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Synthesis, Crystal Structure, and Vibrational and Electron Spin Resonance Study of *tert*-Butylammonium Chromohexamolybdates, $[(CH_3)_3CNH_3]_n[H_{9-n}CrMo_6O_{24}] \cdot mH_2O$ ($n=2$, $m=2$; $n=3$, $m=8$). Effects of Degrees of Protonation and Hydration

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Two *tert*-butylammonium chromohexamolybdates(VI) with the formula $[(CH_3)_3CNH_3]_3[H_6CrMo_6O_{24}] \cdot 8H_2O$ (**1**) and $[(CH_3)_3CNH_3]_2[H_7CrMo_6O_{24}] \cdot 2H_2O$ (**2**), have been synthesised. Crystal data are as follows. Compound **1**: space group $P2_1/n$, $a=14.421(2)$, $b=11.263(6)$, $c=28.954(3)$ Å $\beta=99.70(1)°$, $V=4635(2)$ Å^3, $Z=4$, $R(F_o)=0.053$ and $R_w(F_o)=0.057$; compound **2**: space group $C2/c$, $a=27.923(3)$, $b=11.191(2)$, $c=11.783(3)$ Å, $\beta=102.15(2)°$, $V=3600(1)$ Å^3, $Z=4$, $R(F_o)=0.078$ and $R_w(F_o)=0.077$. A structure in layers showing the existence of hydrophobic layers is clearly seen for both compounds. The structures are stabilised by electrostatic forces and an extensive network of hydrogen contacts involving anions, cations and water molecules. It is interesting to indicate that in both cases the polyanions are joined by means of hydrogen contacts O···O of medium character. Raman and Fourier transform infrared spectra of both compounds have been recorded. The electron spin resonance spectra of compound **1** indicate that the chromophore is distorted with respect to the ideal octahedron, and also demonstrate the existence of a certain contribution of spin–orbit coupling that mixes the fundamental state with the first excited states. For compound **2** the existence of two different chromophores is seen; one of them corresponds to that observed for compound **1** while the other is due to a more distorted environment.

The chromohexamolybdate anion belongs to the family of heteropolyanions with Anderson structure, represented by the general formula $[H_xXM_6O_{24}]^{n-}$; the heteroatom, X, occupies the central octahedral cavity of the crown formed by six edge-sharing MO_6 (M = Mo or W) octahedra. The heteroatom X is an ion in an oxidation state +2, +3, +4, +6 or +7, and the different Anderson anions are classified as a function of the number of protons (x) joined to the central octahedron XO_6 in three groups; series A ($x=0$); series B ($x=6$) and series C ($x=0$–5).

Series A: $[XO_6M_6O_{18}]^{m-}$. This type is observed for X = Te^{VI}, $[TeO_6Mo_6O_{18}]^{6-}$, colourless[1–3] and for X = I^{VII},[4,5] $[IO_6Mo_6O_{18}]^{5-}$. In the case of the tungstate anion, compounds with X = Ni^{IV} and Mn^{IV} are also known. The compounds have been characterised by means of Raman spectroscopy[6] and ^{17}O-NMR.[7] The crystal structures of the following salts have been determined: $(NH_4)_6[TeMo_6O_{24}] \cdot 7H_2O$,[1] $(NH_4)_6[TeMo_6O_{24}] \cdot Te(OH)_6 \cdot 7H_2O$,[2] $Na_4(NH_4)_2[TeMo_6O_{24}] \cdot 16H_2O$,[8] $Li_6[TeMo_6O_{24}] \cdot 18H_2O$ and $Li_6[TeMo_6O_{24}] \cdot Te(OH)_6 \cdot 18H_2O$,[9] $Cs_6[TeMo_6O_{24}] \cdot 2Te(OH)_6 \cdot 4H_2O$,[10] $Rb_6[TeMo_6O_{24}] \cdot 10H_2O$ and $Rb_6[TeMo_6O_{24}] \cdot Te(OH)_6 \cdot 6H_2O$,[11] and $K_5[IMo_6O_{24}] \cdot 5H_2O$.[4]

Series B: $[X(OH)_6M_6O_{18}]^{m-}$ ($X = Mn^{II}$, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Al^{III}, Ga^{III}, Cr^{III}, Fe^{III}, Co^{III}, Rh^{III}). The compounds, generally coloured, are formed from acidified aqueous solutions that contain metallate ions (hot solutions of heptamolybdate and species of the heteroatom at pH 4.5).[12,13] The formation of the compound

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containing Co^{III} requires an oxidant, H_2O_2 or, even better, $S_2O_8^{2-}$. The interval of pH of stability of these compounds varies depending on the heteroatom, those compounds with a trivalent heteroatom being more stable. The following compounds have been described: $Na_3[H_6CrMo_6O_{24}] \cdot 8H_2O$,[13] $K_3[H_6AlMo_6O_{24}] \cdot 7H_2O$,[14] $(NH_4)_4[H_6CuMo_6O_{24}] \cdot 4H_2O$,[15] and $(NH_4)_3[H_6RhMo_6O_{24}] \cdot 6H_2O$.[16] The compounds have been characterised by means of optical spectroscopy,[17,18] IR spectroscopy,[19] NMR spectroscopies[20] and magnetic data.[17,18] The Anderson structure studied for the compound $Na_3[CrMo_6O_{18}(OH)_6] \cdot 8H_2O$[13] consists of an XO_6 octahedron surrounded by a planar ring of six octahedra that share edges. The six hydrogen atoms are not acidic, and they are coordinated to the six oxygen atoms from the central octahedron.

