DALTON
FULL PAPER

Potentiometric studies on the formation and dissociation of the L-cysteine complexes of di-μ-sulfido and di-μ-oxo molybdenum(V) $[Mo_2O_2(\mu\text{-}S)_2(cys)_2]^{2-}$ and $[Mo_2O_2(\mu\text{-}O)_2(cys)_2]^{2-}$

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Potentiometric studies at 25 °C, $I = 0.50$ mol dm^{-3} ($NaClO_4$), on the dissociation of cysteine from $[Mo_2O_2(\mu\text{-}S)_2(cys)_2]^{2-}$, cys = $^-SCH_2CH(NH_2)CO_2^-$ (here L-cysteine), induced by the addition of $HClO_4$ indicated formation of two protonated species prior to $[Mo_2O_2(\mu\text{-}S)_2(H_2O)_6]^{2+}$. In the reverse titration of product solutions with sodium hydroxide, reformation of the cysteine complex was observed with involvement of the same two protonated species. From both sets of data, formation equilibrium constants (log β_{21p} values) for $2cys^{2-} + [Mo_2O_2(\mu\text{-}S)_2(H_2O)_6]^{2+} + pH^+ \rightleftharpoons [Mo_2O_2(\mu\text{-}S)_2(cys)_2H_p]^{p-2}$ are 36.24(3) (β_{210}), 38.63(3) (β_{211}) and 40.63(3) (β_{212}). The first two steps in the dissociation are defined as protonation and dissociation of the cysteine carboxylates, acid dissociation constants 2.00 and 2.39 respectively. In less extensive studies on the di-μ-oxo complex $[Mo_2O_2(\mu\text{-}O)_2(cys)_2]^{2-}$ the two cysteines are more weakly bound to the molybdenum, and a lower $[H^+]$ is required for dissociation. Precipitation of Mo^V_2 is observed at an intermediate stage of the titration. Final products were identified as $[Mo_2O_2(\mu\text{-}O)_2(H_2O)_6]^{2+}$, and for the reverse reaction $[Mo_2O_2(\mu\text{-}O)_2(cys)_2]^{2-}$.

The molybdenum(V) (d^1) dimeric complexes $[Mo_2O_2(\mu\text{-}X)_2(cys)_2]^{2-}$ (X = S or O), with cysteine present as the tridentate ligand $^-SCH_2CH(NH_2)CO_2^-$, can be synthesised as air-stable crystalline materials.[1,2] The di-μ-oxo complex is readily converted to the di-μ-sulfido product *e.g.* by bubbling H_2S through a solution at neutral pH.[1,3] Structures of $Mo_2O_2S_2^{2+}$ core complexes with cysteine $[Mo_2O_2(\mu\text{-}S)_2(cys)_2]^{2-}$ (Fig. 1),[4] histidine $[Mo_2O_2(\mu\text{-}S)_2(his)_2]$,[5] and ethylenediaminetetraacetate $[Mo_2O_2(\mu\text{-}S)_2(edta)]^{2-}$[6] have been determined. Features are the bond lengths Mo–O_t 1.68, Mo–S_b 2.30, and Mo–Mo 2.82 Å consistent with metal–metal bonding (the subscripts indicate terminal and bridging ligands respectively).[7] The MoS_2Mo four-membered ring is non-planar with a dihedral angle between the MoS_2 and MoS_2 planes of 150 to 160°. The $Mo_2O_4^{2+}$ core of $[Mo_2O_4(cys)_2]^{2-}$ is a similar shape (Fig. 1) with Mo–O_t 1.71, Mo–O_b 1.91–1.95, Mo–Mo 2.57 Å, and a dihedral angle between the MoO_2–MoO_2 planes of 151°.[8] The strong Mo–O_t bond results in a lengthening (and weakening) of the *trans* axial bond, which is the position most labile to substitution.[9] The dinuclear complex $[Mo_2O_2(\mu\text{-}S)_2(cys)_2]^{2-}$ with X = S finds extensive use as a precursor in the preparation of cluster complexes *e.g.* $[Mo_4S_4(H_2O)_{12}]^{5+}$ and trinuclear $[Mo_3S_4(H_2O)_9]^{4+}$.[1,10] Dissociation of the cysteine ligands occurs on increasing $[H^+]$, equation (1).

$$[Mo_2O_2(\mu\text{-}X)_2(cys)_2]^{2-} + 6H^+ \rightleftharpoons [Mo_2O_2(\mu\text{-}X)_2(H_2O)_6]^{2+} + 2H_3cys^+ \quad (1)$$

This paper is concerned with the thermodynamics of changes which contribute to reaction (1).

