Inorg. Chem. **2004**, *43*, 4636–4644

Inorganic Chemistry
Article

Preparation and Characterization of 6-Molybdocobaltate and 6-Molybdoaluminate Cobalt Salts. Evidence of a New Heteropolymolybdate Structure

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Received December 15, 2003

Molybdenum and cobalt based heteropolyanions (HPAs) could be used as an alternative to the conventional ammonium heptamolybdate and cobalt nitrate starting materials for friendly environmental preparation of Co–Mo/Al_2O_3 hydrotreating catalysts. In this aim, cobalt salts of molybdocobaltate and molydboaluminate Anderson HPAs have been synthesized and characterized by TGA, XRD, XAS, and vibrational spectroscopies. The crystal structure refinement provided evidence for the formation of a new heteropolyoxomolybdate derived from the well-known Anderson structure.

Introduction

Heteropolyanions are early transition metal oxygen anion clusters that exhibit very interesting properties for catalysis depending on their composition, molecular size, and structure. Molybdenum Keggin type HPAs are particularly used in numerous oxidation or isomerization reactions.[1,2] In the field of hydrodesulfurization (HDS), the HPA applications are less conventional, but it has been shown that preparations based on the use of heteropolyoxomolybdates as starting materials could be an interesting alternative route allowing an improvement of the catalytic performances. In this case, the HPAs replace the usual ammonium heptamolybdate (AHM) and cobalt nitrate precursors. Indeed, the use of phosphomolybdates with Keggin structure[3−5] has been previously proposed, and more recently, Cabello et al. proposed the use of the 6-molybdocobaltate ammonium salt $(NH_4)_3$-$CoMo_6O_{24}H_6$, an heteropolyanion with the Anderson structure.[6] We also developed the preparation of cobalt salts of Keggin phosphomolybdate for the preparation of CoMo based catalysts with a higher Co/Mo ratio. Three different types of HPA were considered, i.e., $Co_{3/2}PMo_{12}O_{40}$, Co_3-$PCoMo_{11}O_{40}H$, and the reduced $Co_{7/2}PMo_{12}O_{40}$.[7,8] Moreover, it is now admitted that well dispersed 6-molybdoaluminate Anderson entities are formed during the classical catalyst preparation with the AHM starting material. It therefore appears interesting to prepare molybdocobaltate and also molybdoaluminate cobalt salts for their direct deposition on an alumina support.

Literature data indicate that the structure, proposed by Anderson[9] for the "XMo_6O_{24}" HPA series (X being the heteroatom), has been verified by Evans for $TeMo_6O_{24}^{6-}$[10] and demonstrated for $NiW_6O_{24}H_6^{4-}$ and for $CrMo_6O_{24}H_6^{3-}$.[11] However, the $(NH_4)_3[AlMo_6O_{24}H_6]$ salt has only been studied by XAS experiments,[12] with structural parameters provided by ADF (Amsterdam Density Functional program) calcula-

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10.1021/ic0354365 CCC: $27.50

tions,[13] and the $(NH_4)_3[CoMo_6O_{24}H_6]$ one has not been extensively characterized. However, interest in Anderson structure based materials is maturing, and the first example of an inorganic−organic hybrid in which the Anderson 6-molybdoaluminate is linked to a transition metal complex with an organic ligand has been recently described.[14] In this work, we therefore tackle the preparation and characterizations of ammonium and cobalt salts of Anderson molybdocobaltate and molybdoaluminate, with the cobalt salts allowing us to increase the Co/Mo atomic ratio. Thus, after the description of their preparation, we will discuss the structural investigations of the bulk salts by XRD and XAS analysis with the help of vibrational spectroscopic and TGA analysis.

Experimental Section

I. Characterizations Techniques. Thermogravimetric Analysis (TGA). The TGA/DSC experiments were carried out on a 2960 SDT thermoanalyzer from TA Instruments. The measurements were carried out in a He flow of 100 mL/min, with a heating rate of 3 °C/min. The temperature was raised to 550 °C.

XRD. The preparation method enables us to obtain well shaped single crystals with suitable size for XRD crystal analysis experiments. For X = Al and X = Co, a single crystal of $[(X^{3+}Mo_6O_{24}H_6)^{3-},(Co^{2+},5H_2O),(H_2O)_6,(Y^+)_1]$, Y being either H_3O^+, NH_4^+, or $(H_3O^+)_z(NH_4^+)_{1-z}$, with $0 \leq z \leq 1$, was mounted on a Bruker Smart three circle diffractometer equipped with a CCD bidimensional detector set at 45 mm from the crystal. One full reciprocal sphere was collected at room temperature [3 × 600 frames at $\varphi = 0-120-240$, 0.3° (scan/frame, 20 s acquisition time)]. Data collection, crystal characteristics, and refinement results are presented in Table 1. Intensities have been integrated from the collected frames and corrected for background Lorentz and polarization effects using SAINT[15] and for absorption using faces indexation and the XPREP software.[16] Data were then recorrected from the detector area absorption with a null *r* value using the program SADABS.[17] Lattice parameters have been refined from the complete data set. For both compounds, the refinements satisfactorily converged in the *Pcab* orthorhombic space group in agreement with the observed systematic extinctions. The metal positions were determined using SIR-97,[18] and the crystal structure was then refined using SHELXTL.[19] The coordination oxygen atoms and interstitial groups were located on the subsequent Fourier difference synthesis calculations. In the last cycles of the refinements, anisotropic thermal parameters were considered for the metal atoms only and an optimized weighting scheme was introduced, yielding R1 = 3.88%, wR2 = 9.25% and R1 = 4.44%, wR2 = 9.67% for X = Co and Al, respectively.

Table 1. Crystal Data, Data Collection, and Structure Refinement Parameters for $[XMo_6O_{24}H_6]^{3-}$ $(Co^{2+}, 5H_2O)$ $(H_2O)_6$ $(H_3O^+)_1$, X = Co^{3+} and Al^{3+}

crystal data	X = Co	X = Al
cryst symmetry	orthorhombic	orthorhombic
space group	*Pcab* (No. 61)	*Pcab* (No. 61)
unit cell (Å)		
a	11.139(2)	11.140(5)
b	22.960(4)	23.002(5)
c	24.486(5)	24.423(5)
V (Å^3)	6262.1	6258.2
Z	8	8
d_{calcd} (g/cm^3)	2.74	2.68
radiation Mo Kα (Å)	0.71073	0.71073
recorded angular range θ (deg)	3.55−29.52	3.57−29.37
no. indep reflns [$I > \sigma(I)$]	4045	2751
no. indep reflns [$I > 2\sigma(I)$]	4045	2751
R merging factor (%)	4.74	6.54
no. refined params	217	217
R1	3.88[a]	4.44[a]
wR2	9.25[b]	9.67[b]
w[c]	$A = 0.05$, $B = 26.91$	$A = 0.05$, $B = 19.91$
isotropic secondary extinction	none	none
max/min $\Delta\rho$ e/Å^3	1.78/−0.79	1.38/−0.84
GOF	1.108	1.121

[a] $R1(F)\ [I > 2\sigma(I)] = \sum||F_o| - |F_c||/\sum|F_o|$ (%). [b] $wR2(F^2)\ [I > 2\sigma(I)] = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)]^{1/2}$ (%). [c] $w = 1/[\sigma^2(F_o^2) + (A \times P)^2 + (B \times P)]$ with $P = [\max(F_o^2, 0) + 2F_c^2)]/3$.

