

Communication

Comment on the reported linkage isomerization in silver hexacyanocobaltate(III) hexadecahydrate

E. Reguera* and G. Quintana

Institute of Materials and Reagents, University of Havana, San Lazaro and L, 10400 Havana, Cuba

J. Fernandez-Bertran

Center of Pharmaceutical Chemistry, P.O. Box 16042, Havana, Cuba

Linkage isomerization in silver hexacyanocobaltate(III) hexadecahydrate during its dehydration has been reported by Kob and House⁽¹⁾. These authors observed that the i.r. spectra of freshly prepared $\text{Ag}_3[\text{Co}(\text{CN})_6] \cdot 16\text{H}_2\text{O}$ has a CN stretching band at 2128 cm^{-1} , which they assigned to the CN linkage in the $\text{Ag}^+ - \text{NC} - \text{Co}^{3+}$ chain, while in dehydrated samples the CN band is observed at 2185 cm^{-1} . This latter absorption band was interpreted as being due to the occurrence of linkage isomerization giving a cobalt salt of the silver cyanide anion, $\text{Ag}^+ - \text{CN} - \text{Co}^{3+}$. However, it is well-known that the CN absorption at 2128 cm^{-1} corresponds to potassium cobalticyanide⁽²⁻⁵⁾ while the absorption at 2185 cm^{-1} belongs to silver cobalticyanide^(5,6). A possible cause of this incongruence could be the occurrence of an exchange between the analyte (silver cobalticyanide hexadecahydrate) and the KBr during the preparation of disks for the i.r. experiment^(6,7), or with the windows when the mulls technique is used. However, since Kob and House specify in their paper that their i.r. spectra were obtained in mulls using NaCl windows^(1,8), if a reaction takes place the lowest frequency band must be observed at 2135 cm^{-1} , corresponding to sodium cobalticyanide⁽⁹⁾. In this communication we shed light on this subject.

$\text{Ag}_3[\text{Co}(\text{CN})_6] \cdot 16\text{H}_2\text{O}$ was prepared according to the procedure described by Kob and House⁽¹⁾. This compound loses water on standing in air or in a desiccator to attain its anhydrous form. All samples were studied in hydrated and anhydrous forms. The i.r. spectra were recorded in Nujol mulls between CaF_2 , KBr and NaCl windows using a Mattson FT-IR spectrometer. Once the i.r. spectra were recorded, the slurry of the sample with Nujol was studied using X-ray diffraction (XRD) as an additional check of possible exchange reactions between the sample and the windows.

When the i.r. spectra of silver cobalticyanide, (hydrated and anhydrous species) are obtained between CaF_2 windows the CN absorption band is always observed at 2185 cm^{-1} (see Figure 1A). However, if KBr windows are used instead of CaF_2 , the hydrated sample has the CN absorption band at 2128 cm^{-1} , while the anhydrous material absorbs at 2185 cm^{-1} (see Figure 1B). The presence of hydration water facilitates the exchange of Ag^+ and K^+ , producing AgBr and $\text{K}_3[\text{Co}(\text{CN})_6]$ as is confirmed by the XRD powder pattern. The same exchange takes place when the windows

used are NaCl plates; in this case the CN absorption is observed at 2135 cm^{-1} . With NaCl windows the absorption at 2185 cm^{-1} also remains since NaCl is less reactive than KBr, giving only a partial exchange. These results discount the occurrence of linkage isomerization in silver hexacyanocobaltate(III) hexadecahydrate during its dehydration process at room temperature and suggest that the windows used by Kob and House⁽¹⁾ in their experiments were KBr instead of NaCl plates. The same results are obtained when the dehydration of the original compound is carried out by heating up to $150\text{ }^\circ\text{C}$. The exchange of the analyte with the windows can also be monitored visually since the resulting silver halide can be observed as a white precipitate between the plates of the alkali halide. Since the occurrence of linkage isomerization in silver hexacyanometallates could be expected on the basis of hard-soft acid-base

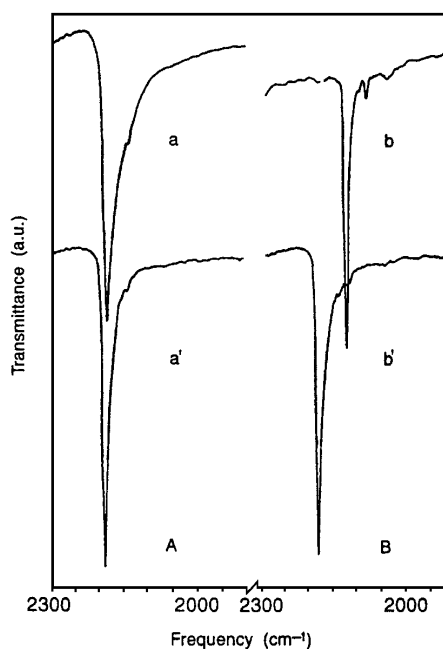


Figure 1. I.r. spectra (CN stretching region) of silver hexacyanocobaltate(III) hydrate (a) and (b) and anhydrous (a' and b'): (A) recorded between CaF_2 plates; (B) recorded between KBr plates. The hydrated complex reacts with the KBr plates producing potassium hexacyanocobaltate(III) (absorption band at 2128 cm^{-1}) and AgBr .

* Author to whom all correspondence should be directed.