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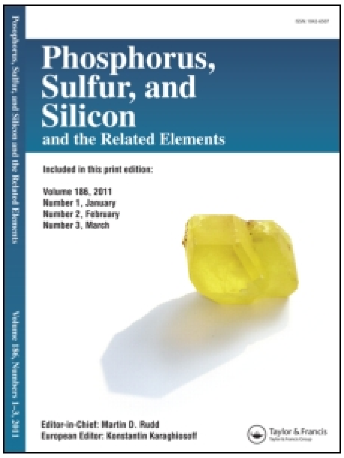

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SELENOCARBOXYLIC ACIDS AND THEIR ALKALI METAL SALTS: SYNTHESIS AND STRUCTURE

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A series of selenocarboxylic acids and their alkali metal salts were prepared. The potassium, rubidium and cesium salts are foundamentaly dimeric structure. Selenocarboxylic acids exist predominantly in selenon acid (selon acid) at low temperature in polar solvent. Selenocarboxylic acids readily react with aryl isocyanates to acyl carbamoyl selenides in good yields.

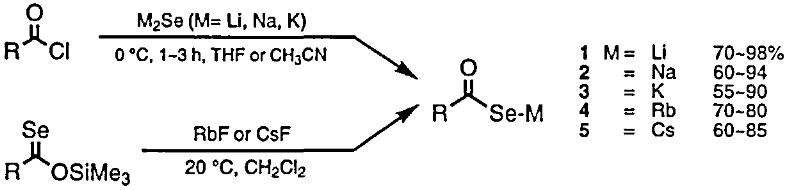
INTRODUCTION

The chemistry of carboxylic and thiocarboxylic acid derivatives has been extensively studied. In contrast, little is known about the chemistry of selenocarboxylic acid derivatives. This paper describes our finding regard to the chemistry of selenocarboxylic acid and its alkali metal salts.

1. Alkali metal selenocarboxylates

The first alkali metal selenocarboxylate was reported in1976 by Hirabayashi et al who synthesized potassium arenecarboselenoates by reacting diacyl selenides with potassium hydroxide.[1] These salts were, however, the green crystals containing a selenium element. We have developed a method for the direct preparation of lithium,[2] sodium,[3] and potasium salts[4] by reacting acyl chloride with the corresponding alkali metal selenide. Unfortunately this method can not be applied to rubidium and cesium selenocarboxylates. We have found that these salts can be obtained in moderate to good yields by reacting the corresponding *O*-trimethylsilyl selenoesters with rubidium and cesium fluorides.[5,6] (Scheme I)

SCHEME I



The resulting alkali metal selenocarboxylates are pale yellow micro solid or crystals. They are unstable toward oxygen. With regard to alkali metal, lithium, sodium and potasium appear to be less stable than rubidium and cesium. The carbonyl stretching frequencies shift to low frequency region in the order Na, K, Rb and Cs. Alkali metal cations do not appear to affect to the carbonyl carbon chemical shift, while the selenium signals show down field shift in the same order as for the carbonyl stretching frequencies.

ORTEP drawings of potassium and cesium 2-methoxybenzenecarboselenoate is shown in Figure I. These salts exibited a dimeric structure in which the ortho methoxy oxygen co-ordinates to the potassium of the opposite molecule. Similar dimeric structure can be observed for rubidium salts. The co-ordination number of these met-

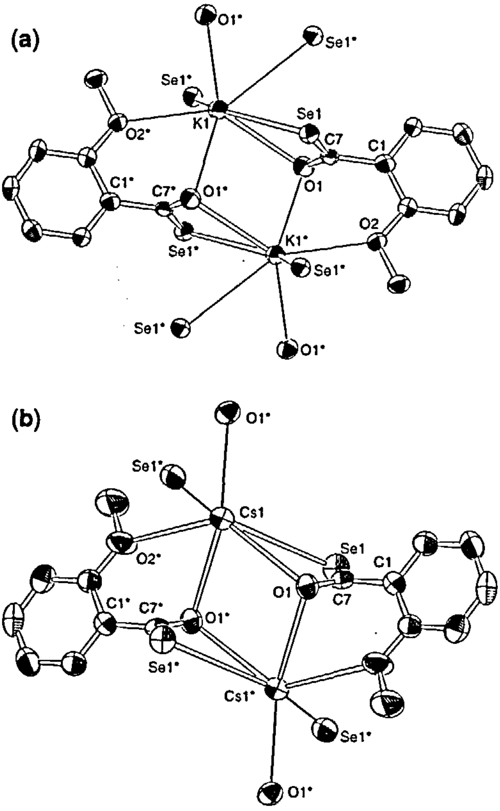
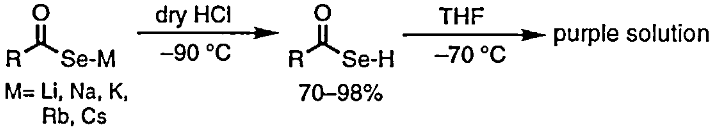


