Alkali Metal Tellurolates: Synthesis and X-Ray Crystal Structures of Monomeric Sodium and Potassium Tellurolates with Sterically Hindered Aryls

Philip J. Bonasia and John Arnold*

Department of Chemistry, University of California, Berkeley, CA 94720, USA

Incorporation of sterically encumbered aryl ligands permits the isolation and characterization of stable sodium and potassium tellurolates; X-ray structures of the monomers $[Na(tmed)_2][Te(2,4,6\text{-}Me_3C_6H_2)]$ and $[K(18\text{-}C\text{-}6)][Te(2,4,6\text{-}Pr^i_3C_6H_2)]$ are described (tmed = *N,N,N′,N′*-tetramethylethylenediamine; 18-C-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane).

The fundamental importance of metal complexes containing alkoxide (RO^-) and thiolate (RS^-) ligands is well documented.[1] In contrast, our knowledge of analogous chemistry with the heavier chalcogenide elements selenium and tellurium is quite limited.[2] Metal selenolate (RSe^-) and tellurolate (RTe^-) complexes have recently attracted attention as precursors to solid-state metal chalcogenides,[3] and as reagents in organic synthesis.[2,4]

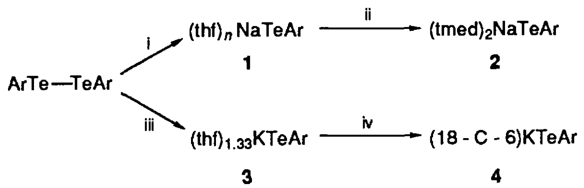
We believe the dearth of well characterized metal tellurolate complexes reflects a lack of suitable synthetic procedures. For alkoxides and thiolates, the most successful approach is a metathesis reaction between a transition metal halide and an alkali metal alkoxide or thiolate.[1c] For tellurolates,[5] however, this approach has been of limited scope since the literature contains only a single example of an isolable lithium tellurolate, the tri-t-butylphenyl derivative $[Li(thf)_3]$-

$[Te(2,4,6\text{-}Bu^t_3C_6H_2)]$ (thf = tetrahydrofuran).[5a] Corresponding sodium tellurolates, prepared *in situ* by reduction of ditellurides, have been known for many years[5d] and have found use in a wide variety of synthetic applications from the preparation of metal tellurolate complexes[6] to formation of carbon–tellurium bonds in organic synthesis.[4]

Hindered aryl ligands with bulky *ortho*-substituents have been gainfully employed in metal alkoxide and thiolate chemistry to prepare soluble monomeric and often highly reactive complexes.[1] The same rationale has now afforded stable, crystallographically characterized sodium and potassium tellurolates. Mesityltellurolate salts were readily isolated by slow cooling of saturated thf solutions prepared *via* the reduction route shown in Scheme 1.

Two equivalents of reducing reagent are consumed per equivalent of ditelluride with the end-point being signalled by an abrupt colour change from dark orange-red to pale yellow. Complex **1** was isolated in 70% yield as air-sensitive pale yellow crystals which rapidly crumbled to a powder on drying at room temperature, thereby precluding complete characterization. To circumvent this problem, crystals of the non-labile tmed† salt **2** were grown from saturated tmed–thf solutions (1 : 5). This material is much more stable, permitting full characterization‡ by NMR spectroscopy, elemental analysis and X-ray diffraction (see below).

Potassium salts were obtained by related methods (Scheme 1). Reduction of ditellurides with potassium tri-s-butylborohydride afforded high yields (typically in the range 70–80%) of the corresponding potassium salts. As an illustrative example, the triisopropylphenyl derivative **3** is quite stable in the solid state, crystallizing from thf with the empirical formula $[K(thf)_{1.33}][Te(2,4,6\text{-}Pr^i_3C_6H_2)]$ as confirmed by elemental analysis, ^1H NMR spectroscopy and X-ray crystallography.[7] Again, the coordinated thf is quite labile and is readily displaced on addition of crown ether (18-C-6) yielding the monomeric tellurolate **4**.



