Systematics of some properties of hexamolybdotellurate(VI) salt hydrates with di- and trivalent metals, $M_x[TeMo_6O_{24}]\cdot nH_2O$

Akira Saito
Chemistry Department, Tokyo Gakugei University, Koganei, Tokyo 184 (Japan)

(Received August 12, 1993; revised October 25, 1993)

Abstract

Due to their anomalously low solubility in water, hexamolybdotellurate(VI) salt hydrates of Mg, alkaline earth and rare earth metals were readily obtained by mixing solutions which contained the heteropoly anion and the nitrate of each metal. The salt hydrates of trivalent lanthanides, $Ln_2[TeMo_6O_{24}]\cdot nH_2O$, were divided into two groups between Gd and Tb by the number of water molecules: for the first half, $n=21$ and the second, $n=31$. To characterize the water of crystallization, thermal analysis was conducted using a DTA-TG apparatus. Solubilities in water were measured at various temperatures. The data for the lanthanide elements were used to evaluate thermodynamic parameters for dissolution. The enthalpy and the entropy of dissolution showed that inclusion of an extra number of water molecules stabilizes the lattice for the heavy lanthanides by filling the increased gaps between the ions. Some characteristic features of salt formation of the related heteropoly molybdates such as $MnMo_9O_{32}^{6-}$ and $CrMo_6O_{24}H_6^{3-}$ were also described.

Key words: Molybdenum complexes; Oxo complexes; Tellurium complexes; Lanthanide complexes; Cluster complexes

Introduction

We have been studying interaction of metal cations with heteropoly anions in aqueous solutions. The stability constants for 1:1 complexes of Ca^{2+}, Eu^{3+}, Th^{4+} and UO_2^{2+} were determined with two heteropolytungstates, $SiW_{12}O_{40}^{4-}$ and $P_2W_{18}O_{62}^{6-}$ [1], and with two heteropolymolybdates, $MnMo_9O_{32}^{6-}$ and $TeMo_6O_{24}^{6-}$ [2]. The results indicated that metal cations bind to the anions primarily by electrostatic interaction with a number of surface oxygen atoms which are arranged in a geometrical framework as a preferred metal binding site.

Since heteropoly anions have ionic sizes of about an order of magnitude larger than common metal cations and show the least possibility of being deformed by the influence of other ions, preparation and structural studies of salts as solid compounds will provide another feature of the metal cation–heteropoly anion interaction. As a general trend, salts of heteropoly anions are found to be extensively hydrated and their solubilities in water are quite high; these properties are attributed to the unmatched ionic sizes and the low surface charge density of the anions [3]. In particular, the heteropolytungstates given above are extremely soluble as acids or as metal salts [4]. By the principal concepts of electrostatic interaction and packing of ions in the lattice formation, cations of high ionic charges and/or large ionic radii are expected to form salts of relatively low solubility. However, experiments to crystallize Ln^{3+} salts of $SiW_{12}O_{40}^{4-}$ and $P_2W_{18}O_{62}^{6-}$ were unsuccessful. On the other hand, the heteropolymolybdates of the structures shown above are less soluble in water; for example, the solubilities of $(NH_4)_6MnMo_9O_{32}\cdot 6H_2O$ and $Na_6TeMo_6O_{24}\cdot 22H_2O$ at room temperature are 5×10^{-3} and 2×10^{-2} M, respectively. As expected, the addition of divalent or trivalent cations such as Mg, alkaline earth metals or lanthanides and Y into the aqueous solution of $Na_6TeMo_6O_{24}\cdot 22H_2O$ produced crystalline precipitates. The anion $MnMo_9O_{32}^{6-}$ [5] has a structure related to $TeMo_6O_{24}^{6-}$ [6], the same negative charge and a very similar ability to bind metal cations as a ligand [2]. However, crystallization of Ln^{3+} salts from the aqueous solutions which contained both ions has not been successful. These observations suggest that the geometrical structure of heteropoly anions may have some relationship to the crystallization of salt lattices.

Trivalent lanthanides are a series of cations with ionic sizes which decrease in a consistent manner. Because of this, they are used as probes to understand

0020-1693/94/$07.00
SSDI 0020-1693(93)03747-X

the nature of phenomena such as ionic hydration in solution or in solid phases and complexation with many organic and inorganic ligands [7]. A wide variety of Ln^{3+} hydrate salts or complexes have been synthesized as a series of compounds [8]. In many such solid compounds, water molecules occupy the first coordination sphere, at least partly, and play an important role in stabilizing the ionic lattices. In the present system, inclusion of more water molecules may be expected because of the significant difference in ionic sizes.

