

Synthesis, Characterisation, Structure, and Magnetic Properties of $[\text{Ni}\{\text{H}_2\text{NCH}(\text{CH}_3)\text{CH}_2\text{NH}_2\}_3][\text{Fe}(\text{CN})_5\text{NO}]\cdot\text{H}_2\text{O}$

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The complex $[\text{Ni}(\text{pn})_3][\text{Fe}(\text{CN})_5\text{NO}]\cdot\text{H}_2\text{O}$ (**1**) was synthesised by the reaction of $[\text{Ni}(\text{pn})_3]\text{Cl}_2$ (pn = racemic propane-1,2-diamine) with $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$ in aqueous solution and has been characterised by IR and Mössbauer spectroscopy and magnetic studies. Single crystal structure analysis revealed octahedrally coordinate cations $[\text{Ni}(\text{pn})_3]^{2+}$ and anions $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$.

Key words: Nitroprusside, Crystal Structure, Nickel Complex, Mössbauer Spectroscopy

Introduction

In the last two decades much attention was paid to the study of molecule-based magnets especially to Prussian blue analogues which are also used in molecular sieves, cation exchangers, electron scavengers, and radionuclide sorbents [1–5]. In these cases metal spin sites are usually bridged by a spacer moiety and a superexchange interaction couples the spin sites. This type of coupling is a function of the spacer consisting organic molecules [6]. The polyfunctionalised spacer controls the magnetic coupling between the spin sites upon photo irradiation and shows an alternative way for the design of communication devices at a molecular level using π conjugated systems in contrast to the traditional electronic communication [7–9]. Hexacyanometallate ions $[\text{M}(\text{CN})_6]^{n-}$ (M = Mn, Fe, Cr *etc.*) act as good building blocks in transition metal complexes containing polydentate amine ligands. Bimetallic assemblies are obtained with structures ranging from clusters to 3D extended networks and discrete polynuclear species with interesting magnetic and magneto-optical properties [10–13]. But the problem in the preparation of these complexes arises from the lack of solubility of cyanide-based assemblies due to the strong tendency of cyanides to form three-dimensional networks. This difficulty has been overcome by introducing capping ligands into the co-ordination sphere of the cation. The capping ligands

can control the topology of metal ions and enhance the solubility of the complexes. Chelating amines such as ethylenediamine (en), propane-1,3-diamine (1,3-pn) or 1,4,8,11-tetraazacyclotetradecane (cyclam) are used for this purpose.

Recently, a few cyanide-bridged compounds based on the nitroprusside anion have been reported which exhibit weak antiferromagnetic interaction between the paramagnetic transitional metal ions through the diamagnetic building blocks like $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$, $[\text{Co}(\text{CN})_6]^{3-}$, $[\text{Ni}(\text{CN})_4]^{2-}$, $[\text{Mo}(\text{CN})_8]^{4-}$, and $[\text{W}(\text{CN})_8]^{4-}$. For instance $[\text{Ni}(\text{en})_2]_3[\text{Fe}(\text{CN})_6]_2\cdot\text{H}_2\text{O}$ [14], $\text{PPh}_4[\text{Ni}(\text{pn})_2][\text{Fe}(\text{CN})_6]\cdot\text{H}_2\text{O}$ [15], $[\text{Ni}(\text{L})_2]_2[\text{Fe}(\text{CN})_6]\text{X}$ (L = pn, 1,1-dimethylethylenediamine; X = ClO_4^- , PF_6^- , *etc.*) [16] have a chain (ropeladder) structure, a 1D zigzag chain structure, or a 2D square sheet structure, respectively. The complexes $[\text{Ni}(\text{cyclam})]_3[\text{Cr}(\text{CN})_6]_2\cdot 20\text{H}_2\text{O}$ and $[\text{Ni}(\text{cyclam})]_3[\text{Fe}(\text{CN})_6]_2\cdot 12\text{H}_2\text{O}$ have layered structures with corrugated sheets [17], and $[\text{Ni}(\text{tren})]_2[\text{Fe}(\text{CN})_6]\cdot 3\text{H}_2\text{O}$ (tren = tris(2-aminoethyl) amine) has a 3D structure consisting of a Fe-CN-Ni-Fe-CN chain [18]. Besides these complexes, $[\text{NiL}_2]_3[\text{Fe}(\text{CN})_6]_2\cdot x\text{H}_2\text{O}$ (L = bpy, $x = 8$; L = phen, $x = 9$) [19], $[\text{Ni}(1,1\text{-dmen})_2]_2[\text{Fe}(\text{CN})_6]\text{X}\cdot y\text{H}_2\text{O}$ (1,1-dmen = 2,2-dimethylethylenediamine, X = CF_3SO_3 , $y = 2$, X = BzO, $y = 6$, X = N_3 , $y = 4$) [16], $[\text{Ni}(\text{baepn})]_{2n}[\text{Fe}(\text{CN})_6]_n(\text{H}_2\text{O})_{8n}$ (baepn = *N,N'*-bis(2-aminoethyl)-1,3-propanediamine) [20], $[\text{Ni}(\text{bpm})]_3[\text{Fe}(\text{CN})_6]_2\cdot 7\text{H}_2\text{O}$ (bpm = bis(1-pyrazol-

