

Fig. 2. A projection of the structure viewed along the *c* axis.

The sugar is associated with an *anti* glycosidic bond rotation. This conformation does not involve notable sugar–base atomic contacts. This is in contrast to the crowded atomic arrangement around the glycosidic bond found in a pyrimidine nucleotide of similar conformation (Sato, 1984*a*). The conformations about the C(4′)–C(5′) and C(5′)–O(5′) bonds are *trans-gauche* and *trans*, respectively.

The bond distances of the adenine base are in agreement (within 0.013 Å) with the ‘standard’ values derived for the neutral form (Taylor & Kennard, 1982). The atoms in the purine ring are coplanar to within 0.019 Å. The glycosidic bond is 0.025 Å shorter than that of 2′-deoxyadenosine (Sato, 1984*b*). This may be due to changes in the sugar puckering and/or in the glycosidic bond rotation (Lo, Shefter & Cochran, 1975). The bond shrinkage seems to be correlated with an elongation (0.020 Å) of the O(4′)–C(1′) bond.

The packing scheme in the crystal is shown in Fig. 2. The ionic groups and the water molecules are arranged close to each other, and form a layer parallel to the *ac* plane, each layer separated from the other by another layer consisting mainly of stacked adenine bases. All

available H atoms participate in intermolecular hydrogen bonds. Among them, N(6)–H(2)⋯O(4′) [N⋯O 3.001 (2), H⋯O 2.27 (3) Å] is noticeable, because, for most cases, the ring oxygen O(4′) does not participate in hydrogen-bond formation. The Ca²⁺ ion is surrounded by seven O atoms [O(1P), O(1P′), O(2P), O(2P′′), O(W1), O(W2) and O(W3)] at distances ranging from 2.302 (2) to 2.581 (2) Å. Apart from those stated above, there are no notable short intermolecular contacts.

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Dipotassium Salt of 3-Hydroxy-4-mercapto-2-thioxo-3-cyclobuten-1-one Dihydrate (Potassium 1,3-Dithiosquarate Dihydrate), K₂[C₄O₂S₂].2H₂O, at 140 K

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Abstract. $M_r = 258.4$, monoclinic, $P2_1/c$, $a = 7.309$ (2), $b = 8.404$ (3), $c = 8.120$ (3) Å, $\beta = 112.6$ (3)°, $V = 460.6$ Å³, $Z = 2$, $D_m = 1.82$, $D_x = 1.86$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 1.43$ mm⁻¹,

$F(000) = 240$. Final $R = 0.026$ for 945 independent observed reflections. The planar 1,3-dithiosquarate dianion is situated on an inversion center; the lengths of the C–C bonds are 1.463 (2) and 1.467 (2) Å. The

Table 1. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters (\AA^2) with *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}^*/B_{\text{iso}}$
K	8769.6 (5)	1556.7 (4)	2713.2 (4)	1.26 (2)
S	5038.5 (5)	3863.7 (5)	3138.0 (5)	1.28 (2)
O(1)	8265 (2)	4422 (1)	843 (1)	1.22 (4)
O(2)	1157 (2)	1650 (2)	625 (2)	1.76 (5)
C(1)	6489 (2)	4744 (2)	391 (2)	1.02 (6)
C(2)	5029 (2)	4557 (2)	1205 (2)	1.02 (6)
H(1)	2024 (38)	2360 (35)	1233 (36)	4.3 (6)
H(2)	1679 (34)	890 (41)	617 (36)	4.3 (7)

* $B_{\text{eq}} = (B_{11} \cdot B_{22} \cdot B_{33})^{1/3}$ for non-H atoms.

C—O and C—S bond distances are 1.236 (2) and 1.672 (2) \AA respectively. Potassium is seven-coordinated by two S atoms [distances 3.469 (1) and 3.445 (1) \AA] and five O atoms [mean distance 2.795 (1) \AA].

