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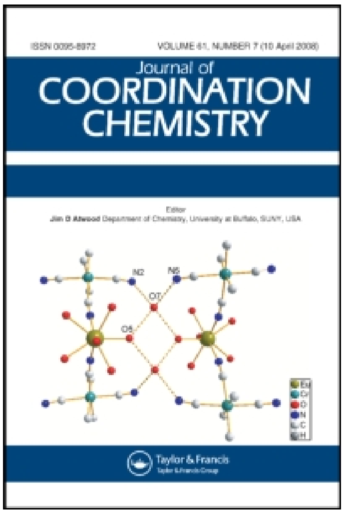

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Spectroscopic Evidence of *in situ* Formation of a Novel Tetrakis(Tetrazolato)Iron Compound

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SPECTROSCOPIC EVIDENCE OF *IN SITU* FORMATION OF A NOVEL TETRAKIS(TETRAZOLATO)IRON COMPOUND

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In an attempt to synthesize the complex $[Fe(CN)_5(N_2)]^{3-}$ by reaction of $Na[Fe(CN)_5(NO)] \cdot 2H_2O$ with azide followed by treatment with $NO[SbCl_6]$, a similar method to that used by Feltham to obtain *trans*-$[RuCl(N_2)(das)_2]Cl_2$ from *trans*-$[RuCl(NO)(das)_2]Cl_2$, we found spectroscopic evidence that excess azide reacts with the CN^- ligands to generate tetrazolato groups *C*-coordinated to Fe. Initial results suggest that the obtained compound is sodium azidotris(2*H*-tetrazolato)(5*H*-tetrazolato)iron(0). The spectroscopic evidence also indicates that these heterocycles are destroyed by reaction with $NO[SbCl_6]$, and the CN^- groups are regenerated. Here we present the characterization of these complexes by IR, ^{13}C NMR, conductivity measurements, elemental analysis and magnetic susceptibility.

Keywords: Iron tetrazolato complexes; Azido cycloaddition; Tetracyanoiron complexes; Nitrosyliron compounds; Dinitrogen complexes

INTRODUCTION

The unexpected synthesis of a tetrakis(tetrazolato)iron(0) complex from $Na_2[Fe(CN)_5(NO)] \cdot 2H_2O$ is noteworthy since it shows how the reactivity of the CN^- groups changes by coordination to a transition metal ion, and by treatment with azide forming *C*-coordinated tetrazolato heterocycles. Tetrazole is an expensive reagent and this could become a useful method for its synthesis. By further treatment with $NO[SbCl_6]$ the tetrazolato heterocycles are decomposed and regenerate the originally coordinated CN groups which could be a novel reaction.

The existence of an iron-only nitrogenase, and the fact that the Haber–Bosch catalyst contains iron, suggests that iron dinitrogen complexes could be intermediates in the synthesis of ammonia [1].

A thorough review of almost 200 end-on dinitrogen complexes, taking into account not only the electron configurations of the metal ions but also a theoretical study of the characteristics of N_2 as compared with those of other isoelectronic diatomic

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ligand species, led to the conclusion that new stable end-on dinitrogen iron(II) complexes can be synthesized [2,3].

In this work we describe the synthesis and characterization of two iron complexes. The work we describe here was based on publications by Douglas *et al.* [4,5], who studied the reactivity of *trans*-[RuCl(NO)(das)$_2$]Cl$_2$ [das, *o*-phenylenebis(dimethylarsine)]; they found that the nitrosyl group, by reaction with hydrazine or sodium azide, could lead to dinitrogen compounds, since the product [RuCl(N$_3$)(das)$_2$] gave the complex *trans*-[RuCl(N$_2$)(das)$_2$]$^{-1}$ by reaction with HCl(g) or NO[PF$_6$].

The starting complex $Na_2[Fe(CN)_5(NO)] \cdot 2H_2O$ has already been studied, and its structure and some reactions on the NO group are known, however processes leading to the synthesis of complexes as described herein are not known [6].