yl)methane) [21], and $[\text{Ni}(\text{bpy})_2]_3[\text{Fe}(\text{CN})_6]_2 \cdot 7\text{H}_2\text{O}$ (bpy = 2,2'-bipyridine) [22a] and $\text{Cu}(\text{H}_2\text{NCH}(\text{CH}_3)\text{CH}_2\text{NH}_2)_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot\text{H}_2\text{O}$ [22b] have also been prepared.

Only few examples of the bimetallic coordination polymers obtained by reaction of nitroprussides with transition metal complexes have been reported so far. In this context we can mention $[\text{Ni}(\text{en})_2][\text{Fe}(\text{CN})_5\text{NO}]\cdot\text{H}_2\text{O}$ which contains a $[\text{Ni}(\text{en})_2]^{2+}$ unit and exhibits a zigzag chain structure [23], $[\text{NiL}_2][\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$ (L = bpy or phen), with weak ferromagnetic exchange interaction [19]. Bimetallic compounds based on rare earth complexes, $[\text{M}^{\text{III}}\text{Fe}(\text{CN})_5\text{NO}(\text{phen})_2(\text{NO}_3)(\text{H}_2\text{O})]\cdot 0.5\text{H}_2\text{O}$ (M = Tb, Eu, Y) [24], which exhibit a zigzag chain structure, have also been reported. Besides these complexes, $[\text{Ni}(\text{C}_6\text{H}_{14}\text{N}_2)_2][\text{Fe}(\text{CN})_5\text{NO}]\cdot 6.5\text{H}_2\text{O}$ (where $\text{C}_6\text{H}_{14}\text{N}_2$ is 1,2-diaminocyclohexane) [25] and $[\text{Ni}(\text{cyclam})][\text{Fe}(\text{CN})_5\text{NO}]\cdot 4\text{H}_2\text{O}$ [25] consist of zigzag chains formed by an alternate array of the paramagnetic cations and $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ anions. Recently our group has reported some nitroprusside complexes of transition and non-transition metals, *e. g.*, $[\text{Zn}(\text{phen})_3][\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}\cdot 0.25\text{MeOH}$, $[(\text{bipy})_2(\text{H}_2\text{O})\text{Zn}(\mu\text{-NC})\text{Fe}(\text{CN})_4(\text{NO})]\cdot 0.5\text{H}_2\text{O}$ [26a], $[\text{Cu}(\text{dmen})_2\text{Fe}(\text{CN})_5\text{NO}]$, and $[\text{Cu}(\text{dmpn})_2\text{Fe}(\text{CN})_5\text{NO}]$ (where dmen = 2-dimethylaminoethylamine and dmpn = 1-dimethylamino-2-propylamine) [26b].

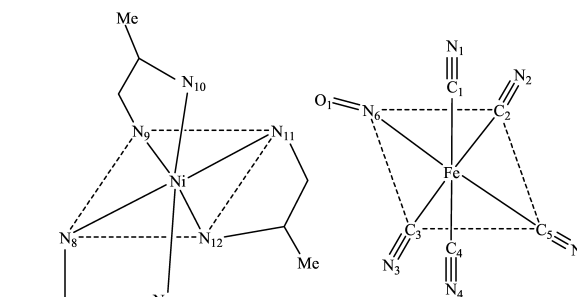
Here we report the preparation, crystal structure and physical characteristics of a discrete double complex $[\text{Ni}(\text{pn})_3][\text{Fe}(\text{CN})_5\text{NO}]\cdot\text{H}_2\text{O}$ with the photochromic anion $[\text{Ni}(\text{pn})_3]^{2+}$.

Result and Discussion

Complex **1** was synthesised by addition of an aqueous solution of sodium nitroprusside to a methanolic solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and racemic propane-1,2-diamine.

