lated supporting the view that substitution reactions of a large number of aquometal ions conform to a two-step mechanism first formulated by Eigen

$$\mathrm{L} + \mathrm{M(H_2O)_6} \xrightarrow{K_{os}} \mathrm{M(H_2O)_6\cdots L} \xrightarrow{k_e} \mathrm{L{-}M(H_2O)_5} + \mathrm{H_2O} \qquad (2)$$

In the first step, the aquometal ion and ligand diffuse together to form an outer-sphere complex with an association constant K_{os}. This process is followed by the rate-determining step, which corresponds to the loss of a coordinated water molecule from the metal ion. According to this mechanism, the second-order formation rate constant k_{M-L} is given by the equation

$$k_{M-L} = K_{os}k_e \qquad (3)$$

where K_{os} is the outer-sphere formation constant and k_e is the rate constant for water exchange of the outer-sphere complex.

The outer-sphere formation constant is given by the equation

$$K_{os} = 4\pi Na^3/3000$$

where N is Avogadro's number and a is the distance of closest approach of the two partners of the outer-sphere complex. For a large number of metal-substitution reactions, K_{os} values of 0.1 have been calculated and the corresponding water-exchange rates account nicely for the magnitude of the second-order substitution rate constant. For the mono(terpyridine)nickel(II) reaction,[3] a K_{os} value of approximately 4 would be required to be consistent with the rate of water exchange reported here for the mono(terpyridine)nickel(II) ion.

If the theoretical equations used to calculate K_{os} values are strictly applicable for outer-sphere formation between mono(terpyridine)nickel(II) and terpyridine, then the unusually large values of K_{os} required to accommodate the water-exchange rate and mono(terpyridine)nickel(II)–terpyridine substitution rate serve as evidence of the breakdown of the general metal ion–ligand complex formation mechanism in this instance. The reaction could then be classified as SN2. However, one cannot rule out the possibility that at least a weak interaction between the two terpyridine molecules in the mono(terpyridine)nickel(II)–terpyridine outer-sphere complex gives rise to an enhanced K_{os}.

It will be of considerable interest to extend substitution studies of the mono(terpyridine)nickel(II) ion to other ligands, particularly monodentates and bidentates, to determine if rapid substitution is general or just characteristic of certain ligands.

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CONTRIBUTION FROM THE SCIENCE DEPARTMENT,
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Potassium Calcium Paramolybdate and Cryoscopy of Paramolybdates

BY ORVILLE W. ROLLINS AND LOUIS C. W. BAKER[1]

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Paramolybdates react, in solution, with various metal cations, especially those of most transition metals, to form heteropoly complexes.[2] It was found that a reproducible new salt forms when a solution containing potassium paramolybdate is treated with calcium ions. Since it has sometimes been contended[3] that spherically symmetrical ions such as Ca^{2+} and Mg^{2+} might also form heteropoly anions with molybdates, it was desirable to subject the new salt to more detailed investigation as a contribution toward settling that point. As expected, this investigation has shown that the new compound is a double salt, $K_4Ca[Mo_7O_{24}]\cdot 7H_2O$, wherein the calcium is not in the anionic complex in solution. This work led to potentiometric, spectrophotometric, and cryoscopic investigations of paramolybdate. The crystallographic unit cell and space group for the new double salt were determined by single-crystal X-ray studies. The combined results add confirmation, by a sensitive independent method, to the formula for paramolybdate which has been proposed in recent years by Lindqvist[4] and Sillén and coworkers.[5]

Experimental Section

Preparation of Potassium Calcium Paramolybdate.—A sample of $K_2CO_3\cdot 1.5H_2O$ weighing 11.48 g (0.0695 mol) was dissolved in water and the solution was heated to boiling, whereupon 10.0 g (0.0695 mol) of MoO_3 was added slowly in small portions. After the evolution of carbon dioxide had ceased, heating was discontinued and concentrated nitric acid was added to the hot solution until methyl red turned orange (pH 5). The solution was diluted to about 200 ml and allowed to cool to 40° or less, and a solution of $Ca(NO_3)_2\cdot 4H_2O$ in about 20 ml of water was added with stirring. The amounts of calcium nitrate used for different preparations were 5.0 g (0.0212 mol), 7.0 g (0.0297 mol), and 8.0 g (0.0339 mol). The pH's of the final solutions were in the range 4.7–5.3. Potassium nitrate was added to each solution to increase the rate of crystallization and the yield. The amount of KNO_3 added was not constant and varied from a few milliliters of a nearly saturated solution to 28 g (0.277 mol) of the salt. Thus, the total amount of K^+ ions used in the preparations was varied from 0.14 to 0.42 mol. The white, crystalline new double salt was filtered onto sintered glass, washed well with cold water followed by ace-

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(1) Addressee for reprints, at Georgetown University

(2) L. C. W. Baker in "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, pp 604–612.

