New Amino-acid Complexes of Molybdenum-(v) and -(vi)

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Anions of the amino-acids iminodiacetic acid, N-methyliminodiacetic acid, nitrilotriacetic acid, aspartic acid, and histidine behave as tridentate ligands towards molybdenum(VI). In neutral solution they give complexes whose compositions and i.r. spectra show them to contain a MoO_3 core. The spectra of the corresponding molybdenum(V) complexes obtained at pH 5.5 point to the presence of a di-μ-oxo-dioxo Mo_2O_4 core. The glycinatomolybdenum-(VI) complex is of the type $[MoO_2(GlyO)_2]$ with two bidentate ligands. At pH 6, uramil-NN-diacetate is tridentate towards Mo^V and Mo^{VI}, but at pH 2 it co-ordinates to a $Mo^{VI}O_2$ core in a quadridentate manner through the additional use of a carbonyl group of the ureide ring.

MOLYBDENUM(VI) complexes may contain either a MoO_2 core, with co-ordination of two bidentate ligands, or a MoO_3 core with one tridentate ligand.[1,2] Molybdenum(v) derivatives have a di-μ-oxo-dioxo Mo_2O_4 core when the ligand is tridentate,[3,4] so that six-co-ordination is maintained. Crystal-structure determinations on

amino-acid derivatives have shown that the molybdenum(vi)–ethylenediaminetetra-acetate (edta) complex has a MoO_3 core (with each end of the ligand co-ordinated to a different molybdenum atom),[5,6] and that the molybdenum(v)–cysteine (Cys)[7,8] and –histidine (His)[9,10] complexes are of the Mo_2O_4 class. In the i.r. spectra of

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[2] W. P. Griffith, *J. Chem. Soc. (A)*, 1969, 211.
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[7] L. R. Melby, *Inorg. Chem.*, 1969, **8**, 349.
[8] J. R. Knox and C. K. Prout, *Acta Cryst.*, 1969, **B25**, 1857.
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[10] L. T. J. Delbaere and C. K. Prout, *Chem. Comm.*, 1971, 162.

oxomolybdenum complexes the strong metal–oxygen absorptions usually stand out from the ligand bands and the type of metal–oxygen core is identifiable from the spectral features. The cis-dioxo MoO_2 group gives two strong bands at 900—950 cm^{-1},[1] the cis-trioxo MoO_3 group gives two bands in the range 800—900 cm^{-1},[2] and the molybdenum(v) Mo_2O_4 core gives $\nu(Mo-O_t)$ at ca. 950 cm^{-1} and Mo–O–Mo bridge vibrations at 700—800 cm^{-1}.[3,4]

We have sought to identify the molybdenum–oxygen core in several new crystalline complexes of amino-acids, since the type of core might be dependent both on the pH of the mother liquor (which affects the relative stability of the co-ordinated MoO_2 and MoO_3 units) and on the number and kind of functional groups in the ligand [11] (which determine its demand for co-ordination sites on the metal). The amino-acids glycine (glycinate anion, GlyO$^-$), iminodiacetic acid (dianion, ida^{2-}) and N-methyliminodiacetic acid (dianion, mida^{2-}), and nitrilotriacetic acid (trianion, nta^{3-}) were used to provide a ligand series with an increasing number of carboxylate groups. Aspartic acid (dianion, AspO$_2^{2-}$), histidine (anion, HisO$^-$),[10] and uramil-NN-diacetic acid (for which it is established that uda^{3-} is the co-ordinating species in neutral solution [12]) allowed the possibility of other variations. Spectra have been recorded for both the molybdenum(v) and molybdenum(vi) derivatives of most of these ligands. For the differing core structures developed by the two oxidation states, comparison of these spectra assisted identification of the Mo–O bands in each molybdenum(v)–molybdenum(vi) pair. Assignment of the Mo–O bands in the edta complexes (of known structure [6,13]) was made on the same basis.