Based on these observations, the hydrate salts of $TeMo_6O_{24}{}^{6-}$ with Mg, alkaline earth metals and the trivalent rare earth elements were prepared. Thermal dehydration was carried out using a DTA-TG apparatus to obtain information on the nature of the water molecules. Then the solubilities in water were measured at various temperatures. Estimation of thermodynamic functions for the dissolution of the Ln^{3+} salts was made to evaluate why these salts are exceptionally insoluble in water.

Experimental

Synthesis of $Na_6[TeMo_6O_{24}]\cdot 22H_2O$

The compound was synthesized by a modified procedure based on the description given in ref. 9. A suspended mixture of $Na_2MoO_4\cdot 2H_2O$ and $Na_2H_4TeO_6$ in a molar ratio of 6:1 was acidified by the addition of conc. HNO_3 until the pH of the solution turned to 7.5, and then it was heated. The nearly clear solution was filtered and heated to reduce the volume to about one third of the original. After being cooled and left to stand overnight, the product that crystallized out was recovered from the supernatant and was further purified by recrystallization from water. The composition of the final product was confirmed by chemical analyses for Te [10] and Mo [11]. *Anal.* Calc. for the above formula: Te, 7.87; Mo, 35.5. Found: Te, 8.08; Mo, 35.6%.

Syntheses of $M_x[TeMo_6O_{24}]\cdot nH_2O$

Crystalline salts of divalent alkaline earths and trivalent rare earths with the heteropoly anion were deposited in the solutions prepared by mixing either nitrates or perchlorates of these metals and 0.02 M solution of $Na_6[TeMo_6O_{24}]\cdot 22H_2O$. Because some of the compounds are efflorescent, they were kept in water until use. Prior to characterization, the solid compounds were taken out and placed on filter paper to dry for 10–20 min in the air. To confirm their compositions, representative samples were analyzed for metals by ICP-AES and for Mo by gravimetry as oxinate [6]. The number of water of crystallization was determined for all samples by thermal analysis using a DTA-TG instrument (Thermoflex, Rigaku, Japan). About 30 mg of the dried compound was packed in a Pt crucible. DTA and TG curves were recorded simultaneously from room temperature to 500 °C in static air atmosphere. The results of the analyses for two representative compounds are as follows. Calc. for $Nd_2[TeMo_6O_{24}]\cdot 21H_2O$: Nd, 16.5; Mo, 32.8; H_2O, 21.6. Found: Nd, 16.2; Mo, 31.4; H_2O, 21.8%. Calc. for $Er_2[TeMo_6O_{24}]\cdot 31H_2O$: Er, 16.9; Mo, 29.1; H_2O, 28.2. Found: Er, 16.7; Mo, 28.9; H_2O, 28.5%.

Solubility measurement

To determine the solubilities of these salts in water, saturated solutions were prepared by agitating the mixture of each salt and triple-distilled water in a thermostatted water bath for over 20 h. The water was boiled to remove CO_2 before use. Equilibration time was determined by sampling aliquots of the supernatant intermittently, and then analyzing for their metal concentration. The contents of Mo of the saturated solutions were determined by ICP-AES and used to calculate the solubilities.

Results

Thermal dehydration of the salts

All the salts, when heated up to about 400 °C, reached constant weights which are assumed to be those of the anhydrous salts. The endothermic effects observed from the start of heating up to 400 °C were typical of dehydration processes. Further heating up to 500 °C did not cause any additional decomposition. However, on the DTA curves of the Sr^{2+} and Ba^{2+} salts, a very sharp exothermic peak was observed at about 450 °C. Because they do not accompany a weight change at all, they must be due to some structural modifications of the amorphous state of the dehydrated salt.

The number of water molecules is generally larger for the salts of the cations of smaller ionic radii, except for the Mg^{2+} salt which has smaller number than the Ca^{2+} salt. The thermal analysis data of the divalent metal salts are reproduced in Fig. 1. Dehydration of the Mg^{2+} salt produced one peak at 170 °C and another at 350 °C which is unusually high. On the other hand, the DTA curve of the Ca^{2+} salt was very complicated. Dehydration begins at as low as 55 °C and the curve has five peaks until the dehydration is completed at 200 °C. Similarly the Sr^{2+} salt begins to release water at around 55 °C and produces rather simple DTA curves with two separated peaks at 100 and 200 °C. A single peak at 200 °C indicates a complete dehydration of the Ba^{2+} salt in a single stage.

