

Inorganic Chemistry

Alkali Metal Dithiocarbamato Carboxylates (DTCCs) – Synthesis, Properties, and Crystal Structures

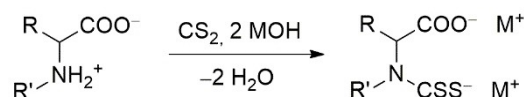
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A series of alkali metal salts of dithiocarbamate-substituted carboxylate (DTCC) anions were prepared by reaction of the parent amino acids with carbon disulfide and an alkali metal hydroxide. The target compounds, which were isolated in anhydrous form or as hydrates, were extensively characterized by elemental analyses, IR and NMR spectroscopy, thermal analyses, cyclic voltammetry, and single-crystal X-ray diffraction. The isolated compounds are more or less hygroscopic and display a varying dehydration and decomposition behavior upon heating. The assumed degradation of the DTCC scaffold was found to depend on the substitution pattern as well as on

the alkali metal counterion, and covers a range between 200 and 340 °C. In aqueous solution, the DTCC anions show irreversible electrochemical oxidations, where the corresponding redox potentials are governed by the substitution pattern of the nitrogen atom. Single-crystal structural analyses of sodium and potassium derivatives revealed that these compounds exist as two- or three-dimensional coordination polymers in the solid state, with the alkali-metal ions adopting typical irregular coordination environments with coordination numbers of six or higher.

Introduction

Dithiocarbamate-substituted carboxylates (DTCCs) are relevant in different fields of research, including biomedical chemistry^[1–3] and material sciences.^[4–6] Moreover, DTCC salts can be used as flotation agents for ore mining.^[7] In transition metal complexes, the dithiocarbamate group is usually coordinated to a late transition metal in a $\kappa S, \kappa S'$ -chelating mode, forming stable square-planar (Ni, Pd, Pt, Cu(II), Au(III)), octahedral (Co–Ir), or polynuclear (Cu(I), Ag(I), Au(I)) complexes.^[8] The carboxylate groups are attached to an oxophilic transition or main group metal ion,^[4–6,9] protonated,^[4,10–12] or esterified.^[1,2] Additionally, main group metal DTCCs are known, e.g. derivatives of β -, γ -, and δ -amino acids with tetravalent tin, in which both the O and S donor groups are metal-coordinated.^[13,14] DTCCs are readily available by allowing a primary or secondary amino carboxylic acid to react with carbon disulfide in alkaline environment (Scheme 1).^[4,8] Alkali



Scheme 1. General synthesis of alkali metal dithiocarbamato-carboxylates (DTCCs) as exemplified at an α -amino acid (R, R' = H or alkyl; M = alkali metal).

metal, alkaline-earth metal, or ammonium DTCC salts derived from natural α -amino acids have been reported throughout the 20th century.^[15,16] Even though these compounds are important intermediates for the preparation of metal complexes, they have been adequately characterized only in few cases. Among alkali metal DTCCs, the vast majority of known compounds are sodium and potassium derivatives, which have been isolated and characterized by NMR spectroscopy in only few studies.^[4,16–18] Lithium DTCCs have been mentioned only very briefly in the previous literature.^[7] With the exception of the sodium, potassium, rubidium, and cesium salts of *N*-dithioato-L-prolinate, none of these compounds has been structurally characterized in the solid state to the best of our knowledge.^[17,18] In order to obtain a detailed picture about alkali metal DTCCs, we report here the preparation and extensive characterization of Li, Na, and K salts of DTCC anions derived from selected amino acids. All compounds were characterized by IR and NMR spectroscopy as well as elemental analyses, and the solid-state structures of a series of compounds are reported. Moreover, we investigated the thermal decomposition and redox properties of the compounds by thermal analyses and cyclic voltammetry, respectively.

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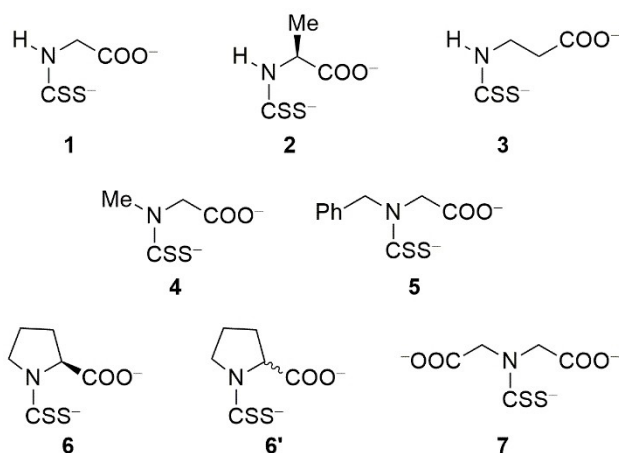
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Results and Discussion

