

Silver Nitroprusside

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ABSTRACT:

Low temperature Raman spectroscopic estimations on silver nitroprusside (AgNP), $\text{Ag}_2[\text{Fe}(\text{CN})_5\text{NO}]$ powders show reversible highlights of an in part changed over metastable state. The outcomes are contrasted and comparatively watched metastable state if there should be an occurrence of sodium nitroprusside (NaNP) and the distinctions have been talked about as far as conceivable protection from metastable state arrangement offered by silver particles based on hard soft acid base (HSAB) hypothesis. The gem structure has two destinations for the silver ion, comparing to its coordination two and three to the N closures of CN gatherings. Figuring of the spiral dissemination capacity and IR and UV-Vis spectra gave the a priori structural data required to help the chose structural model to be refined. Such data was then used to approve the refined structure. The structure of this compound is atypical inside the metal nitroprussides arrangement. The warm deterioration in air and nitrogen air of the title compound was considered from thermogravimetry and IR joined systems. In the strong deposits metallic silver and iron oxide (hematite) were distinguished.

INTRODUCTION:

Silver nitroprusside (AgNP), $\text{Ag}_2[\text{Fe}(\text{CN})_5\text{NO}]$ is a simple of sodium nitroprusside (NaNP), $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$. The outstanding utilizations of the last incorporate its utilization as a Mössbauer alignment standard and as a vasodilator in biomedical sciences. NaNP has likewise drawn an impressive consideration for its potential use as an optical switch data stockpiling material attributable to its light actuated reversible metastable state underneath 160K with a to a great degree long lifetime $\tau > 10^7$ seconds [1].

There are numerous reports in the writing testing the metastable province of NaNP by optical systems like Raman disseminating [2], infrared spectroscopy [3], optical assimilation [4], and time subordinate optical transmission [5] to consider the populace flow. A not very many reports have likewise attempted to clarify the cause of the metastable state [5] and the explanation for its long lifetime [6]. Taken after by this revelation in NaNP, it was accounted for by Zollner et al. [7] utilizing differential checking calorimetry (DSC), that a progression of nitroprussides with various cations and supplanted CN and NO ligands additionally demonstrate comparable metastable states with illumination of light. As far as anyone is concerned, display work is the main report researching light instigated metastable state in nitroprusside group of edifices other than sodium nitroprusside utilizing Raman spectroscopy.

The nitroprusside complex anion shapes an insoluble salt, of equation unit $\text{Ag}_2[\text{Fe}(\text{CN})_5\text{NO}]$, when it responds with a fluid arrangement of Ag^+ . Identified with the high insolubility of silver halides, silver nitroprusside is a decent middle of the road to acquire dissolvable nitroprussides of soluble, antacid earth and trivalent change metals. No different applications for that strong have been accounted for, most likely in light of the fact that its precious stone structure and related properties are obscure. This commitment reports the gem structure for the titled compound from X-beam powder diffraction information and its refinement utilizing the Rietveld method. The structure of this compound is atypical inside the metal nitroprussides arrangement.

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Structure and properties:

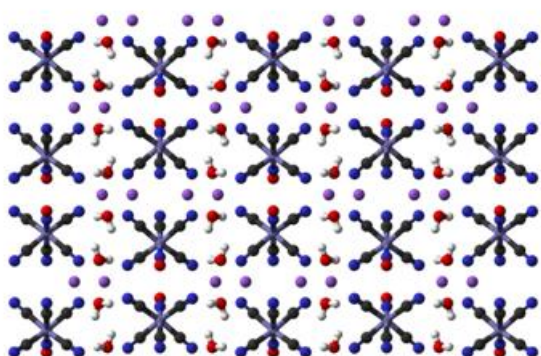


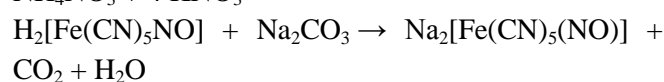
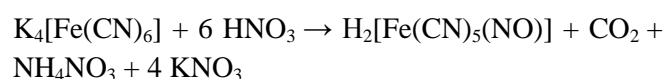
Figure 1: Structure of sodium nitroprusside in the solid state