Experimental

Preparation of molybdenum dimers

Orange crystalline samples of $Na_2[Mo_2O_2(\mu\text{-}S)_2(cys)_2]\cdot 4H_2O$ and $Na_2[Mo_2O_2(\mu\text{-}O)_2(cys)_2]\cdot 5H_2O$ were prepared as previously described, cys = L-cysteine, $^-SCH_2CH(NH_2)CO_2^-$.[1,2] Elemental analyses for C, H, N, S, and UV/VIS absorbance spectra in H_2O were as previously reported, peak positions λ/nm (ε/dm^3 mol^{-1} cm^{-1}) at 229 (3.2×10^4), with shoulders at 280, 310, 370 for the di-μ-sulfido complex, and 306 (2.4×10^4) for the di-μ-oxo complex.[1–3] The corresponding aqua complexes $[Mo_2O_2(\mu\text{-}S)_2(H_2O)_6]^{2+}$ and $[Mo_2O_2(\mu\text{-}O)_2(H_2O)_6]^{2+}$ are identified by absorption peaks at 370 (1940) and 384 (103) respectively.[10,11]

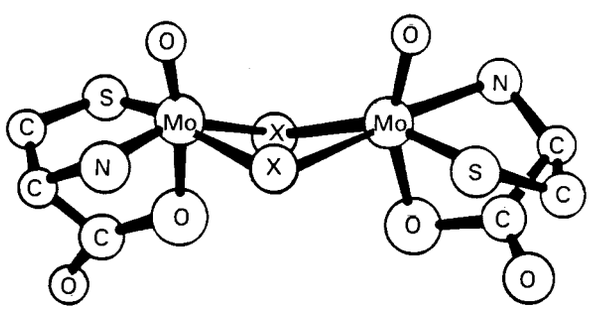

Fig. 1 Structure of the Mo^V_2 complexes $[Mo_2O_2(\mu\text{-}X)_2(cys)_2]^{2-}$, X = O or S[4,8]

Other reagents

These included a solution of $HClO_4$ 0.5 mol dm^{-3} prepared by dilution in doubly glass-distilled water of concentrated $HClO_4$ (70%, Merck), a made-up solution of $NaClO_4$ (Merck analytical grade), and a carbonate free sodium hydroxide solution prepared from titrisol (Merck, ampoule), and standardised against potassium hydrogenphthalate.

Potentiometric titrations

The free H^+ ion concentration in equilibrated solutions was measured by means of the following emf(H) cell: REF//H^+/GE where REF (Radiometer K711 calomel), GE (Ingold L8311), are the reference and glass electrodes, respectively. The experiments were carried out as titrations, where the solution S (at $I = 0.50$ mol dm^{-3} in $NaClO_4$) and the electrode(s) were placed in a 100 mL double-walled glass reactor vessel, thermostatted at 25.0(1) °C by circulating water from a constant temperature bath. An inert CO_2-free argon atmosphere was maintained, and

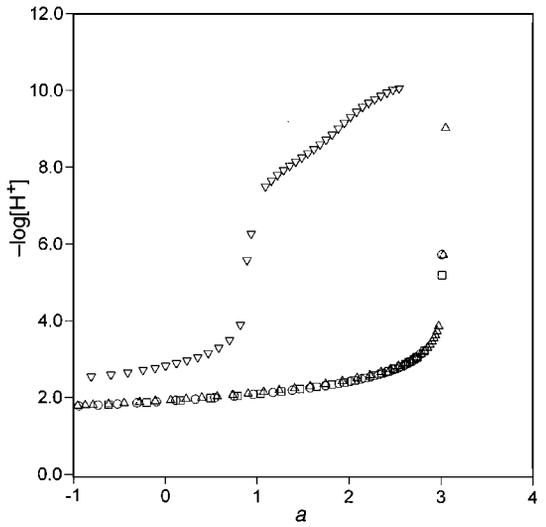

Fig. 2 Titration data showing the variation of measured $-\log[H^+]$ with a (ratio of moles of added NaOH to cysteine). Concentrations ($\times 10^3$) of $[Mo_2O_2(\mu\text{-}S)_2(cys)_2]^{2-}$ were 2.94 (□), 2.88 (△), 2.89 (○) mol dm^{-3} respectively. For comparison the titration of 3.0×10^{-3} mol dm^{-3} free cysteine (H_3L^+) is shown (▽)