Infrared spectrum

The absorption band typical for a free NO is observed at 1876 cm^{-1} and that of NO^- anion is recorded in the range of $1200\text{--}1040\text{ cm}^{-1}$, and the absorption band due to NO^+ cation lies in the range of $1940\text{--}1575\text{ cm}^{-1}$ [27,28]. The nitroprusside anion of $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$ has an Fe-N-O angle of nearly 180° and an IR active NO stretching frequency of 1940 cm^{-1} indicating NO^+ attached to iron(II) with extensive π -bonding. The characteristic terminal



Scheme 1.

$\nu(\text{CN})$ vibration in $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$ appears at 2144 cm^{-1} [29a]. Formation of cyano bridge splits the $\nu(\text{CN})$ stretching band and a blue shift of $\nu(\text{CN})$ occurs [29b].

In the complex **1** we observed stretching vibrations $\nu(\text{CN})$ at 2143 and $\nu(\text{NO})$ at 1940 cm^{-1} . No splitting of the $\nu(\text{CN})$ stretching band indicates the absence of cyano bridging. The spectrum of the complex contains a very strong broad band in the region of $3800\text{--}3000\text{ cm}^{-1}$ indicating the stretching vibrations of the O-H bonds involved in H-bond formation [30]. The strong single peak at 1911 cm^{-1} was assigned to NO stretching implying a linear Fe-N-O bond. The structural diagram of complex **1** is shown in the Scheme 1.

Magnetic susceptibility study

The cryomagnetic behaviour of **1** is explained in Fig. 1. The plot of $\chi_m T$ vs. T appears to be constant ($1.11\text{ emu K mol}^{-1}$) in the temperature range between 2 and 300 K. This value corresponds to the expected value for non-coupled paramagnetic octahedral Ni^{2+} complex ions ($S = 1$, $g = 2.24$), which are magnetically isolated from each other. So, no magnetic exchange interaction occurs in the complex [31, 32].

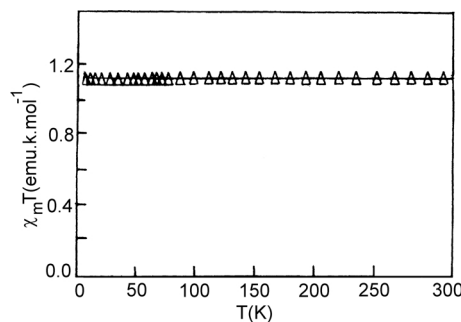


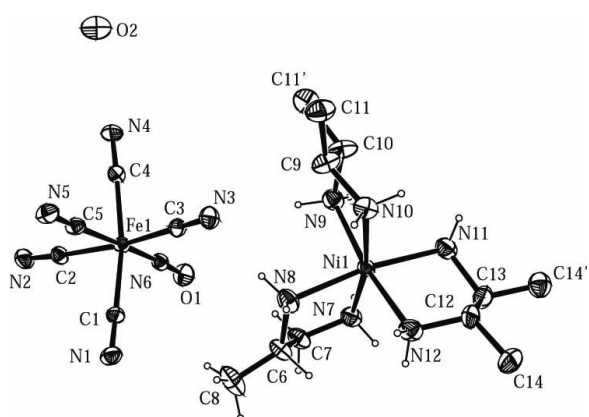
Fig. 1. Plot of the $\chi_m T$ vs. T for compound **1**.

Table 1. Selected bond lengths [Å] and angles [°] for **1**.

