

Mössbauer & Infrared Spectroscopic Studies of Several Nitroprussides

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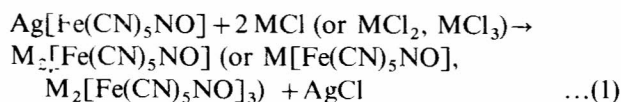
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Mössbauer spectra of several nitroprussides of the general formula $M[Fe(CN)_5NO] \cdot xH_2O$ where $M = Mg, Ca, Sr, Ba, Tl(I), Hg(I \text{ and } II), Al$ and $Ce(III)$ have been studied at room temperature. All the compounds exhibit large quadrupole splitting, $\Delta E_Q = 1.62$ to 1.91 mms^{-1} . Isomer shift varies in a narrow range, $\delta = 0.04$ to -0.04 mms^{-1} relative to sodium nitroprusside. Infrared and magnetic moment data are also reported. Overall structure and geometry of the nitroprusside anion remain unaffected by the presence of different outer cations.

The iron-57 Mössbauer spectroscopy has been used widely in the structural studies of pentacyanonitrosylferrates(III), also known as nitroprussides¹⁻⁸. Recently the authors studied the Mössbauer spectrum of anhydrous nitroprussic acid and explained the observations on the basis of a possible H-bonded model⁹ similar to those of ferro- and ferri-cyanic acids¹⁰. The present studies on some nitroprussides having the general formula, $M[Fe(CN)_5NO] \cdot xH_2O$ where $M = Mg, Ca, Sr, Ba, Hg(I \text{ and } II), Tl(I), Al$ and $Ce(III)$, have been undertaken with a view to investigating the effect of charge and size of the outer cations on the octahedral geometry around the central iron atom and the variation in s -electron density at the iron nucleus due to the presence of these cations.

Materials and Methods

All the chemicals used were of AR(BDH), GR (S Merck or E Merck) or high purity grade. Since most of the nitroprussides were soluble in water, an indirect method of preparing these was adopted (see Eq. 1). Equivalent quantities of metal chloride in solution and purified silver nitroprusside were mixed and stirred vigorously so that corresponding nitroprusside came into solution.



($M = Mg, Ca, Sr, Ba, Ce(III), Tl(I)$ and Al)

The solution was slowly evaporated under infrared lamp whence fine, needle shaped crystals were obtained in most cases. Mercurous nitroprusside was obtained as a pink-coloured precipitate when mercuric sulphate solution was added to an aqueous solution of sodium nitroprusside containing a small amount of nitric acid. Mercuric nitroprusside was obtained by the reaction between mercuric nitrate and sodium nitroprusside in water. As thallos chloride is insoluble

in water, its hot aqueous solution was used for the preparation of thallos nitroprusside. All the nitroprussides gave satisfactory elemental analyses (Table 1).

Mössbauer spectra were recorded at room temperature on a spectrometer consisting of a drive with constant acceleration mode, proportional counter and 512 channel analyser. About 10^5 counts were collected. A 25 mCi ⁵⁷Co(Rh) source was used. The instrument was calibrated using natural iron absorber. All isomer shift values are relative to sodium nitroprusside and have been obtained by adding 0.288 mms^{-1} to the observed values.

Magnetic moments were calculated at room temperature by Gouy method using $Hg[Co(CNS)_4]$ as

