Cu to O(w) is close to 0·4 v.u. In order to saturate its bond strength to 2·0 v.u., O(w) must receive 1·6 v.u., *i.e.* twice the common value (0·8 v.u.) given by H in water molecules. The Jahn–Teller effect on copper leads to four short distances in a square plane $CuO_2(H_2O)_2$. Two long Cu—O distances correspond to less than 16% of the bond strength given by Cu^{2+}. Valence bond calculations also show that hydrogen of water molecules form weak hydrogen bonds with O(2) and O(4). These two latter atoms do not saturate their bond strength, at variance with O(1) and O(3).

From these structural studies, $Cu_3V_2O_8(H_2O)$ appears to be a basic copper pyrovanadate monohydrate, whereas $CuV_2O_6(H_2O)_2$ is a copper metavanadate dihydrate. It is to be noted that the structure of $Cu_3V_2O_8(H_2O)$ differs from that of the isoformula phosphate $Cu_3P_2O_8(H_2O)$ (Riou, Gerault & Cudennec, 1985). Now, it will be interesting to study the thermal dehydration of these copper vanadates and to analyse the structure of the corresponding anhydrous compounds.

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Structures of Two Disulfide-Bridged Compounds

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Abstract. Bis(tetraphenylarsonium) *cis,cis*-1,2,5,6-tetracyano-3,4-dithiahexa-1,5-diene-1,6-dithiolate, $[As(C_6H_5)_4]_2C_8N_4S_4$, (1); $M_r = 1047\cdot0$, monoclinic, $P2/n$, $a = 13\cdot692$ (3), $b = 9\cdot647$ (3), $c = 19\cdot872$ (5) Å, $\beta = 102\cdot71$ (2)°, $U = 2560\cdot5$ (1·0) Å^3, $Z = 2$, $D_x = 1\cdot36$ g cm^{-3}, $\mu(Mo\ K\alpha) = 14\cdot98$ cm^{-1}, $F(000) = 1068$, $R = 0\cdot046$ for 2514 observed reflections. 4,4′,6,6′-Tetramethyl-2,2′-thiopyrimidine, $C_{12}H_{14}N_4S_2$, (2); $M_r = 278\cdot4$, monoclinic, $P2_1/c$, $a = 13\cdot273$ (3), $b = 9\cdot075$ (4), $c = 12\cdot281$ (4) Å, $\beta = 107\cdot66$ (2)°, $U = 1409\cdot7$ (7) Å^3, $Z = 4$, $D_x = 1\cdot31$ g cm^{-3}, $\mu(Mo\ K\alpha) = 3\cdot49$ cm^{-1}, $F(000) = 584$, $R = 0\cdot054$ for 1554 observed reflections. Both compounds were produced by oxidation of thiols by uranyl salts. Dimensions are normal, with C—S 1·759 (6) and 1·782 (4), S—S 2·051 (3) and 2·021 (2) Å respectively, and torsion angles C—S—S—C of 82·7 (4) and 95·7 (4)°.

Introduction. During our studies of compounds containing U—S bonds (Alcock & Pennington, 1989), we investigated the reactions of thiolate anions with uranyl salts. We were unsuccessful in isolating the

intended complexes (even though one had previously been reported), because of the production of compounds containing S—S bonds formed by the oxidation of the ligand. The structures of two such compounds are described here.

Experimental. *Preparation.* (1) was isolated during an attempt to prepare the 1,2-dicyanoethylene-1,2-dithiol salt of uranium(VI). The thiol ligand was prepared using the method described by Davison & Holm (1967). 0·50 g of this ligand in methanol was then added to a solution of uranyl acetate (0·58 g) producing an olive-green-coloured solution. When addition was complete, the mixture was heated at reflux for 2 h. When cool, the volume of solvent was reduced until the first sign of precipitation. The solution was then filtered and tetraphenylarsonium chloride (1·0 g) in methanol added. After further cooling, yellow needle-like crystals had formed, which were shown by structure determination to be the *cis,cis*-disulfide.

