

## PARALLEL STUDY OF THE CONVENTIONAL AND DIFFUSE-REFLECTANCE SPECTRA OF PENTACYANONITROSYL COMPLEXES.

### I. SODIUM PENTACYANONITROSYLFERRATE(II) DIHYDRATE\*

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**A b s t r a c t:** A parallel investigation of the diffuse-reflectance and absorbance spectra of sodium pentacyanonitrosylferrate(II) dihydrate (sodium nitroprusside dihydrate) was carried out in order to reveal whether the pressed-pellets technique may cause (because of the possibility of ion exchange and/or applied pressure during the sample preparation) flaws in the interpretation of the absorbance spectra of the investigated sample. Only slight differences between the diffuse-reflectance and absorbance spectra were detected.

**Key words:** diffuse-reflectance infrared spectra, conventional (absorbance) infrared spectra, sodium pentacyanonitrosylferrate(II) dihydrate, sodium nitroprusside dihydrate, Kubelka-Munk function

#### 1. INTRODUCTION

As is well known, the pellet technique, because of the ease of sample preparation, is the most widely used one for investigating the infrared spectra of inorganic and organic materials. Nevertheless one should always be aware of the flaws it possesses. For example, the scattering and the specular reflectance

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\* Part of the content of this paper has been briefly presented at the XVII Congress of Chemists and Technologists of Macedonia.

of the pellet are not always taken into account, and that can cause problems, especially if quantitative measurements are undertaken.

Furthermore, the MX matrices (M stands for K or Na, and X for Cl or Br) are not always inert toward the substance under investigation [1–4], the ion transfer between the matrix and the sample being the main problem in the case of inorganic samples. The empirical fact is that if the cation of the sample forms a halide salt with a lower solubility product than the alkaline halide of the matrix, the ion exchange will take place. The larger the difference in solubility is, the more rapid and thorough the exchange is.

The increased pressure favors the exchange of ions and this is an important factor since during the pellet preparation quite high pressure is applied in order for the cohesion forces to prevail, a high transparency to be attained and the light diffusion to become negligible.

Finally, especially in the case of crystalline hydrates (when traces of water are always present), redox reactions may take place, the halide anions acting as reducing agents.

The difficulties are usually circumvented by a parallel study of spectra in Fluorolube or Nujol mulls. However, due to the presence of strong absorption bands of the matrix itself, the spectra obtained in such a way do not allow the whole spectrum from 4000 to 370  $\text{cm}^{-1}$  to be observed. In addition to that, the mull is usually spread over alkali halide plates or discs with the consequent possibility of ion exchange and/or occurrence of redox reactions.

The spectra shown on Fig. 1 serve as an example that the  $\text{AgNO}_3$  spectrum cannot be recorded using the pellet technique with alkali halides as a matrix material due to ion exchange. It is obvious that the recorded absorbance spectrum is actually that of  $\text{KNO}_3$ .

Four pentacyanonitrosylferrate(II) (nitroprusside) compounds were chosen for this study: sodium pentacyanonitrosylferrate(II) dihydrate (compound **I**), tris(bipyridine)nickel(II) pentacyanonitrosylferrate(II) tetrahydrate (compound **II**), tris(bipyridine)iron(II) pentacyanonitrosylferrate(II) tetrahydrate (compound **III**) and diamminesilver pentacyanonitrosylferrate(II) (compound **IV**). The diffuse-reflectance spectra of the four compounds were recorded and then compared with the spectra recorded from the same compounds but using the pellet technique. In the present account only the results pertaining sodium nitroprusside dihydrate (compound **I**) will be outlined, while those on the remaining complexes will be discussed in a forthcoming paper.

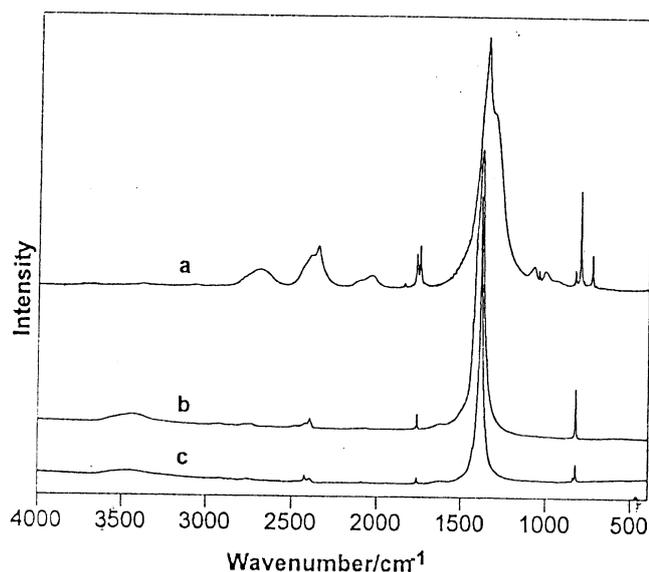


Fig 1. The diffuse-reflectance spectrum of silver nitrate (a); the absorbance spectrum of  $\text{KNO}_3$  in a KBr pellet (b) and the absorbance spectrum of "silver nitrate" in a KBr pellet (c)