RESULTS AND DISCUSSION

Neutral bis(glycinato)dioxomolybdenum(vi), [MoO$_2$-(GlyO)$_2$], was obtained through a ligand-exchange reaction with the butane-2,3-diol (H$_2$bd) complex [14] [MoO$_2$(Hbd)$_2$]·2H$_2$bd under anhydrous conditions. The i.r. spectrum of the glycinate showed two cis-dioxo-bands at 935 and 900 cm^{-1}. The strong bands shown by free Gly in the ν(C=O) and δ(NH$_2$) region at 1 610, 1 585, 1 515, 1 492, and 1 413 cm^{-1} (ref. 15) gave place to a group of frequencies at 1 750, 1 705, 1 605, 1 240, and 1 215 cm^{-1} in the complex. This is indicative of a sharply increased separation of the ν(C=O) frequencies (to above 1 700 cm^{-1} and below 1250 cm^{-1}) and of the existence of δ(NH$_2$) bands at ca. 1 600 and ca. 1 200 cm^{-1}. This in turn is evidence for bidentate co-ordination of the glycinate ligand through one carboxylate oxygen atom and the amino-nitrogen.[16] Involvement of the amine is shown by the displacement of the highest δ(N–H) frequency from 3 160 cm^{-1} in the ligand to 3 250 cm^{-1} in the complex.

On the other hand imino- and N-methylimino-diacetic acid, nitrilotriacetic acid, DL-aspartic acid, and L-histidine all reacted with disodium tetraoxomolybdate in aqueous solution at pH ca. 6 to give hydrated salts whose compositions and spectra (Table 1) show them to contain complex anions having a MoO_3 core co-ordinated with a tridentate ligand (assuming six-co-ordination). The spectra of these complexes usually showed two

TABLE 1

Molybdenum–oxygen bands (cm^{-1}) in complexes of Mo^{VI}

Complex	Bands	Core and ligand type
[MoO$_2$(GlyO)$_2$]	935s, 900s	cis-dioxo, bidentate
Na$_2$[MoO$_3$(ida)]·2H$_2$O	895s, 846s	cis-trioxo, tridentate
Na$_2$[MoO$_3$(mida)]·4H$_2$O	(882ms),[a] 842s, 813s	cis-trioxo, tridentate
Na$_3$[MoO$_3$(nta)]·2.5H$_2$O	(882ms),[a] 860s	cis-trioxo, tridentate
Na$_4$[MoO$_3$(edta)]·8H$_2$O [b]	(900ms),[a] 860s, 840s	cis-trioxo, tridentate
K$_2$[MoO$_3$(AspO$_2$)]·H$_2$O	(912ms),[a] 866s, 826s	cis-trioxo, tridentate
Na[MoO$_3$(HisO)]·H$_2$O	(898m),[a] 840s [c]	cis-trioxo, tridentate
Na$_3$[MoO$_3$(uda)]·3H$_2$O, (I)	870 (sh), 850s	cis-trioxo, tridentate
Na[MoO$_2$(uda)]·2H$_2$O, (II)	950w, 937m, 918s	cis-dioxo, quadridentate
[NH$_4$][MoO$_2$(uda)]·H$_2$O (III)	950m, 937w, 918s	cis-dioxo, quadridentate

[a] Possibly a ligand band. [b] Refs. 5 and 6. [c] Also, barely resolved weak bands at 828 and 810 cm^{-1}.

TABLE 2

Molybdenum–oxygen bands (cm^{-1}) in complexes of Mo^V

Complex	Bands ($Mo-O_t$)	($Mo-O_b$)
Na$_2$[Mo$_2$O$_4$(ida)$_2$]·2H$_2$O	965s, 935ms [a]	765ms, 735ms
Na$_2$[Mo$_2$O$_4$(mida)$_2$]·4H$_2$O	956s	773m, 733m
Na$_4$[Mo$_2$O$_4$(nta)$_2$]·4H$_2$O	970s, 958s	733ms
Na$_4$[Mo$_2$O$_4$(uda)$_2$]·4H$_2$O	960s	775m, 732m
Na$_2$[Mo$_2$O$_4$(edta)]·H$_2$O [b]	952s [c]	758m, 718mw
[Mo$_2$O$_4$(HisO)$_2$]·3H$_2$O [d]	950s, 920m [a]	762m, 735m

[a] A ligand mode may be involved. [b] Ref. 5. [c] The origin of the medium-strong bands at 935 and 907 cm^{-1} is uncertain. [d] Ref. 9.

strong partially overlapping $\nu(Mo-O_t)$ bands in the 800—900 cm^{-1} range, from the cis-trioxo-group. In most cases there was also a band at ca. 900 cm^{-1} which is stronger than expected for a pure ligand mode. For K$_3$[MoO$_3$(nta)]·H$_2$O, a crystal-structure determination [17] has shown that the tridentate nature of nta^{3-} arises from co-ordination of the nitrogen and only two of the three carboxylate groups. The molybdenum(v) complexes of these ligands gave spectra whose Mo–O bands, though collectively differing in detail, all conform to the pattern characteristic of a Mo_2O_4 core (Table 2). There

