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Syntheses of sulfur-bridged tungsten(V) complexes with *syn*-$W_2O_2S_2$ cores. X-ray structures of $K_2[W_2O_2S_2(cys)_2]\cdot 5H_2O$ and $NaNH_4[W_2O_2S_2(edta)]\cdot 2H_2O$

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Abstract

Facile synthetic methods for sulfur-bridged tungsten(V) dimers, $[W_2O_2S_2(cys)_2]^{2-}$ are described, which were obtained directly from sodium tungstate, sodium sulfide, and L-cysteine, together with the description of another route to $[W_2O_2S_2(cys)_2]^{2-}$ using ammonium tetrathiotungstate and L-cysteine. Synthetic methods for the derivative compounds, $W_2O_2S_2^{2+}$(aq) and $[W_2O_2S_2(edta)]^{2-}$ are also described. The X-ray structures of two compounds are determined. The compound $K_2[W_2O_2S_2(cys)_2]\cdot 5H_2O$ (**1**) crystallizes in the monoclinic space group $P2_1$, $a=9.670(1)$, $b=15.993(2)$, $c=6.893(1)$ Å, $\beta=95.02(1)°$, $V=1062.0(3)$ Å^3, $Z=2$, $R=2.76\%$. The compound $NaNH_4[W_2O_2S_2(edta)]\cdot 2H_2O$ (**6**) crystallizes in monoclinic $P2_1/a$, $a=24.522(8)$, $b=12.395(6)$, $c=7.098(2)$ Å, $\beta=104.21(3)°$, $V=2091.5(14)$ Å^3, $Z=4$, $R=4.24\%$. The complex anions $[W_2O_2S_2(cys)_2]^{2-}$ and $[W_2O_2S_2(edta)]^{2-}$ have an approximate symmetry of C_2 and contain the core *syn*-$W_2(O_t)_2(\mu\text{-}S)_2$.

Introduction

The chemistry of molybdenum(V) and tungsten(V) dimers, in particular the di-μ-oxo dimers with $M_2(O_t)_2(\mu\text{-}O)_2$ cores (M = Mo [1], W [2]) have been extensively developed. The μ-oxo-μ-sulfido dimers with $M_2(O_t)_2(\mu\text{-}O)(\mu\text{-}S)$ cores (M = Mo [3], W [2e, 4]) have also been described. Many examples of compounds with $Mo_2(O_t)_2(\mu\text{-}S)_2$ cores, including the cysteinato (cys) and ethylenediaminetetraacetato (edta) complexes $[Mo_2O_2S_2(cys)_2]^{2-}$ and $[Mo_2O_2S_2(edta)]^{2-}$, have been reported [3i, 5], and several tungsten compounds with $W_2(O_t)_2(\mu\text{-}S)_2$ cores have also been described [2e, 6]. However, the syntheses of the tungsten(V) complexes, $[W_2(O_t)_2(\mu\text{-}S)_2(cys)_2]^{2-}$ and $[W_2(O_t)_2(\mu\text{-}S)_2(edta)]^{2-}$ have not yet been reported.

We report here very facile preparative methods for the di-μ-sulfido cysteinato tungsten(V) dimer, $[W_2O_2S_2(cys)_2]^{2-}$, from which the corresponding aqua and edta complexes with $W_2O_2S_2$ cores can easily be prepared. X-ray structure analyses of $K_2[W_2O_2S_2(cys)_2]\cdot 5H_2O$ and $NaNH_4[W_2O_2S_2(edta)]\cdot 2H_2O$ are also described. A few of the results described here have been the subject of preliminary communications [7].

Experimental

Syntheses of compounds

Synthesis of potassium (di-μ-sulfido)bis[(L-cysteinato)-oxotungstate(V)] pentahydrate, $K_2[W_2O_2S_2(cys)_2]\cdot 5H_2O$ (1)

Two methods were used for the synthesis of the tungsten(V) dimer. Air-free conditions are not required for either method.

Method A. Dropwise addition of concentrated HCl (10 ml) with stirring to an aqueous solution (50 ml) containing $(NH_4)_2WS_4$ (5 g, 0.0144 mol) [8] gave a dark slurry, to which L-cysteine hydrochloride monohydrate (3 g, 0.0171 mol) was added, then the mixture was stirred for several minutes. The pH of the slurry was then adjusted to *c.* 7 by use of 10 M KOH, which caused a change in color from brown to yellow–green. Heating the slurry at 50–60 °C for *c.* 30 min changed it to a dark green solution to which KCl (5.0 g) was added. The solution was cooled to room temperature and stored in a refrigerator overnight. Yellow crystals deposited were filtered off and washed with methanol. For recrystallization, the crude sample (*c.* 4 g) was dissolved in hot water (40 ml, >90 °C) and filtered. Addition of KCl (2.0 g) to the filtrate and allowing the solution to stand overnight in a refrigerator gave orange crystals; yield 3.1 g (*c.* 50%). *Anal.* Found: K,

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8.98; N, 3.36; C, 8.36; H, 2.31. Calc.: K, 8.98; N, 3.21; C, 8.27; H, 2.31%.

