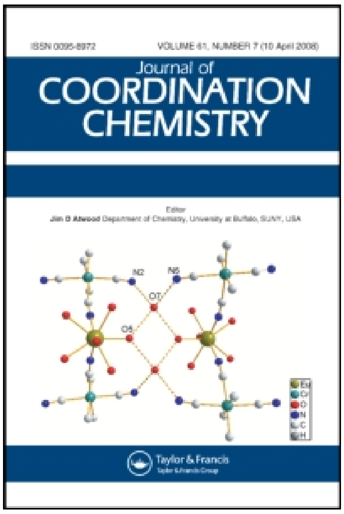

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VIOLURATO COMPLEXES OF Cr(III). SYNTHESIS AND CHARACTERIZATION. PROTONATION-DEPROTONATION EQUILIBRIA OF THE COORDINATED LIGANDS. EVIDENCE OF THE COORDINATION OF VIOLURIC ACID AS A NEUTRAL LIGAND

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VIOLURATO COMPLEXES OF Cr(III). SYNTHESIS AND CHARACTERIZATION. PROTONATION-DEPROTONATION EQUILIBRIA OF THE COORDINATED LIGANDS. EVIDENCE OF THE COORDINATION OF VIOLURIC ACID AS A NEUTRAL LIGAND

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The formation of violurato complexes of Cr(III) has been studied in aqueous solution. Two compounds, $[Cr(H_2V)_3].5H_2O$ and $Na[Cr(H_2V)_2(OH)_2].4H_2O$ have been synthesized and characterized. $[Cr(H_2V)_3]$ behaves in aqueous solution as a triprotic acid but it can also add a proton yielding $[Cr(H_2V)_2(H_3V)]^+$. The acidity constants of this species have been determined: $pK_{a1} = 3.32$, $pK_{a2} = 4.25$, $pK_{a3} = 4.83$ and $pK_{a4} = 6.99$ (25°C, 0.1 M $NaClO_4$). $[Cr(H_2V)_2(OH)_2]^-$ undergoes a deprotonation of the two H_2V^- ligands and a protonation of the hydroxo ligands. The acidity constants of $[Cr(H_2V)_2(H_2O)_2]^+$ have been also determined: $pK_{a1} = 3.5$, $pK_{a2} = 4.6$, $pK_{a3} = 7.1$ and $pK_{a4} = 9.2$ (25°C, 0.1 M $NaClO_4$). The coordination of a violuric acid molecule as a neutral ligand is reported for the first time.

INTRODUCTION

In the last years, the metal complexes of violuric acid, H_3V, (5-oxime,2,4,5,6(1H,3H)-pyrimidinetetrone), with several transition metal ions have been studied.[1-10] In these complexes the ligand is the dihydrogenviolurate anion, H_2V^-, which acts as a strong field bidentate ligand.[1-3] This ligand is linked to the metal ions via the oxime nitrogen atom and one of the neighbor carbonyl oxygen atom[4-6] (Figure 1).

Although H_3V is a triprotic acid[7], both imino groups have a very low acidity ($pK_{a1} = 4.2$, $pK_{a2} = 9.6$, $pK_{a3} = 13.7$), so that, except in a very basic medium, dihydrogenviolurate anion, H_2V^-, is the predominant species in the aqueous deprotonation of violuric acid. However, the coordination of H_2V^- anion to a metal ion increases remarkably the acidity of

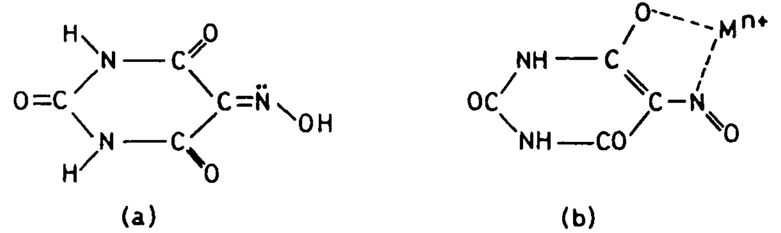

FIGURE 1 a) violuric acid; b) dihydrogenviolurate anion as a bidentate ligand.

one of the NH groups that loses a proton much more easily than when free. Thus, in aqueous solution, $Co(H_2V)_3$ behaves as a triprotic acid, being for pH $\geqslant$ 7 tris(hydrogenviolurato)cobaltate(III), $[Co(HV)_3]^{3-}$, the predominant species.[8]

As there were no previous studies about the chromium(III)-violuric acid interaction, it seemed interesting to perform it and compare the results with those of the previously studied Co(III)-H_3V system.