Introduction. The planar anions with the general formula $\text{C}_n\text{O}_n^{2-}$ are called 'oxocarbons' and have been the subject of many investigations (Schmidt, 1980; Seitz, 1980). Substitution of one or more of the O atoms by heteroatoms like S or N leads to the so-called 'pseudooxocarbons' (Fatiadi, 1980). Oxocarbons and pseudooxocarbons show interesting chemical and electronic, even aromatic properties. In the homologous series $[\text{C}_4\text{O}_{4-n}\text{S}_n]^{2-}$ only the structures with $n = 0$ (Macintyre & Werkema, 1964) and $n = 4$ (Allmann, Debaerdemaeker, Mann, Matusch, Schmiedel & Seitz, 1976) are known so far. The present investigation was undertaken to determine the bonding properties and the degree of electron delocalization in a less symmetrical oxocarbon compound. According to a recent structure determination the two isomeric bis(amides) of dithiosquaric acid, 3,4-di-1-pyrrolidinyl-3-cyclobutene-1,2-dithione (1,2-DTSA) and 2,4-di-1-pyrrolidinyl-3-thioxocyclobutenylium-1-thiolate (1,3-DTSA) contain the planar $\text{C}_4\text{N}_2\text{S}_2$ group with ten π -electrons which are mainly delocalized (Mattes, Altmepfen, Johann, Schulte-Coerne & Weber, 1982).

Experimental. $\text{K}_2[\text{C}_4\text{O}_2\text{S}_2-1,3] \cdot 2\text{H}_2\text{O}$ synthesized according to literature (Seitz, Mann, Schmiedel & Matusch, 1979). Single crystals by slow crystallization from water/ethanol (1:1); density from flotation in $\text{CCl}_4/\text{CBr}_4$; crystal of size 0.3 \times 0.25 \times 0.15 mm in Lindemann tube employed for data collection; Syntex $P2_1$ four-circle diffractometer, graphite monochromator, $\text{Mo K}\alpha$ radiation. Cell dimensions obtained by least squares from 13 reflections ($12 < \theta < 19^\circ$); no absorption correction applied. Intensities of 1085 reflections with $2\theta < 54^\circ$ measured; one standard reflection every 100 reflections, variation less than 2% about its mean; $0 \leq h \leq 9$, $0 \leq k \leq 10$, $-9 \leq l \leq 9$; 945 independent reflections with $I > 1.96\sigma(I)$ considered observed and used in structure determination, 62 unobserved

reflections. Structure solved by direct methods, full-matrix refinement with non-H atoms and anisotropic temperature factors, weighting scheme $w^{-1} = \sigma(F_o) + (0.02F_o)^2$. H atoms from difference synthesis, refined isotropically. Final $R = 0.026$, $R_w = 0.034$ with 63 parameters. Max. and min. height in final difference map 0.26 and -0.35 e \AA^{-3} respectively. Max. least-squares (on F) shift in the last cycle $< 0.1\sigma$. Programs and scattering factors as in the Syntex (1976) *XTL/XTLE* program system used for all calculations.

Discussion. Final positional parameters are given in Table 1,* calculated bond lengths and bond angles in Fig. 1. Fig. 2 shows the packing of the structure. The 1,3-dithiosquarate anion is situated on a crystallographic inversion center and has a highly symmetrical structure. All atoms of the $\text{C}_4\text{O}_2\text{S}_2$ moiety lie within 0.007 \AA in a plane. The difference in the bond lengths between the two nonequivalent C—C bonds is less than 3σ . The planar structure and the individual bond lengths show an extensive delocalization of the π density over the whole anion. The C—C bond lengths fit

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39152 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

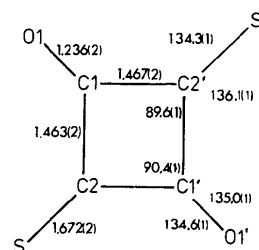


Fig. 1. Interatomic distances (\AA) and bond angles ($^\circ$).