Dimethylthiopyrimidine dimer (2), was formed in an attempt to prepare the dimethylthiopyrimidine product of uranyl nitrate described by Baghlaf,

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Ishaq, Ahmed & Al-Julani (1985). Dimethyl-mercaptopyrimidine (0·71 g) dissolved in methanol (doped with dimethyl sulfoxide) was added to a solution of uranyl nitrate (1·0 g) in methanol. The colour of the solution became yellow-orange. The volume of solvent was reduced by 50%, and the solution allowed to stand. After 48 h, small well defined block-like crystals were observed. Structural study showed these to be the dimeric, oxidized form of the ligand. We are unable to account for the different course of the reaction in our hands.

For both compounds, data were collected with a Syntex $P2_1$ automatic four-circle diffractometer. Maximum 2θ was 50° for each complex. $\omega/2\theta$ scans, range of $\pm 1\cdot1°$ (2θ) around $K\alpha_1$–$K\alpha_2$, scan speed 2·5–29·3° min^{-1} depending on the intensity of a 2 s prescan. Background intensities were measured at each end of the scan for 0·25 of the scan time. Three standard reflections were monitored every 200 reflections. These showed slight changes during data collection; the data were rescaled to correct for this. *hkl* ranges 0/16; 0/11; −23/23 for (1) and 0/16; 0/11; −15/15 for (2). Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 high-angle reflections [28–30° (2θ) for (1) and 25–27° for (2)]. The criterion $I/\sigma(I) \le 3\cdot0$ was used to identify observed reflections, which were corrected for Lorentz, polarization and absorption effects, the last with *ABSCOR* (Alcock, 1972).

Both structures were solved using the direct-methods link of *SHELXTL* (Sheldrick, 1981) on a Data General DG30 computer. Non-H atoms were refined anisotropically. H atoms were inserted at calculated positions with isotropic temperature factors $U = 0\cdot07$ Å^2. Final refinement was on F by cascaded least-squares methods, using a weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$, shown to be satisfactory by weight analysis.

For (1), 4542 unique reflections were recorded, with 2026 considered observed ($R_{int} = 0\cdot019$). 208 parameters were refined, final peaks on a difference Fourier synthesis were +1·1 (on the twofold axis) and −0·5 e Å^{-3}, $wR = 0\cdot047$, $g = 0\cdot0005$, with final maximum shift/e.s.d. of 1·01. Crystal dimensions were 0·47 × 0·14 × 0·28 mm giving rise to maximum and minimum transmission factors of 0·87 and 0·72. The anion has twofold crystallographic symmetry. For (2) 2492 unique reflections were recorded, with 1554 considered observed ($R_{int} = 0\cdot050$). 175 parameters were refined, final peaks on a difference Fourier synthesis were +0·5 and −0·3 e Å^{-3}, $wR = 0\cdot064$, $g = 0\cdot0017$, with final maximum shift/e.s.d. of 0·3. Crystal dimensions were 0·43 × 0·31 × 0·52 mm giving rise to maximum and minimum transmission factors of 0·39 and 0·23. Atomic scattering factors and f', f'' values were taken from *International Tables for X-ray Crystallography* (1974). Atomic

Table 1. *Atomic coordinates* $(\times 10^4)$ *and isotropic thermal parameters* $(\text{Å}^2 \times 10^3)$

