Adsorption of Tetrammine-carbonato and -cis-diaqua and Triethylenetetramine-carbonato and -cis-diaqua Complexes of Cobalt(III) on Titanium Dioxide as Models for the Binding of Uranyl Ions from the Tricarbonatouranyl Complex Ion

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Dedicated to Prof. Dr. W. Beck on the occasion of his 60th birthday

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Anatase, Cobalt(III) Tetrammine Complex Ions, Cobalt(III) Triethylenetetramine Complex Ions, Titanium Dioxide, Uranyl Ion Adsorption

The adsorption of several cobalt(III) complex ions with carbonato or two aqua ligands in cis-position (and related complexes) was studied with the objective of a comparison with the adsorption of UO$_2^{2+}$ ions from [UO$_2$(CO$_3$)$_3$]$^{4-}$ solutions. One CO$_3^{2-}$-group bonded UO$_2^{2+}$ ion was found on the TiO$_2$ surface after vacuum-drying at room temperature. Pre-adsorption of HPO$_4^{2-}$-ions resulted in an increased UO$_2^{2+}$ uptake, whilst coverage of the TiO$_2$ surface with adsorbed Al hydroxo complexes resulted in the opposite effect. The adsorption rate as well as the saturation uptake were higher for the cis-[Co(NH$_3$)$_2$(H$_2$O)$_2$]$^{3+}$ complex than for [Co(NH$_3$)$_3$(CO$_3$)$_2$]$^{3+}$. The diffuse reflectance spectra are similar for both adsorbates. Also with cis-[Co(trien)(H$_2$O)$_2$]$^{3+}$ and [Co(trien)(CO$_3$)$_2$]$^{3+}$ the diaqua is more rapidly adsorbed, whereas the saturation values are very similar. No carbonate is found in the adsorbates with both carbonato complexes, the ammine or trien ligands are retained on the adsorbed Co$^{III}$ ions, however. Temperature-programmed decomposition spectra showed that the bonding of the ammine ligands is weakened in the adsorbed complexes compared to bulk salts of the complex ions. It is concluded that the metal complexes are anchored to the TiO$_2$ surface by bonding to two surface oxygen ions.

Introduction

Titanium dioxide, especially in the form of extensively hydrated hydrolysis products, exhibits a high affinity for uranyl ions or carbonato-uranyl ions [1–5]. Therefore, much research effort has been invested with the objective of a possible application for the recovery of uranium from sea water [6]. However, in recent years the interest seems to have shifted in favor of adsorbents based on polymeric amidoxime derivatives.

Uranium is dissolved in sea water predominantly as the tricarbonato uranyl complex ion, [UO$_2$(CO$_3$)$_3$]$^{4+}$, with an average concentration of 1.39·10$^{-8}$ mol/l [2, 4, 6]. Although there are many publications dealing with this topic, the mechanism of the binding of uranium to the TiO$_2$ surface is not completely understood.

Nearly all investigators agree that some or all of the carbonato ligands are lost in the adsorption process. Keen [7], Maya [8], and Yamashita et al. [4] concluded that UO$_2^{2+}$ or [UO$_2$(OH)$_3$]$^{3-}$ ions are involved in the reaction. There are also references claiming that one carbonato ligand [9] or two carbonato ligands [5, 10, 11] remain with the adsorbed uranyl ion. Surface oxygen atoms of the TiO$_2$ (or Fe$_2$O$_3$) adsorbent become part of the ligand shell encircling the UO$_2^{2+}$ ion. Linking by carbonate bridges has also been suggested [5].

Most of these investigations tried to simulate the conditions in sea water, and therefore low uranium concentrations in the range of 1 μmol/l were used; often bicarbonate was added. We have now studied the adsorption of tricarbonato uranyl ions from relatively concentrated solutions. In order to get a better understanding of the chemisorp-
tion mechanism we have also used several cobalt(III) complexes as model adsorptives. A finely dispersed anatase was used for the present studies since its surface is better characterized than that of "hydrated titanium dioxide", i.e. partly amorphous hydrolysis products. Moreover, our product is non-porous, and exclusion effects due to narrow micropores are avoided. We had shown in early studies that the surface of this TiO₂ material is hydroxylated under normal conditions, and that the hydroxyl population is thermally stable up to 150 °C [12]. The hydroxylated TiO₂ surface is amphoteric, half of the hydroxyl groups have weakly acidic character [13, 14] and half are basic and can be exchanged for other anions such as hydrogen phosphate, hydrogen sulfate [14, 15] or fluoride [16]. The isoelectric point in aqueous dispersion is close to pH 6.5 [13, 14].