The reaction of an amino acid with carbon disulfide and an alkali metal hydroxide to the corresponding DTCC according to Scheme 1 has been conducted previously in methanolic^[4,18,19] or in aqueous solution.^[16,17,20,21] Even though the reaction proceeds relatively slow in water due to the poor solubility of carbon disulfide, using this solvent led to ideal results in our hands. Running the reactions in water with stoichiometric amounts of metal hydroxide and 50% excess CS₂ led to the straightforward formation of the target products. Following this procedure, we prepared lithium, sodium, and potassium DTCCs derived from glycine (1), L-alanine (2), β-alanine (3), sarcosine (4), N-benzylglycine (5), L-proline (6), DL-proline (6'), and iminodi-



Scheme 2. DTCC anions which were investigated in the scope of this study: N-dithioato-glycinate (1), -L-alaninate (2), -β-alaninate (3), -sarcosinate (4), -N-benzylglycinate (5), -L-proline (6), -DL-proline (6'), and -iminodiacetate (7).

acetic acid (7) (Scheme 2). By extraction of the concentrated aqueous solutions with acetone, the products could be isolated as well-defined solid hydrates or in anhydrous form (Table 1). The isolated yields are very high (> 80%) in most cases. Only for 5-K·4H₂O the yield was comparatively low at 56%, which is most likely due to the better solubility of this compound in acetone. The yields for 4-K·2H₂O, 6-K·3H₂O,^[17] and 7-K are virtually quantitative and significantly higher than those reported earlier for the preparation of the same compounds in methanol/water (9:1).^[4] The lower isolated yields using methanol as a solvent, as also discussed by Frank earlier,^[16] are most likely due to the formation of the respective alkali metal methyl xanthate, M(SSC-OMe), as a by-product.^[4,22] The efficient isolation of the solid products from their aqueous solutions is particularly demonstrated with 1-Na, which has been isolated as a liquid trihydrate 1-Na·3H₂O without acetone extraction by Frank,^[16] and was now observed as a solid monohydrate 1-Na·H₂O. On the other hand, a series of N-dithioato-L-prolinates (6) has been previously reported by Tlahuext et al. and characterized as the anhydrous salts.^[18] This report seems questionable in the light of our results, as we identified the respective compounds as the hydrates 6-Li·4H₂O, 6-Na·H₂O, and 6-K·3H₂O.^[17] The specific amounts of crystal water were determined unambiguously through elemental analyses.

Some of the products are significantly hygroscopic, and particularly the lithium compounds 4-Li, 6-Li, and 7-Li showed some tendency towards CO₂ absorption and formation of Li₂CO₃. When stored under an inert atmosphere, all compounds are bench stable at ambient temperature. Thermal analyses under nitrogen revealed a diverse picture. Some hydrated compounds display one or more sharp decomposition steps between 100 and 200 °C, most likely associated with dehydration, whereas others show gradual mass loss within this temperature range (see Table 1 and the Supporting Informa-

Table 1. Isolated yields, and temperatures of decomposition of the title compounds (onset temperatures of the specific processes from TG diagrams; see the Supporting Information). T_{Desolv} represents the assumed release of crystal water, and T_{Degr} gives the assumed degradation of the DTCC scaffold.

Compound	Yield / %	$T_{\text{Desolv.}} / ^\circ\text{C}$	$T_{\text{Degr.}} / ^\circ\text{C}$
1-Na·H ₂ O	90	> 100 (undef.)	227
1-K	97	–	228
2-Na	90	–	201
2-K·1.25H ₂ O	94	96 and 167	202
3-Na·H ₂ O	91	109	234
3-K·H ₂ O	83	> 70 (undef.)	245
4-Li	99	–	247
4-Na·2H ₂ O	93	118	258
4-K·2H ₂ O	99 ^[a]	66 and 139	260 ^[c]
5-Na·4H ₂ O	88	> 100 (undef.)	238
5-K·4H ₂ O	56	123	259
6-Li·4H ₂ O	94 ^[b]	82 and 131	269
6-Na·H ₂ O	97 ^[b]	118	334
6-K·3H ₂ O	> 95 ^{[17] [b]}	67	337 ^[c]
7-Li·H ₂ O	100	–	> 100 (undef.)
7-Na·4H ₂ O	99	141	259
7-K	98 ^[a]	–	329 ^[c]

[a] Yields of previous preparation in methanol/water (9:1): 4-K·2H₂O 84%, 6-K·3H₂O 89%, 6-K 95%.^[4] [b] The corresponding racemic forms were prepared for comparison purposes and single-crystal X-ray structure analysis. Yields: 6'-Li·4H₂O 89%, 6'-Na·4H₂O 98%, 6'-K·4H₂O 96%. [c] These data deviate from previously reported data, which were estimated by the optical behavior of the compounds (melting, color change) and did not differentiate between the specific decomposition steps discussed here.^[4]

Table 2. Anodic (E_{pa}) and cathodic (E_{pc}) peak potentials (vs. Ag/AgCl) observed by cyclic voltammetry in 0.1 mol/l aqueous KCl solution at ambient temperature.

