ATRANS

XXVIII.* 1-HYDROXY-1-OXOMOLYBDATRAN-3,7,10-TRIONIC ACID AND ITS SALTS

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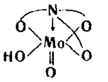
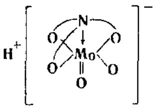
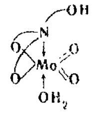
Methods were developed for the preparation of the previously unknown heterocyclic, chelate, mixed anhydride of molybdic and aminotriacetic acids $[\mathrm{HOOCCH_2N(CH_2COO)_2MoO_2 \cdot H_2O}] \cdot 2H_2O$ and its salts. The structures of these compounds in the crystalline state and in aqueous solution were established by IR and PMR spectroscopy, thermography, and potentiometric titration.

Previously, one of us and Lapsin' [2-5] obtained and investigated heterocyclic chelate esters of orthomolybdic acid and tris(2-hydroxyalkyl)amines – 1-hydroxy-1-oxomolybdatrans $[\mathrm{HO(O{=})Mo(OCH_2CH_2)_3N}$ and its C-substituted derivatives].

In the present research, we set out to synthesize and study the similarly constructed mixed anhydride of orthomolybdic and aminotriacetic acids – 1-hydroxy-2-oxomolybdatran-3,7,10-trione (I).†


I


IIa


IIb

The formation of complexes of Mo^{VI} and Mo^{V} with aminotriacetic acid and their stabilities and labilities were previously studied by PMR spectroscopy [6-8]. However, the pure complexes were not isolated.

We have demonstrated that the reaction of aminotriacetic acid (III) with soluble molybdic acid in boiling water gives a light-blue crystalline substance (IV) with the $C_6H_{13}MoNO_{11}$ composition.

Thermographic investigation provides evidence that the IV molecule contains three water molecules. The derivatogram (Fig. 1) shows that one water molecule is lost on heating to 187°. The first endothermic effect is observed at 187-235°, when another 1.5 water molecules are lost. Linking of two molecules of the substance apparently occurs in the process due to formation of an oxygen bridge. The second endothermic minimum at 235-248° is accompanied by the loss of another 0.5 of a water molecule, and the third endothermic minimum at 248-265° corresponds, in our opinion, to further anhydrocondensation of anhydrous substance IV with the loss of still another water molecule.

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*See [1] for communication XXVII.

†Here and elsewhere, N⌒O designates the $-NCH_2COO-$ group.

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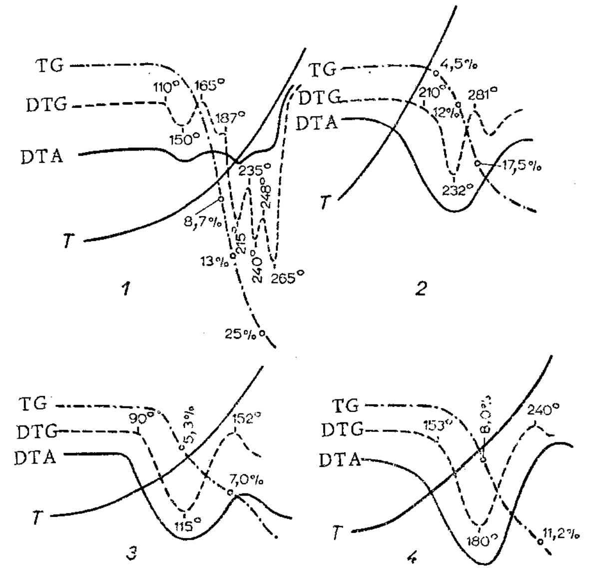

Fig. 1

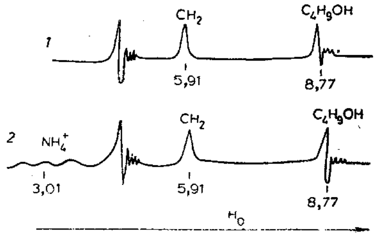

Fig. 2

Fig. 1. Derivatograms of 1-hydroxy-1-oxomolybdatran-3,7,10-trionic acid (1) and its ammonium (2), sodium (3), and disodium (4) salts. The heating rate was 12 deg/min (T is the heating curve, DTA is the differential heating curve, TG is the weight loss curve, and DTG is the derivative curve).

Fig. 2. Proton magnetic resonance spectra of 1-hydroxy-1-oxomolybdatran-3,7,10-trionic acid (1) and its ammonium salt (2).