Method B. Concentrated HCl (25 ml) was slowly added to water (50 ml) containing $Na_2WO_4 \cdot 2H_2O$ (5.0 g, 0.0144 mol) and $Na_2S \cdot 9H_2O$ (17 g, 0.0708 mol). A brown precipitate appears at first but then disappears. L-Cysteine hydrochloride monohydrate (10 g, 0.0569 mol) was then added to the solution. The pH of the solution was raised to *c.* 7 by the addition of 10 KOH, causing a change in color from red–brown to green. Then the solution was heated in a water bath (60–70 °C, 20 min). After filtration, KCl (5.0 g) was added. The crude sample (*c.* 3.0 g) obtained was recrystallized as described in method A. Yield 2.3 g (*c.* 35%).

Synthesis of sodium (di-μ-sulfido)bis[(L-cysteinato)-oxotungstate(V)] trihydrate, $Na_2[W_2O_2S_2(cys)_2] \cdot 3H_2O$ *(2)*

A similar method to that for the potassium salt (method A) was applied, $(NH_4)_2WS_4$ (5.0 g) being used. NaOH and NaCl were used instead of KOH and KCl, respectively. Recrystallization gave the pure product; yield 2.3 g (*c.* 40%). *Anal.* Found: N, 3.48; C, 9.20; H, 2.45. Calc.: N, 3.49; C, 8.98; H, 2.01%.

Synthesis of ammonium (di-μ-sulfido)bis[(L-cysteinato)-oxotungstate(V)] trihydrate, $(NH_4)_2[W_2O_2S_2(cys)_2] \cdot 3H_2O$ *(3)*

A similar method to that for the potassium salt (method A) was applied, $(NH_4)_2WS_4$ (5.0 g) being used. Concentrated NH_3 aq. (28%) and NH_4Cl were used instead of KOH and KCl, respectively. Recrystallization gave the pure product; yield 2.6 g (*c.* 46%). *Anal.* Found: N, 6.90; C, 9.19; H, 3.26. Calc.: N, 7.07; C, 9.09; H, 3.05%.

Synthesis of (di-μ-sulfido)bis[oxotungsten(V)](2+) aqua dimer, $[W_2O_2S_2(H_2O)_6]^{2+}$ *(4)*

Two methods were effectively employed. Air-free conditions are not required for either method.

Method A. One fifth of a gram of the cysteinato complex **1** was dissolved in 1 M HCl (15 ml) with stirring. After the brown precipitates were filtered off, Sephadex G-15 column chromatography (diameter 1.5 cm, length 24 cm) was applied to the filtrate, the eluent being 1 M HCl. The yellow band was collected; yield *c.* 45%. One molar $HClO_4$ can also be used instead of 1 M HCl; yield *c.* 15%.

Method B: $(NH_4)_2WS_4$ (1 g) was dissolved in 1 M HCl (40 ml). After the brown precipitates were filtered off, Sephadex G-15 column chromatography was applied as in method A; yield 6.5%. One molar $HClO_4$ can also be used instead of 1 M HCl; yield *c.* 5.5%.

Synthesis of potassium (μ-ethylenediaminetetra-acetato)-(di-μ-sulfido)bis[oxotungstate(V)] dihydrate, $K_2[W_2O_2S_2(edta)] \cdot 2H_2O$ *(5)*

One molar hydrochloric acid (20 ml) was added to a mixture of the cysteinato tungsten(V) dimer **1** (0.25 g, 2.87×10^{-4} mol/dimer) and $Na_2edta \cdot 2H_2O$ (2.50 g, 6.72×10^{-3} mol). The mixture was heated in a water bath with stirring (50–60 °C, 15 min) to give an orange solution, to which a KOH solution (10 M) was added to raise the pH of the solution up to 4–5. Then the resulting solution was heated again in a water bath (50–60 °C, *c.* 5 min), and the solution was kept in a refrigerator overnight. The orange plate crystals which deposited were filtered by suction and air dried; yield 0.23 g (92%). *Anal.* Found: N, 3.25; C, 13.83; H, 1.87. Calc.: N, 3.23; C, 13.86; H, 1.86%.

Synthesis of ammonium sodium (μ-ethylenediamine-tetraacetato)-(di-μ-sulfido)bis[oxotungstate(V)] dihydrate, $NaNH_4[W_2O_2S_2(edta)] \cdot 2H_2O$ *(6)*

A similar method to the synthesis of the potassium salt **5** was employed and the same starting materials were used except that concentrated NH_3 aq. (28%) was used instead of KOH solution. Yield 69%. *Anal.* Found: N, 5.22; C, 14.40; H, 2.54; Calc.: N, 5.06; C, 14.48; H, 2.43%.