Table 1—Analytical Data of Nitroprussides

Sl No.	Nitroprusside (colour)*	Found (Calc.) (%)		
		M [†]	Fe	C
1	Mg[Fe(CN) ₅ NO].3.5H ₂ O (red)	7.79	18.01	20.87
		(8.02)	(18.42)	(19.78)
2	Ca[Fe(CN) ₅ NO].4H ₂ O (red)	12.82	16.67	18.60
		(12.22)	(17.03)	(18.29)
3	Sr[Fe(CN) ₅ NO].3H ₂ O (red)	23.53	15.42	16.66
		(24.51)	(15.62)	(16.66)
4	Ba[Fe(CN) ₅ NO].H ₂ O (red)	37.18	14.79	15.14
		(36.99)	(15.04)	(16.16)
5	Hg[Fe(CN) ₅ NO].0.5H ₂ O (chocolate)	47.20	12.62	15.04
		(48.16)	(13.41)	(14.41)
6	Hg ₂ [Fe(CN) ₅ NO].2H ₂ O (pink)	60.63	8.76	9.55
		(61.43)	(8.55)	(9.72)
7	Tl ₂ [Fe(CN) ₅ NO].2H ₂ O (red)	60.44	8.56	9.42
		(61.88)	(8.46)	(9.61)
8	Al ₂ [Fe(CN) ₅ NO] ₃ (red)	7.12	23.70	24.89
		(7.69)	(23.88)	(25.65)
9	Ce ₂ [Fe(CN) ₅ NO] ₃ .3H ₂ O (red)	28.53	17.89	19.01
		(28.50)	(18.06)	(19.40)

*Nitroprussides of Hg(I) and Hg(II) are insoluble in water; all other nitroprussides are soluble in water.

†M refers to outer metal cation.

Table 2—Magnetic and Mössbauer Spectral Data of Various Nitroprussides

Nitroprusside*	Magnetic moment (B.M.)	Isomer shift† (δ , mms^{-1})	Quadrupole splitting (ΔE_Q , mms^{-1})	Γ_1 , mms^{-1}	Γ_2 , mms^{-1}
1	0.00	0.04	1.88	0.28	0.30
2	0.58	0.02	1.84	0.21	0.26
3	1.06	0.03	1.78	0.28	0.26
4	1.11	0.02	1.91	0.21	0.29
5	2.57	0.04	1.62	0.25	0.36
6	1.24	0.00	1.66	0.29	0.29
7	1.01	0.04	1.87	0.25	0.22
8	1.06	0.00	1.87	0.29	0.32
9	1.16	0.02	1.91	0.28	0.32

*SI Nos refer to nitroprussides listed in Table 1.

†Relative to that of sodium nitroprusside and obtained by adding 0.288 mms^{-1} , to the observed shift values.

a standard. Infrared spectra were recorded in KBr on a Perkin-Elmer Spectrophotometer, model 580, in the range $4000\text{--}200 \text{ cm}^{-1}$.

Results and Discussion

All the nitroprussides studied presently (see Table 1) exhibit a well-resolved doublet with $\Delta E_Q = 1.62$ to 1.91 mms^{-1} . The Mössbauer parameters and the line widths are reported in Table 2. A typical Mössbauer spectrum of cerous nitroprusside, $\text{Ce}_2[\text{Fe}(\text{CN})_5\text{NO}]_3 \cdot 3\text{H}_2\text{O}$ indicating the quality of Mössbauer spectrum is shown in Fig. 1. Isomer shift values do not vary significantly and are in the small range of 0.04 to -0.04 mms^{-1} . Characteristic IR frequencies with their most probable assignments are given in Table 3.

The crystal structure of sodium nitroprusside has been investigated by Manoharan and Hamilton¹¹ and reinvestigated by Bottomley and White¹². In nitroprusside anion $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ central iron atom, covalently bonded with five CN^- and an NO^+ , is in +2 state with the ground state 1A_1 . The ligands NO and *trans* CN are approximately collinear with iron atom slightly displaced towards NO group (by 0.183 \AA) from the four planar pseudo-equivalent CN^- to form orthorhombic structure and space group P_{nmm} with $a = 6.198 \text{ \AA}$, $b = 11.897 \text{ \AA}$, $c = 15.557 \text{ \AA}$ and $d = 1.71$ for $Z = 4$. Eventhough idealized C_{4v} symmetry is formed, the anion has effective $4mm$ symmetry. The N—Fe—C equatorial angle is 96° , slightly larger than the expected 90° . Although six ligands are bonded to iron by σ -bonds, strong $d_\pi \rightarrow p_\pi$ bonding has been suggested^{13–15} due to the back donation of electrons from the filled metal d_π orbitals. Carbon-13 NMR chemical shift studies¹⁶ of substituted pentacyano-ferrate(II) complexes have indicated strong back