Nitroprusside is an inorganic compound with the formula $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$, normally experienced as the dihydrate, $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$. This red-shaded sodium salt disintegrates in water or ethanol to give arrangements containing the free complex dianion $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$. Nitroprusside is a complex anion that highlights an octahedral iron(III) focus encompassed by five firmly bound cyanide ligands and one linear nitric oxide ligand (Fe-N-O edge = 176.2°). The anion has idealized C_{4v} symmetry. Nitric oxide is a non-guiltless ligand. Because of the straight Fe-N-O point, the moderately short N-O separation of 113 pm[42] and the generally high extending recurrence of 1947 cm^{-1} , the complex is planned as containing a NO^+ ligand. Consequently, press is allotted an oxidation condition of 2+. The iron focus has a diamagnetic low-spin d electron design, in spite of the fact that a paramagnetic seemingly perpetual metastable state has been watched by EPR spectroscopy[8].The chemical reactions of sodium nitroprusside are mainly associated with the NO ligand.

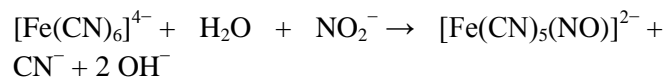
For example, addition of S^{2-} ion to $[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$ produce the violet colour $[\text{Fe}(\text{CN})_5(\text{NOS})]^{4-}$ ion, which is the basis for a sensitive test for S^{2-} ions. An analogous reaction also exists with OH^- ions, giving $[\text{Fe}(\text{CN})_5(\text{NO}_2)]^{4-}$. Roussin's red salt ($\text{K}_2[\text{Fe}_2\text{S}_2(\text{NO})_4]$) and Roussin's black salt ($\text{NaFe}_4\text{S}_3(\text{NO})_7$) are related iron nitrosyl complexes. The former was first prepared by treating nitroprusside with sulfur. This compound decomposes to sodium ferrous ferrocyanide, sodium ferrocyanide, nitric oxide, and cyanogen at about 450°C . It decomposes in aqueous acid to liberate hydrocyanic acid (HCN).[47] Shielded from light, the concentrated solution is stable for more than two years at room temperature. It breaks down rapidly upon exposure to light, although the details are poorly understood. It degrades when heated (e.g. by sterilization in an autoclave), but addition of citric acid is helpful.

Preparation:

Sodium nitroprusside can be synthesized by digesting a solution of potassium ferrocyanide in water with nitric acid, followed by neutralization with sodium carbonate:



Alternatively, ferrocyanide may be oxidized with nitrite as well:



SUMMARY AND EXPLANATION:

The two disorders have different etiologies and clinical signs. So as to start the best possible course of treatment, it winds up critical at that point to recognize the two conditions after a positive outcome in the nitroprusside test. The strategy relies upon the quick decrease of the homocystine disulfide linkage by silver particles. The subsequent free sulfhydryl gatherings can be recognized then with the nitroprusside test.

Cystine isn't lessened under the conditons of the response. The technique shows up very touchy, identifying as meager as 2 mg/dl homocystine. Since different disulfides or sulfhydryl gatherings may respond, the system is prescribed for screening purposes as it were. Any positive result would recommend assist corroborative testing for analysis[9]. The SILVER-NITROPRUSSIDE TEST Technique utilizes a change of the Spaeth strategy. Immersion of the pee example with strong sodium chloride is pointless. The SILVER REAGENT is provided in a steady fluid frame. Examination time is one moment. Bird prescribes the SILVER-NITROPRUSSIDE TEST Strategy be utilized to separate homocystine from cystine after a positive result has been gotten with the NITROPRUSSIDE TEST Method.

PRINCIPLE:

Silver ions reduce the disulfide linkage in homocystine to the free sulfhydryl groups. Cyanide displaces the silver ions and nitroprusside immediately forms a colored complex with the free sulfhydryl groups which appears pink to purple. The color intensity depends on the urinary concentration of homocystine.

