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Bimetallic Cyanide-Bridged Complexes Based on the Photochromic Nitroprusside Anion and Paramagnetic Metal Complexes. Syntheses, Structures, and Physical Characterization of the Coordination Compounds $[Ni(en)_2]_4[Fe(CN)_5NO]_2[Fe(CN)_6]\cdot 5H_2O$, $[Ni(en)_2][Fe(CN)_5NO]\cdot 3H_2O$, $[Mn(3\text{-}MeOsalen)(H_2O)]_2[Fe(CN)_5NO]$, and $[Mn(5\text{-}Brsalen)]_2[Fe(CN)_5NO]$

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The synthesis, crystal structure, and physical characterization of the coordination compounds $[Ni(en)_2]_4[Fe(CN)_5NO]_2[Fe(CN)_6]\cdot 5H_2O$ (**1**), $[Ni(en)_2][Fe(CN)_5NO]\cdot 3H_2O$ (**2**), $[Mn(3\text{-}MeOsalen)(H_2O)]_2[Fe(CN)_5NO]$ (**3**), and $[Mn(5\text{-}Brsalen)]_2[Fe(CN)_5NO]$ (**4**) are presented. **1** crystallizes in the monoclinic space group $P2_1/n$ ($a = 7.407(4)$ Å, $b = 28.963(6)$ Å, $c = 14.744(5)$ Å, $\alpha = 90°$, $\beta = 103.26(4)°$, $\gamma = 90°$, $Z = 2$). Its structure consists of branched linear chains formed by *cis*-$[Ni(en)_2]^{2+}$ cations and ferrocyanide and nitroprusside anions. The presence of two kinds of iron(II) sites has been demonstrated by Mössbauer spectroscopy. **2** crystallizes in the monoclinic space group $P2_1/c$ ($a = 11.076(3)$ Å, $b = 10.983(2)$ Å, $c = 17.018(5)$ Å, $\alpha = 90°$, $\beta = 107.25(2)°$, $\gamma = 90°$, $Z = 4$). Its structure consists of zigzag chains formed by an alternated array of *cis*-$[Ni(en)_2]^{2+}$ cations and nitroprusside anions. **3** crystallizes in the triclinic space group $P\bar{1}$ ($a = 8.896(5)$ Å, $b = 10.430(5)$ Å, $c = 12.699(5)$ Å, $\alpha = 71.110(5)°$, $\beta = 79.990(5)°$, $\gamma = 89.470(5)°$, $Z = 1$). Its structure comprises neutral trinuclear bimetallic complexes in which a central $[Fe(CN)_5NO]^{2-}$ anion is linked to two $[Mn(3\text{-}MeOsalen)]^+$ cations. **4** crystallizes in the tetragonal space group $P4/ncc$ ($a = 13.630(5)$ Å, $c = 21.420(8)$ Å, $Z = 4$). Its structure shows an extended 2D neutral network formed by cyclic octameric $[-Mn-NC-Fe-CN-]_4$ units. The magnetic properties of these compounds indicate the presence of quasi-isolated paramagnetic Ni^{2+} and Mn^{3+}. Irradiated samples of the four compounds have been studied by differential scanning calorimetry to detect the existence of the long-lived metastable states of nitroprusside.

Introduction

Cyanide-bridged bimetallic assemblies based upon hexacyanometalate building blocks, $[M(CN)_6]^{n-}$, provide a rich variety of magnetic materials with structures ranging from clusters to 3D extended networks and interesting magnetic and magnetooptical properties.[1−8] Initial efforts have focused on the preparation of 3D Prussian blue analogues in which the two metal centers are paramagnetic. This family has provided examples of magnets with critical temperatures as high as 315 K.[1] Interesting magnetooptical properties have also been reported for the compound $K_{0.2}Co_{1.4}[Fe(CN)_6]_2\cdot 6.9H_2O$, which undergoes a photoinduced magnetization upon application of light.[2]

To tune the dimensionality of the lattice, $[M(CN)_6]^{n-}$ has been combined with polyamine transition metal complexes containing polydentate ligands. This approach has afforded cyano-bridged complexes with 1D, 2D, and 3D extended structures, as well as discrete polynuclear species. For instance, $[Ni(en)_2]_3[Fe(CN)_6]_2$ (en = ethylenediamine),[3] $PPh_4[Ni(pn)_2][Fe(CN)_6]\cdot H_2O$ (pn = 1,2-propanediamine),[4] $[Ni(L)_2]_2[Fe(CN)_6]X$ (L = pn, 1,1-

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dimethylethylenediamine; X = ClO_4^-, PF_6^-, etc.) present a chain (rope-ladder) structure, a 1D zigzag chain structure, and a 2D square sheet structure, respectively.[5] The complex $[Ni(cyclam)]_3[Cr(CN)_6]\cdot 20H_2O$ and $[[Ni(cyclam)]_3[Fe(CN)_6]\cdot 12H_2O$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) has a layered structure with corrugated sheets,[6] and $[Ni(tren)]_3[Fe(CN)_6]_2\cdot 6H_2O$ (tren = tris(2-aminoethyl)amine) has a 3D structure.[7] Long-range magnetic ordering involving ferro-, ferri-, and metamagnetism has been observed in some cases. As polynuclear species we should mention the series of heptanuclear bimetallic complexes of the type MM'_6 (M = Fe^{III}, Cr^{III}; M′ = Cu^{II}, Ni^{II}, Mn^{II}) exhibiting high-spin ground states.[8]

Mn^{III} and Fe^{III} complexes based upon Schiff bases of the type salen (*N*,*N*′-ethylenebis(salicylideneaminato)) have been also used as paramagnetic building blocks. This kind of complexes has shown a good ability to form bimetallic compounds with $[M(CN)_6]^{3-}$ anions.[9−13] For instance, the compound $[NEt_4][Mn(5\text{-}Clsalen)(H_2O)]_2[Fe(CN)_6]$ is formed by discrete trinuclear species Mn−Fe−Mn, while the compound $\{[NEt_4][Mn(5\text{-}Clsalen)]_2[Fe(CN)_6]\}$ exhibits a 2D bimetallic network and a metamagnetic behavior.[10,11]