Ni(1)-N(11)	2.111(7)	Ni(1)-N(8)	2.114(6)
Ni(1)-N(7)	2.118(7)	Ni(1)-N(12)	2.119(6)
Ni(1)-N(9)	2.134(6)	Ni(1)-N(10)	2.140(7)
Fe(1)-N(6)	1.667(7)	Fe(1)-C(4)	1.929(8)
Fe(1)-C(5)	1.932(9)	Fe(1)-C(3)	1.943(7)
Fe(1)-C(1)	1.949(7)	Fe(1)-C(2)	1.953(8)
O(1)-N(6)	1.114(7)	N(1)-C(1)	1.126(9)
N(2)-C(2)	1.128(9)	N(3)-C(3)	1.095(8)
N(4)-C(4)	1.148(9)	N(5)-C(5)	1.146(9)
N(7)-Ni(1)-N(10)	168.5(3)	N(8)-Ni(1)-N(9)	94.6(3)
N(8)-Ni(1)-N(12)	92.1(3)	N(11)-Ni(1)-N(12)	81.2(3)
N(11)-Ni(1)-N(9)	92.6(3)	N(11)-Ni(1)-N(8)	170.9(3)
N(12)-Ni(1)-N(9)	171.0(3)	N(6)-Fe(1)-C(5)	177.6(3)
N(6)-Fe(1)-C(4)	97.3(3)	N(6)-Fe(1)-C(3)	95.4(3)
N(6)-Fe(1)-C(2)	96.0(3)	N(6)-Fe(1)-C(1)	93.4(3)
C(5)-Fe(1)-C(3)	83.9(3)	C(5)-Fe(1)-C(2)	84.8(3)
C(5)-Fe(1)-C(1)	84.3(3)	C(4)-Fe(1)-C(5)	85.0(3)
C(4)-Fe(1)-C(3)	90.0(3)	C(4)-Fe(1)-C(2)	87.2(3)
C(4)-Fe(1)-C(1)	168.8(3)	C(3)-Fe(1)-C(1)	92.0(3)
C(3)-Fe(1)-C(2)	168.5(3)	C(1)-Fe(1)-C(2)	88.7(3)
O(1)-N(6)-Fe(1)	176.9(6)	Fe(1)-C(1)-N(1)	175.7(7)
Fe(1)-C(2)-N(2)	176.5(7)	Fe(1)-C(3)-N(3)	178.8(7)
Fe(1)-C(4)-N(4)	178.0(6)	Fe(1)-C(5)-N(5)	177.7(7)

Table 2. Crystallographic data and details of the structure determination of complex **1**.

Empirical formula	C ₁₄ H ₃₂ Fe N ₁₂ Ni O ₂
Formula weight	515.08
Temperature [K]	293(2)
Wavelength [Å]	0.71073
Crystal system	monoclinic
Space group	C2/c
Unit cell dimensions	
<i>a</i> [Å]	15.7312(9)
<i>b</i> [Å]	13.6128(6)
<i>c</i> [Å]	23.1023(8)
α [°]	90.0
β [°]	96.651(4)
γ [°]	90.0
<i>v</i> [Å ³]	4914.0(4)
<i>Z</i>	8
Density (calculated) [mg/m ³]	1.392
Absorption coefficient [mm ⁻¹]	1.391
<i>F</i> (000)	2160
Crystal size	0.12 × 0.10 × 0.06 mm
Theta range for data collection [°]	1.77 to 27.51
Index ranges	-20 ≤ <i>h</i> ≤ 20, -17 ≤ <i>k</i> ≤ 17, -29 ≤ <i>l</i> ≤ 29
Reflections collected	53416
Independent reflections	5638 [<i>R</i> (int) = 0.1153]
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	5638 / 24 / 290
Goodness-of-fit on <i>F</i> ²	0.933
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0777, <i>wR</i> 2 = 0.2159
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1703, <i>wR</i> 2 = 0.2823
Largest diff. peak and hole [e·Å ⁻³]	1.052 and -0.777

Fig. 2. Perspective view of **1** with atom numbering scheme (ORTEP drawing). The hydrogen atoms are not shown for clarity. Methyl groups C11, C14 are disordered.

Mössbauer spectrum

There is a quadrupole doublet having an isomer shift $\delta = -0.37$ mm/s and a quadrupole splitting $\Delta Q = 1.91$ mm/s at 80 K. As there is no cyano bridging in the complex, the low δ value is probably due to the higher *s*-electron density around the Fe atom as compared to that of cyano-bridged complexes [33].

Structure of the complex

Single-crystal X-ray structure analysis revealed that the complex [Ni(pn)₃][Fe(CN)₅NO]·H₂O (**1**) is a dou-

ble complex in which the iron(II) is six-coordinated by five carbon atoms from cyanide ligands and by one nitrogen atom from the nitrosyl group (Fig. 2). The Ni(II) ion is coordinated by six nitrogen atoms of three racemic propane-1,2-diamine ligands. Selected bond lengths and angles are given in Table 1. The complex **1** consists of a discrete [Ni(pn)₃]²⁺ cation and a [Fe(CN)₅NO]²⁻ anion. The coordination geometry around the nickel(II) ion can be described as octahedral. The two nitrogen atoms occupying axial positions form an angle of 168.5(3)°. The methyl group on the ring is disordered and its sites are partially occupied. Thus C11 and C11' have site occupancies of 0.65 and 0.35, respectively. Similarly C14 and C14' have occupancies of 0.57 and 0.43, respectively, to count for one carbon. The hydrogens on these two disordered methyl groups were ignored. The Ni–N bond distances range from 2.111–2.140 Å (mean bond length is 2.12 Å), in good agreement with the values reported of other nickel complexes [34–36].

