DALTON

Preparation, structure and reactivity of the di-μ-disulfido Nb^{IV}_2 aqua ion $[Nb_2(\mu\text{-}S_2)_2(H_2O)_8]^{4+}$, the structure of $[Nb_2(\mu\text{-}S_2)_2(NCS)_8]^{4-}$, and properties of the related $(\mu\text{-}S)_2$ aqua ion†

Maxim N. Sokolov, Rita Hernandez-Molina, Mark R. J. Elsegood, Sarah L. Heath, William Clegg and A. Geoffrey Sykes*

Department of Chemistry, The University of Newcastle, Newcastle upon Tyne, UK NE1 7RU

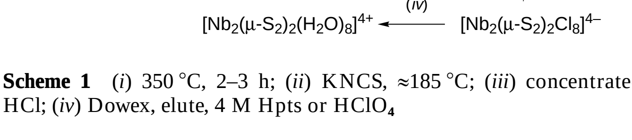
Using $Nb^{IV}S_2Cl_2$ as starting compound, and reaction routes involving aquation of Cl^- (or NCS^-) in 4 M Hpts (Hpts = *p*-toluenesulfonic acid, $CH_3C_6H_4SO_3H$), an aqua ion product was obtained and purified by cation-exchange chromatography. Yellow crystals of $[Nb_2(\mu\text{-}S_2)_2(H_2O)_8](pts)_4{\cdot}4H_2O$ **1**, and orange crystals of the thiocyanato complex $Cs_4[Nb_2(\mu\text{-}S_2)_2(NCS)_8]{\cdot}2H_2O$ **2** were isolated, and the structures of both determined by X-ray diffraction. The compounds have short Nb–Nb distances (2.85–2.90 Å) consistent with metal–metal bonding, two $\eta^2{:}\eta^2$ disulfido bridges (S–S distance 1.99 Å), and **2** has N-bonded thiocyanate. Compound **2** was also shown to be diamagnetic. Conventional time range equilibration studies on the substitution of NCS^- (>10-fold excess) for H_2O on $[Nb_2(\mu\text{-}S_2)_2(H_2O)_8]^{4+}$ indicate $[H^+]^{-1}$-dependent rate laws, $k_f = k_1 + k_2[H^+]^{-1}$ for formation, and $k_{aq} = k_{-1} + k_{-2}[H^+]^{-1}$ for aquation. At 25 °C $k_1 = 0.88\ M^{-1}\ s^{-1}$ and $k_{-1} = 2.4 \times 10^{-3}\ s^{-1}$, $I = 2.00$ M ($LiClO_4$). The slow reaction of the low electron count di-μ-disulfido ion $[Nb_2(\mu\text{-}S_2)_2(H_2O)_8]^{4+}$ is an unusual feature. Neutral S-abstraction reactions from $[Nb_2(\mu\text{-}S_2)_2(H_2O)_8]^{4+}$ with PPh_3 or the water-soluble phenylsulfonate derivative $(3\text{-}SO_3C_6H_4)_3P^{3-}$ ($PR_3{}^{3-}$) have stoichiometries of 2 moles of phosphine per dimer, and give a green product assigned as $[Nb_2(\mu\text{-}S)_2(H_2O)_8]^{4+}$. Stopped-flow studies on the substitution of NCS^- for H_2O on $[Nb(\mu\text{-}S)_2(H_2O)_8]^{4+}$ give a second-order formation rate constant $k = 37\ M^{-1}\ s^{-1}$ in 2.0 M Hpts solutions. On varying $[H^+]$ in the range 1.0–2.0 M, $[Nb_2(\mu\text{-}S)_2(H_2O)_8]^{4+}$ gives a reversible green to yellow colour change with an $[H^+]^{-1}$ dependent rate constant $\approx 4.8 \times 10^{-4}\ s^{-1}$. An irreversible step is incident at $[H^+] < 0.5$ M. Comparisons are made of the inhibitory effect of $\eta^2{:}\eta^2$ μ-disulfido bridges on substitution of H_2O on $[Nb_2(\mu\text{-}S_2)_2(H_2O)_8]^{4+}$ as compared with $[Nb_2(\mu\text{-}S)_2(H_2O)_8]^{4+}$, and reference is made to a similar trend for $[Mo_3(\mu_3\text{-}S)(\mu\text{–}S_2)_3(H_2O)_6]^{4+}$ and $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3(H_2O)_9]^{4+}$. Attempts to prepare the $Mo^V{}_2$ analogue $[Mo_2(\mu\text{-}S_2)_2(H_2O)_8]^{6+}$ gave $[Mo_2O_2(\mu\text{-}S)_2(H_2O)_6]^{2+}$.

There are no known simple ions of Nb (or Ta) with a combination of aqua/hydroxo or oxo ligands. A green trinuclear $Nb^{III}Nb^{IV}{}_2$ cluster believed to be $[Nb_3(\mu_3\text{-}Cl)(\mu\text{-}O)_3(H_2O)_9]^{4+}$,[1] has been prepared by treatment of $[Nb_2Cl_6(tht)_3]$ (tht = tetrahydrothiophene)[2] or $[NbCl_3(dme)]$ (dme = 1,2-dimethoxyethane)[3] with aqueous HCl, followed by cation-exchange chromatography. On treatment with NCS^-, $[Nb_3(\mu_3\text{-}S)(\mu\text{-}O)_3(NCS)_9]^{6-}$ is obtained, and the structure has been determined by X-ray crystallography.[4] Other lower oxidation state M_3X_{13}-type complexes with phosphine ligands, including the six-electron $Nb^{III}{}_3$ cluster $[Nb_3Cl_{10}(PEt_3)_3]^-$, and eight-electron $Nb^{II}{}_2Nb^{III}$ cluster $[Nb_3Cl_7(PEt_2Ph)_6]$ have been prepared.[5] Solution studies carried out on $[Nb_3(\mu_3\text{-}Cl)(\mu\text{-}O)_3(H_2O)_9]^{4+}$ by NMR spectroscopy using ^{17}O labelling have indicated water-exchange processes (two per Nb) of $352\ s^{-1}$, and (one per Nb) $8.3 \times 10^{-3}\ s^{-1}$, at 25 °C. In $HClO_4$ solutions fairly rapid oxidation to Nb^V is observed. Metal–metal bonded dimers are a feature of Nb^{IV} (and Ta^{IV}) chemistry.[6–8] Sulfur-containing compounds are of interest bearing in mind the rich and varied chemistry of neighbouring metals V, Mo and W with S.[9] In the present studies NbS_2Cl_2, which has $\eta^2{:}\eta^2$ di-μ-disulfido ligands between adjacent Nb atoms, and an extended $\{Nb_2(\mu\text{-}S_2)_2Cl_{8/2}\}_x$ structure by chloride sharing,[10] is used as lead-in compound.[11,12] An aqua ion with a $Nb^{IV}{}_2(\mu\text{-}S_2)_2{}^{4+}$ core is characterised in the present studies, and the properties of this ion including its conversion to $Nb^{IV}{}_2(\mu\text{-}S)_2{}^{4+}$ are investigated. Comparisons are made with isoelectronic $Mo^V{}_2$ complexes, and the possibility of converting $Nb^{IV}{}_2(\mu\text{-}S)_2{}^{4+}$ into cuboidal complexes is briefly examined.