Other molecular precursors related to the hexacyanometalates can also be suitable to prepare bimetallic cyanide-bridged systems. One of these complexes is the nitroprusside anion $[Fe(CN)_5NO]^{2-}$. This diamagnetic anion is photochromic. By irradiation with light in the wavelength range 350−580 nm at temperatures below about 160 K, this anion exhibits photoinduced transitions to two extremely long-lived metastable states, MS_1 and MS_2, with lifetimes greater than 10^7 s.[14,15] These light-induced states can be depopulated via a thermal decay channel by heating the sample or by irradiation with laser light in the wavelength range of about 620−760 nm. Similar behaviors have been observed for several Fe, Ru, and Os nitrosyl complexes.[16,17] The nature of these metastable states and their long lifetimes are a subject of current discussion. It has been attributed to a charge-transfer transition from the metal to the NO, accompanied by a change in the coordination mode of the NO group which changes from the nitrosyl isomer in the groundstate, to η^2 nitrosyl and isonitrosyl isomers in the two metastable states.[18]

Most of these physical studies have been performed on simple nitroprusside salts containing an electronically "innocent" cation as charge-compensating counterion (Na^+, Ca^{2+}, Al^{3+}, alkylammonium cations, ...). An interesting possibility is however to connect these photochromic anions with magnetic cations in order to mix photophysical and magnetic properties. In this context, Hashimoto et al. proposed the construction of a switchable molecular spin device in the Prussian blue-like nickel nitroprusside $Ni[Fe(CN)_5NO]\cdot 5.3H_2O$.[19,20] When irradiated with light, this solid exhibited a weak enhancement of the magnetization that was attributed to a spin coupling between the five Ni^{2+} ions directy linked to the nitroprusside due to a photoinduced charge transfer from Fe to NO. A second type of bimetallic materials are the coordination polymers obtained by reaction of nitroprusside with transition metal complexes. This aspect has been loosely investigated and only few examples have been so far reported. We can mention $[Ni(en)_2][Fe(CN)_5NO]\cdot H_2O$ which contains a *trans*-$[Ni(en)_2]^{2+}$ unit and exhibits a zigzag chain structure, and $[Cu_2(oxpn)Fe(CN)_5NO]$ (oxpn is the dianion of *N*,*N*′′-bis(3-aminopropyl)oxamide)), which is formed by parallel sheets, each consisting of a 2D array of Cu(II) and Fe(II) centers bridged by oxpn and cyanide.[21,22] With rare earth complexes the series of bimetallic compounds $[M^{III}Fe(CN)_5NO(phen)_2(NO_3)(H_2O)]\cdot 0.5H_2O$ (M = Tb, Eu, Y) which exhibits a zigzag chain structure has also been reported.[23]

We report here on the preparation, structures, and physical characterization of the first bimetallic complexes of this photochromic anion with the *cis*-$[Ni(en)_2]^{2+}$ complex and with Mn^{III} complexes based upon Schiff bases of the type salen. These bimetallic species can be of interest not only from the point of view of their structural and magnetic properties but also in connection with the photochemistry of the nitroprusside anion, as the coordination of this complex to a Mn(III) or Ni(II) complex is a novel situation that may affect the properties of the photoinduced metastable states of this molecular anion.

Experimental Section

WARNING! Perchlorate salts are potentially explosives and should only be handled in small quantities.

Materials. $Na_2[Fe(CN)_5NO]\cdot 2H_2O$, ethylenediamine, 3-methoxysalicylaldehyde, 5-bromosalicylaldehyde, and ethylenediamine were purchased from commercial sources and used as received. $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ was transformed into the tetrabutylammonium salt $(NBu_4)_2[Fe(CN)_5NO]$ by a metathetic reaction in water. The tetradentate Schiff base ligands 3-MeOsalenH$_2$ and 5-BrsalenH$_2$ were prepared by mixing 3-methoxysalicylaldehyde or 5-bromosalicylaldehyde, respectively, with ethylenediamine in methanol (2:1 molar ratio). [Mn(3-MeOsalen)]ClO_4 and [Mn(5-Brsalen)]ClO_4 were prepared by reaction of $Mn^{III}(OOCCH_3)_3\cdot 2H_2O$ with 3-MeOsalenH$_2$ or 5-BrsalenH$_2$ and $NaClO_4$ (1:1:1 molar ratio) in methanol.

Synthesis. $[Ni(en)_2]_4[Fe(CN)_5NO]_2[Fe(CN)_6]\cdot 5H_2O$ (1). A 10 mL aliquot of an aqueous solution of $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ (361 mg, 1.21 mmol) was added dropwise to 50 mL of an aqueous solution of $[Ni(en)_3]Cl_2$ (0.500 g, 1.6 mmol) prepared as described in the literature.[24] The pH of the resulting solution is around 10. This red-orange solution was allowed to stand for 2 days in the dark to form brown needlelike crystals. IR (KBr): $\nu_{C\equiv N}$(cyanide) 2171, 2130, 2090, 2054 cm^{-1}; ν_{NO}(nitrosyl) 1900 cm^{-1}. Anal. Calcd for $H_{74}C_{32}N_{34}Ni_4Fe_3O_7$: H, 5.10; C, 26.52; N, 32.99. Found: H, 4.93; C, 26.85; N, 32.73.

$[Ni(en)_2][Fe(CN)_5NO]\cdot 3H_2O$ (2). This compound was prepared in a manner similar to **1** except that diluted HCl was added to the final solution until pH = 7.3 was reached. The color of the solution changed from red to brown, and after it was allowed to stand for 2 days in the dark, red prismatic-like crystals were obtained. IR (KBr): $\nu_{C\equiv N}$(cyanide) 2158, 2144, 2133 cm^{-1}; ν_{NO}(nitrosyl) 1925 cm^{-1}. Anal. Calcd for $H_{22}C_9N_{10}NiFeO_4$: H, 4.72; C, 23.62; N, 30.60. Found: H, 4.84; C, 23.74; N, 30.38.

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Table 1. Crystal Data for $[Ni(en)_2]_4[Fe(CN)_5NO]_2[Fe(CN)_6]\cdot 5H_2O$ (1), $[Ni(en)_2][Fe(CN)_5NO]\cdot 3H_2O$ (2), $[Mn(3\text{-}MeOsalen)(H_2O)]_2[Fe(CN)_5NO]$ (3), and $[Mn(5\text{-}Brsalen)]_2[Fe(CN)_5NO]$ (4)

compound	**1**	**2**	**3**	**4**
formula	$H_{74}C_{32}N_{34}Ni_4Fe_3O_7$	$H_{22}C_9N_{10}NiFeO_4$	$C_{41}H_{40}FeMn_2N_{10}O_{11}$	$C_{37}H_{24}Br_4FeMn_2N_{10}O_5$
a, Å	7.407(4)	11.076(3)	8.896(5)	13.630(5)
b, Å	28.963(6)	10.983(2)	10.430(5)	13.630(5)
c, Å	14.744(5)	17.018(2)	12.699(5)	21.420(8)
α, deg	90	90	71.110(5)	90
β, deg	103.26(4)	107.25(2)	77.990(5)	90
γ, deg	90	90	89.470(5)	90
V, Å^3	3079(2)	1977.0(7)	1088.3(9)	3979(3)
Z	2	4	1	4
fw	1449.64	469.94	1014.56	1174.04
space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P4/ncc$
ρ_{calc}, g·cm^{-3}	1.564	1.579	1.548	1.960
λ, Å	0.710 69	0.710 69	0.710 69	0.710 69
μ, cm^{-1}	19.53	17.20	9.72	50.59
R^a	0.0655	0.0478	0.0591	0.0319
R_ω	0.1268^b	0.1340^c	0.1496^d	0.0636^e