Synthesis of sodium (μ-ethylenediaminetetra-acetato)-(di-μ-sulfido)bis[oxotungstate(V)] dihydrate, $Na_2[W_2O_2S_2(edta)] \cdot 2H_2O$ *(7)*

A similar method to the synthesis of the potassium salt **5** was employed and the same starting materials were used except that NaOH solution (13 M) was used instead of KOH solution. Yield 75%. *Anal.* Found: N, 3.36; C, 14.44; H, 1.58. Calc.: N, 3.35; C, 14.40; H, 1.93%.

Synthesis of ammonium (μ-ethylenediaminetetra-acetato)-(di-μ-sulfido)bis(oxotungstate(V)] monohydrate, $(NH_4)_2[W_2O_2S_2(edta)] \cdot H_2O$ *(8)*

A similar method to the synthesis of the potassium salt **5** was employed. The starting materials were $K_2[W_2O_2S_2(cys)_2] \cdot 5H_2O$ (**1**) and H_4edta. Concentrated NH_3 aq. (28%) was used instead of KOH solution. Yield 37%. *Anal.* Found: N, 6.91; C, 14.81; H, 2.97. Calc.: N, 6.95; C, 14.89; H, 2.75%.

Synthesis of calcium (μ-ethylenediaminetetraacetato)-(di-μ-sulfido)bis[oxotungstate(V)] trihydrate, $Ca[W_2O_2S_2(edta)] \cdot 3H_2O$ *(9)*

The corresponding sodium salt **7** (0.05 g, 6×10^{-5} mol/dimer) was dissolved in water (15 ml) and $CaCl_2$

(0.01 g, 9×10^{-5} mol) was added. Heating the mixture (60–70 °C) with stirring till complete dissolution and then allowing it to stand at room temperature gave the product; yield 0.04 g (80%). *Anal.* Found: N, 3.25; C, 13.61; H, 2.42. Calc.: N, 3.31; C, 14.19; H, 2.14%.

Synthesis of magnesium (μ-ethylenediaminetetraacetato)-(di-μ-sulfido)bis[oxotungstate(V)] octahydrate, $Mg[W_2O_2S_2(edta)]\cdot8H_2O$ (10)

A similar method to the synthesis of the calcium salt **9** was employed, $MgCl_2\cdot6H_2O$ being used instead of $CaCl_2$; yield 90%. *Anal.* Found: N, 3.05; C, 13.02; H, 2.89. Calc.: N, 3.04; C, 13.04; H, 3.06%.

Structural determination of $K_2[W_2O_2S_2(cys)_2]\cdot5H_2O$ (1) and $NaNH_4[W_2O_2S_2(edta)]\cdot2H_2O$ (6)

An orange columnar crystal (dimensions $0.25\times0.17\times0.15$ mm) of **1** was mounted on a glass fiber with an adhesive and a yellow columnar crystal (dimensions $0.18\times0.17\times0.17$ mm) of **6** was mounted in a glass capillary with the mother liquor. Systematic absences uniquely identified the space group as $P2_1$ for **1** and $P2_1/a$ for **6**. Cell constants and orientation matrixes for the crystals were obtained from a least-squares refinement, by using setting angles of 23 reflections for **1** and 20 reflections for **6** in the range $20<2\theta<30°$ measured on a RIGAKU AFC-6A diffractometer using Mo Kα radiation ($\lambda=0.71073$ Å). The intensities of standard reflections monitored after every 150 reflections for both crystals did not show any appreciable decay. Intensities were corrected for polarization and Lorentz factors. The corrections for absorption were applied to each crystal with the program CRYSTAN [9].

The coordinates of W and S atoms that composed the cores were determined by means of SHELXS-86 [10] for **1** and **6**, and the remaining non-hydrogen atoms were located from difference maps. No attempt was made to locate hydrogen atoms for each structural determination. The refinement of the structures was performed at the initial stage by the block-diagonal least-squares method using the programs in the UNICS system [11] and at a later stage by the full-matrix least-squares program CRYSTAN [9]. The program ORTEP [12] was used to draw perspective views. Atomic scattering factors for W^0, K^0, S^0, Na^0, O^0, N^0 and C^0 were taken from ref. 13. Computations were performed on a FACOM M380 computer at the Okayama University of Science.

Results and discussion

Synthesis and properties of tungsten(V) complexes with $W_2O_2S_2$ cores

Although more than ten tungsten(V) dimers with *syn*-$W_2(O_t)_2(\mu\text{-}S)_2$ cores have been reported [2e, 6, 7], the number is definitely fewer than that of the corresponding molybdenum compounds with $Mo_2O_2S_2$ cores. The following tungsten sources have been used for the syntheses: $Na_2WO_4\cdot2H_2O$, $(NH_4)_2WO_2S_2$, $(NH_4)_2WOS_3$, $(NH_4)_2WS_4$, $(PPh_4)_2WS_4$ and WCl_2OS; naturally ligand substitution can also be employed to get dimers with the cores.