Powder X-ray diffraction patterns were also recorded using a Siemens D5000 diffractometer with the Cu Kα radiation. Apart from the Kα_2 contribution eliminated by computer postprocessing, the patterns obtained were not subjected to further treatments.

X-ray Absorption Spectroscopy. Mo and Co K-edge EXAFS (extended X-ray absorption fine structure) measurements were carried out in the Laboratoire pour l'Utilisation du Rayonnement Electromagnétique (Orsay) at the EXAFS D42 and D44 beamlines, using synchrotron radiation from the DCI storage ring, running at 1.85 GeV with an average current of 250 mA. At the Mo K-edge, the EXAFS data were taken in the transmission mode through a double crystal monochromator Ge (400) using two ion chambers as detectors. The analysis time for an X-ray absorption spectrum (19 900−20 900 eV) was about 15 min, and three spectra were recorded for each sample. The XANES data were recorded with the same monochromator, using three ion chambers as detectors, a molybdenum foil being placed after the sample to calibrate the energy position. The analysis time for a XANES spectrum (19 900−20 200 eV) was about 10 min, and two spectra were recorded for each sample. At the Co K-edge, the EXAFS data were taken in the transmission mode through a channel-cut monochromator Si (111) using two ion chambers as detectors. The analysis time for an X-ray absorption spectrum (7600−8600 eV) was about 30 min, and five spectra were recorded for each sample. The XANES data were taken in the transmission mode through a double crystal monochromator Si (311) using three ion chambers as detectors, a cobalt foil being placed after the sample to calibrate the energy position. The analysis time for a XANES spectrum (7680−7830 eV) was about 15 min, and two spectra were recorded for each sample.

The Mo and Co K-edge EXAFS regions of the spectra were extracted and analyzed using A. Michalowicz's software packages EXAFS 98 ppc and Round Midnight.[20] The EXAFS spectrum was first transformed from *k*-space (k^3, Kaiser window 3.7−13.3 Å^{-1} for the Mo K-edge and 2.2−14.9 Å^{-1} for the Co K-edge) to *R*-space to obtain the radial distribution function (RDF). The EXAFS

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Table 2. Description and Nomenclature of the HPC Compounds

salt formula	nomenclature	Co/Mo theoretical	Co/Mo (chemical analysis)	N/Mo (chemical analysis)	solubility of Mo mol·L^{-1}
$(NH_4)_3AlMo_6O_{24}H_6$	$AlMo_6Am$			0.50	0.12
$Co_{3/2}AlMo_6O_{24}H_6$	$AlMo_6Co$	0.25	0.19	0.08	0.18
$(NH_4)_3CoMo_6O_{24}H_6$	$CoMo_6Am$	0.17	0.16	0.47	0.17
$Co_{3/2}CoMo_6O_{24}H_6$	$CoMo_6Co$	0.42	0.31	0.10	1.08

spectrum for one or several coordination shells was isolated by inverse Fourier transform of the RDF over the appropriate region and fitted using the single scattering EXAFS equation with amplitude and phase functions calculated by FEFF[21−24] using the interatomic distances deduced from the XRD single-crystal refinement.

Vibrational Spectroscopies. IR. The spectra were recorded using a Nicollet 510 Fourier transform IR spectrometer. The samples were analyzed in the 200−4000 cm^{-1} spectral range using the KBr pellets technique with 1 wt % of the sample in KBr.

Raman. The Raman spectra of the samples, maintained at room temperature, were recorded using a Raman microprobe (Infinity from Jobin-Yvon), equipped with a photodiode array detector. The exciting light source was the 532 nm line of a Nd:YAG laser, and the wavenumber accuracy was 2 cm^{-1}.

II. Preparation. The Anderson ammonium salts $(NH_4)_3[CoMo_6O_{24}H_6]$ (hereafter named $CoMo_6Am$) and $(NH_4)_3[AlMo_6O_{24}H_6]$ (hereafter named $AlMo_6Am$) were obtained according to literature data by precipitation from aqueous solution of ammonium heptamolybdate (AHM), cobalt nitrate, and hydrogen peroxide for the former species[25,26] and of ammonium heptamolybdate (AHM) and aluminum nitrate for the latter species. The recrystallization allows us to purify them and to obtain single crystals of $CoMo_6Am$ for the X-ray structure resolution.

The cobalt salts of the molybdocobaltate and of the molybdoaluminate were obtained by cationic exchanges in aqueous solution according to the following equation:

$$3(NH_4)^+,XMo_6O_{24}H_6{}^{3-} + [3/2Co^{2+},PMo_{12}O_{40}{}^{3-}] \rightarrow 3/2Co^{2+},XMo_6O_{24}H_6{}^{3-} + (NH_4)_3PMo_{12}O_{40}\downarrow$$

The reactants are introduced in stoichiometric quantities and stirred vigorously at 50 °C for 2 h. The solution of the cobalt salt is then filtered to eliminate the $(NH_4)_3PMo_{12}O_{40}$ yellow precipitate. Then, the remaining solution is put at 20 °C in order to obtain $Co_{3/2}CoMo_6O_{24}H_6$ or $Co_{3/2}AlMo_6O_{24}H_6$ single crystals.

The preparation of the cobalt phosphomolybdate salt ($Co_{3/2}PMo_{12}O_{40}$) used for the exchange is described by Griboval et al.[3] It is prepared from the pure heteropolyacid $H_3PMo_{12}O_{40}$ by adding cobalt sulfate to a solution of the purified $H_3PMo_{12}O_{40}$ acid, after neutralization with barium hydroxide. After filtration to eliminate the $BaSO_4$ precipitate, the $Co_{3/2}PMo_{12}O_{40}$ salt is obtained in solution and leads to the bulk compound after evaporation.

In Table 2 are summarized the prepared salts with the nomenclature that will be used hereafter. This table gives the theoretical Co/Mo atomic ratio considering a total exchange and the Co/Mo and N/Mo ratios deduced from the chemical elementary analysis. In this table is also reported the solubility of these salts in water at room temperature.

