

Figure 2. Tetragonal deformation angle ϕ vs. temperature for BaTiO_3 as calculated from the SHG coefficients d_{333} (\square) and d_{311} (\triangle) as well as from the spontaneous polarization P_s (\circ).

$$d_{311} = 44.16[-16.67 \cos \phi \sin^2 \phi + \cos \phi(1 - 3 \cos^2 \phi)]d_{123}(\text{KH}_2\text{PO}_4) \quad (9)$$

which for ϕ near 90° can be approximated to

$$d_{311} = -736d_{123}(\text{KH}_2\text{PO}_4) \cos \phi \quad (10)$$

Using the temperature dependence⁸ of d_{311} we again calculate the temperature dependence of ϕ and compare the results with those found from d_{333} in Figure 2. The agreement is well within the experimental uncertainties⁹ ($\sim 5\%$).

We further relate the observed spontaneous polarization P_s to the microscopic $\text{Ti} \rightarrow \text{O}$ bond dipole moment μ via the same formalism as eq 1, i.e.

$$P_i = \frac{1}{V} A_{ij} \mu_j \quad (11)$$

assuming again that the temperature dependence of μ is small compared to that of A , i.e., $\partial A / \partial T \gg \partial \mu / \partial T$. From eq 11 and Figure 1 we find

$$P = \frac{4\mu}{V} \cos \phi \quad (12)$$

Using the room-temperature value⁷ of the spontaneous polarization ($P_s = 26 \mu\text{C}/\text{cm}^2$) and the previously given values of V and ϕ we find $\mu_{\text{Ti} \rightarrow \text{O}} = -24 \text{ D}$. Hence

$$P_s = (-498 \mu\text{C}/\text{cm}^2) \cos \phi \quad (13)$$

Using the temperature dependence of P_s we thus again determine the temperature dependence of ϕ . This is compared with the results via SHG coefficients in Figure 2. The agreement is excellent.

The large $\text{Ti} \rightarrow \text{O}$ dipole moment (24 D) is due in part to the fact that we have neglected the bond length dependence in eq 11. If we had taken the bond length into account, we would have found $\mu = 14 \text{ D}$ which is quite close to the 13-D value obtained by assuming a 1.33-electron transfer from the Ti to each of the three oxygens (i.e., 100% ionic). The usefulness of this type of a bond dipole model, beyond simplicity, can be seen for example in that we can predict ϕ for the isomorphous ferroelectric PbTiO_3 from the literature¹⁰ value of $P_s = 75 \mu\text{C}/\text{cm}^2$ and eq 13. In this case we predict ϕ to be 98.7° which is fortuitously close to that found by Shirane and co-workers,¹¹ viz., $\phi = 98.6^\circ$. Another example of its utility is the demonstration that $P_s(T) \propto d_{333}(T)$, an experimental result first observed by Miller⁸ which is now

known to occur in a great many crystals.

In summary we have shown that detailed structural information regarding the nature of the solid-state phase transition in BaTiO_3 can be obtained from SHG results by using a three-dimensional hyperpolarizability model. The results are in good agreement with those found via a microscopic bond dipole model which is applied to spontaneous polarization results. We feel that since the experiment (SHG) is so straightforward² (laser light into the crystal—optical second harmonic detected leaving the crystal) and the theory so simple that the technique should prove highly useful as a tool for investigating the microscopic details of solid-state phase transitions. Furthermore, since SHG only arises from the acentric (bonding or valence) electrons, it is indeed possible that the individual β 's will provide new information about the electronic structure of molecules.

Registry No. BaTiO_3 , 12047-27-7.

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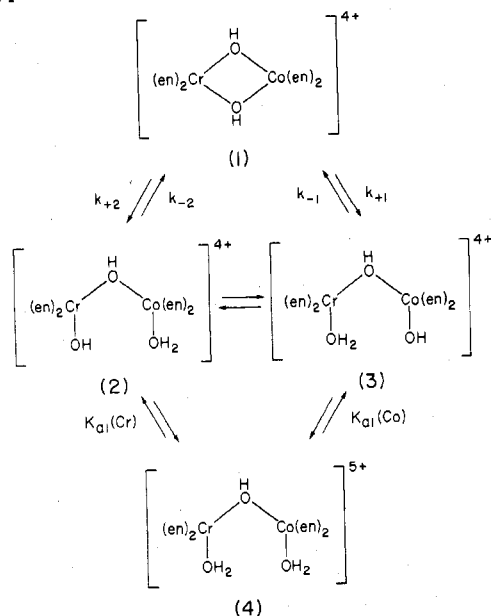
The Di- μ -hydroxo- Λ -bis(ethylenediamine)chromium(III)- Δ -bis(ethylenediamine)cobalt(III) Cation and Its Equilibria with Monobridged Systems

