

On Some Bivalent Transition- and Post-transition Metal Nitroprussides

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The following hydrated nitroprussides are described: $Mn[Fe(CN)_5NO] \cdot 2H_2O$, $Fe[Fe(CN)_5NO] \cdot 4H_2O$, $Co[Fe(CN)_5NO] \cdot 6H_2O$, $Ni[Fe(CN)_5NO] \cdot 4H_2O$, $Cu[Fe(CN)_5NO] \cdot 2H_2O$, $Zn[Fe(CN)_5NO] \cdot 3H_2O$, and $Cd[Fe(CN)_5NO] \cdot 2H_2O$. Spectroscopic and magnetic properties are reported and discussed on the basis of the structures assigned to these compounds. Comparisons are made with previously reported results of some of these and also on related hydrates. The anhydrous compounds are also dealt with briefly.

Introduction

Recently, Inoue *et al.* [1] have dealt with the nitroprussides of divalent transition metals, as part of a series of publications on the bonding nature of coordination polymers. They reported X-ray, infrared, electronic and magnetic data on the dihydrates of the iron, cobalt, nickel, copper and zinc salts and discussed the results on the basis of the face-centered cubic unit cell characteristic of Prussian-blue analogs, with the exception of copper(II) nitroprusside which was found to be tetragonal. Lattice parameters of the manganese, iron, cobalt, nickel and zinc nitroprussides are in fairly good accordance with results previously reported by us [2] and others [3, 4] for different hydrates and anhydrous samples. However, the orderings of the lattice constants found by us ($Fe > Co > Zn > Ni$) and by Inoue *et al.* [1] ($Zn > Fe > Co > Ni$) are not the same. Analogies between their and our own work extend formally to the copper salt (anhydrous for them, dihydrate in the present report) for which we have found also a tetragonal lattice [5]. It is to be noted that Ayers and Waggoner [4] reported for copper(II) nitroprusside (as the monohydrate) a primitive cubic structure. Looking for an independent confirmation of our results we have resorted to the EPR spectrum of the copper salt and found the two signals expected for

a tetragonal structure (see below). It is to be pointed out also that manganese(II) nitroprusside dihydrate which we have reported also as cubic [5] is considered by Inoue *et al.* as having a crystal structure so complicated that its space group had not been determined at the time of the publication. One of the reasons advanced to explain a structure qualified as exceptional [1] was the large diameter of the Mn(II) ion, which was supposed to make the packing in the crystal lattice unfavorable for a cubic structure. The non-cubic character of the lattice of $Cd[Fe(CN)_5NO] \cdot 2H_2O$ is presented as a further example of such a volume effect [1]. In fact, this lattice seems to be orthorhombic (see below).

Previously, we had reported both cadmium and copper nitroprussides as anhydrous [2, 5] just as Khan and Ahmad [6] but further preparations showed that both compounds could be obtained also as the dihydrates. Differences also appeared in the hydration degree of the iron, cobalt, nickel and zinc nitroprussides. We have found in the course of our work a maximal number of 4, 6, 4 and 3 (*cf.* ref. 7) water molecules per formula weight, respectively, for the named compounds. Other hydrates have been also reported [3, 8].

Infrared spectra of nitroprussides from manganese to zinc and of cadmium as various hydrates and also anhydrous have been the subject of previous reports [1, 4, 8, 9]. For the hydrates we are dealing with in this paper complete results, including typical low temperature spectra, are presented. Vibrational properties of the anhydrous compounds in the NaCl region are also reported.

As mentioned above, Inoue *et al.* [1] have also reported electronic spectral data for some nitroprussides. So did also Ayers and Waggoner [4] but only for the u.v. region. As cobalt and nickel nitroprussides suffer dramatic colour changes on dehydration, we believe it is worth reporting and comparing the reflectance spectra of the hydrated and anhydrous forms of these nitroprussides. A novel explanation is advanced for such changes.

Magnetic moments of hydrated and anhydrous cobalt and nickel nitroprussides are also reported and discussed.

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Experimental

Preparative

The compounds were obtained by slow mixing under continuous agitation of equimolecular quantities of 0.1 *M* aqueous solutions of sodium nitroprusside dihydrate and the chlorides or sulphates of the divalent ions. In the case of Mn(II) which forms a nitroprusside partially soluble in water, precipitation was completed by the addition of an equal volume of ethanol to the mother liquor. The solids were washed with water or for Mn(II) with a 1:1 water-ethanol mixture until no nitroprusside and chloride or sulphate ions were detected in the washings. The solids were first air-dried and then kept in a vacuum desiccator over concentrated sulphuric acid. Analytical, spectroscopic and other determinations were delayed until constancy of weight was achieved.

Chemical Analyses

The metallic elements were determined by standard chemical methods [10]. The water content was found gravimetrically by dehydration at 100 °C under high vacuum in a drying pistol or a heatable desiccator until constancy of weight was attained. Completeness of dehydration was checked by running the infrared spectra of the samples in Nujol mulls.

Infrared Spectra

Samples were run in thin KBr disks pressed in a Mini-Die (RIIC) or as Nujol mulls between CsI plates. Two Perkin-Elmer spectrophotometers were used: a 221 model fitted with the NaCl interchange and a 457 model. Survey spectra were run in the standard modes and the spectra for measuring purposes in appropriated expanded modes. Calibration was performed with atmospheric (H₂O, CO₂), polyethylene and indene bands. Wavenumber accuracy is believed to be better than limits stated in the respective instruction manuals.

Low Temperature Infrared Spectra

Nujol mulls or standard KBr disks were cooled down to the boiling point of hydrogen in a AC-3L-110 Cryo-Tip cryostat.

Electronic Reflectance Spectra

Measurements were made between 350 and 700 nm with a Bausch and Lomb Spectronic 20 spectrophotometer provided with the reflectance attachment. Magnesium carbonate was used as the standard. The standard and the samples were finely ground in an agate mortar. The standard measuring cells have been furnished with close fitting plastic caps to avoid contamination of the samples, when anhydrous, with water from the atmosphere. Wavelength calibration of the apparatus was performed with a didymium filter. No correction was required.