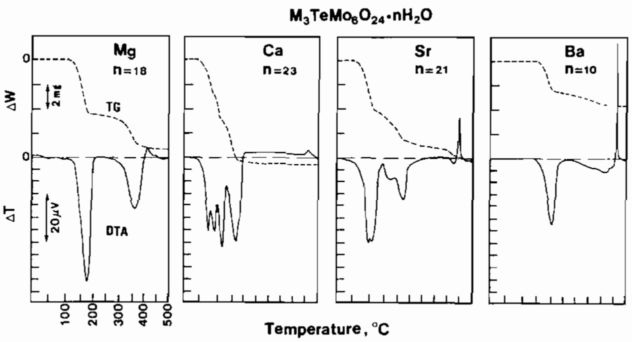

Fig. 1. Thermal analysis of $M_3[TeMo_6O_{24}]\cdot nH_2O$, where M is Mg and alkaline earth metals. Conditions: sample weight, 32.9 ± 0.5 mg; heating rate, 10 °C/min, static air atmosphere.

For trivalent lanthanides, the salts $Ln_2[TeMo_6O_{24}]\cdot nH_2O$ were divided into two groups according to the number of water molecules, i.e. La–Gd with $n=21$, Tb–Lu with $n=31$. The thermal analysis data show that dehydration proceeds generating rather complex DTA curves. Among the lanthanide data we can distinguish four types of curves as seen in Fig. 2. For La–Sm, the main dehydration occurs at around 120 °C with the liberation of nearly a half of the water molecules. The compounds of this group seem to contain two or three water molecules which are not removable up to 270 °C. The DTA curves for Eu and Gd compounds are rather similar to those of the first half, but more properly are considered to be a transitional type. The characteristic of the second group is that a half of the water molecules are dehydrated at temperatures less than 100 °C, and a third at around 170 °C. Though all the DTA curves resemble each other, two major peaks gradually became indistinct from Tb to Lu.

Solubility of the salts

The solubilities of the alkaline earth metal hydrates measured at various temperatures are tabulated in Table 1. They all increase as the temperature increases but only very slightly for those of Mg^{2+} and Sr^{2+}. The Mg^{2+} salt is less soluble than the Ca^{2+} salt and is not in the order expected from the trend observed for the rest of the salts, for generally the solubilities are larger for salts of smaller ionic radii. The solubility of the Ba^{2+} salt is very low so that the addition of $Ba(NO_3)_2$ to the $Na_6[TeMo_6O_{24}]$ solution instantaneously formed a white suspension which was then slowly transformed into a crystalline precipitate on standing for more than a month.

Solubilities measured at various temperatures are given in Fig. 3. Each point was obtained as an average of the values of at least three independent determinations. Errors of the values were all less than 5%.

The solubilities of the light lanthanides do not change much along the series. A notable discontinuity is seen at the middle of the series, where the number of water molecules of the salts changes as well. For the heavy lanthanides, the solubilities and their increasing tendencies with temperature increase are much larger than those for the light lanthanides.

