Cobalt(III) Complexes with Mixed Chelating Ligands

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As recently was reported (1) potassium bis biuretatoco-baltate(III) $[\text{KCo(bi)}_2]$ which shows a striking magnetic behavior having a spin-triplet ground state, forms diamagnetic bis adducts with monodentate nitrogenous bases. The existence of successful addition reactions of this type and our interest (2) in complexes with dithioligands prompted the investigation of the reaction of KCo(bi)$_2$ with N,N-dialkylthiocarbamate ion (R$_2$dtc$^-$) and O-alkylxanthate ion (Rxan$^-$) respectively.

It is found that, when equivalent amounts of KCo(bi)$_2$ and R$_2$dtc$^-$ are reacted in aqueous solution, the initial suspension of KCo(bi)$_2$ disappears, and a blue-violet complex ion $[\text{Co(bi)}_2(\text{R}_2\text{dtc})]^{2-}$ is formed according to the reaction equation:

$$\text{KCo(bi)}_2 + \text{R}_2\text{dtc}^- \rightarrow [\text{Co(bi)}_2(\text{R}_2\text{dtc})]^{2-} + \text{K}^+$$

This reaction had to be carried out at 0$^\circ$, because otherwise the green complex ion Co(bi)(R dtc)$^-$ is rapidly formed. The formation of the latter ion is favored, when two instead of one equivalent R$_2$dtc$^-$ are used and when the reaction is carried out at room temperature. The reaction equation is:
2 H₂O + [Co(bi)₂(R₂dtc)]²⁻ + R₂dtc⁻ \rightarrow [Co(bi)(R₂dtc)]⁻ + biuret + 2 OH⁻

It seemed not preferable to use an excess of R₂dtc⁻ in the latter reaction because in that case the competitive formation of Co(R₂dtc)₃ (insoluble in aqueous solution) becomes important. Often, the isolation of the complex ions appeared to be difficult; we only succeeded in preparing K₂Co(bi)₂(St₂dtc), 3 H₂O and NBu₄Co(bi)(Bu₂dtc)₂ in pure state. These complexes are diamagnetic in the solid state at room temperature, as can be expected for an approximately octahedral Co³⁺ ion with a d⁶ configuration. Conductivity studies, performed in nitrobenzene solution at 25° on NBu₄Co(bi)(Bu₂dtc)₂, proved this compound to be a 1:1 electrolyte.

Using Rtxan⁻ instead of R₂dtc⁻ in the above reactions, products are formed, whose colors (blue-violet and green respectively), suggest the existence of the complex ions [Co(bi)₂(Rtxan)]²⁻ and [Co(bi)(Rtxan)]⁻ respectively. These complex ions have so far not been isolated.

The combined results are clear evidence for the formation of the six-coordinated Co(III) ions Co(bi)₂L⁻² and Co(bi)L₂⁻, when KCo(bi)₂ is reacted with a monoanionic chelating dithioligand L.

It was also possible to prepare Co(Stxan)(St₂dtc)₂ by reacting appropriate amounts of Co(Stxan)₃ and Co(St₂dtc)₃ in chloroform. The PMR spectrum of Co(Stxan)(St₂dtc)₂ proves the octahedral coordination symmetry of the cobalt showing a complicated fine structure for the N—CH₃ proton resonances (fig.). The latter is due to the diastereotropic
nature of the N—CH₂ protons. Such a phenomenon was recently reported (3) for the methylene proton resonance bands of \[ \text{Fe(} \text{Et₄dtc})₂(\text{S₂C₂(} \text{CF₃})₂)²⁻. \]

The AB pattern of the N—CH₂ proton resonances, shown in the figure, may be satisfactorily explained by assuming that the coupling between the diastereotropic protons (14 Hz) is twice as strong as that with the methyl protons (7 Hz). It is rather peculiar, however, that the diastereotropic nature of the O—CH₂ protons did not show in PMR. In this connection it has to be mentioned that for the complexes Co(\text{Et₄dtc})₃, Co(\text{Et₄dtc})₃⁺ and Ni(\text{Et₂dtc})₃⁺ (2) in CDCl₃ at room temperature only one quartet for the methylene proton resonances is observed, which is due to coupling with the methyl protons. The recording of temperature-dependent PMR spectra will be subject of further investigations.