The results indicate that the complex ions are attached to the TiO₂ surface by two oxygen ligands in the metal coordination sphere.

**Experimental**

**Materials**

The TiO₂ sample used was a fine-particle-size anatase produced by Degussa AG by flame hydrolysis of TiCl₄. This material, designated P25, has a surface area of 54 m²/g, and a rutile content of 30%. The concentration of surface hydroxyl groups, determined by deuterium isotope exchange [12, 17], is 480 μmol/g (after outgassing at 130 °C). The surface is contaminated with ca. 10 μmol/g Cl⁻.

(NH₄)₄[UO₂(CO₃)₃] was prepared from pure precursors (Fluka AG) according to ref. [18]. Uranium, carbonate and ammonium contents matched with theory.

K₃[Co(CO₃)₃] is soluble in contrast to the Na salt. Therefore, it is easily decomposed in the solid state [19]. Therefore, a solution was synthesized directly according to refs. [19] and [20] by joining slowly solutions of KHC₂O₃ and of CoCl₂ plus H₂O₂. Gas evolution ceased after 30 min, the UV-VIS spectrum of the green solution agreed with that reported in the literature. Addition of KHC₂O₃ was necessary to stabilize dilute solutions of the complex for extended periods. The necessary HCO₃⁻ concentration was determined by monitoring the spectra over time.

[Co(NH₃)₄(CO₃)₂(SO₄)·3H₂O was prepared in crystalline form according to ref. [21]. The identity of the complex was established from NH₃, content and the UV-VIS and IR spectra. The complex decomposed slowly during storage over half a year. The solutions of the complex were stabilized with NH₄HCO₃.

\[ \text{cis-[Co(NH₃)₄(H₂O)₂(SO₄)·3H₂O]·3H₂O} \]

was synthesized according to ref. [21]. The identity was confirmed by the UV-VIS spectra and NH₃ content. Some decomposition was observed after 6 months storage. The solution reacted with 10⁻² M NH₄HCO₃ within a few minutes to the tetraminecarbonato complex as detected by the shift of the adsorption band from 504 nm to 520 nm. Aqueous solutions of the complex were stable for reasonable times (several hours), and were used without stabilization, therefore.

\[ [\text{Co(NH₃)₄(CO₃)₂(NO₃)·H₂O}] \] was made following ref. [22]. Its identity was confirmed by the UV-VIS and IR spectra and the NH₃ content. UV-VIS spectra of the solutions showed rapid decomposition, but the spectra did not change in 24 h when the solution was 0.1 M in NH₄HCO₃.

\[ \text{K[Co(CO₃)₃(NO₃)]} \] was prepared from [Co(CO₃)₃]³⁻ and KNO₃ and precipitated with methanol [23]. For purification the salt was dissolved in water and reprecipitated.

The triethylenetetramine (trien) complexes of cobalt(III) were synthesized following ref. [24], with slight modifications, in the following sequence:

\[ \text{cis-α-[Co(trien)(NO₂)₂]Cl·H₂O (1) conc. HCl} \]

\[ \text{cis-α-[Co(trien)Cl₂]Cl (2) dil. HClO₄} \]

\[ \text{cis-α-[Co(trien)(H₂O)Cl]⁺ (3, in solution) NaHCO₃} \]

\[ \text{cis-α-[Co(trien)(CO₃)Cl]Cl (4, soln.) NaClO₄} \]

\[ \text{cis-β-[Co(trien)(CO₃)ClO₄·H₂O (5) soln., time} \]

\[ \text{cis-β-[Co(trien)(CO₃)ClO₄·H₂O (6) conc. HClO₄} \]

The α-form of the cis-[Co(trien)(CO₃)²⁺ complex transforms slowly into the stable β-form. In the α-form the terminal amino group of the trien ligand are in trans-position, and in cis-position in the β-form.

