Гласник на хемичарите и технолозите на Македонија **1**, 37—43 (1974)

ГХТМ-5 *Original Scientific Paper*

INFRARED SPECTRA OF THE HYDRATES OF NICKEL, COBALT, IRON AND ZINC NITROPRUSSIDES

B. Šoptrajanov and I. Petrov

Hemiski institut, Prirodno-matematički fakultet, Skopje, Yugoslavia

The infrared spectra of the hydrated nitroprussides (pentacyanonitrosylferrates) of Ni, Co, Fe and Zn are remarkably similar between themselves and similar to the spectra of the corresponding hexacyanometallates as well, so that close similarity of the structures of these compounds is strongly indicated. If the space group in which the nitroprussides crystallize is the *same* as that of the hexacyanides, then some kind of disorder must be present, possibly such that the cyanide and the nitrosyl groups are randomly distributed around the metal atom, forming a pseudoregular octahedron as demonstrated by the appearence of the CN stretching band. Non-equivalent types of water molecules are apparently present in the structure, some of them, probably, being zeolitic in nature. Whilst hydrogen-bonded OH groups of the water molecules must be present (the bonds being formed, probably, between water molecules), essentially non-hydrogen bonded OH groups must also exist. In fact, the OH stretching frequencies observed around 3650 cm^{-1} are among the highest ones ever reported for crystallohydrates.

INTRODUCTION

Being, for some time, interested in the chemistry and particularly the infrared spectra of various pentacyanonitrosylmetallates (*i. e.* compounds containing anions of the type $[M(CN)_5NO]^{n-}$) [1, 2], we decided to study the infrared spectra of the nitroprussides (pentacyanonitrosylferrates) of divalent metals, having the general formula $M[Fe(CN)_5NO].\ xH_2O$ (where M = Ni, Co, Fe and Zn). The existence of such salts has been signallized a long time ago [3], and different water contents (*i. e.* values of x) have been reported. Thus, Ephraim and Rosenberg [3] give 8 molecules of water per formula unit of the air-dried zinc salt, whereas Salvadeo [4] reports a value of $x = 5$ for the Fe and Ni salts and $x = 5.5$ for the Co compound. Khan and Ahmad [5], on the other hand, report that these compounds are dihydrates and such a water content was later confirmed by Gentil, Baran and Aymonino [6] in their note on crystallographic data of these compounds. Besides the compounds mentioned above, Gentil, Baran and Aymonino studied also the manganese compound, but the spectrum of this salt turned out to be appreciably different from the rest of the spectra and, moreover, dependent upon the experimental conditions. We, therefore, decided to study this particular spectrum more closely and leave it out of the present report. When

this communication was already prepared for presentation [7], a paper by Tosi [8] appeared, dealing with the hydrated and anhydrous nitroprussides of Fe, Co, Ni, Zn and Cu.

EXPERIMENTAL

The investigated salts could easly be prepared by mixing solutions of sodium nitroprusside and the corresponding metal(II) salt (we used chlorides), followed by centrifugation, washing and air-drying of the obtained precipitates according the method described in detail by Khan and Ahmad [5].

The infrared spectra from KBr discs were obtained using a Perkin-Elmer Model 521 Infrared Spectrophotometer.

RESULTS AND DISCUSSION

The spectra of all four compounds are remarkably similar, so that Fig. 1 shows only the spectrum of the Ni compound. The frequencies of the observed bands, their approximate intensities and the assignments, based on recent normal-coordinate treatment of $Na_2[Fe(CN)_5NO].2H_2O$ [9, 10] are given in Table I.