Experimental

Preparation of a salt of $[Nb_2(\mu\text{-}S_2)_2(H_2O)_8]^{4+}$

The $Nb^{IV}{}_2$ compounds NbS_2Cl_2 and $[Et_4N]_4[Nb_2(\mu\text{-}S_2)_2(NCS)_8]$ were prepared by procedures described.[11,13] The latter (1 g) was dissolved in hot concentrated HCl (15 cm^3), and heating continued for 30 min until no more H_2S was evolved. The resulting orange solution was allowed to cool to room temperature, when a grey precipitate was filtered off. After diluting to $[H^+] = 0.3$ M the solution was loaded onto a Dowex 50W-X2 cation-exchange column (20 × 1 cm diameter), washed with 0.3 M HCl (100 cm^3), and eluted with 4 M Hpts (Hpts = *p*-toluenesulfonic acid). The reactions can be summarised as in Scheme 1. The solution was kept at room temperature for 5 d during which time crystals of $[Nb_2(\mu\text{-}S_2)_2(H_2O)_8][pts]_4{\cdot}4H_2O$ formed as yellow platelets. These were collected on a glass filter (Found: C, 26.7; H, 3.8. Calc. for $C_{28}H_{44}Nb_2O_{20}S_8{\cdot}4H_2O$: C, 27.6; H, 4.3%). Yield: 0.74 g (79%). The UV/VIS spectrum gave a peak λ/nm (ε/$M^{-1}\ cm^{-1}$ per dimer) at 338 (2000). The ion can also be eluted with 4 M $HClO_4$ peak at 338 (1980), or with 1–2 M HCl peak at 338 (2060).



Scheme 1 (*i*) 350 °C, 2–3 h; (*ii*) KNCS, ≈185 °C; (*iii*) concentrated HCl; (*iv*) Dowex, elute, 4 M Hpts or $HClO_4$

---

† *Non-SI unit employed*: M = mol dm^{-3}.

Preparation of $Cs_4[Nb_2(\mu\text{-}S_2)_2(NCS)_8]\cdot 2H_2O$

To a solution containing $[Nb_2(\mu\text{-}S_2)_2(H_2O)_8]^{4+}$ in 0.5 M HCl (15 cm^3; 0.02 M of dimer), solid CsCl (1 g) was added, and aqueous NH_4NCS (5 cm^3; 1 M) carefully layered on top. The mixture was left undisturbed at ≈5 °C. Orange crystals formed within 1 week. These were collected on a glass filter, washed with a small amount of ice–water and allowed to dry at room temperature. Analyses were obtained for a sample dehydrated over P_2O_5, the Nb and S by inductively coupled plasma atomic emission spectroscopy (Found: C, 7.2; N, 8.3; Nb, 14.3; S, 29.3. Calc. for $C_8Cs_4N_8Nb_2S_{12}$: C, 7.3; N, 8.5; Nb, 14.2; S, 29.3%). Yield 0.35 g (88%). Alternatively the complex could be prepared by fusing together NbS_2Cl_2 (or NbS_2Br_2), with KNCS and subsequent addition of CsCl.[13] The UV/VIS spectrum in 2 M KNCS and 2 M HCl solution gave a peak at 356 nm. Measurements on a Sherwood Scientific Magnetic Susceptibility Balance Mark II indicated that samples were diamagnetic.

Preparation of $[Nb_2(\mu\text{-}S_2)_2(ida)_2(H_2O)_2]$

A solution containing $[Nb_2(\mu\text{-}S_2)_2(H_2O)_8]^{4+}$ (15 cm^3; 0.02 M) in 0.5 M HCl was rota-evaporated to dryness at 80–90 °C (≈30 min), and the solid dissolved in a solution of iminodiacetic acid, H_2ida (0.5 g in 15 cm^3 H_2O). The orange solution was filtered and allowed to evaporate slowly in a conical flask at room temperature. After 1 week a yellow microcrystalline product was collected, washed with a small amount of H_2O and dried in air (Found: C, 16.7; H, 2.3; N, 5.0. Calc. for $C_8H_{14}N_2Nb_2O_{10}S_4$: C, 15.7; H, 2.3; N, 4.6%). Yield 0.13 g (71%). The UV/VIS absorbance peaks at 314 and 360 nm ($A_{314}/A_{360} = 1.5$) were not quantified in terms of ε due to the low solubility.

Preparation of $[Nb_2(\mu\text{-}S_2)_2(H_2edta)_2]\cdot 3H_2O$

A sample of $Cs_4[Nb_2(\mu\text{-}S_2)_2(NCS)_8]\cdot 2H_2O$ (0.38 g) was dissolved in 4 M HCl (10 cm^3) with heating, and H_2O (15 cm^3) added. The solution was filtered and ethylenediaminetetraacetate added as the disodium dihydrogen salt Na_2H_2edta (0.25 g) in hot water (20 cm^3), followed by an additional 20 cm^3 of H_2O. The solution was boiled for 3 min and filtered while hot. After slow cooling (≈1 h), fine crystals were obtained. Recrystallisation was from boiling H_2O (20 cm^3) (Found: C, 25.9; H, 3.5; N, 5.5. Calc. for $C_{20}H_{28}N_4Nb_2O_{16}S_4\cdot 3H_2O$: C, 25.3; H, 3.6; N, 5.9%). Yield 0.10 g (38%).

Preparation of $[Nb_2(\mu\text{-}S)_2(H_2O)_8]^{4+}$

The green $[Nb_2(\mu\text{-}S)_2(H_2O)_8]^{4+}$ ion was obtained by reacting $[Nb_2(\mu\text{-}S_2)_2(H_2O)_8]^{4+}$ with a stoichiometric amount of $Na_3(3\text{-}SO_3C_6H_4)_3P\cdot 4H_2O$ (Strem) (referred to as $PR_3{}^{3-}$) in what is a fast reaction <1 min. Over periods >1 h 1.0–2.0 M $HClO_4$ solutions are not stable, the smell of H_2S is detected and some cloudiness is observed; Hpts solutions were therefore used. Solutions in air show some instability over 1 h (≈10% absorbance increase at 620 nm), and runs were carried out under N_2.

Attempted preparation of $[Mo_2(\mu\text{-}S_2)_2(H_2O)_6]^{6+}$

The complex $[NH_4]_2[Mo_2(\mu\text{-}S_2)_2Br_8]$ was prepared,[14] and a solution (0.37 g) in hot concentrated HCl (35 cm^3) diluted 1 : 2 with H_2O. A dark brown precipitate was filtered off and the filtrate rota-evaporated to dryness. The latter solid was taken up in 0.5 M HCl, diluted to $[H^+] = 0.2$ M and loaded into a Dowex 50W-X2 cation-exchange column. The product eluted with 1 M $HClO_4$ was identified as $[Mo_2O_2(\mu\text{-}S)_2(H_2O)_6]^{2+}$ from the UV/VIS spectrum, peaks λ/nm (ε/M^{-1} cm^{-1} per Mo_2) at 225 (5800), 245 (4120), 280 (5510), 370 (1940).[15,16] Yield 70%. The dark brown precipitate dissolves in KCN (1 g in 10 cm^3 of H_2O), and the product identified as $[Mo_3S_4(CN)_9]^{5-}$ from its UV/VIS spectrum 342 (4500), 377 (5500), 610 (500) (ε values per Mo_3).[17] On stirring $[NH_4]_2[Mo_2(\mu\text{-}S_2)_2Br_8]$ in 4 M $HClO_4$ (4 h; 40 °C) the same $[Mo_2O_2(\mu\text{-}S)_2(H_2O)_6]^{2+}$ product is obtained. Yield 60%.