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(5) Y. Sasaki, I. Lindqvist, and L. G. Sillén, *J. Inorg. Nucl. Chem.*, **9**, 93 (1959).

tone, and then dried by suction. Yields of 6.0 and 7.3 g were obtained when 8.0 g of calcium nitrate was used. This corresponds to yields of 44 and 54% in terms of the molybdenum taken.

Analysis of Potassium Calcium Paramolybdate.—Potassium was determined by flame photometry. Calcium was determined by titration with ethylenediaminetetraacetic acid (EDTA) according to the method of Lewis and Melnick.[6] The EDTA was standardized against standard Zn(II) solution, prepared from ZnO which had been assayed gravimetrically, according to Harris and Sweet.[7] The per cent of calcium in five preparations, which had involved widely varying Ca and K proportions, was very constant, ranging between 2.89 and 2.92% for 11 determinations. Molybdenum was determined using a Jones reductor. The water of hydration was determined by heating samples to constant weight at 500°. The dehydrated samples were white, crystalline, and completely soluble in water. *Anal.* Calcd for $K_4Ca[Mo_7O_{24}]\cdot 7H_2O$: K, 11.35; Ca, 2.905; Mo, 48.76; H_2O, 9.16. Found: K, 11.4; Ca, 2.90; Mo, 48.7; H_2O, 9.20. Results with four other preparations involving widely varying Ca:K proportions in the mother liquor also gave virtually identical agreement with the calculated values.

X-Ray Studies.—A single crystal of potassium calcium paramolybdate was subjected to an X-ray study using Zr-filtered Mo Kα radiation in a precession camera. The crystal proved to be monoclinic: $a = 15.35 \pm 0.03$ Å, $b = 18.60 \pm 0.04$ Å, $c = 10.20 \pm 0.02$ Å, and $\beta = 96° 35' \pm 5'$. The space group is $P2_1/a$. A density of 3.19$_1$ g/ml was measured by the displacement of toluene in a pycnometer. The calculated number of formulas per unit cell is therefore 4.02.

Potentiometric Titrations.—A solution of $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ was passed through an ion-exchange column packed with specially conditioned[8,9] Dowex 50W-X8 (H^+ form). The ammonium paramolybdate (J. T. Baker's Analyzed reagent) was assayed for ammonia and for molybdenum. The micro Kjeldahl method of Pregl and Grant[10] was followed for determination of ammonia. *Anal.* Calcd for $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$: NH_4^+, 8.76; MoO_3, 81.5. Found: NH_4^+, 8.76; MoO_3, 81.5. Aliquots of the acidic effluent (pH 2.85) were analyzed for molybdenum in order to determine the concentration.

A sample of analyzed potassium calcium paramolybdate was dissolved. That solution and an aliquot of the acidic solution prepared from $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ by ion exchange were titrated potentiometrically with standard 0.0996 *M* NaOH solution (Figures 1 and 2). These titrations were run at room temperature, and precautions were taken to exclude carbon dioxide.

Cryoscopy.—Analyzed samples of the double salt and of ammonium paramolybdate were studied cryoscopically, using fused $Na_2SO_4\cdot 10H_2O$ as the solvent. This amounts to investigating the status of the molybdate solute in saturated aqueous Na_2SO_4 solution at 32°. The theory, apparatus, technique, and determination of the cryoscopic constant have been described.[11,12]

Results and Discussion

The symmetry and dimensions of the crystallographic unit cell are such that it could accommodate four paramolybdate anions having the structure proposed by Lindqvist[4] for the anions in $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$.