In the present work, we investigate the formation, syntheses and properties of the chromium(III) violurate complexes as well as the protonation-deprotonation equilibria of the coordinated ligands.

EXPERIMENTAL

Synthesis of Tris(dihydrogenviolurato)chromium(III) Pentahydrate

1.33 g of $Cr(NO_3)_3.9H_2O$ are dissolved in 25 mL of water, and diluted ammonia is added until complete precipitation of chromium(III) hydroxide has occurred. After washing the obtained hydroxide, 1.75 g of violuric acid are added to 75mL of distilled water. The resulting mixture is heated at 40°-50°C in a water bath until complete disolution is obtained. The brown-reddish solution is then taken to dryness. The resulting solid residue is repeatedly washed with water and then with acetone. Finally, the obtained product is dried in an air stream. Yield: 40-50%.

Anal. Calcd.: Cr, 8.52; C, 23.6; N, 20.65. Found.: Cr, 8.45; C, 23.6; N, 20.5.

Synthesis of Sodium di(hydroxo)bis(dihydrogenviolurato)chromate(III) Tetrahydrate

2.15 g of $NaH_2V.2H_2O$ and 2 g of $Cr(NO_3)_3.9H_2O$ are dissolved in 75 mL of water. The brown-reddish solution presents a pH value about 4. Then, $NaHCO_3$ is added until solution pH is ~5.5 appearing very slowly a very light brown precipitate. The obtained compound is filtered, washed first with very cold water and then with acetone. Finally, it is dried in an air stream. Yield: ~30%

Anal. Calcd.: Cr, 10.54; C, 19.47; N, 17.03; Na, 4.66. Found.: Cr, 10.6; C, 19.45; N, 16.95; Na, 4.6.

Violuric acid and sodium dihydrogenviolurate were obtained as previously reported.[2,9] $Cr(NO_3)_3.9H_2O$ and all the other chemicals were Merck reagents p.a. The thermal stability of the isolated complexes was studied with a Setaram balance recording simultaneously the TG, DTG and ATD curves. Magnetic measurements were made by the Gouy method at room temperature; Pascal's constants were used to correct for ligand diamagnetism.

A 0.1*M* carbonate free sodium hydroxide aqueous solution, was used as a titrant. Potential measurements were performed with a Radiometer 84 pH-meter at 25.0 ± 0.1°C in N_2 atmosphere and in 0.1 M $NaClO_4$. Nernst's equation, $E = E^{\circ\prime} + 0.0591 \log[H^+]$ was strictly obeyed by the electrode. Accurate concentration of the basic titrant as well as the $E^{\circ\prime}$ value, were determined with a perchloric acid aqueous solution before each titration series.

The spectrophotometric study of the Cr(III)-H_3V system, was carried out at constant hydrogen ion concentration by adding the adequate buffer just before making the measurements. Since the complex formation was very slow, solutions were allowed to evolve for five days. Absorption spectra were registered with a UV-V Pye Unicam SP 100-8 spectrophotometer. Selected wavelength measurements were made with a Beckman Du spectrophotometer with 1 cm width cells. The measurements at 360 and 370 nm. were corrected for the ligand absorbance.

RESULTS

When mixing aqueous solutions of $[Cr(H_2O)_6](NO_3)_3$ and NaH_2V, appears a brown-reddish colour that slowly intensifies with the time. The absorption spectrum of these solutions is very similar to the one of the free ligand. However, in the 360-400 nm. wavelength range the absorption of a 10^{-4} M ligand solution is negligible whereas the absorption of the complex is considerable. Application of the Job's method in this wavelength range at pH = 5.3 showed the formation of a 1 : 3 (M : L) complex (Figure 2). In this medium the complex is unstable since although very slowly, a progressive diminution in absorption measurements takes place. After a few days decoloration becomes complete. Decomposition goes faster as the solution pH is increased. As a matter of fact, at pH = 8.2 (H_3BO_3-NaOH buffer) the Job curve maximum occurs for 1 : 2 stoichiometry and absorbance values decrease faster than at pH = 5.3. Because, even at pH = 3.5, the complex is unstable in the buffer used, it was added to Cr(III) and H_2V^- solutions that had been allowed to evolve for several days just before performing the absorption measurements. In unbuffered solutions the complex formation brings about an acidification of the solution. It indicates that coordination of H_2V^- to Cr(III) yields the deprotonation of the coordinated ligand (vide infra).