X-Ray crystallography

Crystal data for $[Nb_2(\mu\text{-}S_2)_2(H_2O)_8][pts]_4\cdot 4H_2O$ **1**: $C_{28}H_{52}Nb_2O_{24}S_8$, $M = 1215.0$, triclinic, space group $P1$, $a = 8.7663(6)$, $b = 16.9816(12)$, $c = 23.889(2)$ Å, $\alpha = 82.247(2)$, $\beta = 88.760(2)$, $\gamma = 81.868(2)°$, $U = 3488.4(4)$ Å^3, $Z = 3$, $D_c = 1.735$ g cm^{-3}, $\mu = 0.933$ mm^{-1} (Mo-Kα, $\lambda = 0.710\ 73$ Å), $F(000) = 1866$, $T = 160$ K. A yellow crystal of size 0.44 × 0.25 × 0.22 mm was examined on a Siemens SMART CCD area-detector diffractometer. Cell parameters were refined from observed setting angles of all strong reflections in the complete data set. Intensities were integrated from several series of exposures, each taken over 0.3° ω rotation, covering more than a hemisphere of reciprocal space with $2\theta \leqslant 50°$, and were corrected semiempirically for absorption, based on equivalent and repeated reflections (transmission factors 0.695–0.813), which also indicated no significant intensity decay. 18 299 measured reflections yielded 12 088 unique data ($R_{int} = 0.0237$). The structure was solved by direct methods and refined by least-squares on F^2 values for all data, with weights $w^{-1} = \sigma^2(F_o{}^2) + (0.0359P) + (30.7048P)$, where $P = (2F_c{}^2 + F_o{}^2)/3$. An isotropic extinction coefficient x was refined to 0.002 26(14), whereby F_c is multiplied by $(1 + 0.001x\lambda^3F_c{}^2/\sin 2\theta)^{-\frac{1}{4}}$. Final $R' = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{\frac{1}{2}} = 0.1484$ for all data, conventional $R = 0.0559$ for F values of 9106 reflections having $F_o{}^2 > 2\sigma(F_o{}^2)$, goodness of fit = 1.063 on F^2 for all reflections and 1207 refined parameters. Disordered anions were refined with restraints on geometrical and displacement parameters; isotopic hydrogen atoms were constrained. The largest features in a final difference synthesis (extremes +1.03 and −1.95 e Å^{-3}) were around the disordered anions.

Crystal data for $Cs_4[Nb(\mu\text{-}S_2)_2(NCS)_8]\cdot 2H_2O$ **2**: $C_8H_4Cs_4N_8Nb_2O_2S_{12}$, $M = 1346.4$, monoclinic, space group $P2_1/c$, $a = 15.8752(14)$, $b = 14.4831(13)$, $c = 14.4257(12)$ Å, $\beta = 93.425(2)°$, $U = 3310.9(5)$ Å^3, $Z = 4$, $D_c = 2.701$ g cm^{-3}, $\mu = 5.81$ mm^{-1}, $F(000) = 2472$, $T = 160$ K. Procedures were as for salt **1**, with an orange crystal of size 0.52 × 0.08 × 0.06 mm; transmission factors 0.217–0.279, 17 179 measured reflections, 5831 unique data, $R_{int} = 0.0528$, $w^{-1} = \sigma^2(F_o{}^2) + (0.0334P)^2 + (39.2354P)$, $x = 0.000\ 31(5)$. Some large electron density peaks were interpreted and successfully refined as disorder for two of the Cs^+ ions and as partial substitution of S^{2-} for $S_2{}^{2-}$ ligands in both independent anions; residual peaks (extremes +2.68 and –1.43 e Å^{-3}) were close to heavy atoms. Hydrogen atoms were omitted. Final $R' = 0.1186$ for all data, $R = 0.0492$ for F values of 4618 reflections having $F_o{}^2 > 2\sigma(F_o{}^2)$, goodness of fit = 1.106 on F^2 for all reflections and 366 refined parameters.

Programs were Siemens SMART and SAINT control and integration software and SHELXTL,[18] together with local programs.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/506.

Kinetic studies

All runs were carried out at 25.0 ± 0.1 °C. The aqua ion $[Nb_2(\mu\text{-}S_2)_2(H_2O)_8]^{4+}$ was eluted from a Dowex 50W-X2 cation-exchange column with 4 M $HClO_4$. Stock solutions were as a precaution stored under N_2. Conventional time range runs ($t_{\frac{1}{2}} > 1$ min) were monitored on a Perkin-Elmer Lambda 9 spectrophotometer. Air-free techniques were not required. The reaction of $[Nb_2(\mu\text{-}S_2)_2(H_2O)_8]^{4+}$ in aqueous perchloric acid solutions, $I = 2.00 \pm 0.01$ M ($LiClO_4$), with NCS^-, reactant in >10-fold excess, was monitored at 338 nm, with some check runs at 400 nm. The equilibration of $[Nb_2(\mu\text{-}S)_2(H_2O)_8]^{4+}$ with

Table 1 Selected bond lengths (Å) for salt **1**

Nb(1)–Nb(2)	2.8984(7)	Nb(1)–S(1)	2.4904(15)
Nb(1)–S(2)	2.497(2)	Nb(1)–S(3)	2.515(2)
Nb(1)–S(4)	2.4879(14)	Nb(1)–O(1)	2.175(4)
Nb(1)–O(2)	2.177(4)	Nb(1)–O(3)	2.173(4)
Nb(1)–O(4)	2.156(4)	Nb(2)–S(1)	2.4895(14)
Nb(2)–S(2)	2.512(2)	Nb(2)–S(3)	2.4987(15)
Nb(2)–S(4)	2.4845(14)	Nb(2)–O(5)	2.170(4)
Nb(2)–O(6)	2.170(4)	Nb(2)–O(7)	2.179(4)
Nb(2)–O(8)	2.178(4)	S(1)–S(2)	2.020(2)
S(3)–S(4)	2.022(2)	Nb(3)–Nb(3a)	2.8910(10)
Nb(3)–S(5)	2.4933(15)	Nb(3)–S(5a)	2.4857(15)
Nb(3)–S(6)	2.511(2)	Nb(3)–S(6a)	2.498(2)
Nb(3)–O(9)	2.162(4)	Nb(3)–O(10)	2.174(4)
Nb(3)–O(11)	2.174(4)	Nb(3)–O(12)	2.176(4)
S(5)–S(6)	2.024(2)		

Symmetry transformations used to generate equivalent atoms: *a* $-x + 1, -y + 1, -z + 1$.

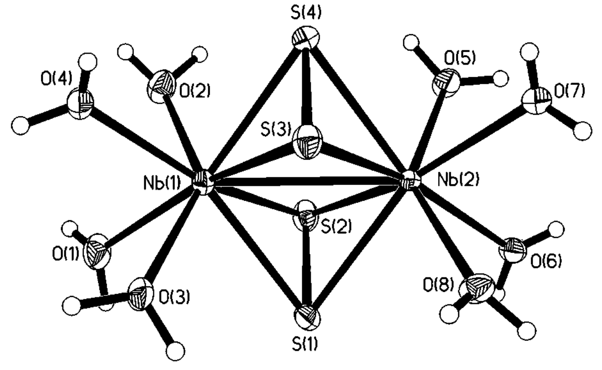


Fig. 1 Structure of one of the cations in salt **1** with 50% displacement ellipsoids and atom numbering

NCS^- was studied in 2.0 M Hpts. The equilibration with $[H^+]$ in the range 0.7–2.0 M $[H^+]$ was also studied by spectrophotometry under similar conditions.

Treatment of data

Unweighted least-squares fitting procedures were used.

Results

Crystal structures

The salt **1** contains two crystallographically independent $[Nb_2(\mu\text{-}S_2)_2(H_2O)_8]^{4+}$ cations, one in a general position, the other on an inversion centre, giving three formula units per unit cell. The two cations are essentially identical, with two symmetrically bridging $\eta^2{:}\eta^2$ disulfido ligands each, Fig. 1. Selected bond lengths are in Table 1. The Nb–O bond lengths to terminal aqua ligands are in the range 2.156(4)–2.179(4) Å; values from 2.133 to 2.318 Å have been found previously in aqua–Nb^V complexes with oxalato ligands.[19,20] There appear to be no previous examples of structurally characterised aqua-Nb^{IV} complexes. An extensive network of hydrogen bonds links the aqua ligands, *p*-toluenesulfonate anions and molecules of water of crystallisation. The anions all display disorder of orientation of their tolyl groups, but their sulfonate groups are held ordered by the hydrogen bonding.

