# Synthesis of Dodecamolybdoantimonate(v) Salts containing the Keggin Structure†

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Ammonium dodecamolybdoantimonate, with a body-centred cubic symmetry, has been synthesized from antimony(III) oxide and ammonium heptamolybdate in aqueous acidic solution. The corresponding potassium, rubidium and caesium salts were prepared by ion exchange. They were characterized by elemental analysis, *X*-ray diffraction, *X*-ray fluorescence, i.r., *X*-ray photoelectron spectroscopy, thermogravimetry, and differential thermal analysis.

The heteropolyacid salts of molybdenum and tungsten possessing Keggin anions have been of interest in recent catalytic research.[1-9] Utilizing such salts as catalysts, processes such as the oxidation of methacrolein (2-methyl-2-propenol) and hydration of propene, isobutene, and 1-butene have already been industrialized.[1] The dependence of catalytic activity and selectivity of these compounds on the elements within the Keggin anion has been discussed.[7,10-12] Thus, acids/salts containing tungsten are found to be effective catalysts for methanol conversion into hydrocarbons, while molybdophosphates are used for oxidation reactions such as those mentioned above. Among molybdenum heteropolyacid catalysts the oxidation reactions are said to be favoured by a lower value of the bond strength between molybdenum and the outer oxygen atoms,[12] which has been shown to be strongly influenced by the electronegativity of the heteroatom. In a comparative study of steady-state catalytic activity, Echigoya and co-workers[11] have shown that ammonium dodecamolybdoarsenate with a less electronegative heteroatom oxidized 10% more isobutyric acid than did ammonium dodecamolybdophosphate.

Keggin salts of antimony(v), which is beneath arsenic in the Periodic Table, and which has a lower electronegativity, have not been reported. In one instance,[13] a non-cubic molybdoantimonic acid was reported to have been prepared, but doubt as to its existence has been cast by Tsigdinos.[14] Tsigdinos[14] also mentioned the necessity of further work to elucidate the exact nature of molybdenum heteropoly compounds containing antimony.

In continuation of our earlier work[15-18] on heteropoly compounds and also in view of the recent catalytic interest in compounds possessing Keggin structures, we report the synthesis of dodecamolybdoantimonate(v) salts of ammonium, potassium, rubidium, and caesium ions all showing a body centred cubic lattice (Keggin Type A[19]). It would be of interest to compare the oxidation catalytic properties of molybdenum heteropolyacid salts with $P^V$, $As^V$, and $Sb^V$ as heteroatoms.

## Experimental

Ammonium heptamolybdate, $[NH_4]_6[Mo_7O_{24}]\cdot4H_2O$ (Wako Pure Chemicals and Fluka AG), and antimony(III) oxide, $Sb_2O_3$ (E. Merck and BDH Chemicals), were used as supplied. All other chemicals used were of analytical grade.

*Synthesis of Ammonium Dodecamolybdoantimonate.*—Antimony(III) oxide (2.9 g, 0.02 mol $dm^{-3}$ Sb) dissolved in *aqua regia* (120 $cm^3$) on a hot plate at 70 °C was added to a solution of ammonium molybdate (42.4 g, 0.24 mol $dm^{-3}$ Mo, in 400 $cm^3$ water). A slightly yellow solution was obtained to which 16 mol $dm^{-3}$ ammonia (50 $cm^3$) was added. A light yellow precipitate was formed. The suspension was further acidified by adding concentrated nitric acid (40 $cm^3$). The light yellow precipitate was left in the mother-liquor for 2 h at 70 °C and for about 15 h at room temperature. Finally the precipitate was filtered off, washed several times with distilled water and dried at 50 °C. Chemical and thermal analyses corresponded to a formulation $[NH_4]_3[Mo_{12}SbO_{40}]\cdot11H_2O$. For comparison studies ammonium dodecamolybdophosphate, $[NH_4]_3[Mo_{12}PO_{40}]\cdot4H_2O$, showing 59.8% (calc. 59.1) Mo and 1.6% (calc. 1.6) P (based on inductively coupled plasma analysis) and pyridinium dodecamolyboarsenate $[C_5H_5NH]_3[Mo_{12}AsO_{40}]\cdot9H_2O$, showing 51.1% (calc. 50.8) Mo and 3.2% (calc. 3.3) As (based on ion chromatographic analysis), were prepared from known methods.