X-ray Diffractograms

Powder diffraction data were collected with a Philips PW 1010 diffractometer using Cu-K α radiation (Ni filter). A rotating support was used with the hydrated samples and a stationary one with the anhydrous samples. In this latter case the samples were covered with Scotch tape to avoid contamination by atmospheric water. Diffractograms of the samples dehydrated *in situ* were also performed with a X-86 NII sample chamber from MRC Manufacturing Corporation. This chamber allows heating the sample under vacuum or in an atmosphere of flowing inert gas (dry nitrogen). Diffraction angle (2θ) was swept between 10 and 60° at a speed of 1 degree/min. Calibration was performed with NaCl as a standard. Relative intensities of the peaks were referred to the most intense peak. Experimental spacings were fitted to the adequate parametric equations [11] to get the unit cell parameters and the indexing of the lines. Results with the anhydrous samples have been checked by the photographic method, filling the anhydrous samples in Lindeman capillaries which were sealed with paraffin wax. All the manipulations have been performed in a dry box.

Densities

Densities of the hydrated samples were determined pycnometrically at 20°C using redistilled benzene or toluene as a working fluid.

Magnetic Susceptibility

A Gouy balance was assembled from a semimicro analytical balance and an electromagnet of about 3000 Gauss field intensity. The standard used was Hg[Co(NCS)₄] [12]. Magnetic moments were calculated as in ref. 13. No correction for diamagnetism was made. Accuracy attained is believed to be ± 0.1 B.M., as judged from control measurements performed on selected paramagnetic compounds.

Electronic Paramagnetic Resonance Spectrum of Cu[Fe(CN)₅NO]·2H₂O

This spectrum has been recorded at room temperature with the home-made spectrometer of the Physics Department (F.C.E. U.N.L.P.) with homodyne detection in the X band ($\lambda = 3$ cm). The magnetic field was modulated at 400 c/sec and 100 kc/sec. The cylindrical resonant cavity worked in the TE 011 mode.

Results and Discussion

Analytical

Analytical results and densities are presented in Table I. Colours of the compounds are also included. For the sake of brevity, from now on the nitroprusside anion will be referred to as Npr. Analytical

TABLE I. Colours, Analytical Results and Densities for $M^{II}[\text{Fe}(\text{CN})_5\text{NO}] \cdot n\text{H}_2\text{O}$.

Sample and Colour	Analysis		Density	
	% calculated	% exp.	calculated ^a	exp.
Mn[Fe(CN) ₅ NO] · 2H ₂ O pale pink	Fe = 18.21 Mn = 17.92 H ₂ O = 11.79	Fe = 18.46 Mn = 17.52 H ₂ O = 12.02	1.73	1.75
Fe[Fe(CN) ₅ NO] · 4H ₂ O brown	Fe = 32.48 H ₂ O = 20.92	Fe = 32.64 H ₂ O = 20.25	1.98	1.99
Co[Fe(CN) ₅ NO] · 6H ₂ O pink	Fe = 14.58 Co = 15.28 H ₂ O = 28.20	Fe = 14.69 Co = 15.46 H ₂ O = 27.51	2.25	2.18
Ni[Fe(CN) ₅ NO] · 4H ₂ O gray	Fe = 16.15 Ni = 16.90 H ₂ O = 20.97	Fe = 15.52 Ni = 16.03 H ₂ O = 21.15	2.11	2.06
Cu[Fe(CN) ₅ NO] · 2H ₂ O pale blue	Fe = 17.70 Cu = 20.05 H ₂ O = 11.40	Fe = 17.40 Cu = 19.83 H ₂ O = 11.65	1.90	1.92
Zn[Fe(CN) ₅ NO] · 3H ₂ O pale pink	Fe = 16.65 Zn = 19.50 H ₂ O = 16.11	Fe = 16.82 Zn = 19.57 H ₂ O = 15.94	2.01	1.98
Cd[Fe(CN) ₅ NO] · 2H ₂ O pale pink	Fe = 15.37 Cd = 30.87 H ₂ O = 9.89	Fe = 15.26 Cd = 29.95 H ₂ O = 10.07	2.66	2.72

^a From X-ray diffraction data.

results and densities are in very good accordance with figures expected from the formulas assigned to the compounds.

Powder Diffraction Data

Results obtained for the cubic nitroprussides reproduce previous findings [2]. Tables II and III show data not reported before for CuNpr · 2H₂O and CdNpr · 2H₂O. These compounds seem to belong to the tetragonal and orthorhombic systems, respectively. Indexing has been done on these grounds. Densities of Table I have been calculated using four as the number of formulas per unit cell (Z). The diffractograms of the cubic nitroprussides are similar to the diffractogram of the Prussian-blue analog K₂Co[Fe(CN)₆] · 6H₂O (according to own measurements). Prussian-blues have been assigned to the O_h-m3m Laue class [14]; systematic extinctions of cubic nitroprussides are also compatible with such a class.

The lattice constants of the cubic nitroprussides increase with the radii of the cations (*cf.* ref. 2), this fact pointing to close contact between counterions in the lattices. In spite of the low symmetry of the nitroprusside anion [15, 16], the cubic symmetry of some of its salts could be explained by a statistical distribution of the NO groups among the six available orientations in each anionic lattice site (see below under infrared spectra, however). It

TABLE II. X-Ray Diffraction Data for Cu[Fe(CN)₅NO] · 2H₂O.^a

h k l	d _{obs}	d _{calc}	I/I ₀
0 0 2	5.23	5.24	90
2 0 1	4.53	4.53	100
2 0 2	3.62	3.63	15
0 0 3	3.51	3.49	10
2 0 3	2.867	2.868	30
0 0 4	2.612	2.620	25
4 0 0	2.520	2.513	40
4 0 1	2.456	2.443	5
4 0 2	2.272	2.266	15
4 2 1	2.230	2.197	10
3 2 3	2.182	2.179	8
2 2 4	2.113	2.109	5
4 2 3	1.910	1.890	8

Unit Cell Parameters^a: a = 10.05 ± 0.02; c = 10.48 ± 0.02

^a Data in Angstrom.

is tempting to trace the tetragonal deformation observed in CuNpr · 2H₂O to the expected Jahn–Teller effect from the *d*⁹ electronic configuration of Cu(II) [17]. The even lower symmetry of CdNpr · 2H₂O could be due to the large size of the Cd(II) ion [18] (*cf.* ref. 1).

