

Synthesis of Isotope Enriched $(\text{CN}_3\text{H}_6)_2[{}^{57}\text{Fe}(\text{CN})_5\text{NO}]$ starting from ${}^{57}\text{Fe}$

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Dedicated to Professor Dr. Kurt Dehnicke on the Occasion of his 70th Birthday

Abstract. A high-yield, mmolar-scale synthesis of pure guanidinium nitroprusside, $(\text{CN}_3\text{H}_6)_2[{}^{57}\text{Fe}(\text{CN})_5\text{NO}]$ (GNP) from iron metal is described. The iron metal contained pieces of 95.3% ${}^{57}\text{Fe}$ together with normal iron so that an isotope enrichment in ${}^{57}\text{Fe}$ of 25% was achieved. Single-crystals of GNP could be grown in cubic shape and dimensions of about $3 \times 4 \times 4 \text{ mm}^3$. The purity of the GNP product and the intermediates $\text{K}_4[{}^{57}\text{Fe}(\text{CN})_6] \cdot 3 \text{H}_2\text{O}$ and $\text{Na}_2[{}^{57}\text{Fe}(\text{CN})_5\text{NO}] \cdot 2 \text{H}_2\text{O}$ was ascertained by ${}^{57}\text{Fe}$ Mössbauer spectroscopy as well as ${}^{13}\text{C}$, ${}^{14}\text{N}$ and ${}^{57}\text{Fe}$ NMR spectroscopy. The ${}^{57}\text{Fe}$ NMR chemical shift for $[{}^{57}\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ in GNP was detected at +2004.0 ppm [vs $\text{Fe}(\text{CO})_5$].

Keywords: Sodium nitroprusside, Guanidinium nitroprusside, Moessbauer spectroscopy (${}^{57}\text{Fe}$); NMR spectroscopy (${}^{57}\text{Fe}$)

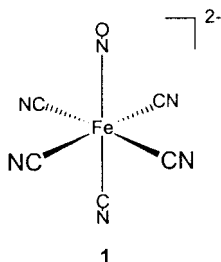
Synthese von Isotopen-angereichertem $(\text{CN}_3\text{H}_6)_2[{}^{57}\text{Fe}(\text{CN})_5\text{NO}]$ ausgehend von ${}^{57}\text{Fe}$

Inhaltsübersicht. Es wird eine Synthese mit hoher Ausbeute und im mmol-Bereich von reinem Guanidiniumnitroprussiat, $(\text{CN}_3\text{H}_6)_2[{}^{57}\text{Fe}(\text{CN})_5\text{NO}]$ (GNP) ausgehend von Eisenmetall beschrieben. Das Eisenmetall enthielt Stücke von 95.3%-igem ${}^{57}\text{Fe}$ und normales Eisen, so dass eine Isotopenanreicherung in ${}^{57}\text{Fe}$ von 25% erreicht wurde. Einkristalle von GNP konnten als Quader mit Abmessungen von etwa

$3 \times 4 \times 4 \text{ mm}^3$ gezüchtet werden. Die Reinheit des GNP-Produktes und der Zwischenprodukte $\text{K}_4[{}^{57}\text{Fe}(\text{CN})_6] \cdot 3 \text{H}_2\text{O}$ und $\text{Na}_2[{}^{57}\text{Fe}(\text{CN})_5\text{NO}] \cdot 2 \text{H}_2\text{O}$ wurde mittels ${}^{57}\text{Fe}$ Mössbauer Spektroskopie und für $\text{K}_4[{}^{57}\text{Fe}(\text{CN})_6] \cdot 3 \text{H}_2\text{O}$ auch mit ${}^{13}\text{C}$, ${}^{14}\text{N}$ und ${}^{57}\text{Fe}$ NMR Spektroskopie überprüft. Die ${}^{57}\text{Fe}$ NMR chemische Verschiebung für $[{}^{57}\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ in GNP wurde bei +2004.0 ppm [vs $\text{Fe}(\text{CO})_5$] detektiert.

Introduction

The complex pentacyanonitrosylferrate(II) or nitroprusside anion $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ (**1**) is a species of high academic [1, 2] and pharmaceutical [3] interest. The sodium salt, $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2 \text{H}_2\text{O}$ (sodium nitroprusside) is given as a medicine to lower the blood pressure e. g. during operations or heart attacks [3, 4].