*Synthesis of Potassium, Rubidium, and Caesium Dodecamolybdoantimonates.*—Small portions of $[NH_4]_3[Mo_{12}SbO_{40}]$ were equilibrated in 0.1 mol $dm^{-3}$ solutions of potassium, rubidium, or a caesium chloride for 4—5 d to ensure complete conversion. These specimens were then washed with distilled water and dried at 50 °C. Chemical and thermal analysis corresponded to $K_3[Mo_{12}SbO_{40}]\cdot9H_2O$, $Rb_3[Mo_{12}SbO_{40}]\cdot7H_2O$, and $Cs_{2.75}[NH_4]_{0.25}[Mo_{12}SbO_{40}]\cdot7H_2O$.

*Elemental Analysis.*—Each of the molybdoantimonates (100 mg) was dissolved in $HF-HNO_3$ (1:1 v/v). After evaporating to half the initial volume the solutions were diluted to 500 $cm^{-3}$ with deionized water and were subsequently analysed for metal ions. A second procedure was also used in which 100 mg of the sample were dissolved in 5.0 mol $dm^{-3}$ NaOH (10 $cm^3$). This solution was then acidified by adding 6.0 mol $dm^{-3}$ hydrochloric acid (6 $cm^3$). The sample was then diluted to 100 $cm^3$ and used for subsequent analyses.

*Apparatus.*—A Phillips PW 1700 automated diffractometer was used for *X*-ray analysis. The diffraction pattern was generated on a vertical goniometer attached to the *X*-ray tube

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† *Supplementary data available* (No. SUP 56770, 6 pp.): *X*-ray powder data, t.g.a., and x.p.s. data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

*Non-S.I. units employed:* eV ≈ 1.60 × $10^{-19}$ J, Torr ≈ 133 Pa.

**Table 1.** Chemical analysis of $[NH_4]_3[Mo_{12}SbO_{40}]\cdot 11H_2O$, prepared from different batches (calc. $NH_4$, 2.6; Mo, 53.2; Sb, 5.60; and $H_2O$, 9.15%)

| | % Mo | | | % Sb | |
|---|---|---|---|---|---|
| Batch | i.c. | i.c.p.s.–a.a.s. | x.r.f. | i.c.p.s.–a.a.s. | x.r.f. |
| 1 | 51.3 | 50.5 | 54.6 | 7.20 | 4.23 |
| 2 | 52.4 | 52.6 | 54.5 | 7.16 | 4.32 |
| 3 | 52.0 | 53.7 | 54.4 | 6.80 | 4.45 |
| 4 | 52.5 | 52.8 | 54.9 | 7.30 | 3.91 |
| 5 | | 51.4 | | 6.40 | |
| Mean | 52.1 | 52.2 | 54.6 | 6.97 | 4.23 |
| Standard deviation | 0.54 | 1.25 | 0.22 | 0.37 | 0.23 |
| Coefficient of variation | 1.0 | 2.4 | 0.4 | 5.3 | 5.4 |

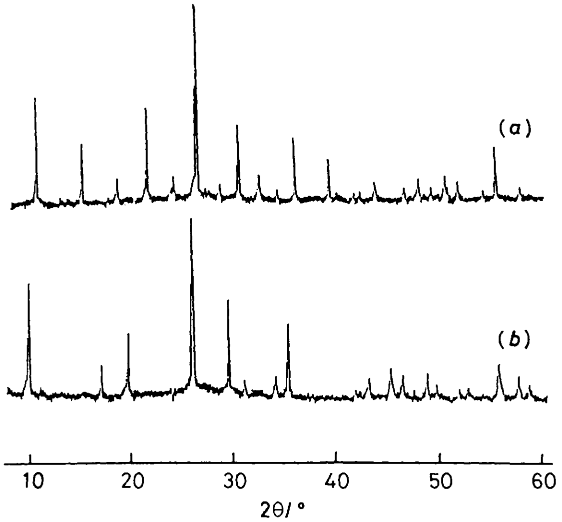

**Figure 1.** $X$-Ray diffraction spectra of ammonium dodecamolybdophosphate (*a*) and ammonium dodecamolyboantimonate (*b*)

with a copper target at 45 kV and 30 mA. The goniometer was controlled by a Digital PDP 11/24 computer and the intensities measured were stored on a RLO2 hard disk. After background removal and $K_{\alpha 2}$ stripping, *d* (interplanar spacing) values were corrected for the instrumental error function which was measured by analysing a standard silicon sample. The *d* values thus evaluated were used to calculate the lattice parameters. Quantitative analyses were performed by matching the x.r.d. pattern of the sample with the patterns of reference compounds.