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Sir:

More than 60 years ago Dubsy¹ made an unsuccessful attempt to prepare a complex in which hydroxide ions bridge a chromium(III) and a cobalt(III) ion. Such an intriguing complex has gained renewed interest because of recent spectral² and magnetic³ studies of bridged chromium(III) complexes. The results of these studies can be accounted for as properties of the individual chromium(III) ions superposed on a superexchange interaction² through the bridges. It is now important to obtain information about the properties of the individual chromium(III) ions in the same site situations but under conditions where the superexchange interaction is absent. The present mixed-metal bridged system provides such a situation. The double-hydroxo-bridged systems have further gained interest by the recent discovery^{4,5} that the double-bridged system of two chromium(III) ions in solution enters into equilibrium with a monobridged system within minutes, i.e., long before other reactions take place. The mixed system therefore gains kinetic interest. The present note describes the preparation of the mixed cation di- μ -hydroxo- Λ -bis(ethylenediamine)chromium(III)- Δ -bis(ethylenediamine)cobalt(III) and its first bridge hydrolysis.

Scheme I



Preparation. Heating¹ of the mononuclear aquahydroxo systems of chromium(III) and cobalt(III) yields the respective binuclear compounds, called the diols. These have recently both been shown to be the meso isomers^{6,7}. In the present study, this knowledge has been used for developing a rational method of synthesis for one of the four isomers of the mixed diol 1, shown in Scheme I. Preliminary experiments showed that heating of cocrystallized dithionate of the chromium- and the cobalt-aquahydroxo cations in the ratio 1:1 produced the chromium diol, the cobalt diol, and the mixed diol 1 in approximately the statistical ratio of 1:1:2. Separation of the reaction mixture to give the pure mixed diol was, however, never achieved. Modification of the above method by use of the optically active forms of the aquahydroxo dithionates finally led to the preparation of a pure salt of the mixed diol, as described below.

A cocrystallized dithionate of Δ -*cis*-[Cr(en)₂(OH)(H₂O)]²⁺ and Δ -*cis*-[Co(en)₂(OH)(H₂O)]²⁺ was obtained by addition of 0.9 M Na₂S₂O₆ (180 ml, 20 °C) and pyridine (160 ml, 0 °C) to a solution of Δ -*cis*-[Cr(en)₂(H₂O)₂](NO₃)₃ (0.06 mol) and of Δ -*cis*-[Co(en)₂(H₂O)₂](NO₃)₃ (0.06 mol) in 0.1 M HNO₃ (130 ml, 0 °C). In order to minimize racemization, which at least in the cobalt system⁸ is much faster for the aquahydroxo species than for the diaqua species, the precipitation was performed with cooling in ice and within 60 s. The solutions of the optically active diaqua ions were obtained by dissolving Δ -*cis*-[Cr(en)₂Cl₂]Cl·H₂O (0.06 mol) and Δ -[Co(en)₂CO₃]I (0.06 mol) in 1.0 M HNO₃ and 2.0 M AgNO₃ (130 ml) at 0 °C.⁹⁻¹² The optically active racemic dithionate of the aquahydroxo ions was treated with acetic anhydride under reflux (30 min) and the resulting diol dithionate was converted to the bromide (with NH₄Br) which then was converted to the perchlorate (with NaClO₄) using the methods reported for the chromium diol and the cobalt diol^{1,7} (yield 42% based upon the dichloro and the carbonate salts, respectively). From the crude perchlorate two fractions were obtained (56% and 23%, in this order) by a fractional precipitation procedure using NaClO₄. The smaller fraction was reprecipitated once using NaClO₄ with a yield of 80% to give the pure mixed diol di- μ -hydroxo- Δ -bis(ethylenediamine)-chromium(III)- Δ -bis(ethylenediamine)cobalt(III) perchlorate.

