

Synthesis and characterisation of the potassium 1,1-dithiolate $C_{12}H_{20}N_2S_2K_2$: a novel $K_{12}S_{12}$ cluster compound

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The carbene adduct **1 reacts with potassium to give the potassium 1,1-dithiolate **2**; its tetrahydrofuran adduct exhibits a cage structure consisting of a hexagonal K_6S_6 prism incorporated into a twelve-membered K_6S_6 ring connected both by direct K–S bonds and vinylidene type bridges.**

Organoalkali-metal compounds are generally made up of ring- and ladder-type fragments.¹ Although a limited number of one- and multi-dimensional ladder structures have been identified for potassium thiolates,² compounds of this class containing ring fragments were previously unknown.

By reduction of the carbene adduct **1**³ with potassium in tetrahydrofuran we have now obtained† the potassium 1,1-dithiolate **2** as a yellow air-sensitive solid. A single-crystal X-ray structural analysis‡ of the solvate complex $2 \cdot 2C_4H_8O \cdot 1/3K_2S_2$ revealed the presence of a hexagonal prism with the composition K_6S_6 as the central unit surrounded by a twelve-membered K_6S_6 ring consisting of alternating potassium and sulfur atoms (Fig. 1). Hexagonal prisms have frequently been observed in

Li_6X_6 compounds ($X = C, N, O, Si, Te$)¹ but for potassium they have to date only been realised in a single structure with a K_6O_6 core.⁴ Previously, hexagonal prisms of the M_6S_6 type were only known in the chemistry of the transition metals.⁵ Of the two sulfur atoms of each dithiolate ligand, one is part of the twelve-membered ring while the second sulfur atom is incorporated into the hexagonal prism. Therefore, the rings and the prisms are connected both through vinylidene bridges and direct K–S bonds. The observed potassium–sulfur contacts (3.023–3.308 Å) are in the expected range. In the hexagonal prism, alternating K–S bond lengths are observed [K(1)–S(1a) 3.023(3), K(1)–S(1b) 3.192(3) Å] for the six-membered rings. Their mean value corresponds well both to the distance of the two six-membered rings in the prism [K(1)–S(1) 3.107(4) Å] as well as to the K–S bond lengths of the surrounding K_6S_6 ring [K(2)–S(2) 3.115(3), K(2)–S(2b) 3.098(3) Å]. The longest K–S distance is observed for the connection of the K_6S_6 ring and prismatic fragments [K(2)–S(1) 3.308(5) Å]. In comparison to the metal structure,⁶ the metal–metal separations are, in part, shortened by up to 0.75 Å and for K(1)–K(2) (3.937 Å) reach the calculated and observed bond lengths for K_2 .⁷ Even under the aspects of electrostatic K–S interactions,⁸ however, such a close approach is not unusual.⁹

A comparison of the 1,1-dithiolate fragment in **2** (Fig. 2) with the structure of the carbene adduct **3**³ reveals a markedly changed distribution of the π electrons; the coplanar orientation of the CS_2 fragment in **2** to the five-membered ring, the significant shortening of the C(1)–C(2) bond [1.375(13) Å] by about 0.12 Å in comparison to that of **3**, and the lengthening of the C–S bonds [C(12)–S(1) 1.803(8) Å, C(12)–S(2) 1.764(11) Å] by the same order of magnitude are all indications of the presence of an exocyclic C–C double bond in **2**. This is further substantiated by the relative widening of the angle N(1)–C(1)–