$X$-Ray fluorescence (x.r.f.) analysis of the samples was carried out on a Phillips PV 9500 energy-dispersive fluorescence spectrometer. The Si(Li) detector had a resolution of 164 eV at 5.9 kV and active area of 10 mm$^2$. The samples were analysed in powder form with a rhodium target excited at 30 kV and 500 mA. The spectra were collected for a total of 200 s without collimator and filter, with the specimen chamber flushed with helium gas during the data collection. Quantitative analysis of the ammonium salt by x.r.f. was performed by using the Claisse–Quintin concentration model. Three standards containing 12 g $MoO_3$ and 1.0, 0.7, and 0.5 g of $Sb_2O_3$ were prepared by homogeneous mixing of the oxides. After establishing the background of the spectra, net intensities of Mo and Sb were determined. Theoretical intensities of Mo and Sb were then calculated using the net intensities of the spectra of the standards and their known weight percentages. The alpha factors, which take into account inter-element effects, were also evaluated. Using these, net intensities of the spectra of the samples were compared with the net intensities of standards, and concentrations of Sb and Mo thus determined by iteration.

The $X$-ray photoelectron spectra of ammonium dodecamolybdoantimonate, antimony trioxide, and antimony pentoxide were obtained on a Perkin-Elmer ESCA 5300 spectrometer equipped with a Mg-$K_\alpha$ $X$-ray source (1 253.6 eV). The $X$-ray power supply was operated at 15 kV and 20 mA. The specimen chamber was evacuated to a pressure of less than $5 \times 10^{-9}$ Torr. The instrumental energy scale was set up by the use of the Au $4f_{\frac{7}{2}}$ signal (83.95 eV). The powdered samples were pressed on indium foil and a carbon contamination peak C 1*s* (284.6 eV) was used as the reference peak for binding energy calibration.

I.r. spectra of the samples as KBr pellets were recorded on a JASCO DS-701G diffraction grating and 60 SX FT-IR spectrophotometers. Thermal analysis was performed on a Rigaku Denki Thermoflex 8002 at a heating rate of 10° min$^{-1}$. Liberated ammonia was identified by passing it into Nessler's reagent solution and its amount was calculated from the weight loss in the corresponding thermogram.

Rubidium and caesium were analysed by emission spectrophotometry in an air–acetylene flame on a Varian Techtron model 1100 atomic absorption spectrophotometer. Potassium, molybdenum, and antimony were determined by atomic absorption spectrophotometry (a.a.s.). A Bausch and Lomb model ARL 3580 inductively coupled plasma spectrometer for the analysis of Mo and Sb and a Dionex 2120i ion chromatograph for the analysis of Mo were also used.

## Results and Discussion

*Chemical Analysis.*—Table 1 shows the results of chemical analysis of $[NH_4]_3[Mo_{12}SbO_{40}]$ prepared from different batches. The small variations in the concentrations of both Mo and Sb obtained by different techniques indicated the good reproducibility of the method of preparation. The results of x.r.f. analysis were not considered quantitative (especially for Sb) and will be discussed later.

From Table 1 the average concentration of Sb, as determined by inductively coupled plasma spectrometry (i.c.p.s.)–a.a.s., is about 25% higher than the calculated value and so results in a lower (9.5) Mo:Sb ratio than expected (12.0) for a dodecaheteropolyacid salt. However, we believe that this increase in the antimony concentration is caused by a small impurity of $Sb_2O_5$ which might have co-precipitated during the preparation of the molybdoantimonate. Such an increase could be caused by just 2% impurity of $Sb_2O_5$. Indeed, this explanation seems likely since, after correction for 2% of $Sb_2O_5$ impurity, the calculated value for Mo, at 52.1% (53.2 × 0.98) compares excellently with values of 52.1 and 52.2% determined by ion chromatography (i.c) and i.c.p.s., respectively.

