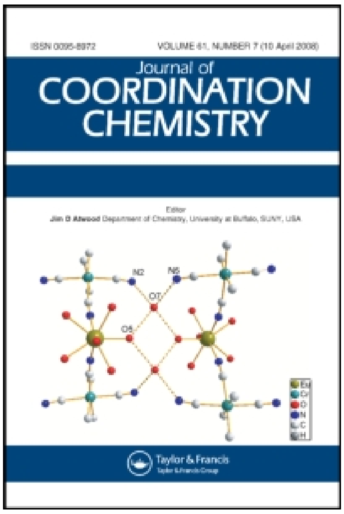

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Maria Fernanda P. Silva[a]; Ana Maria V. Cavaleiro[a]; Júlio D. Pedrosa De Jesus[a]
[a] Departments of Chemistry, University of Aveiro, Aveiro, Portugal

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SYNTHESIS AND CHARACTERISATION OF A NEW NIOBATE COMPLEX WITH CHROMIUM(III)

MARIA FERNANDA P. SILVA, ANA MARIA V. CAVALEIRO* and JÚLIO D. PEDROSA DE JESUS

Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

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A new hexaniobate complex with chromium(III) was prepared and characterised by analytical and spectroscopic techniques. The compound is a violet, non-crystalline solid, formulated as $[Cr_2(\mu\text{-}OH)(H_3Nb_6O_{19})(en)_3(H_2O)]$. It was synthesised in aqueous solution by reaction of $[Cr(en)_3]^{3+}$, en = ethylenediammine, with the hexaniobate anion $[Nb_6O_{19}]^{8-}$, at pH 8. Thermal decomposition yielded a mixture of $CrNbO_4$ and Nb_2O_5. The synthesis of this compound shows that the hexaniobate anion may form complexes at lower pH values than previously reported.

Keywords: Chromium(III) complex; niobate complex

INTRODUCTION

Compounds with hexaniobate anions, $[H_xNb_6O_{19}]^{(8-x)-}$, and transition metals are potential precursors for the synthesis of mixed niobium oxides. Several types of compounds may be envisaged, like salts of the niobates and transition metal complexes or coordination compounds prepared by taking advantage of the coordinating abilities of the polyoxometalate $[Nb_6O_{19}]^{8-}$. This polyoxometalate is known to form complexes in which it is bound to a metal ion as a terdentate ligand, through three bridging oxygen atoms, as shown in Figure 1.[1,2]

Several isostructural polyoxometalate anions $[M_6O_{19}]^{n-}$ are known, with M = Mo, W, V, Nb, Ta.[3] The low basicity of the oxygen atoms on the

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* Corresponding author.

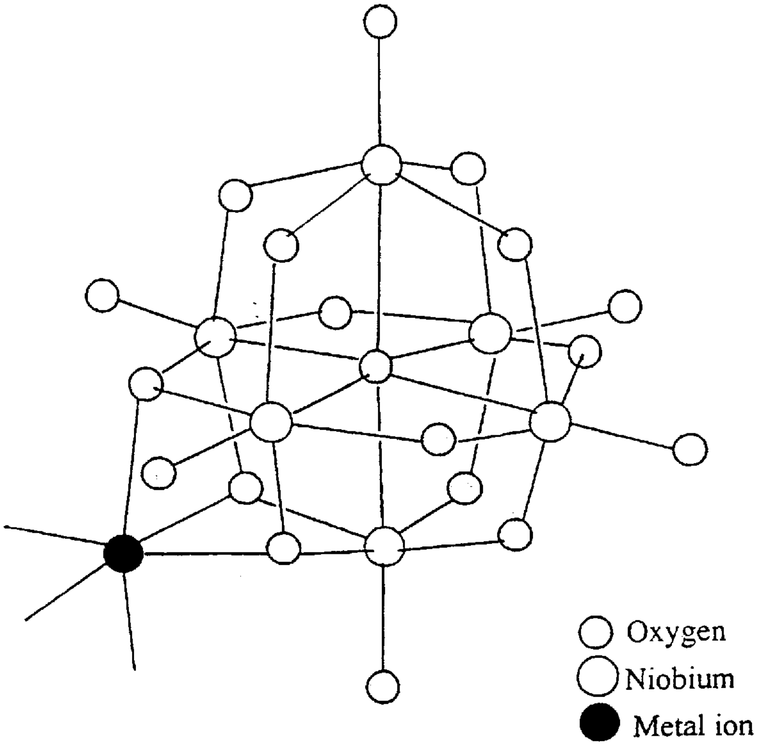

FIGURE 1 Mode of coordination of the hexaniobate anion.

surface of the polyanions makes them poor ligands. Activation of the $[M_6O_{19}]^{n-}$ anions has been achieved by substitution of one or two M atoms by other metals.[4] However, with the unsubstituted isopolyanions only a few complexes with the hexavanadate[5,6] and hexaniobate[1,2,7-9] are known.