EXPERIMENTAL

Instrumentation/Analytical Procedures

The solvents used were appropriately distilled and dried according to published procedures [7]. Melting points were determined in a MELT-TEM apparatus. IR spectra were taken in 1750 Perkin Elmer and PARAGON instruments in the 400–4000 cm^{-1} range as KBr pellets. The ^{13}C NMR spectra were measured on a 600 MHz AC-600 Bruker. Chemical shifts are given in ppm, using TMS as standard and D$_2$O as solvent. C, H, N analysis was made in a CHN-600 Leco instrument. Iron was determined volumetrically by titration with EDTA and salicylic acid [8]. Conductivity measurements were made in a WTW LF 530 conductimeter using a WTW D8120 cell at 25°C. Magnetic susceptibility measurements were performed in an Alfa AESAR Johnson Matthey balance, using Evans's design.

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Synthesis

$Na_2[Fe(CN)_5(NO)] \cdot 2H_2O$ (1)

Complex **1** was purchased from MERCK S.A. $\Lambda_m = 192$ S m^2 mole^{-1} (in water, 25°C); IR, 2173, 2160, and 2143 (C≡N), 1945 (N≡O), 3628, and 3542 (OH) cm^{-1}. ^{13}C NMR (D$_2$O, 25°C): δ 133 (100%) and 131 (30.5%).

$Na_5[Fe(N_3)(CHN_4)_4] \cdot H_2O$ (2)

Compound **2** was unexpectedly obtained when trying to synthesize azido complexes similar to those described by Douglas *et al.* [4]. A 10-fold excess of sodium azide dissolved in 2 mL water is added to a solution of 0.5 g of **1** in 5 mL water. The mixture is allowed to react for 15 min in a water bath at 50–60°C and then the insoluble materials are filtered. The solution is evaporated until a pink purple powder appears. The solid is recrystallized in 3:1 ethanol–water and the purple solid is dried under vacuum at 45–50°C. It decomposes at 245°C. Yield 11%. Elemental analysis: Found: C, 9.51; H, 0.82; N, 52.67; Fe, 11.44%. Calc.: C, 9.51; H, 1.18; N, 52.69; Fe, 11.06%. $\Lambda_m = 444$ S m^2 mole^{-1} (in water, 25°C); IR, 2144 (NNN), 620 (M–N), 3454 (OH) cm^{-1}. ^{13}C NMR (D$_2$O, 25°C): δ 145 (20.6%) and 177 (100%). The complex is diamagnetic.

Isolation of Na[Fe(CN)$_4$(NO)(N$_2$)] (3)

The compound was obtained by a procedure similar to the one described by Douglas *et al.* [5] to transform coordinated azide into coordinated terminal dinitrogen. To 0.1 g of previously synthesized NO[SbCl$_6$] [9], a suspension of 0.5 g of **2** in 10 mL ethanol is added. The mixture is stirred for 24 h at room temperature and the blue precipitate is filtered and dried under vacuum at 45–50°C. The solid decomposes at 240°C. Elemental analysis: Found: C, 19.68; H, 0.05; Fe, 23.02%. Calc.: C, 19.93; N, 40.69; Fe, 23.18%. $\Lambda_m = 162\,\mathrm{S\,m^2\,mole^{-1}}$ (in water, 25°C); IR, 2121 (C≡N), 2028 (N≡O), 2063 (C≡N and N≡N) cm^{-1}. ^{13}C NMR (D$_2$O, 25°C): δ 109.