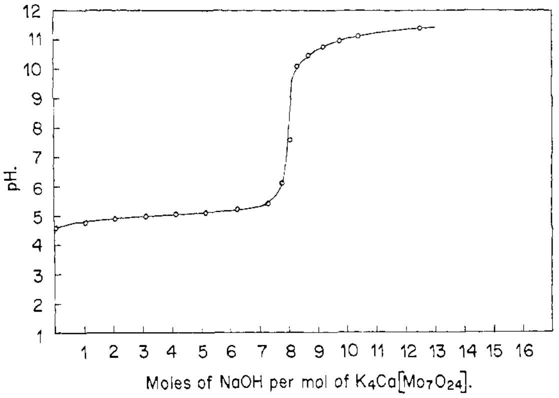

Figure 1.—Titration of 100 ml of 0.000955 *M* $K_4Ca[Mo_7O_{24}]$ solution with 0.0996 *M* NaOH.

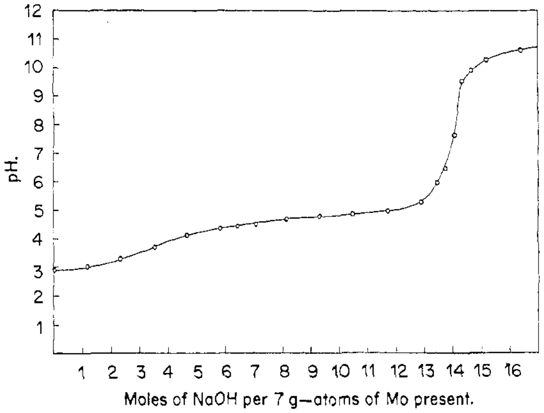

Figure 2.—Titration, with 0.0996 *M* NaOH, of 200 ml of the acidic effluent, 0.002975 *M* in Mo, obtained by passing $(NH_4)_6[Mo_7O_{24}]$ solution through H^+-cycle ion-exchange column.

The first plateau of the potentiometric titration of potassium calcium paramolybdate (shown in Figure 1) corresponds to degradation of the paramolybdate anion. Along this plateau equilibrium was obtained in a few minutes after each addition of the NaOH solution. The reaction for the titration can be written

$$K_4Ca[Mo_7O_{24}] + 8NaOH \longrightarrow 2K_2MoO_4 + 4Na_2MoO_4 + CaMoO_4 + 4H_2O \quad (1)$$

The K_{sp} of $Ca(OH)_2$ was not exceeded. This investigation supports the formulation given above for the new salt and shows that it is not an acid salt.

Figure 2 shows the potentiometric titration of the acidic solution obtained by passing $(NH_4)_6[Mo_7O_{24}]$ solution through a H^+-cycle ion-exchange column. The titration curve for the double salt, Figure 1, is highly similar to the curve for Figure 2 beginning at the point where 6 mol of NaOH had been added per 7 g-atoms of Mo present. The acidic pH at that point and at the start of the double salt titration is caused by very slight hydrolysis of polyanion. The hydrolysis of paramolybdate may be represented as

$$Mo_7O_{24}^{-6} + 4H_2O \rightleftharpoons 7MoO_4^{2-} + 8H^+ \qquad (2)$$

Since the anion degradation occurred at about pH 4.7, this degradation and the neutralization of the hydrogen ions in the solution produced by ion-ex-

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change proceed simultaneously over a broad region.

Results of the cryoscopic studies of potassium calcium paramolybdate and of ammonium paramolybdate are shown in Table I. These data are also plotted in Figure 3. K_0 is the observed depression in the transition temperature of the solvent divided by molality ($\Delta T/m$). This effect was determined at infinite dilution for several known electrolytes by the authors[11,13] by plots similar to that in Figure 3.[14] Division of the K_0 at infinite dilution by ν^* (the number of ions per formula for each solute, not counting Na^+ or SO_4^{2-} ions) gave a value of 3.38°. To obtain accurate conclusions, this constant should be thus evaluated experimentally in any study of this nature employing $Na_2SO_4 \cdot 10H_2O$.[14] The value of K_0 at infinite dilution for the double salt is 20.9°/m, and it is 24.6°/m for ammonium paramolybdate (see Figure 3). For $K_4Ca[Mo_7O_{24}]$, therefore, the experimental $\nu^* = 20.9/3.38 = 6.19$ ions, and for $(NH_4)_6[Mo_7O_{24}]$, the experimental $\nu^* = 24.6/3.38 = 7.27$ ions. Therefore, the double salt is completely ionized into K^+, Ca^{2+}, and $Mo_7O_{24}^{6-}$ ions. We have shown that NH_4^+ ions have a ν^* of 1.00 in this solvent.[11] Thus in the above study the paramolybdate ion is shown to have a ν^* of 1.2–1.3 in saturated Na_2SO_4 solution. The fact that ν^* for paramolybdate was slightly greater than unity may be ascribed primarily to a very small amount of hydrolysis of the type indicated by eq 2. However, the straightness of the two lines in Figure 3 shows that no major hydrolysis or dissociation is taking place over the range of conditions studied. This comparative study affords strong support for formulating the double salt as given above.

