THE COMPOUNDS OF ETHYLENEDIAMINETETRAACETIC ACID WITH HEXAVALENT TUNGSTEN*

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The sodium tungstate–ethylenediaminetetraacetic acid (H_4Y) system was studied using a pH--metric titration method at 25°C and $I = 0\cdot1$. In the pH region $7\cdot0 - 8\cdot1$, complexes WO_3Y^{4-}, WO_3HY^{3-} and $(WO_3)_2Y^{4-}$ are formed; their stability constants were determined. Crystalline salts, $M_4^I[(WO_3)_2Y] \,.\, n\,H_2O$ (M^I = Li, Na, K, NH_4), were also prepared. Their properties agree with a structure analogous to that of hexavalent molybdenum complexes, characterized by bridge Y^{4-} anions and terminal WO_3 groups.

Complexes of hexavalent tungsten with ethylenediaminetetraacetic acid have been investigated predominantly in aqueous solutions. Kula and Rabenstein[1] studied the $Na_2WO_4-Na_2H_2Y$ system potentiometrically and using nuclear magnetic resonance. They found that complexes with W : Y = 1 : 1 and 2 : 1 are formed in a narrow pH range and determined their approximate stability constants. Similar results were obtained by Yano, Takahashi and Nagashima[2] and Busev and Sokolov[3]. Tsunoda and coworkers[4] prepared a crystalline salt, $Na_4[(WO_3)_2Y] \,.\, 7\,H_2O$ and studied it in the solid state and in solution using a number of methods without arriving at an unambiguous conclusion on the molecular structure of the complex anion. Basically there are two possible structures: a type analogous to the complex of hexavalent molybdenum with "terminal" WO_3 groups and the Y^{4-} anion as a bridge or a dimeric unit with the W—O—W bond, surrounded by the Y^{4-} anion.

The present paper was intended as a detailed study of the complexes of hexavalent tungsten with ethylenediaminetetraacetic acid considering a possible analogy to hexavalent molybdenum complexes[5].

EXPERIMENTAL AND RESULTS

Reagents and Apparatus

Tungstic acid (pure, Lachema) was purified and activated by dissolving in a sodium hydroxide solution and precipitation with hot concentrated hydrochloric acid. The substance composition was H_2WO_4 after washing with hot water and drying at 110°C. Deuterium oxide (isotopic purity,

99·7%) and D_2SO_4 (isotopic purity, 95%) were supplied by the Institute for research, preparation and utilization of radioisotopes, Prague. A NaOD solution was prepared by the sodium reaction with D_2O, and DCl solution by introducing gaseous DCl (obtained from NaCl and D_2SO_4) into D_2O. The other chemicals used were of p.a. purity from Lachema and Merck.

The instrumentation employed was described in the previous communications in this series and in ref.[6]. The magnetic susceptibility was measured by the Gouy method at 25°C. The infrared spectra of solutions were taken on the UR 20 instrument using silver chloride cells with polyethylene distance foils 0·04 mm thick. The calculations were performed on an IBM 7040 computer.

Analytical Methods

Tungsten was determined gravimetrically as the oxiquinolate and the Y^{4-} content by titration with manganese (II) sulphate using eriochrome black T at pH 10 (tungsten does not interfere in the determination). The alkali content was determined by argentometric titration of chlorides, obtained by exchange reaction on Dowex 2 in the chloride form after decomposition of the complex by digestion with sulphuric acid. Ammonia was determined by the distillation method and water by drying to a constant weight at temperatures found from thermogravimetric curves.

The Study of Equilibria in Solution

pH- metric titrations of solutions containing $5 . 10^{-3}$M-Na_2H_2Y and Na_2WO_4 in W : Y ratios of 4 : 1, 2 : 1, 1 : 1, 0·5 : 1 and 0 : 1 were performed. The solutions contained sodium perchlorate to adjust the ionic strength to 0·1 and a 0·1M solution of carbonate-free NaOH was used as the titrant. The titrations were performed at
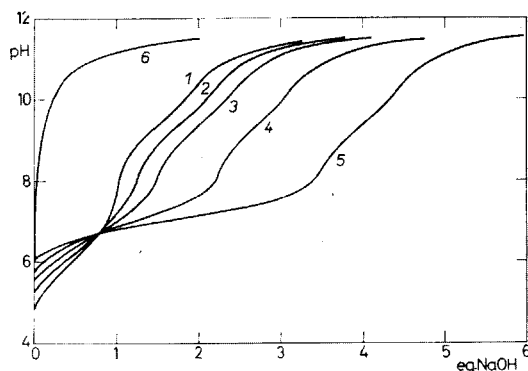