The powder diffractograms of anhydrous MnNpr, FeNpr, CoNpr, NiNpr and ZnNpr reproduce the dif-

TABLE III. X-Ray Diffraction Data for $\text{Cd}[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$.^a

h k l	d_{obs}	d_{calc}	I/I_0
0 1 1	6.24	6.25	5
0 2 0	5.74	5.76	10
2 0 0	5.26	5.27	100
1 2 0	5.02	5.04	50
2 1 0	4.75	4.77	80
2 0 1	4.35	4.34	10
1 2 1	4.19	4.18	25
2 2 0	3.86	3.86	33
0 0 2	3.75	3.74	10
0 3 1	3.41	3.42	8
3 0 1	3.23	3.22	12
0 2 2	3.15	3.14	10
0 4 0	2.878	2.872	25
4 0 0	2.649	2.635	6
2 4 0	2.532	2.520	45
4 2 0	2.402	2.400	8

Unit Cell Parameters^a: $a = 10.52 \pm 0.02$; $b = 11.48 \pm 0.02$;
 $c = 7.48 \pm 0.02$

^a Data in Angstrom.

fractograms of the respective hydrated compounds: water seems therefore to occupy interstitial positions in the cubic lattices, having a zeolitic character (*cf.* infrared spectra, below). On the contrary, when $\text{CuNpr} \cdot 2\text{H}_2\text{O}$ is dehydrated, the powder diffractogram changes as shown by Table IV. This diffractogram could not be indexed as yet [2]. It is difficult to explain such a change if the structure of $\text{CuNpr} \cdot 2\text{H}_2\text{O}$ is supposed as a tetragonal deformation of the basic Prussian blue-like cubic structure. It is interesting to point out that the structure of $\text{K}_2\text{Cu}[\text{Fe}(\text{CN})_6] \cdot x\text{H}_2\text{O}$ changes from cubic ($a =$

TABLE IV. Powder Diffraction Data for Anhydrous $\text{Cu}[\text{Fe}(\text{CN})_5\text{NO}]$.^a

d_{obs}	I/I_0
5.40	50
4.98	100
4.10	10
3.67	25
3.53	12
3.51	12
2.850	12
2.794	100
2.721	25
2.588	5
2.501	35
2.390	20
2.269	20
2.232	20

^a Data in Angstrom.

$9.99 \pm 0.05 \text{ \AA}$) [19] to tetragonal ($a = 9.85 \text{ \AA}$, $c = 10.50 \text{ \AA}$) [20] on dehydration. It is also very interesting that the lattice parameters of anhydrous $\text{K}_2\text{Cu}[\text{Fe}(\text{CN})_6]$ and of $\text{CuNpr} \cdot 2\text{H}_2\text{O}$ are nearly the same (in fact, the c parameters are practically equal and the a parameters differ only by 0.2 \AA) (see comments of above about the anhydrous CuNpr of Inoue *et al.* [1]).

Infrared Spectra

Cubic nitroprussides

In spite of the similarity of the powder diffractograms of $\text{MnNpr} \cdot 2\text{H}_2\text{O}$, $\text{FeNpr} \cdot 4\text{H}_2\text{O}$, $\text{CoNpr} \cdot 6\text{H}_2\text{O}$, $\text{NiNpr} \cdot 4\text{H}_2\text{O}$ and $\text{ZnNpr} \cdot 3\text{H}_2\text{O}$ their infrared spectra are not all alike. These spectra can be divided into two groups which differ distinctly in the bands due to

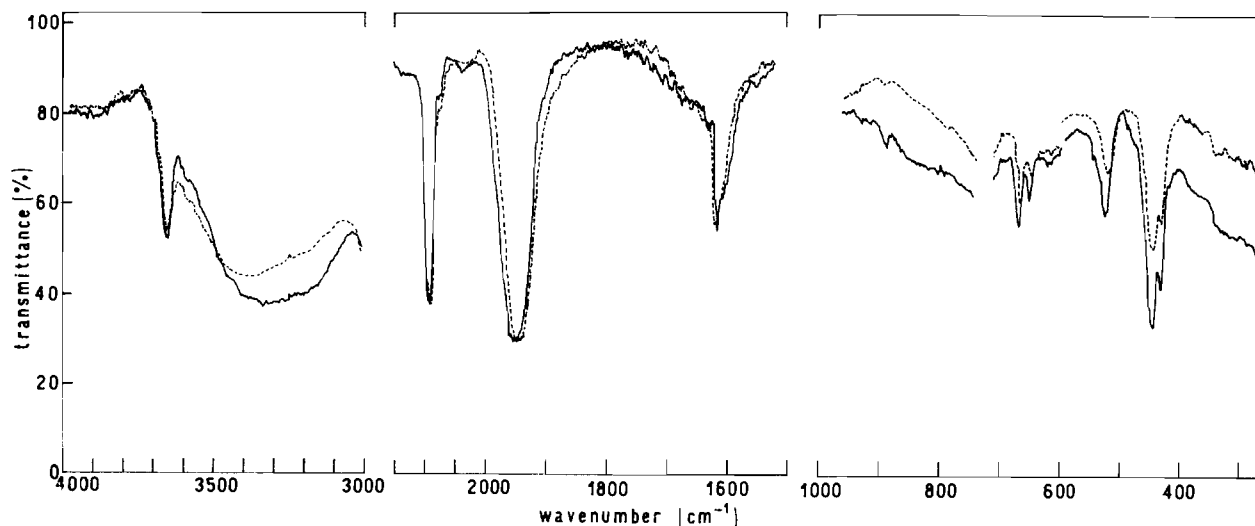


Figure 1. Infrared spectra of $\text{Fe}[\text{Fe}(\text{CN})_5\text{NO}] \cdot 4\text{H}_2\text{O}$. Room temperature - - -, 20 K —.

