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Violurato Complexes of Transition Metals.
III. Synthesis and Characterization of Tris(dihydrogenviolurato)cobalt(III). Deprotonation Equilibria in Aqueous Solution

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The interaction between Co^{2+} aq. and violuric acid (5-isonitroso barbituric) H_3V, in aqueous dilute solution, originates a green complex [1] very easily oxidized by the atmospheric O_2 to a Co(III) complex. Although several authors have studied the formation of this Co(III) complex [2, 3], it has not been isolated nor was its true nature in aqueous solution characterized. Here we report the synthesis and characterization of $Co(H_2V)_3\cdot5H_2O$. It behaves as a triprotic acid in aqueous solution yielding the complex anions $Co(H_2V)_2(HV)^-$, $Co(H_2V)(HV)_2^{2-}$ and $Co(HV)_3^{3-}$. We have studied the deprotonation equilibria and determined the acidity constants of $Co(H_2V)_3$. Although these equilibria are overlapped (see Fig. 4) it is possible to isolate each one of the complex anions by selective precipitation with a suitable counter ion. Thus we have obtained the compounds $Cs[Co(H_2V)_2(HV)]\cdot nH_2O$ (n = 3–4), $[(C_8H_{17})_3(CH_3)N]_2[Co(H_2V)(HV)_2]$ and $[Co(NH_3)_6][Co(HV)_3]\cdot6H_2O$.

Experimental

Synthesis of Tris(dihydrogenviolurato)cobalt(III) Pentahydrate, $Co(H_2V)_3\cdot5H_2O$

A solution of 1.16 g of $Co(NO_3)_2\cdot6H_2O$ in 25 ml of water is added very slowly to a solution of sodium dihydrogenviolurate obtained dissolving 1.88 g of violuric acid in 125 ml of water with excess of $NaHCO_3$. During the addition a stream of air is passed through the solution. The resulting orange–red solution is filtered, if necessary; the filtrate is acidified carefully (pH ~ 3) and allowed to crystallize overnight. The reddish needle shaped crystals are washed with cold water and dried in the air (yield ~ 1.3 g). *Anal.* Found: Co 9.6%; N 20.5%, C 23.4%; H 2.5%. Calc.: Co 9.55%; N 20.41%; C 23.33%, H, 2.59%.

Synthesis of Hexaammincobalt(III) Tris(hydrogenviolurato)cobaltate(III) Hexahydrate, $[Co(NH_3)_6][Co(HV)_3]\cdot6H_2O$

A solution of 1.07 g of $Co(NH_3)_6Cl_3$ is slowly added, with stirring and heating at 60 °C, to a solution of violurato complex of Co(III) obtained as above but without the acidification step. After cooling, the microcrystalline precipitate is filtered, washed with water, ethanol, and dried in the air. *Anal.* Found: Co 14.7%; C 18.30; H 3.95%. Calc.: Co 14.86%; C 18.15%; H 4.16%.

Synthesis of Trioctylmethylammonium Bis(hydrogenviolurato)dihydrogenviolurato Cobaltate(III), $[(C_8H_{17})_3(CH_3)N]_2[Co(H_2V)(HV)_2]$

An ethanolic solution of trioctyl methylammonium chloride (0.8 g in 50 ml) is slowly added, with strong stirring, to a solution of 0.5 g of $Co(H_2V)_3\cdot5H_2O$ in 400 ml of water, heated at 60 °C. The amorphous precipitate is repeatedly washed with water, then ether, and crystallized from a methanol–water (2:1) solution by room temperature evaporation. *Anal.* Found: Co 4,5%; C 60%; H 8.0%. Calc.: Co 4.67%; C 59%; H 8.9%.