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was at least one strong ν(Mo–O) band in the 900—1 000 cm^{-1} region, and bands attributable to bridging oxygen vibrations [3] appeared in the range 700—800 cm^{-1}. All the complexes are therefore similar in this respect to the molybdenum(v)–Cys,[7,8]–His,[9,10] and –edta complexes [5,12,18] for which there is crystallographic or other structural evidence. The i.r. spectra of the anhydrous complexes are closely similar in the ν(Mo–O) regions to those of the corresponding hydrates, showing that in each case the characteristic molybdenum–oxygen core has been retained. The close correspondence in the frequencies suggests that no water molecules are involved in the molybdenum co-ordination sphere. Modifications in the ligand spectra of the anhydrous complexes were reversed on rehydration in the air.

In contrast to the other ligands described, uda^{3-} is able to stabilise two different metal–oxygen cores in co-ordination with Mo^{VI}. At pH 6, from Na$_2$[MoO$_4$] and uramil-NN-diacetic acid, pale pink Na$_3$[MoO$_3$(uda)]·3H$_2$O, (I), was obtained which had ν(Mo–O) frequencies at $<$900 cm^{-1}, characteristic of the usual MoO$_3$ cis-trioxo-core. However, at pH 1—2 the product was yellow Na[MoO$_2$(uda)]·2H$_2$O, (II), with ν(Mo–O) bands at 937 and 917 cm^{-1} in the cis-dioxo-range. Complexes (I) and (II) can be interconverted reversibly with sodium hydroxide and hydrochloric acid. In the presence of ammonium ion at pH 2—2.5, the yellow salt [NH$_4$][MoO$_2$-(uda)]·H$_2$O, (III), was obtained. The two salts, (II)

(III)
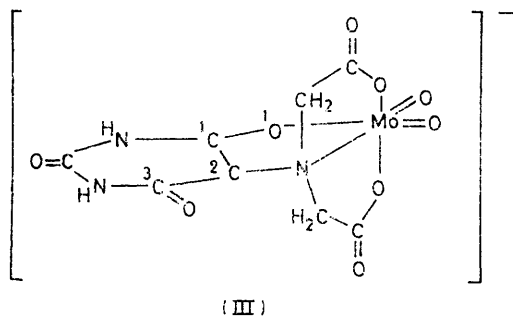
and (III), have the same electronic spectra and very similar i.r. spectra, showing that both contain the same complex anion. A complete X-ray structure determination of (III) by one of us [17] has shown that in this anion the uramil skeleton is almost coplanar with the cis-dioxo MoO$_2$ group and that the ligand occupies four co-ordination positions around the molybdenum with the carbonyl oxygen, O^1, also involved. The C^1–C^2 and C^2–C^3 distances (1.37 and 1.41 Å) are short, as would also correspond with loss of the additional proton originally from C^2, under the strong electron-withdrawing influence of the MoO$_2$ group. The structure determination supports the prediction of Irving and da Silva that uda^{3-} is capable of acting as a quadridentate ligand.[12]

The two salts, (II) and (III), are strongly acidic in solution through partial hydrolysis of the MoO$_2$ core in the absence of added acid. Titration with 0.05 mol dm^{-3} sodium hydroxide gave three end-points. With (II) (0.140 mmol in 10 cm^3; initial pH 2.5), the end-

points were at pH 4.0, 7.5, and 10.0 after addition of 1.00, 2.98, and 3.91 equivalents, respectively. Discharge of the yellow colour was almost complete at the first end-point. The final end-point (4.00 equivalents) corresponds to full conversion of the MoO$_2$ core into [MoO$_4$]$^{2-}$.

Apart from the quadridentate uda derivatives, the molybdenum(vi) complexes are of known structural types.[11] The bidentate glycinate complex is highly susceptible to hydrolysis and no glycinate derivative could be obtained under aqueous conditions (contrasting with α- and β-alanine for which hydroxy-bridged complexes have been isolated from aqueous solution [4]). On the other hand, the formation of molybdenum(vi) complexes of tridentate ligands in aqueous solution shows their greater stability, whether the bonding is through one amine and two carboxylate groups, or one carboxylate and two nitrogen atoms as with histidine. Compared with the molybdenum(vi) complexes, the molybdenum(v) aminoacetato-complexes are less readily obtained pure.[13] Reaction of the ligands with [NH$_4$]$_2$-[MoCl$_5$O],[19] used as the source of Mo^V, may lead also to small amounts of secondary products, and in aqueous solution the complexes themselves are subject to hydrolysis to the free amino-acid.