Both crystallographically independent $[Nb_2(\mu\text{-}S_2)_2(NCS)_8]^{4-}$ anions in **2** lie on inversion centres. There appears to be disorder involving the replacement of a proportion of disulfido $S_2{}^{2-}$ ligands by sulfido S^{2-} ligands; introduction of this into the refinement markedly improved the agreement with the data, removed the very large electron density peaks close to the S–S bond mid-points, produced more reasonable displacement parameters, and led to acceptable geometry. Except for the disorder, the geometry of the anions, Fig. 2, is essentially the same as in the previously reported *N*-ethylquinolinium salt.[13] Selected bond lengths are in Table 2.

Table 2 Selected bond lengths (Å) for salt **2**

Nb(1)–Nb(1a)	2.8669(15)	Nb(1)–S(1)	2.512(3)
Nb(1)–S(1a)	2.505(3)	Nb(1)–S(2)	2.495(3)
Nb(1)–S(2a)	2.503(3)	Nb(1)–N(1)	2.180(8)
Nb(1)–N(2)	2.194(8)	Nb(1)–N(3)	2.180(8)
Nb(1)–N(4)	2.191(8)	S(1)–S(2)	2.010(6)
Nb(2)–Nb(2b)	2.8580(14)	Nb(2)–S(7)	2.515(4)
Nb(2)–S(7b)	2.510(4)	Nb(2)–S(8)	2.524(4)
Nb(2)–S(8b)	2.524(4)	Nb(2)–N(5)	2.182(8)
Nb(2)–N(6)	2.188(8)	Nb(2)–N(7)	2.189(8)
Nb(2)–N(8)	2.191(8)	S(7)–S(8)	1.984(9)

Symmetry transformations used to generate equivalent atoms: *a* $-x + 1, -y + 1, -z + 1$; *b* $-x + 2, -y + 1, -z + 2$.

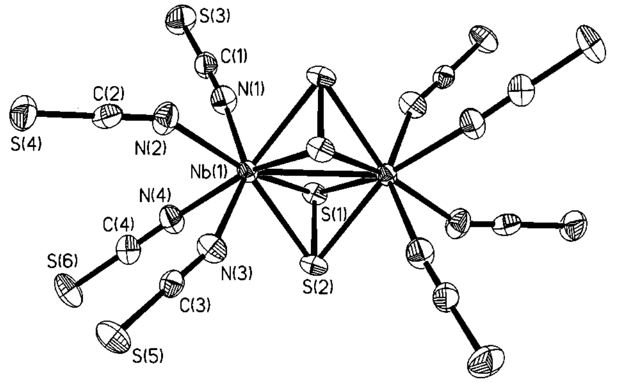


Fig. 2 Structure of one of the anions in salt **2** with 50% displacement ellipsoids. Only the major component is shown

The Nb_2S_4 cores of these two complexes **1** and **2** are essentially the same over all four independent occurrences in the two structures. The Nb–S bond lengths in the range 2.4845(14)–2.524(4) Å, mean 2.497 Å in **1**, 2.511 Å in **2**, are scarcely affected by the exchange of NCS^- for H_2O ligands, and display a symmetrical bridging mode with all S atoms equivalent. The S–S bond lengths lie in the range 1.984(9)–2.024(2) Å, typical of this ligand.

The short Nb–Nb distances in the range 2.8580(14)–2.8984(7) Å are consistent with metal–metal bonding, and are in accord with the observed diamagnetism.

Kinetics of $[Nb_2(\mu\text{-}S_2)_2(H_2O)_8]^{4+}$ with NCS^-

First-order equilibration rate constants k_{eq} (25 °C) for the reaction of $[Nb_2(\mu\text{-}S_2)_2(H_2O)_8]^{4+}$ with NCS^- (reactant in >10-fold excess), Table 3, give first-order dependences on $[NCS^-]$, Fig. 3. No absorbance changes were observed in the stopped-flow range. The linear dependences can be expressed in terms of formation (k_f) and aquation (k_{aq}) rate constants as in equation (1). Values of k_f (slope) and k_{aq} (intercept) obtained are listed in

$$k_{eq} = k_f\,[NCS^-] + k_{aq} \qquad (1)$$

Table 4. Both k_f and k_{aq} give dependences on $[H^+]^{-1}$, Fig. 4, which can be expressed as in equations (2) and (3) respectively.

$$k_f = k_1 + k_2[H^+]^{-1} \qquad (2)$$

$$k_{aq} = k_{-1} + k_{-2}[H^+]^{-1} \qquad (3)$$

Values of $k_1 = 0.88(3)\ M^{-1}\ s^{-1}$, $k_2 = 0.47(2)\ s^{-1}$, $k_{-1} = 2.4(4) \times 10^{-3}\ s^{-1}$, $k_{-2} = 1.8(2) \times 10^{-3}\ M\ s^{-1}$ were obtained. The reaction can be expressed as in equation (4), where k_1/k_{-1} gives an

Table 3 First-order equilibration rate constants k_{eq} (25 °C) from conventional time range studies on the reaction of $[Nb_2(S_2)_2(H_2O)_8]^{4+}$ with NCS^-, $I = 2.0$ M ($LiClO_4$)

$[H^+]$/M	$10^3[NCS^-]$/M	$10^3k_{eq}/s^{-1}$
2.00	0.62	0.38
	1.86	0.51
	2.75	0.63
	3.72	0.72
	7.30	0.78
	6.20	1.00
1.30	0.62	0.45
	1.55	0.51
	3.10	0.57
	7.65	0.83
	6.20	1.18
	7.75	1.36
1.00	0.62	0.50
	1.55	0.66
	3.10	0.90
	7.65	1.03
	6.20	1.31
	7.75	1.40
0.75	0.62	0.58
	1.55	0.81
	3.10	0.95
	3.72	1.08
	7.65	1.17
0.50	3.10	1.13
	7.65	1.30
	6.20	1.65
	7.75	1.75
0.31	0.66	0.98
	1.65	1.13
	3.10	1.45
	4.67	1.88
	6.20	2.20
	7.75	2.42

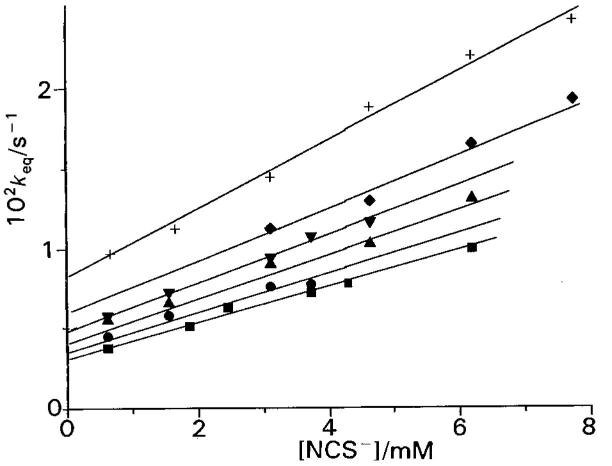


Fig. 3 Dependence of equilibration rate constants k_{eq} (25 °C) on $[NCS^-]$ for the reaction of $[Nb_2(\mu\text{-}S_2)_2(H_2O)_8]^{4+}$ with NCS^-, with $[H^+] = 0.31$ (+), 0.50 (◆), 0.75 (▼), 1.00 (▲), 1.30 (●), 2.00 (■) M, $I = 2.00$ M ($LiClO_4$)

$$[Nb(\mu\text{-}S_2)_2(H_2O)_8]^{4+} + NCS^- \rightleftharpoons [Nb(\mu\text{-}S_2)_2(H_2O)_7(NCS)]^{3+} \qquad (4)$$

equilibrium constant of 370(72) M^{-1} indicating a high affinity for thiocyanate.