The geometry of [Fe(CN)₅NO]²⁻ is in good agreement with those of the previous studies

Table 3. Hydrogen bonds [Å and °] for complex **1**.

D–H...A	d(D–H)	d(H...A)	d(D...A)	∠D–H...A
N7–H7A...N4	0.900	2.620	3.366(10)	141.00
N7–H7B...N5	0.900	2.340	3.162(10)	151.00
N8–H8A...N1	0.900	2.310	3.161(10)	157.00
N8–H8B...N3	0.900	2.450	3.291(11)	156.00
N9–H9B...N3	0.900	2.250	3.139(10)	168.00
N10–H10A...N1	0.900	2.420	3.261(10)	155.00
N10–H10B...N2	0.900	2.490	3.369(11)	164.00
N11–H11A...O2	0.900	1.960	2.862(11)	174.00
N11–H11B...N2	0.900	2.270	3.139(11)	162.00
N12–H12B...N5	0.900	2.400	3.247(11)	158.00

[37–42]. The mean N–O, Fe–N, Fe–C, and C–N bond distances in [Fe(CN)₅NO]^{2–} are 1.114, 1.667, 1.9412, and 1.1286 Å, respectively. As expected, the [Fe(CN)₅NO]^{2–} fragment exhibits a distorted octahedral, pagoda-like coordination geometry around the iron(II) atom (Table 1). The greater electronegativity of the nitrosyl group with respect to the cyanide groups causes a deformation away from the octahedral geometry [43–45].

An important aspect of the present crystal structure is an extensive network of N–H...N/O hydrogen bonds. The key hydrogen bonding contacts for **1** are listed in Table 3. The acceptor (N–H...N/O) and donor...acceptor (H...N/O) distances are in the range of 1.96–2.62 Å and 2.862(11)–3.369(11) Å, respectively, which is within the generally accepted limits of H bonds [45]. The donor–H acceptor angle is in the range of 141–174°. All the amine nitrogen atoms act as donors and the uncoordinated water molecule in the lattice acts as acceptor. The result of this extensive hydrogen bonding is to hold two discrete ions in the crystal and impart overall stability to the system.

Experimental Section

Materials

All chemicals and solvents used for the synthesis were of reagent grade. Sodium nitroprusside Na₂[Fe(CN)₅NO]·2H₂O (Loba Chemie, India), and nickel chloride NiCl₂·6H₂O, (Merck, India) and racemic propane-1,2-diamine (Fluka) were used as received without purification. Since Na₂[Fe(CN)₅NO]·2H₂O has a tendency to decompose on heating and irradiation, the synthesis of the complex was performed at room temperature and crystallization was performed in a dark room.

Physical measurements

The infrared spectra were recorded on a Perkin-Elmer RX-FT-IR spectrophotometer using KBr disc. The C, H, N data were obtained using a Perkin-Elmer 2400 II elemental

analyser. The Ni content was estimated by the standard gravimetric method as dimethyl glyoximate. Magnetic measurements were carried out on polycrystalline samples (20 mg) with a Quantum Design MPMS SQUID magnetometer operating at a magnetic field of 1 T between 2 and 300 K. The contribution of the sample holder was determined separately in the same temperature range and magnetic field. Diamagnetic corrections were estimated from Pascal's constants. The magnetic susceptibility was fitted by least-squares techniques. Mössbauer spectra at 80 K were recorded on a conventional Austin S-600 Mössbauer spectrometer. Co(Pd) was used as the source and all isomer shifts are represented with respect to an α -iron foil.

Synthesis of the complex [Ni(pn)₃][Fe(CN)₅NO]·H₂O (**1**)

To a methanolic solution (40 ml) of NiCl₂·6H₂O (476 mg, 2 mmol), a solution containing propane-1,2-diamine (0.5 ml, 6 mmol) in 40 ml of methanol was added. To the resulting blue solution, a solution of Na₂[Fe(CN)₅NO]·2H₂O (596 mg, 2 mmol) in 40 ml of water was added dropwise. The solution turned violet to dark brown. The brown precipitate was filtered off and the yellow filtrate on slow evaporation for few days yielded reddish brown prism-like crystals, which were filtered off, washed with water and dried in air. Yield: 65.2%. – IR (film): $\nu = 2179, 2157, 2143(\text{CN}), 1940, 1911(\text{NO}), 1615 \text{ cm}^{-1}$. – C₁₄H₃₂FeN₁₂NiO₂ (**1**) (515.08): calcd. C 32.66, H 6.26, N 32.63, Ni 11.38; found C 32.91, H 6.3, N 32.6, Ni 11.40.