## 2. EXPERIMENTAL

The sodium nitroprusside dihydrate was a commercial sample (Merck). The spectra were recorded on a Perkin-Elmer System 2000 Fourier Transform Infrared Spectrometer. The transmission measurements were carried out using the pressed-pellet technique with KBr as a matrix. The diffuse-reflectance spectra were recorded using the Perkin-Elmer diffuse-reflectance accessory. Various sample preparation techniques were tested of which that described below gave the best results.

The diffuse-reflectance spectra were recorded from an intimate mixture of the sample and KBr placed in a holder approximately 3 mm deep, assuming that the measured quantity is  $R_\infty$ , i.e. the reflectance which would be observed if the layer from which the electromagnetic radiation was diffusely reflected was of infinite depth. The samples were ground in an agate mortar separately from the matrix material and the two components were homogenized on a piece of paper. The method of dilution was used to prevent the occurrence of consi-

derable specular reflection. All spectra were recorded against the background of pure KBr also ground in an agate mortar.

### 3. THEORY

It is a well-known fact that scattering occurs when the wavelength of the incident radiation is comparable to the size of the surface particles in the sample. In the case of a sufficiently large scattering density, i.e. for tightly packed particles (which enable diffuse radiation in the system) and multiple scattering, i.e. in the case when

$$\frac{2\pi r}{\lambda} \geq 1 \quad (1)$$

(where  $r$  is the radius of the particles and  $\lambda$  is the wavelength of the used radiation), the only way to describe the scattering is through some phenomenological theory [5].

Using the radiation-transfer equation, Kubelka and Munk [6] derived a widely used expression (called the "Kubelka-Munk function"). In a case when the layer thickness is sufficiently large for no radiation to reach the bottom of the layer, the equation (2) is applicable

$$\frac{K}{S} = \frac{(1 - R_\infty)^2}{2R_\infty} \equiv F(R_\infty) \quad (2)$$

In the above equation  $R_\infty$  is, as mentioned above, the measured reflectance value from the layer of "infinite depth" (this quantity is known as *diffuse reflectance*);  $K$  is the absorption coefficient and  $S$  is the scattering coefficient of the sample.

Because  $F(R_\infty)$  depends linearly on the ratio  $K/S$ , what one obtains is, in a way, the absorbance spectrum of the sample multiplied by a constant that depends on the scattering coefficient  $S$ . The main difference between this and the true absorbance spectrum is that the scattering coefficient may be wavelength-dependent and this may be reflected in the relative intensities of the bands. Thus, if quantitative analysis is to be performed, this should be done on a particular absorption band, i.e. in a specific narrow wavenumber region.

Furthermore, the part of the specular reflection that is present in the emerging radiation depends on the absorption of the sample. The greater the absorption is, the greater the specular component would be and this makes the measured diffuse-reflectance spectra "flattened" and not well resolved. This problem is usually solved using a dilution technique consisting of mixing the investigated material with a non-absorbing matrix resulting in lowering the absorbance and, simultaneously, the specular reflectance.

A knowledge of the nature of the dependence of the scattering coefficient  $S$  on the wavelength of the radiation would, of course, aid the comparison of the absorbance and diffuse-reflectance spectra. In the study of Kortüm and Oelkrug [7], the wavelength dependence of scatter was determined to be  $\lambda^{-2.6}$  to  $\lambda^{-3.6}$  for particles where  $d < \lambda$ ;  $\approx \lambda^{-1}$  for  $d \approx \lambda$  and  $\lambda^{-1}$  to  $\lambda^0$  for  $d > \lambda$ . On the other hand, the same workers [8] found that the effect of the  $\lambda$  dependence of the scatter on the position and the shape of the absorption band was rather small (with the exception of the rather broad bands). It should be pointed out, however, that their work was done in the ultraviolet-visible region of the electromagnetic spectrum, whereas our spectra were recorded in the mid-infrared region.