The identity of the complexes was confirmed by elemental analysis for N and C and by comparison of the IR and UV-VIS spectra with literature data [24, 25]. The positions as well as the relative intensities of the peaks were used for the identification. The α- and β-forms of the trien complexes were identified by their ¹H NMR spectra. The complex-

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Adsorption experiments

The adsorption experiments were performed at room temperature. Usually, 1 g of TiO₂ in 25 ml of solution was agitated for the necessary time predetermined in separate experiments. The TiO₂ was separated from the solution by centrifuging or by filtering through a millipore filter.

Where dry TiO₂ samples with adsorbed complex were needed, the TiO₂ was centrifuged, the cake was rinsed with a little water and then dried in vacuo. Contamination of the sample by crystallized complex seems negligible since dilute solutions were used and the pore volume of the cake is relatively small. During evaporation, the occluded solution is concentrated, resulting in an increased adsorption. Inert salts will finally crystallize, of course.

All adsorption experiments were performed with as little exposure to light as possible. It was shown that near-UV irradiation leads to decomposition of the complexes in the presence of TiO₂ which is known to be a photocatalyst [26-28]. Light of higher-than-band gap energy promotes electrons from the valence band to the conduction band, and the resulting valence band holes are powerful oxidants which can degrade organic compounds or ammonia; the conduction band electrons may reduce metal ions.

Analytical methods

The adsorbed quantities of the various complexes were determined from the concentration difference of the solution before and after the reaction with TiO₂.

UO₂²⁺ ions were determined spectrophotometrically at 454 nm after reaction with K₄[Fe(CN)₆] [29]. [Co(CO)₅]⁻ was determined spectrophotometrically at 260 nm (low concentrations) [30] or 640 nm (higher concentrations). The other cobalt complexes were determined analogously, at 520 nm with [Co(NH₃)₄(CO₃)]²⁺, 504 nm with [Co(NH₃)₄(H₂O)]³⁺, 505 nm with [Co(NH₃)₃(CO₃)]²⁻, 500 nm with [Co(trien)(CO₃)]¹⁻ and [Co(trien)(H₂O)]²⁺, and 506 nm with [Co(trien)(H₂O)Cl]²⁺. Extinctions were measured with a Shimadzu UV-150-02 or a Perkin-Elmer 555 instrument. Path lengths of 2 to 10 mm were chosen, as opportune. The calibration curves gave straight lines in the concentration ranges studied. Diffuse reflectance spectra were taken with a Perkin-Elmer instrument against a BaSO₄ standard. Since the powders did not stick to the support after pressing, the samples were filled into a quartz glass cuvette. The reference spectra of the pure complex salts were measured in solution, if necessary stabilized with NH₄HCO₃.

NH₃ was liberated by addition of NaOH, and steam-distilled into excess standard HCl solution, and determined by back-titration. TiO₂ with adsorbed trien complexes was heated with concentrated H₂SO₄ and an oxidation catalyst tablet (Riedel-de-Haen AG, No. 31817) to produce (NH₄)₂SO₄ (Kjeldahl method).

CO₃²⁻ was decomposed by addition of dilute sulfuric acid, the liberated CO₂ was carried by an N₂ stream into an absorber filled with 1.5·10⁻³ or 3·10⁻³ M Ba(OH)₂ solution, depending on the quantity of CO₂. The decrease of electrical conductivity was measured with a conductivity meter CDM 3 of Radiometer, Copenhagen. The set-up was calibrated by injecting CO₂ with a gas-syringe into the N₂ stream.