Scheme 1 *Reagents and conditions*: i, Na–Hg (2 equiv.) in thf, 20 °C; Ar = $2,4,6\text{-}Me_3C_6H_2$; ii, tmed (excess) in thf; iii, $KBBu^s_3H$ (2 equiv.) in thf, 20 °C; Ar = $2,4,6\text{-}Pr^i_3C_6H_2$; iv, 18-C-6 (1 equiv.) in thf

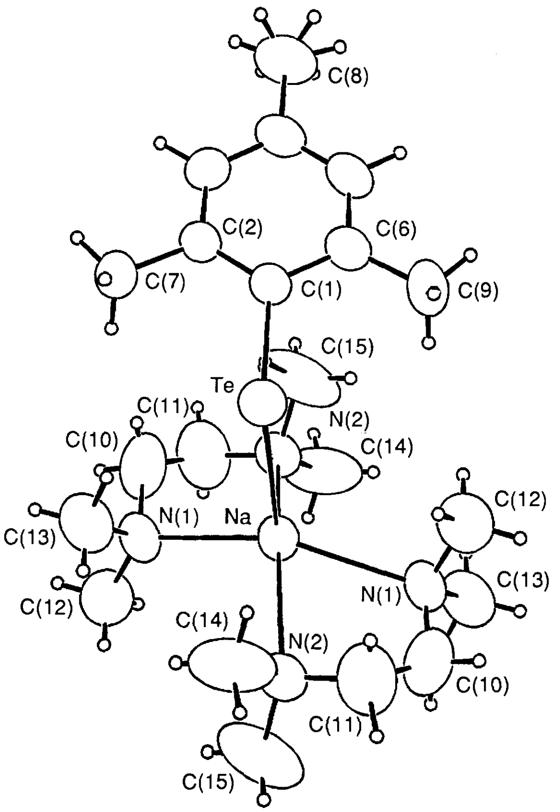


Fig. 1 Crystal and molecular structure of $[Na(tmed)_2][Te(2,4,6\text{-}Me_3C_6H_2)]$ **2**. Thermal ellipsoids depicted at 50% probability level. Selected distances (Å): Te–Na 3.494(3), Te–C(1) 2.135(5), Na–N (av.) 2.540(5). Selected bond angles (°): Na–Te–C(1) 102.26(5), Te–C(1)–C(2) 121.3(3), Te–C(1)–C(6) 120.3(4)

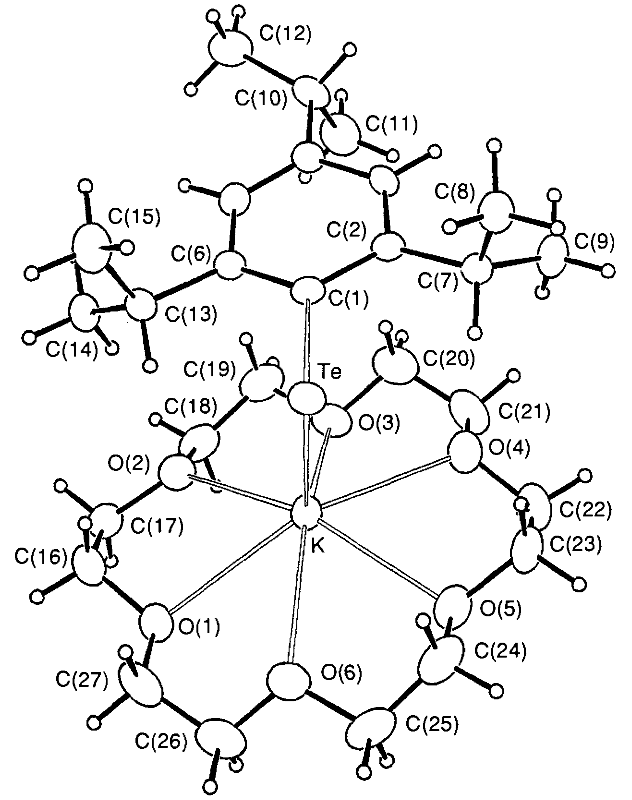


Fig. 2 Crystal and molecular structure of $[K(18\text{-}C\text{-}6)][Te(2,4,6\text{-}Pr^i_3C_6H_2)]$ **4**. Thermal ellipsoids depicted at 50% probability level. Selected distances (Å): Te–K 3.499(1), Te–C(1), 2.150(3), K–O (av.) 2.849(2). Selected bond angles (°): K–Te–C(1) 77.68(7), Te–C(1)–C(2) 120.6(2), Te–C(1)–C(6) 120.8(2)

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† *Abbreviations*: tmed = *N,N,N′,N′*-tetramethylethylenediamine; 18-C-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane.

‡ *Characterization data*: ^1H NMR: (300 MHz; 10^{-3} mol dm^{-3} in C_6D_6; 20 °C). For **2**: δ 6.85 (s, 2H, *m*-H), 2.83 (s, 6H, *o*-Me), 2.26 (s, 4H, tmed), 2.15 (s, 3H, *p*-Me), 2.07 (s, 6H, tmed).