	x	y	z	U*
Compound (1)				
As(1)	1926 (1)	6289 (1)	−383 (1)	48 (1)
N(01)	6643 (4)	9026 (6)	3410 (3)	86 (2)
N(02)	4028 (4)	9690 (6)	2121 (3)	78 (2)
S(1)	6886 (1)	6289 (2)	2097 (1)	59 (1)
S(2)	4842 (1)	6944 (2)	1105 (1)	78 (1)
C(01)	6122 (4)	7619 (6)	2302 (3)	48 (2)
C(02)	5236 (4)	7848 (6)	1851 (3)	52 (2)
C(011)	6424 (4)	8409 (7)	2917 (3)	55 (2)
C(021)	4577 (4)	8880 (7)	2012 (3)	56 (2)
C(11)	1387 (4)	7494 (6)	197 (3)	46 (2)
C(12)	2017 (4)	8027 (7)	787 (3)	55 (2)
C(13)	1623 (4)	8822 (7)	1237 (3)	61 (2)
C(14)	610 (5)	9098 (7)	1094 (3)	62 (3)
C(15)	−10 (4)	8599 (6)	510 (3)	60 (2)
C(16)	374 (4)	7787 (6)	54 (3)	50 (2)
C(21)	3098 (8)	7136 (12)	−587 (5)	50 (4)
C(22)	3907 (4)	6324 (6)	−661 (3)	56 (2)
C(23)	4723 (5)	6988 (7)	−832 (3)	68 (3)
C(24)	4691 (5)	8403 (7)	−924 (3)	82 (3)
C(25)	3913 (5)	9141 (7)	−857 (4)	83 (3)
C(26)	3093 (5)	8544 (7)	−687 (4)	69 (3)
C(31)	935 (4)	6000 (6)	−1220 (3)	53 (2)
C(32)	396 (5)	4774 (7)	−1324 (3)	59 (2)
C(33)	−306 (5)	4595 (8)	−1922 (3)	73 (3)
C(34)	−484 (5)	5616 (9)	−2409 (3)	89 (3)
C(35)	59 (8)	6822 (10)	−2302 (4)	110 (4)
C(36)	772 (6)	7035 (7)	−1708 (3)	88 (3)
C(41)	2212 (4)	4557 (6)	86 (3)	46 (2)
C(42)	2071 (5)	4416 (7)	744 (3)	61 (3)
C(43)	2278 (5)	3188 (7)	1085 (3)	73 (3)
C(44)	2626 (5)	2101 (7)	774 (3)	76 (3)
C(45)	2755 (5)	2213 (7)	111 (3)	77 (3)
C(46)	2549 (5)	3459 (7)	−242 (4)	63 (3)
Compound (2)				
S(11)	7885 (1)	6219 (1)	2796 (1)	70 (1)
C(11)	9104 (3)	5217 (5)	3290 (3)	58 (2)
N(11)	9086 (2)	3787 (4)	3515 (3)	58 (1)
N(12)	9908 (3)	6103 (4)	3402 (3)	45 (1)
C(12)	10046 (3)	3172 (5)	3905 (3)	59 (2)
C(13)	10081 (4)	1586 (6)	4243 (5)	80 (2)
C(14)	10939 (3)	3972 (5)	4017 (4)	66 (2)
C(15)	10845 (4)	5455 (6)	3781 (4)	66 (2)
C(16)	11798 (4)	6441 (7)	3950 (5)	94 (3)
S(21)	6731 (1)	4733 (2)	2716 (1)	71 (1)
N(21)	6761 (2)	4608 (4)	537 (3)	59 (1)
N(22)	5510 (2)	3189 (4)	1125 (3)	63 (1)
C(21)	6307 (3)	4109 (4)	1282 (3)	54 (1)
C(22)	6340 (3)	4072 (5)	−538 (4)	63 (2)
C(23)	6817 (4)	4624 (7)	−1411 (5)	96 (3)
C(24)	5512 (3)	3110 (5)	−799 (4)	66 (2)
C(25)	5087 (3)	2669 (5)	39 (4)	63 (2)
C(26)	4156 (4)	1702 (6)	−164 (5)	88 (2)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

coordinates, and selected bond lengths and angles are given in Tables 1–2.* The anion of (1) is illustrated in Fig. 1, with a packing diagram in Fig. 2. Compound (2) is illustrated in Fig. 3, with its packing diagram in Fig. 4.

Discussion. Complexes (1) and (2) should be viewed as oxidation products. Such oxidations are reported to occur in reactions of thiols with a number of

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates, and full bond lengths and angles for (1) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52037 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Selected bond lengths* (Å) *and angles* (°)

Compound (1)

S(1)—S(1')	2·051 (3)	C(01)—S(1)—S(1')	104·2 (2)
S(1)—C(01)	1·759 (6)	S(1)—C(01)—C(02)	117·1 (4)
C(01)—C(02)	1·359 (7)	S(1)—C(01)—C(011)	121·0 (4)
C(01)—C(011)	1·422 (8)	C(02)—C(01)—C(011)	121·9 (5)
		C(01)—C(011)—N(01)	178·4 (6)
C(011)—N(01)	1·129 (8)	C(01)—C(02)—S(2)	123·8 (5)
C(02)—S(2)	1·704 (5)	C(01)—C(02)—C(021)	118·9 (5)
C(02)—C(021)	1·426 (9)	S(2)—C(02)—C(021)	117·2 (4)
C(021)—N(02)	1·137 (9)	C(02)—C(021)—N(02)	177·7 (5)

S(1') is related to S(1) by the twofold axis at ¾, *y*, ¼.

