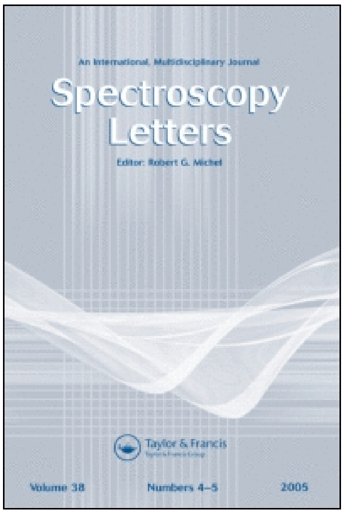

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Mechanochemical Transformations of Ag, Hg AND Pb Cyanometallates in KBr Pressed Disks

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To cite this Article Reguera, E. and Fernàndez-Bertràn, J.(1997) 'Mechanochemical Transformations of Ag, Hg AND Pb Cyanometallates in KBr Pressed Disks', Spectroscopy Letters, 30: 1, 89 — 98

To link to this Article: DOI: 10.1080/00387019708002592

URL: http://dx.doi.org/10.1080/00387019708002592

SPECTROSCOPY LETTERS, 30(1), 89-98 (1997)

MECHANOCHEMICAL TRANSFORMATIONS OF Ag, Hg AND Pb CYANOMETALLATES IN KBr PRESSED DISKS.

Key words: IR spectra, cyano complexes, mechanochemistry, ion exchange reactions.

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ABSTRACT

The mechanochemical transformations of Ag, Hg and Pb cyano complexes (ferro- and ferricyanides, cobalticyanides, nitroprussides, hexacyanoplatinates and tetracyanonickellates) during milling and pressing with KBr have been studied using IR, XRD and Mossbauer techniques as sensors. Exchange of K^+ and the heavy metal cations is observed in all cases.

INTRODUCTION

IR spectra of solids are normally run in pressed KBr disks [1,2]. During the grinding and pressing processes the analyte can undergo mechanochemical changes, the two most common being reduction of the analyte with formation of free Br_2 [3,4] and ionic exchange between the analyte and the KBr matrix [5-7].

IR spectra have been widely used in the study and characterization of hexacyano- and pentacyanometallates and they serve to monitor the mechanochemical changes [8-13]. Ferricyanides are normally reduced to ferrocyanides when milling with KBr [3,4] while cation exchange can take place when an insoluble bromide can be formed [5-8].

Chemists are not generally aware of the possibility of mechanochemical transformation of the analyte in the KBr disk and many pitfalls have been reported on cyano complexes IR spectra [10-14]. In this work we study the mechanochemical transformations taking place between KBr and cyano complexes of heavy metal cations, such as Ag, Pb, Hg hexacyano- and tetracyanometallates and nitroprussides some of whose spectra have been incorrectly interpreted in the literature [10-14].

EXPERIMENTAL

The synthesis of the cyano complexes has been carried out by mixing solutions of soluble cation and cyanometallate salts (K ferrocyanide, ferricyanide, cobalticyanide, hexacyanoplatinate and tetracyanonickelate, and Na nitroprusside). In the case of $Ag_4Fe(CN)_6$ addition of $AgNO_3$ solution to excess $K_4Fe(CN)_6$ solution insures a stable salt. The reverse procedure produces an anomalous silver ferrocyanide [15-17].

IR spectra were recorded in KBr disks and Nujol mulls in an M-40 spectrometer (Carl Zeiss). Mossbauer spectra were taken at room temperature with a ^{57}Co in Rh source, using a constant acceleration spectrometer in the transmission mode. XRD powder patterns were obtained using an HZG-4 diffractometer (Carl Zeiss) and monochromatic CuKα radiation.

The samples for Mossbauer and XRD studies were stoichiometric mixtures of the cyano complex and KBr. The XRD lines were used to determine the disappearance of the initial compounds and the formation of the insoluble bromide as well as the new K cyano complex. In the normal KBr pressed disk the analyte is in a ratio of 1:100 respect to KBr.

RESULTS AND DISCUSSION

A) Reactions of Ag^+ cyanometallates in KBr disks.

The insolubility of AgBr promotes the exchange of the Ag^+ cation for K^+. The ΔH value of the exchange is very large according to Milne [6] (-31 Kcal/mol for Ag_2SO_4 and -18 Kcal/mol for $AgNO_3$ in KBr).