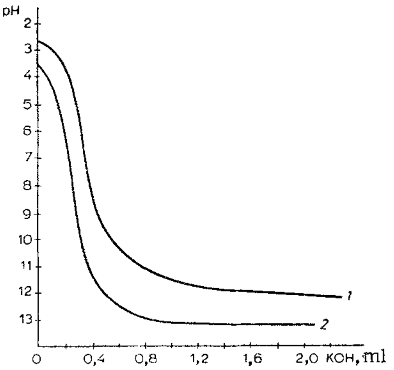

Fig. 3. Titration curves of 1-hydroxy-1-oxomolybdatran-3,7,10-trionic acid (1) and its ammonium salt (2).

According to the ESR data, the molybdenum atom in IV is in a higher degree of oxidation (Mo^{VI}). An investigation of the PMR and IR spectra of IV makes it possible to establish its structure.

The PMR spectrum of an aqueous solution of IV (Fig. 2) coincides with the previously described [8] spectrum of the complex formed in aqueous media in the reaction of III with molybdic acid. At pH ≤ 5, the spectrum contains a single peak from the methylene protons (5.91τ). This indicates the symmetrical structure of the IV molecules in water at pH ≤ 5 and the equilvalence of all the $\overset{\downarrow}{Mo}OCOCH_2N$ half rings of its framework (designated as Mo$\frown$N in the schemes), which excludes the possible 1-hydroxy-1-oxomolybd(VI)atran-3,7,10-trione trihydrate structure (I). We will assume that in aqueous solution IV exists either as the hydrated 1,1-dioxomolybd(VI)atran-3,7,10-trionic acid (IIa) or as acid IIb. In fact, IV in aqueous solution is an acid with pK_a 4.7 that is capable of forming salts.

The specific electrical conductivity of a 0.001 M solution of IV is $5.833 \cdot 10^{-4}\ \Omega \cdot cm^{-1}$ and confirms that this compound is an electrolyte. The specific activity of IV increases markedly on dilution.

The molybdenum atom in the anion of IV has an octahedral configuration. The equivalence of the three $\overset{\downarrow}{Mo}OCOCH_2N$ half rings in IIa and the protons within each of them can be explained by fast dynamic interconversions of the three possible configurations of the hexacoordinated complex [9].

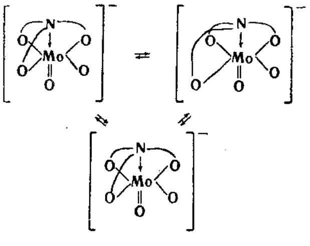

TABLE 1. Frequencies of the Absorption Maxima in the IR Spectra of IV and Its Salts

III	IV	V	Va	VI	VII	VIII	IX	X	XI	XII	Assignment
		417 m	425 s	415 s	435m	420 m	425m	435 m	425 s	420m	
483 m				488 w			450s				
		518 w	520 s		520 m			500 m	525 m	520m	ρ_{COO}, δ_{C-H}
551 m	550vw	559 w	565 s	560 s	560m	565 w			560 s		
591 s				580 m	600				575 s	570 s	
	610s			625 m		635 m	655s	650 vw			δ_{O-C-O}
671 s	670m										
676 s											
		700 w	700 m								
	720m										
744 s	765m	750 w		758s	775vw	775 vw	775vw	780 m	775 vw	780vw	$Mo \leftarrow OH_2$
		790vw	790 vw						790 vw		
				810 m							
				820 m							
863 m	870m	885 m	890 s	840s	880m	890 s	890 vw	850 s	890s	880 w	
900 s				900 vw	905 m			900 vw			
	920vw	918s	920 vw	925 s	920m		920vw		920 vw		$\nu_{Mo=O}$
932 w		938s	940 vw	935 s		930s		930 s	950 m	930 vw	ν_{C-C}
966 s	955vw	950 m									
		970m	970 m	985 w							
		995 w			990s					990 w	
1008 w	1015m	1005 w									
	1040 s										
	1075 w		1075 w	1080w			1030s				
	1085 w	1124m	1125 m	1110w	1125w	1120 w			1120s	1120m	δ_{Mo-O-H}
				1150w			1165w	1150 m			
				1185w						1180w	ν_{CO} (COO⁻)
1204 s	1210 s			1230w	1225s		1230m		1220 vw		
1264 s	1250 vw	1250vw	1255 vw			1250 m			1250s		ρ_{CH_2}, δ_{C-H}
	1290s	1295m	1295 m								
1324 s	1330 w			1310w		1310 w	1320 s	1310 m	1320s	1320m	