TABLE I

Infrared spectra of M [Fe $(CN)_5NO$].$2H_2O$*

M =	Ni	Co	Fe	Zn	Assignment
	3654 m	3658 m	3653 m	3658 m	
	3596 w	3595 w	3591 w	3597 w	OH stretching
	3405 ms	3400 ms	3395 ms	3425 ms	
	2197 vs	2190 vs	2184 vs	2196 vs	CN stretching
	1950 vs	1950 vs	1949 vs	1949 vs	NO stretching
	1618 m	1619 m	1619 m	1620 m	HOH bending
	1612 sh	1612 sh	1612 sh	1613 sh	
	664 m	665 m	665 m	665 m	FeNO bending
	647 m	647 m	646 m	650 m	FeN stretching
	523 m	520 m	519 m	515 m	Oop FeCN bending
	449 s	446 s	445 s	441 s	Ip FeCN bending
	436 s	433 s	433 s	430 s	FeC stretching
	350 vw	340 (?)	340 (?)	339 vw	FeC stretching

* The abreviations which are used in the table have the following meaning:
w — weak; m— medium; s — strong; v — very; Ip — in-plane; Oop—out-of-plane

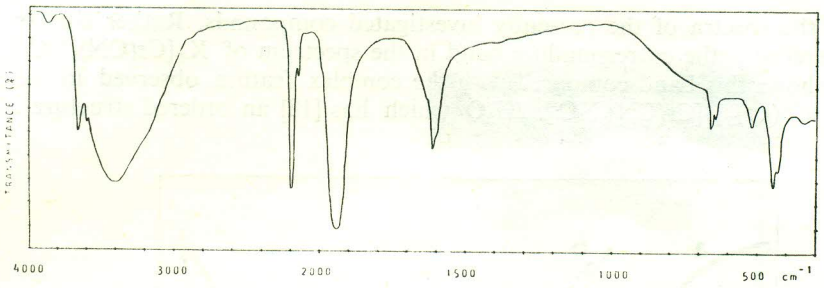

Fig. 1. Infrared spectrum of $Ni[Fe(CN)_5NO].2H_2O$

According to the preliminary crystallographic data of Gentil, Baran and Aymonino [6], the nitroprussides of the divalent metals (formulated as dihydrates) crystallize in the cubic system and have a face-centered unit cell similar to that characteristic for hexacyanometallates of the Prussian Blue type. These latter compounds have been extensively investigated [11—15] and have been found to crystallize, ideally, in the space group $Fm3m$ — O_h^5 (No. 225 in *International Tables* [16]). Thus, in $Co_3[Co(CN)_6]_2.12H_2O$ [14], the outer ions fully occupy the octahedral four-fold sites *a*, whereas the other set of octahedral sites, denoted *b*, is incompletely occupied, the vacancies ocurring at random so that the octahedral symmetry of the space group O_h^5 is preserved. Two kinds of water molecules are present, half of the total number being coordinated to the outer metal ion, the other half being zeolitic in nature. The spectrum of $Co_3[Co(CN)_6]_2.12H_2O$ given by Ludy and Güdel [14] closely resembles our spectra, with the obvious difference with respect to the bands being assigned as NO stretching, FeNO bending and FeN stretching in the spectra of the nitroprussides.

Taken together, the results of Gentil, Baran and Aymonino [6] and the similarity of the infrared spectra would seem to indicate that the space group in which our compounds possibly crystallize is also $Fm3m$ — O_h^5. Thiss would, however, require the pentacyanonitrosylferrate ions to occupy sites with symmetry higher (O_h) than the symmetry of the ideal free ion (C_{4v}), the *b* type sites being, this time, fully occupied, due to the differences in the stoichiometry of the two types of compounds. To accomplish a situation in which the site symmetry is *higher* than the molecular one, disorder of some kind must be present, most probably similar to that existing in the case of $K_3[Cr(CN)_5NO]$ where the cyanide and nitrosyl groups are randomly distributed around the chromium atom [17].