It is interesting to notice the formation of a heteropolyanion of formula $[Co_2O_6(OH)_4Mo_{10}O_{28}]^{6-}$, emerald green in colour, as a byproduct in most of the preparations of the complex salts $[Co^{III}(OH)_6Mo_6O_{18}]^{3-}$. It is the principal product when the oxidation of Co^{II} is carried out with H_2O_2 in the presence of activated carbon or a Raney nickel catalyst. The structure of this anion can be described as two interpenetrating Anderson rings.[20]

Series C: $[XO_{6-n}(OH)_nM_6O_{18}]^{(8-n)-}$ ($X = Pt^{IV}$, n = 0–5). The heteropolymetallates of Pt^{IV} have been obtained not only unprotonated but also protonated, and can adopt two kinds of structure: the planar Anderson structure, point group D_{3d} (α-XM_6O_{24}) and a non-planar form of the Lindqvist type, point group C_{2v} (β-XM_6O_{24}) ($\equiv Mo_7O_{24}^{6-}$).[21] The light yellow salt, $K_{3.5}[H_{4.5}Pt^{IV}Mo_6O_{24}] \cdot 3H_2O$ has the α-structure and the tetraprotonated salt $(NH_4)_4[H_4Pt^{IV}Mo_6O_{24}] \cdot 1.5H_2O$ has the β-type structure. The unprotonated form was obtained for the tungstate.

An heteropolyanion that possesses two types of heteroatoms As^{III} and Co^{II}, and that is intimately related to the Anderson anions, it is the heteropolyanion $[As_6CoMo_6O_{30}]^{4-}$, which consists of one Anderson type unit, $[CoMo_6O_{24}]$, and two triarsenate(III) groups that are joined one above and other below the planar ring.[22]

As a part of a study of polyoxometallates we have isolated and characterised chemically and structurally two compounds with the formulae $[(CH_3)_3CNH_3]_3[H_6CrMo_6O_{24}] \cdot 8H_2O$ (**1**) and $[(CH_3)_3CNH_3]_2[H_7CrMo_6O_{24}] \cdot 2H_2O$ (**2**). The ESR spectra indicate that the chromium(III) ion is found in a distorted octahedral environment with a certain spin–orbit contribution. For compound **2**, two magnetically active centres are observed.

Experimental

Materials. All chemicals were obtained commercially and used without subsequent purification.

Physical measurements. Microanalyses of carbon, nitrogen and hydrogen were performed on a Perkin-Elmer 240 C-, H- and N-analyser, and chromium and molybdenum were determined thermogravimetrically as $MoO_3 + Cr_2(MoO_4)_3$ after thermal decomposition of the samples in a synthetic air atmosphere. The density was measured by flotation in $CHBr_3/CCl_4$. The IR spectrum was recorded in the 4000–400 cm^{-1} range on a Nicolet 740 FTIR spectrometer, and the solid compound was mixed with potassium bromide (Fluka, FTIR spectroscopy grade) into a transparent disk. Raman spectra were obtained on a Nicolet 950 FT Raman spectrometer equipped with a Spectra Physics Nd:YVO_4 laser (1064 nm, 1.5 W) as static powder samples. ESR spectra of both compounds were recorded on powder samples at room temperature with a Brücker ESP 300 spectrometer operating in the X-band (9.75 GHz). The magnetic field was measured with a Brücker BNM 200 gaussmeter, and the frequency inside the cavity was determined using a Hewlett-Packard 5352B microwave frequency counter.

Synthesis.

*Tris(*tert*-butylammonium) chromohexamolybdate(VI) octahydrate, $[(CH_3)_3CNH_3]_3[H_6CrMo_6O_{24}] \cdot 8H_2O$* (**1**). A 1.2 M solution of bis(*tert*-butylammonium) molybdate[23,24] in molybdenum (7.36 g; 24 mmol in 20 mL of H_2O) was prepared, and concentrated HNO_3 was added until the precipitation of a white powder of tetrakis(*tert*-butylammonium) octamolybdate dihydrate.[25] Then, *tert*-butylamine (3.0 mL; 28 mmol) was added and the solution was heated in order to dissolve this precipitate, yielding a colourless solution of pH 5. Alternatively, 1.62 g (4.05 mmol) of $Cr(NO_3)_3 \cdot 9H_2O$ were dissolved in 10 mL of distilled water. The colourless solution of molybdenum, still hot, was added over the dark blue solution of Cr^{III} at room temperature. The colour of the solution turned green and finally dark pink. After 3 h, pink crystals were collected and recrystallized in water. The compound was soluble in water and DMF and insoluble in ethanol and acetone. Crystals were stable to the air and light but they decomposed on exposure to X-rays. Analytical data: Found: C 10.30; H 4.17; N 2.96. Calculated for $C_{12}H_{58}CrMo_6N_3O_{32}$: C 10.41; H 4.22; N 3.04.

*Bis(*tert*-butylammonium) heptahydrogenchromohexamolybdate dihydrate $[(CH_3)_3CNH_3]_2[H_7CrMo_6O_{24}] \cdot 2H_2O$* (**2**). A solution of bis(*tert*-butylammonium) molybdate[24] (3.37 mmol in 50 mL of H_2O) was prepared and acidified up to pH 5 with HCl 1.25 M. $CrCl_3 \cdot 6H_2O$ (0.16 g, 0.58 mmol), in the ratio Mo:Cr = 6:1, was added. Initially, the solution was green, but it changed to pink after being left at room temperature for several hours. After one week, laminar pink crystals were obtained. The crystals were stable to the air, light and X-ray exposure. Analytical data: Found: C 8.25; H 3.05; N 2.40. Calculated for $C_8H_{35}CrMo_6N_2O_{26}$: C 7.99; H 2.93; N 2.33.

Crystallographic data collection and structure refinement. Single crystals of compounds **1** and **2** were obtained as described above. Table 1 summarises crystal data and data collection procedures for both compounds. Intensity data were corrected for Lorentz and polarization effects, and an empirical absorption correction[26] based on the isotropically refined structure was applied.