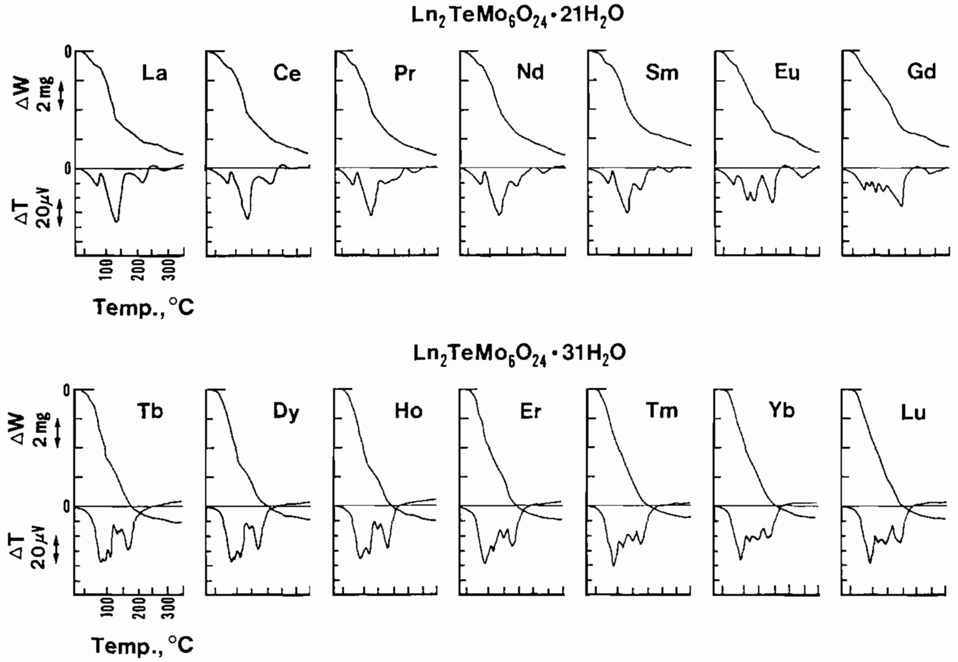

Fig. 2. Thermal dehydration of $Ln_2[TeMo_6O_{24}]\cdot nH_2O$, where Ln denotes trivalent lanthanides. Conditions: sample weight, 31.2 ± 0.5 mg, heating rate, 10 °C/min, static air atmosphere.

TABLE 1. Solubilities, m_s (mol kg^{-1}), of $M_3[TeMo_6O_{24}]\cdot nH_2O$ (M = Mg and alkaline earth metals) at various temperatures

Compound	m_s (15 °C)	m_s (25 °C)	m_s (35 °C)
$Mg_3[TeMo_6O_{24}]\cdot 18H_2O$	3.271×10^{-3}	3.575×10^{-3}	3.909×10^{-3}
$Ca_3[TeMo_6O_{24}]\cdot 23H_2O$	3.639×10^{-3}	8.286×10^{-3}	2.132×10^{-2}
$Sr_3[TeMo_6O_{24}]\cdot 21H_2O$	5.646×10^{-4}	7.696×10^{-4}	1.081×10^{-3}
$Ba_3[TeMo_6O_{24}]\cdot 10H_2O$	3.309×10^{-6}	7.567×10^{-6}	1.867×10^{-5}

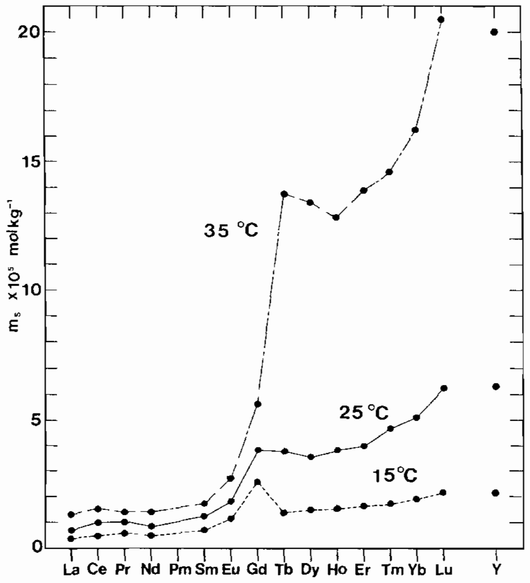

Fig. 3. Solubilities of $Ln_2[TeMo_6O_{24}]\cdot nH_2O$ in water at various temperatures.

Estimation of the thermodynamic functions of solution

Dissolution of the salts is represented as follows:

$$M_x[TeMo_6O_{24}]\cdot nH_2O(s) \rightleftharpoons xM^{z+}(aq) + TeMo_6O_{24}^{6-}(aq) + nH_2O(l) \quad (1)$$

The solubility product, K_s, is expressed as

$$K_s = x^x m_s^{x+1} \gamma_\pm^{x+1} a_w^n \quad (2)$$

where m_s is the molality of the salt at saturation, $\gamma_\pm$ the mean ionic activity coefficient of the solute, a_w the activity of water, which is related to the practical osmotic coefficient of the water in the saturated solution, O_w, by the equation

$$-\ln a_w = (x+1)m_s O_w / n_w \quad (3)$$

where n_w is the number of moles of water associated with m_s moles of solute [12]. This treatment is based on the assumption that $M^{z+}(aq)$ and $TeMo_6O_{24}^{6-}(aq)$ are not associated at all. The stability constants for 1:1 complexation between trivalent lanthanides and the anion are of the order of 10^4 according to our measurement on the Eu^{3+}–$TeMo_6O_{24}^{6-}$ system [2]. Therefore, the above assumption will be valid only to a limited degree, although m_s is very small. Because the stability constants are not known for each of the lanthanides at all temperatures, no correction was made.