We used $(NH_4)_2WS_4$ (method A) or commercially available $Na_2WO_4\cdot2H_2O$ (method B) for the synthesis of **1**. These methods do not require an air-free technique. In method B, a similar procedure to that for the corresponding molybdenum compound [3i] was applied: both 'reduction of tungstate' and 'introduction of sulfide bridges' are achieved by the addition of sodium sulfide to a solution of sodium tungstate. The addition of L-cysteine hydrochloride monohydrate to the resultant solution gives the desired product. Method A gives higher yield than Method B. An intense green coloration was observed in both methods, but the cause of it has not yet been clarified. For the syntheses of **2** and **3**, the starting material $(NH_4)_2WS_4$ gives a moderate yield for both compounds, however, $Na_2WO_4\cdot2H_2O$ gives low yields and is not suitable. The aqua ion **4** was obtained by two methods: (i) by aquation of the corresponding cysteinato complex **1** (or **2**, **3**) followed by Sephadex G-15 separation, (ii) by direct synthesis from $(NH_4)_2WS_4$. The yield of the latter is low.

The edta complexes **5**–**8** were obtained by ligand substitution of $edta^{4-}$ for cys^{2-} of **1**. In the synthesis, the pH of the solution should not exceed 5: at higher pH, recoordination of the cysteinato ligand was observed. The edta complexes **9** and **10** were obtained from the sodium salt **7**. The crystals of **5** have about four waters of crystallization immediately after the isolation of the crystals from the mother liquor, and then lose two waters of crystallization by efflorescence.

The electronic spectra of $[W_2O_2S_2(cys)_2]^{2-}$, $W_2O_2S_2^{2+}$(aq) and $[W_2O_2S_2(edta)]^{2-}$ are shown in Fig. 1. Peak positions, λ_{max} (nm) (ϵ (M^{-1} cm^{-1} per dimer))

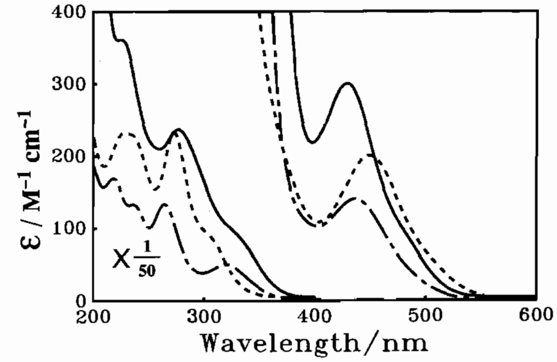

Fig. 1. Electronic spectra of tungsten(V) dimers with $W_2O_2S_2$ cores: ——, $[W_2O_2S_2(cys)_2]^{2-}$ in water; – – – -, $W_2O_2S_2^{2+}$(aq) in 1 M HCl; - - - -, $[W_2O_2S_2(edta)]^{2-}$ in water.

are: 430 (300), 330sh (4560), 278 (11850) for **1**; 435 (140), 320 (2490), 265 (6650), 237 (6630), 218 (8430) for **4**; 450 (200), 310sh (4020), 273 (11660), 229 (11620) for **5**. Each of the spectra of the three tungsten dimers has a characteristic peak at about 430–450 nm, while the corresponding molybdenum dimers have no peaks in the visible region [3i]. A small red shift of the peak position of the aqua ion **4** in the visible region is observed compared to that of $W_2O_4(aq)^{2+}$ (430 nm) [2d], while a large red shift is observed on substitution of bridging sulfur atom(s) for bridging oxygen atom(s) in the complexes having an $Mo_2O_{4-n}S_n$ core ($n=1$–4) (see for example refs. 3a, b, h, 5c, e). The cysteinato complex **1** is fairly resistant toward air oxidation, not only in the solid state but also in solution. The aqua ion **4** in 1 M HCl or in 1 M $HClO_4$ is stable in low concentrations under air. The absorbance of the aqua ion (2×10^{-3} M) remains unchanged for 2 days under air. However, its absorbance increases gradually, when the concentration of the aqua ion exceeds *c*. 3×10^{-3} M. The reason why the absorbance of the solution at higher concentration increases is not clear at present. The aqua ion in 1 M $HClO_4$ or in 1 M HPTS (*p*-toluenesulfonic acid) also has absorption peaks at 435 nm. The solution of the aqua ion in HPTS becomes turbid gradually under both air and dinitrogen atmosphere.

Structures of $K_2[W_2O_2S_2(cys)_2]\cdot5H_2O$ (1) and $NaNH_4[W_2O_2S_2(edta)]\cdot2H_2O$ (6)

The crystallographic and machine data for **1** and **6** are given in Table 1. The atomic coordinates and thermal parameters for **1** are listed in Table 2 and those for **6** in Table 3. The selected interatomic distances and angles for **1** and **6** are collected in Tables 4 and 5, respectively.