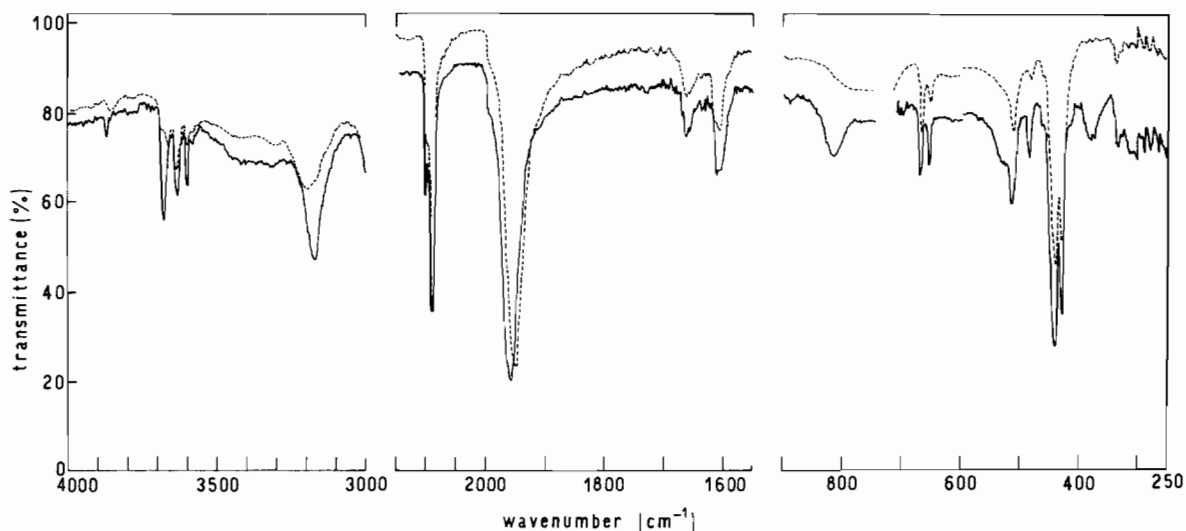


Figure 2. Infrared spectra of $\text{Mn}[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$. Room temperature - - - -, 20 K —.

the anion and specially in the water bands. The two groups can be arranged in the following way: (I) $\text{FeNpr} \cdot 4\text{H}_2\text{O}$, $\text{CoNpr} \cdot 6\text{H}_2\text{O}$ and $\text{NiNpr} \cdot 4\text{H}_2\text{O}$; (II) $\text{MnNpr} \cdot 2\text{H}_2\text{O}$ and $\text{ZnNpr} \cdot 3\text{H}_2\text{O}$. Figures 1 and 2 reproduce, respectively, the infrared spectra both at room and at boiling hydrogen temperatures of $\text{FeNpr} \cdot 4\text{H}_2\text{O}$ and $\text{MnNpr} \cdot 2\text{H}_2\text{O}$, which have been selected as representatives of their groups. Table V gives the wavenumbers and assignments of bands found in the room temperature spectra of the five nitroprussides; it also includes the low temperature spectra of $\text{FeNpr} \cdot 4\text{H}_2\text{O}$ and $\text{MnNpr} \cdot 2\text{H}_2\text{O}$. In Table V we are making no detailed assignments of the $\nu_{\text{M}-\text{C}}$ and δ_{MCN} modes because there seems to exist still a controversy on this subject matter originated in the different assignments made for the hexacyano complexes in this spectral region (*cf.* ref. 21 and references therein). The nitroprussides and the water bands will be dealt with separately in what follows.

a) Nitroprusside bands As expected, the wavenumber of the main CN stretching peak assigned to the doubly degenerate equatorial E mode is greater in the polymeric transition metal nitroprussides than in the nitroprussides where the anion is isolated (*cf.* for instance refs. 21a, d, 22). In the cubic transition metal nitroprussides ν_{CN} reaches a maximum at Co (*cf.* ref. 1; see however ref. 9). This finding is not in exact accordance with the decrease of the unit cell parameters (a) which show a minimum at Ni [2] (*cf.* however ref. 9) as expected from ligand field effects on the cationic radii [17]. Anyway, it is clearly seen the overall effect of the strengthening of the bonding and the increase of the electronic polarization brought about in the CN groups by the transition metal cations bonded to their nitrogen ends [23].

In the spectra of group II nitroprussides, on the high wavenumber side of the main CN (E) stretching band there is a clear inflexion which could be assigned to one of the A_1 CN stretching modes by comparison with $\text{Na}_2\text{Npr} \cdot 2\text{H}_2\text{O}$ [21, 26] and $\text{BaNpr} \cdot 2\text{H}_2\text{O}$ [21a]. By cooling to 20 K the CN stretching region of $\text{MnNpr} \cdot 2\text{H}_2\text{O}$ splits into three bands (see Figure 2 and Table V); this happens also with $\text{ZnNpr} \cdot 3\text{H}_2\text{O}$. The new band appearing on cooling could be due to the second A_1 mode expected for the CN stretchings. In $\text{Na}_2\text{Npr} \cdot 2\text{H}_2\text{O}$ the highest A_1 mode has been assigned to the axial stretching and the lowest to the equatorial mode [9, 24, 25]. However, in $\text{BaNpr} \cdot 2\text{H}_2\text{O}$ the equatorial (A_1) mode was found at a higher wavenumber than the axial (A_1) mode (2172 and 2159 cm^{-1} , respectively [21a]). Due to this contradictory behaviour of the A_1 modes, we are making no distinction in Table V between the axial and equatorial modes. The spectrum in the CN stretching region of $\text{FeNpr} \cdot 4\text{H}_2\text{O}$ (group I, see Figure 1) changes very little on cooling; this is perhaps another difference between groups I and II.