That this can indeed be true could be demonstrated by the rather unusual shape of the cyanide stretching band in the spectra of the divalent-metal nitroprussides (Fig. 2). Namely, whereas in the spectrum of the sodium salt (which is a dihydrate) there are *four* well-resolved bands (*cf.* Fig. 2) and *three* infrared active vibrations are expected in the cyanide stretching region on the basis of the ideal C_{4v} symmetry of the pentacyanonitrosylmetallate ions, only *o n e*, completely unresolved and nicely symmetric band is obser-

ved in the spectra of the presently investigated compounds. Rather similar in appearence is the corresponding band in the spectrum of $K_3[Cr(CN)_5NO]$ (Fig. 3 shows this band compared with the complex feature observed in the case of $[Co(en)_3]$ $[Cr(CN)_5NO]$. $2H_2O$ which has [18] an ordered structure).

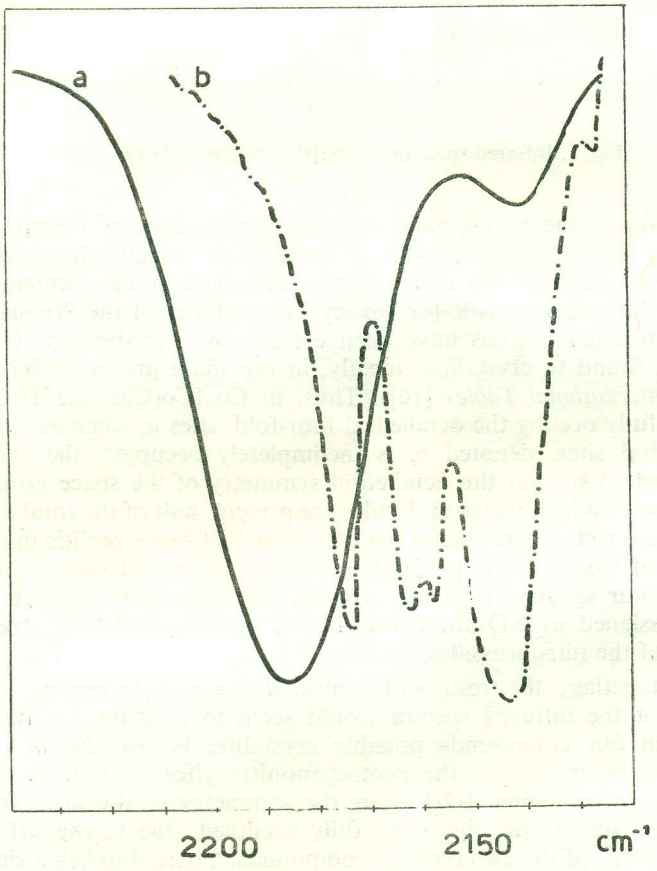

Fig. 2. CN stretching band in the spectra of $Ni[Fe(CN)_5NO]\cdot 2H_2O$ (a) and $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ (b)

The similarity between the structures of the divalent-metal hexacyanometallates and pentacyanonitrosylmetallates in their hydrated form could also explain the similarity in the appearence of the water spectrum in these two classes of compounds. As seen from Fig. 1, in the region of the OH stretching vibrations, two sharp bands at very high frequency (around 3650 and 3595 cm^{-1} respectively) are followed by a broad band centered around 3400 cm^{-1} and exhibiting a rather ill-defined shoulder at around 3300 cm^{-1}. The absorption feature in the HOH bending region has a quite irregular shape, while

a broad absorption, starting somewhat below 1000 cm^{-1}, dominates the low-frequency region, the situation being in almost all respects similar to that found in the case of $Co_3[Co(CN)_6]_2 \cdot 12H_2O$ [14]. Both the appearence of multiple bands in the OH stretching region and the shape of the HOH ben-