The ambidentate NO ligand is normally, i. e. in the ground state, N-bonded to the metal (M) [5]. In

several nitrosyl complexes metastable states have been discovered that can be excited and deexcited by irradiation with light. Due to this property these complexes are promising materials for display devices and for optical memory devices with extremely high capacity. Based on X-ray diffraction and IR data an M-ON linkage isomer has been proposed for at least one of the metastable states [2, 6]. The possibility of M-NO vs. M-ON linkage isomers is especially relevant for metal nitrosyl porphyrins [6] in view of the biological role of NO [7]. For further investigations of these metastable states, e. g. by Mössbauer spectroscopy or nuclear inelastic scattering [8], it is helpful to use ${}^{57}\text{Fe}$ isotope enriched material. Therefore, we describe here the synthesis of guanidinium nitroprusside (GNP), $(\text{CN}_3\text{H}_6)_2[{}^{57}\text{Fe}(\text{CN})_5\text{NO}]$ with isotope enrichment in ${}^{57}\text{Fe}$ starting from ${}^{57}\text{Fe}$ metal. GNP is a standard material for such investigations [9]. GNP offers the advantage over other nitrosyl complexes that all Fe-N-O axes are oriented nearly parallel in its crystalline state [10, 11].

The general synthesis has, of course, already been described in the literature. The problem presented here when using ${}^{57}\text{Fe}$ is to carry out these syntheses with small quantities on a mmol scale. This is not a trivial problem due to, for example, the extremely high

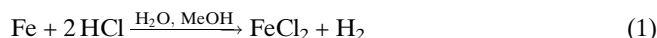
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solubility of some of the intermediates. Furthermore, single crystals of the final GNP product should be made available in a more regular cubic shape with crystal sizes of about $2 \times 2 \times 2 \text{ mm}^3$ instead of the usual needle shape. The purity of the product and of intermediates has been checked by ^{57}Fe Mössbauer and ^{57}Fe NMR spectroscopy with respect to contaminants of other iron compounds and oxidation states.

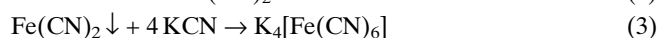
Results and Discussion

The synthetic routes were tested starting with normal iron metal in the same quantity before carrying out the procedure with the expensive ^{57}Fe metal (current price US-\$ 4.00/mg). Thus, each reaction has at least been carried out twice and reproducibility on the given mmol scale can be ensured. An isotope enrichment of about 25% was chosen, so that 0.2 g of ^{57}Fe metal (95.3% isotope purity) were blended with 0.6 g of normal iron metal.

The transformation of iron metal to FeCl_2 was done by reaction with conc. hydrochloric acid in methanol under inert gas (eq. (1)) [12]. To exclude the formation of Fe^{III} impurities, the solution was filtered over iron powder.



The potassium hexacyanoferrate complex was formed from an alkaline solution of FeCl_2 through addition of an about 1.5-fold excess of KCN. An $\text{Fe}(\text{CN})_2$ precipitate could be observed as the intermediate (eq. (2) and (3)).



For the subsequent reaction with HNO_3 , the excess of KCN had to be removed. A presence of KCN prevented the clean formation of the nitroprusside anion. Separation of $\text{K}_4[\text{Fe}(\text{CN})_6]$ and KCN could be achieved dissolving the mixture in water. Through addition of the same volume of methanol the hexacyanoferrate precipitated again while KCN remained in solution. After recrystallization of $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3 \text{H}_2\text{O}$ from hot/cold water the purity with respect to other iron compounds was checked by ^{57}Fe Mössbauer and ^{57}Fe NMR spectroscopy. The Mössbauer spectrum of $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3 \text{H}_2\text{O}$ (Figure 1) shows the expected singlet. The errors given with the Mössbauer parameters in Table 1 may appear rather large. This is, however, due to the large energy window of $\pm 11 \text{ mm/s}$ which was chosen so as to detect any possible impurity.

Usually an analysis of Mössbauer spectra with respect to impurities and an estimation of their content is done by comparing the area of different subspectra, which are for instance fitted with Lorentzian lines.

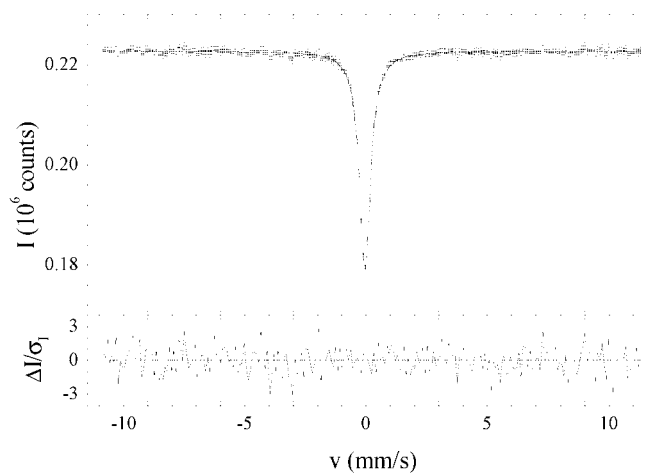


Fig. 1 Mössbauer spectrum of $\text{K}_4[^{57}\text{Fe}(\text{CN})_6] \cdot 3 \text{H}_2\text{O}$ after preparation from iron metal as described (25% enrichment of ^{57}Fe). A single Lorentzian (solid line, parameters in Table 1) is used to fit the experimental data (+). The difference ΔI between experiment and fit is given in units of σ_I .