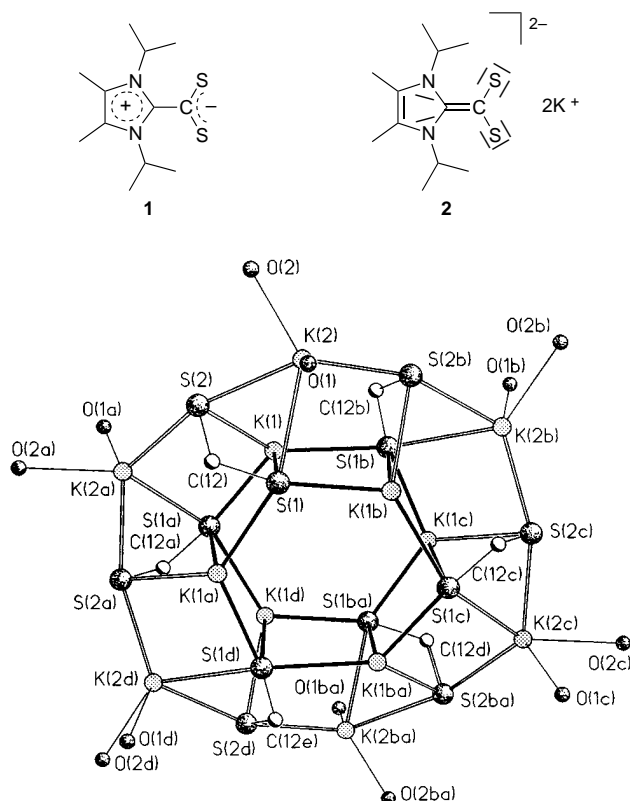


Fig. 1 The $K_{12}S_{12}O_{12}$ core in crystals of $2 \cdot 2C_4H_8O \cdot 1/3K_2S_2$. Selected bond lengths (Å): K(1)–K(2) 3.937(4), K(1)–K(1a) 4.105(4), K(1)–K(1b) 4.105(4), K(1)–K(2a) 4.212(4), K(1)–S(1) 3.107(4), K(1)–S(2) 3.193(4), K(1)–S(1a) 3.023(3), K(1)–S(1b) 3.192(3), K(2)–S(1) 3.308(5), K(2)–S(2) 3.115(3), K(2)–K(2b) 3.098(3), K(2)–O(1) 2.782(13), K(2)–O(2) 2.810(13).

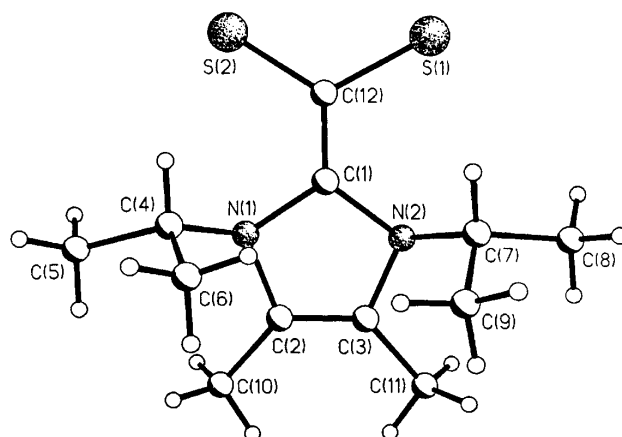
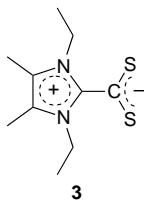
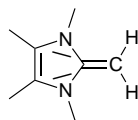


Fig. 2 The structure of the 1,1-dithiolate anion in crystals of $2 \cdot 2C_4H_8O \cdot 1/3K_2S_2$. Selected bond lengths (Å) and angles (°): C(1)–C(12) 1.375(13), C(12)–S(1) 1.803(8), C(12)–S(2) 1.764(11), C(1)–N(1) 1.455(10), N(1)–C(2) 1.454(15), C(2)–C(3) 1.310(16), C(3)–N(2) 1.428(11), N(2)–C(1) 1.428(15); S(1)–C(12)–S(2) 117.6(5), S(1)–C(12)–C(1) 118.0(8), S(2)–C(12)–C(1) 124.4(7).