Synthesis of Cesium Hydrogenvioluratobis(dihydrogenviolurato)cobaltate(III) Trihydrate, $Cs[Co(H_2V)_2(HV)]\cdot3H_2O$

0.38 g of $Co(H_2V)_3\cdot3H_2O$ and 0.06 g of $NaHCO_3$ are dissolved in 15 ml of water heating slightly. Then 10 ml of a saturated solution of CsCl is added, and the resulting solution is left to crystallize for several hours. The crystals are filtered and washed with a few ml of very cold water and dried in the air. *Anal.* Found: Cs 19.5%; C 20.3%; H 1.90%. Calc.: Cs 18.64%; C 20.2%, H 1.54%.

Violuric acid was supplied by Eastman Kodak, trioctyl methylammonium chloride by Serva Feinbiochemica (Heidelberg), and all the other chemicals were Merck reagents. The thermal stability of the isolated complexes was studied with a Setaram balance recording simultaneously the TG, DTG, and ATD curves. Conductivity measurements have been performed with a Radiometer CDM3 conductimeter at 25 ± 0.1 °C and magnetic susceptibility measures with a Gouy balance at room temperature.

The acidity constants of the complex $Co(H_2V)_3$ have been determined by potentiometry, at 25 ± 0.1 °C and NaCl 0.475 *M* as background electrolyte, using a Radiometer 26 pH-meter (precision = ±0.01 pH units). The meter was calibrated as a hydrogen-ion concentration probe [4].

Results and Discussion

The $Co(H_2V)_3\cdot5H_2O$ is a diamagnetic complex stable in the air. It is dehydrated to $Co(H_2V)_3\cdot3H_2O$ when introduced in a $CaCl_2$ desiccator; the pentahydrate crystals are fragmented in others much smaller of trihydrate which retain, however, the same crystalline shape. The study of thermal stability by TG and ATD shows that, in the air, dehydration is produced in two well separated steps:

$$Co(H_2V)_3\cdot 5H_2O \xrightarrow[60\,^{\circ}C]{endo} Co(H_2V)_3\cdot 3H_2O \xrightarrow[100\,^{\circ}C]{endo} Co(H_2V)_3$$

The anhydrous complex is stable up to 250 °C, beginning an exothermic decomposition at this temperature.

The pentahydrate is rather soluble in water ($\sim 10^{-3}$ mol/l) and the 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 evolution and by acidification of concentrated solutions it crystallizes again. A potentiometric and conductimetric titration with NaOH 0.1 *M* shows that the complex behaves as a triprotic acid (see Fig. 1). The potentiometric curve is characterized by a well definite inflection at pH ~ 8, when 3 mol of OH^- per mol of the complex have been added, pointing at the formation of tris(hydrogenviolurato)cobaltate(III):

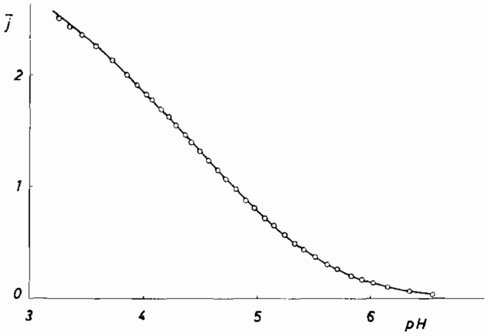

Figure 1. Formation curve $\bar{j}$ (pH) for $Co(H_2V)_3$ at 25 °C in 0.475 *M* NaCl. Circles represent experimental points. The curve is calculated for $\beta_1 = 1.61 \times 10^5$, $\beta_2 = 3.55 \times 10^9$ and $\beta_3 = 9.00 \times 10^{12}$.

$$Co(H_2V)_3 + 3OH^- \rightleftharpoons Co(HV)_3^{3-} + 3H_2O$$

The pH of initial solution as the conductivity decreases (which the NaOH addition produces initially) indicates that aqueous solutions of $Co(H_2V)_3$ are extensively dissociated as follows:

$$Co(H_2V)_3 \; + \; H_2O \rightleftharpoons Co(H_2V)_2(HV)^- + H_3O^+$$

The successive protolysis equilibria are overlapped, small discontinuities in the potentiometric curve at molar ratios OH/Co 1:1 and 2:1 being hardly noticeable. In order to characterize these equilibria quantitatively we have determined the acidity constants of $Co(H_2V)_3$.

