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The Syntheses and Properties of Molybdenum(VI)-Amino Acids Complexes

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New compounds of the $Mo(VI)_2O_7H_3(Am)_n$-type (where HAm=glycine, DL-alamine, DL-Methionine, or L-Leucine) were obtained from an acidic aqueous solution (pH=1) containing sodium molybdate and amino acid. These compounds seem to be isostructural with each other, and all are diamagnetic. Their infrared spectra show characteristic ν(Mo=O) bands.

The ethylenediaminetetraacetato chelates of molybdenum(VI) and (V) have already been studied potentially,[1–3] while studies of the amino acid chelates of molybdenum have appeared only recently. Spence and Lee have studied the solution chemistry of the molybdenum-hystidine system.[4] The molybdenum-cystein complex was obtained in the solid state very recently,[5] and the X-ray structural analysis data[6] as well as its infrared spectral data[7] have also been reported. However the molybdenum chelates of other amino acids are not very stable in a neutral aqueous solution and the solid products have not yet been obtained. The authors found that some amino acids, such as glycine,

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alanine, leucine and methionine, give a very stable product in acidic aqueous media; the solid complexes were thus obtained. They are insoluble in water or organic solvents and consist of two molybdenum atoms per amino acid molecule. From the properties of these complexes, they are expected to be of the polymer type.

Experimental

Instruments. The infrared spectra were obtained by the Nujol or hexachloro-1,3-butadiene mull method using a DS-301 infrared spectrophotometer of the Japan Spectroscopic Co., Ltd. The magnetic susceptibilities of the products were measured with a Gouy balance at room temperature (20°C).

Synthesis of the Complex. *Methoioninato Dimolybdenum (VI)*, $Mo(VI)_2O_7H_3(C_5H_{10}NO_2S)$. One and a half grams (10 mM) of DL-methionine were dissolved into a minimum quantity of 1 N hydrochloric acid. In a separate flask 4.80 g (20 mM) of sodium molybdate dihydrate were dissolved into 10 *ml* of water. The two solutions were mixed and the pH of the supernatant of the mixture was adjusted to about 1 by adding 6 N hydrochloric acid. The mixture was heated and boiled for several minutes, and the original precipitate was dissolved then gradually a fine powder appeared which tended to cling to the wall of the vessel. After the reaction had been completed, the product was filtered off and washed with 0.1 N hydrochloric acid, water, ethanol, and diethyl ether in that order.

The complex thus obtained was dried in a vacuum dessicator for about 24 hr at room temperature. It was pale yellow and was insoluble in water or usual organic solvents, but soluble in an alkaline aqueous solution (in which it decomposed). Although attempts at recrystallization have not yet been successful, this product seems to be a simple compound and not a mixture, because even when the mole ratio of the starting material was changed from 4 : 1 to 1 : 4, the product was found to be identical not only on the basis of the analytical data but also on the basis of the infrared spectra. Moreover, this is supported by the fact that the isostructural complexes were also obtained from other amino acids by the same method.

The glycine, DL-alanine, and L-leucine compounds were obtained by almost the same synthetic method, but they were all white, not yellowish, in color. Using other amino acids, such as glutamic acid, aspartic acid, valine, phenyl-alanine, and histidine, this type of complex has not yet been obtained.

Results and Discussion

The analytical data for these compounds are given in Table 1. These complexes are all diamagnetic at room temperature. The infrared spectral data for the complexes are summarized in Table 2, together with those of several related compounds.

The infrared spectra of amino acid and their metal complexes have already been reported in many papers.[7-10] The assignments of the bands shown n the table were deduced from these references and are only tentative. The ν(N–H) bands near 3200 cm^{-1} of the amino acid complexes of the usual first series of transition elements are rather sharp and in a higher frequency region than those of the free ligand. The bands of these molybdenum(VI) complexes are weak and broad, and the wave number of the peak is less than 3200 cm^{-1}. This is probably due to the fact that the molybdic acid part of the compound makes a strong hydrogen bond with the amino group of an amino acid. The antisymmetric and symmetric stretching bands of $-COO^-$ in the region of 1600—1400 cm^{-1} show a little shift from those of free ligands as usual metal complexes of amino acid, and then the oxygen of the carboxyl group of an amino acid seems to make the coordination bond with the central molybdenum atom in these complexes. The $\delta(-NH_2)$ or $\delta(-NH_3^+)$ peaks can also be recognized in these regions. It seems that the strong bands in the region of 1000—900 cm^{-1} and near 760 cm^{-1} can be identified as ν(Mo=O) and ν(Mo–O–Mo) bands respectively by comparing them with the infrared data of acid complexes of molybdenum reported by many authors;[7,11-16] the rocking band of the methyl group of bands caused by amino acid may also appear near here, but, if so, they should be far less intense. The strong peak near 950 cm^{-1} is likely a band of the terminal Mo=O bond which has almost pure double bond character; however, as there are

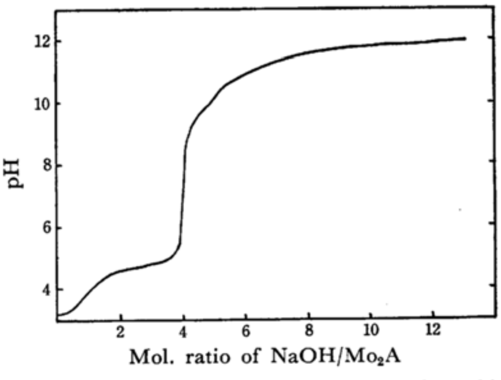

Fig. 1. Alkalimetric titration curve of methioninato dimolybdenum(VI).