Thermal-decomposition spectroscopy

Thermal decomposition of the adsorbed complexes or the reference compounds was studied employing a thermal-desorption spectroscopy (TDS) set-up. The sample (5–20 mg) was heated in vacuo at a constant heating rate of 5 K/min. It was placed in a quartz glass finger of ca. 5 mm width which was connected by wide tubing to a small quadrupole mass spectrometer (Quadruvac of Leybold Co.). Thin NiCr–Ni coax thermoelements were used for temperature measurement and control of the furnace (Thermicon P controller of Heraeus). The sample volume and the quadrupole were each evacuated by a separate turbomolecular pump, the actual pressure never exceeding 10⁻⁴ Pa. Each time a full 10 °C was reached, the mass analyzer was automatically accentuated to measure the mass range from m/e = 1 to 50 which took 100 seconds. The analogue outputs of signal intensity and corresponding mass were digitalized and evaluated with the aid of a PC, taking into account the fragmentation patterns of the gases. The relative signal intensities used for Figs 4–6 were not corrected for the different ionization efficiencies. The samples were outgassed overnight at room temperature prior to the decomposition runs.
Results and Discussion

Adsorption of $[\text{UO}_2(\text{CO}_3)_3]^{4-}$

Fig. 1 shows the adsorption isotherms at 295 K for $(\text{NH}_4)_4[\text{UO}_2(\text{CO}_3)_3]$ solutions. The pH of the starting solution was 8.33 at the lowest concentration (15.8 x 10^{-3} \text{ mol/l}) and 8.09 at a concentration of 112 x 10^{-3} \text{ mol/l}, with the other pH values between 8.25 and 8.15. After saturation adsorption of the uranyl complex, the pH decreased by ca. 0.1 pH units, and less at the highest concentrations. Maximum adsorption was established within 50 minutes. The adsorption isotherm is sigmoid in shape, it seems to reach a plateau near 170 $\mu$mol/g of adsorbed uranium, but rises steeply at the highest concentrations used.

![Fig. 1. Adsorption isotherms for UO$_2$$^{2+}$ ions from solutions of (NH$_4$)$_4$[UO$_2$(CO$_3$)$_3$] on TiO$_2$ P25 (□), on TiO$_2$ P25 with 245 $\mu$mol/g preadsorbed Al hydroxo complex (■), and on TiO$_2$ P25 in the presence of 0.2 M NH$_3$HCO$_3$, pH 9.1-9.05 (∆), or 10^{-2} M Na$_2$HPO$_4$, pH: 9.0-8.4 (▽). The "equilibrium" concentrations at the end of the adsorption experiments are plotted.](image)

Changing the pH of the $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ solution had a profound effect on the quantity of adsorbed uranium. The pH of the 0.04 M uranyl carbonate solution was adjusted to various values by addition of 0.1 M HCl or 0.1 M NH$_3$. A maximum of adsorption was found at a pH of 3.8. The carbonato complex is not stable in acidic solution. Various hydroxo complexes of uranium have been reported for this pH range [32, 33]. The pH dependence was not studied in more detail, therefore. In our experiments, the uranium uptake decreased to very low values at pH 10 or higher, whilst Yamashita et al. [4] observed a distinct minimum of uranium adsorption at pH 8.

It is not clear whether the adsorption process is reversible, and whether a true adsorption equilibrium is established. Ho and Miller [9] found that on raising the pH to 9 after adsorption at a lower pH, the quantity of uranium bound to an Fe$_2$O$_3$ adsorbent was reduced to the value taken up from a solution of pH 9. Adsorbed uranium can be recovered by washing with concentrated NH$_4$HCO$_3$ or NaHCO$_3$ solution [2, 6]. For simplicity, we will use the term "equilibrium concentration" for the concentration established in the solution when the metal uptake did not further increase with time.

It follows also from Fig. 1 that the adsorption isotherms were influenced by additions of other ions. In agreement with an earlier report [2, 4], we found that addition of bicarbonate resulted in a drastic reduction of uranium uptake. At pH ~8, the tricarbonato complex is dissociated in part (especially at low concentrations) [9]. Addition of HCO$_3^-$ inhibits dissociation of $[\text{UO}_2(\text{CO}_3)_3]^{4-}$.