Provided the Lamb-Mössbauer factor and the enrichment of ^{57}Fe are the same for each iron species, the area of a subspectrum is directly proportional to the content of the corresponding species in the sample. In all cases shown here the purity of the compounds did not allow for a fit of any additional subspectrum. The difference $\Delta I(v)$ between the measured count rates $I(v)$ at velocity v and the fit curve resembles a Gauß-type noise. The standard deviation of this noise is close to the standard deviation $\sigma_I = \sqrt{\bar{I}}$ of the mean count rate \bar{I} assuming a Poisson distribution of the count rates (Fig. 1, 2, and 4). In other words the differences between the fit curves and the experimental data give no indication for the existence of any impurities. Only an upper limit for a possible impurity of the sample can be given, e.g. by the relation σ_A/A , where $A = \sum I_\infty - I(v)$ is the area of the fitted spectrum, I_∞ is the count rate off resonance, $\sigma_A = \sigma_I \sqrt{n}$ is the standard deviation of the area, and n is the number of channels used for recording the count rates.

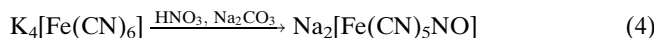
Sodium nitroprusside was obtained from an aqueous solution of $\text{K}_4[\text{Fe}(\text{CN})_6]$ and conc. nitric acid (eq. (4)) [13]. This transformation is the crucial step in the overall synthetic route. With less than the required amount (90% only) of nitric acid an insoluble precipitate occurred. The final solution did not contain the nitroprusside product. With an excess of nitric acid (115%) and an elevated reaction temperature of 98°C a yellow-red product was obtained. At 60°C an excess of nitric acid could still be used without alteration of the product yield. Also, when using the required amount of HNO_3 , the increase in temperature did not effect the nitroprusside product. For the neutralization of the reaction mixture it proved essential to avoid an excess of Na_2CO_3 . Thus, the addition of solid sodium

Table 1 Mössbauer parameters and impurity estimation from Mössbauer spectra

	$\text{K}_4[^{57}\text{Fe}(\text{CN})_6] \cdot 3 \text{H}_2\text{O}^{\text{a}}$	$\text{Na}_2[\text{Fe}(\text{CN})_6] \cdot 2 \text{H}_2\text{O}^{\text{b}}$	GNP ^{a)}
$\delta^{\alpha\text{-Fe}}/\text{mm/s}^{\text{c}}$	-0.05(2)	-0.269 ^{d)} -0.271 ^{e)}	-0.26(2)
$\Gamma/\text{mm/s}^{\text{d)}$	0.55	0.30 (left), 0.32 (right) ^{f)} 0.289 (left), 0.315 (right) ^{g)}	0.50 (left), 0.48 (right)
$\Delta E_Q/\text{mm/s}^{\text{e}}$	0.00	1.722 ^{d)} 1.742 ^{e)}	1.85(2)
A	0.22×10^6	0.87×10^6	1.53×10^6
σ_I	470	935	659
σ_A/A	<2%	≈1%	<1%

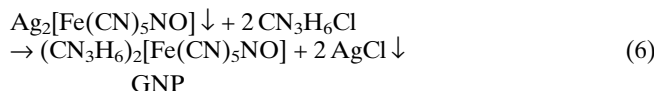
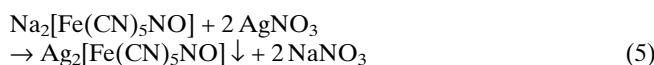
^{a)} Sample with about 25% isotope enrichment in ^{57}Fe ; ^{b)} Sample with natural ^{57}Fe content of 2.1%; ^{c)} Isomer shift referred to α -iron at room temperature; ^{d)} Line width at half-height of maximum (FWHM); ^{e)} Quadrupole splitting; ^{f)} Energy window ± 10 mm/s; ^{g)} Energy window ± 1.6 mm/s

carbonate was monitored with a pH-meter until a value of pH = 7.4 was reached. Addition of methanol to the narrowed reaction solution precipitated the NaNO_3 side product. The sodium nitroprusside could be obtained in crystalline form as the dihydrate by slow solvent evaporation at ambient temperature.