^{a} $R = \sum(F_o - F_c)/\sum(F_o)$. ^{b} $R_\omega = [\sum[\omega(F_o^2 - F_c^2)^2]/\sum[\omega(F_o^2)^2]]^{1/2}$; $\omega = 1/[\sigma^2(F_o^2)+(0.0560P)^2 + 3.440P]$, where $P = (F_o^2 + 2F_c^2)/3$. ^{c} $\omega = 1/[\sigma^2(F_o^2) + (0.0850P)^2 + 4.4382P]$. ^{d} $\omega = 1/[\sigma^2(F_o^2) + (0.1064P)^2+0.9226P]$. ^{e} $\omega = 1/[\sigma^2(F_o^2) + (0.0370P)^2]$.

$[Mn(3\text{-}MeOsalen)(H_2O)]_2[Fe(CN)_5NO]$ (3). A 2 mL aliquot of an aqueous solution of $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ (62 mg, 0.20 mmol) was added dropwise to 40 mL of a methanolic solution of $[Mn(3\text{-}MeOsalen)]ClO_4$ (100 mg, 0.20 mmol). The brown solution was allowed to stand for 2 days in the dark to form brown prismatic crystals. IR (KBr) $\nu_{C=N}$(imine) 1618, 1601 cm^{-1}; $\nu_{C\equiv N}$(cyanide) 2137 cm^{-1}; ν_{NO}(nitrosyl) 1882 cm^{-1}. Anal. Calcd for $C_{41}H_{40}FeMn_2N_{10}O_{11}$: H, 3.94; C, 48.55; N, 13.81. Found: H, 3.85; C, 48.73; N, 13.63.

$[Mn(5\text{-}Brsalen)]_2[Fe(CN)_5NO]$ (4). This synthesis was carried out by a slow diffusion method. $[Mn(5\text{-}Brsalen)]ClO_4$ (100 mg, 0.18 mmol) and $(NBu_4)_2[Fe(CN)_5NO]$ (123 mg, 0.18 mmol) were placed in the compartments of a U type diffusion tube. A mixture of *N*,*N*′-dimethylformamide, acetonitrile, and ethanol (4.3:1.3:1) was used as solvent. After 30 days, dark brown rhombic crystals were obtained. IR (KBr) $\nu_{C=N}$(imine) 1620, 1586 (sh) cm^{-1}; $\nu_{C\equiv N}$(cyanide) 2135 cm^{-1}; ν_{NO}(nitrosyl) 1931 cm^{-1}. Anal. Calcd for $C_{37}H_{24}Br_4FeMn_2N_{10}O5$: H, 2.04; C, 37.85; N, 11.93. Found: H, 1.83; C, 37.64; N, 12.08.

X-ray Data Collection and Structure Refinement. Crystals of **1**, **2**, and **3** were taken directly from their mother liquor and mounted on a CAD4 Enraf-Nonius diffractometer. Preliminary examinations and data collection were performed with Mo Kα radiation. Unit cell parameters and orientation matrixes were determined by a least-squares refinement of the setting angles of 25 independent reflections for the three crystals. Data collection were performed with the ω-scan technique, and three standard reflections were measured every 2 h and showed no significant decay. Lorentz, polarization, and semiempirical absorption corrections (ψ-scan method) were applied to the intensity data. A single crystal of **4** was mounted on a glass fiber in a random orientation. Data collection for **4** was performed at room temperature on a Siemens Smart CCD diffractometer using graphite monocromated Mo Kα radiation with a nominal crystal to detector distance of 4.0 cm. An hemisphere of data was colleted based on three ω-scans runs (starting $\omega = -28°$) at values $\phi = 0$, 90, and 180 with the detector at $2\theta = 28°$ At each of these runs, frames (606, 435, and 230 respectively) were collected at 0.3° intervals and 10 s per frame. The diffraction frames were integrated using the SAINT package (SAINT version 5.0 Bruker Analytical X-ray Systems, Madison, WI.) and corrected for absorption with SADABS (Sheldrick, G. M. SADABS empirical absorption program, University of Gottingen, 1996). Selected experimental parameters and crystal data for all four structures are reported in Table 1. All calculations were performed in a SPARC station 20 (Sun Microsystems). The structures were solved by direct methods using the SIR97 program,[25] and were refined on F^2 using the SHELXL-97 program (Sheldrick, G. M. University of Göttingen, 1997). For **1**, all non-hydrogen atoms were refined anisotropically and the positions for the hydrogen atoms from the organic ethylenediamine ligands were calculated since they could not be found in succesive Fourier differences, with a final R of 6.55 for 2057 reflections with $\sigma(I) > 4$ (4821 total reflections). The better quality of the crystals of **2**, **3**, and **4** allowed us to find the hydrogen atoms from the organic ligands in succesive Fourier differences. Final refinements, anisotropic for all non-hydrogen atoms, gave final R values of 4.78 for 2687 reflections with $\sigma(I) > 4$ (3433 total reflections) (**2**), 5.91 for 2519 reflections with $\sigma(I) > 2$ (3780 total reflections) (**3**), and 3.19 for 1783 reflections with $\sigma(I) > 4$ (3034 total reflections) (**4**), respectively.

Spectra. IR spectra were recorded with a Perkin-Elmer 882 spectrometer in KBr pellets in the 4000−400 cm^{-1} region. Mössbauer spectra at 80 K were recorded using a ^{57}Co/Rh source in a constant acceleration spectrometer equipped with a liquid helium cryostat. The spectra were fitted to Lorentizan lines using a nonlinear minimization iterative routine.

Magnetic Properties. Variable temperature susceptibility measurements were carried out in the temperature range 2−300 K at a magnetic field of 0.1 T on polycrystalline samples with a magnetometer (Quantum Design MPMS-XL-5) equipped with a SQUID sensor. The susceptibility data were corrected from the diamagnetic contributions of the compound as deduced by using Pascal's constant tables.