Sulfur abstraction reactions on $[Nb_2(\mu\text{-}S_2)_2(H_2O)_8]^{4+}$

Reactions with phosphines give abstraction of neutral S-atoms and conversion of $\mu\text{-}S_2^{2-}$ into $\mu\text{-}S^{2-}$.[21] To a solution of $[Nb_2(\mu\text{-}S_2)_2(H_2O)_8]^{4+}$ (1 mM in 4 M Hpts) an excess of water-soluble phenylsulfonate derivative PR_3^{3-} was added (4 mM), and an orange to green colour change was observed in ≈3 min. The alternative two-phase reaction of insoluble PPh_3 (as for a 10 mM solution) to the same 4 M Hpts solution of $[Nb_2(\mu\text{-}S)_2(H_2O)_8]^{4+}$, takes somewhat longer (≈1 h). Titrations of PR_3^{3-} (9 mM; Hamilton microsyringe) with $[Nb_2(\mu\text{-}S_2)_2(H_2O)_8]^{4+}$ (0.3 mM) give a 2:1 stoichiometry, equation (5), and the

$$Nb_2(\mu\text{-}S_2)_2^{4+} + 2PR_3^{3-} \longrightarrow Nb_2(\mu\text{-}S)_2^{4+} + 2SPR_3^{3-} \qquad (5)$$

product can therefore be assumed to have the formula $[Nb_2(\mu\text{-}S)_2(H_2O)_8]^{4+}$, or related (more H_2O's?). The product in 4 M Hpts has a UV/VIS peak at 617 nm (Fig. 5), is stable under N_2, and decomposes only slowly in air. The same reaction is observed in 4 M HCl, peak at 652 nm ($\varepsilon = 31$ M^{-1} cm^{-1} per Nb_2), but in 4 M $HClO_4$ (under N_2) the green solution becomes cloudy within 1 h. Dowex 50W-X2 cation-exchange purification was attempted on the HCl and Hpts solutions. However, on dilution to $[H^+] < 0.5$ M for loading purposes, the green solution became brown, H_2S was evolved, and a decomposition process is evident.

Table 4 Summary of formation (k_f) and aquation (k_{aq}) rate constants (25 °C) for the equilibration of $[Nb_2(S_2)_2(H_2O)_8]^{4+}$ with NCS^-, $I = 2.0$ M ($LiClO_4$)

$[H^+]$/M	$k_f/M^{-1}\,s^{-1}$	$10^2k_{aq}/s^{-1}$
2.00	1.1	0.34
1.30	1.3	0.36
1.00	1.3	0.46
0.75	1.5	0.48
0.50	1.8	0.52
0.31	2.4	0.84

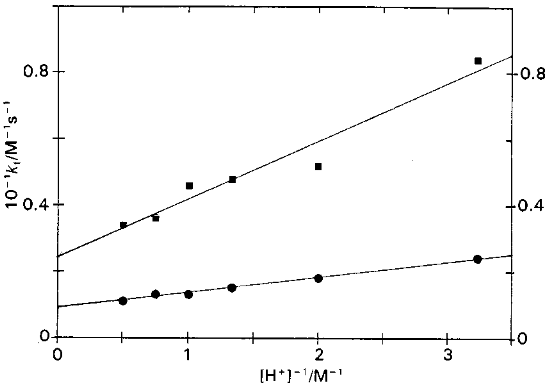


Fig. 4 Dependence of formation rate constants k_f (●, left-hand side scale), and aquation rate constants, k_{aq} (■, right-hand side scale) on $[H^+]^{-1}$ for the reaction (25 °C) of $[Nb_2(\mu\text{-}S_2)_2(H_2O)_8]^{4+}$ with NCS^-, $I = 2.00$ M ($LiClO_4$)

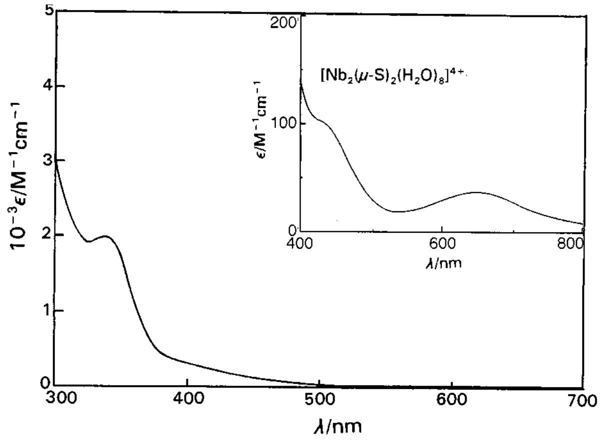


Fig. 5 The UV/VIS spectra of yellow $[Nb_2(\mu\text{-}S_2)_2(H_2O)_8]^{4+}$, and (inset) the green product following S-abstraction with phosphines, assigned as $[Nb_2(\mu\text{-}S)_2(H_2O)_8]^{4+}$ in 4 M Hpts solutions

Table 5 First-order equilibration rate constants k_{eq} (25 °C) for the stopped-flow reaction of $[Nb_2(\mu\text{-}S)_2(H_2O)_8]^{4+}$ (0.35×10^{-4} M) with NCS^-, $I = 2.0$ M (Hpts)

$[NCS^-]$/mM	k_{eq}/s^{-1}
3.5	0.172
4.5	0.200
5.0	0.220
7.5	0.319
10	0.410

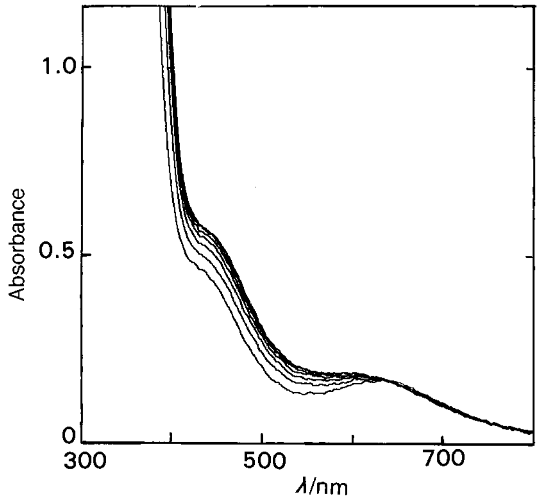


Fig. 6 Showing the increase in absorbance of a solution of $Nb_2(\mu\text{-}S)_2^{4+}$ on decreasing the concentration of HCl from 4 to 1 M (scans every 5 min), corresponding to a green to yellow colour change (complete ≈40 min). On adjusting the HCl from 1 to 4 M by addition of concentrated HCl the green colour is restored. An isosbestic point is observed at 635 nm

Sulfur abstraction is also observed with CN^-, equation (6),

$$Nb_2(\mu\text{-}S_2)_2^{4+} + 2CN^- \longrightarrow Nb(\mu\text{-}S)_2^{4+} + 2SCN^- \quad (6)$$

when the CN^- also replaces the H_2O ligands.[17,22] Two procedures were used. A solution of $[Nb_2(\mu\text{-}S_2)_2(H_2O)_8]^{4+}$ (3 mM) in 2 M HCl was evaporated to dryness under reduced pressure, and the orange solid dissolved in KCN (1 g) in H_2O (10 cm^3). The clear brown solution obtained was, however, stable for only 1–2 min. Subsequently a white precipitate of Nb_2O_5 (or related) separates out, and the smell of H_2S was apparent. Alternatively $[Nb_2(\mu\text{-}S_2)_2(H_2O)_8]^{4+}$ was eluted from an ion-exchange column with a 0.1 M solution of KCN.