TABLE 1. Crystallographic data for $K_2[W_2O_2S_2(cys)_2]\cdot5H_2O$ (**1**) and $NaNH_4[W_2O_2S_2(edta)]\cdot2H_2O$ (**6**)

Formula	$W_2K_2S_4O_{11}N_2C_6H_{20}$	$W_2S_2NaO_{12}N_3C_{10}H_{20}$
Formula weight	870.39	829.09
Space group	$P2_1$	$P2_1/a$
Systematic absences	$0k0$: $k+2n+1$	$h0l$: $h=2n+1$ $0k0$: $k=2n+1$
a (Å)	9.670(1)	24.522(8)
b (Å)	15.993(2)	12.395(6)
c (Å)	6.893(1)	7.098(2)
β (°)	95.02(1)	104.21(3)
V (Å^3)	1062.0(3)	2091.5(14)
Z	2	4
T (°C)	18	18
λ (Mo Kα) (Å)	0.71073	0.71073
D_{obs} (g/cm^3)	2.00	2.64
D_{calc} (g/cm^3)	1.990	2.633
μ (cm^{-1})	118.8	115.1
Transmission factors: max., min.	1.000, 0.885	1.000, 0.891
$R(F_o)$ (%)	2.76	4.24
$R_w(F_o)$ (%)	3.51	6.83

TABLE 2. Atomic coordinates and equivalent isotropic temperature factors for $K_2[W_2O_2S_2(cys)_2]\cdot5H_2O$ (**1**)[a]

Atom	x	y	z	B_{eq} (Å^2)
W1	0.88455(3)	0.0	0.81848(4)	1.294(7)
W2	0.93957(3)	0.17081(3)	0.74088(4)	1.305(7)
S1	0.8798(2)	0.1118(1)	1.0340(3)	1.73(4)
S2	0.8921(2)	0.0658(1)	0.5125(3)	1.86(4)
O1	1.0498(7)	−0.0390(5)	0.850(1)	2.2(2)
O2	1.1176(6)	0.1744(5)	0.785(1)	2.4(1)
S11	0.7950(2)	−0.0871(2)	1.0829(3)	1.93(4)
N11	0.7929(8)	−0.1089(5)	0.646(1)	2.1(2)
O11	0.6488(6)	0.0148(4)	0.754(1)	1.9(1)
O12	0.4510(7)	−0.0568(5)	0.754(1)	2.8(2)
C11	0.5785(9)	−0.0533(6)	0.742(1)	1.8(2)
C12	0.663(1)	−0.1337(6)	0.732(2)	2.1(2)
C13	0.7010(9)	−0.1672(6)	0.937(1)	2.1(2)
S21	0.9331(2)	0.2709(2)	0.4570(3)	1.96(4)
N21	0.9140(8)	0.2954(5)	0.885(1)	2.1(2)
O21	0.7174(6)	0.2075(4)	0.707(1)	1.8(1)
O22	0.5662(7)	0.3134(5)	0.678(1)	2.7(2)
C21	0.6855(9)	0.2846(6)	0.714(1)	1.7(2)
C22	0.8108(9)	0.3436(6)	0.762(1)	2.0(2)
C23	0.873(1)	0.3668(5)	0.573(1)	2.1(2)
K1	1.2955(2)	0.0522(2)	0.9486(4)	3.35(6)
K2	0.5561(3)	0.1176(2)	0.4302(4)	3.77(6)
OW1	0.660(1)	0.2864(7)	0.172(2)	4.4(3)
OW2	0.5244(9)	0.1443(6)	0.022(2)	4.2(2)
OW3	0.498(1)	−0.5253(6)	0.754(2)	4.6(3)
OW4	0.651(1)	−0.2973(8)	0.407(1)	5.1(3)
OW5	0.792(1)	−0.395(2)	0.716(2)	9.8(7)

[a]Equivalent isotropic temperature factors ($B_{eq}=4/3\{\Sigma\Sigma B_{ij}a_ia_j\}$).

The structures of the anion parts of **1** and **6** are shown in Figs. 2 and 3, respectively. The complex anions $[W_2O_2S_2(cys)_2]^{2-}$ and $[W_2O_2S_2(edta)]^{2-}$ have an approximate symmetry of C_2 and contain the core *syn*-$W_2(O_t)_2(\mu\text{-}S)_2$. Only two compounds with *syn*-$W_2(O_t)_2(\mu\text{-}S)_2$ cores have been reported so far: $(Ph_4As)_2W_2O_2S_2Cl_4$ (W–W = 2.844(1) Å) [6a] and $(PPh_4)_2[W_2O_2S_2(S_4)_2]\cdot0.5DMF$ (W–W = 2.856(1) Å) [6m]. Of these four compounds, the edta-coordinated compound has a distinctly short W–W distance (W–W = 2.781(1) Å), by 0.062 Å, than the cys-coordinated compound (W–W = 2.843(1) Å). A similar phenomenon has been observed in the corresponding molybdenum compounds: $Na_2[Mo_2O_2S_2(cys)_2]\cdot2H_2O$ (Mo–Mo = 2.82(0.3) Å) [14], $Cs_2[Mo_2O_2S_2(edta)]\cdot2H_2O$ (Mo–Mo = 2.799(1) Å) [15].