Upon cooling the difference in chemical shift of the diastereotropic dithiocarbamate protons in Co(\text{Et₄dtx})(\text{Et₂dtc})₂ increases slightly. Furthermore one might expect an extra
splitting of the N-bonded ethyl resonances (of the methylene as well as of the methyl proton resonances) due to restricted rotation around the C—N bond (3, 4, 5). At temperatures as low as +9° such a splitting was not observed, probably because at that temperature the hindering of internal rotation is too small. We have indications that the AB pattern is also found for the N—CH₂ dithiocarbamate proton resonances of NB₄Co(bi)(Bu₂dtc)₂. However, due to the overlap with the absorption bands of the cation (N—CH₂) a well-defined interpretation was not possible so far. Moreover, the interpretation will be difficult in view of the coupling of the N—CH₂ dithiocarbamate protons with α, β and γ protons by which the fine structure is broaded considerably with respect to that of the diethyl-dithiocarbamates.

Infrared spectra

In the IR spectra of the various new Co complexes ν(C—N) is a good measure for the electron donating capacity of the ligands with respect to the dithiocarbamate ligand (table I). It is found that in the mixed biuretato-dithiocarbamate complexes no shift of any importance as compared to that determined for Co(Et₂dtc)₃ can be observed. Therefore, it may be concluded that the electron donating capacity of the biuretato ligand will be roughly equal to that of the Et₂dtc⁻ ligand. For Co(Exan)(Et₂dtc)₂ the C—N stretching frequency is found at a higher wavenumber than for Co(Et₂dtc)₃. The C—O stretching frequency, which is characteristic of the xantnate ligand is found to be lower for Co(Exan)(Et₂dtc)₂ than for Co(Exan)₃. Both
findings can be ascribed to the fact that the electron releasing effect of the $-\text{NR}_2$ group is stronger than that of the $-\text{OR}$ group.

**TABLE I**

IR data of some Co(III) complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$v(C\equiv N)$</th>
<th>$v(C\equiv O)$ in cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{K}_2\text{Co(bi)}_2(\text{Et}_2\text{dtc}) \cdot 3 \text{H}_2\text{O}$</td>
<td>1495</td>
<td></td>
</tr>
<tr>
<td>$\text{KCo(bi)}(\text{Et}_2\text{dtc})_2$</td>
<td>1495</td>
<td></td>
</tr>
<tr>
<td>$\text{Co(ET}_2\text{dtc)}_3$</td>
<td>1490</td>
<td></td>
</tr>
<tr>
<td>$\text{Co(Etxan)(Et}_2\text{dtc)}_2$</td>
<td>1505</td>
<td>1230</td>
</tr>
<tr>
<td>$\text{Co(Etxan)}_3$</td>
<td>1505</td>
<td>1250</td>
</tr>
</tbody>
</table>

**TABLE II**

d-d transitions in Co(III) complexes. The band frequencies and $\Delta$ are given in kK, $B$ in K. The molar extinction coefficient is given in parentheses. Unless otherwise reported, the spectra were recorded in CHCl$_3$ solution.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\nu_1$</th>
<th>$\nu_2$</th>
<th>$\Delta$</th>
<th>$B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{K}_2\text{Co(bi)}_2(\text{Et}_2\text{dtc}) \cdot 3 \text{H}_2\text{O} \ast$</td>
<td>15.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{NBu}_4\text{Co(bi)}(\text{Bu}_2\text{dtc})_2$</td>
<td>15.0 (500)</td>
<td>20.8 $\ast$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Co(bi)}_2(\text{Etxan)}^-$</td>
<td>17.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Co(ET}_2\text{dtc)}_3 (7)$</td>
<td>15.5 (600)</td>
<td>20.8 sh</td>
<td>16.3</td>
<td>375</td>
</tr>
<tr>
<td>$\text{Co(Etxan)(ET}_2\text{dtc)}_2$</td>
<td>15.7 (470)</td>
<td>21.1 sh</td>
<td>16.5</td>
<td>380</td>
</tr>
<tr>
<td>$\text{Co(Etxan)}_3$</td>
<td>16.0 (330)</td>
<td>20.7 sh</td>
<td>16.8</td>
<td>328</td>
</tr>
</tbody>
</table>