*X.R.D. and X.R.F. Analyses.*—The ammonium salt prepared from different batches showed very similar diffraction patterns. A typical heteropolyacid salt[2] pattern was obtained with a peak of maximum intensity at $2\theta = 25.83°$ (Figure 1, which also shows the diffraction spectrum of ammonium dodecamolybdophosphate). All the observed lines were sharp and intense and have been indexed for a body centred cubic lattice with a lattice parameter $a_0 = 12.908 \pm 0.01$ Å, a value higher than that reported for ammonium dodecamolybdophosphate.[20] In the light of the larger ionic radius of $Sb^{5+}$ (0.62 Å) than that of $P^{5+}$ (0.35 Å), the higher $a_0$ value in this case is expected.[6,21]

Among heteropolyacid salts, there is a close packing of oxygen atoms in the Keggin anion, yet the anion–anion packing is large enough to accommodate large cations such as $NH_4^+$,

**Table 2.** Chemical analysis * data

| Compound | Analysis (%) | |
|---|---|---|
| $K_3[Mo_{12}SbO_{40}]\cdot 9H_2O$ | K | 5.7 (5.35) |
| | Mo | 54.7 (52.5) |
| | Sb | 6.3 (5.55) |
| | $H_2O$ | 7.4 (7.4) |
| $Rb_3[Mo_{12}SbO_{40}]\cdot 7H_2O$ | Rb | 11.7 (11.2) |
| | Mo | 53.5 (50.2) |
| | Sb | 6.3 (5.3) |
| | $H_2O$ | 5.5 (5.5) |
| $Cs_{2.75}[NH_4]_{0.25}[Mo_{12}SbO_{40}]\cdot 7H_2O$ | Cs | 15.1 (15.15) |
| | Mo | 49.4 (48.0) |
| | Sb | 5.8 (5.1) |
| | $H_2O$ | 5.25 (5.25) |

* Required values are given in parentheses.

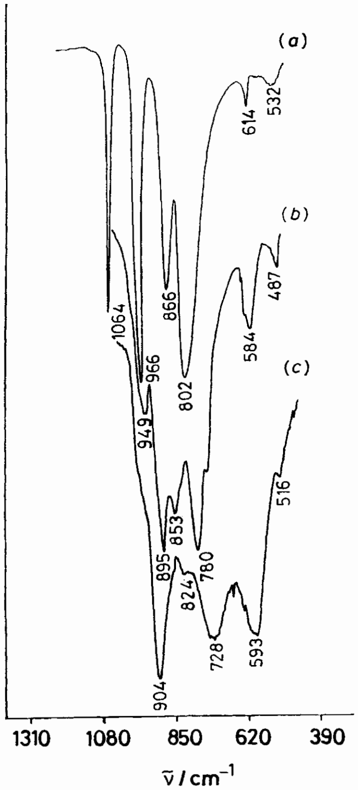

**Figure 2.** I.r. spectra of dodecamolybdophosphate (*a*), dodecamolybdoarsenate (*b*), and dodecamolybdoantimonate (*c*) anions

$K^+$, $Rb^+$, $Cs^+$, $Tl^+$, *etc.* These cations may also move in and out of the lattice and be reversibly exchanged for other cations throughout the entire crystal lattice.[22] Therefore, preparations of potassium, rubidium, and caesium salts were attempted by ion exchange of ammonium ions from $[NH_4]_3[Mo_{12}SbO_{40}]$. Chemical analysis of these compounds (Table 2) shows almost 100% exchange of $NH_4^+$ ions by $K^+$ and $Rb^+$ and about 90% by $Cs^+$.

All these three salts have been found to be isostructural with the ammonium salt (body-centred cubic) with lattice constants, $a_0 = 12.904 \pm 0.01$, $12.931 \pm 0.008$, and $13.000 \pm 0.046$ Å, respectively for $K^+$, $Rb^+$, and $Cs^+$. These results show that the $a_0$ values increase (although only to an extent of < 1%) with increase in ionic diameter of the exchanging cations. This thus confirms some flexibility of the anion–anion packing in these salts to accommodate cations of variable size. However, it has been reported[6] for ammonium dodecamolybdophosphate that above a cation diameter of 4 Å the heteropolyacid salt loses its characteristic cubic structure.