The purity with respect to other iron compounds of a crystalline sample of $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$ was checked by ^{57}Fe Mössbauer spectroscopy. The Mössbauer spectrum shows the expected doublet (Figure 2).

Guanidinium nitroprusside (GNP) was prepared from sodium nitroprusside by twofold cation exchange via the silver nitroprusside [11]. Upon addition of silver nitrate to a solution of sodium nitroprusside, the colorless silver nitroprusside precipitates and, thus, can easily be separated from the soluble sodium nitrate byproduct (eq. (5)). When a slurry of the silver nitroprusside was then reacted with guanidinium chloride the byproduct of silver chloride precipitates and allowed for a facile synthesis of pure GNP (eq. (6)). It was only important here to carry out the reactions mostly in the dark to avoid contamination with elemental silver.



GNP is very good soluble in water (solubility 1800 g/l). This made the growth of large single crystals from a small amount of sample (less than 1 g) difficult. Initially alcohols (ethanol, isopropanol, n-butanol) were tried as solvents. As expected GNP was less soluble in alcohols. However, the nitroprusside was instable in these organic solvents. A black precipitate occurred after 3 to 4 days. Eventually slow solvent evaporation from an aqueous solution by a setup as shown in Figure 3 proved successful in growing large crystals. Instead of needle-shaped crystals [10] large cubic crystals

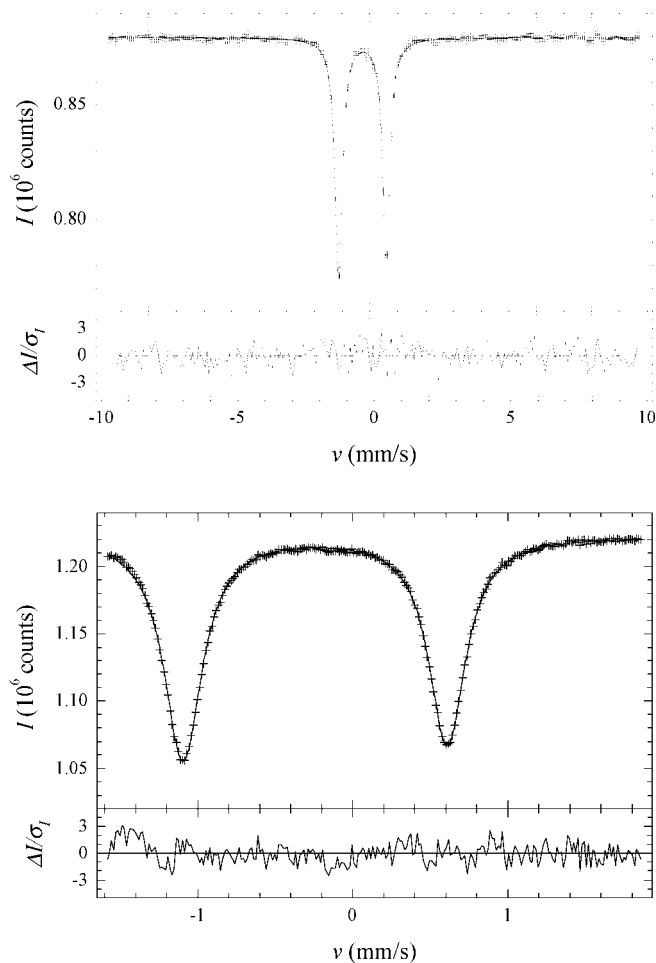


Fig. 2 Mössbauer spectra of $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2 \text{H}_2\text{O}$ after preparation from iron metal as described (natural abundance of 2.1% ^{57}Fe) recorded with large and small energy window (upper and lower graph). A sum of two Lorentzians (solid line, parameters in Table 1) is used to fit the experimental data (+). The difference ΔI between experiment and fit is given in units of σ_I .

tals of dimensions of approximately $3 \times 4 \times 4 \text{ mm}^3$ could be obtained. The surrounding saturated NaCl solution prevented crystal formation at the vertical glass walls.