Compound	Oxidation (E_{pa} / V)		Reduction (E_{pc} / V)	
	1st	2nd	1st	2nd
1-K	+0.92			-0.54
2-K · 1.25H ₂ O	+0.74			-0.66
3-K · H ₂ O	+0.80			-0.58
4-K · 2H ₂ O	+0.53	+1.06	-0.28	-0.57
5-K · 4H ₂ O	+0.51	+1.08	-0.35	-0.67
6-K · 3H ₂ O	+0.55	+1.10		-0.76
7-K	+0.68	+1.13		-0.78
K(SSCNET ₂)	+0.49	+1.19		-0.66

tion). Decomposition at higher temperatures can certainly be attributed to the degradation of the DTCC scaffold, which is presumably initiated by elimination of CS₂.^[4] The corresponding temperatures are very different for the investigated compounds and cover a range between 200 and 340 °C. Following this assignment of the different decomposition steps, the thermally most stable DTCC anions are *N*-dithioato-L-prolinate (6) and *N*-dithioato-iminodiacetate (7). Generally, the DTCCs 4, 6, and 7, which are derived from secondary amines (sarcosine, L-proline, and iminodiacetic acid) are thermally more stable than 1–3, which are derived from primary amines (glycine, L-alanine, and β-alanine). This seems plausible in view of the presence of a reactive N–H moiety in 1–3. It is also less surprising that within a series of a specific DTCC anion the highest decomposition temperature was observed for the potassium compound, as it can be expected that the reactive dithiocarbamate group is ideally stabilized by soft K⁺ counterions. However, the decomposition temperatures of sodium derivatives are often very similar to their potassium analogs, and only the corresponding lithium derivatives are thermally significantly less stable. Compound 7-Li · H₂O shows an entirely undefined decomposition above 100 °C, which suggests that this compound cannot be dehydrated without decomposition.

The IR spectra of solid 1–7 display the bands of the respective DTCC anion and are very similar within a series of the same DTCC with different alkali metal cations (see the Supporting Information for the full spectra). Typical for the carboxylate group are one or two stretching vibrational bands, which were observed between 1630 and 1490 cm⁻¹. In contrast, bands of the dithiocarbamate moiety could not be assigned unambiguously. Beyond 3000 cm⁻¹, usually very broad bands addressed to hydrogen-bonded crystal water were observed. Only the spectra of 1-K and 3-K · H₂O display a sharp ν(N–H) band at 3326 or 3338 cm⁻¹, respectively.

All products 1–7 or their specific hydrates are very soluble in water and lower alcohols. The compounds are usually less soluble in acetone and diethyl ether. A remarkable exception is 5-K · 4H₂O, which is considerably soluble in acetone. In cases where literature data for ¹H and ¹³CNMR data are available, our NMR data are in good agreement with those.^[16,18] Generally, the ¹H and ¹³CNMR spectra of all compounds in D₂O display one signal set of the organic anion and are virtually identical within the series of a specific DTCC, suggesting the presence of

separated DTCC anions and hydrated M⁺ cations. This is also confirmed by the ⁷Li and ²³Na signals of the lithium and sodium compounds, which are very sharp and close to 0 ppm.^[23,24]

In order to study the redox properties of the compounds and their dependency on the ligand substitution pattern, cyclic voltammetry (CV) measurements of the potassium salts in aqueous KCl solution were performed. As a result, all DTCCs derived from secondary amino acids (4–7) show two irreversible oxidation peaks (E_{pa}) at ca. +0.5 V and +1.1 V (vs. Ag/AgCl; see Table 2 and the Supporting Information for the CV diagrams). These oxidation reactions can certainly be assigned to the dithiocarbamate group, as potassium *N,N*-diethyldithiocarbamate (a dithiocarbamate without carboxylate groups) revealed a similar electrochemical behavior. The first oxidation step can most probably be assigned to the formation of a thiuramdisulfide, a product which is readily formed by dithiocarbamate oxidation (Scheme 3a).^[25,26] The electrochemical oxidation of dithiocarbamates has been reported previously by Lieder, who discussed the electrochemical formation of dithiocarbamoyl radicals followed by dimerization to the thiuramdisulfide (EC mechanism).^[27] As potential products of further oxidation, tri- and tetrathian ions have been reported in the previous literature (Scheme 3b).^[25,28,29] For 1–3 (derived from primary amines), the first oxidation peak is significantly shifted to higher positive potentials (around +0.8 V in contrast to ca. +0.5 V for 4–6). This finding meets the expectation in