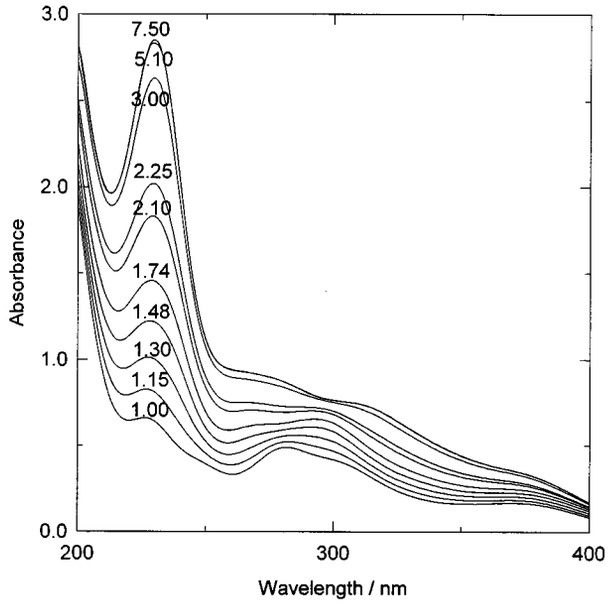

Fig. 3 The effect of decreasing pH on the UV/VIS spectrum of 6.54×10^{-5} mol dm^{-3} $[Mo_2O_2(\mu\text{-}S)_2(cys)_2]^{2-}$ (upper spectrum), and the aquation to $[Mo_2O_2(\mu\text{-}S)_2(H_2O)_6]^{2+}$ (lower spectrum) at 25 °C, $I = 0.50$ mol dm^{-3} ($NaClO_4$)

the solution was magnetically stirred throughout the course of the experiment. Automatic titrations were performed as previously described.[12] In the high concentration ionic medium at 25 °C the emf E (mV) of the cell followed the Nernst equation: $E = E°H + J[H^+] - 59.16\text{pH}$. Here $E°H$ and J are the standard potential and the liquid junction potential, respectively. The values of $E°H$ and J were determined according to the method of Biedermann and Sillén.[13–15] It was found that $pK_w = 13.71$, in accordance with the literature.[16] Treatment of emf(H) data was carried out by means of the program SUPERQUAD.[17]

UV/VIS spectra

The UV/VIS absorption spectra as a function of pH were measured in 0.5 ml dm^{-3} $NaClO_4$, on a Shimadzu UV-2101 PC spectrophotometer. A work flow 10.0 mm path length quartz cuvette was connected *via* Teflon tubing and peristaltic pump to the reactor-vessel containing the emf(H) cell, and a 10.0 mm reference quartz cuvette contained 0.5 mol dm^{-3} $NaClO_4$. The temperature was kept constant at 25.0 °C by means of a temperature controlled cell holder (Shimadzu TTC-260). Spectra were recorded after attainment of constant absorbance readings.

Results

Acid dissociation constants of cysteine

Automatic titrations of cysteine in the concentration range $(1.0\text{–}3.0) \times 10^{-3}$ mol dm^{-3} and in the pH range 2.0–11.0 were carried out. Values of the acid dissociation constants (pK_a) for the cysteine corresponding to equilibria H_3L^+/H_2L, H_2L/HL^-, HL^-/L^{2-} were found to be $pK_1 = 2.00(1)$, $pK_2 = 8.11(7)$ and $pK_3 = 10.10(7)$ respectively, in good agreement with literature values,[18,19] at 25 °C, $I = 0.5$ mol dm^{-3}, of $pK_1 = 1.9$, $pK_2 = 8.13(2)$ and $pK_3 = 10.2(1)$. The pK_1 corresponds to acid dissociation of the CO_2H group; while assignments to pK_2 and pK_3 are less certain,[20] but most likely correspond to the dissociation of SH, and NH_3^+, respectively.