The structure of compound **1** was solved by a combination of direct methods (DIRDIF92)[27] and difference Fourier syntheses and refined by full-matrix least-squares methods based on F.[28] The crystal structure of compound **1** was refined with anisotropic thermal parameters for all the non-hydrogen atoms. The hydrogen atoms belonging to the anion were found by a difference Fourier method. These atoms, together with the hydrogen atoms from the cations and water molecules, geometrically positioned, were included as isotropic contributors. The solution was refined up to an R-value of 5.3%.

The crystal structure of compound **2** was solved using the program DIRDIF92,[27] finding the centrosymmetric anion chromohexamolybdate, one *tert*-butylammonium cation and one water molecule in a general position. Bond orders for the oxygen atoms were calculated, observing that the oxygen atom O(6) has a bond order of 1.48(8). This could mean that this atom and its corresponding centrosymmetric atom could be protonated, giving us the formula $[(CH_3)_3CNH_3]_2[H_7CrMo_6O_{24}]\cdot 2H_2O$. The hydrogen atoms were geometrically positioned, except the seventh hydrogen atom of the anion, and included as isotropic contributors in the final refinement. The rest of the structure was refined by full-matrix least-squares methods based on F with anisotropic thermal parameters for all the non-hydrogen atoms, except an oxygen atom from the polyanion, the water molecule O(13)w and two carbon atoms from the cation. Most calculations were carried out using the XRAY 76[28] system running on a MicroVAXII computer.

Final atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms are given in Tables 2 and 3.

Results and discussion

Vibrational spectroscopy. The infrared spectra and Raman spectra for the compounds are shown in

Table 1. Crystallographic data for compounds **1** and **2**.

	Compound **1**	Compound **2**
Formula	$[(CH_3)_3CNH_3)]_3[H_6CrMo_6O_{24}]\cdot 8H_2O$	$[(CH_3)_3CNH_3)]_2[H_7CrMo_6O_{24}]\cdot 2H_2O$
M_r	1384.23	1203.0
System	Monoclinic	Monoclinic
Space group	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)
a	14.421(2)	27.923(3)
b/Å	11.263(6)	11.191(2)
c/Å	28.954(3)	11.783(3)
β/°	99.70(1)	102.15(2)
V/Å	4635(2)	3600(1)
Z	4	4
$F(0\,0\,0)$	2732	2468
D_o/Mg m^{-3}	2.01(1)	2.23(1)
D_x	1.984	2.220
μ (Mo$K\alpha$)/cm^{-1}	18.417	23.501
Form	Prism	Plate
Dimensions/mm	0.24 × 0.25 × 0.35	0.10 × 0.20 × 0.20
Colour	Pink	Pink
Diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4
Temperature/K	295(1)	295(1)
Radiation (Mo$K\alpha$)	0.71069	0.71069
Monochromator	Oriented graphite	Oriented graphite
Scan mode	ω/2θ	ω/2θ
θ range/°	1–30 (incomplete)	1–30
hkl	0→20; 0→15; −18→18	0→39; 0→15; −16→16
Controls	Intensity and orientation	Intensity and orientation
Reflexions	5 $\bar{1}$ 0; 5 $\bar{4}$ 0	$\bar{1}$ 3 2; 8 2 0
Periodicity	3600 s; 100 reflex	7200 s; 100 reflex
Independent reflexions	8453	5208
Observed reflexions	3697 [$I \geqslant 3\sigma(I)$]	1591 [$I \geqslant 2\sigma(I)$]
No. of variables	448	176
$(\Delta/\sigma)_{max}$	0.65	0.844
$(\Delta/\sigma)_{av}$	0.050	0.050
$(\Delta\rho)$/Å^{-3}	0.48	5.16
Absorption correction (DIFABS)	$T_{min}=0.785$; $T_{max}=1.245$	$T_{min}=0.838$; $T_{max}=1.221$
R	0.053	0.078
R_w	0.057	0.077

Table 2. Compound **1**: atomic coordinates and isotropic temperature factors.