The isolation of quadridentate uda complexes is relevant to the question of metal–carbonyl interactions in flavin-containing enzymes,[20] since the ureide ring of uramil-NN-diacetic acid simulates the quinoid fragment of the flavin structure. The present results indicate that in a suitable environment this carbonyl interaction can be promoted by a MoO$_2$ core, but that this in turn is available only at low pH.

EXPERIMENTAL

Preparations.—Bis(glycinato)dioxomolybdenum(vi). Glycine (2 g) and the butane-2,3-diol (H$_2$bd) complex, [MoO$_2$(Hbd)$_2$]·2H$_2$bd [14] (10 g, m.p. 89 °C), were allowed to react in a closed flask at 100 °C for 6 h. The solidified melt was extracted with four successive portions (each of 20 cm^3) of dry methanol. The product was isolated by addition of diethyl ether and recrystallised from methanol. Exclusion of moisture was essential.

Trioxomolybdenum(vi) complexes. Complexes having a MoO$_3$ core were obtained from the reaction of disodium tetraoxomolybdate with the amino-acid at pH 6, the solution being heated to complete the reaction and reduce the volume. The alternative use of molybdenum trioxide, amino-acid, and sodium or potassium hydroxide in the requisite molar proportions facilitates isolation of a pure product. The ionic products are readily soluble in water and evaporation gives viscous solutions. In some cases the complexes were isolated by crystallisation directly from the aqueous solution [method (A)], but otherwise crystallisation was induced by the use of ethanol [method (B)]. Examples of preparations are given below. The water contents were somewhat variable due to the potentially hygroscopic nature of the complexes and the low stabilities

[18] Y. Sasaki and A. G. Sykes, *J.C.S. Dalton*, 1974, 1468.
[19] P. Klason, *Ber.*, 1901, **34**, 148.
[20] J. T. Spence, *Co-ordination Chem. Rev.*, 1969, **4**, 475.

of some of the hydrates. Analyses were made on re-crystallised samples which had been conditioned to constant weight in the air, except for the particularly hygroscopic aspartato- and the uramil-*NN*-diacetato-complexes which were dried over potassium hydroxide. Water of crystallisation was determined by weight loss under high vacuum at up to 160 °C.

Sodium histidinatotrioxomolybdate(VI)*–water* (1/1). Molybdenum trioxide, sodium hydroxide, and L-histidine (each 18 mmol) were boiled in water (30 cm³) until the oxide dissolved. The solution was filtered and allowed to evaporate [method (A)]. The clear tabular crystals were

washed with dilute hydrochloric acid, ethanol, and diethyl ether. The ammonium salt, (III), was conveniently obtained by reaction of the acid (5 mmol) with hexa-ammonium heptamolybdate(6−) − water (1/4) (5 mmol of molybdenum) in water (20 cm³). The product recrystallised as short yellow prisms.

Molybdenum(V) *complexes*. These were obtained using the amino-acid and [NH₄]₂[MoCl₅O] in equimolar proportions. The pH of the solutions was adjusted to 5.5 by slow addition of 5% sodium hydroxide (with stirring) so that the molybdenum(V) hydroxide redissolved. These complexes are again very soluble in water and give solutions