REAGENTS: FOR IN-VITRO DIAGNOSTIC

USE:

Reactive Set Cat. No. N-110 includes:

SILVER REAGENT - (Cat. No. N-21)

REACTIVE INGREDIENTS:

12 mM silver nitrate. Ammonium salts added.

PRECAUTIONS:

Causes irritation. Avoid contact with eyes, skin and clothing.

STORAGE AND STABILITY:

Store at 2 - 8° C. Stable until expiration date if sealed tightly. PROTECT FROM LIGHT.

DETERIORATION:

The reagent should be a clear, colorless solution. Turbidity or a gray-black coloration would indicate deterioration, and the solution should not be used.

HOMOCYSTINE SOLUTION - (Cat. No. N-22)

REACTIVE INGREDIENTS:

50 mg/dl homocystine. Stabilizer added.

PRECAUTIONS:

For in-vitro diagnostic use.

STORAGE AND STABILITY:

Store at 2 - 8° C. Stable until expiration date if sealed tightly.

DETERIORATION:

The solution should be clear and colorless. Turbidity would indicate deterioration, and the solution should not be used.

CYSTINE SOLUTION - (Cat. No. N-13)

REACTIVE INGREDIENTS:

50 mg/dL cystine. Stabilizer added.

PRECAUTIONS:

Causes irritation. Avoid contact with skin, eyes and clothing. In case of contact, wash with large amounts of water.

STORAGE AND STABILITY:

Store at 2 - 8° C. Stable until expiration date if sealed tightly.

DETERIORATION:

The solution should be a clear, colorless solution. Turbidity would indicate deterioration, and the solution should not be used.

SPECIMEN COLLECTION

PRECAUTIONS:

1. Freshly collected urine is recommended.

2. The specimen should not be contaminated with feces.
3. For screening newborns, specimens should be collected at 10 - 14 days after birth, and at 3 - 4 weeks of age.

SAMPLE STORAGE:

Refrigerate the specimen as soon as possible after collection. If testing is delayed longer than 24 hours after collection, freeze the sample.

INTERFERING SUBSTANCES:

Free sulfhydryl gatherings or any disulfide linkage equipped for being lessened by silver may respond. Creatinine, CH₃)₂CO and acetacetate don't meddle. Acetaminophen, salicylates, phenobarbital, ampicillin and antibiotic medication are inert. Uric acid levels over 2 g/l and pees from patients accepting ascorbic acid may meddle with the test affectability.

PROCEDURE

MATERIALS PROVIDED:

SILVER REAGENT (Cat. No. N-21), and HOMOCYSTINE SOLUTION (Cat. No. N-22).

MATERIALS REQUIRED BUT NOT PROVIDED:

1. Spot plate
2. Dropper pipets
3. Applicator sticks
4. NITROPRUSSIDE TEST KIT (Cat. No. N-10)

PREPARATION OF HOMOCYSTINE

REFERENCE SAMPLE:

A Homocystine Reference Sample should be prepared by adding 1 drop of the HOMOCYSTINE SOLUTION to 10 drops of a normal urine and mixing well[10]. The homocystine concentration is approximately 5 mg/dL in the Reference Sample. It is recommended that a normal urine and the Reference Sample be included in each test series.

MANUAL PROCEDURE:

1. Add 2 drops of urine specimen to the spot plate cavity.

2. Add 1 drop of SILVER REAGENT . Use an applicator stick to mix well.
3. Wait 1 minute. Add 1 drop of NITROPRUSSIDE REAGENT.
4. Observe for color change.

INTERPRETATION OF RESULTS:

A prompt pink to purple shading upon the expansion of NITROPRUSSIDE REAGENT would demonstrate the nearness of homocystine. Shading power relies upon urinary focus. Typical pee has a slight pink shading due to the NITROPRUSSIDE REAGENT. The test ought to be viewed as positive if the shading force breaks even with or surpasses that of the 5 mg/dL Homocystine Reference Test[11].