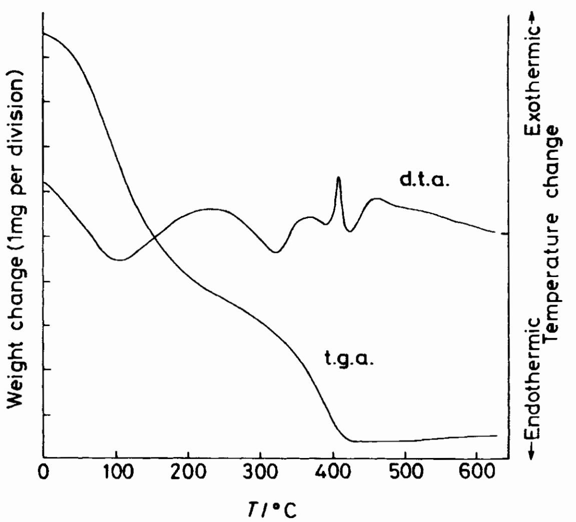

**Figure 3.** Thermal behaviour of the ammonium salt in air. Sample weight 0.066 g

Results of x.r.f. analysis of Mo and Sb in the ammonium salt, synthesized from different batches, are reported in Table 1 alongside the chemical analysis. This shows that x.r.f. results for Mo are about 4.6% higher than those obtained by i.c. and i.c.p.s. methods. Considering the difference between the matrices of standards (mixtures of $MoO_3 + Sb_2O_3$) and the sample (ammonium salt), these results may be accepted within experimental error. However, antimony concentrations obtained from x.r.f. measurements are about 40% lower than those obtained by i.c.p.s. Therefore, the x.r.f. method was not found to be suitable for the absolute quantification of Mo and Sb in the ammonium salt. Nevertheless, due to its speed and ease of operation, it was found helpful in looking for variations in the concentrations of Mo and Sb during the synthesis of the ammonium salt.

*Infrared Analysis.*—Characteristic i.r. peaks of anionic tetrahedra of dodecaheteropolyacids can be seen in the region 1 100—500 $cm^{-1}$ due to four different types of oxygen bonding. For example, in the case of the ammonium salt the four different oxygen types can be classified as: four $O_i$ (internal oxygen) connecting Sb and Mo, 12 $O_e$ (edge sharing) connecting Mo, 12 $O_c$ (corner sharing) connecting $Mo_3O_{13}$ units, and 12 $O_t$ (terminal) bonding to one Mo atom only. According to Rocchiccioli-Deltcheff *et al.*[23] the bands which have been observed for ammonium salt (Figure 2) in the above mentioned region can be assigned as follows: 944(sh) ($Mo–O_t$), 824 ($Mo–O_c–Mo$), 728 ($Mo–O_e–Mo$), 904 (Sb–O),[24] and 593 $cm^{-1}$ ($Mo–O_i–Sb$). A comparison of this i.r. spectrum with those of dodecamolybdophosphate and dodecamolybdoarsenate (Figure 2) shows that the intensity of the M=O peak has decreased from dodecamolybdophosphate to dodecamolybdoantimonate and all the characteristic peaks have also shifted to lower wavenumbers in that order. The potassium, rubidium and caesium salts also show similar i.r. spectra for the Keggin anion. Peaks due to OH bending (1 590—1 605 $cm^{-1}$) and stretching (3 600—2 000 $cm^{-1}$) occur for all the compounds; NH bending (1 395 $cm^{-1}$) and stretching (3 100 $cm^{-1}$) observed in the i.r. spectra of the ammonium and caesium salts confirmed the presence of $NH_4^+$ ions in these compounds.

**Table 3.** Chemical analysis* of $12MoO_3 \cdot 0.5Sb_2O_3$, the product obtained after the decomposition of the ammonium salt during t.g.a. and d.t.a. experiments up to 660 °C

| | Analysis (%) | | |
|---|---|---|---|
| | I | II | |
| Mo | 63.8 | 64.5 | (63.0) |
| Sb | 7.4 | 7.8 | (6.4) |

* Required values are given in parentheses.