Kinetics of $[Nb_2(\mu\text{-}S)_2(H_2O)_8]^{4+}$ with NCS^-

Solutions of $[Nb_2(\mu\text{-}S)_2(H_2O)_8]^{4+}$ were first prepared by reacting $[Nb_2(\mu\text{-}S_2)_2(H_2O)_8]^{4+}$ (1.6 mM; 5 cm^3) with a two-fold amount of PR_3^{3-} (8.4 mM; 2 cm^3), both in 2.0 M Hpts. The yellow to green colour change was complete in ≈3 min, and solutions were stable for days. No further purification was carried out. Equilibration rate constants, k_{eq} (25 °C) for substitution of H_2O with NCS^- are given in Table 5. The reaction can be expressed as in equation (4). A linear dependence of the form shown in equation (7), is observed, with $k_f = 37.4(8)$ M^{-1} s^{-1}, $k_{aq} =$

$$k_{eq} = k_f[NCS^-] + k_{aq} \quad (7)$$

0.036(6) s^{-1}, in 2.0 M Hpts, giving an equilibrium constant (k_f/k_{aq}) of $1.04(20) \times 10^3$ M^{-1}.

Effect of $[H^+]$ on $[Nb_2(\mu\text{-}S)_2(H_2O)_8]^{4+}$

Absorbance changes were identified on diluting freshly prepared solutions of green $[Nb_2(\mu\text{-}S)_2(H_2O)_8]^{4+}$ in 4.0 M HCl (under N_2) to (*a*) 2.0 and (*b*) 1.0 M HCl, and recording UV/VIS spectra every 5 min, *e.g.* Fig. 6. A colour change to yellow was observed (≈40 min) with isosbestic points at ≈330 and 635 nm. Absorbance increases at 430 nm indicate that the reaction proceeds further in 1.0 than in 2.0 M HCl. The peak at 652 nm is retained with little change. When the [HCl] is restored to 4.0 M by addition of concentrated acid the green product reforms with the same isosbestic points and at about the same rate. At $[H^+] < 0.5$ M an irreversible decay process is observed. Kinetic equilibration studies on the green to yellow change were carried out by preparing a solution of $[Nb_2(\mu\text{-}S)_2(H_2O)_8]^{4+}$ in 4 M Hpts, and diluting to $[H^+]$ values in the range 0.80–2.00 M, $I = 2.00$ M (Lipts). Relevant data are shown in Table 6. Smaller absorbance increases during the first 10–20 min of reaction (insert to Fig. 7) are attributed to the aquation of pts^- ligands, some complexing of which occurs in 4 M Hpts. Kinetic plots for subsequent absorbance changes define first-order rate constants k_H, Table 6. From a plot of k_H against $[H^+]^{-1}$, Fig. 7, the slope is $4.2(2) \times 10^{-4}$ M^{-1} s^{-1}. The forward reaction can be expressed as in equations (8) and (9), in which case the slope is k_3K_a. Acid

Table 6 First-order rate constants k_H (25 °C) from absorbance changes on decreasing the $[H^+]$ of solutions of $[Nb_2(\mu\text{-}S)_2(H_2O)_8]^{4+}$, $I = 2.00$ M (Lipts)

$[H^+]$/M	$[Nb_2(\mu\text{-}S)_2^{4+}]$/mM	10^4k_H/s^{-1}
0.80	0.92	5.8
0.85	0.61	5.4
0.90	0.80	4.9
1.00	0.95	4.8
1.20	0.80	4.1
1.50	2.3	3.5
1.70	0.80	2.9
2.00	0.80	2.4

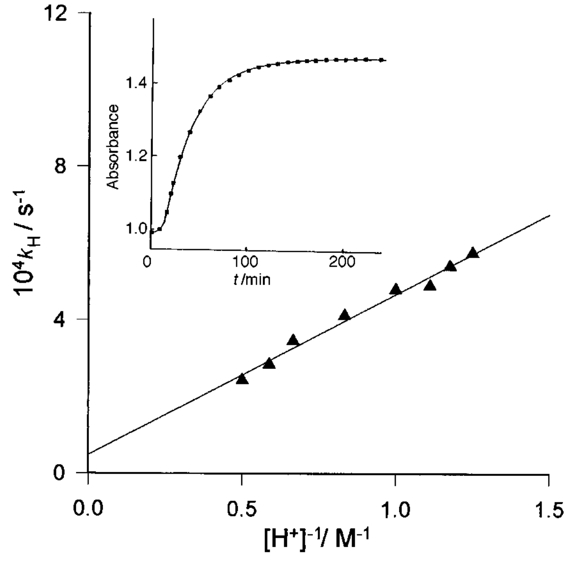


Fig. 7 The variation of rate constants k_H (25 °C) obtained on adjusting the $[H^+]$ of solutions of $[Nb_2(\mu\text{-}S)_2(H_2O)_8]^{4+}$, $I = 2.00$ M (Lipts). The inset shows absorbance changes at 350 nm for a run with $[Nb_2(\mu\text{-}S)_2(H_2O)_8^{4+}] = 0.80$ mM, $[H^+]$ adjusted from 4.0 to 0.90 M Hpts, and illustrates the initial stage of reaction (up to 20 min) prior to k_H

$$[Nb_2(\mu\text{-}S)_2(H_2O)_8]^{4+} \overset{K_a}{\rightleftharpoons} [Nb_2(\mu\text{-}S)_2(H_2O)_7OH]^{3+} + H^+ \quad (8)$$

$$[Nb_2(\mu\text{-}S)_2(H_2O)_7OH]^{3+} \xrightarrow{k_3} \text{product} \quad (9)$$

dissociation as in equation (8) is generally very fast. The intercept (k_{-3}) in Fig. 7 corresponds to the back reaction in equation (9) and is $0.50(20) \times 10^{-4}$ s^{-1}. The equilibrium constant k_3K_a/k_{-3} is 8.4 M^{-1}

Conversion of $[Nb_2(\mu\text{-}S)_2(H_2O)_8]^{4+}$ into cuboidal products

Reduction of $[Nb_2(\mu\text{-}S_2)_2(H_2O)_8]^{4+}$ (1 mM; 10 cm^3) in acid with $NaBH_4$ (100-fold excess) was attempted, *cf.* the reaction of $[Mo_2O_2(\mu\text{-}S)_2(cys)_2]^{2-}$ (cys = cysteine) with BH_4^-, when the Mo_4S_4 cube is generated.[23] A dichroic brown-violet solution was obtained, peak at 737 nm. On decreasing the $[H^+]$ to 0.3 M in order to load a Dowex 50W-X2 cation-exchange column, a decay process was observed.

Aquation of the $[Mo_2(\mu\text{-}S_2)_2(Br)_8]^{2-}$ analogue

On diluting solutions of $[NH_4]_2[Mo_2(\mu\text{-}S_2)_2Br_8]$ in concentrated HBr or HCl, $[Mo_2O_2(\mu\text{-}S)_2(H_2O)_6]^{2+}$ was identified in 60–70% yields,[15,16] together with a second solid which with CN^- gives $[Mo_3S_4(CN)_9]^{5-}$.[17] The same products were obtained on stirring the bromide complex with 4 M $HClO_4$. There was no evidence for the formation of $[Mo_2(\mu\text{-}S_2)_2(H_2O)_8]^{6+}$.