Atom	*x*	*y*	*z*	U_{eq}[a]
Mo(1)	0.50329(7)	0.4704(1)	0.62659(5)	396(6)
Mo(2)	0.70884(8)	0.4660(1)	0.59035(5)	383(6)
Mo(3)	0.86047(7)	0.6891(1)	0.61582(5)	383(6)
Mo(4)	0.80362(7)	0.9174(1)	0.67878(5)	390(6)
Mo(5)	0.59650(7)	0.9210(1)	0.71607(5)	407(6)
Mo(6)	0.44510(7)	0.6993(1)	0.68890(5)	433(6)
Cr(1)	0.6544(1)	0.6930(2)	0.65402(8)	280(8)
O(1)	0.5778(5)	0.5869(7)	0.6864(3)	32(3)
O(2)	0.5967(5)	0.6045(7)	0.5975(3)	31(3)
O(3)	0.7605(5)	0.5820(7)	0.6540(3)	35(3)
O(4)	0.7280(5)	0.7993(7)	0.6207(3)	35(3)
O(5)	0.7115(5)	0.7841(7)	0.7099(3)	32(3)
O(6)	0.5484(5)	0.8032(7)	0.6522(3)	31(3)
O(7)	0.6266(6)	0.4012(7)	0.6300(4)	45(4)
O(8)	0.7739(5)	0.5998(8)	0.5694(3)	38(4)
O(9)	0.8817(5)	0.7810(8)	0.6739(4)	45(4)
O(10)	0.6801(6)	0.9874(7)	0.6765(4)	41(3)
O(11)	0.5302(6)	0.7869(8)	0.7360(4)	47(4)
O(12)	0.4264(6)	0.6083(8)	0.6311(3)	42(4)
O(13)	0.4638(7)	0.3764(9)	0.6646(5)	69(5)
O(14)	0.4497(7)	0.4253(9)	0.5730(5)	64(5)
O(15)	0.6521(7)	0.4216(9)	0.5360(4)	57(4)
O(16)	0.7978(7)	0.3656(9)	0.6053(4)	61(4)
O(17)	0.9485(6)	0.5896(9)	0.6304(4)	68(5)
O(18)	0.9016(7)	0.7850(9)	0.5790(4)	60(4)
O(19)	0.8382(6)	1.0110(8)	0.6384(4)	51(4)
O(20)	0.8584(7)	0.9675(9)	0.7325(4)	56(4)
O(21)	0.6519(7)	0.9669(9)	0.7697(4)	66(5)
O(22)	0.5071(7)	1.0182(9)	0.6994(4)	63(4)
O(23)	0.3583(6)	0.7996(9)	0.6738(4)	70(5)
O(24)	0.4030(7)	0.6049(9)	0.7259(4)	74(5)
$O(25)_w$	0.205(1)	0.2702(9)	0.2034(5)	116(7)
$O(26)_w$	0.152(1)	0.600(2)	0.0381(7)	128(9)
$O(27)_w$	0.012(1)	0.800(1)	0.0172(5)	87(6)
$O(28)_w$	0.024(2)	0.424(2)	0.9271(8)	146(10)
$O(29)_w$	0.230(3)	0.364(5)	0.016(2)	271(18)
$O(30)_w$	0.095(3)	0.028(4)	0.489(1)	222(13)
$O(31)_w$	0.219(2)	0.832(3)	0.980(1)	199(11)
$O(32)_w$	0.101(4)	0.365(5)	0.086(2)	285(22)
N(11)	0.0675(7)	0.7688(9)	0.3333(4)	40(4)
C(12)	0.0198(8)	0.7730(9)	0.3554(6)	45(6)
C(13)	−0.0793(9)	0.671(1)	0.3356(8)	77(8)
C(14)	−0.0676(9)	0.8914(9)	0.3424(7)	58(6)
C(15)	0.009(1)	0.765(2)	0.4071(9)	91(6)
N(21)	0.0239(7)	0.7363(9)	0.7536(4)	40(4)
C(22)	0.1231(8)	0.7267(9)	0.7441(6)	41(5)
C(23)	0.139(2)	0.831(2)	0.713(1)	130(15)
C(24)	0.1316(1)	0.609(2)	0.7176(7)	72(8)
C(25)	0.1871(1)	0.7262(3)	0.7889(9)	116(12)
N(31)	0.2147(9)	0.153(2)	0.9492(6)	91(8)
C(32)	0.3091(9)	0.135(2)	0.9400(8)	91(9)
C(33)	0.334(2)	0.253(3)	0.915(1)	145(11)
C(34)	0.312(3)	0.034(4)	0.906(2)	169(13)
C(35)	0.378(2)	0.128(3)	0.984(1)	125(9)

[a] $U_{eq} = 1/3 \Sigma U_{ij} a_i^*, a_j^* \cos(a_i, a_j)$ (Å$^2 \times 10^4$ for Cr and Mo; 10^3 for O atoms).

Table 3. Compound **2**: atomic coordinates and isotropic temperature factors.

Atom	*x*	*y*	*z*	U_{eq}[a]
Mo(1)	0.1876(1)	0.4826(2)	−0.1392(1)	199(6)
Mo(2)	0.1268(1)	0.2501(2)	−0.0577(2)	247(6)
Mo(3)	0.1895(1)	0.0123(2)	0.0780(1)	218(6)
Cr(1)	0.2500(−)	0.2500(−)	0.0000(−)	19(1)
O(1)	0.2486(6)	0.3487(12)	0.1410(11)	19(4)
O(2)	0.1955(5)	0.3564(13)	0.0207(13)	21(5)
O(3)	0.1941(6)	0.1395(14)	−0.0714(14)	29(5)
O(4)	0.2490(6)	0.5507(13)	−0.0526(13)	26(3)
O(5)	0.1440(6)	0.3412(15)	−0.1829(13)	32(5)
O(6)	0.1464(5)	0.1534(16)	0.0863(13)	29(5)
O(7)	0.1891(5)	0.5353(17)	−0.2768(13)	31(5)
O(8)	0.1486(6)	0.5750(18)	−0.0849(14)	39(6)
O(9)	0.0917(6)	0.3486(16)	−0.0029(19)	44(6)
O(10)	0.0899(6)	0.1483(21)	−0.1418(19)	52(7)
O(11)	0.1489(7)	−0.0778(16)	−0.0149(15)	39(6)
O(12)	0.1885(7)	−0.0394(17)	0.2140(16)	40(6)
$O(13)_w$	0.7250(11)	0.2134(48)	0.1321(40)	133(14)
N(11)	0.6092(7)	0.2044(22)	0.0818(20)	43(7)
C(12)	0.5550(10)	0.2032(28)	0.0490(26)	47(7)
C(13)	0.5404(18)	0.1762(57)	−0.0779(50)	97(16)
C(14)	0.5397(14)	0.1040(63)	0.1326(29)	110(23)
C(15)	0.5364(18)	0.3485(41)	0.0650(54)	108(23)

[a] $U_{eq} = 1/3 \Sigma U_{ij} a_i^*, a_j^* \cos(a_i, a_j)$ (Å$^2 \times 10^4$ for Cr and Mo; 10^3 for O atoms).