The syntheses of two complexes of 1 : 3 and 1 : 2 stoichiometry, has been attained in agreement with the solution data. $Cr(H_2V)_3.5H_2O$ is a paramagnetic, brown-reddish compound with μ_{eff} = 3.7 BM. The TG curve reveals that, in N_2 atmosphere, dehydration starts at 60°:

$$Cr(H_2V)_3 \cdot 5H_2O \xrightarrow[60°C]{endo-} Cr(H_2V)_3 \xrightarrow[225°C]{exo-} \text{decomp.}$$

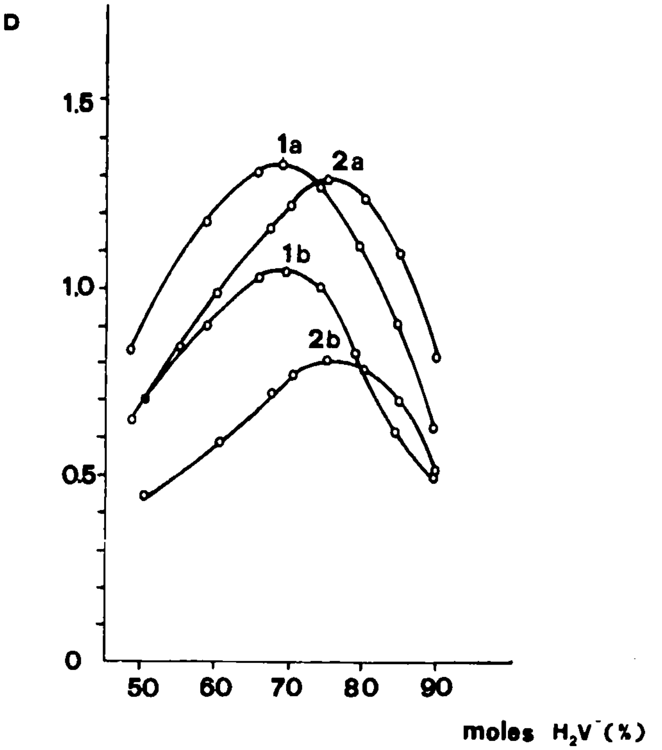

FIGURE 2 Job plots: a) λ = 360 nm, b) λ = 370 nm, 1) pH = 8.2, 2) pH = 5.3.

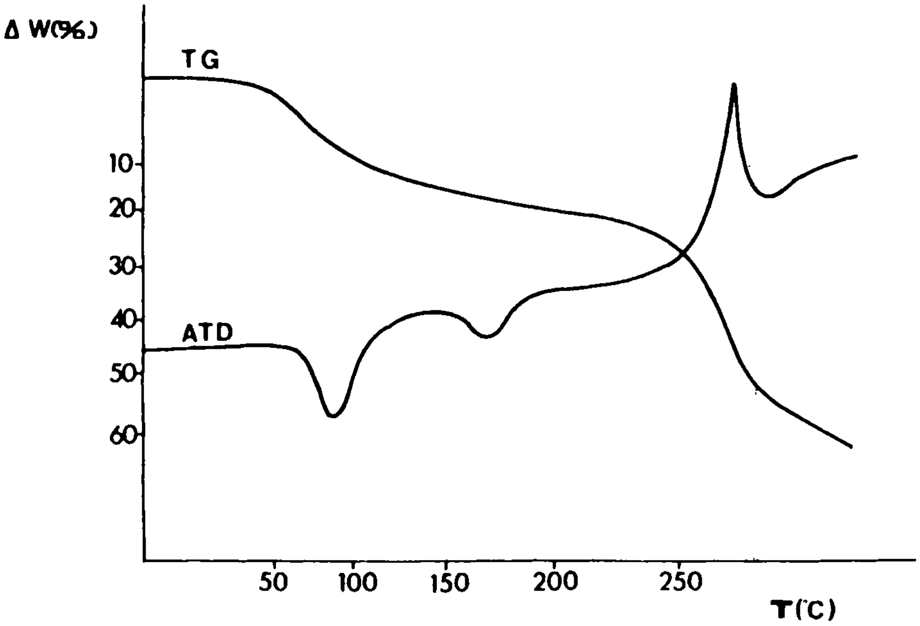

FIGURE 3 TG and ATD curves for $Na[Cr(H_2V)_2(OH)_2].4H_2O$. Endothermic weight losses correspond to four and one water molecules respectively for each Cr(III).