The fundamental NO stretching band increases by coordination to metal cations less than the CN stretching bands and it seems to follow no trend in the cubic nitroprussides. Anyway, not much significance should be put on this point due to the uncertainty involved in locating the maxima of relatively broad bands. The shape of the fundamental NO stretching band does not differ appreciably between groups I and II although this is not the case with its first overtone because in the spectra of group I this band is broader than in group II. The broadness and weakness of $2\nu_{\text{NO}}$ in group I renders this band practically unobservable in the

TABLE V. Infrared Absorption Data of Hydrated Divalent Mn, Fe, Co, Ni and Zn Nitroprussides.^a

Assignment	Mn[Fe(CN) ₅ NO]·2H ₂ O		Fe[Fe(CN) ₅ NO]·4H ₂ O		Co[Fe(CN) ₅ NO]·6H ₂ O		Ni[Fe(CN) ₅ NO]·4H ₂ O		Zn[Fe(CN) ₅ NO]·3H ₂ O	
	Room Temp.	20 K	Room Temp.	20 K	Room Temp.	20 K	Room Temp.	20 K	Room Temp.	20 K
2 ν _{NO}	3858 vw	3867 vw	ca. 3851 vw, br		ca. 3880 vw, br		ca. 3852 vw, br		3860 w	
	3683 sh 3665 vw 3632 w 3596 vw 3576 sh ca. 3430 vw, br ca. 3310 vw, br 3199 w, br	3675 w 3633 sh 3626 w 3595 w 3575 vw ca. 3420 br ca. 3300 vw, br 3169 m	3653 m	3653 m	3653 w		3644 s		ca. 3693 sh 3675 m 3633 m 3599 w 3581 vw 3320 vw, br 3224 m, br	
ν _{HO}			ca. 3371 s, br ca. 3170 sh, br	ca. 3300 s, br	3411 vs, br		ca. 3380 vs, br			
			2199 sh 2180 vs		2190 s 2154 vw		2187 vs ca. 2150 sh		2196 sh 2186 vs ca. 2155 sh	
ν _{CN}			1943 vs	1945 vs	1944 vs		1939 vs		1944 vs	
			1660 w 1604 w	1662 vw 1607 w	1616 m		1616 m		1662 m 1607 s 1600 s	
δ _{H₂O}			ca. 781 sh, br	ca. 843 sh, br					796 w, br	
			664 w 651 vw	669 w 654 w	664 w 648 vw		663 vw 648 vw		667 m 656 w	
L-H ₂ O ^b			ca. 520 sh, br	ca. 530 sh, br					ca. 525 sh	
			510 w 483 vw	516 w 485 w 467 sh	521 w		521 vw		515 m 487 vw	
ν _{FeC:δFeCN} ^b			438 s 426 s	444 vs 431 s	441 m 428 w		449 m 433 w, sh		439 s 425 s	
			335 vw	380 vw, br 336 vw	ca. 335 vw, sh		ca. 375 sh		342 vw	
L-H ₂ O ^b			310 vw	310 vw	ca. 265 vw		ca. 315 vw, br		338 vw	
					ca. 270 vw, br		ca. 270 vw, br		285 vw	

^a Data in cm⁻¹. ^b See text. Abbreviations: vw = very weak; w = weak; m = medium; s = strong; vs = very strong; br = broad; sh = shoulder; L = Libration.

TABLE VI. Infrared Absorption Spectra of Anhydrous Cubic Nitroprussides (NaCl region).^a

Assignments	Mn[Fe(CN) ₅ NO]	Fe[Fe(CN) ₅ NO]	Co[Fe(CN) ₅ NO]	Ni[Fe(CN) ₅ NO]	Zn[Fe(CN) ₅ NO]
ν_{CN}	{ 2215 sh 2188 sh 2182 vs	2191 vs	2198 vs	2194 vs	2219 s
					2192 vs
					2147 vw
ν_{NO}	{ 1946 vs	1939 vs	1937 vs	1927 vs	1937 vs
		1915 vs	1913 vs	1901 vs	1932 sh
δ_{FeNO}	664 vw	663 w	665 w	662 w	666 vw
ν_{FeN}	656 vw				653 vw

^a Data in cm^{-1} . vs = very strong; s = strong; m = medium; w = weak; sh = shoulder.

spectra at low sample concentration such as in Figure 1 (*cf.* Figure 2).

It is to be noted that the bands due to the anion are displaced towards higher wavenumbers on cooling, as expected from the shrinkage suffered by the crystalline lattices.

The spectra of the anhydrous cubic nitroprussides also sustain the proposed division into two groups because in anhydrous FeNpr, CoNpr and NiNpr (group I) the NO stretching band splits into two peaks of approximately the same intensities, while in group II this band remains unsplit although its shape and wavenumber are different from those in the hydrated substances. The splitting of the NO stretching band had not been reported previously. It could be due to some degree of ordering of the NO groupings in the crystal lattice. Table VI presents infrared data for the anhydrous cubic nitroprussides as obtained with the Perkin-Elmer 221 spectrophotometer with NaCl optics. These results are in good accordance with previous reports [4, 9] and confirm the systematic increase of ν_{CN} produced by dehydration [9]. On the contrary, ν_{NO} decreases, the manganese salt being an exception because an increase in ν_{NO} is noted in this case. The FeNO deformation band and the FeN stretching band change little on dehydration.

b) Water bands Differences in the infrared behavior of water between the two groups of cubic nitroprussides are still more marked than for the anion. It is very suggestive that group I gathers together the nitroprussides with the higher hydration degrees (FeNpr·4H₂O, CoNpr·6H₂O, NiNpr·4H₂O) while group II includes the two compounds with the lowest numbers of water molecules (MnNpr·2H₂O, ZnNpr·3H₂O). It is also very interesting that group II includes cations with half-filled or complete *d* subshells. Spectra of group I are far simpler than group II spectra; these latter show more details and a better definition than group I and also they seem to be much more affected by the cooling of the samples (see Figures 1 and 2).

On cooling, bands assigned to H-bonded HO stretchings suffer a displacement towards lower wavenumbers and a strong increase in intensity. The free HO stretching bands experience also a noticeable increase in intensity for group I nitroprussides, while the wavenumbers do not change much. The HOH deformation bands do not change appreciably on cooling. The librational bands, again, increase in intensity and in the group II nitroprussides they shift clearly to higher wavenumbers; this could also be the case for group I nitroprussides as expected for H-bonded water molecules.