Supplementary material

More information on the structure determinations is available from author T.S. on request.

TABLE 3. Atomic coordinates and equivalent isotropic temperature factors for $NaNH_4[W_2O_2S_2(edta)]\cdot 2H_2O$ (**6**)[a]

Atom	x	y	z	B_{eq} (Å^2)
W1	0.22426(2)	0.25104(4)	0.19657(7)	1.22(1)
W2	0.33690(2)	0.23766(4)	0.39514(7)	1.29(1)
S1	0.3010(2)	0.2285(3)	0.0621(5)	1.54(7)
S2	0.2599(2)	0.2084(3)	0.5220(5)	1.71(8)
O1	0.2152(5)	0.3872(8)	0.192(2)	2.0(3)
O2	0.3531(5)	0.3706(7)	0.440(2)	2.6(3)
N1	0.2061(6)	0.0582(8)	0.165(2)	1.7(3)
O11	0.1429(4)	0.2296(8)	0.240(2)	2.2(2)
O12	0.1758(4)	0.2234(7)	−0.084(1)	1.7(2)
O13	0.0655(5)	0.129(1)	0.188(2)	3.6(4)
O14	0.1290(5)	0.1150(8)	−0.319(1)	2.0(2)
C11	0.1183(6)	0.139(1)	0.219(2)	1.8(3)
C12	0.1638(6)	0.130(1)	−0.159(2)	1.7(3)
C13	0.1548(7)	0.040(1)	0.230(3)	2.6(4)
C14	0.1941(6)	0.035(1)	−0.049(2)	1.5(3)
C15	0.2473(6)	−0.023(1)	0.278(2)	2.0(4)
N2	0.3507(5)	0.0441(8)	0.373(2)	1.1(2)
O21	0.4180(4)	0.2193(8)	0.342(2)	2.1(2)
O22	0.3866(5)	0.1843(8)	0.665(1)	2.0(3)
O23	0.4905(5)	0.113(1)	0.329(2)	2.9(3)
O24	0.4246(5)	0.0542(9)	0.876(2)	2.4(3)
C21	0.4403(7)	0.126(1)	0.330(2)	2.0(4)
C22	0.3935(6)	0.086(1)	0.715(2)	1.6(3)
C23	0.4038(7)	0.030(1)	0.303(2)	2.0(4)
C24	0.3620(6)	0.005(1)	0.576(2)	1.6(3)
C25	0.3050(6)	−0.024(1)	0.240(2)	1.6(3)
N3	0.5349(6)	0.155(1)	1.001(2)	2.6(4)
NaA	0.0	0.0	0.0	4.1(3)[b]
NaB	0.5456(6)	0.242(1)	0.638(2)	2.7(2)[b]
OWA	0.030(1)	−0.132(2)	0.242(4)	4.8(5)[b]
OWB	0.057(1)	−0.001(2)	−0.498(4)	4.7(5)[b]
OWC	0.044(1)	−0.068(2)	−0.260(4)	6.7(7)[b]

[a] Equivalent isotropic temperature factors ($B_{eq} = 4/3\{\Sigma\Sigma B_{ij}a_i a_j\}$). [b] Isotropic temperature factors were used. The following occupancy factors were used for the disordered atoms: NaA, 0.5; NaB, 0.5; OWA, 0.667; OWB, 0.667; OWC, 0.667.

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TABLE 4. Selected interatomic distances (Å) and angles (°) in $[W_2O_2S_2(cys)_2]^{2-}$