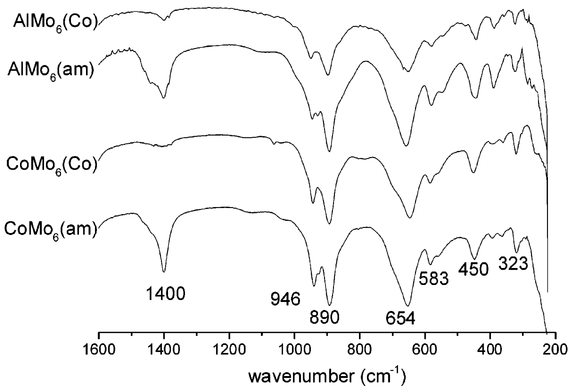

Figure 1. IR spectra of the salts of Anderson HPAs.

Chemical analysis results of the ammonium salts are in agreement with the theoretical expected values while, whatever the HPA, the Co/Mo atomic ratio of the cobalt salts is lower than the theoretical one. This suggests an incomplete exchange of the ammonium by the Co atoms as revealed by the IR study. Indeed, the IR spectra of the four heteropolycompounds (HPC) $AlMo_6Am$, $AlMo_6Co$, $CoMo_6Am$, and $CoMo_6Co$ reported in Figure 1 exhibit the band at 1400 cm^{-1} characteristic of the $NH_4{}^+$ ions. Its intensity is, however, largely reduced in the cobalt salts by comparison to the starting ammonium salts. This incomplete exchange is also confirmed by the N/Mo ratio deduced from the elemental analysis (Table 2). Indeed, for the cobalt salts, an unexpected N/Mo ratio around 0.08 is obtained. Taking into account the Co/Mo ratio, we may consider that only two ammonium groups have been replaced by cobalt(II) ions. Chemical analysis suggests that, around the HPA unit $[(Al/Co)Mo_6O_{24}H_6]^{3-}$, there is an average environment of $1Co^{2+}$,$1/2NH_4{}^+$, which implies also $1/2H^+{}_{aq}$ in order to ensure the electroneutrality.

Results and Discussion

I. XRD Analysis. The crystal data collection and the structure refinement parameters of the molybdoaluminate and molybdocobaltate Anderson cobalt salts are reported in Table 1. The nominal formula of the HPA deduced from the crystal structure refinements is $[XMo_6CoO_{29}]$,O_7, where X is a Co or an Al atom. The hydrogen atom positions have not been refined, but these atoms are located near oxygen atoms from crystal-chemistry considerations. The pertinent distances related to the structure and bond valence sums calculations from the Brese and O'Keeffe data[27] are reported in Table 3. The new structure consists of new heteropolyoxomolybdates units derived from the well-known Anderson structure.[10] Figure 2a shows the $[Al/Co^{III}Mo^{VI}{}_6(OH)_6O_{18}Co^{II}(H_2O)_5]^-$

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Table 3. Selected Distances (Å) for $[XMo_6O_{24}H_6]^{3-}$ $(Co^{2+},5H_2O)(H_2O)_6(H_3O^+)_1$, X = Co and Al[a]

	X = Co	X = Al		X = Co	X = Al
Mo1−O1	1.697(7) 1.76	1.692(11) 1.79	Mo4−O17	1.696(7) 1.77	1.696(10) 1.77
Mo1−O2	1.709(6) 1.71	1.701(10) 1.75	Mo4−O18	1.700(7) 1.75	1.697(11) 1.76
Mo1−O3	1.927(5) 0.95	1.928(11) 0.94	Mo4−O4	1.933(5) 0.93	1.920(9) 0.97
Mo1−O4	1.946(5) 0.90	1.954(9) 0.88	Mo4−O19	1.948(5) 0.90	1.936(9) 0.92
Mo1−OH5	2.280(5) 0.36	2.29(1) 0.36	Mo4−OH20	2.284(5) 0.36	2.288(9) 0.36
Mo1−OH6	2.315(5) 0.33	2.334(9) 0.32	Mo4−O5	2.293(5) 0.35	2.29(1) 0.36
	$\sum S_{ij} = 6.02$	$\sum S_{ij} = 6.03$		$\sum S_{ij} = 6.06$	$\sum S_{ij} = 6.14$
Mo2−O7	1.692(6) 1.79	1.683(10) 1.83	Mo5−O21	1.707(6) 1.72	1.702(11) 1.74
Mo2−O8	1.708(7) 1.71	1.692(10) 1.79	Mo5−O22^{i}	1.713(6) 1.70	1.708(11) 1.71
Mo2−O9	1.944(5) 0.90	1.930(9) 0.94	Mo5−O19	1.912(5) 0.99	1.903(9) 1.01
Mo2−O10	1.948(5) 0.90	1.934(9) 0.93	Mo5−O15^{i}	1.914(5) 0.98	1.908(9) 1.00
Mo2−OH11	2.272(5) 0.37	2.267(10) 0.38	Mo5−OH20	2.280(5) 0.36	2.282(9) 0.36
Mo2−OH12	2.301(5) 0.34	2.318(9) 0.33	Mo5−OH16^{i}	2.289(5) 0.36	2.306(9) 0.34
	$\sum S_{ij} = 6.02$	$\sum S_{ij} = 6.20$		$\sum S_{ij} = 6.10$	$\sum S_{ij} = 6.16$
Mo3−O13	1.699(7) 1.75	1.685(10) 1.82	Mo6−O23	1.699(6) 1.75	1.682(10) 1.84
Mo2−O14	1.702(7) 1.74	1.701(11) 1.75	Mo6−O24	1.729(6) 1.62	1.712(10) 1.69
Mo2−O9	1.937(5) 0.92	1.938(9) 0.92	Mo6−O10^{i}	1.905(5) 1.01	1.899(9) 1.02
Mo2−O15	1.941(5) 0.91	1.941(9) 0.91	Mo6−O3	1.942(5) 0.91	1.926(10) 0.95
Mo2−OH11	2.259(5) 0.39	2.267(10) 0.38	Mo6−OH6	2.244(5) 0.40	2.249(9) 0.40
Mo2−OH16	2.294(5) 0.35	2.309(9) 0.34	Mo6−OH12^{i}	2.319(5) 0.33	2.335(10) 0.31
	$\sum S_{ij} = 6.07$	$\sum S_{ij} = 6.11$		$\sum S_{ij} = 6.02$	$\sum S_{ij} = 6.21$
Co1−O24	2.039(7) 0.39	2.063(11) 0.37	Co/Al2−OH6	1.904(5) 0.58	1.89(1) 0.52
Mo2−H2O1	2.055(6) 0.37	2.066(10) 0.36	Co/Al2−OH16^{i}	1.908(5) 0.57	1.895(9) 0.52
Mo2−H2O2^{ii}	2.090(8) 0.34	2.099(12) 0.33	Co/Al2−OH11^{i}	1.910(5) 0.57	1.900(9) 0.51
Mo2−H2O3^{iii}	2.104(7) 0.33	2.111(11) 0.32	Co/A12−O5	1.911(5) 0.57	1.901(10) 0.51
Mo2−H2O4^{iv}	2.128(7) 0.31	2.127(10) 0.31	Co/A12−OH20	1.916(5) 0.56	1.903(10) 0.51
Mo2−H2O5^{iv}	2.129(7) 0.31	2.142(10) 0.30	Co/A12−OH12^{i}	1.922(5) 0.55	1.91(1) 0.50
	$\sum S_{ij} = 2.05$	$\sum S_{ij} = 1.99$		$\sum S_{ij} = 3.39$	$\sum S_{ij} = 3.06$
Co/Al2−Mo4	3.308(1)	3.301(9)			
Co/Al2−Mo1	3.321(1)	3.316(9)			
Co/Al2−Mo6	3.291(1)	3.294(4)			
Co/Al2−Mo2	3.312(1)	3.312(9)			
Co/Al2−Mo3	3.300(1)	3.294(9)			
Co/Al2−Mo5	3.297(1)	3.295(4)			
Mo6Co1	3.768(1)	3.761(10)			