Titration of $[Mo_2O_2(\mu\text{-}S)_2(cys)_2]^{2-}$

Solutions typically 3×10^{-3} mol dm^{-3} of the complex were titrated with 0.498 mol dm^{-3} $HClO_4$ by the automatic method described in order to monitor removal of the cysteine ligands. To study the reformation solutions a predefined $[H^+]$ was added to remove the cysteine ligands (typically a 10-fold excess over the concentration of molybdenum complex), and excess then back-titrated with sodium hydroxide. Titration curves for the complex and a comparison with the titration curve for free cysteine are shown in Fig. 2 as a *vs.* $-\log[H^+]$ plots (a = mole ratio of NaOH to cysteine). Changes in UV/VIS spectra are indicated in Fig. 3. The fitting of data was carried out for three separate full cycle titrations (149 experimental points). The equilibrium (2) for complex formation was used in

$$r\,cys^{2-} + [Mo_2O_2(\mu\text{-}S)_2(H_2O)_6]^{2+} + pH^+ \overset{\beta_{rlp}}{\rightleftharpoons} [Mo_2O_2(\mu\text{-}S)_2(cys)_rH_p]^{p+2-2r} \quad (2)$$

the analysis of the experimental data by SUPERQUAD. The following species incorporating one cysteine (ratio 1:1) 110, 111, 112, and two cysteines (ratio 2:1) 210, 211, 212, 213 and 214 were considered. The formation of hydroxo complexes has been established in basic medium for the $Mo_2O_2(\mu\text{-}O)_2$ core.[21,22] The formation of 21 − 1 and 21 − 2 hydroxo complexes was therefore also introduced into the model. The analysis of the experimental data by SUPERQUAD shows that the 1:1 species (110, 111 and 112) can be rejected. Only the species 210, 211 and 212 are accepted, and a good fit is achieved for these three species ($\sigma_E = 2.64$, $\chi^2 = 15.89$ as in SUPERQUAD), with $\log\beta_{210} = 36.24(3)$, $\log\beta_{11} = 38.63(3)$ and $\log\beta_{212} = 40.63(3)$, and all three thermodynamically very stable. From these values acid dissociation pK_a's of 2.00 and 2.39 are obtained for reactions (3) and (4) respectively.

$$[Mo_2O_2(\mu\text{-}S)_2(cys)_2H_2] \rightleftharpoons [Mo_2O_2(\mu\text{-}S)_2(cys)_2H]^- + H^+ \quad (3)$$

$$[Mo_2O_2(\mu\text{-}S)_2(cys)_2H]^- \rightleftharpoons [Mo_2O_2(\mu\text{-}S)_2(cys)_2]^{2-} + H^+ \quad (4)$$

A species distribution diagram as a function of pH is shown in Fig. 4. We note that at pH 3 the unprotonated complex is 80% of the total, and that complete formation is observed at pH 5.

Titration of $[Mo_2O_2(\mu\text{-}O)_2(cys)_2]^{2-}$

Similar experiments were carried out for the di-μ-oxo complex. However addition of H^+ to the cysteine complex under the

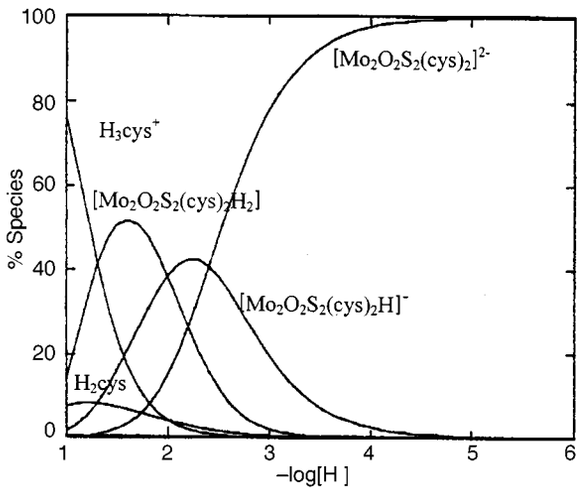

Fig. 4 Species distribution diagram as a function of $-\log[H^+]$ for $[Mo_2O_2(\mu\text{-}S)_2(cys)_2]^{2-}$ 3×10^{-3} mol dm^{-3}, using cysteine as reference

same conditions gave precipitation at an intermediate stage prior to completion of the titration. Also on adding sodium hydroxide to $[Mo_2O_2(\mu\text{-}O)_2(H_2O)_6]^{2+}$ and 2 equivalents of free cysteine in acid solution precipitation was observed before completion of the titration. The cysteine ligands are more extensively dissociated at the higher pH, and conversion of ligated H_2O to OH^- followed by precipitation is presumably occurring. Similar observations hold for the reverse process with precipitation at an intermediate stage before co-ordination of the cysteine becomes sufficiently extensive.