A few samples were isolated by centrifugation, redispersed in 25 ml of water, and again centrifuged. After drying at room temperature, the carbonate content of the samples was estimated by adding 1 M H$_2$SO$_4$ and determining the liberated CO$_2$ conductometrically. The results in Table I show that slightly less than one carbonate group was found per adsorbed uranyl ion. This carbonate content decreases slowly during storage at room temperature, more rapidly at 40 °C. About 30-50% of the original value was found after three days at 40 °C. Pure TiO$_2$, with no adsorbed uranium, contained only 6 $\mu$mol/g CO$_3^{2-}$ after analogous treatment with a 0.05 M NH$_4$HCO$_3$ solution, although treatment with a 0.05 M NH$_3$HCO$_3$ solution, although 360 $\mu$mol/g CO$_3^{2-}$ had been adsorbed in equilibrium with the solution.

A sample of TiO$_2$ P25 was covered with adsorbed aluminium. As shown earlier, aluminium is strongly adsorbed on TiO$_2$ from so-called basic aluminium chloride solutions of the formal composition Al(OH)Cl$_2$ or Al(OH)$_2$Cl [12]. Such solutions are quite complex and contain several species including polynuclear hydroxo complexes. This is a hydrolytic adsorption, very little chloride is co-adsorbed, and it can be washed out quite easily. A sample with 245 $\mu$mol/g of adsorbed aluminum showed a significant decrease in uranium uptake. Obviously, the binding of uranyl ions is much
### Table I. Carbonate contents of isolated TiO₂ samples after adsorption experiments with (NH₄)₃[UO₂(CO₃)₃].

<table>
<thead>
<tr>
<th>Drying temperature and time</th>
<th>Uranium content ( \mu \text{mol/g} )</th>
<th>Carbonate content ( \mu \text{mol/g} )</th>
<th>Ratio ( \text{CO}_3^{2-}/\text{UO}_2^{2+} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>R.T. 4 h</td>
<td>277</td>
<td>231</td>
<td>0.84</td>
</tr>
<tr>
<td>R.T. 1 year</td>
<td>277</td>
<td>22</td>
<td>0.08</td>
</tr>
<tr>
<td>R.T. 4 h</td>
<td>122</td>
<td>118</td>
<td>0.97</td>
</tr>
<tr>
<td>R.T. 4 h</td>
<td>210</td>
<td>193</td>
<td>0.92</td>
</tr>
<tr>
<td>40 °C 3 d</td>
<td>147</td>
<td>49</td>
<td>0.33</td>
</tr>
<tr>
<td>40 °C 3 d</td>
<td>249</td>
<td>120</td>
<td>0.48</td>
</tr>
<tr>
<td>TiO₂ 250 ( \mu \text{mol/g} ) PO₄³⁻</td>
<td>190</td>
<td>23</td>
<td>0.12</td>
</tr>
<tr>
<td>R.T. 3 h</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO₂ 250 ( \mu \text{mol/g} ) AsO₄³⁻</td>
<td>196</td>
<td>42</td>
<td>0.21</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Preadsorbed species</th>
<th>Final concentration ( \text{mmol/l} )</th>
<th>Adsorbed uranium ( \mu \text{mol/g} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>32.4</td>
<td>137</td>
</tr>
<tr>
<td>250 ( \mu \text{mol/g} ) H₃PO₄ (impregnation)</td>
<td>37.0</td>
<td>207</td>
</tr>
<tr>
<td>250 ( \mu \text{mol/g} ) HPO₄²⁻ (gas phase)</td>
<td>41.8</td>
<td>202</td>
</tr>
<tr>
<td>250 ( \mu \text{mol/g} ) H₃AsO₄ (impregnation)</td>
<td>37.5</td>
<td>196</td>
</tr>
<tr>
<td>245 ( \mu \text{mol/g} ) Al (from solution)</td>
<td>35.6</td>
<td>98</td>
</tr>
<tr>
<td>250 ( \mu \text{mol/g} ) Fe (from solution)</td>
<td>36.6</td>
<td>127</td>
</tr>
</tbody>
</table>

weaker on surfaces that resemble alumina surfaces. Similar results were obtained with a sample with hydrolytically adsorbed ferric ions (see Table II).