Compound (2)

S(11)—C(11)	1·793 (4)	S(11)—S(21)	2·021(2)
C(11)—N(11)	1·328 (6)	C(11)—N(12)	1·310 (6)
N(11)—C(12)	1·340 (5)	N(12)—C(15)	1·326 (6)
C(12)—C(13)	1·494 (6)	C(12)—C(14)	1·361 (6)
C(14)—C(15)	1·374 (7)	C(15)—C(16)	1·512 (7)
S(21)—C(21)	1·771 (4)	N(21)—C(21)	1·319 (6)
N(21)—C(22)	1·359 (5)	N(22)—C(21)	1·315 (5)
N(22)—C(25)	1·365 (6)	C(22)—C(23)	1·487 (8)
C(22)—C(24)	1·364 (6)	C(24)—C(25)	1·376 (8)
C(25)—C(26)	1·474 (7)		

C(11)—S(11)—S(21)	105·7 (2)	S(11)—C(11)—N(11)	119·6 (3)
S(11)—C(11)—N(12)	110·3 (3)	N(11)—C(11)—N(12)	130·1 (4)
C(11)—N(11)—C(12)	114·0 (3)	C(11)—N(12)—C(15)	114·3 (4)
N(11)—C(12)—C(13)	116·5 (4)	N(11)—C(12)—C(14)	121·2 (4)
C(13)—C(12)—C(14)	122·2 (4)	C(12)—C(14)—C(15)	118·7 (4)
N(12)—C(15)—C(14)	121·7 (4)	N(12)—C(15)—C(16)	116·2 (4)
C(14)—C(15)—C(16)	122·1 (4)	S(11)—S(21)—C(21)	105·6 (2)
C(21)—N(21)—C(22)	114·3 (3)	C(21)—N(22)—C(25)	115·9 (4)
S(21)—C(21)—N(21)	120·3 (3)	S(21)—C(21)—N(22)	110·4 (3)
N(21)—C(21)—N(22)	129·3 (4)	N(21)—C(22)—C(23)	116·2 (4)
N(21)—C(22)—C(24)	121·5 (5)	C(23)—C(22)—C(24)	122·3 (4)
C(22)—C(24)—C(25)	119·7 (4)	N(22)—C(25)—C(24)	119·4 (4)
N(22)—C(25)—C(26)	116·6 (5)	C(24)—C(25)—C(26)	124·0 (5)

one-electron oxidizing agents, producing in the first instance with 1,2-dicyanoethylene-1,2-dithiol the *cis,cis*-disulfide (1). The uranyl ion in the reactions producing (1) and (2) presumably serves as this one-electron oxidant, and is itself reduced to uranium(V). However, this species is relatively unstable and disproportionates to give uranium(IV) and uranium(VI), which could then be used in further oxidation reactions. Spectroscopic characterization of the final solutions to identify the uranium species present were not performed, but these would be expected to be predominantly uranium(VI), since any uranium(IV) species produced would be oxidized under the reaction conditions.

The survey of bond distances by Allen, Kennard, Watson, Brammer, Orpen & Taylor (1987) shows that the parameters of CSSC groups are relatively variable. The principal determinant of the C—S distance is the hybridization at C, and the values of 1·759 (6) Å in (1) and 1·782 (4) Å in (2) are standard for C(sp^2) and C(aromatic)—S.
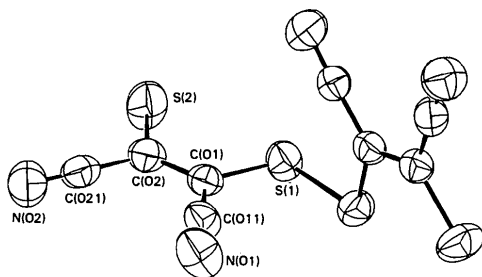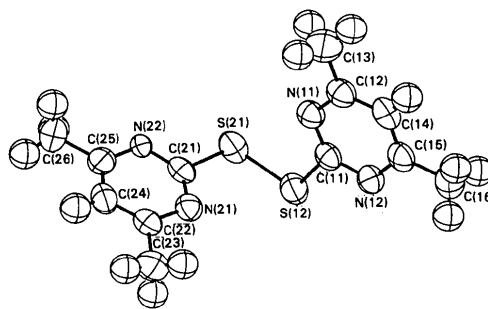

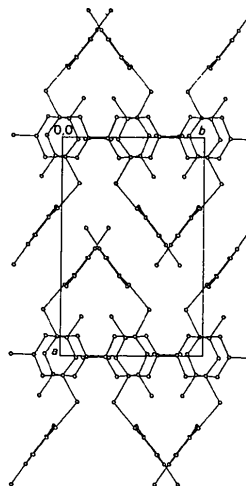Fig. 3. View of (2) showing atomic numbering scheme.