Group I nitroprussides. In group I the stretching and deformation regions look much like in some zeolites at low water content [28] and in the ternary systems inert solvent-water-organic base at low concentrations of the solutes present at a 1:1 respective ratio [29]. The sharp band of highest wavenumber in the HO stretching region has been assigned to free HO groups and the broad and most intense band at the lowest wavenumber to the hydrogen-bonded groups. The hydrogen bonds are directed to the oxide groups in the zeolites and the organic base in the inert solvent solutions, respectively [28, 29]. In the complexes formed by nitriles and proton donors, it is supposed that the association takes place through the π -electrons of the CN group [28]. This could be also the case for the transition metal nitroprussides, *i.e.*, the π -electrons of the CN and NO groups could be acceptor sites for hydrogen bonding in addition to the electron lone pairs of the oxygen atoms of the water molecules. Shifts suffered by the CN and NO stretching bands on dehydration could be taken as an evidence of the suggested π -H interaction. This supposition is also supported by the changes noted in the electronic spectra of cobalt and nickel nitroprussides (see below) when they are dehydrated.

In the librational region, the group I nitroprussides present no definite bands in the room temperature spectra. At 20 K there is a general decrease of the transmittance between 1000 and 250 cm^{-1} , although some features are insinuated in the same region where

nitroprussides of group II have definite bands (*vide infra*).

Group II nitroprussides. The surprisingly high number of sharp peaks in the high-wavenumber part of the HO stretching region points to the existence of different types of free or nearly free HO groups. At lower wavenumbers, the two broad bands indicate two types of strongly bonded HO groups. In correspondence with such a complicated HO stretching region the bending region shows two well defined peaks, the one at highest wavenumber being possible related to the HO stretching band of lowest wavenumber. The better definition of the spectra of group II nitroprussides compared with group I is perhaps related to the lower number of water molecules present in the lattices of the nitroprussides of group II. In the manganese salt there is, for instance, one molecule per interstice. Different sites must be therefore available for this single molecule. In the region below 900 cm^{-1} , bands due to librations of the water molecules are easily identified in group II spectra due to the strong temperature dependence of their intensities. The bands located at the highest wavenumbers (*ca.* 800 and *ca.* 520 cm^{-1}) should be related to the HO stretchings of lowest wavenumbers and to the HOH bendings of highest wavenumbers, *i.e.*, they are possibly due to the tightest bonded water molecules. Interestingly enough, a librational band at a wavenumber as high as 800 cm^{-1} has been observed in ice and in water strongly bonded to cations [29]. Information available does not allow us presently to distinguish between different librational modes and between modes belonging to different water molecules.

Non-cubic nitroprussides

$\text{Cu}[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$ The infrared spectrum of $\text{CuNpr} \cdot 2\text{H}_2\text{O}$ is quite similar to the spectra of group I nitroprussides. The main differences lie in the relative intensities of the δ_{FeNO} and ν_{FeN} bands: in the spectra of group I nitroprussides the first of these bands is stronger than the second one while in $\text{CuNpr} \cdot 2\text{H}_2\text{O}$ the relative intensities are reversed. In this compound the separation and differences in intensities of the bands assigned to the $\text{Fe}(\text{CN})_5$ moiety are larger than in the other nitroprussides. Another difference between the spectra of $\text{CuNpr} \cdot 2\text{H}_2\text{O}$ and the group I nitroprussides is the splitting of the deformation band of water.

Wavenumbers and tentative assignments of bands found in the spectra appear in Table VII. On dehydration, the infrared spectrum of copper(II) nitroprusside does not change much: the strong CN stretching band shifts upwards to 2209 cm^{-1} and the ν_{NO} band downwards to 1943 cm^{-1} . In the low-wavenumber region, the FeN stretching and FeNO deformation bands reverse their relative intensities; at the same time the separation between them decreases.

TABLE VII. Infrared Spectra of Dihydrate and Anhydrous $\text{Cu}[\text{Fe}(\text{CN})_5\text{NO}]$.

Assignments	$\text{Cu}[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}^a$	$\text{Cu}[\text{Fe}(\text{CN})_5\text{NO}]^b$
$2\nu_{\text{NO}}$	3880 vw	3860 vw
ν_{HO}	$\left\{ \begin{array}{l} 3652\text{ w} \\ 3449\text{ w, br} \end{array} \right.$	
ν_{CN}	$\left\{ \begin{array}{l} 2204\text{ vs} \\ 2175\text{ vw} \\ 2161\text{ vw} \\ 2154\text{ vw} \\ 2146\text{ vw} \\ 2135\text{ vw} \end{array} \right.$	$\left\{ \begin{array}{l} 2209\text{ vs} \\ 2195\text{ m} \\ 2166\text{ vw} \end{array} \right.$
ν_{NO}	1956 vs	1943 vs
$\delta_{\text{H}_2\text{O}}$	$\left\{ \begin{array}{l} 1607\text{ vs} \\ 1593\text{ w} \end{array} \right.$	
δ_{FeNO}	662 vw	661 vw
ν_{FeN}	639 w	647 vw
ν_{FeC} δ_{FeCN}^c	$\left\{ \begin{array}{l} 528\text{ w} \\ 460\text{ s} \\ 417\text{ vw} \end{array} \right.$	

^a Perkin-Elmer 457. ^b Perkin-Elmer 221 (NaCl region).

^c See text. vw = very weak; w = weak; m = medium; s = strong; vs = very strong; br = broad.

$\text{Cd}[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$. This spectrum looks like the group II spectra although it is a little more complicated. In the HO stretching region, for instance, there are two more bands in this spectrum than in group II spectra: one sharp band at the higher wavenumbers and a second broad and strong band at the lower wavenumbers. Wavenumbers and assignments of bands appear in Table VIII both for the hydrated and anhydrous cadmium nitroprussides; both ν_{CN} and ν_{NO} increase when cadmium nitroprusside is dehydrated, as in the case of MnNpr .