X-ray crystallography

Crystallographic measurements were made at 150 K using a Bruker-Nonius Kappa diffractometer equipped with a CCD area detector with graphite monochromatised Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) and ω -scan technique. The lattice constants were determined by least squares refinements of the setting angle for 25 reflections ($1.77 \geq \theta \geq 27.51^\circ$). The data were corrected for absorption effects by using the program SORTAV [46a]. The structure was solved by direct methods (SHELXS-96) [46b] and refined on F^2 by full-matrix least-squares (SHELXL-96) [46c] of all unique data. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included in calculated positions (riding mode). The crystal showed almost no decomposition during data collection. Selected bond lengths and angles are presented in Table 1. The crystal data and details of data collection and structure refinement are summarised in Table 2. A general view of the structure is presented in Fig. 2.

Supplementary material

Crystallographic data has been deposited at the Cambridge Crystallographic Data Centre with deposition number 260162. Copies of the information may be ob-

tained free of charge from The director, CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Conclusion

The complex, [Ni(pn)₃][Fe(CN)₅NO]·H₂O (**1**) crystallizes in the monoclinic *C*₂/*c* space group (*C*⁶_{2h}). The anions occupy *C*_s sites in the lattice and present the usual distorted octahedral structure and the geometrical parameters (bond distances and angles) as in several nitroprussides. The cation, which has also a distorted octahedral structure, and one water molecule, also occupy a *C*_s site. The structure of the cation is similar as found in other complexes but the average N-O distance (1.148 Å) seems to be somewhat longer (1.131 Å) as reported elsewhere [23].

The coordination chemistry of the photochromic nitroprusside anion, [Fe(CN)₅NO]²⁻, has been extended

to its association with the paramagnetic [Ni(pn)₃]²⁺ cation in this work. The versatile nature of the nitroprusside ion as a building block to form bimetallic complexes of various dimensionalities, has again been proven.

The complex **1** is a double complex with two discrete ions as in [Ni(bpy)₃][Fe(CN)₅NO]·3H₂O (bpy = 2,2'-bipyridine) [23]. In contrast, the analogous complexes [Ni(en)₂][Fe(CN)₅NO]·3H₂O [23] and [Cu(1,2-pn)₂Fe(CN)₅NO]·H₂O [43] are a cyano-bridged polymer with a zigzag chain structure, and dimer, respectively. Thus the formation of a discrete or cyano bridged polymeric double complex is a function of the nature of the ligand of the cation. In complex **1** the steric demand of the methyl groups of racemic propane-1,2-diamine molecules perhaps blocks the formation of cyano bridges between the ions.

