

Mössbauer Spectroscopic Evidence of Hydrogen Bonding in Nitroprussic Acid

D V PARWATE & A N GARG*

Department of Chemistry, Nagpur University, Nagpur 440 010

Received 26 June 1984; revised 12 October 1984; accepted 31 December 1984

Room temperature Mössbauer spectrum of anhydrous nitroprussic acid ($\text{H}_2[\text{Fe}(\text{CN})_5\text{NO}]$) exhibits a well-resolved quadrupole doublet with $\Delta E_Q = 1.85 \pm 0.03 \text{ mms}^{-1}$ and $\delta = 0.015 \pm 0.010 \text{ mms}^{-1}$ (with reference to sodium nitroprusside dihydrate). This large ΔE_Q value, in comparison to the ΔE_Q of alkali metal nitroprussides has been attributed to intermolecular hydrogen bonding in the acid. Infrared spectral measurements also support these conclusions.

Mössbauer¹, infrared^{2,3} and refractometric⁴ studies have conclusively proved the presence of unsymmetrical intermolecular hydrogen bonding in anhydrous hydrogen hexacyanoferrate(II) and hydrogen hexacyanoferrate(III). This is in contrast to the behaviour of alkali metal hexacyanoferrates (II and III). Garg and Goel⁵ studied several alkali metal and transition metal nitroprussides and pointed out⁶ that the highly unstable and difficult to prepare nitroprussic acid, $\text{H}_2[\text{Fe}(\text{CN})_5\text{NO}]$ should also show intermolecular hydrogen bonding. We have now prepared $\text{H}_2[\text{Fe}(\text{CN})_5\text{NO}]$ in the solid state and studied its Mössbauer and infrared spectra at room temperature.

All the chemicals used were of AR(BDH), GR (S Merck) grade or of high purity. Nitroprussic acid was prepared by first precipitating silver nitroprusside and then reacting it with required quantity of conc. HCl. The dark red solution was slowly evaporated under infrared lamp at $\sim 70^\circ\text{C}$ whence shining dark red coloured crystals of the acid were obtained (Found: C, 26.85; H, 1.15; Fe, 25.09. Calc.: C, 27.54; H, 0.92; Fe,

25.64%). These crystals decomposed to form blackish product on prolonged standing.

Mössbauer spectrum was recorded with a constant velocity transducer driven spectrometer (ECIL, Hyderabad) using a $\sim 5 \text{ mCi } ^{57}\text{Co}(\text{Rh})$ source (Amersham, UK). The spectrometer was calibrated by recording the spectra of iron foil and recrystallized sodium nitroprusside as standards. Infrared spectra were recorded on SPECORD 75 model spectrophotometer in nujol mull in the range $4000\text{--}400 \text{ cm}^{-1}$. Magnetic measurements were carried out on a Guoy balance using $\text{Hg}[\text{Co}(\text{CNS})_4]$ as the calibrant.

The room temperature Mössbauer spectrum of nitroprussic acid exhibits a well-resolved quadrupole doublet (Fig. 1). Mössbauer parameters, δ (with reference to sodium nitroprusside) and ΔE_Q are given in Table 1 alongwith measured linewidths (FWHM). Also given in Table 1 are the parameters for other alkali metal nitroprussides and hydrogen hexacyano-

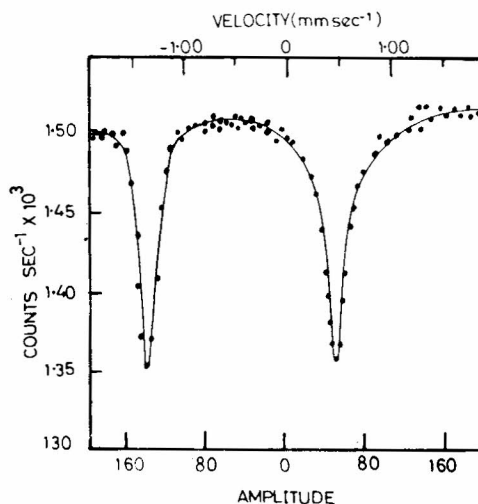


Fig. 1—Mössbauer spectrum of $\text{H}_2[\text{Fe}(\text{CN})_5\text{NO}]$ at room temperature