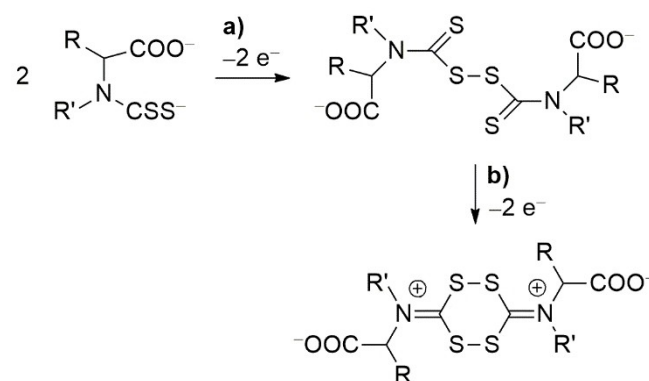
**Scheme 3.** Possible products of the electrochemical oxidation of DTCC anions (R, R' = H or alkyl): a) a thiuramdisulfide, b) a 1,2,4,5-tetrathian ion.

Table 3. Selected geometric parameters in the crystal structures of the reported compounds.

Compound	Coord. number of M ^[a]	M–S/pm	M–O(OC)/pm	Coord. mode of N-CSS [−]	Coord. mode of COO [−]
4-Na·2H ₂ O	Na1: 6 [S ₂ O ₄]	292.53(5) and 307.12(5)	236.95(7)–247.82(8)	κ ⁵ S,S':S:S:S	κ ⁴ O,O':O:O
	Na2: 6 [S ₂ O ₃]	297.25(5)–314.40(4)	232.83(8) and 242.48(8)		
4-K·2H ₂ O	K1: 6 [SO ₃ (η ³ -NCS)]	347.7(1) (σ) and 339.2(1) (π)	269.1(2) and 280.1(2)	κ ⁶ N,C,S:S':S':S'	κ ⁵ O,O':O:O:O'
	K2: 7 [S ₂ O ₅]	330.6(1) and 347.9(1)	274.7(2)–282.3(2)		
6'-Na·4H ₂ O	Na1: 7 [SO ₃ (η ² -CS)]	299.5(1) (σ) and 322.9(1) (π)	244.2(1) and 277.6(2)	κ ⁴ C,S:S:S	κ ⁵ O,O':O:O:O'
	Na2: 7 [SO ₆]	303.5(1)	232.4(2)–310.6(1)		
6'-K·4H ₂ O	K1: 7 [SO ₃ (η ² -CS)]	323.8(1) (σ) and 330.5(1) (π)	274.8(1) and 281.0(2)	κ ⁴ C,S:S:S	κ ⁵ O,O':O:O:O'
	K2: 7 [SO ₆]	318.1(1)	262.0(1)–306.1(1)		
6-K·3H ₂ O ^[17]	K1: 7 [O ₆ (η ³ -CSS)]	329.6(1) and 344.6(1) (π)	267.5(2)–335.8(2)	κ ⁶ C,S,S':S,S':S	κ ⁴ O,O':O:O'
	K2: 8 [S ₂ O ₅]	321.8(1)–346.6(1) (σ)	–		
7-K	K1: 5 [O ₆ (η ³ -CSS)]	329.6(1) and 344.6(1) (π)	265.1(2)–270.1(2)	κ ⁷ C,S,S':S:S:S:S'	κ ⁸ O,O':O,O':O:O:O':O'
	K2: 7 [SO ₆]	335.9(1)	273.4(2)–300.6(2)		
	K3: 8 [SO ₇]	333.8(1)	283.2(2)–316.0(3)	κ ¹⁰ C,S,S':S,S':S,S':S:S:S'	κ ⁸ O,O':O,O':O:O:O':O'
	K4: 7 [S ₂ O ₄ (η ³ -CSS)]	323.8(1) and 327.5(1) (σ)	268.4(3)–277.1(3)		
	K5: 7 [S ₂ O ₄]	346.6(1) and 346.8(1) (π)	–	–	–
	K6: 7 [S ₂ O ₄]	320.1(1)–358.7(1)	271.6(2)–282.9(3)	–	–
K6: 7 [SO ₆]	328.7(1)	272.6(2)–312.5(2)	–	–	

[a] A η²- or η³-coordinated group is counted as one ligating entity.