Phosphoric acid as well as \( \text{H}_3\text{PO}_4^- \) and \( \text{HPO}_4^{2-} \) ions are also specifically adsorbed on titanium dioxide [15]. The saturation uptake from the adsorption isotherms corresponds to half the total quantity of surface hydroxyl groups. Apparently, the basic \( \text{OH}^- \) groups of the surface are replaced by hydrogen phosphate ions. It has been shown that TiO₂ with adsorbed hydrogen phosphate ions exhibits a strong Bronsted acidity [34–36]. The adsorption isotherm in the presence of \( 10^{-2} \text{M Na}_3\text{HPO}_4 \) shows a drastically increased uranium uptake. The pH after “equilibration” was in the range of 8.7 to 8.4.

Samples with preadsorbed \( \text{H}_3\text{PO}_4 \) or \( \text{H}_3\text{AsO}_4 \) were prepared by the impregnation method: the TiO₂ powder was mixed with the calculated quantity of concentrated \( \text{H}_3\text{PO}_4 \) solution and vacuum-dried at 100 °C. Another sample was covered with adsorbed phosphate by vacuum-distilling \( \text{POCl}_3 \) (at its vapour pressure at room temperature) over the TiO₂, which was kept at 100 °C, followed by hydrolysis with water vapour [37]. It is shown in Table II that all these samples adsorbed more uranium at comparable concentrations than the original, untreated TiO₂. The carbonate content of these samples, subsequent to drying at room temperature, was significantly lower than with untreated TiO₂, see Table I (PO₄³⁻ and AsO₄³⁻ loading by impregnation).

### Adsorption of cobalt(III) carbonato and ammine complexes

The triscarbonato cobalt(III) complex is stable only in the presence of excess carbonate or bicarbonate. The cobalt uptake from such solutions was strongly dependent on the NaHCO₃ concentration, as expected. In the presence of 0.4 M KHCO₃ 42 \( \mu \text{mol/g} \) of cobalt were adsorbed at a \( \text{K}_3[\text{Co(CO}_3]_3] \) concentration of 58 mmol/l.

Tetrammine-carbonato cobalt(III) and cis-tetrammine-diaqua cobalt(III) ions were applied as the sulfates, \([\text{Co(NH}_4]_4\text{CO}_3\text{SO}_4·3\text{H}_2\text{O}] \) and \([\text{Co(NH}_4]_4(\text{H}_2\text{O})_2\text{SO}_4·2\text{H}_2\text{O}] \), respectively. The
carbonato complex was stabilized with NH₄HCO₃ (0.5 M). The diaqua complex was not stabilized since it was transformed into the carbonato complex already in 10⁻² M NH₄HCO₃, as made evident by the UV-VIS spectrum. As Fig. 2 shows, more cobalt was adsorbed from the solution of the diaqua complex. Saturation was not established at a concentration of 50 mmol/l of the complex ion. Interestingly, there was a significant difference in the rate of adsorption. Whereas the final adsorption value was established within ca. 45 min with the carbonato complex, 10–15 min were sufficient with the diaqua complex. This is an indication that it is the diaqua complex which really reacts with the surface. A fairly rapid adsorption (ca. 20 min) was also observed with [Co(NH₃)₅(CO₃)]NO₃ with a monodentate carbonato ligand. 47 μmol/g of Co were adsorbed at a residual concentration of 18 mmol/l from a solution 0.12 M in NH₄HCO₃.

An anionic complex, [Co(CO₃)₂(NO₂)₂]⁻, was taken up in a similar quantity, 42 μmol/g at a concentration of 25–36 mmol/l (see Fig. 2). This solution was stabilized by added KHCO₃ and KNO₂ (0.5 M in each species). About one hour was needed for the adsorption.

Cationic and anionic complexes are adsorbed in similar quantities, also the magnitude of charge seems to be of no importance. Anionic complex ions are adsorbed at pH values near 8, when the TiO₂ surface is negatively charged. This indicates that the binding of the complexes is not due to an ion exchange mechanism.