Table 1—Mössbauer Parameters for Various Nitroprussides at Room Temperature

Compound	Isomer shift δ , mms^{-1}	Quadrupole splitting ΔE_Q mms^{-1}	Linewidths (FWHM) mms^{-1}	Reference
$\text{H}_2[\text{Fe}(\text{CN})_5\text{NO}]$	0.015 ± 0.01	1.85 ± 0.03	0.21, 0.23	This work
$[\text{Li}_2[\text{Fe}(\text{CN})_5\text{NO}].3\text{H}_2\text{O}]$	0.05 ± 0.02	1.62 ± 0.03	0.26, 0.24	5
$\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}].2\text{H}_2\text{O}$	0.00 ± 0.02	1.705 ± 0.002	0.24, 0.26	19
$\text{K}_2[\text{Fe}(\text{CN})_5\text{NO}].2\text{H}_2\text{O}$	0.07 ± 0.02	1.74 ± 0.03	0.30, 0.32	5
$\text{Rb}_2[\text{Fe}(\text{CN})_5\text{NO}]$	0.13 ± 0.02	1.78 ± 0.02	0.26, 0.24	5
$\text{Cs}_2[\text{Fe}(\text{CN})_5\text{NO}]$	0.40 ± 0.02	2.00 ± 0.03	0.24, 0.22	5
$\text{H}_4[\text{Fe}(\text{CN})_6]$	0.13 ± 0.01	0.23 ± 0.02	0.19, 0.20	1
$\text{H}_3[\text{Fe}(\text{CN})_6]$	0.20 ± 0.02	0.20 ± 0.03	0.22, 0.22	1

ferrates (II) and (III) for comparison. Magnetic measurements showed the compound to be diamagnetic.

Structurally nitroprussides of several elements have been widely studied by X-ray crystallography⁷⁻⁹, infrared^{5,10-12} and Mössbauer spectroscopic^{13,14} techniques. Basic unit of nitroprussides is the nitroprusside anion $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ where iron is bonded to five CN^- and one NO^+ ligands in an octahedral geometry. The ligands NO^+ and *trans* CN^- are approximately collinear with the central iron atom slightly displaced in the direction of the NO group from the plane of the four pseudo equivalent CN groups (in the case of sodium nitroprusside this displacement is 0.2 Å). Nitroprussic acid is also found to be diamagnetic like all other nitroprussides¹⁵. This is attributed to strong $d_\pi \rightarrow p_\pi$ bonding due to back donation of electrons from the filled metal d_π -orbitals (also termed as e and b_2) to the empty ligand antibonding p_π -orbitals^{16,17}. Manoharan and Gray¹⁷ have shown the energy separation between e and b_2 to be mainly responsible for generating an asymmetry at the iron nucleus. The asymmetric expansion of the e and b_2 electrons towards the NO ligand causes a large quadrupole splitting.

Alkali metal nitroprussides have ΔE_Q values in the range 1.62-2.00 mms^{-1} (Table I). The observed $\Delta E_Q = 1.85 \pm 0.03 \text{ mms}^{-1}$ for nitroprussic acid is higher than that for sodium nitroprusside (Table I). Mössbauer spectrum of $\text{H}_4\text{Fe}(\text{CN})_6$ yields a doublet unlike that of the other alkali metal hexacyanoferrates(II) which all give a singlet¹. In view of the similarity of Mössbauer spectrum of nitroprussic acid and hydrogen hexacyanoferrate(II), it is reasonable to presume intermolecular unsymmetrical hydrogen bonding in nitroprussic acid. The high ΔE_Q value is due to higher asymmetry generated in nitroprussic acid as a result of intermolecular hydrogen bonding. There can be two possibilities: (i) two hydrogen atoms are bound to any two CN ligands (both equatorial or one axial and one equatorial) and thus a three dimensional network may be formed (see Fig. 2A) and (ii) out of the two hydrogens, one is bound to a CN and the other to NO ligand, thus forming a three dimensional network (see Fig 2B). The isomer shift value of $\text{H}_2[\text{Fe}(\text{CN})_5\text{NO}]$ ($\delta = 0.015 \pm 0.010 \text{ mms}^{-1}$) is close to the isomer shift values of other nitroprussides and is the lowest (Table I). This may be explained if hydrogen is assumed to be bonded to any of CN or NO ligand in the proposed model. In that case it will be electropositive and will withdraw some electronic charge from the d -orbitals of iron atom, thereby decreasing δ -value. This is in agreement with our proposed model.