To calculate the ionic mean activity coefficients for the Ln^{3+} salts, the Debye–Hückel equation in the following form was used:

$$\ln \gamma_\pm = \{-z_1 z_2 A I_m^{1/2}\}/\{1 + \mathring{a} B I_m^{1/2}\} \quad (4)$$

In this equation, z_1 is the charge of the cation (i.e. +3), z_2 is the negative charge of the anion (i.e. +6), I_m is the ionic strength which is equal to $27m_s$, $\mathring{a}$ is the distance between ions at closest approach, A and B are parameters dependent only on the relative dielectric constant of water [13] and temperature. K_s at 25 °C was calculated by eqn. (1) and then converted to ΔG_s by the equation: $\Delta G_s = -RT \ln K_s$. Regression analysis for the linear relationship between $\ln K_s$ and $1/T$ was used to estimate ΔH_s at 298.15 K. The correlation coefficients were larger than 0.99 in every calculation. The entropy change at 298.15 K was calculated by the relationship $\Delta S_s = (\Delta H_s - \Delta G_s)/T$. The results of the calculations are given in Table 2 in which the mean ionic activity coefficients are also included.

Discussion

Heteropoly anions are relatively large ions with high formal negative charges. Their unique geometrical frameworks are composed of MoO_6 or WO_6 octahedra sharing edges, vertices or faces. Therefore, these anions are considered to be unsusceptible to deformation even under the influence of other ions. The cations used in the present study as typical hard acids have ionic radii in the range of 0.7 to 1.4 Å which are still too small to form crystal lattices with the heteropoly anions. Therefore, the inclusion of water molecules, in addition to the electrostatic principle, is very significant for the effective packing. Some of the water molecules are coordinated to the cation and at the same time they are partly hydrogen bonded to the anion oxygen atoms. The other water molecules are hydrogen bonded only to the anion or to other water molecules.

The number of water molecules of the lanthanide salts also reflects the decreasing ionic radii of the cations; the heavy lanthanides form the salts with a larger number of water molecules. Even though the ionic size decreases consistently with increasing atomic number, the compositions are divided only into two groups at the middle of the series. The salts of each group look very similar in appearance and may have crystal structures closely related with each other. In spite of this, the DTA data imply that structural modifications are apparent with a gradual decrease in ionic radius.

TABLE 2. Thermodynamic data for the dissolution of $Ln_2[TeMo_6O_{24}]\cdot nH_2O$ at 298.15 K

Ln	m_s (mol kg^{-1})	$\gamma_\pm$	K_s	ΔG_s (kJ mol^{-1})	ΔH_s (kJ mol^{-1})	ΔS_s (J K^{-1} mol^{-1})
La	6.759×10^{-6}	0.755	5.323×10^{-16}	87.18	104.2	57.01
Ce	1.011×10^{-5}	0.711	1.483×10^{-15}	84 64	99.36	49.35
Pr	1.069×10^{-5}	0.704	1.704×10^{-15}	84.30	71.75	−42.11
Nd	8.372×10^{-6}	0.732	9.216×10^{-16}	85.82	89.38	11.93
Sm	1.260×10^{-5}	0.683	2.554×10^{-15}	83.30	79.40	−13.80
Eu	1.841×10^{-5}	0.633	6.320×10^{-15}	81.05	74.26	−22.78
Gd	3.829×10^{-5}	0.521	3.175×10^{-14}	77.05	56 59	−68.62
Tb	3.777×10^{-5}	0.523	3.087×10^{-14}	77.12	167.0	301.6
Dy	3.535×10^{-5}	0.534	2.690×10^{-14}	77.46	157.4	268.1
Ho	3.824×10^{-5}	0.521	3.167×10^{-14}	77.05	151.1	248.3
Er	3.997×10^{-5}	0.514	3.468×10^{-14}	76.83	151.3	249.9
Tm	4.704×10^{-5}	0.487	4.808×10^{-14}	76.02	147.9	241.1
Yb	5.128×10^{-5}	0.473	5.689×10^{-14}	75.60	143.2	226.6
Lu	6.257×10^{-5}	0.439	$8\ 267\times10^{-14}$	74.68	139.5	217.5
Y	6.308×10^{-5}	0.437	8.390×10^{-14}	74.64	141.9	225.7