$Ag_3Fe(CN)_6$ reacts rapidly with KBr and KCl to form $K_3Fe(CN)_6$ and the Ag halide. The process has been monitored by IR, Mossbauer and XRD techniques. See Table 1 and Fig. 1a-b. With excess of KBr and prolonged milling, the exchange reaction is followed by reduction of $K_3Fe(CN)_6$ to anhydrous $K_4Fe(CN)_6$ with a complex multiband IR spectra (A_{1g}, E_{2g}, F_{1u}). See Fig. 1c and Table 1. Reduction of ferricyanides to ferrocyanides by milling with KBr is observed for other cations [4], not only for K, and has been the cause of the erroneous interpretation of IR spectra of these complex salts [18].

$Ag_4Fe(CN)_6$ obtained by adding the $AgNO_3$ solution to excess $K_4Fe(CN)_6$ solution, is a white stable powder with υ_{CN} at 2095 cm^{-1} in Nujol mulls (normal silver ferrocyanide). In KBr disks it transforms to anhydrous $K_4Fe(CN)_6$ with formation of AgBr. IR spectra of the reaction products show the six absorption band pattern characteristic of anhydrous $K_4[Fe(CN)_6]$. See Fig. 1c. Differences in IR spectra of silver ferrocyanide obtained using KBr disks and Nujol mulls have been reported [13] but without an explanation about their origin.

TABLE 1.

υ_{CN} frequencies of Ag cyanometallates in Nujol mulls and KBr disks.

Complex	Nujol mulls υ_{CN} [cm^{-1}]	KBr disks υ_{CN} [cm^{-1}]	Assignment
$Ag_3[Fe(CN)_6]$	2170	2118	$K_3[Fe(CN)_6]$
		2092	$K_4[Fe(CN)_6]$
		2072	$K_4[Fe(CN)_6]$
		2060	$K_4[Fe(CN)_6]$
		2042	$K_4[Fe(CN)_6]$
		2024	$K_4[Fe(CN)_6]$
$Ag_4[Fe(CN)_6]$	2095	2092	$K_4[Fe(CN)_6]$
(Normal)		2072	$K_4[Fe(CN)_6]$
		2060	$K_4[Fe(CN)_6]$
		2042	$K_4[Fe(CN)_6]$
		2024	$K_4[Fe(CN)_6]$
$Ag_4[Fe(CN)_6]$	1990-2015	2030-2070	$K_4[Fe(CN)_6]$
(Abnormal)		2083	$KFe[Fe(CN)_6]$
		2110	$K_2Ag(CN)_3$
		2140	$KAg(CN)_2$
		2175	AgCN
$Ag_3[Co(CN)_6]$	2186	2128	$K_3[Co(CN)_6]$
$Ag_2[Fe(CN)_5NO]$	2176, 2164	2136	$K_2[Fe(CN)_5NO]$
$Ag_2[Ni(CN)_4]$	2164	2135	$K_2[Ni(CN)_4]$
$Ag_2[Pt(CN)_6]$	2204	2190	$K_2[Pt(CN)_6]$
AgCN	2175	2110	$K_2Ag(CN)_3$
		2140	$KAg(CN)_2$
		2080	KCN

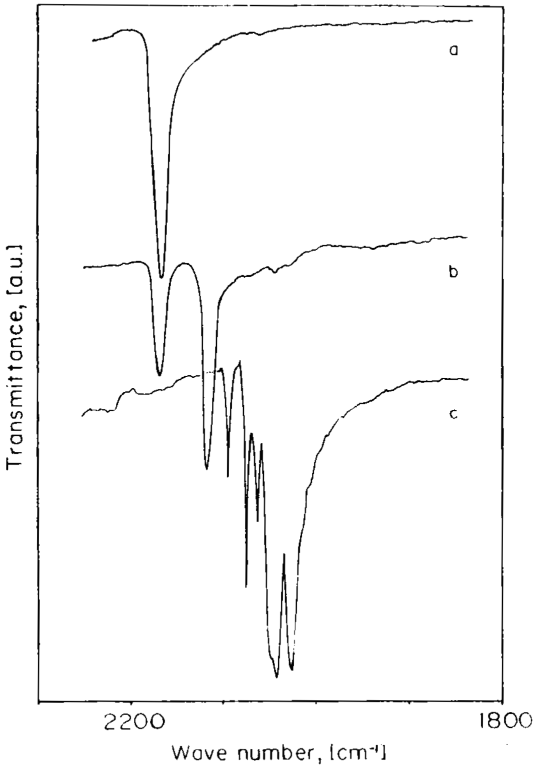

FIG. 1. Infrared spectra (CN stretching region) of: a) $Ag_3[Fe(CN)_6]$ recorded in Nujol mulls; b) $Ag_3[Fe(CN)_6]$ milled and pressed with KBr (a partial exchange of Ag^+ and K^+ is observed); c) $Ag_3[Fe(CN)_6]$ after a prolonged milling with excess of KBr (the characteristic six absorption bands spectrum of anhydrous $K_4[Fe(CN)_6]$ is observed).