view of the electron-donating nature of the N-alkyl substituent in 4–7 instead of a hydrogen atom in 1–3, leading to the result that adjacent dithiocarbamate group is more easily oxidized in the former derivatives. For the same reason, for 1–3 the second electrochemical oxidation peak might be situated beyond the oxidation potential of water, that is, the corresponding oxidation products are presumably not redox-stable in water. At negative potentials, the CV curves display one or two irreversible reduction peaks (E_{pc} ; see Table 2 and the Supporting Information). These peaks can be most likely interpreted as the respective dimerized oxidation products are reduced back to the starting dithiocarbamate. Overall, the oxidation-reduction steps observed for the title compounds are electrochemically irreversible, even though we surmise that the oxidation of the dithiocarbamate group is chemically reversible.

Single crystals suitable for X-ray structural analyses were obtained for 4-Na, 4-K, 6'-Na, 6'-K, and 7-K directly from their aqueous solutions. Experimental details on structure determinations are summarized in Table S1 in the SI, and selected structural parameters are given in Table 3. In all compounds, both the carboxylate and the dithiocarbonate carbon atoms exhibit a typical trigonal-planar environment. The same applies to the dithiocarbamate nitrogen atom, which is therefore best described as sp²-hybridized. The C–O bond lengths within the carboxylate groups are almost identical, confirming the picture of predominantly ionic binding to the metal atoms, with the negative charge being efficiently delocalized over the O–C–O fragment. The same is true for the S–C–S fragment of the dithiocarbamate group. For both COO[−] and CSS[−], the interatomic distances correspond to a bond order between one and two (C–O: 125–126 pm; C–S: 171–173 pm).^[30]

Structure elucidation of the crystalline hydrates of the sarcosine-derived compounds 4-Na and 4-K revealed the presence of two equivalents of crystal water in both cases, which is identical with the water content of the isolated bulk products. In both 4-Na·2H₂O and 4-K·2H₂O, the asymmetric

unit contains one DTCC moiety and two alkali metal atoms. In 4-Na·2H₂O (Figure 1), both of the two crystallographically independent sodium atoms are six-coordinated. While Na1 is attached to two S atoms, three carboxylate O atoms and one μ-bridging H₂O ligand in a somewhat octahedral fashion, Na2 is bonded less symmetrically by three S atoms, two carboxylate O atoms and one terminal H₂O ligand. The dithiocarbamate group of the {SSC–N(Me)–CH₂COO}^{2−} anion is coordinated to four Na atoms, while the carboxylate group has three Na atoms as direct neighbors. In 4-K·2H₂O (Figure 2), one potassium atom in the asymmetric unit (K2) adopts an irregular seven-coordination by two S atoms, three carboxylate O atoms, and two μ-bridging H₂O ligands. Atom K1 is pseudo-six-coordinated by one S atom, two carboxylate O atoms, two μ-bridging H₂O ligands, and a π-coordinated S–C–N fragment of a dithiocarbamate group. Both the increase of the coordination number to values larger than six and an enhanced tendency towards π-

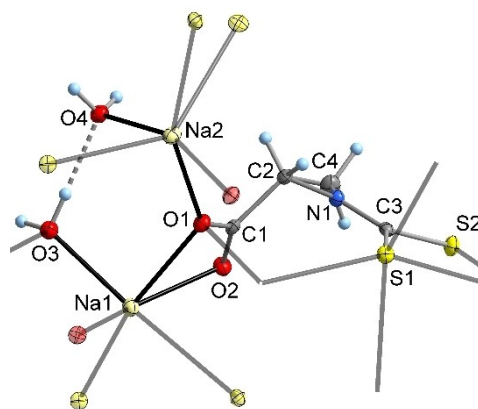


Figure 1. The asymmetric unit in the crystal structure of 4-Na·2H₂O, showing the atom numbering scheme as well as bonds to symmetry-equivalent atoms. Displacement ellipsoids are drawn at the 50% probability level, hydrogen atoms as spheres of arbitrary size.

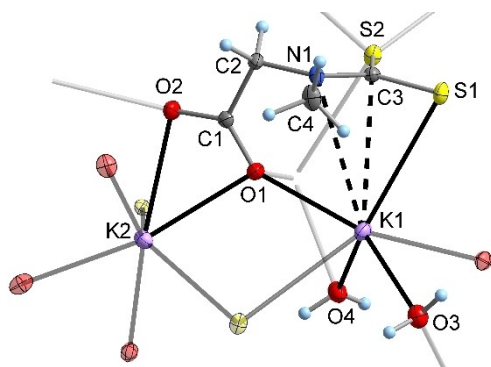


Figure 2. The asymmetric unit in the crystal structure of $4\text{-K}\cdot 2\text{H}_2\text{O}$, showing the atom numbering scheme as well as bonds to symmetry-equivalent atoms. Displacement ellipsoids are drawn at the 50% probability level, hydrogen atoms as spheres of arbitrary size.