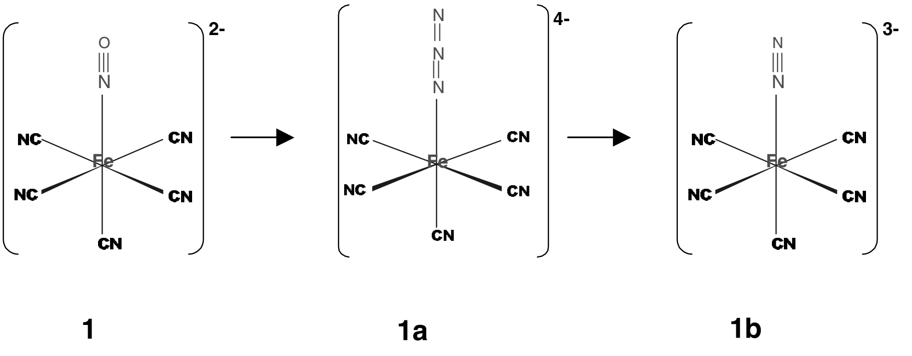
RESULTS AND DISCUSSION

Compound **1** (Scheme 1) was characterized with the same equipment and methods used for the new compounds in order to facilitate the assignment of signals. The IR spectrum of the compound, shows three bands of 2A$_1$ and E symmetry (C_{4v}), as expected, at 2173, 2160, and 2143 cm^{-1}, corresponding to ν(C≡N). The reported bands for these groups range between 2200 and 2000 cm^{-1}, depending on the ability of the central ion to accept electron density in the unoccupied *d* orbitals (e$_g$ in O_h point group), to form σ bonds, and to back-donate it from filled t$_{2g}$ orbitals to the π^* ligand orbitals. It is noteworthy that the suggestions of Poveda *et al.* [3] based on theoretical considerations of isoelectronic ligands such as CN$^-$, N$_2$, and NO$^+$ are confirmed:

- Electron donation in these ligands takes place from the $2\sigma^*$ orbital and not from the 3σ, that is by similar symmetry rather than by similar energy. These ligands accept charge density in the π^* orbital.
- CN$^-$ acts as a better donor than acceptor, whereas CO and N$_2$ are better acceptors than donors, and NO$^+$ is almost exclusively an acceptor.

The $2\sigma^*$ donor properties of CN$^-$ strengthen the C≡N bond, which shifts from 2080 cm^{-1} in the free ion to 2143, 2160, and 2173 cm^{-1} in **1**.

The ^{13}C NMR spectrum shows two signals at 131 and 133 ppm with an intensity of 30.5 and 100%, respectively. These values indicate that the carbons are unshielded in a similar way, being almost chemically equivalent but not symmetry equivalent.



SCHEME 1 Expected compounds according to the reactions carried out in this work.

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Therefore the carbons in the equatorial plane are symmetry equivalent (133 ppm) whereas the one located on the C_4 axis is not equivalent (131 ppm).

The molar conductivity in water (192 S m^2 mole^{-1}) indicates the presence of three ions in solution. The NO ligand is considered a cationic species (NO$^+$), isoelectronic with N_2 and CN$^-$, therefore the oxidation state for the metal ion is 2+.

When **1** was treated with ten-fold excess of sodium azide, Complex **1a** was expected, according to Scheme 1. The IR spectrum showed signals at 2144 cm^{-1} ν(NNN), and at 639 cm^{-1} ν(M–N), due to azide coordination. In conjunction, the disappearance of the ν(NO) band at 1947 cm^{-1} suggested that **1a** was obtained. However, the high nitrogen content and the low Fe indicate that the reaction not only took place on the NO group but also on the cyano groups. The conductivity (444 S m^2 mole^{-1}) indicates the presence of more than three ions in solution. The ^{13}C NMR spectrum shows only two signals at 145 (20.69%) and 177 (100%) ppm, indicating the presence of two non-equivalent C. It is known that cyano groups can react with hydrazoic acid to form tetrazole rings, as shown in Fig. 1. These rings can also be obtained according to the reaction shown in Fig. 2 [10].

In addition, Douglas *et al.* [4] suggest the formation of the heterocycle shown in Fig. 3, as part of the mechanism of the reaction of N_3^- on coordinated NO. Some coordination compounds with tetrazole as ligands are known [11], but in this case the tetrazolato groups are formed *in situ*, suggesting that they are attached to the iron through the carbon atoms.