The anhydrous complex is stable up to 225°C beginning an exothermic decomposition at this temperature. The pentahydrate is rather soluble in water and its solutions have acid character. It is much more soluble in hot water and in basic medium; it is dissolved instantaneously in aqueous $NaHCO_3$ with CO_2 release. $Na[Cr(H_2V)_2(OH)_2].4H_2O$ is a paramagnetic, light-brown solid with $\mu_{eff} = 3.8$ BM the TG and ATD curve (Figure 3) reveal that, in N_2 atmosphere, dehydration starts at 80°C with a first weight loss involving four water molecules; at 165°C a second loss involving one water molecule starts. This second loss originates by intermolecular condensation yielding probably a dioxobridged dimer. The formation of oxo or hydroxo bridges is well known in the coordination chemistry of Cr(III) [11].

$$Na[Cr(H_2V)_2(OH)_2]\cdot 4H_2O \xrightarrow[80^\circ C]{\text{endo-}} Na[Cr(H_2V)_2(OH)_2]$$

$$\xrightarrow[165^\circ C]{\text{endo-}} 1/2\, Na_2[Cr(H_2V)_2O]_2 \xrightarrow[240^\circ C]{\text{exo-}} \text{decomp.}$$

The resulting compound is stable up to 240°C beginning an exothermic decomposition at this temperature. The tetrahydrate is rather soluble in water. It is much more soluble in hot water and in basic or acid medium.

Protonation–Deprotonation Equilibria of the Coordinated Ligands

We have titrated $\sim 10^{-3}$ M $[Cr(H_2V)_3].5H_2O$ solutions, with or without adding a strong acid, using as a titrant NaOH 0.1 M. The protonation curve of the system, $(\bar{j}, -\log[H^+])$, has been obtained from experimental data; $\bar{j}$ is the average number of protons bound to each base, in this case to $Cr(H_2C)_3^{3-}$. The complex deprotonation could not be followed for $\bar{j} \leq 0.6$ values