1370 s 1380 m 1410 m 1435 s	1350 vw 1380 vw 1420 vw	1358 m 1380 s 1400 s 1430 m	1350 s 1375 s 1400 s	1400 vw 1430 vw	1390 vw	1380 vw	1400 s	1350 m 1430 vw	1340 vw 1400 s 1430 vw	1350 vw	ν_s (COO$^-$), δ_{CH_2}, δ_{NH^+}
1460 m	1450 s 1635 vw	1455 s 1595 vw 1655 vw	1450 vw 1595 vw 1640 vw	1630 vw	1450 w 1490 m 1630 vw	1450 w 1610 vw 1650 vw	1445 vw 1480 s 1600 vw 1650 s	1470 vw 1520 vw 1630 vw	1455 s 1600 vw 1680 vw	1450 s 1640 vw	ν_{as} (COO$^-$), δ_{H-O-H}
1728 vw	1740 vw	1725 w 2570 w 2640 w 2750 w	1725 w 2570 m 2650 m 2760 m		1730 w		1730 w		1750 s 2560 s 2630 s 2750 s		ν_{COOH} COOH
2954 w 2984 w 3040 m	2965 m 3030 m	2870 m 2950 m 3060 m	2950 m 3050 m	2850 w 3000 w	2870 m 3065 m		3090 m	3070 s	2960 m		ν_{C-H}
		3181 s 3260 s	3270 m	3200 m		3250 m					ν_{NH^+}
	3460 vw	3445 s	3450 s	3460 m	3480 w	3470 m	3470 w	3470 m	3450 s†	3450 s†	ν_{O-H} in the crystallization water
	3490 m	3530 s		3530 s							ν_{O-H} in the coordination water

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*The following abbreviations were used: s is strong, m is medium, w is weak, and vw is very weak.

†A broad band, which indicates a polyassociated state for ν_{O-H}.

It is more likely, however, that IV has structure IIb. The equivalence of the methylene protons of the free bonded (to the molybdenum atom) CH_2COO groups in this case can be explained by their rapid exchange. One water molecule enters into the inner sphere of the molybdenum atom in the IIb molecule, while aminotriacetic acid figures as a tridentate ligand rather than as a tetradentate ligand. Two molecules of crystallization water are tied up with the oxygen atoms of the CH_2COO groups of the hydrogen bond. The increased acidity of IIb should be explained by the I effect of the $Mo \leftarrow N$ and $Mo \leftarrow OH_2$ bonds, which promote protonation of the hydrogen atom in the free carboxyl group and protonation of the $Mo \leftarrow OH_2[Mo-OH)^-H^+]$ group.

When the pH of the solution of IV increases above five, the intensity of the proton signals in the PMR spectrum decreases, and a peak of the CH_2 protons of the aminotriacetate anion appears at stronger field. This is evidence for the partially ionic character of the $Mo-O(COCH_2)$ bonds in IV, which, at $pH > 5$ are inclined to cleavage accompanied by breaking of the $Mo \leftarrow N$ coordinate bond.

In the crystalline state, IV most likely has the IIb structure, which is confirmed by IR spectroscopy (Table 1). The spectrum of IV contains two absorption bands at 3450 and 3528 cm^{-1}, which correspond to the stretching vibrations of the hydroxyl group in the molecules of coordinately bonded and crystallization water. The peak at 1740 cm^{-1} corresponds to the absorption of the free carboxyl group. The absorption band at 920 cm^{-1} corresponds to the stretching vibrations of the $Mo=O$ bond [10, 13].

The reaction of III with ammonium molybdate in boiling water gives a colorless, crystalline substance (V) with the composition $C_6H_{15}MoN_2O_{10.5}$ [mol. wt. (by cryoscopy in water) 229, 231]. The specific conductivity of a 0.001 M solution of V is $5.049\ 10^{-4}\ \Omega \cdot cm^{-1}$ and increases on dilution. When a solution of V is highly diluted, V dissociates into five ions with disintegration of the atran skeleton. In dilute solution, V therefore has the properties of an acid with pK_a 3.7.