Differential Scanning Calorimetry. The radiationless decay of the metastable states of nitroprusside was detected with a modified differential scanning calorimeter (Mettler DSC 30, TA 3000), equipped with two quartz windows inside and outside of the oven. The absolute calibration of the enthalpy H and temperature T was controlled by measuring the phase-transitions of In, Hg, pentane, hexane, and KH_2PO_4. During the illumination the sample was kept at $T = 100$ K in a dry nitrogen atmosphere and subsequently heated with constant heating rate $q = dT/dt = 5$ K/min. The measured exothermal heatflow is the time derivative of the enthalpy H. To obtain only the contribution of the enthalpy of the metastable state, the enthalpy of the unirradiated sample was subtracted from that of the irradiated one. The residual enthalpy was evaluated by fitting to an Arrhenius law modified for dinamic measurements.

$$\dot{H}(T) = H_{tot} Z \exp[-\{(Z/q) \int_{T_0}^{T} \exp(-E_A/k_B T') + (E_A/k_B T)\}]$$

$$(Z = \text{frequency factor}, E_a = \text{activation energy}, K_B = \text{Boltzmann constant})$$

The light exposure, Q, given by the product of constant light intensity, I, and irradiation time, t, has an value of $Q = 2000$ J/cm^2. With this exposure the saturation of the population is reached. As a light source we have used a metal-vapor lamp (HMI 575, Osram) filtered by dichroitic filters to the blue-green spectral range of 410−500 nm with a constant intensity of 200 mW/cm^2 on the sample.

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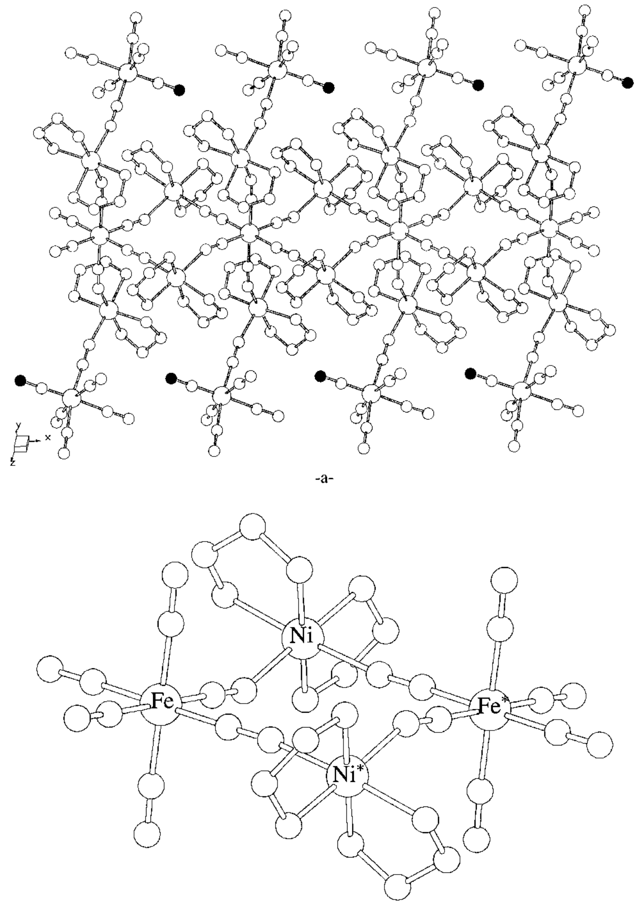

Figure 1. (a) View of the structure of the branched chains of **1**. (b) View of the rhomblike core of the chains of **1**. Black atoms are O atoms from the NO group.

Results and Discussion

Synthesis and Structural Characterization. Compound **1** is obtained by reaction of $[Fe(CN)_5NO]^{2-}$ with $Ni(en)_3Cl_2$ in aqueous solution. The slow disociation of $[Ni(en)_3]^{2+}$ into $[Ni(en)_2]^{2+}$ leads to the growth of crystals suitable for X-ray diffraction. This is a general method to obtain cyanide-briged bimetallic assemblies.[3] In the present case the final pH of the solution is around 10. When the above solution is neutralized by addition of diluted HCl, compound **2** is obtained.

The structure of compound **1** shows branched linear chains running along the *a* axis (Figure 1a). The core of these chains shows a rhomb-like repeating unit comprising two ferrocyanide anions (Fe1, Fe1*) and two *cis*-$[Ni(en)_2]^{2+}$ cations (Ni1, Ni1*) (Figure 1b). The four equatorial CN^- groups from the ferrocyanides act as bridging ligands giving rise to the polymerization of the chain. The branches of the chains are formed by two bimetallic $[Ni(en)_2][Fe(CN)_5NO]$ dimers linked to the central ferrocyanide complex through the two axial CN^- ligands which connect the nickel complex with the iron one. The bimetallic dimers are formed by a *cis*-$[Ni(en)_2]^{2+}$ complex and a nitroprusside anion connected through a CN^- bridging ligand in such a way that this bridge is cis to the terminal NO group.

From the X-ray diffraction analysis, the nature of these peripheral iron complexes (Fe2) as nitroprusside anions is well established, since the NO group is perfectly located among the six possible coordinating positions. The Fe−N distance (1.65 Å) is much shorter than the other five Fe−C distances, which are between 1.90 and 1.96 Å. These values are in good agreement with other polymeric structures reported for nitroprusside.[21,22] In contrast, the central iron site (Fe1) cannot be well-characterized from the structural analysis. We found an octahedral iron atom coordinated by six dinuclear groups, with equivalent Fe−ligand distances. Although this structure could be attributed to a nitroprusside anion with its NO group disordered among the six different possitions, this possibility is quite unlikely to happen. It would imply that the NO group is acting as a bridging ligand, and as far as we are aware, a bridging NO group has never been reported to date for nitroprusside. So, we have assumed that this iron complex is indeed ferrocyanide. The presence of two different anions in the structure, $[Fe(CN)_5NO]^{2-}$ and $[Fe(CN)_6]$,$^{4-}$ could be explained as result of the partial decomposition of the nitroprusside anion in the basic aqueous solution (pH = 10) produced by the ethylenediamine ligand. In fact, this feature has already been observed in other instances.[26,27] This point will be confirmed by Mössbauer spectroscopy. According to this, the formula for the polymeric chain would be $\{[Ni(en)_2]_4[Fe(CN)_5NO]_2[Fe(CN)_6]\}_n$, with an overall neutral charge. Between the parallel infinite chains, several solvent molecules (water) were also found.