The experimental data $\bar{j}$ (pH) are shown in Figure 1, besides the theoretical curve calculated with the computed constants; $\bar{j}$ is the average number of protons bound to each base [5], in this case to $Co(HV)_3{}^{3-}$. The global constants β_j (association) have been computed by the extrapolation method suggested by Rossotti and Rossotti [5]. The values obtained are $\beta_1 = 1.61 \times 10^5, \beta_2 = 3.55 \times 10^9$ and $\beta_3 = 9.00 \times 10^{12}$ (25 ± 0.1 °C, 0.475 *M* NaCl) corresponding to the acidity contants (dissociation) $Ka_1 = 3.9 \times 10^{-4}$, $Ka_2 = 4.5 \times 10^{-5}$ and $Ka_3 = 6.2 \times 10^{-6}$ It is apparent that the coordination to Co(III) causes a strong acidity increase of the violurate ligand H_2V^- (see Fig. 2), that loses a second proton easily whereas the free ligand only is additionally deprotonated in very basic media (Ka_2 for $H_3V \sim 10^{-10}$). Recently S. Sueur, C. Bremard and G. Nowogrocki [6] have reported a similar behaviour, although less accentuated in agreement with the lower charge on the metal ion, for the isoelectronic $Ru(H_2V)_3^-$.

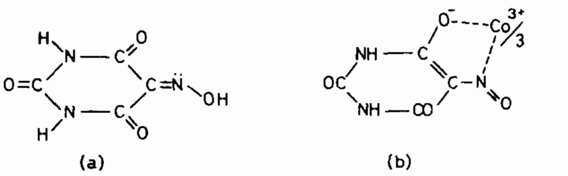

Figure 2. a) Violuric acid H_3V; b) dihydrogenviolurate, H_2V^-, as bidentate ligand.

The distribution diagram α(pH) for the species in solution is plotted in Figure 4. Although the deprotonation equilibria are overlapped it is possible to isolate each one of the complex anions from the solution by selective precipitation with a suitable counterion. We attempted the precipitation of $Co(H_2V)_2(HV)^-$ with the voluminous quaternary ammonium $(C_8H_{17})_3(CH_3)N^+$, previously proved to be effective in the isolation of $Fe(H_2V)_3^-$ by us [7], but curiously the precipitated anion was $Co(H_2V)$-

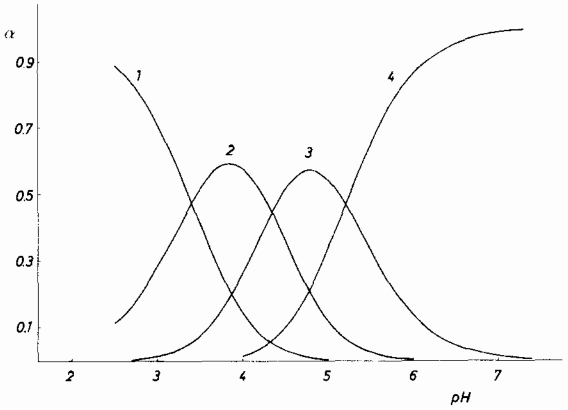

Figure 3. Distribution diagram α(pH) for $Co(H_2V)_3$ solutions. 1) $Co(H_2V)_3$, 2) $Co(H_2V)_2(HV)^-$, 3) $Co(H_2V)(HV)_2^{2-}$, 4) $Co(HV)_3^{3-}$.

$(HV)_2^{2-}$ even to pH values (~ 3) where its equilibrium concentration is nearly negligeable. On the other hand, however, the alkali metal ion Cs^+ allows the crystallization of a water soluble salt of the single charged anion, and the hexaammincobalt(III) cation precipitates $Co(HV)_3^{3-}$ (see Experimental).

Acknowledgments

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