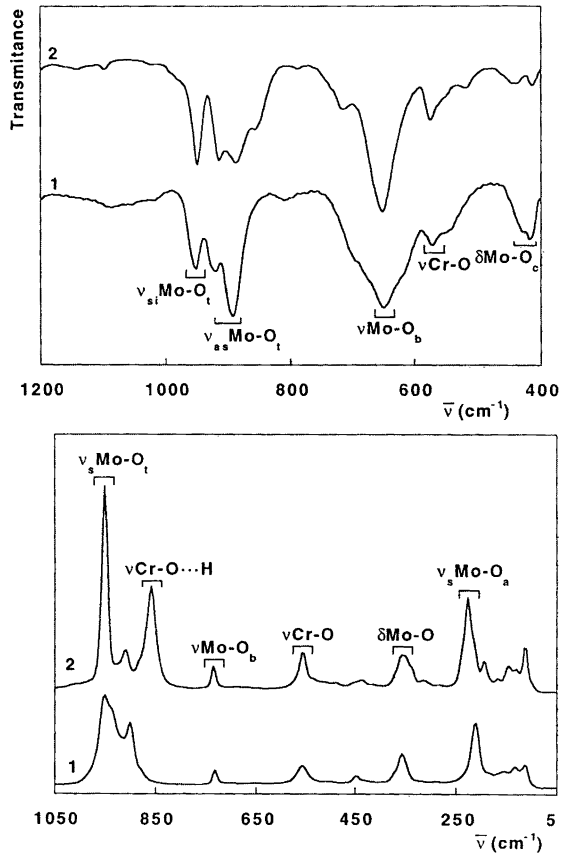

Fig. 1. IR and Raman spectra for both anions.

Fig. 1. These spectra are characteristic of the Anderson anions of formula $[H_6X^{III}Mo_6O_{24}]^{3-}$ and $[H_6X^{II}Mo_6O_{24}]^{4-}$.[19,29,30] In the infrared spectrum, the bands associated with the Mo–O_t bonds are displaced towards higher wavenumbers as the size of the central atom

increases.[30] Table 4 lists the values of the frequencies of the stretching modes for both compounds.

Description of the crystal structures. The X-ray structural analysis reveals that the asymmetric unit of compound **1** is composed of an acentric chromohexamolybdate, three *tert*-butylammonium cations and eight water molecules, while the asymmetric unit of compound **2** consists of half a chromohexamolybdate anion, one *tert*-butylammonium cation and one water molecule.

Figure 2 shows both chromohexamolybdate anions, together with the atom numbering scheme.

The chromium atom occupies the central octahedral cavity of the crown formed by the six octahedra MoO_6 that share edges. All the metallic centres, Cr and Mo, are located in the same plane. In both anions, the central octahedron CrO_6 is the most regular one (1.97–1.98 Å for compound **1** and 1.99–2.03 Å for compound **2**), while the MoO_6 octahedra show three types of distances, short (1.69–1.72 Å for **1** and 1.69–1.73 Å for **2**) with the terminal oxygen atom, medium (1.92–1.95 Å for **1** and 1.93–2.00 Å for **2**) with the doubly shared oxygen atoms and long (2.28–2.31 Å for **1** and 2.27–2.34 for **2**) with the triply shared oxygen atoms (with the Cr atom and two Mo atoms); thus, only one type of MoO_6 octahedron exists.

It is seen that the most regular Cr–O distances are those of the $[H_6CrMo_6O_{24}]^{3-}$ from compound **1**. On the other hand, the intermediate Mo–O distances are longer for the Anderson anion of compound **2**. In addition, in this anion the longest Cr–O distance is the one that the O(3), shared with the molybdenum atoms Mo(2) and Mo(3), molybdenum atoms that also share the same oxygen atom, O(6).

The bond orders for all oxygen atoms for both anions have been calculated,[31–33] confirming that the six protons are joined to the oxygen atoms belonging to the CrO_6 octahedron[13] (bond orders: 1.17(2)–1.20(3) for compound **1** and 1.11(5)–1.14(3) for compound **2**). Additionally, the oxygen atom O(6) of the Anderson anion of compound **2** has a bond order of 1.48(8). Thus it is possible that this oxygen atom and its centrosymmetric partner, would be protonated at 50%, yielding the anion $[H_7CrMo_6O_{24}]^{2-}$ or the existence of two anions with different degrees of protonation: $[H_8CrMo_6O_{24}]^{-}$ and $[H_6CrMo_6O_{24}]^{3-}$, as the ESR spectra of this compound indicate.

Table 4. Some assignments in the vibrational spectra of the Anderson $[H_{9-n}CrMo_6O_{24}]^{n-}$ anions.

Assignment	**1**	**2**	NH_4^+
IR bands			
ν_s (Mo–O_t)	948 (s)	948 (s)	945 (s)
ν_{as} (Mo–O_t)	891 (vs)	891 (vs)	894 (vs)
ν_{as}(Mo–O_b–Mo)	706 (vw)		706 (sh)
	650 (vs)	650 (vs)	657 (vs)
ν (Cr–OH)	577 (w)	577 (m)	578 (m)
ν(Mo–O_c–Mo)	519 (w)	519 (w)	415 (w)
	445 (w)	445 (w)	
Raman bands			
ν_s (Mo–O_t)	951 (vs)	951 (vs)	941 (vs)
ν_{as} (Mo–O_t)	963.5 (m)	959 (s)	897 (s)
		942 (m)	
	907 (w)		
ν (Mo–O_b–Mo)	735 (vw)	735 (vw)	731 (w)
ν (Cr–OH)	557 (w)	557 (w)	558 (w)
δ (Mo–O)	357 (w)	357 (w)	360 (w)
ν_s (Mo–O_a)	215 (s)	226 (s)	215 (s)