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- [1] M. Ohba, H. Ōkawa, *Coord. Chem. Rev.* **198**, 313 (2000).
- [2] A. H. Yuan, J. Z. Zou, B. L. Li, Z. G. Zha, C. Y. Duan, Y. J. Liu, Z. Xu, S. Keizer, *Chem. Commun.* 1297 (2000).
- [3] D. F. Mullica, P. K. Hayward, E. L. Sappenfield, *Inorg. Chim. Acta* **237**, 111 (1995).
- [4] J. Narbutt, J. Siwinski, B. Bartos, A. Bilewicz, *J. Radioanal. Nucl. Chem.* **101**, 41 (1986).
- [5] a) M. Verdager, A. Bleuzen, V. Marvaud, J. Vaisermann, M. Seuleiman, C. Desplanches, A. Scullier, C. Train, R. Garde, G. Gelly, C. Lomenech, I. Rosenman, P. Veillet, C. Cartier, F. Villain, *Coord. Chem. Rev.* **190**, 1023 (1999); b) Z.-Z. Gu, O. Sato, T. Iyoda, K. Hashimoto, A. Fujishima, *Chem. Matter.* **9**, 1092 (1997).
- [6] J. S. Miller, A. J. Epstein, *Angew. Chem. Int. Ed. Engl.* **33**, 385 (1994).
- [7] A. C. Benniston, V. Gouille, A. Harriman, J.-M. Lehn, B. Marczinke, *J. Phys. Chem.* **98**, 7798 (1994).
- [8] A. P. de Silva, H. Q. N. Gunaratne, C. P. McCoy, *Nature* **364**, 42 (1993).
- [9] N. S. Hush, A. T. Wong, G. B. Bacskay, J. R. Reimers, *J. Am. Chem. Soc.* **112**, 4192 (1990).
- [10] a) H.-Z. Kou, S. Gao, B.-Q. Ma, D.-Z. Liao, *Chem. Commun.* 713 (2000); b) Z. J. Zhong, H. Seino, Y. Mizobe, M. Hida, A. Fujishima, S. Ohkoshi, K. Hashimoto, *J. Am. Chem. Soc.* **122**, 2952 (2000); c) J. Larionova, M. Gross, M. Pilkington, H. Andres, H. Stoeckli-Evans, H. U. Güdel, S. Decurtins, *Angew. Chem. Int. Ed.* **39**, 1605 (2000); d) P. A. Berseth, J. J. Sokol, M. P. Shores, J. L. Heinrich, J. R. Long, *J. Am. Chem. Soc.* **122**, 9655 (2000).
- [11] a) N. Matsumoto, Y. Sunatsuki, H. Miyasaka, Y. Hashimoto, D. Luneau, J.-P. Tuchagues, *Angew. Chem. Int. Ed.* **38**, 171 (1999); b) D. W. Knoepfel, J. Liu, E. A. Meyers, S. G. Shores, *Inorg. Chem.* **37**, 4828 (1998); c) E. Colacio, J. M. Domínguez-Vera, M. Ghazi, R. Kiveväs, M. Klinga, J. M. Moreno, *Chem. Commun.* 1071 (1998); d) D. G. Fu, J. Chen, X. S. Tan, L. J. Jiang, S. W. Zhang, P. J. Zheng, W. X. Tang, *Inorg. Chem.* **36**, 220 (1997).
- [12] a) B.-Q. Ma, S. Gao, G. Su, G.-X. Xu, *Angew. Chem. Int. Ed.* **40**, 434 (2001); b) A. K. Sra, M. Andruh, O. Kahn, S. Golhen, L. Ouahab, J. V. Yakhmi, *Angew. Chem. Int. Ed.* **38**, 2606 (1999); c) H. Miyasaka, H. Ōkawa, A. Miyazaki, T. Enoki, *Inorg. Chem.* **37**, 4878 (1998); d) H.-Z. Kou, W.-M. Bu, D.-Z. Liao, Z.-H. Jiang, S.-P. Yan, Y.-G. Fan, G.-L. Wang, *J. Chem. Soc., Dalton Trans.* 4161 (1998); e) Z. N. Chen, J. L. Wang, J. Qiu, F. M. Miao, W. X. Tang, *Inorg. Chem.* **34**, 2255 (1995).
- [13] a) N. Fukita, M. Ohba, H. Ōkawa, K. Matsuda, H. Iwamura, *Inorg. Chem.* **37**, 842 (1998); b) S.-W. Zhang, D.-G. Fu, W.-Y. Sun, Z. Hu, K.-B. Yu, W.-X. Tang, *Inorg. Chem.* **39**, 1142 (2000); c) A. K. Sra, G. Rombaut, F. Lahitête, S. Golhen, L. Ouahab, C. Mathonière, J. V. Yakhmi, O. Kahn, *New J. Chem.* **24**, 871 (2000); d) M. Ohba, N. Usuki, N. Fukita, H. Ōkawa, *Angew. Chem. Int. Ed.* **38**, 1795 (1999).