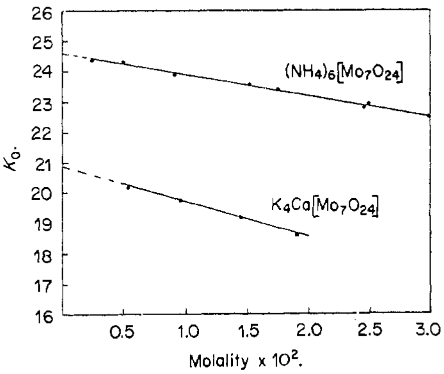

Figure 3.—Cryoscopy in $Na_2SO_4 \cdot 10H_2O$. K_0 *vs.* molality for $K_4Ca[Mo_7O_{24}]$ and for $(NH_4)_6[Mo_7O_{24}]$.[14]

TABLE I

RESULTS OF CRYOSCOPY IN SODIUM SULFATE DECAHYDRATE[14]

Solute	Molality[a]	ΔT, °C	K_0
$(NH_4)_6[Mo_7O_{24}]$	0.00254	0.062	24.4
	0.00521	0.127	24.4
	0.00919	0.220	23.9
	0.01527	0.360	23.6
	0.01750	0.409	23.4
	0.02460	0.560	22.8
	0.02480	0.570	22.9
	0.03060	0.690	22.5
$K_4Ca[Mo_7O_{24}]$	0.00555	0.122	20.2
	0.00960	0.190	19.8
	0.01455	0.280	19.3
	0.01905	0.355	18.6

[a] Moles of solute per 1000 g of $Na_2SO_4 \cdot 10H_2O$.[14]

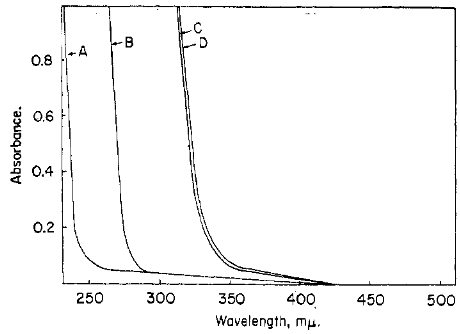

Figure 4.—Absorption spectra: A, 7.15 × 10^{-4} M $Ca(NO_3)_2$; B, 5.0 × 10^{-3} M Na_2MoO_4; C, 7.15 × 10^{-4} M $(NH_4)_6[Mo_7O_{24}]$; D, 7.15 × 10^{-4} M $K_4Ca[Mo_7O_{24}]$.

The absorption spectrum of the $K_4Ca[Mo_7O_{24}]$ salt in solution is compared with absorption spectra of known molybdates in Figure 4. The spectrum of the double salt is almost identical with the spectrum of ammonium paramolybdate. These two spectra are quite different from that of orthomolybdate, MoO_4^{2-}. The absorption spectra of 6-molybdonickelate(II), 6-molybdoaluminate(III), 6-molybdoferrate(III), and 6-molybdochromate(III) have been reported by Tsigdinos.[12] These show that the highly absorbing charge-transfer region, caused by the heteropolymolybdate skeleton, begins in each case before wavelengths as low as 380 mμ are reached. The paramolybdate absorption shoulder begins below 350 mμ (Figure 4). This comparative study also lends support to the formulation of the new compound as a double salt of the paramolybdate anion.

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(13) M. T. Pope, O. W. Rollins, and L. C. W. Baker, paper in preparation.

(14) In this article molalities for the cryoscopy are in terms of moles of solute per 1000 g of $Na_2SO_4 \cdot 10H_2O$ (as solvent) potentially present. Alternatively, the molalities could have been expressed in terms of moles of solute per 1000 g of H_2O present (an equally correct form). To convert the molalities given in the text to the latter basis, multiply each of them by 1.79, and divide each K_0 by the same factor. On that basis the K_0 per ν^* at infinite dilution, for known compounds in the procedure used, becomes 3.38/1.79 = 1.89° per m. The ν^* values, of course, come out identically on either basis.