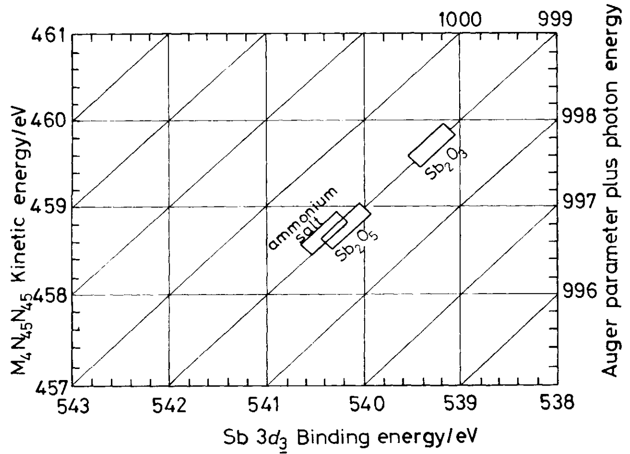

**Figure 4.** Chemical-state plot of the binding energy of the $3d_{\frac{3}{2}}$ line against the kinetic energy of the $M_4N_{45}N_{45}$ Auger line for the ammonium salt, $Sb_2O_3$, and $Sb_2O_5$

*Thermal Analysis.*—The t.g.a. of the ammonium salt (Figure 3) shows that water of hydration was eliminated up to about 240 °C with a 9% loss in weight for the sample. Loss of water was found consistent with an endothermic peak (maximum at 105 °C) in d.t.a. Release of ammonia occurred over the temperature range 240—360 °C, and was confirmed by a colour test (after passing the released ammonia into Nessler's reagent). This process corresponded to a 2.6% loss in weight. A second endothermic peak in d.t.a. (maximum at 320 °C) confirmed the elimination of ammonia. After this the ammonium salt was decomposed into the oxides of Mo and Sb with the removal of 1.5 mol of bound water with a weight loss of 1.3%. However, a further loss in weight (about 1.2%) was also observed which may be attributable to the loss of some oxygen atoms. A small endothermic peak (maximum at 400 °C) combined with a sharp exothermic peak in d.t.a. confirmed the elimination of bound water and the change in the crystallinity of the ammonium salt. The total loss in weight up to 660 °C was found to be 13.9%, which compared well with a 14.5% weight loss in a static experiment. Table 3 shows the chemical analysis of the decomposed ammonium salt after thermal analysis experiments up to 660 °C. The concentrations of Mo and Sb are consistent with the expected mixture of $12MoO_3 \cdot 0.5Sb_2O_5$.

X.r.d. spectra of the ammonium salt heated above 400 °C matched that of $MoO_3$ and no diffraction lines for any possible antimony oxides[25] were observed. The absence of an antimony oxide phase can be attributed (*i*) to its amorphous nature, since amorphous $Sb_2O_5$ remains poorly crystalline[24] below 700 °C, (*ii*) to the formation of a solid solution with $MoO_3$, (*iii*) to its presence as Senarmontite (formation of $Sb_2O_3$ is possible due to the loss of oxygen from $Sb_2O_5$) the highest-intensity peak of which, at 3.22 Å, overlaps with the highest-intensity peak of $MoO_3$, or (*iv*) to its presence at only low level which cannot be determined by x.r.d. All these possibilities may arise, however, in the light of the absence of the highest-intensity peak of crystalline antimonic acid ($Sb_2O_5 \cdot 4H_2O$) at $2\theta = 14.8°$ in a mixture with $MoO_3$ in 1:9 ratio (same as the ratio of Sb:Mo in the heated ammonium salt), (*iv*) would seem to be the most likely explanation. Significantly also the total *X*-ray cross-section of Sb is much lower than for Mo and therefore detection by x.r.d. of small quantities of antimony oxides in the large amount of molybdenum oxide would be difficult.

The thermograms (SUP 56770) of the salts of $K^+$, $Rb^+$, and $Cs^+$ revealed that water of hydration in all the compounds was eliminated up to 250 °C. Removal of this water and a small amount of ammonia (in the $Cs^+$ salt) has been confirmed by the corresponding peaks in their respective d.t.a.s. At 400 °C all three compounds are partially converted into $MoO_3$ (confirmed by x.r.d.) as indicated by exothermic peaks in their d.t.a. curves due to the consequent change in crystallinity. Sharp endothermic peaks in the d.t.a. curves at about 550, 525, and 500 °C for the $K^+$, $Rb^+$, and $Cs^+$ salts were observed due to melting.

