Stabilization of cobalt(II) chloro-complexes with the butanedi-ammonium cation

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Summary

Cobalt(II) chloro-complexes with empirical formulae (bnH2)2CoCl6·2H2O (1) and (bnH2)2CoCl4 (2), where \( \text{bnH}_2^+ \) represents the diprotonated species of putrescine (1,4-butanediamine), were prepared.

The visible spectra in the solid state and measurement of the magnetic moments permit the assignment of an octahedral geometry for cobalt in (1) and a tetrahedral geometry for (2).

Introduction

In its + 2 oxidation state, cobalt gives rise to a d\(^7\) configuration which is specially apt for forming tetrahedral complexes since the difference in stabilization energy between the octahedral and tetrahedral fields is smaller than for other transition metal ions.

Putrescine is an aliphatic diamine involved in numerous biological processes, particularly in its diprotonated form, which is the one usually present at physiological pH. In the present work, it was precisely the diprotonated form of this amine that was used as the stabilizing cation for the above-mentioned cobalt chloro-complexes. In the present work (1) and (2) were obtained and characterized. Compound (1) contains the octahedral species \([\text{CoCl}_3(\text{H}_2\text{O})_2]^{2-}\) instead of the tetrahedral species \([\text{CoCl}_4]^{2-}\) present in (2). In the series of compounds prepared previously with the formula \([\text{NH}_3(CH_2)NH_3]\text{CoCl}_4\), where \(n = 2, 3, 5-10\), in no cases were any hydrated compounds obtained and unlike (1), studied in the present paper, the tetrahedral \([\text{CoCl}_4]^{2-}\) ion is present in all of them.

Discussion

The diffuse reflectance spectra of both compounds (1) and (2) are shown in Figure 1 together with that corresponding to CoCl\(_2\)·6H\(_2\)O. The spectrum of (1), the hydrated complex, is compatible with an octahedral environment for cobalt(II) and is similar to the spectrum of hexahydrated cobalt chloride which can be formulated as \([\text{CoCl}_3(\text{H}_2\text{O})_2]·2\text{H}_2\text{O}\). According to these spectra, it is possible to propose a formula for this compound similar to \([\text{NH}_3(CH_2)NH_3]\text{CoCl}_4\) prepared by Fogel et al.\(^{(7)}\). In view of this, the hydrated compound (1) may be written \((\text{bnH}_2)\text{CoCl}_4(\text{H}_2\text{O})_2\text{Cl}_2\) and in it the cobalt would be surrounded equatorially by four chlorine atoms and axially by two molecules of water, jointly forming a tetragonally distorted octahedron with axial compression. This structure is also observed in CoCl\(_2\)·2H\(_2\)O\(^{(8)}\) and is that offered by Fogel for his ammonium compound. In other cobalt halo-complexes, which crystallize with molecules of water, cobalt has a tetrahedral geometry in the form of the tetrachlorocobal-tate ion, as is the case of the compound with cinchoninium (cin), which may be formulated as \((\text{cin})\text{CoCl}_4\)·2H\(_2\)O\(^{(21)}\). Cinchonine is an alkaloid which as a diprotonated species stabilizes the CoCl\(_2^+\) ion in the compound in question\(^{(21)}\). This species, like 1, 4-butanediarnonium, contains two nitrogen atoms separated by four carbon atoms, although the structure of both cations is different such that the different packing of the corresponding crystal networks would stabilize the CoCl\(_2^+\) ion in one case, and the CoCl\(_2(\text{H}_2\text{O})_2^2+\) ion in our case. The species \([\text{CoCl}_3(\text{H}_2\text{O})_2]^{2-}\) has only been found in (1) and Fogel's compound\(^{(10)}\). With the remaining \(\alpha,\omega\)-alkanediammonium compounds it is possible to obtain the tetrachlorocobaltates mentioned\(^{(10)}\) containing the tetrahedral CoCl\(_2^+\) ion. Similarly, Khvostova et al.\(^{(10)}\) have detected the presence of the species \([\text{CoCl}_3(\text{H}_2\text{O})_2]^{2-}\) in \(\text{H}_2\text{O}/\text{EtOH}\) and \(\text{H}_2\text{O}/\text{DMSO}\) solutions of cobalt chloride. According to the above literature references, the visible spectrum obtained has been interpreted by attributing the band whose centre is at 18520 cm\(^{-1}\) to \(v_3\) to the \(4T_{1g} \rightarrow 4T_{2g}(P)\) transition (1) and appears as a weak flat band ranging from 11000 cm\(^{-1}\) when it is joined to the intense \(v_2\) band. In the visible spectrum zone corresponding to the \(v_2\) band, it is noteworthy that transitions to doublet states may take place; these arise mainly from the \(2G\) and \(2H\) states of the free ion. However, the assignment of this band to \(v_3\) or \(v_2\) transition is in agreement with the same assignment made by Fogel for the corresponding ammonium salt. Furthermore, the \(v_2/v_3\) ratio in our case