W1–W2	2.843(1)	S2–W1–S11	159.3(1)
W1–S1	2.328(2)	S1–W2–S21	158.5(1)
W1–S2	2.364(2)	mean	158.9[6]
W2–S1	2.348(2)	S1–W1–O1	105.6(3)
W2–S2	2.319(2)	S2–W1–O1	100.0(3)
mean	2.340[20]	S1–W2–O2	100.4(3)
W1–O1	1.711(7)	S2–W2–O2	106.1(3)
W2–O2	1.723(6)	mean	103.0[33]
mean	1.717[8]	S1–W1–O11	88.3(2)
W1–S11	2.508(2)	S2–W1–O11	83.6(2)
W2–S21	2.525(2)	S1–W2–O21	83.6(2)
mean	2.517[12]	S2–W2–O21	89.3(2)
W1–O11	2.296(6)	mean	86.2[30]
W2–O21	2.219(6)	S11–W1–O11	78.3(2)
mean	2.258[54]	S21–W2–O21	78.0(2)
W1–N11	2.246(8)	mean	78.2[2]
W2–N21	2.251(8)	S1–W1–N11	154.7(2)
mean	2.249[4]	S2–W2–N21	156.7(2)
S11–C13	1.823(10)	mean	155.7[14]
S21–C23	1.846(10)	S2–W1–N11	85.2(2)
mean	1.835[16]	S1–W2–N21	86.0(2)
O11–C11	1.284(11)	mean	85.6[6]
O12–C11	1.244(11)	S11–W1–N11	78.9(2)
O21–C21	1.274(11)	S21–W2–N21	77.6(2)
O22–C21	1.245(11)	mean	78.3[9]
mean	1.262[20]	O1–W1–S11	94.8(3)
N11–C12	1.489(13)	O2–W2–S21	94.1(3)
N21–C22	1.470(12)	mean	94.5[5]
mean	1.480[13]	O1–W1–O11	164.2(3)
C11–C12	1.528(13)	O2–W2–O21	162.4(3)
C12–C13	1.526(14)	mean	163.3[13]
C21–C22	1.549(12)	O1–W1–N11	96.0(3)
C22–C23	1.532(14)	O2–W2–N21	92.3(3)
mean	1.534[10]	mean	94.2[26]
W2–W1–S1	52.9(1)	N11–W1–O11	68.8(3)
W2–W1–S2	51.9(1)	N21–W2–O21	70.7(3)
W1–W2–S1	52.2(1)	mean	69.8[13]
W1–W2–S2	53.3(1)	W1–S1–W2	74.9(1)
mean	52.6[6]	W1–S2–W2	74.7(1)
W2–W1–S11	138.8(1)	mean	74.8[1]
W1–W2–S21	139.7(1)	W1–S11–C13	100.2(3)
mean	139.3[6]	W2–S21–C23	100.4(3)
W2–W1–O1	100.7(2)	mean	100.3[1]
W1–W2–O2	101.5(3)	W1–O11–C11	115.8(5)
mean	101.1[6]	W2–O21–C21	119.2(5)
W2–W1–O11	93.6(2)	mean	117.5[24]
W1–W2–O21	94.5(2)	W1–N11–C12	107.8(6)
mean	94.1[6]	W2–N21–C22	107.7(6)
W2–W1–N11	135.9(2)	mean	107.8[1]
W1–W2–N21	137.5(2)	S11–C13–C12	109.4(7)
mean	136.7[11]	S21–C23–C22	109.2(6)
S1–W1–S2	103.4(1)	mean	109.3[1]
S1–W2–S2	104.1(1)	O11–C11–O12	123.8(9)
mean	103.8[5]	O21–C21–O22	125.0(8)
S1–W1–S11	86.3(1)	mean	124.4[8]
S2–W2–S21	86.7(1)		
mean	86.5[3]		

TABLE 4. (*continued*)

O11–C11–C12	115.9(8)	N21–C22–C21	106.5(7)
O12–C11–C12	120.1(9)	N21–C22–C23	108.8(7)
O21–C21–C22	114.2(7)	mean	107.3[16]
O22–C21–C22	120.7(8)	C11–C12–C13	109.8(8)
mean	117.7[32]	C21–C22–C23	108.7(8)
N11–C12–C11	105.5(7)	mean	109.3[8]
N11–C12–C13	108.4(7)		

TABLE 5. Selected interatomic distances (Å) and angles (°) in $[W_2O_2S_2(edta)]^{2-}$