There are two discontinuities (the first at the equivalence point at $pH \approx 6.7$, the second, which is only slightly expressed, at $pH \sim 10$) on the titration curve of V (Fig. 3). Ammonium molybdate gives the same titration curve. The titration curve of IV, which does not contain ammonium ions, has only the first expressed discontinuity at pH 6.9 (Fig. 3). The titration curves of H_2MoO_4 and $N(CH_2COOH)_3$ (a $4 \cdot 10^{-3}$ M solution of III has pH 3.0) were obtained for comparison. There is one expressed discontinuity (equivalence point at pH 6.7) on the titration curve of III. The amount of alkali consumed during neutralization at the equivalence point is 2 mole; i.e., 2 moles of alkali are consumed per mole of III.

Compound V contains 2.5 molecules of crystallization water, which was confirmed by thermography, by a study of the PMR spectra of solutions of V in D_2O, and by IR spectroscopy [14].

The dehydration curve of V is presented in Fig. 1 by the derivatogram. Up to 210°, V loses one molecule of crystallization water and loses the second molecule at 210-232°. The last 0.5 mole of water is eliminated at 281°. Ammonia is liberated at a higher temperature at which decomposition of the substance is already occurring. The endothermic minimum at 210-232°, which corresponds to the loss of a second molecule of water, is accompanied by the evolution of a gas.

Compound Va, which has the same structure as V but is the monohydrate, can be obtained by dehydration of V by heating to constant weight under a high vacuum or in refluxing decalin. The IR spectra of the two compounds are practically identical.

There are two signals in the PMR spectrum of acidified aqueous solutions of V (Fig. 2) — a singlet of the CH_2 protons (τ 5.91) and a triplet of the protons of the NH_4^+ ion (τ 3.01; $J_{14} = 55$ Hz). As in the case of IV, increasing the pH of the medium leads to the appearance of the peak of the anion of free acid III and, of course, to the disappearance of the fine structure and, eventually, to merging of the signal of the NH_4^+ protons with the H_2O peak.

The PMR spectra of solutions of IV and V in dimethyl sulfoxide contain a broad signal of the CH_2 protons, which attests to the presence of a certain amount of paramagnetic Mo^V impurity. The ESR method confirms that this sort of impurity is a compound of pentavalent molybdenum, the percentage of which in a 0.5 M solution of IV or V does not exceed 10^{-10} mole/liter. The Mo^V impurity is not detected by ESR spectroscopy in aqueous solutions and in crystals of pure IV or V. The transition of hexavalent molybdenum to the pentavalent state consequently occurs due to the reducing action of dimethyl sulfoxide on IV and V.

The equality of the chemical shifts of the methylene protons in the PMR spectrum of IV and V attests to the identical structure of their anions; i.e., it is evidence that V has the ammonium salt structure (IIa) in solution.

TABLE 2. Salts of V with Ammonia and Amines

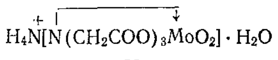
Salt	Amine	Empirical formula	Found, %				Calc., %				Yield, %
			C	H	N	Mo	C	H	N	Mo	
VI	NH_3	$C_6H_{15}MoN_3O_9 \cdot H_2O$	18,6	4,9	11,3	23,9	18,6	4,4	10,9	24,8	95
VII	$N(CH_3)_3$	$C_9H_{20}MoN_3O_9$	27,1	4,8	10,0	23,1	26,4	4,9	10,3	23,4	90
VIII	$C_5H_{11}N$	$C_{11}H_{22}MoN_3O_9 \cdot H_2O$	29,8	5,6	8,7	20,9	29,1	5,3	9,2	21,1	92
IX	$C_{10}H_8N_2$	$C_{16}H_{19}MoN_4O_9$	37,7	3,7	11,9	18,5	37,9	3,8	11,0	18,9	86
X	$C_{12}H_8N_2$	$C_{18}H_{19}MoN_4O_9$	40,9	3,4	10,6	18,8	40,7	3,6	10,5	18,0	95

In addition, the presence of the NH_4^+ ion in the V molecule can be judged from the absorption bands at 3000-3200 cm^{-1}.

A band at 415-435 cm^{-1}, which might have been assigned to the vibrations of the $Mo \leftarrow N$ coordinate bond, is observed in the low-frequency region of the IR spectra of almost all of the investigated compounds. However, it is more likely that this vibration is displayed in the still lower-frequency region.