When the reverse process of addition is used (a solution of $K_4Fe(CN)_6$ is added to a $AgNO_3$ solution), a bluish precipitate is formed which has a complex IR spectrum. The main band is in the region between 1990 and 2015 cm^{-1}, being its position dependent on the operating conditions; time of mixing, excess of $AgNO_3$, aging of the precipitate, etc. [17]. Mossbauer spectra of the precipitate show the presence of high spin Fe^{2+} which indicates partial decomposition of the ferrocyanide [15]. However, the nature of the absorption near 2000 cm^{-1}, should correspond to a CN compound. Milling the bluish precipitate with KBr gives rise to a complex IR spectrum whose bands can be assigned to: anhydrous and hydrated $K_4Fe(CN)_6$ (2020-2070 cm^{-1}), ferric ferrocyanide (2083 cm^{-1}), $K_2Ag(CN)_3$ (2110 cm^{-1}), $KAg(CN)_2$ (2140 cm^{-1}) and AgCN (2175 cm^{-1}). The mechanochemical reaction proves that there is decomposition of $Ag_4Fe(CN)_6$ by Ag^+ as postulated by Emschwiller [15] and that the amorphous solid with absorption at 1990-2015 cm^{-1} is a silver ferrocyanide of unknown structure; perhaps the low υ_{CN} frequency is due to binding of the Ag^+ cations to the π cloud of the CN ligand instead of the sp orbital of the N atom [19].

$Ag_3Co(CN)_6$ undergoes a simple transformation to $K_3Co(CN)_6$ in KBr disks without any reduction process of the complex anion. See Table 1. In a study on the linkage isomerization and dehydration of silver hexacyanocobaltate(III) hexadecahydrate, Kob and House Jr. [14] report υ_{CN} absorptions at 2128 cm^{-1} and 2185 cm^{-1} for hydrated and dehydrated samples respectively. Erroneously they assigned the first absorption to the hydrated silver salt and interpretated the second one as occurrence of a linkage isomerization process which produces the cobalt salt of a silver cyanide complex anion. The absorption at 2128 cm^{-1} is due to potassium hexacyanocobaltate (III) which probably results from an exchange reaction of Ag^+ and K^+ during the preparation of the sample for IR spectroscopy. In such case the exchange reaction could be highly facilitated by the presence of water of crystallization. The role of the crystallization water in solid state reactions in cyano complexes is known [20,21]. The absorption at 2185 cm^{-1} is originated from the dehydrated silver cyano complex without flipped CN ligands as suppose these authors [14].

Exchange reactions are also observed for $Ag_2Fe(CN)_5NO$, $Ag_2Ni(CN)_4$ and $Ag_2Pt(CN)_6$. See Table 1. Due to this exchange reaction, Ayers and Waggoner [12] and Garg and Goel [10] have reported IR spectra for $Ag_2Fe(CN)_5NO$ which really belong to $K_2Fe(CN)_5NO$. In the case of AgCN a complex substitution process is observed when milled slowly with small amount of KBr, leading to the disappearance of the 2175 cm^{-1} of AgCN and the appearance of new bands at 2140 cm^{-1} [$KAg(CN)_2$], 2110 cm^{-1} [$K_2Ag(CN)_3$] and finally 2080 cm^{-1} (KCN). See Table 1

B) Reactions of Pb^{2+} cyanometallates in KBr disks.

The insolubility of $PbBr_2$ is less than AgBr but still produces ion exchange in KBr disks. Milne has estimated the ΔHs in Kcal/mol for the reactions of KBr with $PbSO_4$ (-1.7) and $Pb(NO_3)_2$ (-6.7) [6].