Two types of complexes with hexaniobate and first-row transition metals have been reported, with ligand to metal ratios of 1 and 2, respectively. Examples of each type are $[M(Nb_6O_{19})(en)]^{5-}$, M = Cr^{III}, Co^{III}, en = ethylenediamine[8] and $[M(Nb_6O_{19})_2]^{12-}$, M = Mn^{IV}, Ni^{IV}.[1,7,9]

In this paper we report the synthesis and characterisation of a new hexaniobate complex with chromium(III), with the formula $[Cr_2(\mu\text{-}OH)(H_3Nb_6O_{19})(en)_3(H_2O)]$. This compound was prepared from aqueous solutions with lower pH (pH ≈ 8) than all the known compounds with the hexaniobate, including the related coordination compound, $Na_5[Cr(Nb_6O_{19})(en)] \cdot 18H_2O$.[8]

EXPERIMENTAL

Analysis and Physical Measurements

Elemental analysis of Nb and Cr were performed by ICP spectrometry (University of Aveiro, Central Laboratory of Analysis). Hydration water was determined from the weight loss up to 180°C. Total weight loss was calculated from thermogravimetric analysis performed to 800°C, assuming decomposition to a mixture of oxides. Thermogravimetric analyses (TG) between 30–800°C were carried out in air, at $10^\circ C\,min^{-1}$ heating rate, on a Mettler M3 thermobalance equipped with a TC 10A microprocessor. Diffuse reflectance spectra ($200–900\,cm^{-1}$) were registered on a Shimadzu 3100 spectrophotometer, using MgO as reference. Infrared absorption spectra ($400–4000\,cm^{-1}$) were recorded on a Mattson 7000 FTIR spectrometer, using KBr pellets. KBr disks were heated in a oven to 150°C to obtain the spectra of the dehydrated compound. Magnetic susceptibilities were measured by the Evans method, at room temperature, with a Johnson Mattey magnetic susceptibility balance, calibrated against $[HgCo(NCS)_4]$.[10] Diamagnetic corrections were taken from Meites.[11] Magnetic moments were determined assuming that the simple Curie law is obeyed. X-ray powder diffraction patterns were measured on a RigakuD/Max III instrument, using CuKα radiation, in the range $2\theta = 3–50^\circ$.

Synthesis

All chemicals were used as received from suppliers. The following compounds were prepared by reported procedures: $[Cr(en)_3]Cl_3 \cdot 3.5H_2O$,[12] $K_7HNb_6O_{19} \cdot 10H_2O$.[13]

$[Cr_2(\mu\text{-}OH)(H_3Nb_6O_{19})(en)_3(H_2O)] \cdot 11H_2O$

Aqueous solutions of $K_7HNb_6O_{19} \cdot 10H_2O$ (0.55 g, $400\,cm^3$) and $[Cr(en)_3]Cl_3 \cdot 3.5H_2O$ (0.49 g, $50\,cm^3$) were mixed, with stirring. To the resulting solution nearly $3\,cm^3$ of HCl ($0.01\,mol\,dm^{-3}$) were added very slowly, until pH 8 was reached. The solution was concentrated by evaporation on a hot plate, until the formation of a violet precipitate was observed. A gelatinous violet compound precipitated overnight. The obtained solid was filtered and washed with dilute hot aqueous KOH (pH 8), ethanol/water (50%), ethanol and acetone and dried in a vacuum desiccator. Yield: 90%. *Anal.* found (%): Nb, 38,7; Cr, 7.4; C, 5.46; H, 3.52; N, 6.13; hydration H_2O, 14.42;

% weight loss, 31.29. Calcd. (%): Nb, 40.3; Cr, 7.5; C, 5.22; H, 3.79; N, 6.08; hydration H_2O, 14.34; % weight loss (TG), 31.30. The absence of K^+ in the compound was confirmed by ICP analysis.