Since an absorption band at 890 cm^{-1}, which corresponds to the Mo=O vibrations in the $[MoO_4]^{2-}$ anion [8, 10] (895 and 935 cm^{-1}), is observed in the spectrum of $(NH_4)_2MoO_4$, we assigned the bands at 918 cm^{-1} (V) and 900 cm^{-1} (VI) to the vibrations of the Mo=O bonds [10, 13].

In accordance with the results of IR spectroscopy and thermography, the structure of the monohydrated form of ammonium salt IIa can be ascribed to crystalline Va, while the structure of the dihydrate of IIa, the two molecules of which are linked by the hydrogen bonds of still another molecule of crystallization water, can be ascribed to V.



$$H_4\overset{+}{N}[N(CH_2COO)_3MoO_2] \cdot H_2O$$

Va

$$H_2O \cdot Va \cdots H{-}O{-}H \cdots Va \cdot H_2O$$

V

As should have been expected, the absorption of the free COOH group at 1740 cm^{-1} is absent in the IR spectrum of crystalline V, but extremely intense peaks, which correspond to the ν_{as} and ν_s (COO^-) vibrations respectively, are present at 1630 and 1400 cm^{-1}. This may indicate the presence in the V molecule of three equivalent CH_2COO^- groupings, the bond of which with the molybdenum atom has predominantly ionic character.

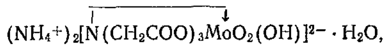
An intense absorption band, which is related to the NH_4^+ vibrations, is observed at 1400-1450 cm^{-1} in the spectra of V and the diammonium salt VI described below [as well as in the spectrum of $(NH_4)_2MoO_4$].

The structure of V is also confirmed by its formation during the neutralization of IV with ammonium hydroxide.

Diammonium salts VI-X (Table 2) are formed when V reacts with excess boiling ammonium hydroxide, trimethylamine, or piperidine. Compound VI is also formed in the reaction of IV with excess ammonia.

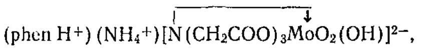
Salts VI and VIII contain one molecule of crystallization water, while salt VII is anhydrous.

Diamines — α,α′-dipyridyl (IX) and o-phenanthroline (X) — form similar salts that do not contain crystallization water. The structures of VI and X can be represented by the formulas



$$(NH_4^+)_2[N(CH_2COO)_3MoO_2(OH)]^{2-} \cdot H_2O,$$

VI

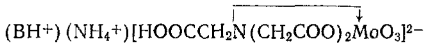


$$(phen\,H^+)(NH_4^+)[N(CH_2COO)_3MoO_2(OH)]^{2-},$$

X

(phen = phenanthroline)

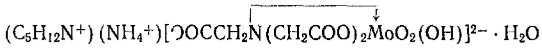
which are confirmed by the presence in the IR spectrum of only one very strong ν_{as} (COO^-) absorption band at 1630 cm^{-1}. The salt of V with o-phenanthroline (X) has a similar structure, and its IR spectrum contains only one ν_{as} (COO^-) band at 1630 cm^{-1}. Salts VII and IX contain a free carboxyl group, which is indicated by the weak absorption band in the IR spectrum at 1730 cm^{-1}. The simultaneous presence of a strong band at 1630 cm^{-1} makes it possible to ascribe the following structure to it.



$$(BH^+)(NH_4^+)[HOOCCH_2N(CH_2COO)_2MoO_3]^{2-}$$

VII $B=N(CH_3)_3$ IX $B=C_{10}H_8N_2$

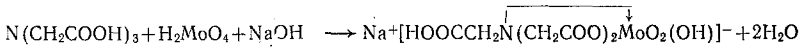
Two intense bands at 1610 and 1650 cm^{-1} are contained in the spectrum of the salt of V with piperidine (VIII) in the region of the carboxyl group vibrations. This makes it possible to ascribe the following structure to this salt.



$$(C_5H_{12}N^+)(NH_4^+)[OOCCH_2N(CH_2COO)_2MoO_2(OH)]^{2-} \cdot H_2O$$

VIII

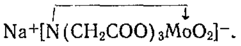
The reaction of III with an equimolar amount of molybdic acid (or its anhydride) in the presence of 1 mole of NaOH in aqueous solution gives the monosodium salt of IV (XI).