TABLE 3

Elemental analyses, with calculated values in parentheses

Complex [a]	Method of isolation	Colour	Analysis(%) C	H	Mo [b]	N	Na [c]	H₂O [d]
[MoO₂(GlyO)₂]	e	White	17.8 (17.4)	3.1 (2.9)	34.8 (34.8)	10.1 (10.1)		
Na₂[MoO₃(ida)]·2H₂O	(B)	White	13.3 (13.45)	2.9 (2.5)	25.7 (26.9)	3.6 (3.9)	12.8 (12.9)	1.97
Na₂[MoO₃(mida)]·4H₂O	(A), (B)	White	15.4 (14.7)	3.9 (3.7)	23.1 (23.6)	3.5 (3.4)	11.4 (11.3)	3.86
Na₃[MoO₃(nta)]·2.5H₂O	(B)	White	15.4 (16.1)	2.75 (2.5)	21.4 (21.5)	2.8 (3.1)	16.2 (15.5)	2.52, 2.61 [f]
Na₃[MoO₃(uda)]·3H₂O	(B)	White [g]	18.7 (18.4)	2.6 (2.3)	18.3 (18.4)	7.6 (8.0)	13.0 (13.2)	3.10 [h]
K₂[MoO₃(AspO₂)]·H₂O	(B)	White	12.8 (12.9)	2.55 (2.0)	25.4 (25.9)	3.75 (3.6)		1.36 [h, i]
Na[MoO₃(HisO)]·H₂O	(A), (B)	White	21.2 (21.2)	3.00 (2.95)	27.5 (28.3)	12.6 (12.4)	6.0 (6.8)	1.10
Na[MoO₂(uda)]·2H₂O	e	Yellow	22.1 (21.7)	2.5 (2.3)	21.7 (21.7)	9.6 (9.5)	5.0 (5.2)	1.96
[NH₄][MoO₂(uda)]·H₂O	e	Yellow	22.6 (22.9)	2.8 (2.85)	22.8 (22.9)	13.3 (13.3)		
Na₂[Mo₂O₄(ida)₂]·2H₂O	(C)	Orange-brown	16.5 (16.0)	2.8 (2.5)	30.8 (31.9)	4.3 (4.7)	6.9 (7.6)	0.97
Na₂[Mo₂O₄(mida)₂]·4H₂O	(C)	Orange-brown	18.9 (18.1)	3.3 (3.3)	27.6 (28.9)	4.0 (4.2)	6.7 (6.6)	1.98 [j]
Na₄[Mo₂O₄(nta)₂]·4H₂O [k]	(B)	Orange-brown	18.3 (18.1)	3.1 (2.5)		3.7 (3.5)		
Na₄[MoO₄(uda)₂]·4H₂O	(C)	Orange-brown	20.9 (20.6)	3.0 (2.5)	20.7 (20.6)	9.6 (9.0)	10.0 (9.8)	2.08 [l]
[Mo₂O₄(HisO)₂]·3H₂O	m	Amber	23.6 (23.3)	3.8 (3.6)		13.3 (13.6)		

[a] GlyO = C₂H₄NO₂, ida = C₄H₅NO₄, mida = C₅H₇NO₄, nta = C₆H₆NO₆, uda = C₈H₆N₃O₇, AspO₂ = C₄H₅NO₄, and HisO = C₆H₈N₃O₂. [b] Determined as the oxinate. [c] Determined by atomic absorption. [d] As the ratio H₂O : Mo, determined by weight loss. [e] See text. [f] Values from different preparations. [g] With a faint pink cast. [h] For the hygroscopic complex dried over K[OH]. [i] The evidence for the stoicheiometric hydrate is uncertain; progressive loss of water over P₄O₁₀. [j] One mole was lost over K[OH]. [k] Needle crystals gave: C, 17.7; H, 3.1; N, 3.9%. [l] One mole was lost in air at 40 °C. [m] Refs. 9 and 10.

washed with a little water. They became opaque on standing in air through partial loss of water of crystallisation to leave the monohydrate.

Trisodium (*nitrilotriacetato*)*trioxomolybdate*(VI)*–water* (2/5). Disodium tetraoxomolybdate (5 mmol) and nitrilotriacetic acid (5 mmol) were dissolved in water (10 cm³) and the pH of the solution was adjusted to 6 with 5% sodium hydroxide (4.9 mmol). Ethanol (30 cm³) was then added. The concentrated aqueous layer which separated was stirred with successive fresh portions of ethanol to induce crystallisation [method (B)].

Sodium dioxo(*uramil-*NN-*diacetato*)*molybdate*(VI)*–water* (1/2), (II), *and ammonium dioxo*(*uramil-*NN-*diacetato*)-*molybdate*(VI)*–water* (1/1), (III). These complexes, obtained at low pH, are of lower solubility than the trioxo-complexes and crystallise readily. Yellow needles of (II) separated from a solution (pH *ca.* 1.7) containing molybdenum trioxide, sodium hydroxide, and uramil-*NN*-diacetic acid (each 5 mmol) in water (20 cm³). The crystals were

which separate into two phases on addition of ethanol. The complexes were crystallised by stirring the concentrated orange-red lower layer with ethanol, followed by trituration with propan-2-ol [method (C)]. The imino-diacetato- and *N*-methyliminodiacetato-complexes are slightly soluble in anhydrous ethanol and may be purified by continuous extraction with boiling solvent. The amount of water of crystallisation in the complexes was variable (footnotes to Table 3). The nitrilotriacetato-complex was obtained in acceptable purity from only the later fractions of the lower liquid layer which were separated by successive additions of ethanol [method (B), as above]. In some cases, minute needles of the complex also crystallised from the dilute residual mother liquor.