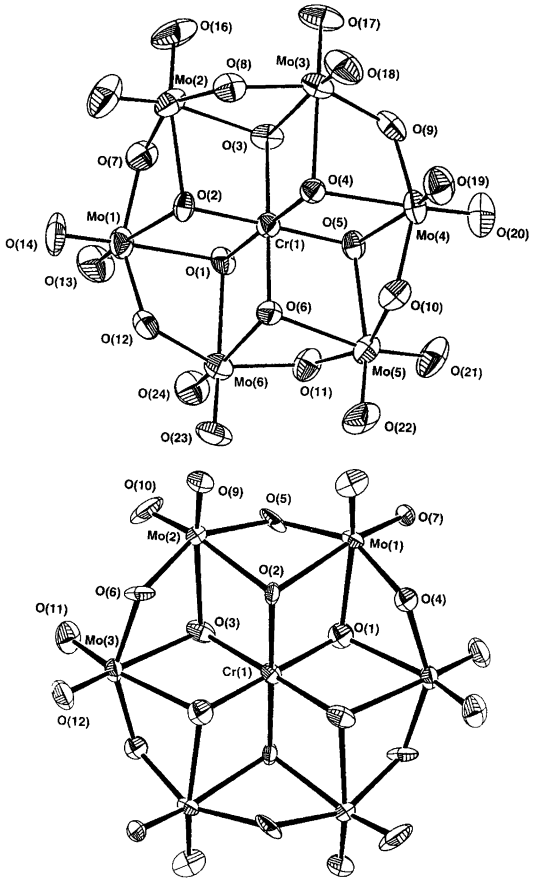

Fig. 2. ORTEP views for $[H_6CrMo_6O_{24}]^{3-}$ anion (top) and $[H_7CrMo_6O_{24}]^{2-}$ anion (bottom) with atom labelling.

The chromohexamolybdate anion has a D_{3d} ideal symmetry, with the molybdenum and chromium atoms located on the same plane. It is seen that for the acentric anion, the Cr atom deviates most (0.036 Å) from the average plane formed by the six molybdenum atoms and the Cr atom, while in the case of the centrosymmetric anion, the Cr atom is the one that deviates less (0.0006 Å) from the plane defined by the Mo and Cr atoms. On the other hand, in the case of the acentric anion, all the doubly shared oxygen atoms are located at 0.91–0.93 Å from the plane of atoms of Cr and Mo; however, in the centrosymmetric anion the oxygen atom O(6) is at 0.98 Å, while the other two doubly shared oxygen atoms, O(4) and O(5), are at 0.92 and 0.95 Å, respectively. This

fact could be due to the protonation of the oxygen atom O(6).

The crystal structure of compound **1** projected onto the plane (0 1 0) is shown in Fig. 3(a). The whole structure has a pronounced two-dimensional character and can be viewed as a succession along the [1 0 −1] direction of layers of polyanions and separated by hydrophobic layers of cations. The existence of two hydrophobic zones is observed. The water molecules are hydrogen bonded to the anions of the same layer.

The anions are disposed in zigzag rows along the *b*-axis [Fig. 3(b)]. The anions $[H_6CrMo_6O_{24}]^{3-}$ are connected by means of hydrogen bonds involving their OH groups, cations 1 and 2, and the water molecule O(13)w. Cation 3 and the remaining water molecules link the adjacent zigzag rows through a hydrogen-bonded 'waterfall'.

The three-dimensional arrangement in compound **2** is very similar to that of compound **1** and consists of layers of polyanions and cations parallel to the (1 0 0) plane following the sequence –cation–anion–cation–[(Fig. 4(a)]. The hydrophobic groups of the cations are

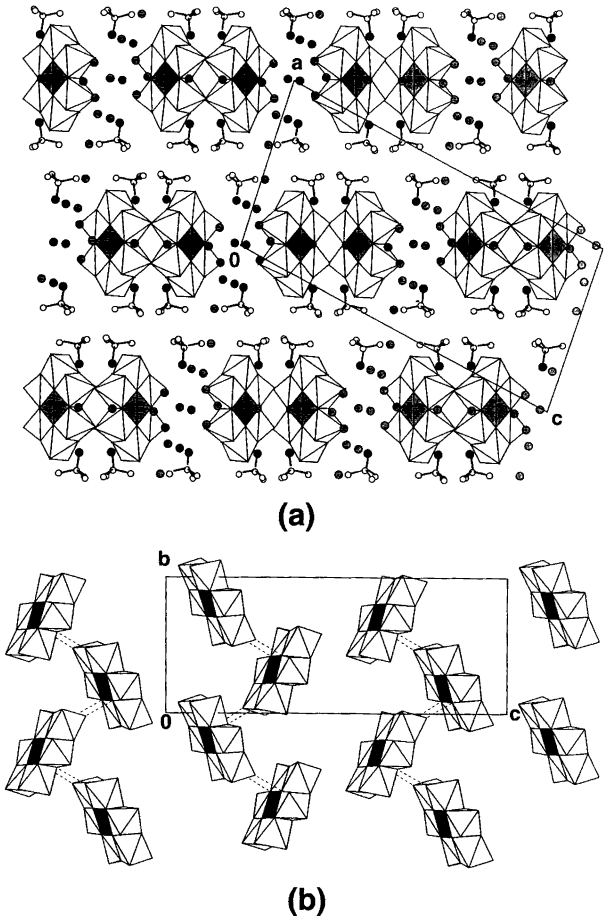

Fig. 3. Compound **1**: (a) view along the *b*-axis. N atoms in filled circles and water molecules in grey circles; (b) arrangement of polyanions in layers parallel to the (1 0 −1) plane, dotted lines correspond to hydrogen bonding of type O_{poly}–H···O_{poly}.