$$N(CH_2COOH)_3 + H_2MoO_4 + NaOH \longrightarrow Na^+[HOOCCH_2N(CH_2COO)_2MoO_2(OH)]^- + 2H_2O$$

XI

The structure of salt XI is confirmed by the presence of the absorption band of a free carboxyl group at 1750 cm^{-1} in its IR spectrum. The derivatogram of XI (Fig. 1) contains one endothermic minimum at 115-152°, which corresponds to the loss of 1 mole of water. In the process, XI is apparently converted to



$$Na^+[N(CH_2COO)_3MoO_2]^-.$$

The disodium salt of IV (XIII) is formed in the reaction of III with sodium molybdate in aqueous solution.

$$N(CH_2COOH)_3 + Na_2MoO_4 \longrightarrow Na_2^+[N(CH_2COO)_3MoO_2(OH)]^{2-} \cdot H_2O$$

XII

The structure of this compound is confirmed by its derivatogram and IR absorption spectrum, which contains one very intense ν_{as} (COO$^-$) band at 1665 cm^{-1}. Thus the XII molecule contains three equivalent atran half rings, the bond of which with the molybdenum atom is primarily ionic.

The derivatogram of XII (Fig. 1) contains an endothermic minimum at 153-190-240°, which corresponds to the loss of 1.5 molecules of water. The substance decomposes with gas evolution on heating to 300°.

Lead and mercuric acetates give white precipitates with IV and V in aqueous media, the composition of which is

$$M[N(CH_2COO)_3MoO_2]_2, \text{ where } M = Pb, Hg.$$

EXPERIMENTAL

Starting Reagents. Aminotriacetic acid was obtained by the method in [15] and purified by recrystallization from water. Ammonium molybdate was a chemically pure preparation. The soluble molybdic acid was obtained by the method in [11].

Analysis. Carbon and hydrogen were determined by combustion in one weighed sample in a stream of oxygen both without a catalyst and in the presence of chromium oxide. Nitrogen was determined by the Dumas micromethod using nickel oxide or cobalt oxide. Molybdenum was determined as the oxide remaining after thorough calcination of the substance in a stream of oxygen at 1000°. In addition to this, molybdenum was determined as follows. A weighed sample of the substance was treated with concentrated HNO_3 and, after slow evaporation, was calcined thoroughly at 600-700° twice for 30 min (gravimetric form of MoO_3).

The crystallization water was determined by heating a weighed sample of the substance in a stream of dry, oxygen-free nitrogen with subsequent absorption of the water vapors by magnesium perchlorate.

The potentiometric titration was carried out with a TTT-1 automatic titrator with an SBR-2 titrigraph and a TTA-2 titrating apparatus. The substance was titrated with 0.4 N and 2 N KOH solutions, which were prepared from Ag_2O and KCl. The KOH solutions did not contain carbonate impurities.

Derivatograms. The derivatograms were obtained with the derivatograph of the system in [12].

PMR Spectra. The PMR spectra of 0.5 M solutions were obtained with a Perkin-Elmer R-12A spectrometer (60 MHz) at 36°. tert-Butyl alcohol (τ 8.77 ppm) was used as the internal standard for the aqueous solutions, while cyclohexane was used as the internal standard for the dimethyl sulfoxide solutions.

To determine the crystallization water by integration, the intensities of the signals of H_2O and the CH_3 protons of the standard were compared before and after the addition of the substance to a solution of tert-butyl alcohol in heavy water. The amount of excess water was then compared with the intensity of the peak of the methylene protons of the substance. The accuracy in the integration was no lower than 2.5%.

IR Spectra. The IR spectra of KBr pellets were recorded with a UR-10 spectrophotometer at 400-3500 cm^{-1}.

Mixed Anhydride of Orthomolybdic and Aminotriacetic Acids (IV; IIb · $3H_2O$). An 11.2-g (0.07 mole) sample of soluble molybdic acid was added gradually with stirring to a refluxing solution of 13.4 g (0.07 mole) of III in 500 ml of water, after which the mixture was refluxed for another 8 h. The resulting dark-blue solution was filtered, and the filtrate was evaporated to dryness in a rotary vacuum evaporator. The residue was suspended in alcohol, and the suspension was evacuated. The solid was dried and recrystallized from water to give 17.5 g (66%) of blue crystals. Found: C 19.1; H 3.5; Mo 26.5; N 3.5%. $C_6H_{13}MoNO_{11}$. Calculated: C 19.4; H 3.5; Mo 25.8; N 3.8%.