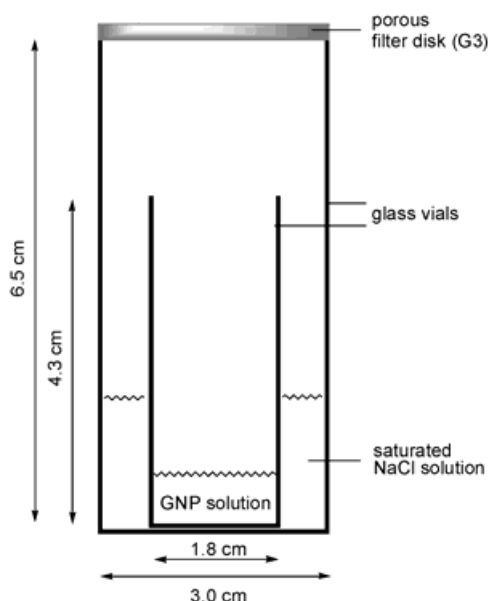


Fig. 3 Setup for the crystal growth of GNP.

A Mössbauer spectrum was collected from one of the crystals (Figure 4). The purity of the sample was estimated as described above for $\text{K}_4[(^{57}\text{Fe}(\text{CN})_6) \cdot 3\text{H}_2\text{O}]$. Again, the estimate of at the most 1% impurity (Table 1) is a rough upper limit. From the Mössbauer spectra it can clearly be stated that there is no significant indication for an iron-containing impurity.

^{13}C , ^{14}N , and ^{57}Fe NMR spectroscopy

Chemical shifts and coupling constants measured from aqueous solutions of $\text{K}_4[(^{57}\text{Fe}(\text{CN})_6)]$ and GNP are given in Table 2.

The ^{13}C NMR signals of both compounds are sharp and the broad ^{14}N NMR signal of $[\text{Fe}(\text{CN})_6]^{4-}$ is approximately in the same place as reported [14]. In the presence of paramagnetic $[\text{Fe}(\text{CN})_6]^{3-}$, both ^{13}C and ^{14}N NMR signals would be markedly affected [15]. The ^{57}Fe NMR spectra of both compounds are shown in Figure 5. The $\delta^{57}\text{Fe}$ value of 2455.3 for $[\text{Fe}(\text{CN})_6]^{4-}$ differs slightly from the value given in the literature (+2497, measured from a 1 M aqueous solution at pH = 12 [16]). The $\delta^{57}\text{Fe}$ value of ferrocene as a second

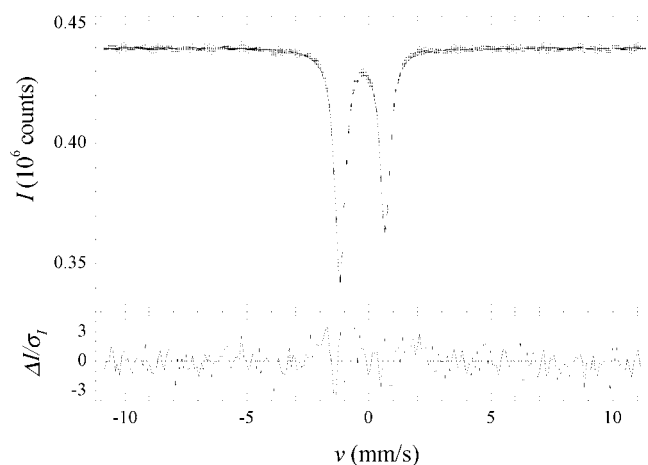


Fig. 4 Mössbauer spectrum of $(\text{CN}_3\text{H}_6)_2[(^{57}\text{Fe}(\text{CN})_5\text{NO})]$ (GNP) after preparation from iron metal as described (25% enrichment of ^{57}Fe). A sum of two Lorentzians (solid line, parameters in Table 1) is used to fit the experimental data (+). The difference ΔI between experiment and fit is given in units of σ_I .

external reference was determined ($\delta^{57}\text{Fe} = 1541.7$ for a 0.8 M solution in CDCl_3) and found in reasonable agreement with reported values [$\delta^{57}\text{Fe} = 1535.2$ (1 M solution in THF); = 1532.4 (in C_6H_6)] [16, 17]. Therefore, it appears that the $\delta^{57}\text{Fe}$ value of $[\text{Fe}(\text{CN})_4]^{4-}$ is dependent on the pH value of the solution. The extremely sharp ($h_{1/2} \leq 0.6$ Hz) ^{57}Fe NMR signal of $[\text{Fe}(\text{CN})_6]^{4-}$ was detected after less than 10 min of spectrometer time by the single pulse (30°) method, whereas the ^{57}Fe NMR signal of GNP was not visible under the same conditions. The ^{14}N NMR signal of the NO ligand is sharp, and since scalar ^{57}Fe - ^{14}N coupling cannot be neglected [see the substantial values of $^1J(^{57}\text{Fe}, ^{13}\text{C})$ in Table 2], broadening of the ^{57}Fe NMR signal can be expected. Together with a long relaxation time $T_1(^{57}\text{Fe})$, difficulties can arise for recording of this ^{57}Fe NMR signal, at least for samples with ^{57}Fe at natural abundance. Indeed, it is reported that this particular ^{57}Fe NMR signal of $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ had not been found [16]. Therefore, a very small pulse angle (15°) was used, and data were collected for ca. 3 h. The result was a weak signal at $\delta^{57}\text{Fe} = 2004$; this signal was reproduced under different experimental conditions (spectral