coordination modes is typical for the heavier alkali metals.^[31] In spite of the different coordination patterns in $4\text{-Na}\cdot 2\text{H}_2\text{O}$ and $4\text{-K}\cdot 2\text{H}_2\text{O}$, both compounds form two-dimensional polymeric

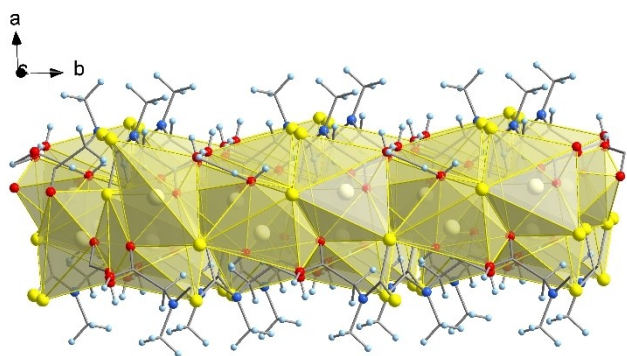


Figure 3. 2D polymeric structure of $4\text{-Na}\cdot 2\text{H}_2\text{O}$ (a), viewed in a projection on (0 0 1). The layer extends parallel to (1 0 0).

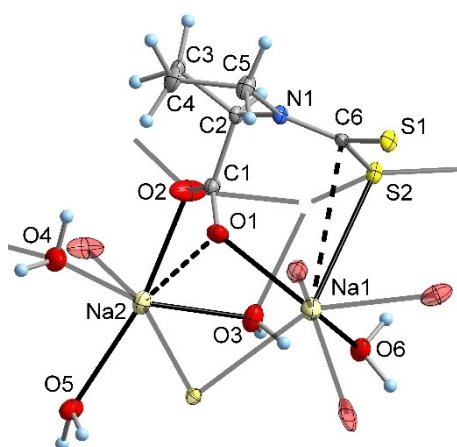


Figure 4. The asymmetric unit in the crystal structure of $6'\text{-Na}\cdot 4\text{H}_2\text{O}$, showing the atom numbering scheme as well as bonds to symmetry-equivalent atoms. Displacement ellipsoids are drawn at the 50% probability level, hydrogen atoms as spheres of arbitrary size.

structures in the solid state, with the apolar methyl groups being situated at the surface of the layers (Figure 3).

The DL-proline-derived compounds $6'\text{-Na}$ and $6'\text{-K}$ crystallize isotypically as tetrahydrates (Figures 4 and 5). It is worth mentioning that the enantiopure compound 6-K , whose solid-state structure has been reported previously, crystallized as a trihydrate.^[17] In compounds $6'\cdot 4\text{H}_2\text{O}$, for one of the two metal atoms in the asymmetric unit (Na1 or K1) a distorted octahedral six-coordination is realized by one S atom, two carboxylate O atoms, and three H_2O ligands. For Na2 or K2, respectively, the coordination is increased to an irregular seven-coordination, formed by two S atoms, two carboxylate O atoms, and three H_2O ligands. However, in the case of $6'\text{-Na}\cdot 4\text{H}_2\text{O}$ one Na–O contact is very long at 310.6(1) pm (Na2–O1), and therefore the coordination can also be described as a “6+1” coordination. While one of the two S-donating groups is coordinated in typical “end-on” orientation, the other sulfur group is attached to the metal center in a “side-on” orientation, thus being best described as η^2 -type π -coordination of the corresponding C=S fragment. Despite the different environment of the two sulfur atoms of the dithiocarbamate group, the C–S bond lengths differ only marginally between non-coordinated ($6'\text{-Na}\cdot 4\text{H}_2\text{O}$: C6–S1 172.6(2) pm; $6'\text{-K}\cdot 4\text{H}_2\text{O}$: C6–S2 172.9(2) pm) and metal-coordinated ($6'\text{-Na}\cdot 4\text{H}_2\text{O}$: C6–S2 171.2(2) pm; $6'\text{-K}\cdot 4\text{H}_2\text{O}$: C6–S1 170.5(2) pm) sulfur atoms. The COO^- group in the two compounds $6'\cdot 4\text{H}_2\text{O}$ is coordinated to a total of four metal atoms, while is only three metal atoms for the N-CSS[−] group. In the closely related compound $6\text{-K}\cdot 3\text{H}_2\text{O}$, a η^3 -CSS coordination has been seen, and the COO^- group connects only three instead of four K^+ ions.^[17] Similar as for the sarcosine-derived compounds $4\text{-Na}\cdot 2\text{H}_2\text{O}$ and $4\text{-K}\cdot 2\text{H}_2\text{O}$ as well as for $6\text{-K}\cdot 3\text{H}_2\text{O}$,^[17] two-dimensional infinite layer structures exist in the solid-state structures of $6\text{-Na}\cdot 4\text{H}_2\text{O}$ and $6\text{-K}\cdot 4\text{H}_2\text{O}$.