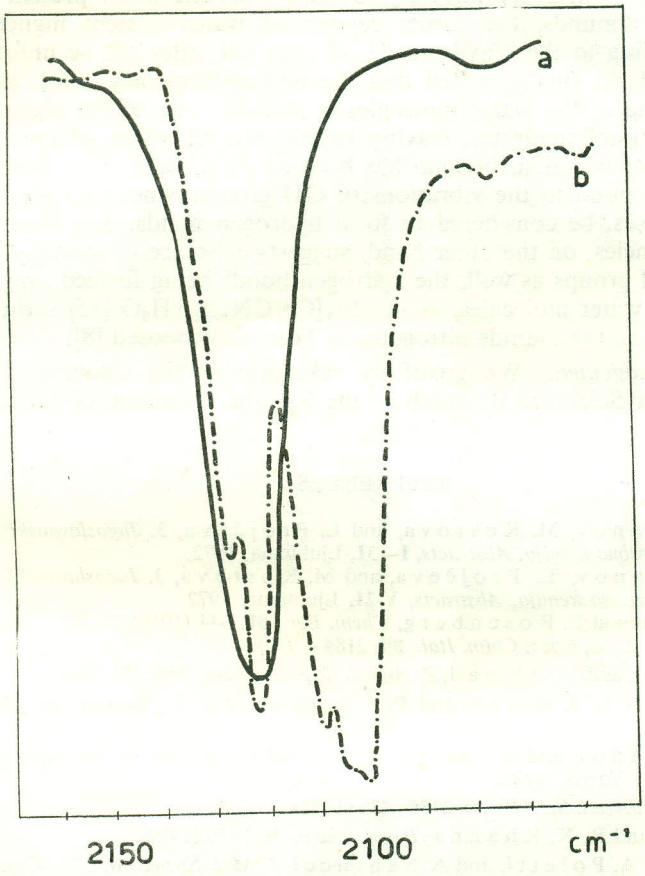

Fig. 3. CN stretching band in the spectra of $K_3[Cr(CN)_5NO] \cdot 2H_2O$ (a) and $[Co(en)_3][Cr(CN)_5NO] \cdot 2H_2O$ (b)

ding band suggest the existence of non-equivalent water molecules, whereas the broad, featureless band in the low-frequency region to which the nitroprusside bands are supperimposed is quite reminescent of the spectrum of liquid water (see, *e. g.* in Brun [19]). It would, thus, seem, that what one sees in the low-frequency region is, in fact, the spectrum of zeolitic-type water (similar to that existing in the structure of the hexacyanometallates [14, 15]). As mentioned before, however, in the structure of the latter compounds there is a second type of water molecules, being situated at (or near) one third of the

24-fold special position *e* and coordinated to the outer ion. All together, there are eight water molecules which were placed in this way in the structure of the hydrates of hexacyanometallates [14, 15], but this is the full water content of the metal(II) nitroprussides if they are considered to be dihydrates and, following Gentil *et al.* [6], the number of formula units in the unit cell is taken to be $Z = 4$. Since there is, obviously, zeolitic water present in the investigated compounds, the earlier reports of water content higher than that corresponding to the dihydrates [3, 4] may not, after all, be unfounded.

It should be, finally, noted that the highest-frequency band, ascribed to OH stretching of the water molecules is certainly one of the highest ever observed for crystallohydrates, leaving behind the dihydrate of the sodium nitroprusside, for which such claim has been advanced [20]. This band must, therefore, correspond to the vibrations of OH groups which can not, for all practical purposes, be considered to form hydrogen bonds. The broad band at lower frequencies, on the other hand, suggests existence of strongly hydrogen-bonded OH groups as well, the hydrogen bonds being formed, most probably, between water molecules, as in $Mn_3[Co(CN)_6]_2.xH_2O$ [15] rather than between water and the cyanide nitrogens, as Tosi has proposed [8].

Acknowledgement. We greatfully acknowledge the financial support by the Fund for Scientific Research of the Socialist Republic of Macedonia.