Fig. 1

pH-Metric Titrations of Na_2H_2Y and Na_2WO_4 Solutions

1 $5 . 10^{-3}$M-Na_2H_2Y;   *2* $5 . 10^{-3}$M-Na_2H_2Y + $1·25 . 10^{-3}$M-Na_2WO_4;   *3* $5 . 10^{-3}$M-Na_2H_2Y + $2·5 . 10^{-3}$M-Na_2WO_4;   *4* $5 . 10^{-3}$M-Na_2H_2Y + $5 . 10^{-3}$M-Na_2WO_4; *5* $5 . 10^{-3}$M-Na_2H_2Y + $1 . 10^{-2}$M-Na_2WO_4;   *6* $5 . 10^{-3}$M-Na_2WO_4.

$25 \pm 0.1^\circ$C with a precision of ± 0.01 pH and ± 0.002 ml. The pH values were recalculated to $-\log[\text{H}^+]$, using the tabulated activity coefficient value[7].

It is evident from the titration curves in Fig. 1 that an interaction between the tungstate and ethylenediaminetetraacetic acid anions takes place. The pH region in which the complex formation is unaffected by other processes is apparently very narrow; at pH < 7 tungstate condenses[8] and at pH > 8.2 tungsten is present in solution solely as WO_4^{2-}, since the shape of the curves at pH > 8.2 is no longer dependent on the tungsten concentration and hence reflects only gradual dissociation of H_2Y^{2-}.

Therefore only experimental points in the pH range, $7.0-8.2$, were selected for further treatment of the titration data using the SCOGS program[9], which systematically looks for the complex particles and their stability constants which best fit the experimental titration curve. The average deviation of the calculated titrant consumption from the experimental value (residual) serves as the criterion which is minimized by the program employing the non-linear least squares method.

TABLE I

The Stability Constants of the Complexes at 25°C and I 0·1

The constant (charges are omitted)	$\log K \pm 3\sigma$	Ref.[1] (35°C, $I = 1 - 3$)
$K_1 = [\text{WO}_3\text{Y}]/[\text{WO}_3][\text{Y}]$	9.92 ± 0.06	10.8 ± 0.2
$K_2 = [(\text{WO}_3)_2\text{Y}]/[\text{WO}_3]^2[\text{Y}]$	18.41 ± 0.04	19.6 ± 0.4
$K_3 = [\text{WO}_3\text{HY}]/[\text{WO}_3\text{Y}][\text{H}]$	7.31 ± 0.03	7.5 ± 0.2

TABLE II

The Wavenumbers of $\nu_a(\text{COO})$ in the Infrared Spectra of $\text{Na}_4[(\text{WO}_3)_2\text{Y}]$ Solutions in D_2O at Various pD

pD	—COO$^-$	$^+$NHCH$_2$COO$^-$	—COO—W
5·1	—	1 630 vs	1 650 sh
6·0	—	1 635 s	1 655 m
7·2	—	1 640 sh	1 655 vs
8·0	1 590 sh	1 630 m	1 652 s
9·2	1 585 vs	1 628 s	—

The optimum description of the experimental data involves a system of three complex particles, the composition and stability constants of which are given in Table I. During the computation, the residual was invariant after six iteration cycles and equaled 0·039 ml. If the assumption of the existence of a further complex, *e.g.* $WO_3H_2Y^{2-}$ or $(WO_3)_2HY^{3-}$, was introduced in the computation, the residual increased and values for the stability constant of these complexes were divergent.

In order to check the region in which complex $(WO_3)_2Y^{4-}$ is stable, the infrared spectra of $Na_4[(WO_3)_2Y]$ solutions in deuterium oxide were measured at various pD values, adjusted with NaOD and DCl solutions. The measurements were carried out in the region of the carboxylic group antisymmetrical stretching which is diagnostically important for determining the structure of complexes of this type[10]. The results are given in Table II and indicate that the complex anion is stable at least in the pH range $7·2-8·0$. The maximum at $1590\ cm^{-1}$ corresponds to HY^{3-} and Y^{4-} ions, that at $1630\ cm^{-1}$ to the $N^+HCH_2COO^-$ zwitterion $(H_2Y^{2-}$ and $HY^{3-})$ and that at $1655\ cm^{-1}$ to the carboxylic group bound covalently to tungsten.