Table 2 ^{57}Fe , ^{14}N and ^{13}C NMR data^{a)} for $\text{K}_4[(^{57}\text{Fe}(\text{CN})_6)]$ and GNP^{b)}

Compound	$\delta^{57}\text{Fe}$	$\delta^{14}\text{N}$	$\delta^{13}\text{C}$	$^1J(^{57}\text{Fe}, ^{13}\text{C})$
$\text{K}_4[\text{Fe}(\text{CN})_6]$ (saturated in D_2O ; pH = 7)	+2455.3 $h_{1/2} > 0.6$ Hz	-105 ± 8 $h_{1/2} > 1500$ Hz	178.8	15.8
GNP (0.1 g in 0.5 ml of D_2O)	+2004.0 $h_{1/2} = 2.5 \pm 0.5$ Hz	-5.1 ± 0.2 (NO) ^{c)} $h_{1/2} = 7 \pm 1$ Hz	134.6 (<i>cis</i> -CN) 132.6 (<i>trans</i> -CN) 158.2 (CN_3)	15.5 (<i>cis</i> -CN) 12.2 (<i>trans</i> -CN)

^{a)} Chemical shifts $\delta^{57}\text{Fe}$ (± 0.1), $\delta^{13}\text{C}$ (± 0.1), and coupling constants $^1J(^{57}\text{Fe}, ^{13}\text{C}) \pm 0.3$ Hz; ^{b)} Both samples had an ^{57}Fe content of about 25%; ^{c)} A very broad hump around $\delta^{14}\text{N} = -100$ represents the unresolved ^{14}N NMR signals of the CN ligands in *cis* and *trans* positions relative to NO. $\delta^{14}\text{N}$ (NH_2) = -310 ± 2 .

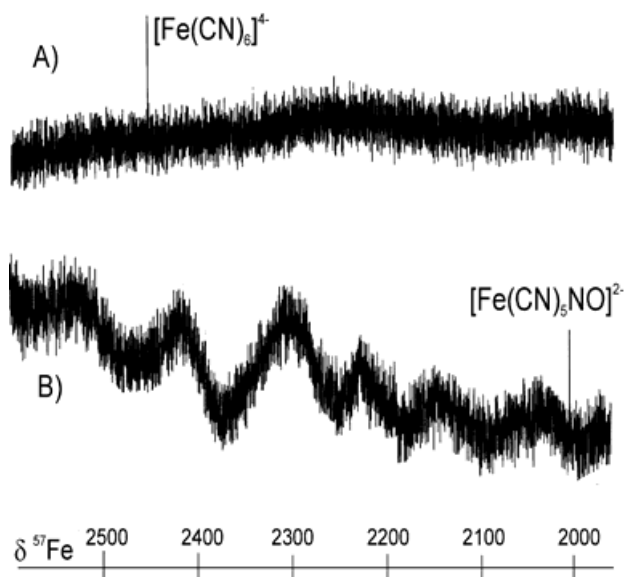


Fig. 5 16.1 MHz ${}^{57}\text{Fe}$ NMR spectra of $\text{K}_4[\text{Fe}(\text{CN})_6]$ (saturated in D_2O) (A), and of GNP (0.1 g in 0.5 ml of D_2O) (B), both measured at $23 \pm 1^\circ\text{C}$.

A) Result of 800 transients (acquisition time 0.8 s; 30° pulses; line broadening 0.3 Hz).

B) Result of 6000 transients (acquisition time 1.6 s; 15° pulses; line broadening 1.5 Hz). The rolling baseline is due to acoustic ringing, typical of NMR spectra of low- γ nuclei if the NMR signal is weak.

width, pulse offset, acquisition time), including an experiment lasting 12 h in order to double the signal-to-noise ratio. The ${}^{57}\text{Fe}$ NMR signal of GNP is broader ($h_{1/2} = 2.5 \pm 0.5$ Hz) than the one for $[\text{Fe}(\text{CN})_6]^{4-}$. The rolling baseline in Figure 5B) can in principle be corrected by applying certain pulse sequences [18]; however, these experiments tend to reduce the signal-to-noise ratio which is critical in the case of ${}^{57}\text{Fe}$ NMR spectroscopy.