The heteropoly anion, $CrMo_6O_{24}H_6^{3-}$, has the same structure as $TeMo_6O_{24}^{6-}$, though it includes six hydrogen atoms bound to six oxygen atoms of the central CrO_6 octahedron [15]. The Ln^{3+} salts, $Ln[CrMo_6O_{24}H_6]\cdot nH_2O$, readily crystallized from aqueous solutions. This series of salts can also be divided into two groups based on their number of water molecules: La–Tb, $n=11$ and Dy–Lu, $n=15$. This demonstrates that the dividing position in the series is determined only by the cationic size relative to that of the anion.

The Y^{3+} salt has no anomaly in composition, thermal dehydration behavior or solubility. However, a few attempts to prepare the Sc^{3+} salt of $TeMo_6O_{24}^{6-}$ were not successful. The concentration of Sc^{3+} was increased up to 0.013 M in the presence of an equi-molar concentration of $TeMo_6O_{24}^{6-}$, but no crystallization occurred. Preparation of Ln^{3+} salts with another typical heteropolymolybdate, $MnMo_9O_{32}^{6-}$, from solutions of various compositions was not successful. Their solubilities are estimated to be of the order of 10^{-5} M or less according to the extrapolation from those of the NH_4^+ salt (1×10^{-3} M) and of the Sr^{2+} salt (7×10^{-5} M). The specific geometry of the anion may prohibit the crystallization of Ln^{3+} salts possibly for kinetic reasons.

When hydrate salts are heated, water molecules which have gained enough energy escape from the surface of the crystal lattice. Since the size disparity between the cation and the anion in this system is so large, the relative configuration of the ions must be rather limited. Therefore, the basic structure will not change even after it has been thermally dehydrated. The temperature at which the dehydration occurs will be an indication of how strong they are bound in the crystal lattice. According to the DTA-TG data, all the lanthanide salts contain a nearly equal number of firmly bound water molecules, whereas the salts of the second half of the series have a larger number of structural water. Such a characteristic was also found for the lanthanide salts of $CrMo_6O_{24}H_6^{3-}$ when studied by the same technique for comparison; the salts with 11 H_2O were dehydrated in one stage giving rise to a single DTA peak at 160 °C, whereas those with 15 H_2O showed two peaks on their DTA curves at 100 and 160 °C corresponding to the losses of 5 and 10 water molecules, respectively. This indicates that the extra number of water molecules must be loosely bound in the lattice to fill the gaps between the constituent ions.

It is generally accepted that heteropoly acids and their salts are highly soluble in water [4]. However, all types of salts of the anion $TeMo_6O_{24}^{6-}$ seem to have comparatively low solubility in water. In particular, the solubility of $La_2[TeMo_6O_{24}]\cdot 21H_2O$ is exceptionally small compared with those reported for La^{3+} salt hydrates of other heteropoly anions such as $La[PMo_{12}O_{40}]\cdot 10H_2O$ (0.16 M) [15], $La_4[SiMo_{12}O_{40}]_3\cdot 82H_2O$ (0.427 M) [15] and $La[CrMo_6O_{24}H_6]\cdot 11H_2O$ (1.13×10^{-3} M) [16]. The unique arrangement of seven octahedra seems to give the anion a rather compact ionic size compared to other heteropoly anions such as $SiW_{12}O_{40}^{4-}$ and $P_2W_{18}O_{62}^{6-}$. Since the surface of the anion can be regarded as flat, close-packed arrays of oxygen atoms, the most basic oxygen atoms [17], which define the central TeO_6 octahedron, are accessible to metal cations or water molecules providing relatively strong interaction sites.