[a] (i) $1 + x, y, z$; (ii) $1 - x, 0.5 - y, 0.5 + z$; (iii) $2 - x, 0.5 - y, 0.5 + z$; (iv) $1.5 - x, y, 0.5 + z$; (v) $-1 + x, y, z$; (vi) $1 - x, 0.5 - y, -0.5 + z$; (vii) $2 - x, 0.5 - y, -0.5 + z$; (viii) $1.5 - x, y, -0.5 + z$; (ix) $2 - x, -y, -z$; (x) $-0.5 + x, -y, 0.5 - z$; (xi) $0.5 + x, 0.5 - y, z$; (xii) $-0.5 + x, 0.5 - y, z$; (xiii) $-1.5 + x, -y, 0.5 - z$.

unit fully labeled. The central unit has a hexagonal plane structure composed of a central Co/Al cation surrounded by six octahedral $Mo(1-6)O_4(OH)_2$ groups forming a crown. It is well-known that the coordination polyhedron of this central cation is formed by six hydroxyl OH^- anions.[9] Each MoO_6 shares an O−OH edge with each of its two neighboring MoO_6 moieties and another edge OH−OH with the central $Co/Al(OH)_6$. Inside each $Mo(OH)_2O_4$ octahedron, three kinds of Mo−O distances are observed. Two long Mo−OH distances ~2.3 Å with corners shared by two $Mo(OH)_2O_4$ moieties and the central $Co/Al(OH)_6$ octahedron, two medium Mo−O distances ~1.9 Å with corners shared by two $Mo(OH)_2O_4$ species, and two short Mo−O distances ~1.7 Å, with oxygen terminal atoms. One should deduce a significant shifting of the central Mo(1−6) cation from the center of its polyhedron toward external apices of the crown.

Bond valence sums calculations confirm the expected III oxidation state of the central Co/Al atom and the VI oxidation state of the Mo cations. An additional $Co(1)^{2+}$ cation (from bond valence calculations) shares its O(24) corner with $Mo(6)(OH)_2O_4$. Its five remaining corners are linked to water molecules in order to preserve the electroneutrality, i.e., $H_2O(1-5)$. The Co(1)−Mo(6) distance is close to 3.76 Å for both salts (X = Co^{III} and Al^{III}), and the $Co(1)^{II}-O$ distance ~2.1 Å is largely superior to the $Co^{III}/Al^{III}-O$ distances ~1.9 Å, as expected from the ionic radii for Co^{III} (0.54 Å) and Co^{II} (0.74 Å) in octahedral coordination.[28] Valence bond sums calculations performed on H_2O (1−5) considering the unique Co^{II} bonded cation lead to values in the 0.30−0.36 range showing a underbonded feature and assuring the presence of two protons of the water molecules. The same calculation performed for O(24) (with Co(1) and Mo(6) neighbors) leads to 2.05 in good agreement with its oxo nature.

Figure 2b shows the eight units cell generated by *Pcab* symmetry. Seven water molecules surround the HPA groups (labeled H_2O_{A-G}) with distances to the HPA cations higher than 3.6 Å. The water molecule assignment of counter entities is driven with respect to the electroneutrality. Therefore, with the HPA electric charge being negative, and bond sum calculations on oxygen of the HPA giving no evidence of a lacking H^+ on any of the anions (in agreement with the $6OH^-/18O^{2-}/5OH_2$ distribution), one should conclude that one of the interstitial H_2O molecules is in fact an H_3O^+ cation. H_2O and NH_4^+ are hardly distinguishable by XRD, and the presence of one NH_4^+ cation instead of one H_2O

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[28] Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

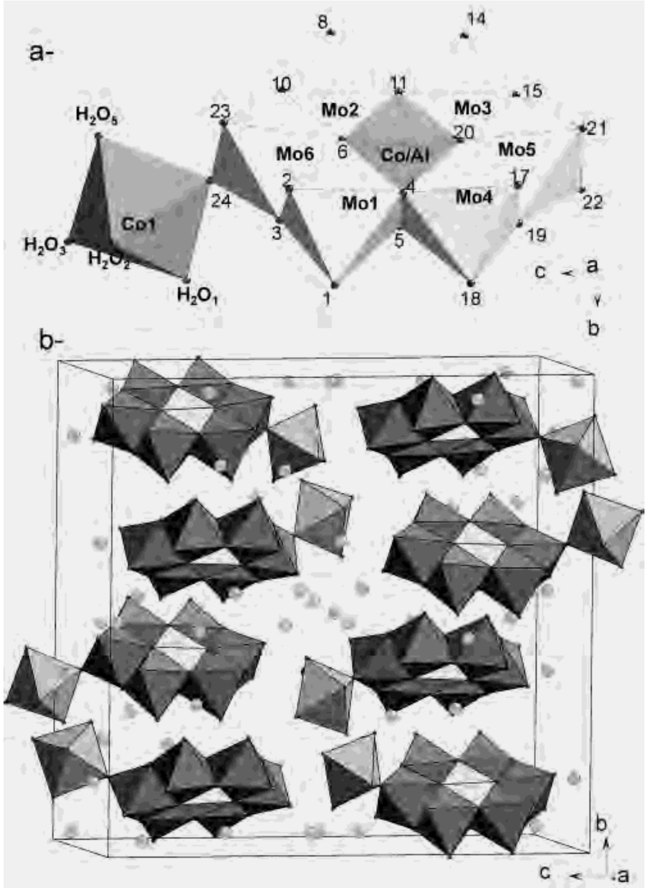

Figure 2. (a) $[XMo_6O_{24}H_6]^{3-}$ $(Co^{2+},5H_2O)$ heteropolyanion (X = Al or Co) label scheme. H_2O_{1-5} form the Co1 coordination octahedron. H_2O_{a-g} are the solvate water molecules represented with $Mo-OH_2$ broken lines bonds shorter than 4 Å. Labels 1−24 stand for O or OH according to the Table 2 nomenclature. (b) The eight equivalent HPA according to the *Pcab* symmetry, surrounded by the H_2O_{a-g} hydration molecules (gray circles).