- [14] a) M. Ohba, N. Maruono, H. Ōkawa, T. Enoki, J.M. Latour, *J. Am. Chem. Soc.* **116**, 11566 (1994); b) M. Ohba, N. Fukita, H. Ōkawa, *J. Chem. Soc., Dalton Trans.* 1733 (1997).
- [15] M. Ohba, N. Usuki, N. Fukita, H. Ōkawa, *Inorg. Chem.* **37**, 3349 (1998).
- [16] M. Ohba, N. Maruono, H. Ōkawa, *J. Am. Chem. Soc.* **119**, 1011 (1997).
- [17] a) S. Ferlay, T. Mallah, J. Vaissermann, F. Bartolome, P. Veillet, M. Verdaguer, *Chem. Commun.* 2481 (1996); b) E. Colacio, J.M. Domínguez-Vera, M. Ghazi, R. Kikeväs, F. Lloret, J.M. Moreno, H. Stoeckli-Evans, *Chem. Commun.* 987 (1999).
- [18] M. S. El Falah, E. Rentschler, A. Caneschi, R. Sessoli, D. Gatteschi, *Angew. Chem., Int. Ed. Engl.* **35**, 1947 (1996).
- [19] Z. Smékal, F. Březina, Z. Šindelář, R. Klička, D. Krausová, M. Nádvořník, *Polish J. Chem.* **70**, 725 (1996).
- [20] J.-E. Koo, D.-H. Kim, Y.-S. Kim, Y. Do, *Inorg. Chem.* **42**, 2983 (2003).
- [21] K. Van Langenberg, S. R. Batten, K. J. Berry, D. C. R. Hockless, B. Moubaraki, K. S. Murray, *Inorg. Chem.* **36**, 5006 (1997).
- [22] a) K. Van Langenberg, D. C. R. Hockless, B. Moubaraki, K. S. Murray, *Synthetic Metals*, **122**, 573 (2001); b) M. Clemente-León, E. Coronado, J. R. Galán-Mascarós, C. J. Gómez-García, Th. Woike, J. M. Clemente-Juan, *Inorg. Chem.* **40**, 87 (2001).
- [23] H. L. Shyu, H. H. Wei, Y. Wang, *Inorg. Chim. Acta* **258**, 81 (1997).
- [24] T. Yi, Z. Wang, S. Gao, X. Chen, B. Ma, C. Liao, C. Yan, *Mol. Cryst. Liq. Cryst.* **335**, 211 (1999).
- [25] F. Bellouard, M. Clemente-León, E. Coronado, J. R. Galán-Mascarós, C. J. Giménez-Saiz, C. J. Gómez-García, Th. Woike, *Polyhedron* **20**, 1615 (2001).
- [26] a) A. Datta, S. Mitra, G. Rosair, *Z. Naturforsch.* **58b**, 916 (2003); b) N. Mondal, M. K. Saha, S. Mitra, V. Gramlich, M. S. El. Fallah, **19**, 1935 (2000).
- [27] P. N. Hawker and M. V. Twigg, in S. G. Wilkinson, R. Gillard, J. A. McCleverty (Eds), *Comprehensive Coordination Chemistry*, Vol. 4, p. 1187, Pergamon, Oxford (1989).
- [28] J. B. Ayers, H. Waggoner, *J. Inorg. Nucl. Chem.* **31**, 2045 (1969).
- [29] a) S. Zhan, X. Chen, A. Viji, D. Guo, Q. Meng, *Inorg. Chim. Acta* **292**, 157 (1999); b) K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed., Wiley-Interscience, New York (1997).
- [30] Yu. N. Kukushkin, *Chemistry of Coordination Compounds*, Moscow, Vysshaya Shkola (1985).
- [31] A. Meyer, A. Gleizes, J. J. Girerd, M. Verdaguer, O. Kahn, *Inorg. Chem.* **21**, 1729 (1982).
- [32] O. Kahn, *Molecular Magnetism*, p. 257, VCH, New York (1993).
- [33] N. N. Greenwood, T. C. Gibb, *Mössbauer Spectroscopy*, p. 183, Chapman and Hall, London (1971).
- [34] C.-H. Kim, S.-G. Lee, *Acta Crystallogr.* **C57**, 382 (2001).
- [35] M. Ohba, H. Ōkawa, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **25**, 423 (1996).
- [36] K. M. A. Malik, S. Mitra, R. K. Bhuban Singh, *J. Chem. Crystallogr.* **29**, 877 (1999).
- [37] M. R. Pressprich, M. A. White, Y. Vekhter, P. Coppens, *J. Am. Chem. Soc.* **116**, 5233 (1994).
- [38] A. G. Sharpe, *The Chemistry of Cyano Complexes of the Transition Metals*, Academic Press, New York (1976).
- [39] C. R. Johnson, C. M. Jones, S. A. Asher, J. E. Abola, *Inorg. Chem.* **30**, 2120 (1991).
- [40] S. Das, S. Ganguli, M. Bhattacharya, *J. Phys. Chem. Solids*, **143**, 46 (1985).
- [41] Y. Y. Yang, J. I. Zink, *J. Am. Chem. Soc.* **107**, 4799 (1985).
- [42] A. Navaza, G. Chevrier, P. M. Alzan, P. J. Aymonino, *Acta Crystallogr. Sec. C* **45**, 839 (1989).
- [43] Z. Smékal, Z. Trávníček, J. Marek, M. Nádvořník, *Aust. J. Chem.* **53**, 225 (2000).
- [44] a) J. E. Huheey, *J. Phys. Chem.* **69**, 3284 (1965); b) J. E. Huheey, *J. Phys. Chem.* **70**, 2086 (1966).
- [45] K. Takahashi, Y. Nishida, K. Kida, *Bull. Chem. Soc. Jpn.* **57**, 2628 (1984).
- [46] a) R. H. Blessing, *Acta Crystallogr. A* **51**, 33 (1995); b) G. M. Sheldrick, *Acta Crystallogr. A* **46**, 467 (1990); c) G. M. Sheldrick, *SHELXL-96, Program for Crystal Structure Refinement*, University of Göttingen, Germany (1996).