The iminodiacetic-derived compound 7-K , which crystallizes from aqueous solution in anhydrous form, exhibits a highly complex 3D network structure with two $\{\text{SCC-N}(\text{CH}_2\text{COO})\}_2^{3-}$ anions and six K^+ cations in the asymmetric unit (Figure 6). Five out of these metal ions adopt coordination numbers larger

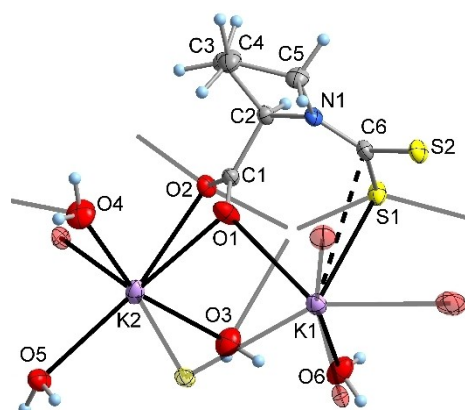


Figure 5. The asymmetric unit in the crystal structure of $6'\text{-K}\cdot 4\text{H}_2\text{O}$, showing the atom numbering scheme as well as bonds to symmetry-equivalent atoms. Displacement ellipsoids are drawn at the 50% probability level, hydrogen atoms as spheres of arbitrary size.

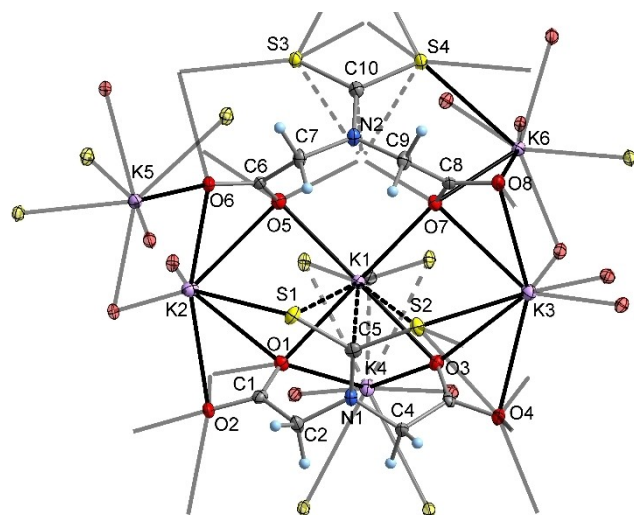


Figure 6. The asymmetric unit in the crystal structure of **7-K**, showing the atom numbering scheme as well as bonds to symmetry-equivalent atoms. Displacement ellipsoids are drawn at the 50% probability level, hydrogen atoms as spheres of arbitrary size.

than six, which is realized by highly bridging coordination modes of the dithiocarbamate and carboxylate groups (at least seven K^+ ions per $N\text{-CSS}^-$ and six K^+ ions per COO^- group; Figure 7). Both dithiocarbamate groups in the asymmetric unit display η^3 -type π -coordination of the CSS fragment, while the coordination of the carboxylate groups is restricted to chelating and non-chelating σ -coordination modes. The coordination patterns of the dithiocarbamate group to the respective alkali metal ions observed for the reported compounds are characteristic and have been observed previously for other dithiocarbamates,^[32–35] as well as for related dithiocarbonates.^[22]

As it is typical for the alkali metals which prefer usually ionic bonding in their compounds, both the $M\text{-S}$ and the $M\text{-O}$ distances cover wide ranges (see Table 3. For the sodium salts, the Na-O separations are in ranges of 232.83(8)–247.82(8) pm (**4-Na**·2H₂O) and 232.4(2)–310.6(1) pm (**6'-Na**·4H₂O). The relatively long bonds in the DL-proline derivative can be addressed to the metal's high coordination number of seven, whereas the two Na^+ cations are only six-coordinated in the