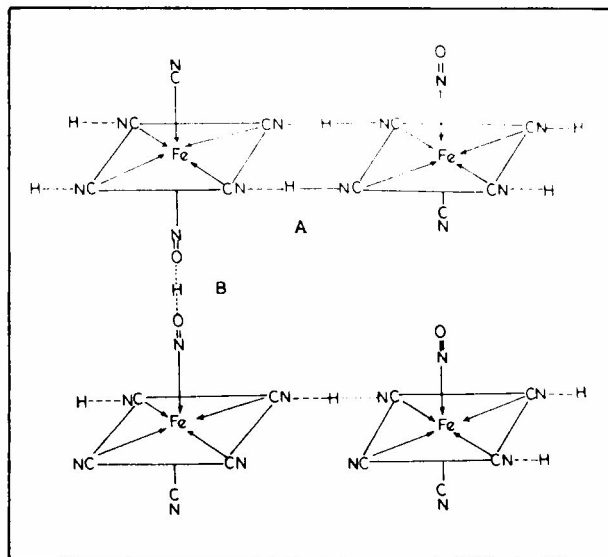


Fig. 2—Three dimensional model for $\text{H}_2[\text{Fe}(\text{CN})_5\text{NO}]$ showing inter-molecular unsymmetrical hydrogen bonding in two ways: (A) where any two CN ligands are involved in H-bonding and (B) where one CN and another NO are involved

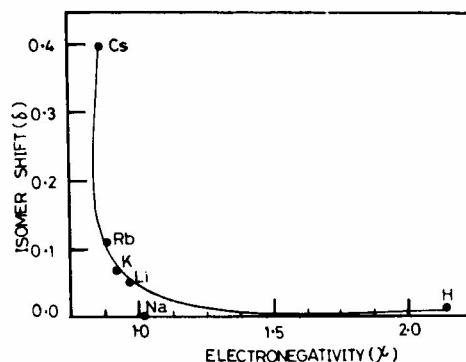


Fig. 3—Correlation of isomer shift and electronegativity (χ) of the outer cation in alkali metal nitroprussides

The plot of isomer shift values of various alkali metal nitroprussides versus electronegativities (χ) of the outer cations, (Fig. 3) shows that δ -values decrease with increase in electronegativities of the cations. This trend is similar to that observed in alkali metal hexacyanoferrates(II) and hexacyanoferrates(III)¹. Monaghan and Fanning¹⁸ have attributed the observed differences in δ values of alkali metal ferrocyanides partially to difference in the second order Doppler shift part of the δ -values. It has been further stated that $\text{H}_4\text{Fe}(\text{CN})_6$ is most covalent amongst all the alkali metal hexacyanoferrates(II). Presumably the same argument may be extended to the present case of alkali metal nitroprussides where $\text{H}_2[\text{Fe}(\text{CN})_5\text{NO}]$ having the lowest δ -value will be most covalent and $\text{Cs}_2[\text{Fe}(\text{CN})_5\text{NO}]$ will be the most ionic compound. Similarly the plot of ΔE_Q versus χ in Fig. 4 is linear for all the alkali metal nitroprussides