Fig. 1. View of the anion of (1) showing atomic numbering scheme.
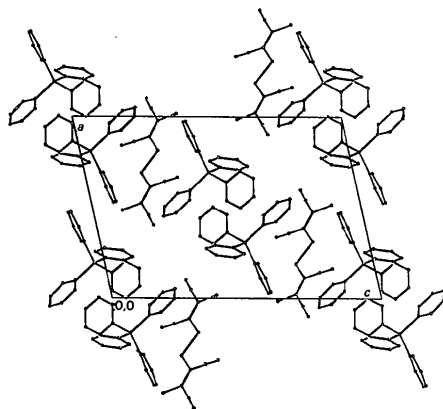
Fig. 2. Packing diagram for (1), viewed down **b**.

Fig. 4. Packing diagram for (2), viewed down **c**.

For S—S, the present values bracket the mean of 2·029 Å ($\sigma = 0·015$ Å). We have collected values for the C—S—S—C torsion angle for 72 occurrences in the Cambridge Structural Database (Allen *et al.*, 1979) (all having C—S—S—C in a non-cyclic system with $R \le 0·075$). The values cover a wide range (50–119°) and our results [82·4 (4)° (1) and 95·7 (4)° (2)] lie relatively close to the mean of 87° ($\sigma = 13°$).

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Neutron Diffraction Study of Potassium Oxalate Monoperhydrate at 123 K*

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Abstract. $K_2C_2O_4.H_2O_2$, $M_r = 200·24$, monoclinic, $C2/c$, $a = 8·858$ (2), $b = 6·505$ (2), $c = 10·872$ (2) Å, $\beta = 108·38$ (1)°, $V = 594·57$ (4) Å^3, $Z = 4$, $D_x = 2·23$, $D_m = 2·18$ g cm^{-3}, $\lambda = 1·0559$ (2) Å, $\mu = 0·348$ cm^{-1}, $F(000) = 400$, $T = 123·0$ (2) K, $R = 0·0251$ for 2196 unique reflections. The hydrogen peroxide molecule has a skew conformation, the H—O—O—H torsion angle being 101·6°; O—O = 1·4578 (4), O—H = 1·0117 (5) Å, and O—O—H = 100·69 (3)°. The oxalate ion is centrosymmetric and planar; the two C—O distances are 1·2635 (3) and 1·2460 (3) Å, differing by 0·0175 Å, the longer one being the hydrogen-bond acceptor. The C—C distance is long, 1·5675 (5) Å.

Introduction. The structure of the title compound $K_2C_2O_4.H_2O_2$ has been dertermined from film intensity data by Pedersen (1967). We are now determin-

ing the deformation electron density of the hydrogen peroxide molecule in different conformations to look for possible differences. We therefore have refined the X-ray crystal structure of the title compound at 123 K as well as the structure based on neutron diffraction data. The single-crystal neutron diffraction study was also inspired by the publication of neutron diffraction powder data for the deuterated compound apparently in error, as the authors claim the O—O distance of the hydrogen peroxide molecule to be 1·355 (8) Å (Adams, Ramdas & Hewat, 1980), compared to the old film-data value of 1·441 (9) Å (Pedersen, 1967). The neutron diffraction study is reported here.

Experimental. Potassium oxalate (p.a. Merck) was dissolved in perhydrol (30% H_2O_2). Crystals of $K_2C_2O_4.H_2O_2$ were formed by slow evaporation. The crystals had a diamond-like form with the longest direction along a diagonal in the crystal lattice. The density was measured at room temperature by the flotation method. The crystals were grown in Norway and transported to the BNL High Flux Beam Reactor, USA. The dimensions of the