



PS5.10 — MO

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MOLYBDENUM(VI) COMPLEXES OF (R)-CYSTEINE IN AQUEOUS SOLUTION

Complex formation between molybdate ions and (R)-cysteine has been studied, in aqueous solution, over a range of concentrations and pH, at 298K and $I=1 \text{ mol dm}^{-3}$ (NaCl), using UV, CD and NMR techniques. One main species is evident for $\text{pH} > 6.5$, in which cysteine is bonded as a tridentate ligand to Mo(VI), forming a 1:1 complex. This compound has a formation constant $\log K_f = 18.23 \pm 0.12$, determined by CD measurements. In solutions with pH values between 4.5 and 6.5, apart from this complex, there is evidence for at least three other species.

INTRODUCTION

Complexes of molybdenum(VI) with (R)-cysteine have been studied by a number of authors [1-5], as possible models for molybdenum-containing enzymes.

An early report [1], based on spectrophotometric studies, claimed the formation of complexes where ligand:Mo(VI) ratio varies from 3:1 to 1:1, in aqueous solutions, at pH values between 4.6 and 6.5. Conflicting results about the nature of the species formed and the pH region adequate for their study, have been subsequently reported [4,5]. Circular dichroism proved to be a very informative technique and was used over a wide pH range (4.5-9.5), with varying metal and ligand concentrations. A number of UV and NMR experiments linked our work with previous studies. We found

that redox chemistry, although being important in all conditions in which this and previous work have been carried out, has not been properly considered in previous studies.

At pH values higher than 6.5, a single complex, with Mo(VI):cysteine ratio equal to 1:1, has been identified and its formation constant determined. This species, and at least a second complex of Mo(VI), is present at lower pH values. However, in more acidic solutions (pH between 4.5 and 6.5) reduction of Mo(VI) is much faster, resulting in the formation of the known compound $[\text{Mo}_2\text{V}_2\text{O}_4(\text{cys})_2]^{2-}$.

RESULTS AND DISCUSSION

SPENCE and CHANG [1] have studied the complexes formed over a pH range from 4 to 6. Using Job's method of continuous variation they have suggested the formation of species where ligand:metal ratio varies from 3:1 to 1:1 and have estimated the formation constant for the first complex. We have used the same method for studying the species present in solutions with pH varying from 6.4 to 8.5 and concentrations of Mo(VI) and cysteine similar to those used by Spence and Chang. Some of the results are shown in Fig. 1. The molar ratios corresponding to the maxima of the curves vary with pH, total concentration and wavelength chosen. These results could be inter-

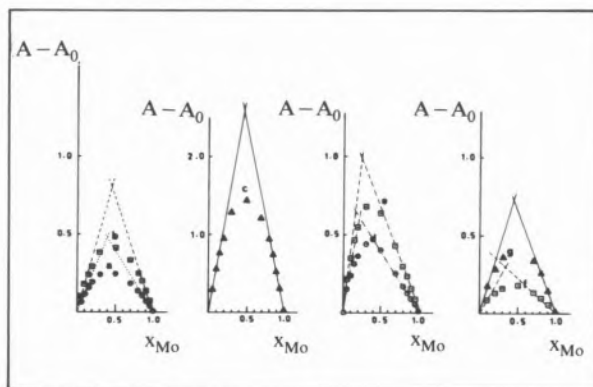


Fig. 1

Job's plots of absorbances for solutions of sodium molybdate and (R)-cysteine where

- $C_{\text{Mo}} + C_{\text{cys}} = 0.04 \text{ mol dm}^{-3}$, $\text{pH} = 8.5$, $l = 10 \text{ mm}$, and
(a) $\lambda = 370 \text{ nm}$, (b) $\lambda = 360 \text{ nm}$, (c) $\lambda = 340 \text{ nm}$;
- $C_{\text{Mo}} + C_{\text{cys}} = 0.04 \text{ mol dm}^{-3}$, $\text{pH} = 6.4$, $l = 5 \text{ mm}$, and
(d) $\lambda = 380 \text{ nm}$, (e) $\lambda = 360 \text{ nm}$;
- $C_{\text{Mo}} + C_{\text{cys}} = 0.016 \text{ mol dm}^{-3}$, $\text{pH} = 6.4$, $l = 5 \text{ mm}$,
(f) $\lambda = 360 \text{ nm}$, (g) $\lambda = 340 \text{ nm}$

preted as meaning that complexes with ligand:metal ratios varying from 1:1 to 3.5:1 have been formed. However we have other evidence for the occurrence of fast redox processes in these solutions, with formation of Mo(V) complexes of cysteine, namely the well known $[\text{Mo}_2\text{O}_4(\text{cys})_2]^{2-}$ compound. This complex absorbs strongly in the region of our measurements, and at higher wavelengths than the Mo(VI) species. It has also been found that the reduction is faster for higher total concentrations, higher ligand:metal ratios and lower pH values. All these results explain the deviation of the Job's plot maximum from a molar ratio close to 1:1, when we increase total concentration and/or decrease pH. This means that these results should not be used by themselves to support the presence of species with Cys:Mo(VI) ratio higher than 1:1.

CALLIS and WENTWORTH [5] studied this system using ^1H NMR and found that reduction of Mo(VI) occurred for $\text{pH} < 8.5$. Using solutions with $\text{pH} = 9.40$, they have claimed evidence for the formation of a 1:1 and a 3:1 complex. Having studied the first species in detail, they have found that the ligand should be tridentate and calculated a formation constant, $\log K_f = 19.88 \pm 0.06$, for the complex $[\text{MoO}_3(\text{cys})]^{2-}$. Using analogous conditions, we have obtained NMR spectra similar to those described by Callis *et al.* However, other signals were always present which could be assigned for cysteine and $[\text{Mo}_2\text{O}_4(\text{cys})_2]^{2-}$.