FIGURE I. ORTEP Drawings of Potassium (a) and Cesium 2-Methoxybenzenecarboselenoates (b) als are seven for K and Rb, and eight for Cs. The C–O and C(O)–Se bond lengthes of the selenocarboxyl group are 1.227–1.231 Å and 1.712–1.872 Å, respectively. The former is almost identical to those of common ester carbonyl and the later values are in the range of C–Se single bond length. This suggests the possibility of the localization of negative charge on the selenium atom.

2. Selenocarboxylic acids

The first synthesis of selenocarboxylic acid was reported in 1972 by Jensene and his co-workers who prepared selenobenzoic acid and observed SeH proton chemical shift at δ 2.38.[7] We also independently prepared the same acid by acidolysis of *O*-trimethylsilyl selenobenzoate with hydrogen chloride and observed νSe-H band at 2310 cm^{-1}.[8] However, their isolation had been hampered for long time, most likely due to the extreme instability. To isolate selenoacrboxylic acids, pure alkali metal selenocarboxylates was required. After several attempts at acidolysis of these alkali metal salts **2** with hydrogen chloride, we have succeeded in isolating a series of selenocarboxylic acids as yellow to reddish orange liquid or solid[9,10] (Scheme II). They are very unstable and quickly oxidized at room temperature to afford diacyl selenide and diselenide with liberating red selenium.

SCHEME II



In the IR spectra, νSeH and νC=O bands are observed at 2290–2360 and 1680–1740 cm^{-1}, respectively. The SeH proton, carbonyl carbon and selenium chemical shifts are observed at δ 2.08–4.75, 184–208 and 500–800 regions, respectively.

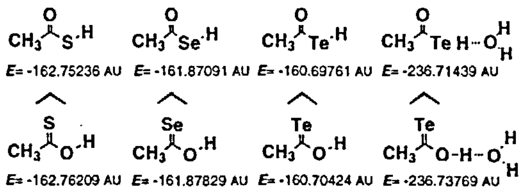
Interestingly when a polar solvent such as ether, tetrahydrofuran, methanol and acetone etc. was added to selenocarboxylic acids, the pale yellow or reddish orange of these acids immediately changed to purple. The IR and NMR spectra of these purple solutions do not show any signals due to the expected carbonyl and SeH groups. Instead, new signals attributable to the OH proton and the selenocarbonyl carbon and selenium were observed (Table I). Based on these spectral data, we determined that the structure of the purple compounds was selenocarboxylic OH-acid (selenon or selon acid). The notation that selon acid is more stable than the corresponding seleno acid was supported by a STO 3G molecular orbital calculation (Table II). As shown in the table, selonacetetic acid is 16 kJ/mol more stable than selenoacetic acid. A similar proximities can be observed for thio- and telluro-acetic acids.

TABLE I. Spectral Data of 4-Methoxyselenobenzoic acid

Solvent	Vis [nm]^a λmax	NMR [δ]^a ^1H	^{13}C	^{77}Se
$CDCl_3$		2.59 (SeH)	189.6 (C=O)	427.5
d_8THF	502 (n -π*)	15.40 (OH)	222.2 (C=Se)	754.0

^{a}–70 °C.

TABLE II. Themodynamic Stability of Monochalcogenocarboxylic Acids (STO-3G)



ΔE= 25.9 ΔE= 19.8 ΔE= 17.7 ΔE= 62.0 kJ/mole

ACKNOWLEDGEMENT

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