Figure 1. Reflectance spectra of the cobalt compounds. (——) \([\text{bnH}_2)_2\text{CoCl}_4\text{Cl}_2\), (—and——) \([\text{bnH}_2)_2\text{Co(H}_2\text{O)}_2\text{Cl}_4\text{Cl}_2\), (———) \([\text{Co(H}_2\text{O)}_4\text{Cl}_2\text{]}·2\text{H}_2\text{O}\).
Table 1. Electronic spectra and magnetic moments of the cobalt compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>$v_1$</th>
<th>$v_2$</th>
<th>$v_3$</th>
<th>$10D_q$</th>
<th>$B$</th>
<th>$B/B_0$</th>
<th>$\mu$(MB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[bnH$_2$]$_2$CoCl$_6$ 2H$_2$O</td>
<td>5954</td>
<td>12870</td>
<td>18416</td>
<td>6937</td>
<td>894</td>
<td>0.92</td>
<td>4.73</td>
</tr>
<tr>
<td>[bnH$_2$]$_2$CoCl$_6$</td>
<td>3828</td>
<td>6603</td>
<td>15128</td>
<td>3828b</td>
<td>671</td>
<td>0.69</td>
<td>4.59</td>
</tr>
</tbody>
</table>

$^a$Data taken from the diffuse reflectance spectrum; $^b$Calcd from: $\mu = 3.87 \times (1 - 4\rho/10D_q)$.

Table 2. I.r. bands and their assignments of bn, bnH$_2$Cl$_2$ and cobalt complexes (cm$^{-1}$)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$v$(O-H)</th>
<th>$v$(N-H)</th>
<th>$\delta$(O-H)</th>
<th>$\delta$(N-H)</th>
<th>$\delta$(C-H)</th>
<th>$\delta$(C-H)</th>
<th>$v$(C-N)</th>
<th>$\rho$(N-H)</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>bn</td>
<td>3340s</td>
<td>1590m</td>
<td>1465w</td>
<td>1380w</td>
<td>1080sh</td>
<td>865s, b</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>bnH$_2$Cl$_2$</td>
<td>3200m</td>
<td>1602m</td>
<td>1465s</td>
<td>1340w</td>
<td>1030m</td>
<td>870s</td>
<td>1990m, b</td>
<td>1280s</td>
<td></td>
</tr>
<tr>
<td>[bnH$_2$]$_2$CoCl$_6$ 2H$_2$O</td>
<td>3400m</td>
<td>1600w</td>
<td>1480s</td>
<td>1375w</td>
<td>1030m</td>
<td>880m</td>
<td>2020w, b</td>
<td>1290m</td>
<td></td>
</tr>
<tr>
<td>[bnH$_2$]$_2$CoCl$_6$</td>
<td>3150sh</td>
<td>1580m</td>
<td>1480s</td>
<td>1370m</td>
<td>1090m</td>
<td>855m</td>
<td>2010w</td>
<td>1110w</td>
<td>1020w</td>
</tr>
</tbody>
</table>

equals 2.16, which is within the range generally accepted for other octahedral complexes; i.e. between 1.9 and 2.2.$^{(10)}$ Both $v_2$ and $v_3$ bands appear in the spectrum of (1). Accordingly, Lever's method$^{(11)}$ was employed to calculate the splitting energy of the $10D_q$ crystalline field, the interelectronic repulsion parameter $B$ and the nephelauxetic ratio $B/B_0$, which measures interelectronic repulsion with respect to the free ion ($B_0 = 971$ cm$^{-1}$). The nephelauxetic ratio measures the ionic participation in the formation of the complex; this becomes greater as the ratio approaches unity. Table 1 shows the transitions and the calculated crystal field parameters, and the values are in agreement with those proposed by Fogel et al. for the analogous ammonium complex.