#### 4. RESULTS AND DISCUSSION

The diffuse-reflectance and absorbance spectra of the four studied compounds,  $\text{Na}_5[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$ ,  $[\text{Ni}(\text{bpy})_3][\text{Fe}(\text{CN})_5\text{NO}] \cdot 4\text{H}_2\text{O}$ ,  $[\text{Fe}(\text{bpy})_3][\text{Fe}(\text{CN})_5\text{NO}] \cdot 3\text{H}_2\text{O}$  and  $[\text{Ag}_2(\text{NH}_3)_2][\text{Fe}(\text{CN})_5\text{NO}]$ , were recorded and, for each compound, a comparison was made between the two kinds of spectra.

The study started with the relatively thorough investigation of compound I and, as noted above, the present paper is devoted to this compound only. In Fig. 2 the diffuse-reflectance (in Kubelka-Munk units) and the absorbance spectra of sodium nitroprusside are presented and the spectra of the remaining compounds will be dealt with at a later date.

As is clearly seen, the two spectra are almost identical, including the two sharp bands due to the water stretching vibrations. The only noticeable difference is present in the H-O-H stretching region in which a broad band with a maximum at  $3442 \text{ cm}^{-1}$  is present in the absorbance spectrum and is absent in the diffuse-reflectance one. However, the difference is not an important one since it is customary to observe such a band in the absorbance spectra of many compounds and to interpret it as due to vibrations of the molecules of water adsorbed on the sample or, more likely, on the alkaline halide matrix.

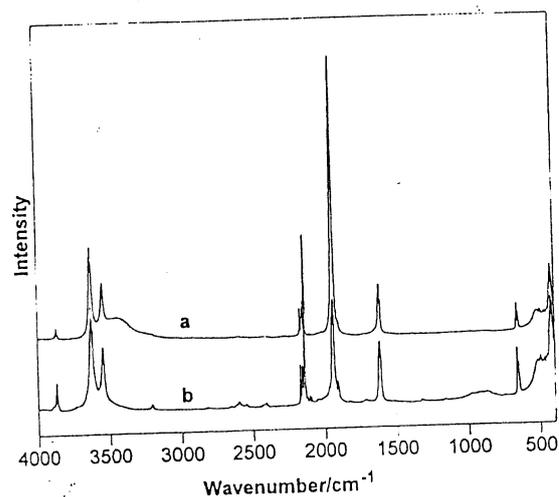


Fig. 2. Infrared spectra of sodium nitroprusside dihydrate:  
(a) absorbance spectrum; (b) diffuse-reflectance spectrum

As for the similarity of the two types of spectra, this may be an indication that there is no significant ion exchange between  $\text{Na}^+$  ions of the sample and  $\text{K}^+$  ions of the matrix<sup>1</sup>. It should be noted that the number of bands originating from the vibrations of the complex anion and their positions are practically identical except for the splitting of the NO stretching band which is clearly seen in the diffuse-reflectance spectrum and almost unobservable in the absorbance one. There is an additional difference between the absorbance and the diffuse-reflectance spectra for the investigated sample I. As seen in Fig. 1, some bands in the diffuse-reflectance spectra have an appreciable intensity whereas they are much weaker in the absorbance spectrum. Incidentally, this may be the reason for the visibility of the doublet of the NO stretching band in the diffuse-reflectance spectrum that is not observed in the absorbance spectrum.

The work of Kortüm and co-workers [7–9] has shown that (at least in the visible and ultraviolet region) the scattering coefficient  $S$  depends on the diameter of the particles of the reflecting substance and the wavelength  $\lambda$  of the incident radiation, the dependence being given by the equation

$$S = c \lambda^k \quad (3)$$

<sup>1</sup> Chacón Villalba et al. [11] came to a similar conclusion.

where  $c$  is a constant and  $k$  has values dependent on the size of the reflecting particles. Thus, when the diameter of the particles is smaller than the wavelength,  $k$  takes values between  $-2.6$  and  $-3.6$ ; for  $d$  close to the wavelength,  $k = -1$  whereas  $k = 0$  for  $d > \lambda$ .

Assuming that a similar dependence holds in the infrared region as well, we decided to estimate the size of the particles of sodium nitroprusside dihydrate by comparing the appearance of the absorbance spectrum with that of the absorbance spectrum corrected with several values of  $k$ . To do that, a program was written<sup>2</sup> using the Array Basic suite of programs [10] with the aid of which the spectra can be redrawn for values of the scattering coefficient  $S$  obtained for chosen values of  $k$  in the equation (3) given above. The results are shown in Fig. 3.