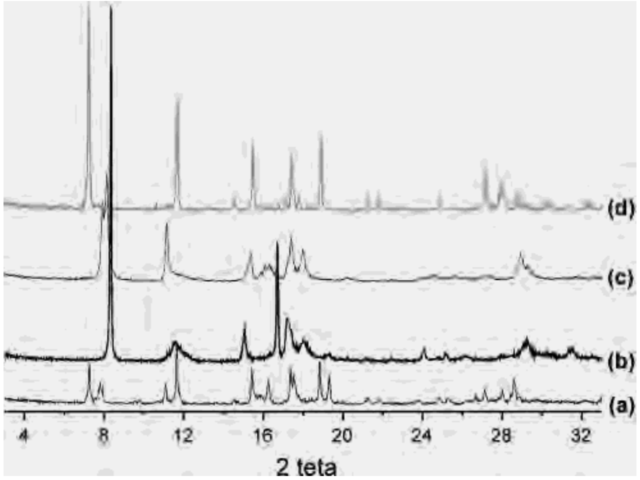

Figure 3. HPC's XRD patterns: (a) $AlMo_6Co$, (b) $AlMo_6Am$, (c) $CoMo_6Am$, and (d) $CoMo_6Co$.

cannot be excluded with regard to the uncompleted NH_4^+ removal evidenced by infrared spectroscopy and elemental analysis.

Powder diffraction patterns of the $AlMo_6$ and $CoMo_6$ salts have been recorded, and their diagrams are presented in Figure 3. The indexations deduced from the refinement of the cobalt salt XRD patterns by using the single crystal orthorhombic unit cell described above leads to the following lattice parameters for each compound: for $CoMo_6(Co)$, $a = 11.235(-)$ Å, $b = 23.007(-)$ Å, $c = 24.524(-)$ Å; for $AlMo_6(Co)$: $a = 11.125(-)$ Å, $b = 22.932(-)$ Å, $c = 24.322(-)$ Å.

The parameters are determined with good accuracy and confirm the homogeneity and the purity of the powdered samples in agreement with a microinfrared spectroscopic study which did not give evidence for the existence of a microdomain containing only the ammonium salt. Indeed, the spectra (not reported here) were quite similar however the microcrystal analyzed. Moreover, the $AlMo_6Am$ and $CoMo_6Am$ XRD patterns are in agreement with previous works published by Plazenet.[12] Nevertheless, the $CoMo_6Am$ XRD pattern is different from the one previously reported by Cheng et al.[29] corresponding to the JCPDS file 04-0226. However, these authors only deduced the formula from the chemical analysis and did not perform any XRD structure resolution. La Ginestra et al. also discussed the synthesis of an ammonium molybdocobaltate salt, but the XRD pattern of their compound is different from the present one. Moreover, these authors proposed a different formula from ours in which the central Co atom had a 2+ oxidation state, leading to a total charge of 4− for the HPA ($CoMo_6O_{24}H_6^{4-}$).[30,31] Our crystal structure refinement and the XRD powder study allows us to consider that we obtain homogeneous samples of cobalt salts of 6-molybdoaluminate and molybdocobaltate despite the incomplete removal of ammonium ions of the initial HPC.

II. Thermogravimetric Analysis. The TGA patterns of the 6-molybdocobaltate and 6-molybdoaluminate cobalt salts are shown in Figure 4. The two curves are similar and present four domains corresponding to (i) the departure of the hydration water (12% weight loss), (ii) the departure of the coordination water of Co^{2+} (penta aquo coordinated species determined by XRD), and (iii) the removal of the (NH_4^+) groups and the formation of NH_3 and N_2. The total weight loss is around 20%. This value is in agreement with the decomposition of $CoMo_6Co$ into MoO_3 and $CoMoO_4$ on one hand and $AlMo_6Co$ into MoO_3, $CoMoO_4$, and $Al_2(MoO_4)_3$ on the other hand, according to the following equations:

$$(NH_4^+,Co^{2+})(AlMo_6O_{24}H_6^{3-}),xH_2O \rightarrow (1/2)Al_2(MoO_4)_3 + CoMoO_4 + (7/2)MoO_3 + NH_3 + (x + 7/2)H_2O$$

$$(NH_4^+, Co^{2+})(CoMo_6O_{24}H_6^{3-}),xH_2O \rightarrow 2CoMoO_4 + 4MoO_3 + (2/3)NH_3 + (x + 4)\ H_2O + (1/6)N_2$$

The presence of the oxides MoO_3, $Al_2(MoO_4)_3$, and $CoMoO_4$ has been confirmed by Raman spectroscopy on the powders obtained after TGA.

III. X-ray Absorption Spectroscopies. After deposition on the alumina, the HPC becomes XRD silent, and EXAFS

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(31) La Ginestra, A.; Gianetta, F.; Fiorucci, P. *Gazz. Chim. Ital.* **1968**, *98*, 1197.