Experimental:

The titled compound was set up by the precipitation technique from watery arrangements (0.01 M) of silver nitrate and sodium nitroprusside, both from Sigma–Aldrich. The shaped accelerate was matured inside the mother alcohol for seven days in the haziness and after that isolated by centrifugation and washed a few times with refined water. The got pale strong was dried in air in the obscurity until the point when it has steady weight. The idea of coming about fine powder as Ag₂[Fe(CN)₅NO] was built up from X-beam energydispersed (EDS) and IR spectroscopies[12]. As per EDS spectra, the Ag:Fe nuclear proportion in the strong is 2:1, while the recorded IR range is commonplace of metal nitroprussides. The chronicle of the thermogravimetric (TG) bend, X-beam powder example, and UV– Vis range finished the material portrayal. The material deterioration on warming, in both nitrogen and air environment, was observed by joined TG and IR methods. IR range was recorded with a Pike ATR gadget utilizing a Perkin spectrophotometer. UV– Vis range was gathered with the mix circle strategy. The TG bend was recorded both in air and under a N₂ stream (1 L/min) utilizing a TA Instrument (IR-5000) worked in the HR mode. The XRD powder designs were gathered in Bragg–Brentano geometry at room temperature with both Cu

Ka and Mo Ka radiation. The examples recorded with this last radiation was utilized to compute the Radial Distributed Function (RDF) keeping in mind the end goal to acquire from the earlier data on the interatomic separations including overwhelming molecules. The unit cell was already identified and its parameters computed amid the Mill operator records task with the assistance of TREOR and DICVOL calculations. The interatomic separations got from the RDF figuring were utilized to segregate between all the conceivable space gatherings to be considered in the structural refinement.

The structural model was at long last distinguished utilizing a worldwide enhancement process in the immediate space (mimicked toughening) actualized in the EXPO09 program. The gem structure was refined utilizing the Rietveld technique with the FULLPROF program. Points of interest on the XRD information recording and handling are accessible from Supplementary data. As of now said, change metal nitroprussides have gotten certain consideration as model of permeable solids for hydrogen stockpiling, and in that sense, H₂ adsorption isotherms were recorded at 75 K keeping in mind the end goal to investigate a conceivable hydrogen particle communication with the silver molecule in the structure of silver nitroprusside[13].

Material behavior on heating:

The conduct or the behavior of metal nitroprussides on warming is very much recorded. The warm decay of a strong is identified with the crack of substance bonds as outcome of an expanding plentifulness for the vibrations of molecules around their balance positions because of the expansion of the warm vitality (kT). From this reality, for metal nitroprussides the unbridged NO ligand develops at generally low temperature, for the most part beneath 200 C, and furthermore the pivotal CN gathering in the event that it remains unbridged or feebly clung to a metal focus. The unbridged ligands are especially defenseless to develop on warming.

The loss of the NO ligand prompts development of moderate metal cyanide buildings of differing stoichiometry, depending of the included metals. On dynamic warming, the framed metal cyanides break down with development of cyanide ligands. The evolved cyanide radicals have decreasing character coming about the arrangement of C₂N₂ and diminished types of the included metals[14].

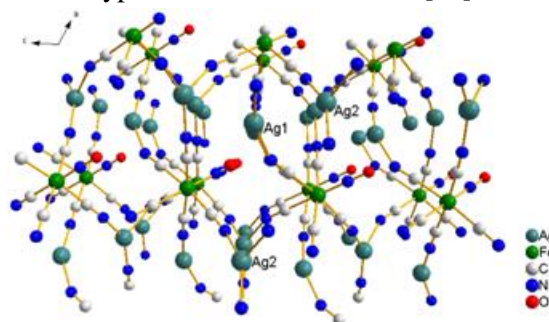


Figure 2: Framework of silver nitroprusside and coordination environments for the involved metals (Fe and Ag).