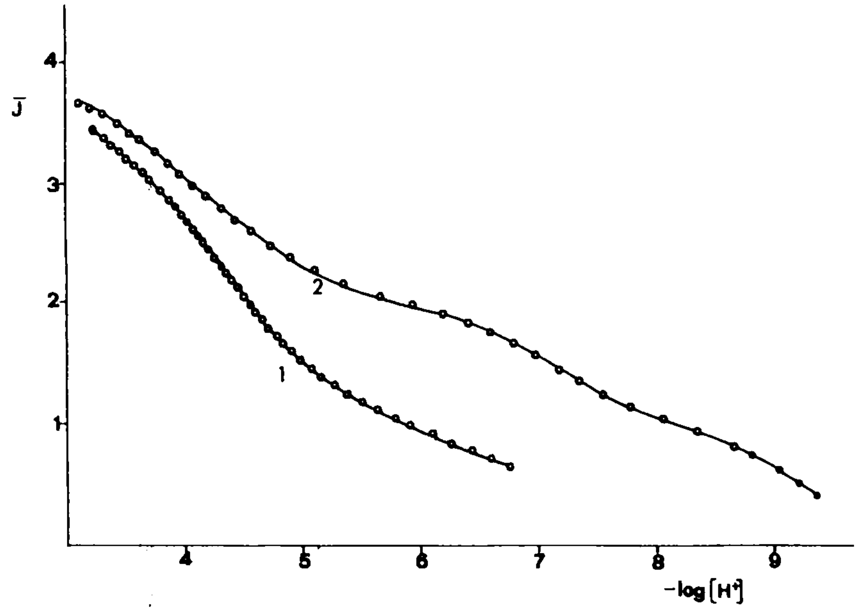

FIGURE 4 Protonation curves for Cr(III)-violurato complexes at 25°C and 0.1 M $NaClO_4$. Circles represent experimental points. The curves are calculated for the computed constants. 1) $[Cr(H_2V)_2(H_3V)]^+$ Only a fraction of the experimental points are plotted. $\beta_1 = 9.7 \times 10^6$, $\beta_2 = 6.5 \times 10^{11}$, $\beta_3 = 1.1 \times 10^{16}$ and $\beta_4 = 2.4 \times 10^{19}$. 2) $[Cr(H_2V)_2(H_2O)_2]^+$, $\beta_1 = 1.6 \times 10^9$, $\beta_2 = 2.1 \times 10^{16}$, $\beta_3 = 9.0 \times 10^{20}$ and $\beta_4 = 3.1 \times 10^{24}$.

because in this range, experimental data were not reproducible. This fact agrees with the observed instability of the complex in basic medium. The obtained results (Figure 4) indicate that $[Cr(H_2V)_3].5H_2O$ similarly to $[Co(H_2V)_3].5H_2O$ behaves in aqueous solution as a triprotic acid losing a proton for each coordinated ligand. However, the j values tend to a maximum of 4 whereas in the Co(III) case it tended to 3. It means that $Cr(HV)_3^{3-}$ anion can get four protons. Therefore, the initial $Cr(H_2V)_3$ species not only bears a deprotonation but a protonation to give the cationic $[Cr(H_2V)_2(H_2V)]^+$ species in which one of the ligands has to be a violuric acid molecule instead of a dihydrogenviolurate anion. The overall association constants β_j were determined by using a combination of the Rossotti and Rossotti's extrapolation graphic method[12] and one electronic computation method based on a no linear regression program. The obtained values are $\beta_1 = 9.7 \times 10^6$, $\beta_2 = 6.5 \times 10^{11}$, $\beta_3 = 1.1 \times 10^{16}$ and $\beta_4 = 2.4 \times 10^{19}$ ($NaClO_4$ 0.1 M, 25°C) corresponding to the following $[Cr(H_2V)_2(H_3V)]^+$ acidity constants $pk_{a1} = 3.32$, $pk_{a2} = 4.25$, $pk_{a3} = 4.83$ and $pk_{a4} = 6.99$. In these calculations 95 experimental points from three independent titrations have been used. The theoretical protonation curve calculated from the computed constants fits very well the experimental data (standard deviation $\sigma = 0.017$). The distribution (α_n, $-\log[H^+]$) for the species in solution is plotted in Figure 5.

In a similar way, titrating acidified solutions of $[Cr(H_2V)_2(OH)_2]^-$ with NaOH 0.1 M. we have determined the protonation curve that is plotted in Figure 4. It seems apparent that the initial dihydroxo-complex suffers a double protonation to give the cationic diaqua species, $[Cr(H_2V)_2(OH_2)^+$, as well as a double deprotonation to give the anionic $[Cr(HV)_2(OH)_2]^{3-}$ complex. The calculations have been performed with 36 experimental points from a single titration and the agreement between the calculated values and the experimental ones is good ($\sigma = 0.01$). However, reproducibility is not as good as in the 1 : 3 complex and results