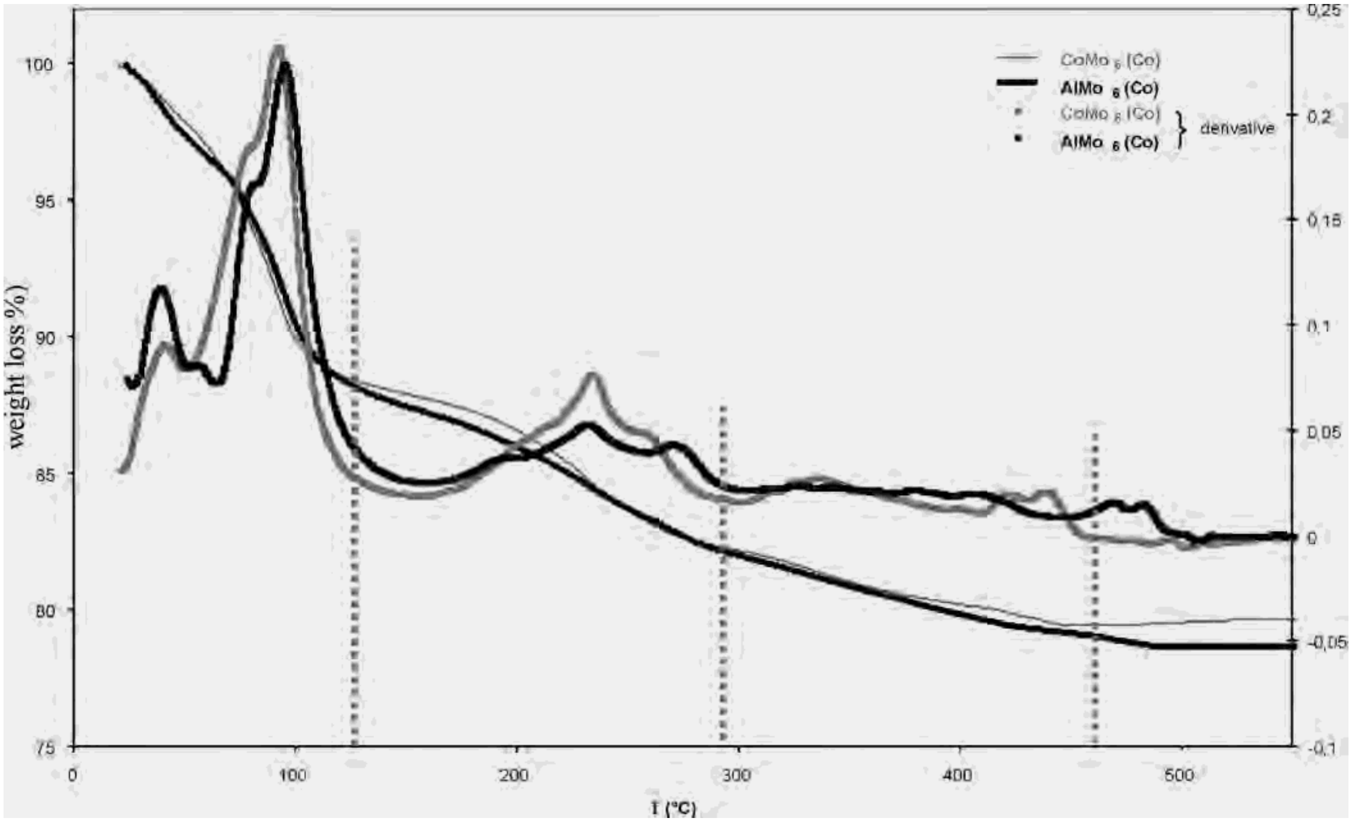

Figure 4. TGA experiments conducted on $CoMo_6(Co)$ (grey line) and $AlMo_6(Co)$ (black line), with the derived curves (dotted lines).

Table 4. Refinement of the EXAFS Signals of the Co Salts at the Mo K Edge

$CoMo_6(Co)$	Mo−O(1)	Mo−O(2)	Mo−O(3)	Mo−Mo	Mo−Co
N	1.90	2.07	2.15	2.13	1.10
R (Å)	1.70	1.93	2.30	3.32	3.28
$\Delta\sigma$ (Å)	0.03	0.09	0.05	0.08	0.09
ΔE (eV)			−0.32		
residue			0.01		

$AlMo_6(Co)$	Mo−O(1)	Mo−O(2)	Mo−O(3)	Mo−Mo	Mo−Al
N	2.00	1.99	2.03	2.01	0.90
R (Å)	1.70	1.93	2.30	3.32	3.41
$\Delta\sigma$ (Å)	0.04	0.08	0.06	0.06	0.09
ΔE (eV)			−0.42		
residue			0.009		

measurements are generally used to characterize the preservation of the heteropolyanionic structure after deposition. EXAFS study of the bulk starting HPC has therefore been performed in order to obtain data for the EXAFS characterization of the catalyst oxidic precursor. The crystallographic data were used for the EXAFS simulations of the EXAFS spectra of the powdered samples. Successful EXAFS simulation confirmed the X-ray single crystal analysis.

III.A. EXAFS at the Mo K-Edge. For all the simulations, the crystallographic data deduced from the XRD study, number of neighbors, and distances have been used to create amplitude and phase functions with the FEFF program in order to fit the experimental EXAFS oscillations with the software “Round Midnight”.

The Mo K edge EXAFS spectra of $AlMo_6$ salts and $CoMo_6$ ones are reported in Figure 5a,b, respectively. The spectra of the cobalt salts are similar to those of the ammonium salts, confirming that the HPA structure is maintained upon the ionic exchange of the counterions. In both cases, the refinement was successful, as shown in Table 4, in which are reported the main parameters of the refinement process, i.e., the number of neighbors *N*, the distance *R* between Mo and its neighbors, the Debye−Waller factor $\Delta\sigma$, the shift in energy ΔE, and the residue after fitting. The modulus of the Fourier transform (Figure 5) presents the coordination shells around the Mo atoms. The first shell contains 3 contributions due to the 3 different Mo−O distances (1.71, 1.93, 2.31 Å) whereas the second shell contains the contributions of Mo and Co neighbors for $CoMo_6$ salts and Mo and Al neighbors for $AlMo_6$ salts. Moreover, from the modulus of the Fourier transform, it is clear that the $Mo-Co^{2+}$ distances (cobalt as counterions) are too large (around 3.76 Å) to have a significant contribution in the examined EXAFS oscillations. If the EXAFS study at the Mo K-edge allows us to discern between $CoMo_6$ and $AlMo_6$ HPA, it does not allow us to make the distinction between the ammonium and the cobalt salt whatever the HPA considered. EXAFS experiments at the Co K-edge have therefore been performed.

III.B. XAS at the Co K-edge. (a) XANES. The position and the shape of the Co K absorption edge provide information about the charge and geometry of the Co species. Indeed, it is easy to distinguish Co^{2+} from Co^{3+} ions; the nonbonded and antibonded levels of the Co^{3+} are less stabilized whereas the 1s level is more stabilized, leading to a higher transition energy. So, in Figure 6, the peak at 7725 eV for $AlMo_6Co$ (Figure 6a) is attributed to Co^{2+} whereas the peak visible at 7733 eV for $CoMo_6Am$ (Figure 6c) is