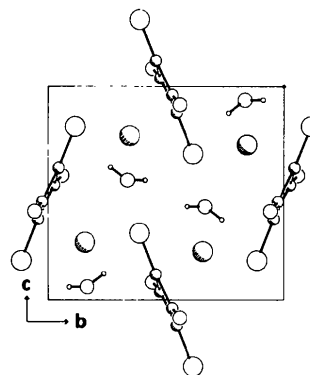


Fig. 2. Projection of unit-cell contents (large shaded circles: K, large open circles: S, small shaded circles: C, small open circles: O).

nically in the series of squaric-acid derivatives so far characterized structurally, *i.e.* $C_4O_4^{2-}$ (Macintyre & Werkema, 1964), $C_4S_4^{2-}$ (Allmann *et al.*, 1976), 1,2-DTSA and 1,3-DTSA (Mattes *et al.*, 1982), where mean C—C distances from 1.438 (7) to 1.461 (4) Å have been found. The C—S bond length [1.672 (2) Å] is slightly longer than in 1,2-DTSA and 1,3-DTSA, where the values 1.645 (3) and 1.652 (7) Å have been found and no hydrogen bonds can be formed. In the present case, the S atom is engaged in a hydrogen bond [S...O(2): 3.352 (1) Å, S—H(1)...O(2): 167 (2)°]. The same is valid in $C_4S_4^{2-}$ with the C—S bond length 1.663 (8) Å.

The C—O bond length [1.236 (2) Å] agrees well with the estimated bond order 1.5. Potassium is seven-coordinated by two S atoms at distances 3.469 (1) and 3.445 (1) Å and five O atoms [mean distance 2.795 (1) Å]. In the three-dimensional lattice, the

planes of the dianions are aligned nearly parallel to the *a* axis, with an approximate angle of 45° between neighboring anions (see Fig. 2).

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Structures of Azidobis(dimethylglyoximato)(triphenylphosphine)cobalt(III), $C_{26}H_{29}CoN_7O_4P$, and [4,5-Bis(methoxycarbonyl)-1,2,3-triazolato]-bis(dimethylglyoximato)(triphenylphosphine)cobalt(III), $C_{32}H_{35}CoN_7O_8P^*$

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Abstract. $(PPh_3)Co(DH)_2N_3$, $M_r = 593.5$, orthorhombic, $Pca2_1$, $a = 15.156$ (8), $b = 11.120$ (6), $c = 16.557$ (8) Å, $U = 2790$ (3) Å³, $Z = 4$, $D_m = 1.42$ (floatation), $D_x = 1.41$ g cm⁻³, $Mo K\alpha$, $\lambda = 0.7107$ Å, $\mu = 7.5$ cm⁻¹, $F(000) = 1232$, $T = 298$ K, $R = 0.025$ for 1988 independent reflections. $(PPh_3)Co(DH)_2(trz)$, $M_r = 735.6$, triclinic, $P\bar{1}$, $a = 10.261$ (6), $b = 18.190$ (9), $c = 10.425$ (6) Å, $\alpha = 76.01$ (6), $\beta = 88.15$ (6), $\gamma = 110.19$ (6)°, $U = 1758$ (2) Å³, $Z = 2$, $D_m = 1.41$ (floatation), $D_x = 1.39$ g cm⁻³, $Mo K\alpha$, $\lambda = 0.7107$ Å, $\mu = 6.2$ cm⁻¹, $F(000) = 764$, $T = 298$ K, $R = 0.037$ for 4469 independent reflections. The cobalt atom is octahedrally distorted with the $(DH)_2$ (DH = monoanion of dimethylglyoxime) units at the equatorial positions in both compounds. The N—Co—P fragment is characterized by Co—P, Co—N bond lengths of 2.311 (1) and 2.014 (4) Å, respectively, and an N—Co—P angle of 175.4 (1)° in the azido

derivative(I). The corresponding figures for the triazolato (trz) derivative (II) are 2.333 (1), 1.953 (3) Å and 178.0 (1)°, respectively. The *trans* influence of the axial ligands is discussed and compared with that of other ligands.

Introduction. The reaction products of substituted alkynes with $LCo(DH)_2N_3$ complexes (L = neutral ligand) have been characterized by elemental analyses. IR and ¹H NMR spectroscopy (Beck, Nelson, Takach, Kemmerich, Boehme & Jablonski, 1982). These data suggest that a 1,3-dipolar cycloaddition takes place, yielding complexes in which the substituted triazolato is coordinated to cobalt. Spectroscopic data suggested that the coordination takes place through the central N atom of the triazolato ring. Furthermore, it was suggested that the triazolato group has a greater *trans* labilizing ability than azide does. Since the determination of the molecular geometry may give an

* Dimethylglyoxime is 2,3-butanedione dioxime.