3



4

N(2) [109.3(7)°] and, above all, by the marked contraction by around 12° of the angle S(1)–C(12)–S(2) [117.6(5)°]. The ethylene structure causes a strong steric interaction between the isopropyl substituents and the sulfur atoms which results in a pronounced protrusion of the carbon atoms C(4) and C(7) by 1.112 and 1.023 Å, respectively, out of the plane defined by the five-membered ring. As a consequence from steric hindrance, the methyl protons of the isopropyl substituents appear as two broad signals in the NMR spectrum. We consider this reorientation of the CS₂ fragment upon reduction of the carbene adduct (in **3** the planes of the ring and the CS₂ fragment are perpendicular to each other) to be in a causal relationship with the quasireversibility that can be recognized in cyclic voltammetric studies.¹⁰ It certainly proceeds in concert with the electron transfer and increases the activation barrier. The close analogy to the structure of the methyleneimidazoline **4**,¹¹ which reacts similarly to an ylide, excludes the take-up of π-electron density by the five-membered ring as is typical for conventional 1,1-dithiolates and makes the electronic argument for the bending of the isopropyl groups (sp³ hybridisation of the nitrogen atoms) less favourable.

The geometry of **2** is indicative of a bonding situation that can be interpreted with regard to the electron distribution as an 'unpolarisation' in comparison to conventional 1,1-dithiolates. We will report elsewhere on the results of cyclic voltammetry and the chemical properties of **2** which all support this hypothesis.

Footnotes

† All reactions were performed under anaerobic and anhydrous conditions; **1** was prepared by a published procedure.³

To a suspension of 1.026 g (4 mmol) **1** in 30 ml tetrahydrofuran 0.20 g (5.12 mmol) potassium were added. The mixture was stirred for 16 h at room temperature. After separation of excess potassium and reducing to a small volume *in vacuo*, 30 ml diethyl ether were added. The resulting yellow solid was filtered off and washed three times with 20 ml of diethyl ether to give 1.562 g (81%) C₂₀H₄₀K₂N₂O₂S₂ (2·2Et₂O), identified by potassium and sulfur analysis. ¹H NMR (250 MHz, [²H₈]tetrahydrofuran, SiMe₄ ext.): δ 4.74 [m, 2 H, CH(CH₃)₂], 1.72 [s, 6 H, 4,5-CH₃], 1.24, 1.05 [2 br s, 12 H, CH(CH₃)₂]; in addition, signals at δ 3.38 (q) and 1.10 (t) are observed arising from 2 equiv. of Et₂O. The compound decomposes readily in polar solvents like acetone and acetonitrile. At ca. 90 °C, potassium sulfides and unidentified organic compounds are formed. Crystals of 2·2C₄H₈O·1/3 K₂S₂ have been obtained by slow evaporation of a tetrahydrofuran solution of 2·2Et₂O.

‡ Crystal data for C₂₀H₃₆K_{2.667}N₂O₂S_{2.667} (2·2C₄H₈O·1/3K₂S₂), *M* = 526.27, trigonal, space group *P*3̄, *a* = 19.145(8), *c* = 13.753(6) Å, *U* = 4365.55 Å³, *Z* = 6, *D*_c = 1.201 g cm⁻³, μ(Mo-Kα) = 0.63 mm⁻¹, Siemens P4RA four-circle diffractometer, rotating anode generator, Mo-Kα radiation (λ = 0.71073 Å), graphite monochromator, scintillation counter, *T* = 150 K, empirical absorption corrections; direct methods, full matrix least-squares refinements, non-hydrogen atoms anisotropic, H atoms at idealized positions, one common isotropic temperature factor for H within each residue, one extinction parameter, one scaling factor; transmission range 0.714–0.516, 2θ_{max} = 48°, ω scan, crystal dimensions ca. 0.75 × 0.65 × 0.21 mm, 3556 unique reflections, *R*(*R*_w) = 0.0884 (0.0857) for 2358 reflections with *I* > 2σ(*I*), 287 variables. The atomic displacement parameters indicate a possible disorder of the C₄H₈O molecules which could not be resolved in terms of a physically meaningful superposition. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/383.

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