RESULTS AND DISCUSSION

Synthesis and Characterisation

The chromium complex reported in this paper, containing hexaniobate and ethylenediamine as ligands, is a violet, non-crystalline solid, insoluble in water, ethanol or acetone. Elemental and thermogravimetric analysis are in accordance with the proposed formula $[Cr_2(\mu\text{-}OH)(H_3Nb_6O_{19})(en)_3(H_2O)] \cdot 11H_2O$ (I). This compound was synthesised from a dilute aqueous solution of hexaniobate and $[Cr(en)_3]^{3+}$, at pH 8, after prolonged heating.

The infrared spectra present bands characteristic of the hexaniobates and of ethylenediamine. Hexaniobate anions give rise to bands in the 400–900 cm^{-1} region assigned to Nb=O and Nb–O–Nb stretching vibrations.[14–16] Spectra represented provide evidence for the presence of the intact $[Nb_6O_{19}]^{8-}$ moiety in the complex, most probably di- or tri-protonated. The relevant frequencies are listed in Table I, together with those of some potassium niobates.

Frequencies associated with hexaniobate anions have been found to depend on protonation and also on the degree of hydration of the salts.[16] Thus, comparisons with simple niobate salts have to be made with care. Nevertheless, the positions of the bands between 500 and 900 cm^{-1} in the spectra of complex (I) are slightly shifted to higher frequencies when compared with those of $[H_xNb_6O_{19}]^{(8-x)-}$, $x = 1\text{–}3$, anions in potassium or sodium salts,[15,17] whereas the band around 400 cm^{-1} moves to lower frequencies.

One strong band observed at 3420 cm^{-1} was first attributed to ν(OH) of the hydration water. However, after heating the compound at 150°C, this band was still present, albeit with lower intensity, whereas the corresponding

TABLE I Characteristic infrared absorption frequencies[†] in the 900–400 cm^{-1} spectra

Assignment[‡]	*Complex* (I)	$K_7[HNb_6O_{19}] \cdot 10H_2O$	$K_6[H_2Nb_6O_{19}] \cdot 13H_2O$	$K_5[H_3Nb_6O_{19}] \cdot 10H_2O$
$\nu(Nb\text{–}O_t)$	870s	858vs	860vs	860vs
			842s	840sh
$\nu(Nb\text{–}O_b)_{asym}$	770sh	770sh	770sh	780m
	685vs	670vs	670vs	663vs
$\nu(Nb\text{–}O_b)_{sym}$	543s	526vs	520vs	525vs
$\nu(Nb\text{–}O_c)$	< 400s	414s	406s	414s

[†] In cm^{-1}; [‡] t = terminal, b = bonding, c = central.

band at 1630 cm^{-1}, due to the water bending mode, had almost completely disappeared. This indicates the presence of other OH groups. Several of these groups are possibly present, either in the protonated niobate or a Cr–OH–Cr bridge.[18]

Usually Cr–OH–Cr bridges absorb at 550–580 cm^{-1},[18–20] but this could not be observed in this complex due to strong Nb–O–Nb vibrations. Careful comparison of the spectrum of compond (I) with those of all the $[H_xNb_6O_{19}]^{6-}$ anions (potassium salts, $x = 0–3$) shows that the former has two weak bands, observed as shoulders, in the 500–520 cm^{-1} range, not present in the latter. These values seem too low to correspond to the Cr–OH–Cr deformation. They are possibly, due to the coordination of the bridging oxygens of the hexaniobate.

Values of the magnetic moment and diffuse reflectance spectra are typical of Cr(III) complexes. The magnetic moment at 20°C (per chromium atom) was $\mu = 3.48$ BM. This is comparable to those of other monobridged dinuclear chromium complexes.[20,21] The visible spectrum has two bands, centred at $\lambda = 400$ and 557 nm. The positions of these bands are near those reported for the $[Cr(Nb_6O_{19})(en)(H_2O)]^{5-}$ anion.[8] In O_h symmetry those bands correspond to the $^4T_{2g} \leftarrow {}^4A_{2g}$ and $^4T_{1g} \leftarrow {}^4A_{2g}$ transitions. As commonly found for *cis*-$[Cr(en)_2X_2]^x$ and other related complexes, no splitting due to lowering of symmetry was observed.[21] Thus, for comparison, the values $\Delta = 17950$ cm^{-1}, $B = 704$ cm^{-1} and $\beta = 0.77$ were determined as for O_h complexes.[22] These compare with $\Delta = 18900$ cm^{-1} for $[Cr_2(\mu\text{-}OH)_2(en)_4]^{4+}$ [21] and $\Delta = 17800$ cm^{-1}, for $[Cr(Nb_6O_{19})(en)(H_2O)]^{5-}$.[8]