To calculate the solubility products, the mean activity coefficients of the ions and the activity of water must be estimated. Since the solubilities are quite low, the latter value is taken as unity. The formal charge of the anion is so large that it brings significant contributions to the ionic strength of the solution, and henceforth to the activity coefficients of the ions. In a study of the aqueous solution of $H_4SiW_{12}O_{40}$, the activity coefficients were obtained by ultracentrifugation and were found to agree with the results calculated by the Debye–Hückel equation for a 1:4 electrolyte with $\mathring{a} = 7.6$ Å. The magnitude of the parameter $\mathring{a}$ approaches the ionic radius of this spherical anion [18]. In the present system, however, the anion is not spherical but of a disk-shaped structure. Therefore, it is even more difficult to definitely determine the closest approach of the ions. In applying the Debye–Hückel equation of the form given in eqn. (4), the second term in the denominator is still small enough so that, regardless of the value selected as the parameter $\mathring{a}$, it will not affect the results significantly. On the other hand, the solubilities of the alkaline earth salts except for Ba^{2+} are much higher than those of the lanthanide salts. The application of the Debye–Hückel equation would result in mean activity coefficients of the order as low as 10^{-3}. Accordingly, the use of the same equation will not be appropriate. At present, an estimation of the thermodynamic parameters was not attempted for these salts.

The large positive values of ΔG_s are principally ascribed to the highly endothermic nature of the dissolution. Along the lanthanide series, ΔG_s values show only a slight decrease. As seen in Fig. 4, the enthalpy of solution, ΔH_s, is not continuous, but a distinct change is observed between the light and heavy lanthanides which exactly coincides with the discontinuity in the number of water of crystallization. This means, therefore, that the larger enthalpy changes of the heavy lanthanide salts (of about 70 kJ mol^{-1} more than the light ones) are almost compensated for by their entropy increase.

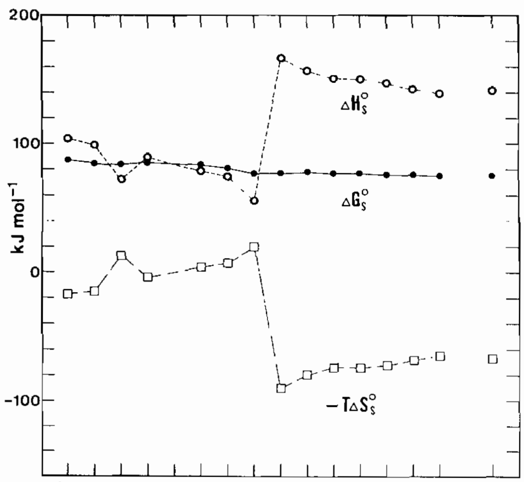

Fig. 4. Thermodynamic functions of solution for $Ln_2[TeMo_6O_{24}] \cdot nH_2O$ at 298.15 K.

The enthalpy of solution which reflects the difference between the lattice enthalpy (ΔH_{latt}) and the enthalpy of hydration of the constituent ions, $\Delta H_{hyd}(TeMo_6O_{24}{}^{6-})$ and $\Delta H_{hyd}(Ln^{3+})$, is related by the following equation:

$$\Delta H_{latt} + \Delta H_{hyd}(TeMo_6O_{24}{}^{6-}) \\ = \Delta H_s - 2\Delta H_{hyd}(Ln^{3+}) - n\Delta H_v(H_2O) \qquad (5)$$

where $\Delta H_v(H_2O)$ is the enthalpy of vaporization of water. All terms on the right-hand side of this equation are known, so that the trends in the lattice enthalpy will be observable though there are no available data for $\Delta H_{hyd}(TeMo_6O_{24}{}^{6-})$. The enthalpy of hydration for Ln^{3+} decreases almost linearly with increasing atomic number [19]. When compared to $\Delta H_{hyd}(Ln^{3+})$, ΔH_s is so small that its slight decrease in each group is not manifested in ΔH_{latt}. Therefore, ΔH_{latt} in each group of salts increases linearly and there is a discontinuity between Gd and Tb. The difference of ΔH_{latt} for each of the heavy lanthanides from the values extrapolated from that for the light lanthanides amounts to 510 kJ mol^{-1}. This must be the contribution from the extra number of water molecules. Though the ionic sizes of the cations and the anion become less proportionate as the atomic number increases, the inclusion of more water molecules enables effective packing possibly by forming hydrogen-bonded aggregates and the reduction of repulsive force between the anions as found in the acid $H_3PW_{12}O_{40} \cdot 29H_2O$ [20].