W1–W2	2.781(1)	W2–W1–O11	140.9(3)
W1–S1	2.326(4)	W2–W1–O12	137.6(3)
W1–S2	2.321(3)	W1–W2–O21	140.6(3)
W2–S1	2.314(3)	W1–W2–O22	139.4(3)
W2–S2	2.311(4)	mean	139.6[15]
mean	2.318[7]	W2–W1–N1	97.1(3)
W1–O1	1.702(10)	W1–W2–N2	99.4(3)
W2–O2	1.707(9)	mean	98.3[16]
mean	1.705[4]	S1–W1–S2	103.7(1)
W1–O11	2.110(11)	S1–W2–S2	104.3(1)
W1–O12	2.083(9)	mean	104.0[4]
W2–O21	2.124(12)	S1–W1–O1	103.1(4)
W2–O22	2.111(9)	S2–W1–O1	104.9(4)
mean	2.107[17]	S1–W2–O2	104.6(4)
W1–N1	2.431(11)	S2–W2–O2	104.6(5)
W2–N2	2.433(10)	mean	104.3[8]
mean	2.432[1]	S1–W1–O11	159.1(3)
O11–C11	1.260(17)	S2–W1–O12	154.4(3)
O12–C12	1.279(16)	S1–W2–O22	154.6(3)
O13–C11	1.265(20)	S2–W2–O21	160.3(3)
O14–C12	1.256(16)	mean	157.1[30]
O21–C21	1.287(19)	S1–W1–O12	85.2(3)
O22–C22	1.267(17)	S2–W1–O11	88.0(3)
O23–C21	1.243(21)	S1–W2–O21	87.3(3)
O24–C22	1.274(16)	S2–W2–O22	86.6(3)
mean	1.266[14]	mean	86.8[12]
N1–C13	1.461(24)	S1–W1–N1	89.6(4)
N1–C14	1.506(19)	S2–W1–N1	83.2(3)
N1–C15	1.510(18)	S1–W2–N2	84.8(3)
N2–C23	1.515(22)	S2–W2–N2	90.6(3)
N2–C24	1.479(17)	mean	87.1[36]
N2–C25	1.529(16)	O1–W1–O11	90.2(5)
mean	1.500[25]	O1–W1–O12	96.1(4)
C11–C13	1.517(21)	O2–W2–O21	87.2(5)
C12–C14	1.505(18)	O2–W2–O22	94.3(4)
C15–C25	1.503(23)	mean	92.0[40]
C21–C23	1.477(21)	O11–W1–O12	77.3(4)
C22–C24	1.487(18)	O21–W2–O22	76.7(4)
mean	1.498[16]	mean	77.0[4]
W2–W1–S1	53.0(1)	O1–W1–N1	162.5(5)
W2–W1–S2	52.9(1)	O2–W2–N2	159.1(5)
W1–W2–S1	53.4(1)	mean	160.8[24]
W1–W2–S2	53.3(1)	N1–W1–O11	74.4(4)
mean	53.2[2]	N1–W1–O12	72.7(4)
W2–W1–O1	100.2(4)	N2–W2–O21	74.5(4)
W1–W2–O2	101.2(4)	N2–W2–O22	72.0(4)
mean	100.7[7]	mean	73.4[12]

TABLE 5. (*continued*)

W1–S1–W2	73.6(1)	O21–C21–O23	123.6(14)
W1–S2–W2	73.8(1)	O22–C22–O24	123.8(12)
mean	73.7[1]	O11–C11–O13	123.2(13)
W1–O11–C11	122.5(10)	O12–C12–O14	123.0(12)
W1–O12–C12	124.4(8)	mean	123.4[4]
W2–O21–C21	122.7(10)	O11–C11–C13	117.2(13)
W2–O22–C22	124.0(8)	O13–C11–C13	119.5(13)
mean	123.4[9]	O12–C12–C14	117.4(11)
W1–N1–C13	106.1(9)	O14–C12–C14	119.5(12)
W1–N1–C14	105.5(8)	O21–C21–C23	118.5(14)
W1–N1–C15	121.8(8)	O23–C21–C23	117.7(14)
W2–N2–C23	106.2(8)	O22–C22–C24	117.2(11)
W2–N2–C24	105.1(8)	O24–C22–C24	118.9(12)
W2–N2–C25	119.3(7)	mean	118.2[10]
mean	110.7[77]	N1–C13–C11	113.5(13)
C13–N1–C14	108.6(12)	N1–C14–C12	108.9(11)
C13–N1–C15	104.1(12)	N1–C15–C25	116.3(13)
C14–N1–C15	110.1(11)	N2–C23–C21	114.0(12)
C23–N2–C24	108.1(10)	N2–C24–C22	111.3(11)
C23–N2–C25	106.9(11)	N2–C25–C15	117.9(12)
C24–N2–C25	110.8(10)	mean	113.7[33]
mean	108.1[24]		

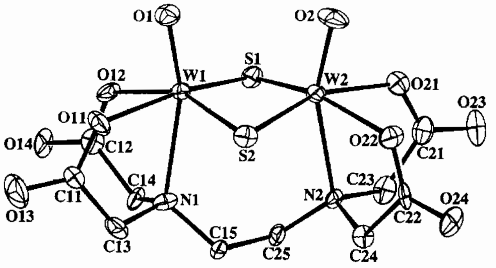

Fig. 2. Perspective view of $[W_2O_2S_2(cys)_2]^{2-}$ (the anion of **1**) showing the atom-labelling scheme.

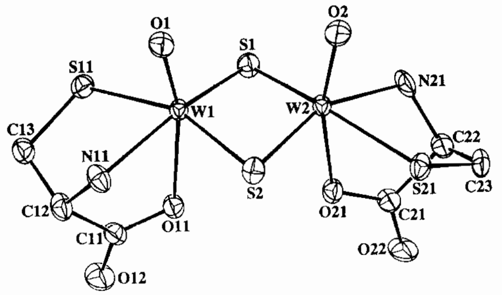

Fig. 3. Perspective view of $[W_2O_2S_2(edta)]^{2-}$ (the anion of **6**) showing the atom-labelling scheme.

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