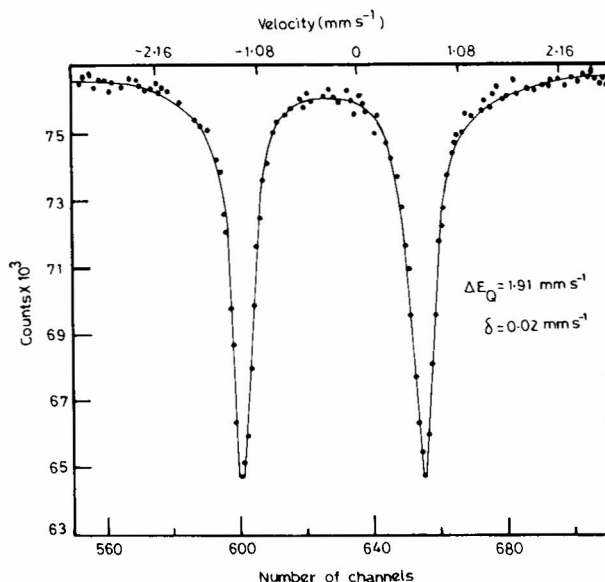


Fig. 1—Mössbauer spectrum of cerous nitroprusside at room temperature

bonding supporting Mössbauer and electronic spectral conclusions. Extensive MO calculations¹³ of the $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ anion have shown the ground state configuration to be $(d_{xz}, d_{yz})^4 (d_{xy})^2$ or $(e)^4 (b_2)^2$, with energy separation of 4570 cm^{-1} between e and b_2 levels. An asymmetry at the iron nucleus is generated resulting in large quadrupole splitting.

No significant change in isomer shift and quadrupole splitting values is observed in most of the nitroprussides, except for mercuric and mercurous nitroprussides which not only exhibit comparatively small ΔE_Q values but also smaller δ -values. This may possibly be due to completed $3d$ shell configuration in mercury which may be affecting back donation. Hg^{2+} has a large ionic radius (1.10 \AA) and this is expected to distort the geometry of nitroprusside anion to a large extent, thus affecting ΔE_Q . However, it appears that mercurous and mercuric ions are situated at a distance from the nitroprusside ion so as not to cause any distortion in the geometry of the nitroprusside anion. Similarly, charge on outer cation does not seem to affect any of the Mössbauer parameter. Barium and Ce nitroprussides show largest quadrupole splittings of $\Delta E_Q = 1.91 \text{ mms}^{-1}$, indicating that possibly these ions are situated closer to nitroprusside anion, and this may affect its geometry only slightly.

In homologous compounds such as the nitroprussides of Mg, Ca, Sr and Ba no uniform trend is observed. Detailed X-ray analysis of strontium nitroprusside dihydrate indicates crystal parameters⁸ comparable to those of sodium nitroprusside¹². Strong H-bonding has been suggested for molecules of water of crystallization. No such indication is available

Table 3—Characteristic Infrared Frequencies for Various Nitroprussides

Nitroprusside*	$\nu\text{C}\equiv\text{N}$	$\nu\text{N}=\text{O}$	$\nu\text{Fe}-\text{N}$	$\delta\text{Fe}-\text{C}-\text{N}$	$\nu\text{Fe}-\text{C}$	$\delta\text{H}-\text{C}-\text{H}$	$\nu\text{M}-\text{O}$
1	2180s	1980s	660w 650w	515w	450b	1615vw 1600w	340w
2	2195m 2160s 2140vw	1960s	660w	510w	435m	1620m	325w
3	2145s	1965s	660w	505w	420sh	1605s	320w
4	2140s 2100vw	1960s	660s 640vw	500vw	410sh	1610s	320w
5	2160vw 2140s	1960s	655s 645vw	470vw	410w	1610s	310w
6	2160s 2140s	1960s	655m 645w	510m	415m	1610vs	320m
7	2140m 2125vw	1940b	660s 640w	510w	405s	1620w	330vw
8	2200w 2145w	1950sh	650w	560b,sh	440w	1620s	305vw
9	2160s 2125w	1955w 1930w	660w 640w	510w	440w	1606m,b	330w