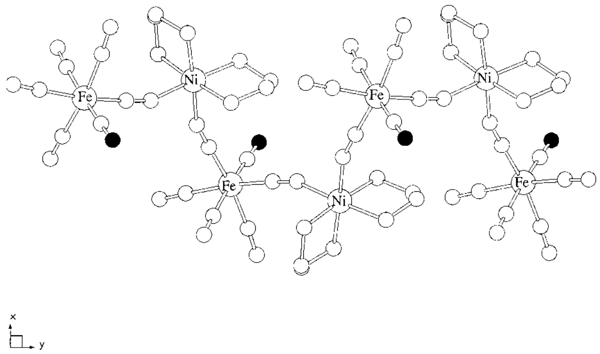

Figure 2. Projection of the structure of **2** onto the *xy* plane. Black atoms are O atoms from the NO group.

More evidence about the presence of ferrocyanide is found in the IR spectrum, which shows four sharp ν_{CN} peaks. The two peaks at 2171 and 2130 cm^{-1} correspond to the presence of bidentate and monodetante CN^- ligands from the nitroprusside anion, while the two peaks at 2090 and 2054 cm^{-1} would correspond to those of the $[Fe(CN)_6]^{4-}$ anion. These two peaks are at higher frequencies than the peak observed in $K_4[Fe(CN)_6]$, in agreement with the bridging nature of these cyano groups. On the other hand, the presence of two peaks, instead of one, accounts for the lowering of the local symmetry of the ferrocyanide complex in this structure. For example, in the $[Ni(en)_2]_3[Fe(CN)_6](PF_6)_2$ compound all the CN^- groups are equivalent, and a single CN^- peak at 2060 cm^{-1} is observed.[28] Besides the peaks associated with CN^-, a strong peak at 1900 cm^{-1} is also observed in the spectrum, which can be assigned to the NO stretching vibration of the $[Fe(CN)_5NO]^{2-}$ anion. This value is lower than that found in the sodium salt (1940 cm^{-1}). Similar values have also been observed for other nitroprusside compounds such as $[Ni(bpy)_3][Fe(CN)_5NO]\cdot 3H_2O$ (1911 cm^{-1}).[21]

The structure of compound **2** shows polymeric zigzag chains running along the *b* axis (Figure 2). It is formed by an alternated

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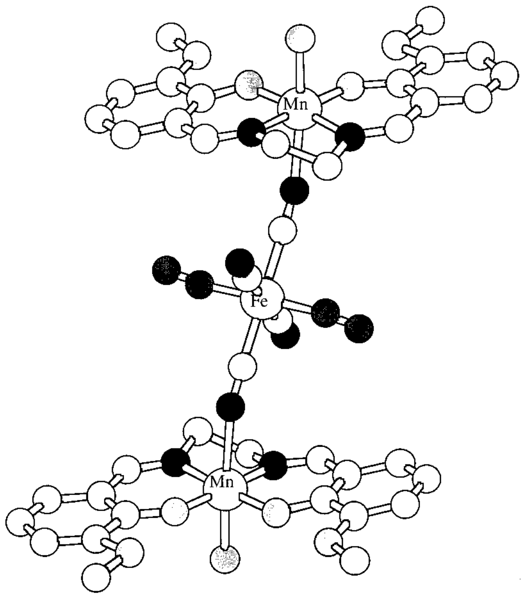


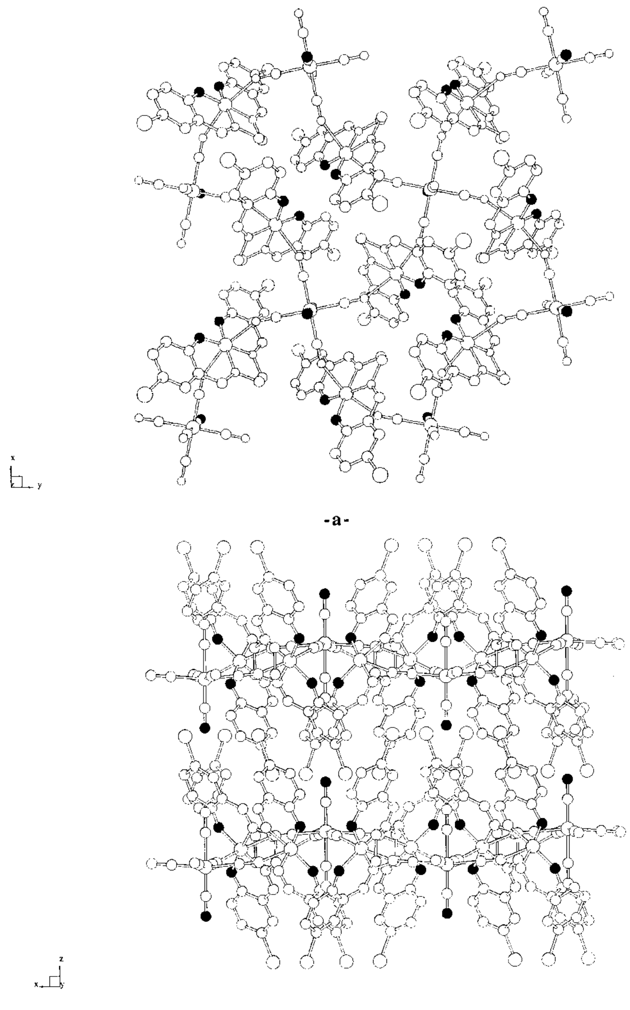
Figure 3. View of the structure of the trimeric unit of **3**: white atoms (C), black atoms (N), and light gray atoms (O). Dark gray atoms represent the disorder between NO and CN groups in nitroprusside anion.

array of *cis*-$[Ni(en)_2]^{2+}$ cations and $[Fe(CN)_5NO]^{2-}$ anions. Nitroprusside anions are bridged to two *cis*-$[Ni(en)_2]^{2+}$ units (Ni, Ni*) through two CN^- equatorial ligands in cis. The NO ligand and the other three CN^- ligands are monodentate. As in the nitroprusside anion of **1**, the NO group is perfectly located among the six possible coordinating positions. The Fe−N distance found (1.63 Å) is much shorter that the other five Fe−C distances, which are between 1.92 and 1.95 Å. The two *cis*-$[Ni(en)_2]^{2+}$ units are bridged to other two nitroprusside anions (Fe, Fe*) through the cyanide groups, and this coordination gives rise to the zigzag chain. The other polymeric compound of $[Ni(en)_2]^{2+}$ and $[Fe(CN)_5NO]^{2-}$ already known shows a different chain structure. The synthetic procedure used in that case afforded a chain that contains the *trans*-$[Ni(en)_2]^{2+}$ isomer.[21] This trans complex is the one formed in situ by adding the en ligand to an aqueous solution of nickel chloride.