Ammonium Salt of IV (V). A 3.92-g (0.02 mole) sample of ammonium molybdate was added with stirring to a refluxing solution of 3.82 g (0.02 mole) of III in 500 ml of water, during which vigorous ammonia evolution was observed. The resulting blue solution was filtered hot, and the filtrate was evaporated with a rotary vacuum evaporator. The solid residue was suspended in alcohol, and the suspension was filtered by suction. The solid was vacuum dried and recrystallized from hot water to give 8.9 g (87%) of white crystals. Found: C 19.4; H 3.8; Mo 26.0; N 7.5%. $C_6H_{12}MoN_2O_{19} \cdot 1.5H_2O$. Calculated: C 19.0; H 3.9; Mo 25.2; N 7.4%.

Diammonium Salt of V (VI). A 1.0-g (2.5 mmole) sample of V was added to 10 ml of 20% ammonium hydroxide, and the mixture was refluxed for 1 h. The solution was evaporated to dryness in a vacuum rotary evaporator, and the solid residue was suspended in alcohol. The alcohol suspension was filtered by suction, and the solid was vacuum dried and recrystallized from 50% alcohol to give 0.91 g (95%) of colorless crystals.

Trimethylammonium Salt of V (VII). A 1.0-g (2.5 mmole) sample of IV was added to a mixture of 5 ml of trimethylamine and 3 ml of water. The resulting yellowish solution was refluxed for 15 min, cooled, and filtered. The filtrate was evaporated to dryness, and the solid residue was recrystallized from 50% alcohol to give 0.95 g (90%) of colorless shiny crystals.

Piperidine Salt of V (VIII). A total of 10 ml of a mixture of piperidine and water (1 : 1) was added to 1.0 g (2.5 mmole) of V, and the solution was refluxed for 1 h. The solvent was removed by vacuum distillation to dryness, and the residual light-yellow crystals were recrystallized from piperidine—water (1 : 3). The crystals were removed by suction filtration and vacuum dried to give 1.2 g (92%) of pure product.

Salt of V with α,α'-Dipyridyl (IX). A 0.41-g (2.5 mmole) sample of α,α'-dipyridyl was added to a solution of 1.0 g (2.5 mmole) of V in 20 ml of water. The precipitate was removed by suction filtration, washed with water and alcohol, and vacuum dried to give 1.20 g (86%) of slightly rosy crystals.

Salt of V with o-Phenanthroline (X). A 1.0-g (2.5 mmole) sample of V was dissolved in 20 ml of water, and a solution of 0.45 g (2.5 mmole) of o-phenanthroline in 10 ml of water was added. The precipitate was removed by suction filtration and recrystallized from 50% alcohol. The crystals were vacuum dried to give 1.36 g (95%) of colorless crystals.

Monosodium Salt of IV (XI). A solution of 7.19 g (0.05 mmole) of MoO_3 and 2.0 g (0.05 mole) of NaOH in 10 ml of water was added to a hot solution of 9.5 g (0.05 mole) of III in 400 ml of water, and the mixture was refluxed for 4 h. The resulting light-blue solution was evaporated to dryness in a vacuum evaporator, and the solid residue was suspended in alcohol. The suspension was filtered by suction, and the solid was recrystallized from hot water to give 13.0 g (70%) of colorless crystals that became pinkish-flesh colored on standing in the air. Found: C 21.2; H 2.1; N 4.2%. $C_8H_8MoNO_9Na$. Calculated: C 20.2; H 2.2; N 3.9%.

Disodium Salt of IV (XII). A solution of 7.19 g (0.05 mole) of MoO_3 (or 7.89 g of H_2MoO_4) and 4.0 g (0.1 mole) of NaOH in 20 ml of water was added to a hot solution of 9.5 g (0.05 mole) of I in 400 ml of water. The mixture was refluxed for 4 h, and the resulting blue solution was evaporated in a vacuum rotary evaporator. The solid residue was suspended in alcohol, and the suspension was filtered by suction. The solid was then recrystallized from 50% alcohol to give 15.0 g (76%) of pinkish crystals. Found: C 18.1; H 2.7; N 3.3%. $C_6H_{10}NMoO_{10}Na_2$. Calculated: C 18.1; H 2.5; N 3.5%.

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