$\ast$ = reflectance spectrum (in BaSO$_4$); $\ast\ast$ recorded in aqueous solution.
UV-VIS spectra

For the series of complexes Co(\textit{Et}_2\textit{dtc})_3, Co(\textit{Et}xan)_3 and Co(\textit{Et}xan)(\textit{Et}_2\textit{dtc})_2 the crystal field splitting energy $\Delta$ and the Racah parameter $B$ were calculated from UV-VIS spectral data (according to Jørgensen (6)) assuming a low spin $d^6$ Co$^{3+}$ ion with a local $O_h$ symmetry. The tabulated values of $\Delta$ and $B$ of Co(\textit{et}xan)(\textit{Et}_2\textit{dtc})_2 show a good correspondence with those of Co(\textit{Et}_2\textit{dtc})_3 and Co(\textit{Et}xan)_3 (table II).

Unfortunately, only one $d$-$d$ transition is observed in the spectra of the Co(\textit{bi})_2L$^{-2}$ and Co(\textit{bi})L$^{-1}$ complex ions (table II), so no calculations could be performed.

EXPERIMENTAL

The PMR spectra were recorded with a Varian HA-100 spectrometer operating at 100 MHz. As external reference HMDS was used. The IR data were obtained using a Perkin-Elmer 157 spectrophotometer. UV-VIS spectra were measured with the Cary 14 spectrometer. Magnetic measurements were performed according to the Gouy method.

For preparation of KCo(\textit{bi})_2 (8), Co(\textit{Et}_2\textit{dtc})_3 (9) and Co(\textit{Et}xan)_3 (10), the procedures given in the literature were used.

K$_2$Co(\textit{bi})_2(\textit{Et}_2\textit{dtc})_3 H$_2$O.

To a stirred suspension of KCo(\textit{bi})_2 (1 mole) in an ethanol-water mixture (1:1) a solution of K(\textit{Et}_2\textit{dtc}) (1 mole) in the same solvent was added. The reaction temperature had to be kept at 0\(^\circ\). After half an hour the solution is filtered and on cooling to -5\(^\circ\) blue-violet crystals slowly separated. Upon heating the product decomposed near 130\(^\circ\).

Found: Co 11.0; C 19.4; H 3.9; N 17.4; S 11.6. Calc. for K$_2$Co$_9$H$_{22}O_3N_7S_2$ (541.6): Co 10.9; O 20.0; H 4.1; N 18.1; S 11.8.

NBu$_4$Co(\textit{bi})(\textit{Bu}_2\textit{dtc})_2.
Two moles of Na(Bu₂dtc) were added to a suspension of KCo(bi)₂ (1 mole) in water. After the color of the solution had changed from blue-violet to green, an excess of NBu₄Br was added resulting in the precipitation of a green solid substance. This precipitate was filtered off and purified by dissolving in CHCl₃ and reprecipitation with petroleum ether (40–60°). The crystals thus obtained melted at 136–140°.

Found: Co 7.4; C 50.9; H 9.1; N 10.3. Calc. for CoC_{36}H_{75}-N₂O₂S₄ (811.2): Co 7.3; C 53.3; H 9.3; N 10.3.

Co(Etxan)(Et₂dtc)₂.

Two moles of Co(Et₂dtc)₃ and one mole of Co(Etxan)₃ were refluxed for 10 minutes in a chloroform solution. The solvent was evaporated and the separated green crystals melted at 131–132°.

Found: Co 12.5; C 33.6; H 5.4; N 6.2. Calc. for CoC_{13}H_{25}-N₂O₆ (462.2): Co 12.7; C 33.8; H 5.5; N 6.1.

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REFERENCES