The IR spectra of **2** is clearly different from that of **1**, as expected from the crystal structure. It shows three strong bands at 2158, 2144, and 2133 cm^{-1} corresponding to bidentate and monodentate cyanide ligands of the $[Fe(CN)_5NO]^{2-}$ anion and a strong band at 1925 cm^{-1} coming from the NO stretching vibration of the $[Fe(CN)_5NO]^{2-}$ anion.

Two different strategies have been used for the synthesis of **3** and **4**. The first one consists of mixing a methanolic solution of $[Mn(3\text{-}MeOsalen)]^+$ with an aqueous solution of $[Fe(CN)_5NO]^{2-}$. Slow evaporation of the resulting solution in the dark affords crystals of compound **3**. The second procedure consists of conducting the synthesis in the absence of water in a mixture of organic solvents. Thus, by slow diffusion of $[Mn(5\text{-}Brsalen)]^+$ and $[Fe(CN)_5NO]^{2-}$ in a mixture of DMF/acetonitrile/ethanol, compound **4** is obtained.

The structure of compound **3** is formed by neutral trinuclear bimetallic complexes (Figure 3). The trinuclear unit comprises one central $[Fe(CN)_5NO]^{2-}$ anion linked to two $[Mn(3\text{-}MeOsalen)]^+$ cations through two trans CN^- ligands. Both kinds of metal sites are octahedral. The Fe atom of nitropusside occupies an inversion center giving rise to a disorder of the nitrosyl group between two positions in trans. The corresponding Fe−N/C distances (1.80 Å) are intermediate between the Fe−N and Fe−C distances typically observed in the $[Fe(CN)_5NO]^{2-}$ anion.[29] The other Fe−C distances are similar to those observed in other nitroprusside compounds. These Fe−C distances are 1.90 Å for the two CN^- terminal ligands and 1.93 Å for the two CN^- bridging ligands. The manganese site exhibits an octahedral distorted geometry due to the strong Jahn−Teller effect of Mn^{III}. In the equatorial positions of the Mn site this metal is coordinated by the N_2O_2 donor atoms of the Schiff base. Mn−O distances of the $[Mn(3\text{-}MeOsalen)]^+$ cations are 1.86 and 1.86 Å while Mn−N distances are 1.97 Å. The two axial positions are occupied by one N from a CN^- bridging ligand of nitroprusside and by one water molecule.



-a-

-b-

Figure 4. Projection of the structure of **4** onto the *xy* plane (a) and onto the *xz* plane (b). Black atoms are O atoms.

In contrast to **3**, the structure of compound **4** shows an extended two-dimensional neutral network formed by cyclic octameric $[-Mn-NC-Fe-CN-]_4$ units with Fe atoms at the corners and Mn atoms at the edges of a deformed square grid in the *ab* plane (Figure 4a). In this compound, $[Mn(5\text{-}Brsalen)]^+$ cations are coordinated to two $[Fe(CN)_5NO]^{2-}$ anions through the nitrogen atoms of two cyano groups in the axial positions while $[Fe(CN)_5NO]^{2-}$ anions are linked to four $[Mn(5\text{-}Brsalen)]^+$ cations through the four equatorial CN^- ligands.

The nitroprusside anion contains four symmetrically equivalent equatorial bridging CN^- ligands at Fe−C distances of 1.95

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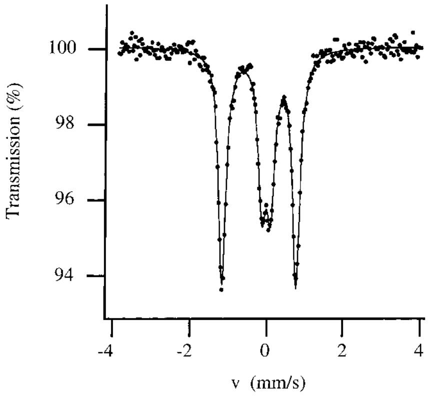

Figure 5. Mössbauer spectrum of **1**. The solid line represents the best fit to two doublets.

Å related by a C_4 axis that pass through the NO and CN^- axial ligands. In this case the Fe−N distance (1.66 Å) is much shorter than the other Fe−C distance (1.95 Å). Hence, the NO ligand is perfectly localized in the structure. It is always oriented parallel to the *c* axis pointing toward the neighboring layer and even partially penetrating into it (Figure 4b). Interestingly, the CN^- group axial to the NO ligand does not penetrate into the layer. This suggests some kind of interaction between the NO groups and the $[Mn(5\text{-}Brsalen)]^+$ cations. In fact, the NO is surrounded by Br atoms from $[Mn(Brsalen)]^+$ cations with four short contacts Br···O of 3.26 Å which are smaller than the sum of the van der Waals radii (3.37 Å).

The Mn(III) ion has an octahedral geometry with a strong axial distortion. In the equatorial plane it is coordinated by the N_2O_2 donor atoms from the tetradentate Schiff base Brsalen. The Mn−O and Mn−N distances are 1.86 and 1.99 Å, respectively, which are quite similar to those of **3**. The coordination is completed by two equivalent nitrogen atoms of CN^- bridging ligands of the nitroprusside at 2.378(2) Å. These distances are slightly longer than Mn−NC distances of **3** (2.36 Å).

The above 2D network closely resembles that exhibited by the bimetallic compound obtained from $[Mn(5\text{-}Clsalen)]^+$ and $[Fe(CN)_5]^{3-}$ by Okawa et al.[11] The main difference lies is the fact that in this last compound the bimetallic Mn_2Fe layers have a negative charge which needs to be compensated by a monocation, while in our case the layers are neutral and therefore the interlayer distance is shorter.

Mössbauer Spectroscopy. ^{57}Fe Mössbauer spectroscopy is a very powerful technique to study the electronic properties of iron complexes, since it provides information about the oxidation state, coordination sphere and local environment of this metal ion. In the present case we have used this technique to distinguish between the different iron sites postulated in compound **1**. As expected, the Mössbauer spectrum shows two different signals (Figure 5), indicating the presence of two different iron sites in the structure. One signal corresponds to a quadrupolar doublet centered at −0.01 mm/s with a very small quadrupole splitting, $\Delta E_Q = 0.22$ mm/s. Such spectrum is typical of low-spin Fe(II) and can be assigned to the ferrocyanide anion.[30] The other signal is a quadrupolar doublet centered at −0.2 mm/s which exhibits a much larger quadrupole splitting, $\Delta E_Q = 1.88$ mm/s. These are the typical parameters found for nitroprusside.[31] The ratio between the intensities of these signals is 1:2. Providing the Debye−Weller factors of both ^{57}Fe central atoms are equal, this result is in excellent agreement with the stoichiometry proposed for compound **1** constituting so an unambiguous experimental evidence of our initial hypothesis.