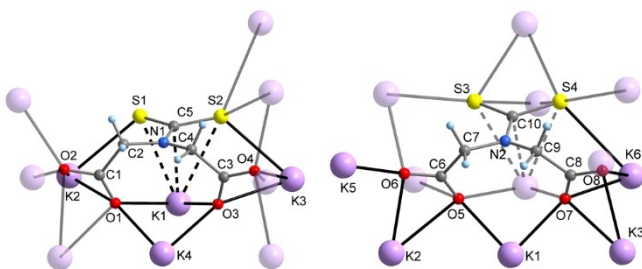


Figure 7. Illustration of the coordination environment of the two crystallographically independent $\{\text{SSC-N}(\text{CH}_2\text{COO})_2\}^{3-}$ ligands in **7-K**.

sarcosine derivative. A similar trend is seen with the Na-S distances, being 292.53(5)–314.40(4) pm for **4-Na**·2H₂O and 299.5(1)–322.9(1) pm for **6'-Na**·4H₂O. Thereby, the longest Na-S contact is that to the π -coordinated dithiocarbamate group. All the observed Na-O and Na-S bond lengths are within the ranges reported for related compounds deposited in the Cambridge Structural Database (CSD).^[36] For the potassium salts, a less clear dependency of the bond lengths on the coordination number was observed. The K-O distances in **4-K**·2H₂O, **6'-K**·4H₂O and **7-K** are all in a range of 262.0(1)–316.0(3) pm. Similarly, for the K-S separations no systematic dependency on the coordination mode of the ligating group was observed, as the intervals of interatomic distances are comparable for σ -coordinated (318.1(1)–358.7(1) pm) and π -coordinated (329.6(1)–346.8(1) pm) sulfur groups. Similar values of K-O and K-S distances have been observed in the previously reported **6-K**·3H₂O,^[17] as well as in related potassium compounds deposited in the CSD.^[36]

Conclusion

Summarizing the results reported here, we investigated the synthesis and properties of lithium, sodium, and potassium salts with different dithiocarbamate-carboxylate (DTCC) anions, in order to reveal a complete picture of this widely useful class of compounds. As a result, we have seen that among the different alkali metals the potassium salts are usually most easily handled and thermally most stable. This finding is less surprising and in agreement with the fact that K salts have been frequently used in past studies. However, we have shown that also the sodium and lithium salts are potentially interesting for future studies due to their different properties. Single-crystal structure elucidation disclosed the first two crystal structures of sodium DTCCs to the best of our knowledge, and three more entries of potassium DTCCs in addition to the one structure which has been reported earlier.^[17,18] These results reflect the typical coordination-chemical properties of the alkali metals, where steric saturation by ligands is more important than defined coordination polyhedra.^[31] Increasing coordination numbers and a rising tendency towards π -coordination modes (including rather unusual binding including the dithiocarbamate nitrogen atom) in going from Na to K were also seen and are typical for this series of metals. The same applies for the decreasing tendency of hydrate formation in going from the lighter to the heavier alkali metals. The fact that some potassium derivatives could readily be isolated in anhydrous form (as seen with **1-K** and **7-K**) or can be dehydrated without decomposition by heating makes these compounds particularly interesting as starting materials for synthesis under anhydrous conditions. For solubility issues, such syntheses are often limited to lower alcohols. However, it was shown that the introduction of large organic substituents such as benzyl, as it was illustrated by the acetone-soluble *N*-benzylglycine derivative **5-K**, opens pathway for reactions in aprotic media. The selection of amino acids in the scope of this study allowed for the comparison of DTCCs derived from amino acids having primary (NH_2) and secondary (N-H) amino groups, α - and β -

amino acids, as well as aminomono- and aminodicarboxylic acids. As a result, we have seen that the DTCC anions derived from secondary amino acids are thermally more stable than those derived from primary amino acids. In contrast, cyclic voltammetry disclosed that the DTCCs derived from primary amino acids are more redox stable, that is, they are electrochemically less easily oxidized than those derived from secondary amino acids. The latter finding does not necessarily mean that metal compounds with such DTCC anions or ligands are thermodynamically generally more stable than their secondary-amine analogs, since the reactive N–H moiety opens pathways for other potential decomposition reactions.^[37,38] Regarding the comparison of α - and β -amino acid-derived DTCCs, an increasing distance between the functional groups within the molecule might result in an increased thermal stability, as it was seen with the β -alanine derivatives 3.

Supporting Information Summary

The Supporting Information file (PDF) contains the full experimental procedures, IR and NMR spectra, TG and CV diagrams, and details in the single-crystal X-ray structural analyses.

Deposition numbers 2100764 (for 4-Na·2H₂O), 2100765 (for 4-K·2H₂O), 2100766 (for 6'-Na·4H₂O), 2100767 (for 6'-K·7H₂O), and 2100768 (for 7-K) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Center and Fachinformationszentrum Karlsruhe. <http://www.ccdc.cam.ac.uk/services/structures>

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: amino acid · crystal structure · cyclic voltammetry · dithiocarbamate · thermal analysis

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