Discussion

There is an almost total lack of kinetic/mechanistic studies on Nb-containing complexes in aqueous solution. The complexes investigated have as an added interest $\mu\text{-}S_2^{2-}$ and $\mu\text{-}S^{2-}$ ligands. The disulfido S_2^{2-} group shows a remarkable degree of flexibility in its co-ordination chemistry stemming no doubt from its electron lone pairs. One of the most common forms is with S_2^{2-} bonded sideways to a single metal (M), but variations are observed in different M_2, M_3 and M_4 situations, and Müller and Diemann[24] have indicated ten different structural variants. Examples of $\eta^2{:}\eta^2$ S_2^{2-} bridging two metal atoms are fairly numerous (eleven examples[24]). Crystal structures of the two $Nb_2(\mu\text{-}S_2)_2^{4+}$ complexes reported give an average S–S distance of 2.01 Å, in accord with the listing for other complexes in the range 1.98–2.05 Å (Table 1 in ref. 24). Both the binuclear Nb^{IV} (d^1) complexes have short Nb–Nb distances consistent with metal–metal bonding, confirmed by the diamagnetism. Although the S_2^{2-} ligand has only a small co-ordination angle at the metal, the increased co-ordination number may help protect the metal atoms from nucleophilic attack. In addition the S_2^{2-} ligands have π-donor properties, with π_y^* and π_z^* S_2^{2-} donations to the two Nb atoms. Such a depopulation of π* orbitals leaves the S_2^{2-} ligands susceptible to nucleophilic attack by PR_3^{3-} and CN^-, when abstraction of neutral S atoms occurs. The S_2^{2-} π donations to the Nb atoms also influences the substitution of H_2O on $[Nb_2(\mu\text{-}S_2)_2(H_2O)_8]^{4+}$, as will now be discussed.

Studies on the substitution of NCS^- for H_2O on $[Nb_2(\mu\text{-}S_2)_2(H_2O)_8]^{4+}$ give a formation rate constant $k_1 = 0.88$ M^{-1} s^{-1}. The enhancement in rate provided by the $[H^+]^{-1}$ term is explained by H_2O conjugate-base formation, and labilisation by the OH^- ligand.[25] This is normal expected behaviour. The acid dissociation does not appear to be extensive, since no curvature is observed for the plots in Fig. 4. The most significant observation concerns the slowness of k_1 for substitution on $[Nb_2(\mu\text{-}S_2)_2(H_2O)_8]^{4+}$. The slowness is explained by the high oxidation state of the Nb^{IV}, and by the π-electron donation from S_2^{2-} to the Nb^{IV}. As a general rule low d-electron d^1 and d^2 hexaaqua metal ions undergo fast substitution, where water-exchange rate constants for $[Ti(H_2O)_6]^{3+}$ ($\approx 10^5$ M^{-1} s^{-1})[26] and $[V(H_2O)_6]^{3+}$ (1.6×10^3 M^{-1} s^{-1})[27] are good examples.

The substitution of NCS^- for H_2O on $[Nb_2(\mu\text{-}S)_2(H_2O)_8]^{4+}$ was also studied, and gives a 34-fold increase in k_f as compared to $[Nb_2(\mu\text{-}S_2)_2(H_2O)_8]^{4+}$ at $[H^+] = 2.00$ M. This is a measure of the relative influence of $\mu\text{-}S^{2-}$ and $\mu\text{-}S_2^{2-}$ ligands. Studies were in Hpts because of the instability in ClO_4^- solutions, but little effect is expected to result from this change. With the less extensive π donation for the μ-S ligands the rate constant is more in line with what might be expected for substitution on Nb^{IV}.

Table 7 Comparisons of formation (k_f) and aquation (k_{aq}) substitution rate constants (25 °C) for $[Nb^{IV}{}_2S_4(H_2O)_8]^{4+}$ with those for other 1:1 NCS^- (or as indicated) reactions of $Mo^V(d^1)$ (binuclear) and $Mo^{IV}(d^2)$ (trinuclear) complexes, $I = 2.00$ M

Reactant	$k_f/M^{-1}\ s^{-1}$	k_{aq}/s^{-1}	Ref.
$[Nb^{IV}{}_2(\mu\text{-}S_2)_2(H_2O)_8]^{4+}$	0.88^a	$2.4 \times 10^{-3\,a}$	This work
$[Nb^{IV}{}_2(\mu\text{-}S)_2(H_2O)_8]^{4+}$	37.4^b	0.036^b	This work
$[Nb^{III}{}_2Nb^{IV}(\mu_3\text{-}Cl)(\mu\text{-}O)_3\text{-}(H_2O)_9]^{4+}$	352^c $8.3 \times 10^{-3\,c}$		1
$[Mo^V{}_2O_2(\mu\text{-}O)_2(H_2O)_6]^{2+\,d}$	2.9×10^4	1.2×10^2	28
$[Mo^V{}_2O_2(\mu\text{-}S)_2(C_2O_4)_2\text{-}(H_2O)_2]^{2+\,d}$	2.1×10^5	3.5×10^4	16
$[Mo^{IV}{}_3(\mu_3\text{-}O)(\mu\text{-}O)_3(H_2O)_9]^{4+\,e,f}$	0.80	1.51×10^{-3}	29
$[Mo^{IV}{}_3(\mu_3\text{-}S)(\mu\text{-}S)_3(H_2O)_9]^{4+\,e,g}$	212	0.092	30
$[Mo^{IV}{}_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3(H_2O)_6]^{4+\,h}$	5.5×10^{-4}	0.47×10^{-4}	21

[a] k_1 and k_{-1} as defined in equations (2) and (3). [b] In 2.0 M Hpts. [c] Units s^{-1}. [d] No $[H^+]^{-1}$ dependence. [e] At $[H^+] = 2.0$ M. [f] Substitution of the more labile H_2O ligands *cis* to μ_3-O. [g] Substitution of the more labile H_2O ligands *cis* to μ_3-S. [h] Reaction with Cl^-. One H_2O only to each Mo is replaced at $[Cl^-] = 2.0$ M.

As far as previous studies on metal–metal bonded binuclear Mo^V (d^1) complexes are concerned, fast substitution of NCS^- for H_2O on $[Mo_2O_2(\mu\text{-}O)_2(H_2O)_6]^{2+}$ (2.9×10^4 M^{-1} s^{-1}),[28] and $[Mo_2O_2(\mu\text{-}S)_2(C_2O_4)_2(H_2O)_2]^{2-}$ (2.1×10^5 M^{-1} s^{-1})[25] has been observed. These reactions are, however, fast because of the labilising influence of the terminal oxo groups. Comparisons can also be made of the $Mo^{IV}{}_3$ clusters $[Mo_3O_4(H_2O)_9]^{4+}$ and $[Mo_3S_4(H_2O)_9]^{4+}$, when an overall labilising effect of $\mu\text{-}O^{2-}$ and $\mu\text{-}S^{2-}$ ligands is indicated, Table 7. In the latter case however the rate constant (212 M^{-1} s^{-1})[29] for NCS^- substitution is very much bigger than for $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3(H_2O)_6]^{4+}$ (5.5×10^{-4} M^{-1} s^{-1})[21] (factor of 4×10^5). There have been no previous studies on $Nb^{IV}{}_2$ complexes, but we note that the faster water-exchange (two H_2O per Nb) on the $Nb^{III}Nb^{IV}{}_2$ cluster $[Nb_3(\mu_2\text{-}Cl)(\mu\text{-}O)_3(H_2O)_9]^{4+}$ gives a rate constant of 352 s^{-1}.[1] It is concluded that $\mu\text{-}S_2^{2-}$ ligands bring about a marked decrease in rate constants for H_2O substitution.

Since Mo^V binuclear complexes with a $Mo_2(\mu\text{-}S_2)_2$ core are quite common,[24,30,31] and are isoelectronic with $Nb_2(\mu\text{-}S_2)_2$, we also explored the possibility of generating the aqua ion $[Mo_2(\mu\text{-}S_2)_2(H_2O)_8]^{6+}$ by aquation of $[Mo_2(\mu\text{-}S_2)_2Br_8]^{2-}$. From the experiments carried out this is clearly not straightforward, and aquation of Br^- yields instead $[Mo_2O_2(\mu\text{-}S)_2(H_2O)_6]^{2+}$ in 60–70% yields. The other product is trinuclear $Mo^{IV}{}_3S_4^{4+}$. When no terminal π-donor or anionic ligands are present the highly charged 6+ $Mo_2(\mu\text{-}S_2)_2$ core appears to be unstable.