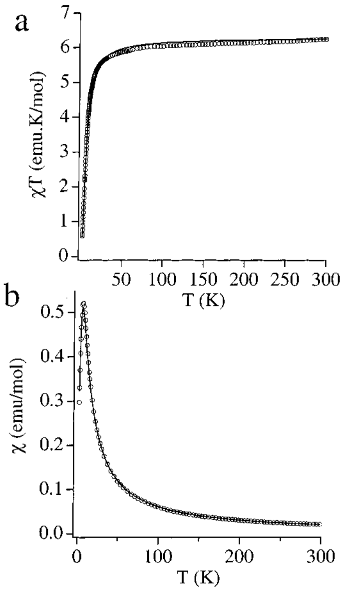

Figure 6. Plot of χT product vs *T* for **3** (a) and χ vs *T* for **3** (b). Solid line represents the theoretical curve with the parameters $D = -2.62$ cm^{-1}, $J = -0.44$ cm^{-1}, and $g = 2.05$.

Magnetic Properties. A constant value of χT of ca. 4.7 emu K mol^{-1} is observed from room temperature to 12.7 K for compound **1**. This value agrees with the presence of four magnetically independent high-spin ($S = 1$) Ni^{2+} centers. At the same time, it provides an additional proof of the presence of diamagnetic $[Fe(CN)_6]^{4-}$ anions. The *cis*-$[Ni(en)_2]^{2+}$ are separated by diamagnetic $[Fe(CN)_6]^{4-}$ anions and linked to $[Fe(CN)_5NO]^{2-}$ anions which are also diamagnetic. Distances between neighboring $[Ni(en)_2]^{2+}$ units (minimun distance 6.86 Å) are too large to allow significant magnetic interactions. Only below 13 K does the χT product show a small increase with a value at 2 K of 4.95 emu·K·mol^{-1}. This increase is indicative of the presence of weak ferromagnetic exchange interactions between Ni^{2+} ions through ferrocyanide anions. The ability of ferrocyanide to promote ferromagnetic Ni−Ni interactions has already been observed[28] for the 3D compound $[Ni(en)_2]_3[Fe(CN)_6](PF_6)_2$.

For compound **2** a constant χT value of 1.3 emu K mol^{-1} has been observed down to ca. 25 K. This behavior indicates that the octahedral Ni^{2+} complexes are magnetically isolated from each other, in agreement with the structure that shows that these paramagnetic centers are separated by diamagnetic $[Fe(CN)_5NO]^{2-}$ anions. Below 25 K, χT decreases upon cooling. This behavior may be attributed to the combined effect of weak antiferromagnetic Ni−Ni interactions through the nitroprusside bridge and zero field splitting of Ni^{2+}.

Magnetic properties of **3** are plotted in Figures 6 and 7. In the temperature range 300−50 K the χT product stays almost constant with a value of 6.0−6.2 emu·K·mol^{-1}, which corresponds to the expected value for two noninteracting Mn^{III} ions (6.0 emu·K·mol^{-1} for $g = 2$, $S = 2$). At lower temperatures, χT shows a sharp decrease upon cooling, reaching a value of 0.6 emu·K·mol^{-1} at 2 K (Figure 6a). The χ vs *T* curve exhibits a maximum at 6.1 K (Figure 6b). The above behavior cannot be explained by the zero-field-splitting of the Mn^{III} and suggests the presence of a weak antiferromagnetic coupling between the Mn^{III} ions. Taking into account both effects and using the

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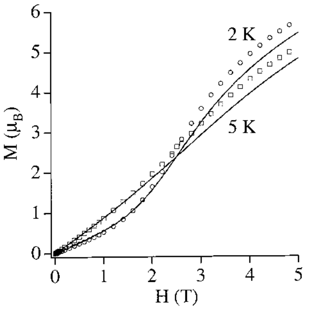

Figure 7. Field dependence of the magnetization of **3** at 2 (empty circles) and 5 K (empty squares). The solid line represents the theoretical curve with the parameters derived from susceptibility measurements.

computational program recently developed in our group,[32] we have obtained an excellent fit of the experimental data from the following parameters $D = -2.62$ cm^{-1}, $J = -0.44$ cm^{-1}, and $g = 2.05$ (solid line in Figure 6b). Notice that the negative sign of the D value agrees with recent studies of high-frequency EPR of Mn^{III} compounds with a tetragonally elongated octahedral symmetry.[33] On the other hand, the small antiferromagnetic coupling between Mn^{III} ions cannot be only attributed to dipolar interactions between trinuclear complexes as the shortest intermolecular $Mn^{III}-Mn^{III}$ distance is too large (4.684 Å) to account for the observed effect (the estimated dipolar interaction is of the order of 0.01 cm^{-1}). Therefore, an intramolecular exchange interaction through the diamagnetic $[Fe(CN)_5NO]^{2-}$ anion is expected to be the dominant interaction pathway.

The magnetic characterization has been completed with the study of the field dependence of the magnetization performed at 2 and 5 K (Figure 7). We observe that the increase of the magnetization with the magnetic field at 2 K is very slow below 1 T, in agreement with the nonmagnetic ground spin state. Above 1 T the magnetization increases more rapidly due to the population of excited states having higher spin multiplicities. At 5 K the increase of magnetization is steeper due to the population of excited states. The theoretical curves calculated by using the parameters derived from susceptibility measurements closely reproduces these trends at 2 and 5 K. These results support the validity of the magnetic parameters derived from the fitting to the susceptibility data.

The temperature dependence of the χT product of compound **4** is shown in Figure 8a. A constant value of ca. 6.1 emu·K·mol^{-1} is obtained at high temperatures which agrees with the presence of two noninteracting Mn^{III} per formula. At temperatures below 30 K there is a decrease of χT similar to that found for compound **3** but not so important. Thus, the χT value of this compound at 2 K is larger than that of compound **3** (1.84 compared to 0.61 emu·K·mol^{-1}). These differences are seen more clearly in the χ vs T plot (Figure 8b). Thus, while compound **3** shows a maximum at 6.1 K, the susceptibility of compound **4** increases continuously down to 2 K. It is possible to fit the temperature dependence of the susceptibility of compound **4** taking into account only ZFS of Mn^{III}. However, the obtained D value ($D = -10$ cm^{-1}) is clearly too large suggesting that a weak antiferromagnetic exchange through the nitroprusside anions is also operative, as in the previous case. The resulting exchange network involves an extended 2D lattice in which each Mn^{III} can be antiferromagnetically coupled to the three Mn^{III} ions linked to each one of the two diamagnetic nitroprusside anions acting as bridging groups. Obviously, a quantitative theoretical treatment of this 2D magnetic lattice cannot be carried out due to the complexity of the problem.