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TABLE 1. ANALYSIS OF COMPLEXES (Figures are given in %.)

		Mo	C	H	N	S
$Mo_2O_7H_3(Met)$	Calcd	42.16	13.20	2.88	3.08	7.05
	Found	41.70	13.44	2.73	3.10	7.07
$Mo_2O_7H_3(Gly)\cdot H_2O$	Calcd	48.09	6.02	2.27	3.51	
	Found	48.10	6.28	1.96	3.51	
$Mo_2O_7H_3(Ala)$	Calcd	48.58	9.12	2.30	3.54	
	Found	48.00	9.41	2.09	3.57	
$Mo_2O_7H_3(Leu)\cdot H_2O$	Calcd	42.16	15.84	3.77	3.08	
	Found	42.30	15.71	3.97	3.22	

HMet: DL-methionine, HGly: Glycine, HAla: DL-alanine and HLeu: L-leucine

TABLE 2. INFRARED SPECTRA OF COMPLEXES (Figures are given in cm^{-1}.)

$Mo_2(Met)$	$Mo_2(Gly)$	$Mo_2(Ala)$	$Mo_2(Leu)$	Glycine	Methionine	$Ni(Met)_2$	$Na_2MoO_4\cdot 2H_2O$	$(NH_4)_6(Mo_7O_{24})\cdot 4H_2O$	Tentative assignment
3160 w	3200 w	3170 w	3180 w	3180 s	3160 sh	3338) s			ν(N-H)
						3276)			
							1675 s	1635 br	
1607 s	1625) s	1616 s	1625) s	1620 br	1620 s	1617 s			$\nu(\text{-COO})_{\text{antisym.}}$
	1607)		1613)						
1570 sh, m	1575 s	1572 s		1590 br	1675 s			1400 s	$\delta(NH_2)$ or others
1503 s	1495 s	1505 s)	1520 br, m	1505 s	1580 s	1580 s			
		1498 s)			1515 s	1560 sh			
1445 w	1448 s	1463 s	1433 s	1400 s	1413 s	1425 s			$\nu(\text{-COO})_{\text{sym}}$
1430 s	1415 s	1426 s				1408 s			
1360 m	1352 s	1387 m	1390 m	1328 s	1343 s	1350 s			$\nu(C{=}N)+\delta(CH_3)$
1337 m		1362 s	1373 m			1331 w			
			1358 s			1315 w			
950 vs	952 vs	955 vs	955 vs	1033 m	1010 m	1151 s			ν(Mo=O)
917 vs	930 s	930 s	925 s	911 m	925 m	948 s	905 m	915 s	
	910 s	915 s	910 s						
898 s	902 s	898 sh	895 w	893 m	873 m	877 m	856) vs	890) vs	
789 w						798 s	820)	870)	
							800 sh	837 s	
760 s	767 s	761 s	765 m		778 w	765 w			ν(Mo-O-Mo) or others
					775 w				
				700 m	738 w				

vs=very strong, s=strong, m=medium, w=weak, br=broad.
$Mo_2(Met)$, for example, shows the methionine complex having the composition shown in Table 1.

some other bands of lower frequencies in this region too, Mo-O bonds with less of a double-bond character may also exist.[7,12,14,16)] The band near 760 cm^{-1} seems to be due to the Mo–O–Mo bridge,[12,15)] this Mo–O bond should have rather a single-bond character.

The results of the alkalimetry of the methionine complex are shown in Fig. 1.[*2] After the mole ratio of NaOH : Mo_2A (where Mo_2A means the complex) exceeds 2 : 1, the suspended solid begins to dissolve into the solution; after the alkaline standard solution had been added, it takes a few minutes until a stabilized pH value is observed. At the point where the ratio is 4 : 1 all the solid is dissolved and a clear solution is obtained: the pH of the solution suddenly rises there.

As (1) the solid complexes are obtained from an acidic aqueous solution of about pH=1, (2) these complexes are insoluble in water, and (3) the mole ratio of molybdenum and the amino acids in the complexes is 2 : 1, these complexes are probably in the polymer form. However, the behavior of these complexes in alkalimetry is a little different from those of isopolymolybdate, as the reaction with alkali in an aqueous solution is faster and as a big pH change is observed at the point where NaOH : Mo_2A=4 : 1.

The complex seems to be less stable than usual isopolymolybdate. Moreover, in an alkaline solution the presence of polymolybdate ions or complex anions is not probable, as the metal molybdate precipitated immediately from the solution when barium or lead salt was added and as the attempt to isolate the sodium salt of the complex by adding organic solvents to the solution was not successful. On the basis of these results, Fig. 2 shows a tentative model of these complexes, though the exact structure must be determined by a subsequent X-ray structural analysis.

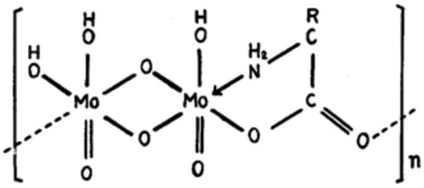

Fig. 2. Structure of molybdenum(VI)-amino acid complexes.

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[*2] 0.1 mM sample suspended in 100 ml of water was titrated by 0.1 N sodium hydroxide. Almost the same results were obtained by the other three complexes, too (at 20°C).