Evidence that this compound actually is a mixed diol was obtained from elemental analyses, visible spectra (spectrum independent of [H⁺] in the region 10⁻³ M < [H⁺] < 1 M for

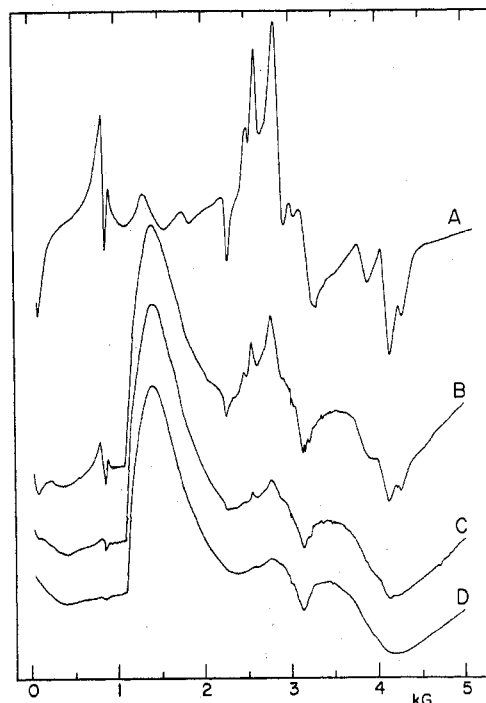


Figure 1. Electron spin resonance spectra of *ms*-[(en)₂Cr(OH)₂-Cr(en)₂](ClO₄)₄ (A), mixed diol artificially contaminated with 4.6% (B) and 1.2% (C) of chromium diol, respectively, and pure mixed diol Δ , Δ -[(en)₂Cr(OH)₂Co(en)₂](ClO₄)₄ (D). Solutions (0.01 M in 1:1 glycerol-10⁻³ M aqueous HClO₄) were made up at 0 °C within 1 min and then frozen to a glass and measured at -140 °C. The spectra therefore are those of the diols, the amounts of monools formed by this procedure being negligible. The measurements were done at 9.111 GHz using a JEOL JES-ME-1X spectrometer.

which the (ϵ , λ)_{max} values are (230, 528) and (149, 383); ϵ in l. mol⁻¹ cm⁻¹ and λ in nm), and powder diffraction patterns (great similarity with those of the meso chromium diol with anions perchlorate and dithionate). The chirality symbols are derived from those of the parent ions. The purity was further supported by the fact that the compound showed an optical rotation ($[\alpha]^{20D}$ -215°, 0.1% solution in 10⁻³ M HClO₄-1 M NaClO₄; $[\alpha]$ obtained by extrapolation to time of dissolution) which did not change on further reprecipitation. All this evidence does not exclude a small contamination of nearly equimolar amounts of chromium and cobalt diols. However, the impurity of chromium diol could be estimated through the ESR spectra. From the relative peak heights (Figure 1) the content of chromium diol in the sample was determined to be 0.2 ± 0.05%. On the basis of the very accurate metal analyses of the anhydrous perchlorate salt an estimate of 0.2% as the upper limit of the contamination with cobalt diol can be made. *Anal.* Calcd: Cr, 6.64; Co, 7.53. Found: Cr, 6.65; Co, 7.51.

Bridge Cleavage. In the following, it will be discussed how the mixed diol enters into equilibrium with its corresponding monools 2-4.

The visible absorption spectra of freshly prepared acid solutions (10⁻⁴ M ≤ [H⁺] ≤ 1.0 M; μ = 1.00 M adjusted with sodium perchlorate) of the mixed diol changed with time showing up to four isobestic points, whose number and positions were dependent upon [H⁺]. At 0 °C constant spectra were measured after 2-4 h. First-order plots of log (OD_t - OD_∞) vs. time were linear to ca. 90% completion, and from the gradients ($k_{\text{obsd}}/2.303$), values of the rate constants, k_{obsd} , were calculated. These rapid changes in spectra can by analogy with the chromium diol system^{4,5} be interpreted as due to an equilibration reaction between the mixed diol and its corresponding monools, 2-4.