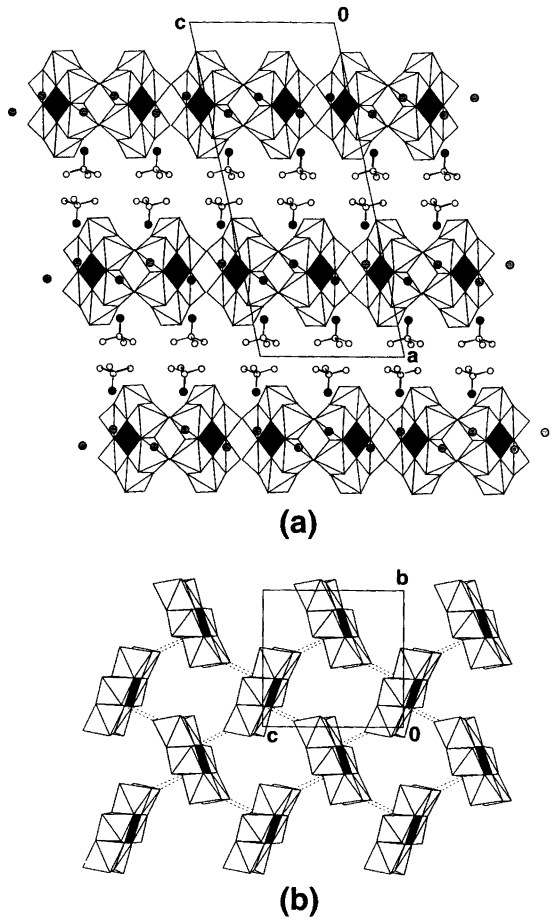

Fig. 4. Compound **2**: (a) view along the *b*-axis. N atoms in filled circles and water molecules in grey circles; (b) arrangement of polyanions in layers parallel to the (1 0 0) plane, dotted lines correspond to hydrogen bonding of type O_{poly}–H···O_{poly}.

directed to the regions $x=0$ and $x=1/2$. As can be seen in the Fig. 4(b), each polyanion forms eight hydrogen bonds with the nearest four polyanions (medium character, O–O 2.72–2.74 Å), giving rise to a two-dimensional arrangement of polyanions. The links between these polyanions are reinforced by the hydrogen contacts involving the *tert*-butylammonium cation and the water molecule.

ESR spectral measurements. The observed spectrum for compound **1** is characteristic of an $S=3/2$ system with an appreciable zero-field splitting, of the same order as the microwave energy employed in the experiment ($h\nu=0.32\ cm^{-1}$). Four ESR signals centred about 1900, 3600, 6000 and 6800 G were detected [Fig. 5(a)]. The positions of these lines have been analysed in terms of the following spin Hamiltonian:

$$H = g\beta Hs + D[S_z^2 - \tfrac{1}{3}S(S+1)] + E[S_x^2 - S_y^2]$$

and the deduced assignations are marked on Fig. 5(a). Assuming an isotropic *g*-tensor, as it is usually observed for Cr^{III} compounds, the observed spectrum is consistent

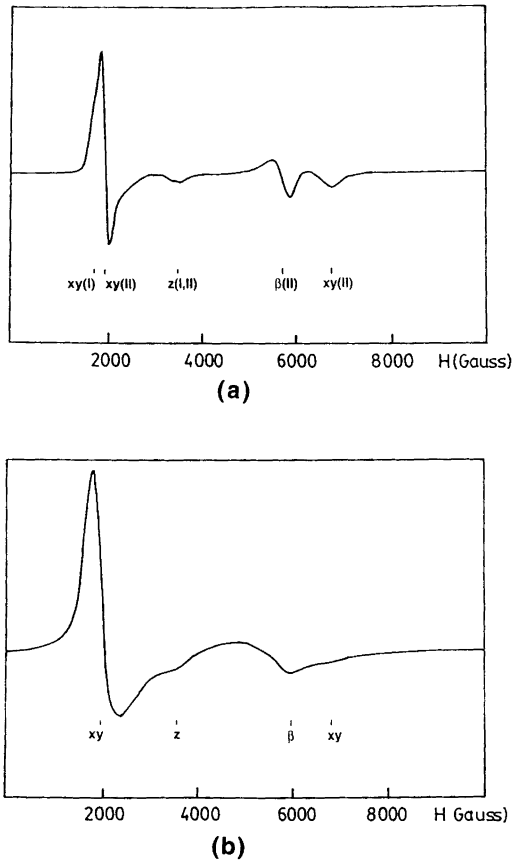

Fig. 5. X-Band ESR spectra for both compounds.

with a g-value of 1.91 and a zero-field splitting parameter $|D| = 0.34\ cm^{-1}$. The observation of only four lines suggests that the rhombic E parameter is close to zero, even if the rather large linewidth could preclude the observation of the corresponding splitting.

With the structural parameters having been taken into account, the observed D-value can be attributed not only to the distortion of the chromophore with respect to the ideal octahedron but also to the existence of a certain contribution of spin–orbit coupling that mixes the fundamental state with the first excited states. This last contribution is also reflected in the reduction that the value of g undergoes with respect to the expected value for the free electron (2.0023).

Finally, it is not possible to deduce the sign of the D-parameter, or determine which is the Kramer doublet of lowest energy ($M_s = \pm\frac{1}{2}$ or $M_s = \pm\frac{3}{2}$) at zero field. Usually, $M_s = \pm\frac{1}{2}$ is the state that stays at lowest energy, but to solve this problem it would be necessary to make the measurement at a temperature for which $KT \approx 2D$ ($T = 0.5$ K).

The ESR spectrum of compound **2** is shown in Fig. 5(b). The existence of two different chromophores is seen, both with approximately the same g-value but with a clearly different zero-field splitting term.