Conclusions

${}^{57}\text{Fe}$ isotope enriched nitroprusside compounds can be prepared in high-yield and in high purity on a small scale by starting from iron metal as the ${}^{57}\text{Fe}$ source. Large single crystals of guanidinium nitroprusside (GNP) were grown by slow solvent evaporation from a saturated aqueous GNP solution in the presence of a saturated NaCl solution. ${}^{13}\text{C}$, ${}^{14}\text{N}$, and ${}^{57}\text{Fe}$ NMR shifts and coupling constants have been measured from aqueous solutions of ${}^{57}\text{Fe}$ -isotope enriched $\text{K}_4[\text{Fe}(\text{CN})_6]$ and $(\text{CN}_3\text{H}_6)_2[\text{Fe}(\text{CN})_5\text{NO}]$ (GNP).

Experimental

The solvent water was deionized and degassed. Methanol was degassed. In both solvents the dissolved air was removed by five cycles of evacuation and refilling with nitrogen. The nitrogen inert gas had a purity of 99.999% (5.0

and was used without further purification. ${}^{57}\text{Fe}$ was obtained from AMT (Advanced Materials Technologies, Kiryat Ono, Israel) as iron foil in pieces of 2×0.10 g. The isotope purity was certified to 95.3% in ${}^{57}\text{Fe}$. Hydrochloric acid (HCl) was obtained from J. T. Baker (36–38%, Baker analyzed), HNO_3 from Riedel-de-Haën (65%, analytical reagent), $(\text{CN}_3\text{H}_6)\text{Cl}$ from Aldrich (99%).

An isotope enrichment for ${}^{57}\text{Fe}$ of 25% was aimed for the samples by mixing the isotope enriched iron foil with the normal iron. The temperatures given refer to the temperature of the heating bath.

${}^{57}\text{Fe}$ Mössbauer spectroscopy: ${}^{57}\text{Fe}$ Mössbauer spectra were recorded with a conventional spectrometer in constant-acceleration mode with a ${}^{57}\text{Co}[\text{Rh}]$ source. The velocity calibration was performed with a $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$ single crystal for which the quadrupole splitting (ΔE_Q) and the isomer shift (δ) are known with high accuracy. The measured isomer shifts are referred to an α -Fe standard at room temperature ($\delta^{\alpha\text{-Fe}} = 0.11 \pm 0.01$ mm/s + $\delta^{\text{Fe/Rh}}$). The experimental spectra were fitted by a sum of Lorentzian lines by means of a least-squares procedure.

${}^{13}\text{C}$, ${}^{14}\text{N}$ and ${}^{57}\text{Fe}$ NMR spectroscopy: ${}^{13}\text{C}$ (125.8 MHz) and ${}^{14}\text{N}$ (36 MHz) NMR spectra were recorded for aqueous solutions of $\text{K}_4[\text{Fe}(\text{CN})_6]$ and GNP using a Bruker DRX 500 NMR spectrometer equipped with a standard 5 mm multinuclear probehead [$\delta^{13}\text{C}$ values are given relative to external TMS ($\delta^{13}\text{C} = 0$ for Ξ 25.145004 MHz), and $\delta^{14}\text{N}$ values relative to external neat MeNO_2 ($\delta^{14}\text{N} = 0$ for $\Xi = 7.226324$ MHz)]. The ${}^{57}\text{Fe}$ NMR spectra were measured using the same instrument with a low-frequency 5 mm probehead tunable to frequencies in the range for ${}^{187}\text{Os}$ to ${}^{13}\text{C}$. Routine experimental parameters were used to record the ${}^{13}\text{C}$ and ${}^{14}\text{N}$ NMR spectra. In the case of ${}^{57}\text{Fe}$ NMR, the length of the 90° pulse ($80 \mu\text{s}$) was calibrated by measuring the ${}^{73}\text{Ge}$ NMR signal of GeCl_4 (17.5 MHz), assuming that this parameter does not change significantly when the probehead is tuned for ${}^{57}\text{Fe}$ (16.1 MHz). The frequency $\Xi({}^{57}\text{Fe}) = 3.237798$ MHz given in the literature [19] for neat $\text{Fe}(\text{CO})_5$ was used as an external reference. The ${}^{57}\text{Fe}$ NMR spectrum of the $[\text{Fe}(\text{CN})_6]^{4-}$ anion was readily obtained by using 30° pulses, whereas under these conditions the ${}^{57}\text{Fe}$ NMR signal of GNP could not be detected. Application of 15° pulses and ca. 3 h of spectrometer time were necessary to obtain a weak ${}^{57}\text{Fe}$ NMR signal (see Figure 5).