Discussion

An application of ^{18}O labelling techniques to the study of Mo^V complexes with $Mo_2O_2(\mu\text{-}S)_2$ and $Mo_2O_2(\mu\text{-}O)_2$ cores has demonstrated that both the oxo and sulfido core ligands are inert to substitution.[9] This contrasts with the substitution properties of terminal ligands such as the H_2O's of $[Mo_2O_2(\mu\text{-}S)_2(H_2O)_6]^{2+}$ and $[Mo_2O_2(\mu\text{-}O)_2(H_2O)_6]^{2+}$ which are labile.[2,23] In particular those axial Mo–OH_2 bonds which are *trans* to Mo–O_t are elongated (Fig. 1), and as a result are very labile.[24–26] In the case of $[Mo_2O_2(\mu\text{-}S)_2(cys)_2]^{2-}$ and $[Mo_2O_2(\mu\text{-}O)_2(cys)_2]^{2-}$ the carboxylates of the cysteine ligands occupy positions *trans* to the Mo–O_t bonds (Fig. 1). Not only are the carboxylates more labile because of this, but the CO group of the carboxylate is available as a possible site for protonation.[27,28]

The model that best fits the experimental data considers only the formation of $[Mo_2O_2(\mu\text{-}S)_2(cys)_2]^{2-}$, $[Mo_2O_2(\mu\text{-}S)_2(cys)_2H]^-$, and $[Mo_2O_2(\mu\text{-}S)_2(cys)_2H_2]$, and no other species were identified. The rejection by the program of other species indicates that if such forms are present they are in negligible amounts. Highly sensitive rapid scan UV/VIS spectrophotometry would be required to identify the possible existence of such transients. The absence of 1:1 species in detectable amounts indicates that both cysteine ligands become attached practically simultaneously to the core. The carboxylate group is bound *trans* to Mo–O_t, Fig. 1. The pK_a values of 2.00 and 2.39, reactions (3) and (4) respectively, are similar to pK_1 for acid dissociation of the CO_2H group of an unco-ordinated cysteine. This suggests that dissociation of the complex can be interpreted in terms of protonation of the carboxylate groups of the cysteines which are weakly bonded to the $Mo_2O_2(\mu\text{-}S)_2$ core. Dissociation of one of the carboxylates ($pK_a = 2.39$) occurs prior to the other ($pK_a = 2.00$). That no 213 and 214 species are identified indicates that the N and S atoms undergo similar protonation steps[20] at about the same pH's with dissociation of the two cysteines, Fig. 4. Fig. 2 is consistent with the near-simultaneous dissociation of the S and N atoms of the cysteine from the $MoO_2(\mu\text{-}S)_2$ core at very acid pH values. The species distribution diagram, Fig. 4, illustrates that the formation of unprotonated $[Mo_2O_2(\mu\text{-}S)_2(cys)_2]^{2-}$ occurs mainly at pH > 2.5 and is complete at pH 5.

On titration of $[Mo_2O_2(\mu\text{-}O)_2(cys)_2]^{2-}$ with $HClO_4$ the final product is likewise the aqua ion, in this case $[Mo_2O_2(\mu\text{-}O)_2(H_2O)_6]^{2+}$. However dissociation of the cysteine occurs more readily (at higher pH), and acid dissociation of the aqua product and precipitation at an intermediate stage prevents accurate potentiometric monitoring of the reaction. A full explanation of this behaviour and that observed for the reverse reaction may include hard–soft acid–base effects of the core oxo as opposed to sulfido ligands,[29] as well as the *trans* effect of the μ-oxo as opposed to μ-sulfido ligands.[25]

Acknowledgements

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