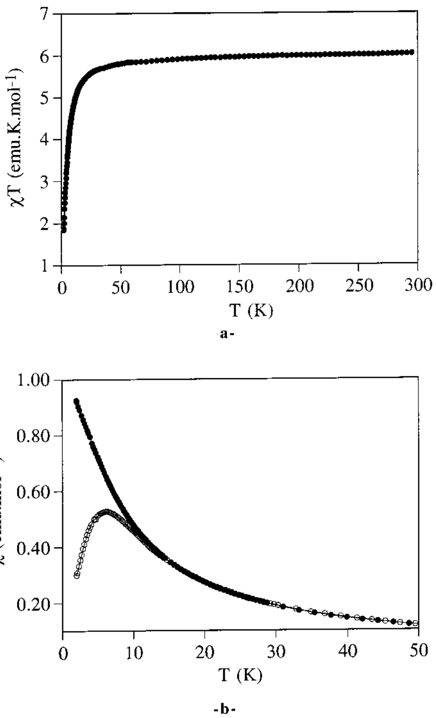

Figure 8. Plot of the χT product vs T for **4** (a) and χ vs T for **3** (empty circles) and **4** (filled circles) (b).

Differential Scanning Calorimetry (DSC). This technique has already been used to detect the existence of metastable states in the nitroprusside anion.[34,35] With DSC, we can determine the amount of energy which heats the lattice during the thermal decay of the metastable states. In the present case, the two irradiated compounds exhibit a thermal decay behavior (Figure 9) in the temperature range of 160−195 K for **1** and 155−200 K for **2**. In each case, an exothermic peak is measurable in the plot of the heat flow vs temperature that corresponds to the decay of the first metastable state (MS_1). The decay of the second metastable state (MS_2), that in the sodium salt occurs at 151 K, is not observed. The peak maxima observed during the decay are lying at about $T_M = 184$ K for **1** and at 190 K for **2**, very close to those observed in the sodium nitroprusside salt (203 K). Since the decay is exponential in time under isothermal conditions, the depopulation processes are first order reactions and can be conveniently described with an Arrhenius law. In the present case a fit of the experimental data allows us to evaluate the activation energy and the frequency factor for the state MS_1 of compound **1** [**2**]. We obtain $E_a = 0.57 \pm 0.2$ [0.34 ± 0.2] eV, and $Z = (9 \pm 3) \times 10^{13}$ [$(8 \pm 3) \times 10^{6}$] s^{-1}. These high activation energies are within the range of those estimated for other nitroprusside salts and account for the stability at low temperature of the induced metastable state MS_1. The frequency factors are much lower, compared to the sodium salt, especially for **2**, which results in a much broader temperature range of the decay. Short contacts between NO groups and neighboring atoms that could justify this effect are not observed. Thus, the NO group is surrounded by CN^-, water solvent molecules and

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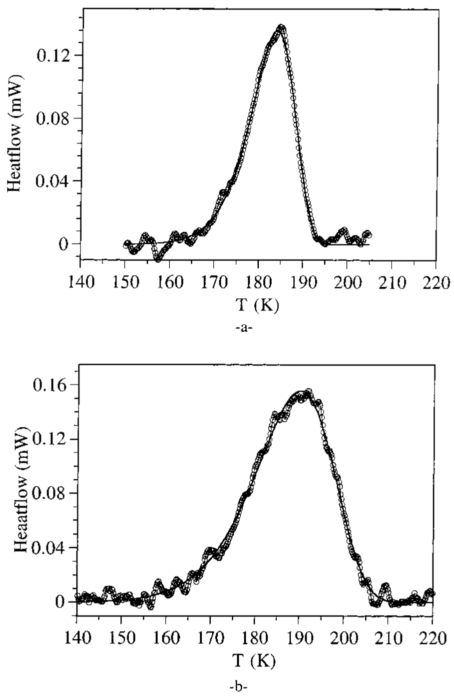

Figure 9. (a) Differential scanning calorimetry after irradiation of **1** (b) and **2** (b). The solid line represents in each case the best fit to an Arrhenius law.

ethylenediamine at distances of 3.22 (O···N), 3.45 (O···O), and 3.66 Å (O···C) in **1** and by two water solvent molecules at 2.92 (O···O) and 3.44 Å (O···O) in **2**. All these distances are significantly higher than the sum of the van der Waals radii. Therefore, we assume that the magnetic environment is responsible for the decrease of T_M and Z. More additional examples are still required before the factors influencing the stabilities of the photoinduced metastable states in these nitrosyl complexes can be understood.

DSC measurements performed on irradiated samples of the two Mn^{III} complexes do not show any exothermic peak corresponding to the decay of the metastable states of nitroprusside. This behavior is in sharp contrast with that obtained in the two Ni^{II} coordination compounds. Such a difference may be related with the surroundings of the nitroprusside anion in the crystal structure or with the presence of Mn^{III} Schiff base complexes linked to the nitroprusside. The first factor could explain the behavior of **4** since very short contacts between NO group and bromine atoms from the Schiff base have been observed that may prevent NO group to rotate from the N-bound isomer to the O-bound isomer under light irradiation. However, the lack of an exothermic peak has also been observed in compound **3**, despite the fact that the environment around the NO group does not show any short intermolecular contact. Therefore, the second factor, i.e., the coordination to Mn^{III}, needs to be invoked. In compounds **3** and **4** the nitroprusside anion is directly connected to Mn^{III} through CN^- bridging ligands situated in cis to the NO group. A similar coordination mode has been observed in **1** and **2**. Thus, the difference in behavior may be related with the nature of the coordinated metal ion—Mn^{III} instead of Ni^{II}—rather than with the coordination mode.

Conclusions

In this work, the coordination chemistry of the photochromic nitroprusside anion, $[Fe(CN)_5NO]^{2-}$, has been extended to its association with the paramagnetic $[Ni(en)_2]^{2+}$ complex and Mn^{III} complexes based upon Schiff bases. Four novel bimetallic compounds have been reported which have illustrated the versatility of nitroprusside as building block to obtain in a controlled way bimetallic complexes of various dimensionalities. On the other hand, we have seen that the stability of photoinduced metastable states of nitroprusside is significantly affected by the presence of Mn^{III} ions linked to the nitroprusside via the cyanide groups. Thus, in contrast to what is observed when Ni^{II} ions are present, no metastable states have been detected in complexes containing Mn^{III}.

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Supporting Information Available: Four X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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