For **3**: δ 7.13 (s, 2H, *m*-H), 4.26 (septet, *J* 7 Hz, 2H, *o*-C*H*Me$_2$), 3.54 (m, 3H, thf), 2.91 (septet, *J* 7 Hz, 1H, *p*-C*H*Me$_2$), 1.45 (d, *J* 7 Hz, 12H, *o*-CH*Me*$_2$), 1.39 (m, 3H, thf), 1.34 (d, *J* 7 Hz, 12H, *p*-CH*Me*$_2$).

For **4**: δ 7.13 (s, 2H, *m*-H), 5.05 (septet, *J* 7 Hz, 2H, *o*-C*H*Me$_2$), 3.11 (s, 24H, 18-C-6), 2.96 (septet, *J* 7 Hz, 1H, *p*-C*H*Me$_2$), 1.56 (d, *J* 7 Hz, 12H, *o*-CH*Me*$_2$), 1.40 (d, *J* 7 Hz, 12H, *p*-CH*Me*$_2$). All compounds were analytically pure.

The above procedures are quite general for a range of substituted aryls with varying degrees of steric bulk, and we have now isolated and characterized lithium, sodium and potassium derivatives with mesityl, triisopropylphenyl and tri-t-butylphenyl substituents.

These tellurolate salts can be stored indefinitely under nitrogen at ambient temperature; however, they are rapidly oxidized (in solution or the solid state) to the deep orange-red ditellurides on exposure to air. They serve as useful reagents for the preparation of transition metal tellurolates, details of which will be reported at a later date.[7]

X-Ray crystallography[§] provided valuable structural information on compounds **2** and **4** (Figs. 1 and 2). Both are monomeric with little evidence for interactions between molecules. [The Na(tmed)$_2$ unit is disordered about a crystallographic mirror plane containing the planar aryl ligand and the tellurium.] In both cases the relatively long M–Te distances suggest a fairly weak interaction between the alkali metal and the tellurolate anion. Thus, for **2**, d(Na–Te) = 3.494(3) Å and for **4** d(K–Te) = 3.499(1) Å. These data may be compared with bond lengths based on ionic radii of 3.16 Å for d(Na–Te) and 3.54 Å for d(K–Te).[8] Parameters associated with the tellurolate anions in both molecules are quite constant and the Te–C distances are identical within experimental error [av. = 2.143(5) Å]. The angles M–Te–Ar vary across a wide range from 102.26(5)° in **2** to 77.68(7)° in **4** suggesting that bonding between the alkali metal and tellurium is essentially non-directional. In the absence of more extensive data, we tentatively ascribe the remarkably acute K–Te–Ar angle in **4** to crystal packing forces.

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[§] *X-Ray structure determinations.* For **2**: $C_{21}H_{43}N_4NaTe$: space group $P2_1/m$ with $a = 8.712(2)$, $b = 15.579(2)$, $c = 9.787(2)$ Å, $\beta = 96.20(1)°$, $V = 1320.6(6)$ Å^3, $D_c = 1.26$ g cm^{-3}, $Z = 2$ and $T = -82$ °C. Data were collected on an Enraf-Nonius CAD-4 diffractometer at -85 °C with Mo-Kα ($\lambda = 0.709\,26$ Å) radiation. A 2θ range from 3 to 45° gave 1803 unique data. The structure was solved by Patterson methods and refined by least squares and Fourier techniques for 142 variables using 1469 observed data [$F^2 > 3\sigma(F^2)$], to give $R = 4.54\%$, $R_w = 5.23\%$ and GOF = 2.34. The aryl ligand and the Te atom lie in the crystallographic mirror plane at $y = \frac{1}{4}$ and so are constrained to be exactly planar. While there are Na atoms both above and below this plane in the average/disordered structure, for any given Te atom there is only one Na atom, either above or below. To prevent solvent loss the crystal was mounted under a film of Paratone-N as described in: H. Hope, in *Experimental Organometallic Chemistry*, eds. A. L. Wayda and M. Y. Darensbourg, American Chemical Society Symposium Series 357; Washington, 1987, p. 257.

For **4**: $C_{27}H_{47}KO_6Te$: space group $P\bar{1}$ with $a = 8.7134(9)$, $b = 10.273(2)$, $c = 19.323(2)$ Å, $\alpha = 75.30(1)$, $\beta = 80.31(1)$, $\gamma = 65.95(1)°$, $V = 1523.6(4)$ Å^3, $D_c = 1.38$ g cm^{-3}, $Z = 2$ and $T = -114$ °C. The structure was solved by Patterson methods for 316 variables using 3407 observed data [$F^2 < 3\sigma(F^2)$; 3980 unique], to give $R = 2.20\%$, $R_w = 2.58\%$ and GOF = 1.10. The crystal structures were determined by Dr. F. J. Hollander, staff crystallographer at the U. C. Berkeley Crystallographic Facility (CHEXRAY).

Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.