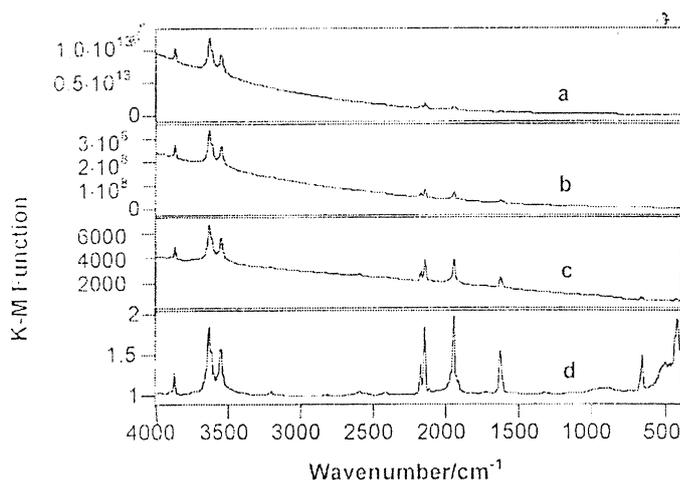


Fig. 3. Corrected diffuse-reflectance spectra of sodium nitroprusside dihydrate using eq. 3: The values of the exponent  $k$  are:  $k = -3.6$  (a);  $k = -2.6$  (b);  $k = -1$  (c);  $k = 0$  (d)

As seen, the major change in the spectra seem, to be confined to the baseline which becomes less and less horizontal as the value of  $k$  increases.

To test whether there are additional changes, the baseline was numerically corrected and the results are shown in Fig. 4.

<sup>2</sup> The program was kindly written for us by Professor Vladimir Petruševski of the Institute of Chemistry, Faculty of Science of the "Sts Cyril and Methodius" University in Skopje.

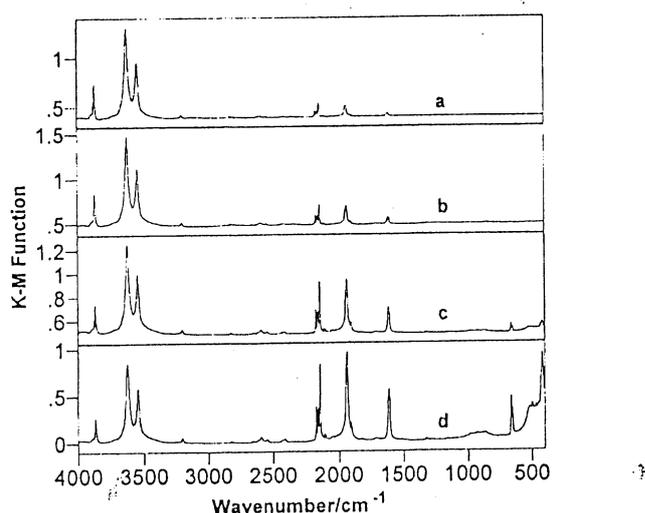


Fig. 4. Corrected diffuse-reflectance spectra of sodium nitroprusside dihydrate with base-line correction included: The spectra are labeled as in Fig. 3

By comparing the absorbance spectrum (Fig. 2) with its various diffuse-reflectance counterparts (Fig. 4), it is obvious that the intensities of the bands in the region below  $2500\text{ cm}^{-1}$  progressively decrease with the increased (in absolute value) exponent in the equation  $S = c \lambda^k$ . Thus the similarity between the absorbance and the diffuse reflectance spectrum is the most pronounced if the value of the exponent  $k$  is taken to be equal to zero.

If, then, the dependence of eq. (3) is indeed applicable in the infrared region, the above observation would lead to the conclusion that the diameter of the reflecting particles is larger than the wavelength of the incident radiation in the whole mid-infrared region, a conclusion which is fully in line with the intuitive expectations. It would be interesting to check whether the application of different grinding techniques and different grinding times would have an effect on the similarity of the absorbance and the diffuse-reflectance spectra.

The assignment of the bands in the infrared spectra (be it absorbance or diffuse-reflectance) is a straightforward task, because of the numerous experimental and theoretical studies on the infrared spectra of sodium nitroprusside dihydrate, of other pentacyanonitrosyl compounds (see e.g. [11] and references given therein) and of the vibrations of the nitroprusside ion [12–14]. A simplified assignment of the bands in the  $4000\text{--}400\text{ cm}^{-1}$  region is given in Table 1 in which only the major contributors to the potential energy are given.