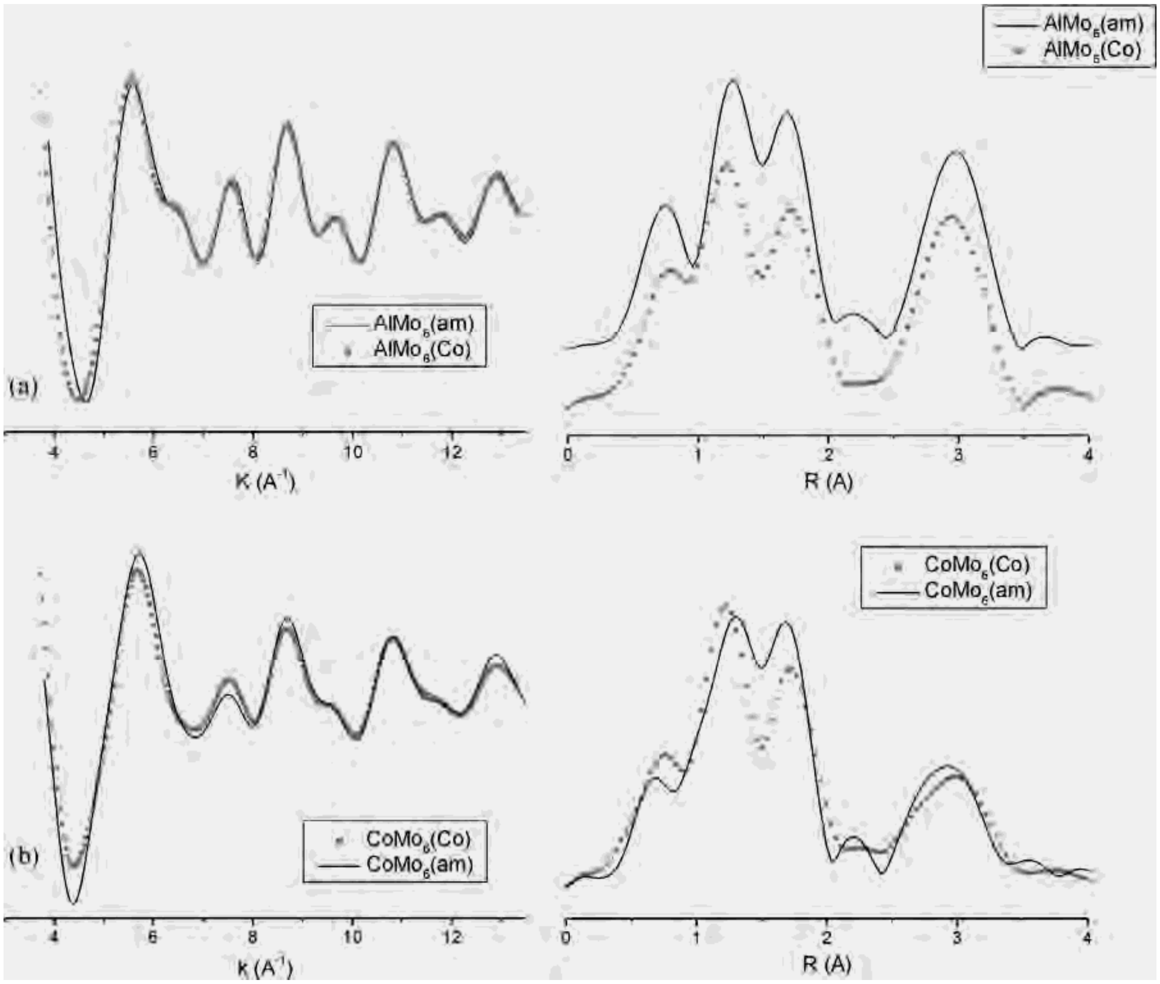

Figure 5. EXAFS at the Mo K-edge.

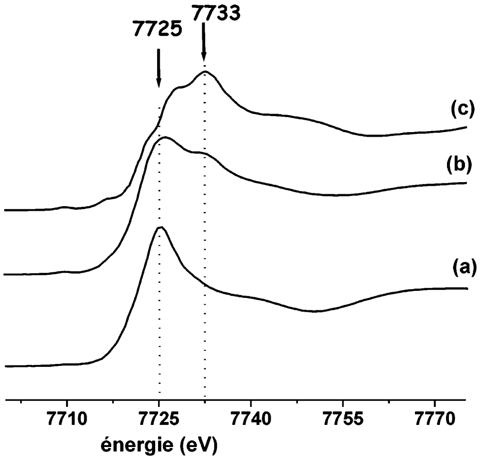

Figure 6. XANES at the Co K-edge (a, $AlMo_6Co$; b, $CoMo_6Co$; c, $CoMo_6$-Am).

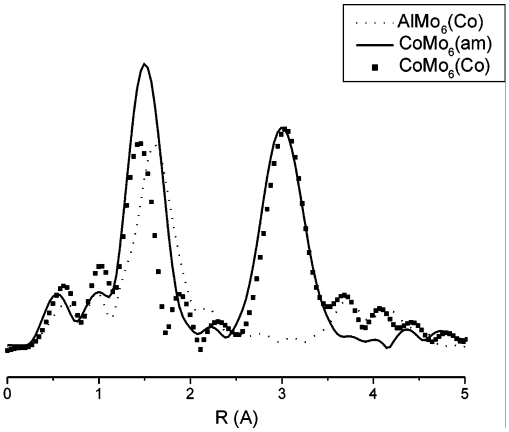

Figure 7. Modulus of the Fourier transforms of the EXAFS signals at the Co K-edge.

characteristic of Co^{3+}. The absorption spectrum of the 6-molybdocobaltate cobalt salt that contains both Co^{2+} and Co^{3+} ions presents two maxima corresponding to each cobalt oxidation state, as shown in Figure 6b. These results are in agreement with UV−vis characterizations, the spectra (not reported here) exhibiting the bands characteristic of Co^{2+} (at 510 nm) and Co^{3+} (at 400 and 600 nm).

(b) EXAFS. In Figure 7 are reported the Fourier transform (FT) modulus of the $AlMo_6Co$, $CoMo_6Am$, and $CoMo_6Co$ samples. For the three samples, the refinement of the Co K-edge spectra was successful as shown in Table 5. The FT of $AlMo_6Co$ presents only one shell corresponding to the first oxygen shell contribution and no contribution at higher distances. However for the simulation, two Co−O distances had to be taken into account (2.14 and 2.36 Å), the second distance being larger than the one proposed by XRD analysis (2.14 Å). The necessity to introduce a new Co^{2+}−O distance could be assigned to the presence of a small amount of cobalt hydroxide for which such a Co^{2+}−O value is expected.