The analysis of the signals of one of the centres indicates that it is the same centre as that described for compound **1** and that it is characterised for $g = 1.98$ and $D = 0.337\ cm^{-1}$. The other centre only yields two lines, one of them for a field value corresponding to $g = 1.98$ and the other at approximately half that value (1750 G). This situation is characteristic of a centre with a value of the zero field splitting higher than radiofrequency energy used in the measurement ($D \gg h\nu$). The negative observation of other XY and intermediate orientation bands at fields lower than 10 kG implies that the D-parameter is larger than $0.70\ cm^{-1}$, meaning that this centre must show a more distorted environment.

Conclusions

The hydrophobic methyl groups of the *tert*-butylammonium cation tend to pack forming hydrophobic regions. The compounds described in this work show a two-dimensional arrangement of anions and cations in which the distance between anion layers of 13.65 Å for both compounds, and consequently single crystals of these compounds are quite easily exfoliated. Some differences can be noticed with respect to the polyanion layers: in compound **1** the polyanions form rows through $O_{poly} \cdots O_{poly}$ hydrogen bonds, following the b-axis, which are connected by the water molecules, while in compound **2** the polyanions are disposed in a two-dimensional arrangement, based on $O_{poly} \cdots O_{poly}$ hydrogen bonds, in which the water molecule and the *tert*-butylammonium cation reinforce these contacts. The influence of protonation is clearly visible in the degree of hydration. The higher the polyanion's degree of protonation, the smaller is the number of water molecules in the compound.

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References

1. Evans, H. T. *J. Am. Chem. Soc. 70* (1948) 1291.
2. Evans, H. T. *Acta Crystallogr., Sect. B 30* (1974) 2095.
3. Tsigdinos, G. A. *Top. Curr. Chem. 76* (1978) 1.
4. Kondo, H., Kobayashi, A. and Sasaki, Y. *Acta Crystallogr., Sect. B 36* (1980) 661.
5. Angus, H. J. F., Briggs, J. and Weigel, H. *J. Inorg. Nucl. Chem. 33* (1971) 697.
6. Filowitz, M., Klemperer, W. G., Messerie, L. and Shum, W. *J. Am. Chem. Soc. 98* (1976) 2345.
7. Filowitz, M., Ho, R. K. C., Klemperer, W. G. and Shum, W. *Inorg. Chem. 18* (1979) 93.
8. Robl, C. and Frost, M. *Z. Anorg. Allg. Chem. 619* (1993) 1132.
9. Robl, C. and Frost, M. *Z. Anorg. Allg. Chem. 619* (1993) 1137.
10. Robl, C. and Frost, M. *Z. Anorg. Allg. Chem. 619* (1993) 1624.
11. Robl, C. and Frost, M. *Z. Anorg. Allg. Chem. 619* (1993) 1834.

12. Matajevic, E., Kerker, M., Beyer, H. and Theubert, F. *Inorg. Chem. 2* (1963) 581.
13. Perloff, A. *Inorg. Chem. 9* (1970) 2228.
14. Lee, H. Y., Park, K. M., Lee, U. and Ichida, H. *Acta Crystallogr., Sect. C 47* (1991) 1959.
15. Ito, F., Ozeki, T., Ichida, H., Miyamae, H. and Sasaki, Y. *Acta Crystallogr., Sect. C 45* (1989) 946.
16. Ozawa, Y., Hayashi, Y. and Isobe, K. *Acta Crystallogr., Sect. C 47* (1991) 637.
17. Baker, L. C. W., Foster, G., Tan, W., Scholnick, F. and McCutheon, T. P. *J. Am. Chem. Soc. 77* (1955) 2136.
18. Weakley, T. J. R. *Struct. Bonding 18* (1974) 131.
19. Botto, I. L., García, A. C. and Thomas, H. J. *J. Phys. Chem. Solids 53* (1992) 1075.
20. Pope, M. T. *Heteropoly and Isopolyoxometalates*, Springer-Verlag, New York 1983.
21. Lee, U. and Sasaki, Y. *Chem. Lett.* (1984) 1297.
22. Jeannin, Y., Herve, G. and Proust, A. *Inorg. Chim. Acta 198–200* (1992) 319.
23. Román, P., San José, A., Luque, A. and Gutiérrez-Zorrilla, J. M. *Acta Crystallogr., Sect. C 50* (1994) 1189.
24. Wéry, A. S. J. *Ph.D. Thesis*, Universidad del País Vasco, Bilbao 1995.
25. Román, P., San José, A., Luque, A. and Gutiérrez-Zorrilla, J. M. *Z. Kristallogr. 234* (1993) 179.
26. Walker, N. and Stuart, D. *Acta Crystallogr., Sect. A 39* (1983) 158.
27. Beurkens, P. T., Admiraal, G., Beurkens, G. Bosman, W. P., García-Granda, S., Gould, R. O., Smits, J. M. M. and Smykalla, C. The DIRDIF program system. Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands 1992.
28. Stewart, J. M., Machin, P. A., Dickinson, C. W., Ammon, H. L., Heck, H., Flack, H. The XRAY 76 System, Technical report TR-446, Computer Science Center, University of Maryland, College Park, MD 1976.
29. Cabello, C. I., Botto, I. L. and Thomas, H. J. *Thermochim. Acta 232* (1994) 183.
30. Nomiya, K., Takahashi, T., Shirai, T. and Miwa, M. *Polyhedron 6* (1987) 213.
31. Brown, I. D. and Wu, K. K. *Acta Crystallogr., Sect. B 32* (1976) 1957.
32. Gutiérrez-Zorrilla, J. M. *Ph.D. Thesis*, Universidad del País Vasco, Bilbao 1984.
33. Brown, I. D. *Chem. Soc. Rev. 7* (1978) 359.

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