Electronic Spectra

The colour of the nitroprusside anion is red-brown as seen in the nitroprussides of the alkaline and alkaline-earth metals. In the visible part of the spectrum sodium nitroprusside presents two main bands at 497 and 395 nm which are assigned to the transitions: $^1\text{A}_1 \rightarrow ^1\text{E}$ [$2b_2 \rightarrow 7e$ ($\pi^*\text{NO}$)] and $^1\text{A}_1 \rightarrow ^1\text{A}_1$ ($6e \rightarrow 7e$) [30]. The nitroprussides of the transition metals have more complicated spectra and a variety of colours (see Table I) due to the superposition of the absorptions due to the cations and the common anion. The colours of some of these nitroprussides depend surprisingly on the hydration state, this being the case for the cobalt(II) and nickel(II) compounds. In the first case the colour of the hexahydrate is pink while the anhydrous compound is dark blue-violet; nickel nitroprusside is gray when

TABLE VIII. Infrared Spectra of Dihydrate and Anhydrous Cd[Fe(CN)₅NO].

Assignment	Cd[Fe(CN) ₅ NO]·2H ₂ O ^a	Cd[Fe(CN) ₅ NO] ^b
2ν _{NO}	3863 w	3854 vw
ν _{HO}	3665 m	
	3628 s	
	3598 m	
	3577 m	
	ca. 3420 sh, br	
ν _{CN}	3315 m	
	3217 s	
	2198 s	2207 w
	2179 vs	2180 vs
ν _{NO}	2145 vw	
	2135 vw	
	1956 sh	
δ _{H₂O}	1945 vs	1948 vs
	1650 w	
L _{H₂O}	1603 s	
	750 vw, br	
δ _{FeNO}	663 m	666 w
ν _{FeN}	649 w	654 vw
ν _{FeC} , δ _{FeCN} ^c	506 m	
L _{H₂O}	477 vw	
ν _{FeC} , δ _{FeCN} ^c	436 s	
	421 s	
	327 w	

^a Perkin-Elmer 457. ^b Perkin-Elmer 221. ^c See text.
vw = very weak; w = weak; m = medium; s = strong; vs = very strong; br = broad; sh = shoulder; L = libration.

hydrated while green when anhydrous. These striking differences are unexpected because the crystal structures of the hydrated and anhydrous compounds are the same and the water molecules seem to be of zeolitic nature (see above). The dehydration process should not bring about therefore any change in the coordination state of the cations in the lattices unless the ligand strengths of the terminal O and N atoms from the NO and CN groups which surround the cations in the Prussian-blue-like lattice of the bivalent nitroprussides are changed by some mechanism. It is to be noted that a similar colour change from pink to blue occurring upon dehydration of hydrated cobalt(II) hexacyanocobaltate(III) has been ascribed to a modification of the coordination of the interstitial cobalt(II) ions. These ions are supposed to be coordinated octahedrally to water in the hydrate and to the π electrons of three CN groups in the anhydrous compound [31].

In Figure 3 are reproduced the visible reflectance spectra of hydrated and anhydrous cobalt(II) and

nickel(II) nitroprussides. The spectrum of Na₂Npr·2H₂O is also included for the sake of comparison. Due to the low resolution attained in the spectra only the main bands due to the cations are considered in what follows. The cations located in the octahedral holes left by the nitroprusside anions are surrounded by N and O atoms. In the Prussian-blues and related polymeric cyanides the ligand strength of the nitrogen atoms has been estimated as lower than ammonia but slightly greater than water [32], and comparable with other nitrogen ligands such as NCO⁻, NCS⁻ and NCSe⁻ [33]. The terminal oxygen atom of the nitrosyl groups should have a lower strength (a partial positive charge is usually recognized on this group [30] (*cf.*, however, ref. 34). In accordance with these expectations the absorption band ν₃[⁴T_{1g}(F) → ⁴T_{1g}(P)] of Co²⁺ in CoNpr·6H₂O should contribute to the main absorption band in the corresponding spectrum of Figure 3 because the same band in [Co(OH₂)₆]²⁺ appears at 515 nm and in [Co(NH₃)₆]²⁺ at 474 nm [35]. Upon dehydration, the minimum of the band at 510 nm shifts to 580 nm. There is therefore a decrease of the ligand field strength. The same seems to occur although to a different extent in nickel nitroprusside on dehydration. In NiNpr·4H₂O the main visible absorption band which appears at 582 nm should be assigned to the ν₂[³A_{2g} → ³T_{1g}(F)] transition. This figure should be compared with wavelengths reported for ν₂ in [Ni(OH₂)₆]²⁺ (725 nm), [Ni(NH₃)₆]²⁺ (571 nm), [Ni(NCCH₃)₆]²⁺ (574 nm) [35].

On dehydration, ν₂ of NiNpr·4H₂O shifts to 620 nm, the displacement being smaller than in the case of cobalt(II) nitroprusside. In spite of the relatively slight shift of ν₂, nickel(II) nitroprusside changes appreciably its colour upon dehydration due to the increase of the reflectance in the green (see Figure 3).

The wavelengths of the main bands we are reporting for CoNpr·6H₂O and NiNpr·4H₂O are about 20 nm higher than values given by Inoue *et al.* It is to be noted that the band observed by them at 571 nm in NiNpr·2H₂O is assigned to the ³A_{2g} → ¹E_g transition in spite of its high intensity which points to a spin-allowed [³A_{2g} → ³T_{1g}(F)] transition.

Interestingly, the compounds K₂M^{II}[Fe(CN)₆]·xH₂O, where the divalent metallic cations (M^{II}) are in octahedral positions of the crystalline lattice and the potassium ions and the water molecules in the interstices, also experience spectacular changes of colour on dehydration when M^{II} = Co and Ni. According to our own observations the colour of the cobalt compound changes from light chocolate-brown to dark green on dehydration and the nickel compound from blue-green to brown (*cf.* ref. 32). It is worth mentioning that the infrared behaviour of water in these compounds is the same as in the nitroprussides