The recorded TG bend in a nitrogen climate for silver nitroprusside. As per the subsidiary of that bend, the warm disintegration of the strong under investigation happens in four soaks. The principal warm impact is seen from 150 C with a most extreme decay rate near 200 C[15]. The weight reduction for this impact is 13% and is attributed to the development of the unbridged NO ligand and to the pitifully reinforced hub CN gathering. The second weight reduction has a most extreme at 250 C and it was appointed to decay of a middle of the road metal cyanide of low warm soundness. At that point, from 280 C an articulated weight reduction happens, which has a most extreme at 325 C. This impact is additionally attributed to disintegration of middle of the road cyanide metals. The fourth impact is distinguished from 350 C as a slight articulation in the TG bend. It appears, the disintegration of the last middle cyanide has a low active and a generally high warm solidness. In a non-oxidant air, under a nitrogen stream for example, the normal last results of the warm decay of metal cyanides are the included metals in metallic state identified with the diminishing impact of the cyanide

radicals. The arrangement of IR spectra relating to the advanced gases amid the warm deterioration process. For all the temperature extend an exceptional doublet near 2300 cm⁻¹ is watched, which compare to cyanogen (C₂N₂) species. The IR spectra profile has four maxima which could be identified with the four articulations saw in the recorded TG bend, comparing to the as of now said strong decay through four warm impacts.

The arrival of the NO gathering is identified as moderately frail flag in the 1827– 1734 cm⁻¹ unearthly district because of essence of nitrogen monoxide species (see Supplementary data). A simple conduct is watched for the strong decay under an air environment. In the TG bend four warm impacts are obviously distinguished while the IR spectra of the developed gases are ruled by the cyanogen doublet.

| Atom | Site | X | Y | Z | Biso | Occ |
|------|------|----------|-----------|----------|---------|-----|
| Fe | 2a | 0.893(2) | 0.488(2) | 0.811(2) | 1.34(2) | 1 |
| Ag1 | 2a | 0.337(2) | -0.061(2) | 0.686(2) | 2.45(2) | 1 |
| Ag2 | 2a | 0.486(2) | 1.004(2) | 0.477(2) | 2.81(3) | 1 |
| C1 | 2a | 0.673(4) | 0.298(5) | 0.769(3) | 3.94(3) | 1 |
| N1 | 2a | 0.547(4) | 0.178(5) | 0.740(3) | 3.94(3) | 1 |
| C2 | 2a | 0.772(4) | 0.647(6) | 0.897(4) | 3.94(3) | 1 |
| N2 | 2a | 0.699(4) | 0.742(6) | 0.949(4) | 3.94(3) | 1 |

As per XRD information (see Supplementary data), the strong deposit for both, the examples warmed under a nitrogen air and in air, is shaped by metallic silver and iron oxide (hematite). The nearness of Fe₂O₃ as definite iron stage under a nitrogen environment, proposes that metallic iron is shaped by the decreasing impact of the developed cyanide radicals, which is then oxidized when the buildup is presented to air.

Such conduct has been watched for the warm disintegration of Prussian blue under nitrogen and in vacuum. No signs from cyanide metal edifices were found in the deposits[16]. Table 2 Nuclear positions and temperature and occupation factors got from the Rietveld refined precious stone structure for Ag₂[Fe(CN)₅NO][17].

CONCLUSIONS:

Silver nitroprusside, Ag₂[Fe(CN)₅NO], solidifies with a monoclinic unit cell in the Pc space gathering. The unit cell contains two equation units of the compound. In the gem structure, to kinds of silver molecules are discovered; Ag1 straightly planned to the N closures of the tropical CN gatherings, and Ag2 likewise organized to the pivotal CN ligand, through a weaker collaboration. This last coordination collaboration underpins the material 3D system. The precious stone structure of silver nitroprusside is atypical inside metal nitroprusside arrangement; with two kinds of coordination (2 and 3) for the metal connected at the N end of the CN gathering. The refined precious stone structure is bolstered by the accessible spectroscopic data. On the strong warming, NO and the pivotal CN bunches develop from around 160 C and after that the warm decay is finished by advancement of likewise the hub CN gatherings. In the strong buildups metallic silver and iron oxides were recognized. The concentrated strong was considered as a model to reveal insight into the conceivable coordination connection between the silver particle and hydrogen atoms. In any case, the permeable structure of silver nitroprusside comes about unavailable to the hydrogen particle.

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