**Table 1**  
*Wavenumber values of bands in the absorbance and diffuse-reflectance spectra of sodium pentacyanonitrosylferrate dihydrate*

Absorbance spectrum		Diffuse-reflectance spectrum		Assignment*	
Wavenumber/cm <sup>-1</sup>	Relative intensity	Wavenumber/cm <sup>-1</sup>	Relative intensity		
3871.7	w	3871.4	m		
3630.2	s	3626.8	vs	$\nu(\text{H}_2\text{O})$	
3546.2	m	3546.8	s	$\nu(\text{H}_2\text{O})$	
		3445.0	br	Adsorbed water	
3204.0	vvw	3205.0	w		
3825.2	vvw	3825.0	w		
3657.4	vvw	3657.3	w		
2618.1	vvw	2617.3	w	<i>Overtones and/or combinations</i>	
2596.1	vvw	2597.7	w		
2547.2	vvw	2548.2	w		
2429.0	vvw	2429.5	w		
2408.6	vvw	2407.8	w		
2173.0	w	2172.8	m		$\nu(^{12}\text{C}^{14}\text{N})$
2161.2	w	2160.1	m		$\nu(^{13}\text{C}^{14}\text{N})$
2156.8	w	2157.0	m		$\nu(^{12}\text{C}^{14}\text{N})$
2143.8	s	2143.0	s		$\nu(^{12}\text{C}^{14}\text{N})$
2126.0	vw	2124.8	w		$\nu(^{12}\text{C}^{15}\text{N})$
2109.0	vw	2109.3	w	$\nu(^{12}\text{C}^{15}\text{N})$	
2098.2	vw	2097.8	w	$\nu(^{12}\text{C}^{15}\text{N})$	
1941.0	vs	1947.3	vs,sh	$\nu(^{14}\text{N}^{16}\text{O})$	
		1939.9	vs	$\nu(^{14}\text{N}^{16}\text{O})$	
1909.6	?	1909.1	w	$\nu(^{15}\text{N}^{16}\text{O})$	
1624.5	m,sh	1624.8	s,sh	$\delta(\text{HOH})$	
1617.8	m	1617.3	s		
1612.5	m,sh	1612.3	s,sh		
663.2	w	662.7	m	$\delta(\text{FeNO})$	
651.9	w	652.7	m	$\nu(\text{FeN})$	
520.6	w,br	518.8	m,br	$\text{H}_2\text{O}$ libration	
498.4	m	499.2	m	$\delta(\text{FeCN}_{\text{ax}})$	
467.2	m	467.7	m	$\nu(\text{FeC}_{\text{ax}})$	
		454.2	m	$\delta(\text{FeCN})$	
432.4	s,sh	432.0	s,sh	$\delta(\text{FeCN})$	
423.4	s	423.4	s	$\nu(\text{FeC})$	
418.3	s	415.2	s	$\nu(\text{FeC})$	

\* The assignments are based on the work of Chacón Villaba et al. [11]. The symbols have their usual meaning:  $\nu$  denotes a stretching vibration and  $\delta$  is used as a symbol for a bending mode.

Another point concerning Table I should be mentioned. It is important to note, namely, that the number of observable bands which can be assigned to vibrations of the isotopic species containing  $^{15}\text{N}$  is somewhat larger in the case of the diffuse-reflectance than in the absorbance spectra.

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#### Резиме

### ПАРАЛЕЛНО ИЗУЧУВАЊЕ НА КОНВЕНЦИОНАЛНИТЕ И СПЕКТРИТЕ НА ДИФУЗНА РЕФЛЕКТАНЦА НА ПЕНТАЦИЈАНОНИТРОЗИЛНИ КОМПЛЕКСИ

#### I. НАТРИУМ ПЕНТАЦИЈАНОНИТРОЗИЛФЕРАТ(II) ДИХИДРАТ

Паралелно се изучувани конвенционалните инфрацрвени спектри на натриум нитропрусид дихидрат, т.е. натриум пентацијанонитрозилферат(II) дихидрат, од една страна, и спектрите снимени при дифузиона рефлексција,

од друга. Основната идеја беше да се испита применливоста на методата на дифузна рефлексија и нејзината евентуална предност пред техниката на пресувани таблети. Во конкретниот случај, забележени се само мали разлики меѓу двата вида спектри, додека таму каде што е можна размена на јони и/или редокс реакции, разликите се значителни. Врз основа на зависноста на коефициентот на расејување од брановата должина, направена е проценка за големината на честичките од испитуваната супстанца.

**Клучни зборови:** инфрацрвени спектри при дифузна рефлексија, натриум пентацијанонитрозилферат(II) дихидрат, натриум нитропрусид дихидрат, функција на Кубелка–Мунк.

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