REFERENCES

1. B. Šoptrajanov, M. Kostova, and L. Projčeva, 3. *Jugoslavanski kongres za čisto in uporabno kemijo, Abstracts*, I—**31**, Ljubljana, 1972.
2. B. Šoptrajanov, L. Projčeva, and M. Kostova, 3. *Jugoslavanski kongres za čisto in uporabno kemijo, Abstracts*, V-**21**, Ljubljana, 1972.
3. F. Ephraim and E. Rosenberg, *Chem. Ber.* **51**, 644 (1918).
4. P. G. Salvadeo, *Gazz. Chim. Ital.* **89**, 2184 (1959).
5. M. M. Khan and N. Ahmad, *Z. Anorg. Allgem. Chem.* **354**, 301 (1967).
6. L. A. Gentil, E. J. Baran, and P. J. Aymonino, *Z. Naturforsch.* **23B**, 1264 (1968).
7. B. Šoptrajanov and I. Petrov, *V National Conference on Spectroscopy, Abstracts*, p. 139, Varna, 1972.
8. L. Tosi, *C. R. Acad. Sci. (Paris)* **275C**, 439 (1972).
9. J. B. Bates and R. K. Khanna, *Inorg. Chem.* **9**, 1376 (1970).
10. G. Paliani, A. Poletti, and A. Santucci, *J. Mol. Struct.* **8**, 63 (1971).
11. J. F. Keggin and E. D. Miles, *Nature (London)* **137**, 577 (1935).
12. A. K. van Bever, *Rec. Trav. Chim. Pays-Bas* **57**, 1259 (1938).
13. H. B. Weiser, W. O. Milligan, and J. B. Bates, *J. Phys. Chem.* **46**, 99 (1942).
14. A. Ludi and H. U. Güdel, *Helv. Chim. Acta* **51**, 2006 (1968).
15. A. Ludi, H. U. Güdel, and M. Ruegg, *Inorg. Chem.* **9**, 2224 (1970).
16. N. F. M. Henry and K. Lonsdale (Eds.), *International Tables for X-Ray Crystallography, Vol. I*, Kynoch Press, Birmingham, 1965.
17. N. G. Vannerberg, *Acta Chem. Scand.* **20**, 1571 (1966).
18. J. H. Enemark, M. S. Quinby, L. L. Reed, M. J. Steuck, and K. K. Walthers, *Inorg. Chem.* **9**, 2397 (1970).
19. G. Brun, *Rev. Chim. Minér.* **5**, 899 (1968).
20. M. Holzbecher, O. Knop, and M. Falk, *Can. J. Chem.* **49**, 1413 (1971).

ИЗВОД

ИНФРАЦРВЕНИ СПЕКТРИ НА ХИДРАТИТЕ НА НИТРОПРУСИДИТЕ НА НИКЕЛ, КОБАЛТ, ЖЕЛЕЗО И ЦИНК

Б. Шоптрајанов и И. Петров

Инфрацрвените спектри на хидратите на нитропрусидите (пентацијанонитрозилферати) на некои двовалентни метали (Ni, Co, Fe и Zn) се извонредно слични како меѓу себе, така и со оние на соодветните хексацијанометалати, така што, веројатно, постои сличност и во структурата на овие соединенија. Ако просторната група во која кристализираат нитропрусидите би била *и с т а* со онаа на хексацијанидите, тогаш структурата би морала да биде несредена. Веројатно цијанидните и нитрозилните групи се статистички распоредени околу централниот железен атом, образувајќи псевдоправилен октаедар. Во полза на ваквата препоставка зборува изгледот на лентата што се должи на цијанидната валентна вибрација. Нееквивалентни типови на молекули вода се присутни во структурата, при што некои се, најверојатно, зеолитски по карактер. Иако некои хидроксилни групи секако учествуваат во водородно сврзување (врските се образуваат, веројатно, меѓу молекули вода), постојат и практички несврзани со водородни врски ОН групи. Всушност, најдените околу 3650 cm^{-1} ленти спаѓаат, по својата фреквенција, меѓу највисоките досега најдени кај кристалохидрати.

ХЕМИСКИ ИНСТИТУТ
ПРИРОДНО—МАТЕМАТИЧКИ ФАКУЛТЕТ
СКОПЈЕ