Titanium dioxide samples with adsorbed cobalt complex ions were isolated by filtration and washed with very little water, and vacuum-dried at room temperature. A TiO₂ sample with 41 μmol/g of adsorbed [Co(NH₃)₅(CO₃)]⁺ complex was analyzed for its ammonia content: 238 μmol/g. The cobalt content estimated from the difference in complex concentration before and after the adsorption experiment agreed very well with an AAS determination of the isolated adsorbate. Since the adsorption medium was 0.12 M in NH₄HCO₃, a reference sample of TiO₂ was equilibrated with a pure NH₄HCO₃ solution, and the quantity of ammonia (or ammonium ions) was determined that remained on the surface after a similar treatment: 79 μmol/g. After correcting the first analysis for this “blank” value, a ratio of 3.88 NH₃ molecules per Co atom is obtained. Clearly, the ammonia ligands are retained during adsorption of the complex.
Infrared spectra of the samples taken by dusting a thin layer of the material between two KBr discs were not very informative because of the presence of water and the closing near 1300 cm\(^{-1}\) of the “window”, due to TiO\(_2\) absorption. UV-VIS diffuse reflectance spectra showed a shift of the absorption peaks to longer wavelengths in the case of adsorption of [Co(NH\(_3\))\(_4\)CO\(_3\)]\(^+\) and [Co(NH\(_3\))\(_4\)(H\(_2\)O)\(_2\)]\(^3+\) (see Fig. 3). The spectra of the TiO\(_2\) with adsorbed complex were practically identical with both compounds, and also for adsorbed [Co(NH\(_3\))\(_5\)(CO\(_3\))]\(^+\) (not shown).

Temperature-programmed decomposition in vacuo of TiO\(_2\) samples treated with the [Co(NH\(_3\))\(_4\)(CO\(_3\))]\(^+\), [Co(NH\(_3\))\(_4\)(H\(_2\)O)\(_2\)]\(^3+\), and [Co(NH\(_3\))\(_5\)(CO\(_3\))]\(^+\) solutions showed decomposition patterns quite different from those of the solid sulfates of these ions (Fig. 4–6). Evolution of NH\(_3\), CO\(_2\) and H\(_2\)O is shifted to lower temperatures. In the case of [Co(NH\(_3\))\(_4\)(CO\(_3\))]\(^+\)-treated TiO\(_2\), the signals for NH\(_3\) and H\(_2\)O can be separated into four peaks at ca. 100 °C, 160 °C, 180 °C, and 370 °C, whereas there is only one sharp peak at 190 °C for the bulk salt (plus a H\(_2\)O peak around 100 °C for the water of hydration). The CO\(_2\) peak at 95 °C has a relatively small area compared to the total NH\(_3\) intensity, and this seems to originate only from a minor contamination of the sample. Very likely, the complex is stripped of its carbonato ligand during adsorption (see below). Attempts to determine the carbonate content gave badly reproducible results. Furthermore, a little HCO\(_3^-\) is retained by the TiO\(_2\) itself.

![Fig. 4. Temperature-programmed decomposition of TiO\(_2\) after adsorption of [Co(NH\(_3\))\(_4\)(CO\(_3\))]\(^+\) ions. The spectrum for solid [Co(NH\(_3\))\(_4\)(CO\(_3\))]\(^+\)SO\(_4\)·3H\(_2\)O is shown for comparison. For clarity the curves for the various gas species are vertically displaced by a constant distance.](image1)

![Fig. 5. Temperature-programmed decomposition of TiO\(_2\) with adsorbed [Co(NH\(_3\))\(_4\)(H\(_2\)O)\(_2\)]\(^3+\) ions and of the parent salt (see legend to Fig. 4).](image2)
Adsorption of cobalt(III) triethylenetetramine complexes

In order to avoid the problems with the insufficient stability of the carbonato and ammine complexes of cobalt, a series of adsorption experiments was performed with cobalt(III) complexes with triethylenetetramine (trien) as a quadridentate ligand. The two remaining coordination sites in cis position were filled with bidentate carbonate or water and/or chloride.

The complex [Co(trien)CO₃]ClO₄ was used in the stable β-form (the terminal amino groups are coordinated in cis position). The adsorption isotherm shown in Fig. 7 can be very well represented by a Langmuir isotherm. A plot c/x vs. c was linear.
over the whole concentration range (see also Fig. 8), and a saturation uptake of 23.7 μmol/g was estimated from its slope (c = equilibrium concentration, x = adsorbed quantity of Co per g TiO₂). In principle, the Langmuir equation should not be applicable in the case of adsorption of charged species. Its good fit gives evidence that the ions bound to the surface are spatially well separated from each other so that electrostatic repulsion becomes negligible.