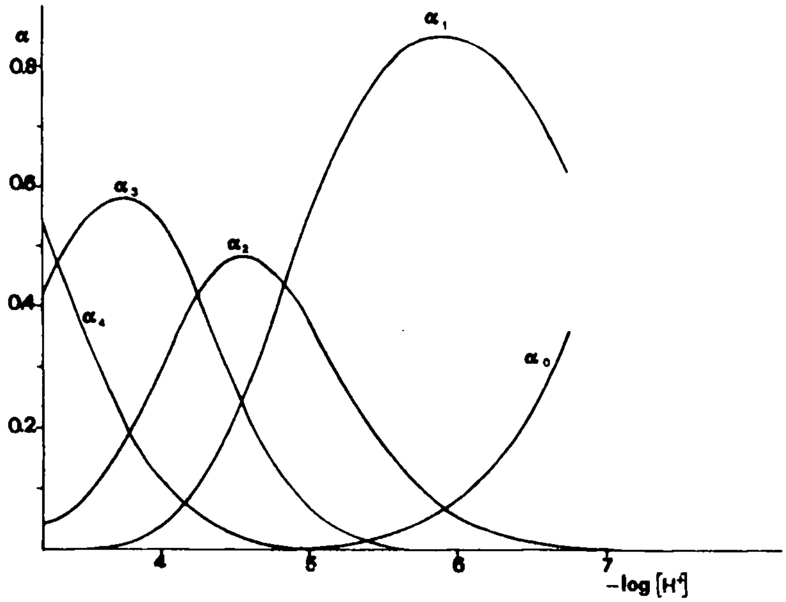

FIGURE 5 Distribution Diagram for the 1 : 3 complex: α_4) $[Cr(H_2V)_2(H_3V)]^+$, α_3) $[Cr(H_2V)_3]$, α_2) $[Cr(HV)(H_2V_2]^-$, α_1) $[Cr(HV)_2(H_2V)]^{2-}$ and α_0) $[Cr(HV)_3]^{3-}$.

obtained from distinct titrations are slightly different. It can be attributed to the fact that a great part of the deprotonation takes place at pH > 7, range in which the complex is not completely stable. These deviations are affecting the pk_a second decimal figures. So, the computed constants are less accurate than the ones obtained for the 1 : 3 complex. The

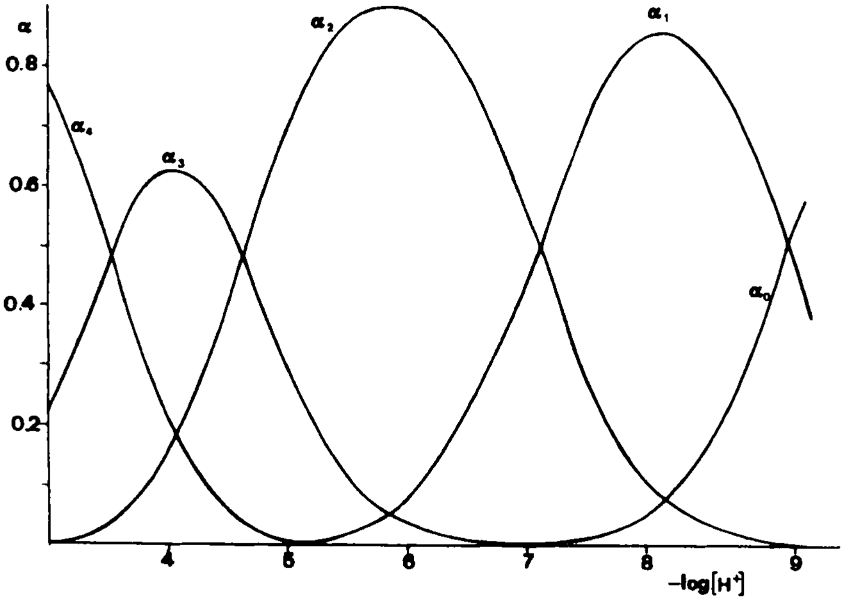

FIGURE 6 Distribution Diagram for the 1 : 2 complex. α_4) $[Cr(H_2V)_2(H_2O)_2]^+$, α_3) $[Cr(H_2V)_2(OH)(H_2O)]$, α_2) $[Cr(H_2V)_2(OH)_2]^-$, α_1) $[Cr(HV)(H_2V)(OH)_2]^{2-}$ and α_0) $[Cr(HV)_2(OH)_2]^{3-}$.

obtained values for the acidity constants of the $[Cr(H_2V)_2(H_2O)_2]^+$ complex are, $pk_{a1} = 3.5$, $pk_{a2} = 4.6$, $pk_{a3} = 7.1$ and $pk_{a4} = 9.2$ ($NaClO_4$ 0.1 M, 25°C). The distribution diagram for the species in solution is plotted in Figure 6.

DISCUSSION

Although Cr(III) forms with H_3V a complex $[Cr(H_2V)_3]$, similar to the one of Co(III), $[Co(H_2V)_3]$, its chemical behavior is fairly different. The Cr(III) complex is much less stable than the one of Co(III), as a result, in the presence of an acetic-acetate buffer (pH ~ 5) it slowly decomposes. It is also more labile suffering in basic medium a fast decomposition.