*X.P.S. Analysis.*—Though antimony(III) in the starting material used for the preparation of the ammonium salt was oxidized to $Sb^V$ by dissolving $Sb_2O_3$ in hot *aqua regia* and further the analysis of ammonium and other cations in these compounds confirmed the presence of $Sb^V$, in view of the existence of antimony(III) heteropolyacid salts[19] a further confirmation of the valency of Sb in the ammonium salt by *X*-ray photoelectron spectroscopy (x.p.s.) was thought desirable.

X.p.s. binding energies of the $3d$ and $3p$ lines and the kinetic energy of the $M_4N_{45}N_{45}$ Auger line were determined for $Sb_2O_3$, $Sb_2O_5$ (synthesized according to Agrawal and Abe[26]), and $[NH_4]_3[Mo_{12}SbO_{40}]$. The chemical-state plot introduced by Wagner *et al.*[27] provides a useful format for displaying x.p.s. data. In this format the kinetic energy of the most prominent *X*-ray excited Auger line is plotted against the binding energy of the photoelectron lines. Accordingly, two plots, one for the high-binding-energy $3p_{\frac{3}{2}}$ line and another for the low-binding-energy, $3d_{\frac{3}{2}}$ line *vs.* the kinetic energy of the $M_4N_{45}N_{45}$ Auger peak were constructed. Due to the overlapping of the Sb $3d_{\frac{5}{2}}$ with the O $1s$ peak its binding energy could not be determined accurately and therefore the Sb $3d_{\frac{5}{2}}$ line was not included for comparison. Figure 4 shows a representative plot for the $3d_{\frac{3}{2}}$ line. According to Wagner *et al.*[27] chemical states which have lines located more than 1 eV away from the data points of the unknown can generally be excluded from consideration. In both chemical-state plots, the ammonium salt was located more than 1 eV away from $Sb_2O_3$ and therefore $Sb_2O_3$ (trivalent Sb) was excluded from consideration. Due to the unavailability of similar data on other compounds, the sensitivity of Sb $3d$ and Sb $3p$ to environmental effects could not be determined; however, since the ammonium salt lies closer to $Sb_2O_5$, this suggests an oxidation state $Sb^V$ in the ammonium salt, which is in accord with the chemical analysis.

Confirmation of $Mo^{VI}$ in the ammonium salt was derived from the sharpness of the signals of Mo $3d_{\frac{5}{2}}$ and $3d_{\frac{3}{2}}$ levels in the *X*-ray photoelectron spectrum as well as by its similarity to the spectrum of unreduced $K_3[Mo_{12}PO_{40}]$.[28] Reduced molybdenum in heteropolyacid salts and oxides generally show broad peaks.[29,30] An effort to use x.p.s. for the determination of elemental concentrations at the surface of the ammonium salt was also made. Table 4 shows the percentage atomic concentrations of different elements in a sample from batch 1 (Table 1; the impurity In might be due to contamination from the indium foil). The atomic ratio of Mo:Sb of 8.5:1 was consistent with the chemical analysis for this sample (Table 1 Mo:Sb = 8.95).

In conclusion, dodecaheteropolyacid salts of antimony(V) with body centred cubic symmetry (Keggin type A) have been prepared and characterized. The results of chemical analysis,

**Table 4.** Atomic percentages of different elements in the ammonium salt prepared in batch 1 (Table 1) as determined by x.p.s.

| Element | Concentration, % | Sens. Factor |
|---|---|---|
| C (1*s*) | 37.23 | 0.250 |
| In (3*d*5$_{\frac{5}{2}}$) | 1.25 | 3.900 |
| O (1*s*) | 49.59 | 0.660 |
| Mo (3*d*) | 10.66 | 2.750 |
| Sb (3*d*$_{\frac{3}{2}}$) | 1.27 | 3.300 |

x.r.d., x.r.f., thermal analysis, i.r., and x.p.s. have indicated that the compounds are dodecaheteropolyacid salts isostructural to ammonium dodecamolybdophosphate (with a small impurity of $Sb_2O_5$ present). These species are of possible catalytic applicability.

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