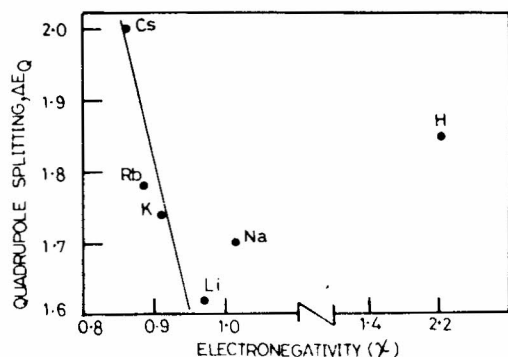


Fig. 4—Correlation of quadrupole splitting and electronegativity (χ) of the outer cation in alkali metal nitroprussides

except nitroprussic acid suggesting an anomalous behaviour. While all the alkali metal nitroprussides are ionic, some covalency factor is present in $\text{H}_2[\text{Fe}(\text{CN})_5\text{NO}]$.

Infrared spectrum of $\text{H}_2[\text{Fe}(\text{CN})_5\text{NO}]$ in nujol shows three very strong peaks at 2175, 1940 and 415 cm^{-1} corresponding to νCN , νNO and $\nu\text{Fe}-\text{C}$ respectively. A weak band at 630 cm^{-1} has been assigned to $\nu\text{Fe}-\text{N}$ and another at 500 cm^{-1} to deformation of $\text{Fe}-\text{C}\equiv\text{N}$ bonding. The νCN is quite sharp and symmetric but νNO is broad and asymmetric. This observation inter alia supports structure (B) over structure (A) for nitroprussic acid.

We are grateful to the CSIR, New Delhi for sponsoring this research project.

References

- 1 Garg A N & Goel P S, *J inorg nucl Chem*, **31** (1969) 697; **32** (1970) 1597.
- 2 Ginsberg A P & Koubek E, *Inorg Chem*, **4** (1965) 1186.
- 3 Beck W & Smedel H S, *Z Naturforsch*, **20B** (1965) 109.
- 4 Bastanov S S, *Vestn mosk gos Univ*, (1958) 117; *Refractometry and chemical structure* (English Translation—P P Sutton) (Van Nostrand, New York) 1966.
- 5 Garg A N & Goel P S, *Inorg Chem*, **10** (1971) 1344.
- 6 Garg A N, *Mössbauer effect studies of chemical bonding in some iron complexes*, Ph.D. Thesis (Indian Institute of Technology, Kanpur) 1970.
- 7 Manoharan P T & Hamilton W C, *Inorg Chem*, **2** (1963) 1043.
- 8 Bottomley F & White P S, *Acta Crystallogr*, **B35** (1979) 2193.
- 9 Castellano E E, Piro O E, Podjarny A D, Rivero B E, Aymonino P J, Lesk J H & Varette E L, *Acta Crystallogr*, **B34** (1978) 2673.
- 10 Brown D B, *Inorg Chem*, **14** (1975) 2582.
- 11 Gentil L A, Baran E J & Aymonino P J, *Inorg chim Acta*, **20** (1976) 251.
- 12 Waiké T, Krasser W, Beehthold P S & Hawsuehl S, *Solid State Comm*, **45** (1983) 503.
- 13 Boughton C A, Bradey G R, Matejczyk D E, Reed C R, McKinney B J & Lombardi J C, *J inorg nucl Chem*, **38** (1976) 427.
- 14 Long J C, Thomas J L & Lombardi J C, *J inorg nucl Chem*, **40** (1978) 1627.
- 15 Parwate D V & Garg A N (unpublished results).
- 16 Tosi L & Danon J, *Inorg Chem*, **3** (1964) 150.
- 17 Manoharan P T & Gray H B, *J Am chem Soc*, **87** (1965) 3340.
- 18 Monaghan C P & Fanning J C, *J phys Chem*, **82** (1978) 1043.
- 19 Grant R W, Housley R M & Gonser U, *Phys Rev*, **178** (1969) 523.