Preparation of the Complexes

Salts with the general composition $M_4^I[(WO_3)_2Y].n\ H_2O$ were prepared by mixing equivalent amounts of an alkali hydroxide (carbonate), tungstic acid and ethylenediaminetetraacetic acid, heating the water suspension slightly until the solid particles dissolved and crystallizing from dilute ethanol. The preparation of the sodium salt was reproduced according to the method of Tsunoda and coworkers[4]. Attempts to prepare the rubidium and caesium salts were unsuccessful because of the precipitation of sparingly soluble hexatungstates. The compositions and analyses of the prepared substances are summarized in Table III.

TABLE III

Analyses of the Prepared Compounds

Compound	Calculated/Found			
	% W	% Y	% M^I	% H_2O^a
$Na_4[(WO_3)_2Y].7\ H_2O$	37·91	29·71	9·48	13·00
	37·28	29·13	9·28	12·98
$K_4[(WO_3)_2Y].8\ H_2O$	34·94	27·39	14·86	13·69
	34·76	27·05	14·72	13·38
$(NH_4)_4[(WO_3)_2Y].4\ H_2O$	41·03	32·16	8·05	8·04
	40·70	31·82	7·95	—
$Li_4[(WO_3)_2Y].6\ H_2O$	41·42	32·47	3·13	12·18
	40·97	32·09	3·08	12·30

^{a} The water content was determined from thermogravimetric curves.

TABLE IV
Thermal Decomposition of the Prepared Compounds

Compound	Dehydration at a const. temperature	°C (number of liberated H_2O molecules)			Decomposition, °C		
		GTA	DTA	product	GTA	DTA	product
$Li_4[(WO_3)_2Y].6 H_2O$	200 (6)	200 (6)	210 endo	$Li_4[(WO_3)_2Y]$	280	295 exo 680 endo	Li_2WO_4
$Na_4[(WO_3)_2Y].7 H_2O$	120 (7)	150 (7)	160 endo	$Na_4[(WO_3)_2Y]$	280	290 exo 385 exo 550 endo 650 endo	Na_2WO_4 (s) Na_2WO_4 (l)
$K_4[(WO_3)_2Y].8 H_2O$	40 (5) 100 (8)	120 (8)	50 endo 100 endo	$K_4[(WO_3)_2Y]$	270	410 exo	K_2WO_4
$(NH_4)_4[(WO_3)_2Y].4 H_2O$	beginning 120, follows continuously up to				290	270 endo 300 exo 515 exo	WO_3

Properties of the Prepared Compounds

The complexes obtained are white crystalline solids, incongruently soluble in water, except for the lithium salt, which dissolves without decomposition, its solubility being 44·3 g/100 ml solution at 25°C. They are diamagnetic and their molar susceptibilities agree almost exactly with the values calculated from the Pascal constants[11]. Their thermal decomposition in the air is summarized in Table IV. During this decomposition, all the substances are first dehydrated and then their organic component decomposes. The final products are alkali tungstates or tungstic oxide (with the ammonium salt). The products were identified by chemical analysis and by the X-ray powder method. The characteristic groups of bands in the infrared spectra are given in Table V. From the powder patterns it follows that none of the substances are isostructural and their patterns also differ from those of analogous hexavalent molybdenum compounds[5].

TABLE V

Characteristic Band Groups in the Infrared Spectra of the Crystalline Complexes

| Compound	$\nu_a(WO_3)$	$\nu(C{-}N)$	$\nu_a(COO)$	$\nu(H_2O)$
$Li_4[(WO_3)_2Y].6\ H_2O$	925 m	1 075 w	1 625 s	3 445 s, b
		1 105 w	1 660 sh	
$Na_4[(WO_3)_2Y].7\ H_2O$	910 s	1 065 w	1 655 vs	3 185 w, b
		1 108 w		3 385 s, b
$K_4[(WO_3)_2Y].8\ H_2O$	910 m	1 070 w	1 650 s	3 225 w, b
		1 110 w		3 500 s, b
$(NH_4)_4[(WO_3)_2Y].4\ H_2O$	912 s	1 050 w	1 640 s	3 450 s, b
		1 070 vw		
		1 102 vw		