Identical values for k_{obsd} were found for $[\text{H}^+] = 10^{-3}$ and 10^{-4} M ($\mu = 1.0$ M, adjusted with sodium perchlorate) with $k_{\text{obsd}} = 0.30 \text{ min}^{-1}$ at 20°C and $k_{\text{obsd}} = 0.03 \text{ min}^{-1}$ at 0.8°C . k_{obsd} was interpreted as $k_{\text{obsd}} = k_f + k_r$, where (Scheme I) $k_f = k_{+1} + k_{+2}$ and $k_r = (k_{-1}k_{-2})(k_{+1} + k_{+2})/(k_{+1}k_{-2} + k_{-1}k_{+2})$ are composite constants for the bridge cleavage reaction and the bridge formation reactions, respectively. (The same value for k_{obsd} at 20°C was measured using optical rotation at the D line indicating that the racemization reactions are unimportant at the time scale of k_{obsd}^{-1} .) At 0.8°C the pH region of the kinetic measurements was extended ($10^{-4} \text{ M} \leq [\text{H}^+] \leq 1.0 \text{ M}$), and a decrease of k_{obsd} with increasing $[\text{H}^+]$ was then observed. These data were consistent with the rate expression⁵

$$k_{\text{obsd}} = k_f + k_r \left[\frac{K_{a_1}}{K_{a_1} + [\text{H}^+]} \right]$$

where $k_f = 0.024 \text{ min}^{-1}$, $k_r = 0.006 \text{ min}^{-1}$, and $K_{a_1} = 0.05 \text{ M}$. The rate expression is consistent with the reaction mechanism shown in Scheme I, k_f and k_r defined as above, and K_{a_1} defined as the acid dissociation constant of **4**

$$K_{a_1} = \frac{[2 + 3][\text{H}^+]}{[4]} = K_{a_1}(\text{Cr}) + K_{a_1}(\text{Co})$$

This interpretation implies that equilibria involving a protonated diol, i.e., a μ -aqua- μ -hydroxo-bridged cation, can be ignored. In agreement with that, the visible absorption spectra of the perchlorate salt of the mixed diol at 0°C in 1 M HClO_4 and 10^{-3} M HClO_4 - 1 M NaClO_4 , when extrapolated back to the time of dissolution, were identical.

From the values of k_f and k_r it follows that $K_{\text{eq}} = 4 \pm 1$ where $K_{\text{eq}} \equiv [\text{monool}]/[\text{diol}] = k_f/k_r$, and $[\text{monool}] \equiv [2 + 3]$. This kinetically established equilibrium constant could also be directly determined by base titration of the monools at equilibrium. The constant found in this way was $K_{\text{eq}} \approx 3.5$ at 0°C . A prerequisite for such a titration procedure to be valid is that the diol itself does not exhibit buffer capacity within the pH region in question and this was found to be the case. The $\text{p}K_1$ of the diol was found to have a lower limit of 10 and the $\text{p}K_{a_2}$ of the aquahydroxo monools was found to be about 8, where K_{a_2} is defined as

$$K_{a_2} = \frac{[(\text{OH})(\text{en})_2\text{Cr}(\text{OH})\text{Co}(\text{en})_2(\text{OH})^{3+}][\text{H}^+]}{[2 + 3]}$$

In conclusion, it is noted that the properties of the mixed diol with regard to the kinetics and thermodynamics of its first bridge cleavage reaction are very similar to those of the chromium diol. The cobalt diol is in these respects quite different and its behavior, in spite of many studies, is still an unsolved problem.¹³

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Registry No. Λ, Δ - $[(\text{en})_2\text{Cr}(\text{OH})_2\text{Co}(\text{en})_2](\text{ClO}_4)_4$, 59109-94-3; *ms*- $[(\text{en})_2\text{Cr}(\text{OH})_2\text{Cr}(\text{en})_2](\text{ClO}_4)_4$, 57159-02-1; Λ -*cis*- $[\text{Cr}(\text{en})_2(\text{H}_2\text{O})_2](\text{NO}_3)_3$, 59202-59-4; Δ -*cis*- $[\text{Co}(\text{en})_2(\text{H}_2\text{O})_2](\text{NO}_3)_3$, 59109-95-4; Λ -*cis*- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$, 59109-96-5; Δ -*cis*- $[\text{Co}(\text{en})_2\text{CO}_3]\text{I}$, 15351-65-2.

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