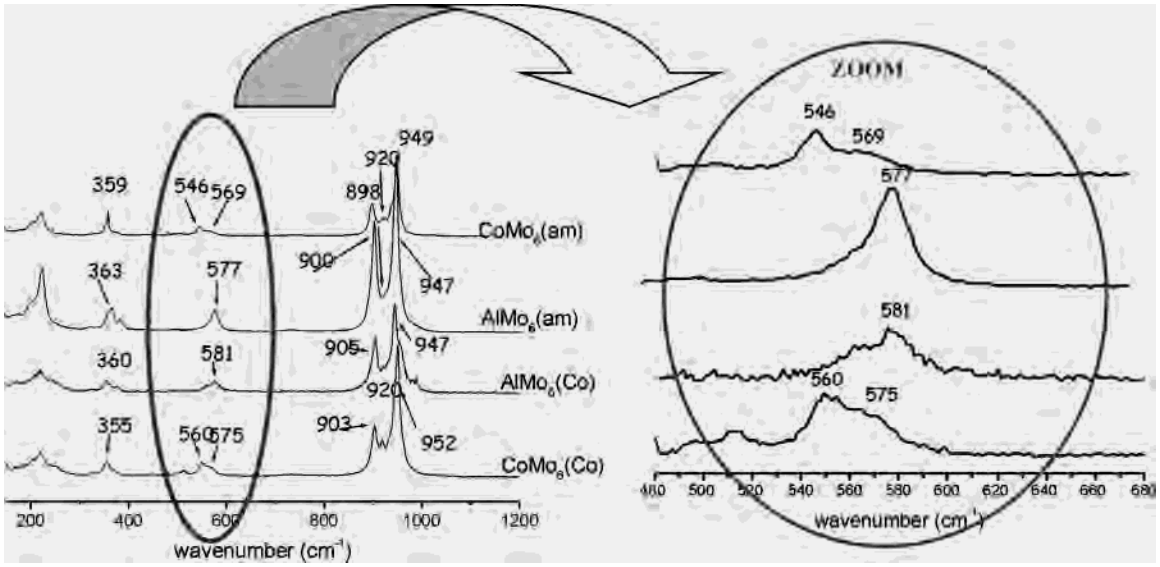

Figure 8. Raman spectra of the salts of Anderson HPA.

Table 5. Refinement of the EXAFS Signals of the Co Salts at the Co K-Edge

$CoMo_6(Co)$	Co−O(1)	Co−O(2)	Co−Mo
N	5.01	2.32	3.00
R (Å)	1.93	2.14	3.29
$\Delta\sigma$ (Å)	0.08	0.06	0.06
ΔE (eV)	−1.75		
residue	0.035		

$AlMo_6(Co)$	Co−O(1)	Co−O(2)
N	3.87	2.18
R (Å)	2.10	2.36
$\Delta\sigma$ (Å)	0.05	0.1
ΔE (eV)	0.68	
residue	0.02	

$CoMo_6(Am)$	Co−O	Co−Mo
N	5.61	5.70
R (Å)	1.93	3.34
$\Delta\sigma$ (Å)	0.06	0.05
ΔE (eV)	1.71	
residue	0.07	

Table 6. Vibrational Spectroscopy Assignments[a]

(s) Assignments of the Vibrations of IR and Raman Spectra of $CoMo_6Am$

IR (cm^{-1})	Raman (cm^{-1})	assignment
946 (vs)	949 (vs)	ν_{sym} Mo−O_{2t} (stretching)
890 (sh)	898 (sh)	ν_{as} Mo−O_{2t} (stretching)
654−583 (m)	569−546 (m)	ν Mo−O−Co
450−392−360	359 (w)	δ Mo-$O2_t$ (bending)

(b) Assignments of the Vibrations of Raman Spectra of XMo_6Am and XMo_6Co

XMo_6Am		XMo_6Co	
X = Co	X = Al	X = Co	X = Al
949 (vs)	947 (vs)	952 (vs)	947 (vs)
898 (sh)	900 (sh)	903 (sh)	905 (sh)
569−546 (m)	577 (m)	575−560 (m)	581 (m)
359 (w)	363 (w)	355 (w)	360 (w)

[a] vs, very strong; m, medium; w, weak; sh, shoulder.

In the $CoMo_6Am$ and $CoMo_6Co$ Fourier transform modulus, two shells are clearly visible, the first one around 1.5 Å corresponding to the first oxygen shell contribution whereas the second one is due to the first Mo shell contribution. We can note that the position and the relative intensity of the second shell are similar in both solids whereas intensity and position of the first shell differ, in agreement with the aforementioned description of the HPA structure. Indeed, in $CoMo_6Co$, 50% of the cobalt atoms are Co^{3+} that have 6 oxygen neighbors at 1.91 Å and 6 molybdenum neighbors at 3.30 Å, whereas the remaining Co atoms are Co^{2+} ones having only 6 O neighbors at 2.10 Å. The refinement was satisfactory for the two shells, the Co−O distances being in very good agreement with those provided by structural analysis even if in the first shell the contribution of Co^{3+} is overestimated. It is well recognized that the EXAFS technique is reliable and accurate concerning the distance determination whereas the number of neighbors is given with less accuracy. In $CoMo_6Am$, according to the refinement, each Co has 6 O neighbors at 1.93 Å and 6 Mo neighbors at 3.34 Å confirming the nature of the Anderson heteropolyanionic structure in $CoMo_6Am$.

IV. IR and Raman Spectroscopic Characterizations. The IR and Raman spectra are reported in Figures 1 and 8, respectively. The IR spectra of $CoMo_6Am$ and $CoMo_6Co$ (Figure 1) are similar. The former one, which is similar to the one previously reported by Cabello et al.,[32] exhibits the bands characteristic of the ammonium counterions. As mentioned, the intensity of this band is lower in the spectrum of the cobalt salt, but the similarity of both the IR and Raman features of the cobalt and ammonium HPA salts is also new evidence for the preservation of the Anderson structure upon the cation exchange. On the basis of previous work,[32,33] an assignment of the main vibrational modes of the HPA is given in Table 6a,b. The main features of the Mo−O_{2t} (where t stands for terminal) and the Mo−O−X (X = Co or Al) are visible in both IR and Raman spectra. A strong similarity is observed between the Al and Co Anderson HPA, the

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(32) Botto, I. L.; Garcia, A. C.; Thomas, H. J. *J. Phys. Chem. Solids* **1992**, *53* (8), 1075−1080.

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Raman spectra of which are characteristic of the Anderson structure according to the literature data.[34] Small differences are, however, observed, which allow us to make the distinction between the 6-molybdoaluminate and the 6-molybdocobaltate entities. The vibrational mode characteristic of the bond between the Mo and the central heteroatom is observed at 577 cm^{-1} for $AlMo_6Am$, whereas a doublet at 569 and 546 cm^{-1} is present for $CoMo_6Am$.

Conclusion

In this study, our attention has been particularly focused on the Anderson 6-molybdocobaltate and 6-molybdoaluminate cobalt salts, which were prepared through the ionic exchange in aqueous solution of the ammonium counterions of the starting ammonium salts ($Al/CoMo_6O_{24}H_6{}^{3-},3NH_4{}^+$). It has been shown that the HPA structure is preserved after the exchange, but the preparation method does not lead to the complete exchange as shown by IR spectroscopy. Elemental analysis also suggests that $1/2NH_4{}^+$ per HPA unit remains, and to ensure the electroneutrality, the presence of an interstitial $1/2H_3O^+$ group per HPA unit is required. The X-ray resolution structure shows that each $AlMo_6$ or $CoMo_6$ HPA unit is also surrounded by a $[Co(H_2O)_5]^{2+}$ group directly linked through a bridged oxygen atom to the $CoMo_6$ unit. It has been deduced that the unit cell contains eight units and respects the *Pcab* symmetry. EXAFS analysis also confirms this structure. These new entities were characterized by various techniques giving us a database for the characterization of the HDT oxidic precursors obtained by their deposition on alumina.

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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