Thermal decomposition occurred in three steps. The first was attributed to the loss of hydration water. Decomposition of the organic part of the complex occurred between 200°C and 420°C. The last step, observed around 520°C, corresponds to the final decomposition to oxides. The residue obtained after decomposition at 800°C was shown to be a mixture of Nb_2O_5 and $CrNbO_4$ by powder X-ray diffraction.[23]

Structure of the Complex

Elemental analyses of the prepared compound showed that the solid had both Nb/Cr = 3 and Cr/en = 1.5 ratios. Infrared spectra gave evidence that the hexaniobate anion was intact in the complex and visible spectra showed that it is coordinated to chromium. The simplest structure in accordance with these facts is represented in Figure 2. A water molecule coordinated to one of the chromium atoms completes the coordination of this metal. The protonated form $[H_3Nb_6O_{19}]^{5-}$ is known to be the predominant form in aqueous solutions of pH 8–9.[24,25]

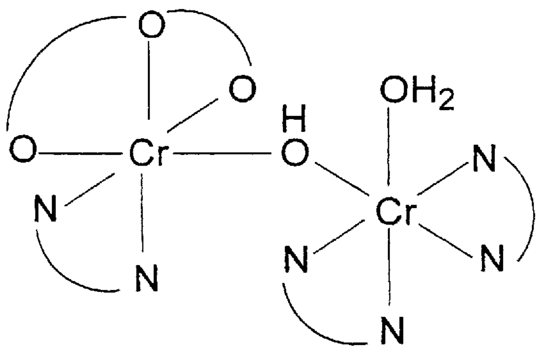

FIGURE 2 Schematic representation of $[Cr_2(\mu\text{-}OH)(H_3Nb_6O_{19})(en)_3(H_2O)]$.

The formation of dimeric chromium complexes with hydroxide or oxide bridges is very common and is well-established.[21,26] It is assumed to occur for complex (I) in view of the stoichiometric Nb/Cr ratio and the fact that chromium complexes prepared in neutral or slightly alkaline aqueous solutions are usually dimeric. Evidence for the presence of an OH^- bridge is not clear-cut. Under the synthetic conditions employed, however, the formation of a O^{2-} bridge seems to be more improbable. The observed magnetic moment is more in accordance with hydroxide than with an oxide bridge.[20,21] We excluded the possibility of formation of other possible compounds, such as hexaniobate salts of known chromium complexes $[Cr_2(\mu\text{-}OH)_2(en)_4]^{4+}$, $[Cr_2(\mu\text{-}OH)(en)_4(H_2O)_2]^{5+}$ or even $[Cr_4(\mu\text{-}OH)_6(en)_6]^{6+}$ on the basis of the stoichiometry and electronic spectroscopy.[21,26]

The reaction of $[Cr(en)_3]^{3+}$ with the hexaniobate anions, in alkaline conditions, was used by Flynn and Stuck to synthesise $Na_5[Cr(Nb_6O_{19})(en)(H_2O)]\cdot 18H_2O$.[8] We have used almost the same reactants, but in more dilute solutions (to prevent the precipitation of an intermediate compound) and have lowered the pH to about 8. Equations (1) and (2) represent the reaction under the conditions reported here and those used by Flynn and Stuck and show clearly the possible formation of the two different compounds:

$$2[Cr(en)_3]^{3+} + H[Nb_6O_{19}]^{7-} + H^+ + 2H_2O \rightarrow [Cr_2(\mu\text{-}OH)(H_3Nb_6O_{19})(en)_3(H_2O)] + 3en \qquad (1)$$

$$[Cr(en)_3]^{3+} + H[Nb_6O_{19}]^{7-} + OH^- \rightarrow [Cr(Nb_6O_{19})(en)(H_2O)]^{5-} + 2en \qquad (2)$$

Acknowledgements

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