*SI Nos refer to nitroprussides listed in Table 1.

from the present measurements. Incidentally, strontium nitroprusside exhibits a smaller ΔE_Q compared to ΔE_Q s of other nitroprussides in this homologous series. This may be ascribed to the fact that the number of molecules of water of crystallization in strontium nitroprusside may be different from those present in the nitroprussides of Hg, Ca and Ba. No good correlation is observed between δ and ΔE_Q for alkaline earth metal nitroprussides, similar to that observed in transition metal nitroprussides⁷.

The nitroprusside anion is diamagnetic because all the six d -electrons of the central metal remain paired up. The low magnetic moments observed for some nitroprussides (Table 2) may be primarily due to orbital contribution of the outer cations¹⁷. For mercuric nitroprusside, $\mu_{\text{eff}} = 2.5$ B.M. is quite high.

The infrared spectra of all the nitroprussides exhibit νNO and $\nu\text{C}\equiv\text{N}$ modes in the regions 1980-1930 and 2195-2125 cm^{-1} , respectively. The bands in the region 1980-1930 cm^{-1} can be assigned to NO^+ . The occurrence of νNO in the region 1980-1930 cm^{-1} indicates that back bonding properties of NO^+ are affected slightly by the presence of outer cations³.

The $\nu\text{Fe}-\text{N}$, $\delta\text{Fe}-\text{C}\equiv\text{N}$ and $\nu\text{Fe}-\text{C}$ modes appear in the regions 660-640, 515-470 and 450-405 cm^{-1} , respectively, in conformity with literature reports^{15,17,18}. For aluminium nitroprusside a broad shoulder with splitting appears at 560 cm^{-1} . In most cases splitting with separation of about 20-40 cm^{-1} in $\nu\text{C}\equiv\text{N}$ mode may be attributed to difference in the behaviour of equatorial and axial nature of CN groups. Brown¹⁵ has argued that NO^+ should be

assigned as NO and concluded that formal charge on iron should be +3. However, our Mössbauer isomer shift data, in confirmation with other recent works^{18,19} do not support this view. If iron is in +3 low spin state in nitroprusside ion then its magnetic moment would correspond to 1.73 B.M. Similarly IR bands would also be considerably shifted in the two oxidation states. The IR and magnetic data clearly indicate that formal charge on iron is +2.

The presence of water of crystallization is confirmed by the appearance of $\nu\text{O}-\text{H}$ in the region 3600-3560 cm^{-1} and $\delta\text{O}-\text{H}$ in the region 1600-1620 cm^{-1} (see ref. 18). Further, there is no significant change in major band positions with the change in outer cation, confirming our view that the outer cations are not involved in any type of bonding or interaction as has been observed for some other nitroprussides⁷.

The shift in $\nu\text{C}\equiv\text{N}$ modes by 20-40 cm^{-1} relative to that of sodium nitroprusside clearly indicates the presence of bridging cyanide structure in the nitroprussides studied presently. It is observed that νNO modes also shift to higher wavenumbers ($\Delta\nu = 10$ -40 cm^{-1}), suggesting the presence of bridging nitrosyl ligand. Inoue *et al.*²⁰ have shown that O-M bond does not exist in Fe, Ni, and Zn nitroprussides but the possibility of significant interaction may not be ruled out. A very weak band observed in the region 305-340 cm^{-1} may possibly be attributed to $\nu\text{M}-\text{O}$.

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