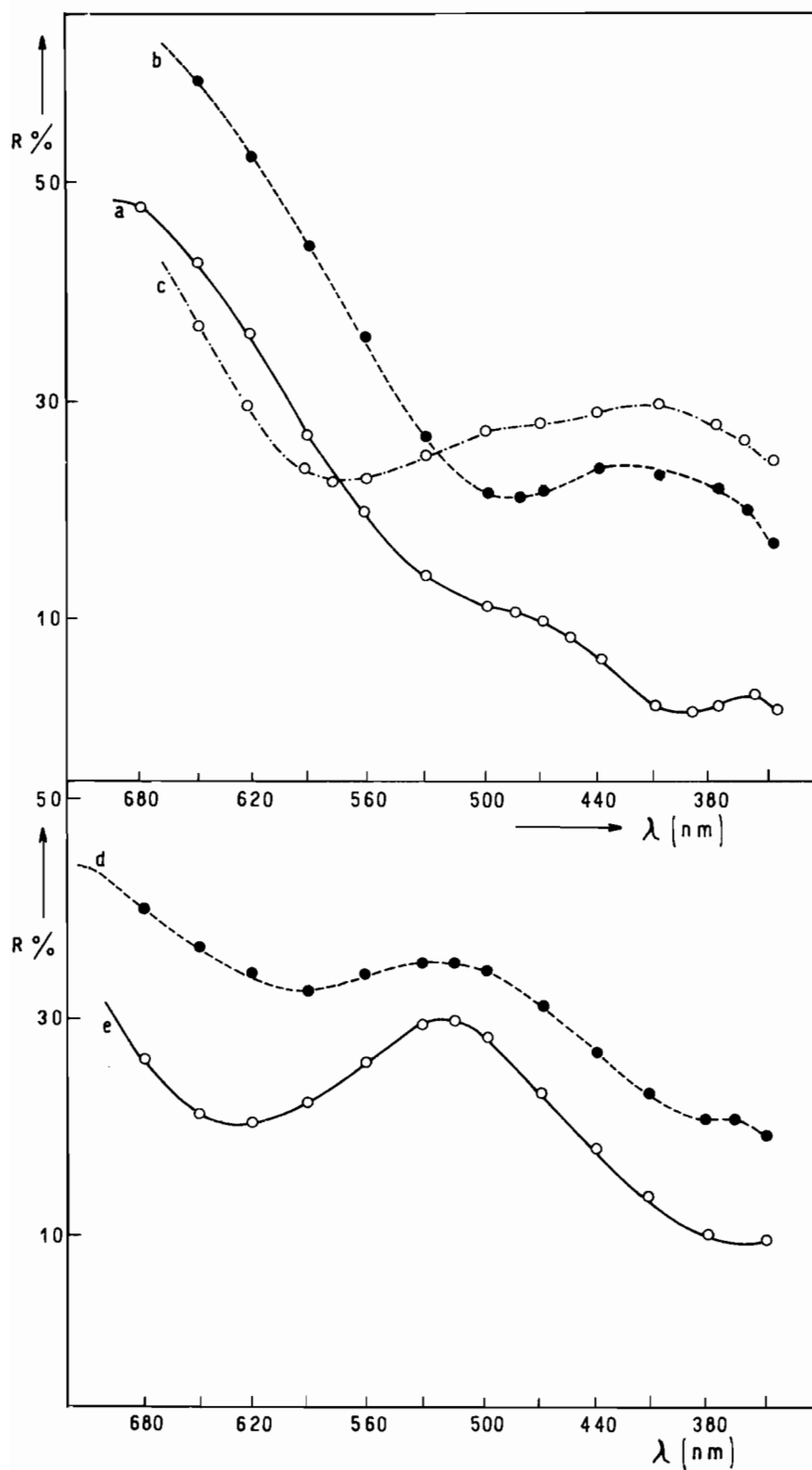


Figure 3. Visible reflectance spectra of nitroprussides: a) $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$, b) $\text{Co}[\text{Fe}(\text{CN})_5\text{NO}] \cdot 6\text{H}_2\text{O}$, c) $\text{Co}[\text{Fe}(\text{CN})_5\text{NO}]$ (anhydrous). d) $\text{Ni}[\text{Fe}(\text{CN})_5\text{NO}] \cdot 4\text{H}_2\text{O}$, e) $\text{Ni}[\text{Fe}(\text{CN})_5\text{NO}]$ (anhydrous).

of group II. As advanced above, the only explanation at hand to justify the described spectral changes and concomitant colour modifications is a decrease of the ligand field strength of the terminal N and O atoms of the CN and NO groups. This could be due to the interaction suggested above between the water molecules and the groups coordinated to the cations through hydrogen bonds directed to the π electrons. This interaction could bring about modifications also in the electronic levels of the nitroprusside ion leading to shifts in the bands assigned to the anion. Unfortunately, the quality of our spectra does not allow to draw any conclusions on this subject matter (see however ref. 1).

Magnetic Moments

Water seems to have no noticeable effect on the magnetic susceptibilities of cobalt and nickel nitroprussides because differences found between the magnetic moments of the hydrated and anhydrous samples are within the accuracy of our measurements (values in Bohr magnetons are, respectively: Co, 4.7 and 4.5; Ni, 2.8 and 2.9).

Electronic paramagnetic resonance spectrum of $\text{Cu}[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$

g values obtained from the first derivative of the EPR spectrum are as follows: $g_{\parallel} = 2.328$, $g_{\perp} = 2.066$. The relative values: $g_{\parallel} > g_{\perp} > g_0$ [g_0 (spin free value) = 2.0023] point to an axial elongation (stabilization of the d_{z^2} orbital) of the coordination octahedron around the Cu(II) ions [36] (cf. ref. 1).

From the mean value $\bar{g} = \sqrt{(g_{\parallel}^2 + 2g_{\perp}^2)}/3 = 2.2$ there results a calculated magnetic moment $\mu = 2.2 \sqrt{3}/2 = 1.9 \text{ BM}$, just equal to the experimental value (our own measurement).

The similarity found between $\text{CuNpr} \cdot 2\text{H}_2\text{O}$ and anhydrous $\text{K}_2\text{Cu}[\text{Fe}(\text{CN})_6]$ from the crystallographic point of view extends also to the EPR behaviour because for $\text{K}_2\text{Cu}[\text{Fe}(\text{CN})_6]$ the following g values have been reported: $g_{\parallel} = 2.24$, $g_{\perp} = 2.06$ [20].

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For note added in proof see overleaf

Note added in Proof (October 1, 1976)

Recently, D. B. Brown, *Inorg. Chem.*, 14, 2582 (1975), assigned a tetragonal structure to manganese(II) nitroprusside, and described two tetragonal forms of cupric nitroprusside. Our results compare better with data reported for Form II than for Form I.