Adsorption was quite slow, about 15–20 h were needed to achieve the final adsorption values. The carbonate concentration in solution (free and complex-bound CO₃²⁻) did not change during adsorption. This is firm evidence that the carbonate ligand is stripped from the adsorbed complex. The ratio of N:/Co in the adsorbed complex was 4, as expected.

When cis-[Co(trien)(H₂O)₂](ClO₄)₃ was used, the adsorption isotherm was nearly identical with that of the carbonate complex, as was also the case with the aqua-chloro complex [Co(trien)(H₂O)Cl]Cl₂. The adsorption isotherms for these complexes are not shown, therefore. Saturation values of 24.5 μmol/g (diaqua complex), and 21.7 μmol/g (aqua-chloro complex), respectively, were estimated from the plots of the linearized Langmuir isotherms. As an example, the Langmuir plot of the adsorption isotherm measured with cis-[Co(trien)(H₂O)₂]³⁺ is shown in Fig. 8. No chlorine was adsorbed on the surface in the case of the aqua-chloro complex.

The saturation uptakes were still smaller than those observed with the cobalt ammine complexes. The small scattering of the saturation values suggests that it is always the same species that is adsorbed. However, there were distinct differences in the adsorption rates. As shown in Fig. 9, the diaqua complex was adsorbed more rapidly than the carbonate complex, the final adsorption values being established within ca. 4 h (at a concentration of 10⁻² M) while almost 24 h were needed with the carbonate complex. It should be kept in mind that the diaqua complex contained a considerable admixture of the carbonate complex. With the aqua-chloro complex even 30 min were sufficient.

The dinitro complex cis-[Co(trien)(NO₂)₂]Cl was not adsorbed at all, very likely because dissociation of the nitro ligands from the complex is very small.

Conclusions

The experiments with the cobalt(III) complexes show that a similar adsorption mechanism is effective as with the triscarbonato uranyl ions. Especially the triethylenetetramine complexes were useful because this multidentate uranyl ions. Usually the triethylenetetramine complexes were useful because this multidentate ligand does not dissociate to a measurable extent. No stabilization of the complexes by added excess ligand ions was necessary, and it could be shown by simple analytical methods that carbonato or chloro ligands are stripped off the complex ions in the process of adsorption. Quite obviously, the complexes are fixed by displacement of two water molecules (or OH⁻ or Cl⁻ ions) in the ligand sphere of the complex by two oxygen ligands of the oxide surface:

$$\text{OH}^- \quad \text{OH}^-$$

The affinity of the TiO₂ surface for uranyl ions is considerably higher than that for cobalt(III) complex ions, as shown by the significantly higher capacity for uranyl ions. This may be attributed to the higher formal positive charge on the uranium atoms. Similarly, the triscarbonato complex of cobalt(III) is much less stable than the corresponding uranyl complex.
The affinity of the TiO₂ surface for uranyl ions is higher than that of an alumina-like surface, as shown by the experiments with the TiO₂ adsorbent carrying hydrolytically adsorbed aluminum ions on the surface. Again, the difference in positive charge of the cations seems to be responsible. In contrast, when phosphate or phosphoric acid with pentavalent phosphorus was adsorbed on the TiO₂ surface, still more uranium was taken up from the solution of the carbonato complex.

The binding of the other ligands is loosened by the adsorption of the complexes on the TiO₂ surface, as was shown clearly by the thermodecomposition experiments with the adsorbed cobalt(III) ammine complexes. This confirms the conclusion of Yamahita et al. [4] that the bond strength of carbonate to uranium is reduced by the binding of uranium to the oxide surface. Samples isolated from solution and dried in vacuo at room temperature contained approximately one carbonate ligand per uranium atom, but this was gradually lost during storage. However, it cannot be excluded that two carbonate ligands are bound to the chemisorbed uranyl ion when the TiO₂ is still in suspension. Very little carbonate was found when TiO₂ with preadsorbed phosphoric acid was used as the adsorbent.

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