A literature search for similar compounds shows that Losartan, a very important medication, has a tetrazole ring that is obtained by cycloaddition of a nitrile with azide [12–15]. There are also several complexes formed *in situ*. Among them,

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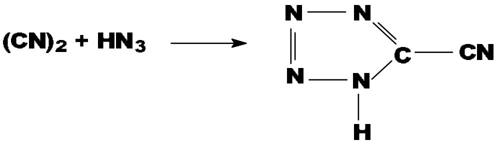

FIGURE 1 Formation of 5-cyanotetrazol.

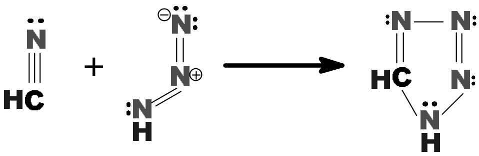

FIGURE 2 Tetrazole formation.

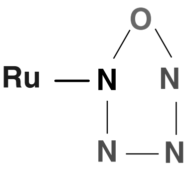

FIGURE 3 Heterocycle proposed by Douglas *et al.* [4].

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Treichel *et al.* [16] by reaction of $[(\text{phos})_2\text{Pt}(\text{CNCH}_3)_2]^{2-}$ with NaN_3 obtained the mono- or bis-1-methyl substituted *C*-coordinated tetrazolato; Beck *et al.* [17] by reaction of azido gold complexes such as $[\text{Au(III)}(\text{N}_3)_4]^{1-}$ with isonitriles obtained 1-substituted *C*-coordinated tetrakis(tetrazolato)Au(III) compounds. The structure of $[\text{Au(III)}(\text{CN}_4\text{CH}_3)_4]^{1-}$ was confirmed by Fehlhammer [18], by X-ray crystallography. *In situ* azido cycloaddition was published by Purcell *et al.* [19], who reacted a pentaammineacetonitrilecobalt(III) compound with NaN_3 to produce a *C*-substituted *N*-coordinated tetrazolato that presents an interesting case of linkage isomerism. We did not find any report of cycloaddition of a cyano metal complex to form the corresponding tetrazolato compound.

The above facts suggest that the most probable structure for **2** consists of tetrazolato rings coordinated to the metal ion through the C atoms. The anion charge and the elemental analysis suggest that there are four tetrazolato ligands and one azido ligand in the compound. In order to assign the two above mentioned ^{13}C NMR signals for **2** it is necessary to take into account the various positions of the H on the tetraazalato ring, 1*H*-, 2*H*-, or 5*H*-, as shown in Fig. 4. The chemical shift difference of more than 30 ppm suggests the presence of both 5*H*-tetrazolato with saturated carbons, and 1*H*- or 2*H*-tetrazolato with unsaturated carbons. The structure of octahedral Fe(II) with four tetrazolato rings of two different types was initially considered but it was ruled out since more than two ^{13}C NMR signals should be obtained. A d^8 five-coordinated Fe(0) with four tetrazolato rings was considered, for which two geometries are possible, a trigonal bipyramid, C_{3v} (two signals in ^{13}C NMR), or a square pyramid (three signals in ^{13}C NMR) (Fig. 5). Furthermore, the most stable and the one with the lowest conformational energy is the trigonal bipyramid, probably because of the bulky ligands.[1] Reduction of Fe(II) to Fe(0) could be possible because sodium azide, a strong reducing agent, was used in a large excess (10:1). The loss of the fifth CN^- ligand when going from **1** to **2** (Scheme 2 and Fig. 5) is possible since when the latter is allowed to react with NO^+ to form **3** (Fig. 6), only 4 CN^- equivalent ligands are detected as expected if **2** had only four tetrazolato groups.