The blue anhydrous compound, herein designated (2), shows a broad intense band corresponding to the $v_3$ transition, $^4A_2 \rightarrow ^4T_1(P)$, which is characteristic of tetrahedral complexes, and more particularly of the tetrachlorocobaltate ion.$^{(6,13)}$ The same method as described above permitted calculation of the crystal field parameters, shown in Table 1. The values are in agreement with the data cited in the literature for other tetrachlorocobaltates.$^{(13)}$

The magnetic moment measured for anhydrous (2) corresponds to the presence of CoCl$_2^{-}$.$^{(12,13)}$ For the hydrated (1) the magnetic moment measured was 4.73 BM; this value is in the lower interval range assigned for the magnetic moments of cobalt(II) for high spin octahedral field (4.7–5.2 BM). In an octahedral field, the $^4T_{1g}$ fundamental state is degenerate and produces an angular momentum contribution to the spin moment and, hence, the experimental magnetic moments are greater than the magnetic moment due to spin alone (3.88 BM) and lower than the corresponding value with contribution of the orbital, which would be $[4S(S + 1) + L(L + 1)]^{1/2}$ and would be 5.2 BM when $S = 3/2$ and $L = 3$. The small magnetic moment obtained for (1) is interpreted as a loss of symmetry from $O_h$ to $D_{4h}$ (octahedron with tetragonal distortion)$^{(7,14,15)}$.

Table 2 shows the main bands of the i.r. spectrum and their assignations. Of note is the effect of protonation of the amine groups and the formation of hydrogen bonds on the $v$(N-H) both in the hydrated and anhydrous compounds. Also, the bands corresponding to the coordinated water appear in the hydrated compound. The broad band situated at 385 cm$^{-1}$ in the hydrated compound is assigned to the Co–OH$_2$ stretching mode.$^{(15)}$ This same zone of the i.r. spectrum is also exhibited by the Ni–OH$_2$ vibration.$^{(20,22)}$

In the i.r. spectrum, the complex ion [CoCl$_4$(H$_2$O)$_2$]$^{2-}$ shows a single band corresponding to the vibration modes of the coordinated water when this species adopts a $D_{4h}$ symmetry; i.e., when both molecules of water are trans. On the other hand, for the cis complex the symmetry adopted would be $C_{2v}$ and two bands would be expected.$^{(16)}$ The hydrated (1) shows only one band in the zone of coordinated water, such that the geometry adopted by the complex ion in this compound would be trans-$^{[CoCl_4(H_2O)_2]^{2-}}$ in agreement with the corresponding ammonium compound prepared by Fogel.$^{(7)}$ Likewise in the far i.r. the hydrated compound exhibits a band at 300 cm$^{-1}$ (Figure 2) which we assign to the Co–Cl stretching vibration, in agreement withSacconi, Watt et al.$^{(18,19)}$

Protonation and the formation of hydrogen bonds result in displacement of $v$(N–H) towards lower values compared with the unprotonated diamine.$^{(4,17)}$ Figure 2 illustrates the recordings of the compounds obtained.

In the t.g. curve of the hydrated compound (Figure 3) it is possible to observe an initial loss of weight at 100° C corresponding to two molecules of water; this gives rise to a plateau $b$ corresponding to anhydrous (2), a transformation analogous to that occurring for (N$_3$H)$_2$$[^2CoCl_4(H_2O)_2]$ as expressed by the following reaction:

(bnH$_2$)$_2$[CoCl$_4$(H$_2$O)$_2$]Cl$_2$

$\Rightarrow$ (bnH$_2$)$_2$[CoCl$_4$]Cl$_2$ + 2H$_2$O

The reaction is reversible such that by leaving the blue compound in air it again produces the