The variation of ΔS_s along the series parallels that of ΔH_s. According to the Born–Haber cycle, dissolution of hydrate salts is described by the succession of the following processes: (i) transformation of the crystal to hypothetical gaseous state, (ii) its decomposition to gaseous ions and water molecules, (iii) formation of hydrated ions and liquid water. Entropy increases in the first two processes, whereas in the last one it decreases. For the light lanthanides, ΔS_s values are between +60 and −70 J K^{-1} mol^{-1} dispersed around the average of −4.0 J K^{-1} mol^{-1}. On the other hand, for the heavy lanthanides, the entropy change is a large positive value which is large enough to almost compensate for the even larger endothermic enthalpy changes so that it causes only a slight increase in solubility. The entropies of hydration of Ln^{3+} decrease slightly as the ionic radius decreases along the series, nevertheless, they can also be regarded as being approximately constant for the light and for the heavy lanthanides with values of about −478 and −512 J K^{-1} mol^{-1}, respectively [21]. The difference between the two is about 34 J K^{-1} mol^{-1}. Hence the notable difference of ΔS_s by 250 J K^{-1} mol^{-1} among the two groups is principally associated with the disordering of lattice water as a result of the dissolution of the salts.

References

1 A. Saito and G.R. Choppin, *Inorg. Chem*, *30* (1991) 4564.

2 A. Saito and G.R. Choppin, Interaction of metal cations with heteropolymolybdate ions, $MnMo_9O_{32}^{6-}$ and $TeMo_6O_{24}^{6-}$, in preparation.

3 L. Barcza and M.T. Pope, *J. Phys. Chem.*, *79* (1975) 92.

4 G.A. Tsigdinos, *Heteropoly Compounds of Molybdenum and Tungsten, Topics in Current Chemistry,* Vol. 76, Springer, Berlin, 1978, p. 10.

5 J.L.T. Waugh, D.P. Shoemaker and L. Pauling, *Acta Crystallogr.*, *7* (1954) 438.

6 H.T. Evans, Jr., *J Am. Chem. Soc.*, *90* (1968) 3275; *Acta Crystallogr., Sect. B*, *30* (1974) 2095.

7 G.R. Choppin, in J.-C. G. Bünzli and G.R. Choppin (eds.), *Lanthanide Probes in Life, Chemical and Earth Sciences, Theory and Practice,* Elsevier, Amsterdam, 1989, p. 12.

8 L. Niinisto and M. Leskelä, in K.A. Gschneidner, Jr. and L. Eyring (eds.), *Handbook on the Physics and Chemistry of Rare Earths,* North-Holland, Amsterdam, Vol. 8, 1986, Ch. 56, p. 203; Vol. 9, 1987, Ch. 59, p. 91.

9 H.T. Evans, Jr., *J. Am. Chem. Soc.*, *70* (1948) 1291.

10 T.E. Green and M.E. Turley, in I.M. Kolthoff and P.J. Elving (eds.), *Treatise on Analytical Chemistry*, Part II, *Analytical Chemistry of the Elements,* Vol. 7, Interscience, New York, 1961, p. 162.

11 W.J. Williams, *Handbook of Anion Determination,* Butterworths, London, 1979, p. 108.

12 D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Shum, I. Halow, S.M. Bailey, K.L. Churney and R.L. Nuttall, *The NBS Tables of Chemical Thermodynamic Properties, J. Phys. Chem. Ref. Data,* Vol. 11, Suppl. 2, American Chemical Society and American Institute of Physics, Washington, DC, 1982, p. 2-12.

13 D. Eisenberg and W. Kauzmann, *The Structure and Properties of Water*, Oxford University Press, Oxford, 1969, p. 189.

14 A. Perloff, *Inorg Chem.*, *9* (1970) 2228.

15 G.A. Tsigdinos, *Ind. Eng. Chem*, *Prod. Res. Develop.*, *13* (1974) 267.

16 A. Saito, Tokyo Gakugei University, 1993, unpublished data.

17 M. Filowitz, R.K.C. Ho, W.G. Klemperer and W. Shum, *Inorg. Chem.*, *18* (1979) 93.

18 J.S. Johnson, K.A. Kraus and G. Scatchard, *J. Phys. Chem.*, *64* (1960) 1867.

19 L.R. Morss, *J. Phys. Chem.*, *75* (1971) 392.

20 J.W. Linnett, *J Chem. Soc*, (1961) 3796.

21 Y. Marcus, *Ion Solvation,* Wiley, Chichester, UK, 1985, p. 125.