Iron(II) chloride, $({}^{57}\text{Fe})\text{FeCl}_2$. A 50 ml Schlenk-flask was charged with ${}^{57}\text{Fe}$ (0.20 g, 3.58 mmol) and normal iron (0.60 g, 11.00 mmol). The flask was evacuated and refilled with nitrogen. This procedure was repeated three times. Then degassed methanol (10 ml) and hydrochloric acid (37%, 4.0 ml, 48.3 mmol) was added. The mixture was stirred for 5 h at 60°C . After this time most of the iron metal had dissolved. The resulting light-green solution was filtered under nitrogen over a glass frit covered with 1–2 g of iron powder. The solvent was removed from the filtrate in vacuum. A light-green solid was obtained. Yield 1.70 g (13.41 mmol, 93%).

Potassium hexacyanoferrate(II), $\text{K}_4[({}^{57}\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$. Under nitrogen gas $({}^{57}\text{Fe})\text{FeCl}_2$ (1.70 g, 13.41 mmol) was dissolved in water (10 ml). To this solution was added solid NaOH (1.00 g, 25.00 mmol) and a solution of KCN (6.10 g, 93.88 mmol) in degassed water (20 ml). A yellow solid precipi-

pitated immediately. Warming to 50 °C gave a yellow solution. The solvent was removed in vacuum. The product was separated from excess KCN by dissolving the mixture in the minimum quantity of water at room temperature. To this solution was added the same amount of methanol. The slurry was heated to 50 °C to give a clear solution which was slowly cooled to room temperature. The light-yellow precipitate formed was collected by filtration and recrystallized again from hot/cold water to give a light-yellow crystalline solid. Yield 5.50 g (13.02 mmol, 96%).

The product was studied by ^{57}Fe Mössbauer and ^{57}Fe NMR spectroscopy. No iron(III) impurities or other iron(II) compounds could be detected.

Sodium pentacyanonitrosylferrate(II), $\text{Na}_2[^{57}\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$. $\text{K}_4[^{57}\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ (1.70 g, 4.00 mmol) was dissolved in water (5 ml). The solution was warmed to 60 °C and concentrated nitric acid (65% HNO_3 , 1.0 ml) was added. The mixture was stirred for 6 h at 60 °C and for 2 d at room temperature. A blue-brown solution was obtained. With addition of solid Na_2CO_3 the pH of the solution was set to 7.2 under the control of a pH-meter. This solution was heated to reflux for 5 min. The color changed to red. About 70% of the solvent water were removed in vacuum at a bath temperature of 45 °C. The remaining solution was cooled to room temperature. To it were added 30 ml of methanol to precipitate the NaNO_3 side product. The filtrate was evaporated at ambient temperature in an oil pump vacuum to dryness to give the product which was used without further purification. The reaction was carried out twice. Yields 1.00 g and 1.06 g (85% and 90%).

The purity of a sample which was obtained from normal iron metal according to the same procedure was studied by ^{57}Fe Mössbauer spectroscopy. No iron(III) impurities could be detected.

Silver pentacyanonitrosylferrate(II), $\text{Ag}_2[^{57}\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$. Solid silver nitrate (1.40 g, 8.24 mmol) was added to a solution of $\text{Na}_2[^{57}\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$ (1.00 g, 3.36 mmol) in water (20 ml). The mixture was stirred for 3 h at 50 °C in the dark. A colorless precipitate was obtained which was collected by centrifugation and decantation. The precipitate was washed five times with 5 ml of water each. The product was used without further purification. Yield 1.40 g (3.00 mmol, 88%).

Guanidinium pentacyanonitrosylferrate(II), $(\text{CN}_3\text{H}_6)_2[^{57}\text{Fe}(\text{CN})_5\text{NO}]$. In the dark (!), solid guanidinium chloride, $\text{CN}_3\text{H}_5 \cdot \text{HCl}$ (0.80 g, 8.37 mmol) was added to a slurry of $\text{Ag}_2[^{57}\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$ (1.40 g, 2.99 mmol) in water (20 ml). The mixture was stirred for 24 h at room temperature. A redish solution with solid AgCl was obtained. The latter was separated by centrifugation and decantation. The clear solution was narrowed to about 5 ml in vacuum at ambient temperature.

Large crystals could be grown from this solution by slow solvent evaporation in a glass vial as shown in Figure 3. The crystal yield was 0.65 g (60%).

One of the single crystals was studied by ^{57}Fe Mössbauer spectroscopy. No iron(III) impurities or other iron(II) compounds could be detected.

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