The other isolated complex, $[Cr(H_2V)_2(OH)_2]^-$, presents 1 : 2 stoichiometry, and it surely means the first step in the basic hydrolysis of the 1 : 3 complex. It is very easily isolated because of the relatively low solubility of its sodium salt. Since t_{2g} orbitals are differently filled in the Cr(III) complex (t_{2g}^3) and in the Co(III) complex (t_{2g}^6), the great stability difference between both complexes is perhaps revealing the importance of π-bonding in these complexes. In this sense, it is significant that the violurato complexes up to now studied are those with metal ions having five or more d electrons Ru(II), Ru(III),[6,7] Fe(II),[3,5] Fe(III),[10] Co(II),[3] Co(III),[8] Ni(II),[2,9] Cu(II),[4] being favorable a low spin configuration with maximum t_{2g} orbitals occupancy.

The acid behavior of $Cr(H_2V)_3$ can be represented by means of the following equations:

$$Cr(H_2V)_3 + H_2O \longrightarrow [Cr(H_2V)_2(HV)]^- + H^+_{aq} \qquad pk_a = 4.25$$

$$Cr(H_2V)_2(HV)^- + H_2O \longrightarrow Cr(H_2V)(HV)_2^{2-} + H^+_{aq} \qquad pk_a = 4.83$$

$$Cr(H_2V)(HV)_2^{2-} + H_2O \longrightarrow Cr(HV)_3^{3-} + H^+_{aq} \qquad pk_a = 6.99$$

These equations correspond to the deprotonation of the three H_2V^- ligands to HV^{2-}. It is apparent that the acidity of the coordinated H_2V^- is much higher than that of the free ligand. $Co(H_2V)_3$ behaves in a similar way, although in this complex due to the higher polarizing power of the Co(III) ion, a stronger increase of the ligand's acidity is produced (pk_a 3.40, 4.34 and 5.20). At pH 4 an additional protonation takes place in the Cr(III) complex. This protonation can only take place on one of the H_2V^- ligands yielding a H_3V molecule. It is the first time that coordination of violuric acid as a neutral ligand has been observed. It is possible because, unlike what happens with most protonable ligands, dihydrogenviolurate anion is attached to the proton and to the metal ion via different donor atoms, the oxime oxygen atom to the proton, the oxime nitrogen atom and one of the carbonyl oxygen atom to the metal ion (Figure 1). Therefore, the metal and hydrogen ions do not exclude each other, although, obviously ligand protonation will modify its coordinating behavior.

Similarly to what happens with H_2V^- anion, the acidity of violuric acid when coordinated to Cr(III) ($pK_a = 3.32$) is higher than when free. From this pk_a value it can be concluded that cationic $[Cr(H_2V)_2(H_3V)]^+$ species will start to be significant in aqueous solution from pH ~ 4 (Figure 5). This protonation has not been found in the study of the Co(III) – H_3V system because due to the Co(III) polarizing power its pk value should be fairly lower than 3.32, and the protonation of the coordinated H_2V^- only could have taken place for very acid pH.

The distribution diagram (Figure 5) reveals that an aqueous $Cr(H_2V)_3$ solution (pH ~ 4) is not only containing two deprotonated species ($\alpha_2 \sim 0.3$, $\alpha_1 \sim 0.05$) but also the protonated species ($\alpha_4 \sim 0.1$). It means that $Cr(H_2V)_3$ simultaneously behaves as an acid and a base. Approximately only a half rests in its molecular form ($\alpha_3 \sim 0.5$). It allows us to realize the reason why in the synthetic procedure it was necessary to evaporate to dryness for obtaining the compound. Once isolated this compound only solubilizes very slowly.

In the case of the $[Cr(H_2V)_2(OH_2)_2]^+$ complex, the ligands bearing deprotonation first are the water molecules. The obtained acidity constants $pk_{a1} = 3.5$, $pk_{a2} = 4.6$ do not differ much from those of the simple hydrated ion $pk_{a1} = 4$, $pk_{a2} = 5.6$.[13] The coordinated H_2V^- ligand are fairly less acid than in the 1 : 3 complex case, being the acidity of the second violurate very similar to the one it has when free. Thus, it can be inferred that the presence of the two hydroxo ligands affects remarkably the acidity of the coordinated H_2V^-. The distribution diagram (Figure 6) allows a better understanding of the synthesis of $Na[Cr(H_2V)_2(OH)_2]$, since $[Cr(H_2V)_2(OH)_2]^-$ is the predominant species at pH = 5.8.

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