Solutions of (R)-cysteine and Mo(VI), with pH values between 6.5 and 9.2 give CD spectra which can be assigned to a single species. The spectra recorded for solutions where $C_M = 10^{-2} \text{ mol dm}^{-3}$, $C_L:M_{\text{Mo}}$ varied from 0.4 to 6 and $I = 1 \text{ mol dm}^{-3}$ (NaCl) were used to calculate a formation constant value, $\log K_f = 18.23 \pm 0.12$, for a complex 1:1. This compound had the stoichiometry confirmed by applying ASMUS's method [6] in the treatment of these results, and we believe that it is the species $[\text{MoO}_3(\text{cys})]^{2-}$ described by other authors [1,5].

In solutions where pH varies from 4.5 to 6.5, quite distinct CD spectra ($\lambda > 250 \text{ nm}$) are observed. These spectra were resolved into four components: One, made of one negative ($\lambda_{\text{max}} = 277 \text{ nm}$) and one positive ($\lambda_{\text{max}} = 325 \text{ nm}$) band, is the spectrum of the species 1:1 observed at $\text{pH} > 6.5$.

A second component is a new positive band ($\lambda_{\text{max}} = 412 \text{ nm}$) and is tentatively assigned to a dimeric complex of Mo(VI), $[\text{Mo}_2\text{O}_5(\text{cys})_2]^{2-}$. Two negative bands, centred at 357 and 385 nm, respectively, are associated with Mo(V) complexes of (R)-cysteine. This last assignment is further supported by the developments in the spectrum with time, which eventually turn it into that of $[\text{Mo}_2^{\text{V}}\text{O}_4(\text{cys})_2]^{2-}$.

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PS5.11 — TU

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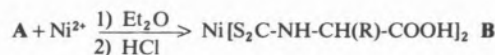
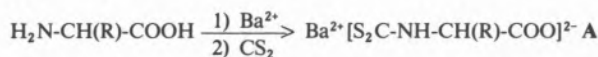
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NEW NICKEL(II) COMPLEXES WITH DITHIOCARBAMATE-DERIVATIVES OF α -AMINOACIDS

Although little is known about the role of nickel *in vivo*, it has been recognized that it is essential in the growth of experimentation animals [1] and its deficiency impairs iron absorption, reducing the haemoglobin level; on the other hand, its ability in changing its coordination geometry (D_{4h} , T_d , O_h) may make it important in a fine control over metabolic activity, and is also useful as a substituent for Mg^{2+} because of their close radii [2,3].

In an attempt to fathom its biochemistry, complexes formed by Ni(II) and dithiocarbamate derivatives of α -aminoacids have been synthesized according to:



All reagents were from Fluka (*p.a.*) and were used without any further purification.

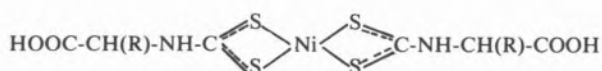
Synthesis of compounds **A** has been described elsewhere [4,5]. To obtain compounds **B**, an aqueous solution of $NiCl_2 \cdot 6H_2O$ is dropwise added on **A** dissolved in H_2O ($Ni:Ba = 1:2$ molar ratio). Addition of Et_2O and then HCl 0.1 M

(stoichiometrically to yield $BaCl_2$ formation) leads to extraction of compounds **B** in the organic phase. A fine olive-green powder is obtained after room temperature evaporation of Et_2O . The product is purified by recrystallization in Et_2O and acetone (final yield 70%). However, when glycine is used, if addition of HCl and Et_2O is not carried out, evaporation of water yields $Ba[Ni(S_2C-NH-CH_2-COO)_2]$, while decomposition products are obtained with alanine and 2-aminobutyric acid ($R = Me, Et$).

Chemical analysis (C, H, N, S, Ni) data agree with the expected formula. Characterization of the complexes has been carried out by IR spectroscopy (KBr pellets, Beckman Acculab-10), UV-Vis spectroscopy (in H_2O or Et_2O , Shimadzu UV-240), 1H NMR (Hitachi Perkin-Elmer R-24B) and magnetic measurements (at room temperature, Stanton MC-5 Gouy-type balance).

Nickel(II) (d^8) complexes may exhibit three different geometries: square planar (D_{4h}), octahedral (O_h) and tetrahedral (T_d), the former being diamagnetic.

Compounds **B** are diamagnetic, and our IR results (see below) indicate the presence of free $-COOH$ groups. With these results, the structure below can be suggested.



The main features of the IR spectra have been collected in the Table.

Table

Compound	ν_{COOH}	ν_{COO^-}		ν_{CS}	ν_{NiS}
		ν_a	ν_s		
Ba(gly dtc)	—	1620(s)	1410(s)	620(m)	—
Ni(gly dtc) ₂	1700(s)	—	—	615(m)	380(w)
Ba[Ni(gly dtc) ₂]	—	1580(s)	1410(s)	645(m)	380(w)
Ba(DL-ala dtc)	—	1615(s)	1405(s)	620(m)	—
Ni(DL-ala dtc) ₂	1700(s)	—	—	625(m)	370(w)
Ba(DL-2-am.but dtc)	—	1625(s)	1400(s)	635(m)	—
Ni(DL-2-am.but dtc) ₂	1695(s)	—	—	655(m)	370(w)

s = strong; m = medium; w = weak.

The ν_a and ν_s bands of the COO^- groups in the ligands (compounds **A**) have been recorded at 1625-