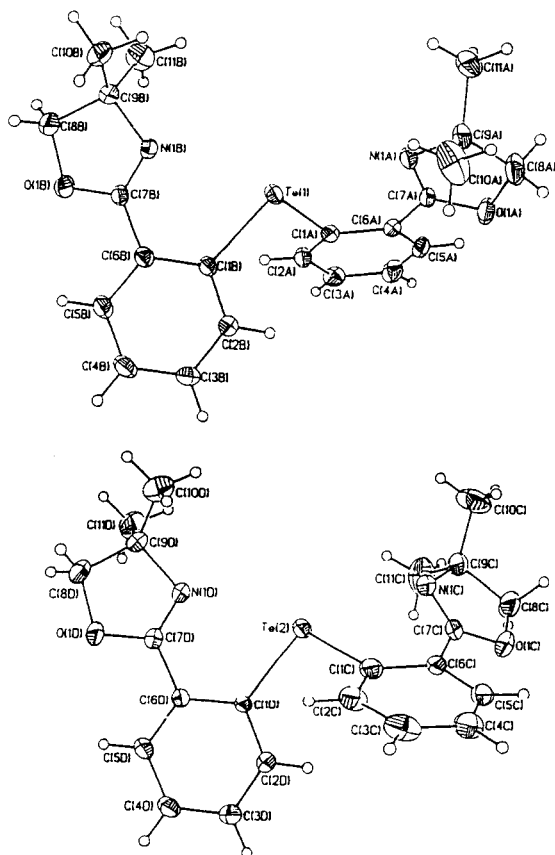


Fig. 1 Crystal Structure of **3**: selected bond lengths (Å) and bond angles (°): Te(1)–C(1A) 2.136(3), Te(1)–C(1B) 2.135(3), Te(2)–C(1C) 2.140(3), Te(2)–C(1D) 2.131(3), N(1A)–C(7A) 1.261(4), N(1B)–C(7B) 1.265(4), N(1C)–C(7C) 1.262(5), N(1D)–C(7D) 1.264(4), O(1A)–C(7A) 1.355(4), O(1B)–C(7B) 1.363(4), O(1C)–C(7C) 1.366(5), O(1D)–C(7D) 1.351(4), C(1B)–Te(1)–C(1A) 93.63(11), C(1D)–Te(2)–C(1C) 94.14(12), C(2A)–C(1A)–Te(1) 117.9(2), C(2B)–C(1B)–Te(1) 118.4(2), C(2C)–C(1C)–Te(2) 119.0(3), C(2D)–C(1D)–Te(2) 119.3(2), C(6A)–C(1A)–Te(1) 123.3(2), C(6B)–C(1B)–Te(1) 122.7(2), C(6C)–C(1C)–Te(2) 122.3(3), C(6D)–C(1D)–Te(2) 122.0(2)

polarization and absorption effects. Crystallographic data for **3**: triclinic, spacegroup: P1 (bar), $a = 11.4837(19)$ Å, $b = 11.9237(16)$ Å, $c = 16.879(3)$ Å, $\alpha = 76.124(10)^\circ$, $\beta = 76.985(12)^\circ$, $\gamma = 85.312(11)^\circ$, $V = 2185.2(6)$ Å³, $Z = 4$, $D_c = 1.447$ Mg/m³, $R(R_w) = 0.0924$.

An ORTEP view of **3** is shown in Fig. 1. In the unit cell of **3** there are two asymmetric units. The geometries around the Te atoms are V-shaped. The C–Te–C bond angles [C(1A)–Te(1)–C(1B) = 93.63(11)°; C(1C)–Te(2)–C(1D) = 91.14(5)°] for both the asymmetric units are found to be comparable. The nitrogen atoms of both the oxazoline moieties are directed towards Te atoms in both the units. While the Te⋯N distances [(Te(1)⋯N(1A) = 3.014, (Te(1)⋯N(1B) = 2.923, (Te(2)⋯N(1C) = 2.976, (Te(2)⋯N(1D) = 2.949 Å] are close to each other, these distances are much shorter than the van der Waals distance (3.61 Å). This indicates that both the nitrogen atoms in each unit involve in nonbonded interactions with tellurium giving rise to a 12-Te-4 tellurane structure. Interestingly, this is in contrast to the observations made for bis[2-(4'-methoxyphenyl)iminomethinylphenyl] telluride and bis(2-isopropyliminomethinylphenyl) telluride where in spite of two possible Te⋯N interactions, only one interaction exists and gives rise to a 10-Te-3 tellurane structure.² The Te⋯N distances in **3** are, however, higher than that of bis[2-(4'-methoxyphenyl)iminomethinylphenyl] telluride [2.702(3) Å

Table 2 Significant bond lengths (Å) and bond angles (°) for **3**

Te(1)–C(1A)	2.136(3)	Te(1)–C(1B)	2.135(3)
Te(2)–C(1C)	2.140(3)	Te(2)–C(1D)	2.131(3)
N(1A)–C(7A)	1.261(4)	N(1B)–C(7B)	1.265(4)
N(1C)–C(7C)	1.262(5)	N(1D)–C(7D)	1.264(4)
O(1A)–C(7A)	1.355(4)	O(1B)–C(7B)	1.363(4)
O(1C)–C(7C)	1.366(5)	O(1D)–C(7D)	1.351(4)
C(1B)–Te(1)–C(1A)	93.63(11)	C(1D)–Te(2)–C(1C)	94.14(12)
C(2A)–C(1A)–Te(1)	117.9(2)	C(2B)–C(1B)–Te(1)	118.4(2)
C(2C)–C(1C)–Te(2)	119.0(3)	C(2D)–C(1D)–Te(2)	119.3(2)
C(6A)–C(1A)–Te(1)	123.3(2)	C(6B)–C(1B)–Te(1)	122.7(2)
C(6C)–C(1C)–Te(2)	122.3(3)	C(6D)–C(1D)–Te(2)	122.0(2)

and bis(2-isopropyliminomethinylphenyl) telluride [2.720(2) Å] but less than that of bis[(N,N-dimethylamino)benzyl] telluride (3.048 and 3.134 Å)^{1e} where the nitrogen is in sp³ state. The Te⋯N distances are also higher than that in *p*-ethoxyphenyl-2-(2-pyridyl)phenyl telluride [2.695 (4) Å], an unsymmetric telluride, where the pyridine nitrogen interacts with Te.^{1d} The average Te–Cl bond lengths in **3** [Te(1)–Cl = 2.136 Å, Te(2)–Cl = 2.136 Å] relate well to that suggested by Pauling (2.14 Å).⁵

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Techniques used: NMR, X-ray diffraction

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Table 1: Crystal and structure refinement data for **3**

Table 2: Significant bond lengths and angles for **3**

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