DISCUSSION

The determination of the stability constants carried out in the present paper is more precise than the results of Kula and Rabenstein[1] for two reasons: *1)* the effects of tungstate condensation were eliminated and *2)* a large number of experimental data was treated statistically. The composition of the hexavalent tungsten complexes with ethylenediaminetetraacetic acid is identical to that for hexavalent molybdenum and the mutual ratio of the stability constants is also analogous. The two WO_3 groups in the $(WO_3)_2Y^{4-}$ complex are coordinated almost equally strongly, which can be explained by their bonding at the opposite ends of Y^{4-} anion. The acid dissociation constant of the WO_3HY^{3-} complex corresponds unambiguously to the proton-to-nitrogen bond. In agreement with the infrared spectra of solutions it has further been verified that the complexes are stable only in a narrow pH region.

Preparation of salts with the complex anion $[(WO_3)_2Y^{4-}]$ is substantially more difficult than with molybdenum, because of their narrow stability range. Moreover, these substances dissolve incongruently, except for the lithium salt, and are partially converted into hexatungstates on prolonged contact with the mother liquor. The impossibility of preparing the rubidium and caesium salts is apparently related to the pronounced decrease in the solubility of hexatungstates in the Li—Cs series.

The powder pattern of the sodium salt is practically identical with the data of Tsunoda and coworkers[4]. However, their conclusion that the substance exhibits tetragonal symmetry was not verified. The powder pattern could not be indexed in the tetragonal system and the number of molecules in the unit cell, $Z = 3$, given by Tsunoda, is principally impossible in the tetragonal symmetry. Either the lattice parameter values reported by Tsunoda are incorrect, or the substance crystallizes in a system of a lower symmetry than tetragonal; the large number of lines in the powder pattern seems to support the latter suggestion.
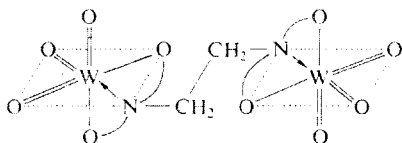
Summarization of the results of the study of hexavalent tungsten complexes with ethylenediaminetetraacetic acid leads to proposed molecular structures in solution and in the solid state:
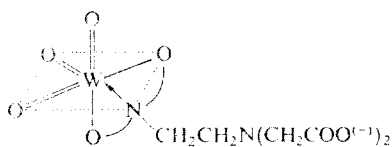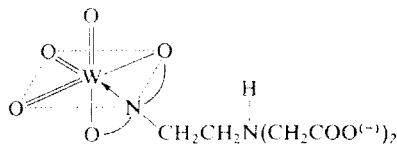
WO_3Y^{4-} in solution WO_3HY^{3-} in solution

$(WO_3)_2Y^{4-}$ in solution and in the solid state

The following are the chief arguments supporting the above formulas: *1*) The stability constant values discussed above; *2*) the process of thermal decomposition, suggesting that the hydrate water is not coordinated; *3*) the infrared spectra of the crystalline salts, which are practically identical with those of the molybdenum complexes[5] and contain bands corresponding to vibrations of the following characteristic groups:

antisymmetrical valence vibrations of terminal WO_3 groups (W—O—W bridge vibrations were not observed), splitting of the C—N valence vibration band typical of coordinated nitrogen, the $\nu_a(COO)$ vibration corresponding to the carboxyl-tungsten covalent bond and finally the $\nu(H_2O)$ vibration in the region corresponding to uncoordinated water molecules forming weak hydrogen bonds; *4*) diamagnetism of all the compounds, characteristic of tungstic oxide and tungstates. On the other hand, compounds with W—O—W bonds are usually weakly paramagnetic[11].

Thus it can be concluded that the hexavalent tungsten complexes with ethylene-diaminetetraacetic acid have the same structure as those of hexavalent molybdenum, with which the "terminal" type has been confirmed by X-ray structure determination[12]. A similar analogy has also been found with pentavalent tungsten[6] and molybdenum[13], which, however, belong to an entirely different structural type.

We thank Dr J. Podlaha for stimulating advice and critical comments provided throughout the work.

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