In Pb cyano metallates, exchange of K for Pb takes place in KBr disks, leading to erroneous spectral assignment in the literature. For example Ayers and Waggoner [13] give incorrect bands for $Pb_2Fe(CN)_6.H_2O$ which correspond to $K_4Fe(CN)_6$. We have studied this exchange in cobalticyanide and ferro- and ferricyanides, comparing IR spectra recorded using KBr disks and Nujol mulls methods and always the exchange reactions takes place in KBr. Results are shown in Table 2. In contrast with Ag^+ ferricyanide, in the case of Pb^{2+} the reactivity of the exchange and oxidation-reduction reactions seems to be similar since these two processes can not be separated through the milling time.

C) Reactions of Hg^+ and Hg^{2+} cyanometallates in KBr disks.

The cyano complexes of Hg^{2+} in KBr are reduced to Hg^+ salts and finally transformed to the K salts. We also have observed the

TABLE 2

υ_{CN} frequencies of some Pb and Hg cyanometallates in Nujol mulls and KBr disks.

Complex	Nujol mulls $\upsilon_{CN}[cm^{-1}]$	KBr disks $\upsilon_{CN}[cm^{-1}]$	Assignment
$Pb_3[Co(CN)_6]_2$	2179 2164 2153 2145 2138 2126	2128	$K_3[Co(CN)_6]$
$Pb_2[Fe(CN)_6]$	2085	2092	$K_4[Fe(CN)_6]$
		2072	$K_4[Fe(CN)_6]$
		2060	$K_4[Fe(CN)_6]$
		2042	$K_4[Fe(CN)_6]$
		2024	$K_4[Fe(CN)_6]$
$Pb[Ni(CN)_4]$	2172	2135	$K_2[Ni(CN)_4]$
$Hg_3[Co(CN)_6]_2$	2180	2128	$K_3[Co(CN)_6]$
$Hg[Fe(CN)_5NO]$	2158, 2140	2134	$K_2[Fe(CN)_5NO]$
$Hg_2[Fe(CN)_5NO]$	2160, 2140	2134	$K_2[Fe(CN)_6NO]$

reduction of the outer cation in cyano complex salts by milling with alkali halides for other heavy metals, for instance, Ti^{4+}, Fe^{3+} and Cu^{2+}. The reduction of the outer cation in hexacyanometallates can be monitored by IR spectra since the valence change introduces a shift of about (10-15) cm^{-1} in the υ_{CN} stretching [9, 22], however, the same shift is not observed in nitroprussides since the NO ligand dominates the spectral properties of these last compounds. Differences in IR spectra of Hg^{2+} and Hg^{+} nitroprussides can be observed in the bending region [19].

Milne calculated a ΔH of -27 Kcal/mol for the reaction of Hg_2SO_4 in KBr [6]. Ayers and Waggoner [13] reported the spectra of $Hg_4Fe(CN)_6$ which really corresponds to $K_4Fe(CN)_6$, and the spectra of $Hg_3Fe(CN)_6$ which is really a mixture of $Hg_3Fe(CN)_6$, $Hg_4Fe(CN)_6$ and $KHg_3Fe(CN)_6$. In another article [12] they also report the spectra of $Hg_2Fe(CN)_5NO$ which corresponds to $K_2Fe(CN)_5NO$. Parwate and Garg [11] report spectra of $HgFe(CN)_5NO$ and $Hg_2Fe(CN)_5NO$ which correspond to mixture of Hg^{+} and K nitroprussides.

In Table 2 we collect our data in KBr and Nujol mulls for the compounds $Hg_3[Co(CN)_6]_2$, $HgFe(CN)_5NO$ and $Hg_2Fe(CN)_5NO$, in which complete exchange has taken place.

Since the driving force of the above discussed exchange reactions is the higher insolubility of the Ag, Pb and Hg halides, similar behaviour is expected for salts of other cyano complex anions.

CONCLUSIONS

Cyanometallates of Ag^{+}, Hg^{+}, Hg^{2+} and Pb^{2+} undergo cation exchange reactions with alkali halides when they are milled and pressed together. Also oxidation-reduction reactions can be present. These reactions are source of pitfalls in interpretation of IR spectra of cyanometallates when they are recorded in alkali halide disks. A best option to obtain the true IR spectra of these cyano complexes is the method of Nujol mulls.

ACKNOWLEDGMENTS

The authors like to thank the help of L. Nuñez and A. Gomez in the preparation of the manuscript.

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Received: June 12, 1996
Accepted: July 18, 1996