Complexes of $Nb_2(\mu\text{-}S_2)_2^{4+}$ were also prepared with two edta or two ida ligands attached. The formula for the edta complex suggests a structure similar to the Re^{IV} dimer $Ba_2[Re_2(\mu\text{-}O)_2(edta)_2]\cdot 4.5H_2O$,[32] or Tc^{IV} dimer $[Tc_2(\mu\text{-}O)_2(H_2edta)_2]$,[33] which have edta co-ordinated in a tetradentate fashion to each metal with two carboxylates unco-ordinated. These structures are different from those of the single μ-edta $Mo^V{}_2$-containing $[Mo_2O_2(\mu\text{-}O)_2(edta)]^{2-}$ and related complexes,[34–36] which have an 'open-basket' six-co-ordination of the edta.

Finally in an attempt to generate cuboidal Nb_4S_4 and/or incomplete cuboidal Nb_3S_4 products, the reduction of $[Nb_2(\mu\text{-}S_2)_2(H_2O)_8]^{4+}$ with BH_4^- was explored. In this procedure it was assumed that a first stage involving reduction of $\mu\text{-}S_2^{2-} \longrightarrow \mu\text{-}S^{2-}$ occurs. The approach is similar to that adopted for generating Mo_4S_4 by BH_4^- reduction of $[Mo_2O_2(\mu\text{-}S)_2(cys)_2]^{2-}$,[23] which has protective (tridendate) cysteine ligands. A brown-violet product was obtained, but this is not sufficiently stable to allow purification by cation-exchange chromatography. Attempts to co-ordinate cysteine to the $Nb_2(\mu\text{-}S_2)_2^{4+}$ core gave a red-brown solution, followed by precipitation and a smell of H_2S indicating core decomposition. The experiments are regarded as encouraging, and further studies are planned.

Acknowledgements

We are grateful to EPSRC for research grants and financial support to (M. N. S.)

References

1 S. Minhas and D. T. Richens, *J. Chem. Soc., Dalton Trans.*, 1996, 703.
2 E. T. Maas and R. E. McCarley, *Inorg. Chem.*, 1973, **12**, 1096.
3 E. J. Roskamp and S. F. Pederson, *J. Am. Chem. Soc.*, 1987, **109**, 6551.
4 F. A. Cotton, M. P. Diebold, R. Llusar and W. J. Roth, *J. Chem. Soc., Chem. Commun.*, 1986, 1276.
5 F. A. Cotton, M. P. Diebold, X. Feng and W. J. Roth, *Inorg. Chem.*, 1988, **27**, 3414.
6 See, for example, E. Babayan-Kibala and F. A. Cotton, *Inorg. Chim. Acta*, 1991, **81**, 77; M. G. B. Drew, D. A. Rice and D. M. Williams, *J. Chem. Soc., Dalton Trans.*, 1985, 417; F. A. Cotton, M. P. Diebold and W. J. Roth, *Inorg. Chem.*, 1987, **26**, 3319.
7 See, for example, F. A. Cotton, E. Babayan-Kibala, L. R. Favello and M. Shang, *Inorg. Chem.*, 1990, **29**, 2591.
8 See, for example, F. A. Cotton and S. A. Duraj, *Inorg. Chem.*, 1984, **23**, 3592; M. G. B. Drew, D. A. Rice and D. M. Williams, *Acta Crystallogr., Sect. C*, 1984, **40**, 1547.
9 G. Wilkinson, R. D. Gillard and J. McCleverty (Editors), *Comprehensive Coordination Chemistry*, Pergamon, Oxford, 1988, vol. 3.
10 J. Rijnsdorp, G. L. DeLange and G. A. Wiegers, *J. Solid State Chem.*, 1979, **30**, 365.
11 W. Beckmann and H. Z. Schäfer, *Z. Anorg. Allg. Chem.*, 1966, **347**, 225.
12 H.-G. von Schnering and W. Beckmann, *Z. Anorg. Allg. Chem.*, 1966, **347**, 231.
13 M. Sokolov, A. Virovets, V. Nadolinnyi, K. Hegetschweiler, V. P. Fedin, N. Podberezskaya and V. Fedorov, *Inorg. Chem.*, 1994, **33**, 3503.
14 V. Fedin, Y. Mironov and V. Fedorov, *Zh. Neorg. Khim.*, 1989, **34**, 2984.
15 B. Spivack and Z. Dori, *J. Chem. Soc., Chem. Commun.*, 1973, 909.
16 F. A. Armstrong, T. Shibahara and A. G. Sykes, *Inorg. Chem.*, 1978, **17**, 189.
17 A. Müller, R. Jostes, W. Eltzner, C.-S. Nie, E. Diemann, H. Bögge, M. Zimmermann, D. Dartmann, V. Reinsch-Vogell, S. Che, S. J. Cyvin and B. N. Cyvin, *Inorg. Chem.*, 1985, **24**, 2872.
18 G. M. Sheldrick, SHELXTL mannual, Siemens Analytical X-ray Instruments Inc., Madison, WI, 1995.
19 N. Galesic, N. Brnicevic, B. Matkovic, M. Herceg, B. Zelenko, M. Sljukic, B. Prelesnik and R. Herak, *J. Less-Common. Met.*, 1977, **51**, 259; B. Kojic-Prodic, R. Liminga and S. Scavnicar, *Acta Crystallogr., Sect. B*, 1973, **29**, 864.
20 L. Eriksson, G. Svensson and V. Tabachenko, *Acta Chem.Scand.*, 1993, **47**, 1038.
21 D. N. Saysell, V. P. Fedin, G. J. Lamprecht, M. N. Sokolov and A. G. Sykes, *Inorg. Chem.*, in the press.
22 V. P. Fedin, G. J. Lamprecht, T. Kohzuma, W. Clegg, M. R. J. Elsegood and A. G. Sykes, 1997, 1747.
23 M. Martinez, B.-L. Ooi and A. G. Sykes, *J. Am. Chem. Soc.*, 1987, **109**, 4615.
24 A. Müller and E. Diemann, *Adv. Inorg. Chem.*, 1987, **31**, 89–122.
25 See, for example, B.-L. Ooi and A. G. Sykes, *Inorg. Chem.*, 1988, **27**, 310.
26 A. M. Chmelnick and D. Fiat, *J. Chem. Phys.*, 1969, **51**, 4238; H. Diebler, *Z. Phys. Chem. N.F.*, 1969, **68**, 64.
27 A. M. Chmelnick and D. Fiat, *J. Magn. Reson.*, 1972, **8**, 325; W. R. C. Patel and H. Diebler, *Ber. Bunsen-Ges. Phys. Chem.*, 1972, **76**, 1035.
28 Y. Sasaki, R. S. Taylor and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1975, 396.
29 B.-L. Ooi and A. G. Sykes, *Inorg. Chem.*, 1989, **28**, 3799.
30 C. G. Young, T. O. Kocaba, X.-F. Yan, E. R. T. Tiekink, L.-W. Wei, H. H. Murray III, C. L. Coyle and E. I. Stiefel, *Inorg. Chem.*, 1994, **33**, 6252.
31 D. Coucouvanis, A. Hadjikyriacou, A. Toupadakis, S.-M. Koo, O. Ileperuma, M. Draganjac and A. Salitoglou, *Inorg. Chem.*, 1991, **30**, 754.
32 S. Ikari, T. Ito, W. McFarlane, M. Nasreldin, B.-L. Ooi, Y. Sasaki and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1993, 2621.
33 H.-B. Bürgi, G. Anderegg and P. Blauenstein, *Inorg. Chem.*, 1981, **20**, 3829.
34 Y. Sasaki and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1974, 1468.
35 T. Shibahara and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1978, 95.
36 G. G. Kneale, A. J. Geddes, Y. Sasaki, T. Shibahara and A. G. Sykes, *J. Chem. Soc., Chem. Commun.*, 1975, 356.

Received 2nd *January* 1997; *Paper* 7/00063D