In order to confirm the above assignment the ^{13}C NMR spectra of the model structures shown in Fig. 7 were simulated.[1] Structure **A** (1*H*- and 2*H*-), shows two signals of equal intensity at 123 (C4) and 119 ppm (C6). Structures **C** (2*H*- and 5*H*-), and **B** (1*H*- and 5*H*-) have one unsaturated and one saturated carbon and show two signals at 146 (25%) and 114 ppm (100%) for C4 and C6, respectively. The signal at 114 ppm would correspond to the saturated C in 5*H*-tetrazolato. Molecular modeling

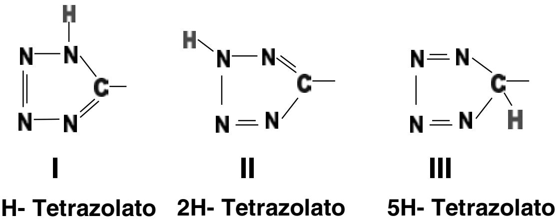

FIGURE 4 Tautomeric forms of the tetrazolato anion.

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[1] ACD/CNMR Predictor, Software for spectra simulation from the molecular structure.

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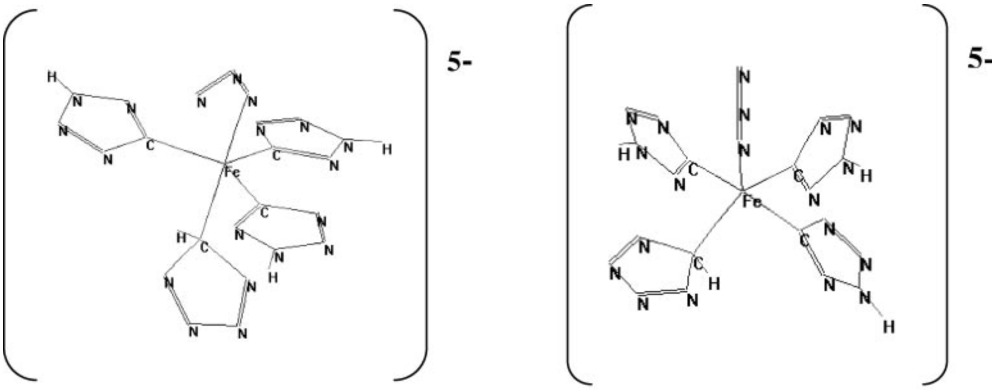
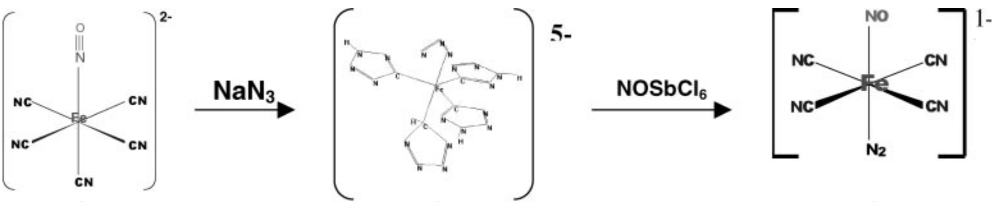


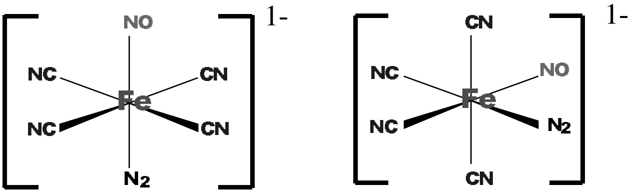
2 **2a**

FIGURE 5 Trigonal bipyramid and square pyramidal geometries for the tetrakis(tetrazolato) complex.



1 **2** **3**

SCHEME 2 Obtained compounds.



3 **3a**

FIGURE 6 *trans*- and *cis*-geometries for the $[Fe(CN)_4(NO)(N_2)]^-$ anion.

(HyperChem)[2] indicates that structure **C** has lower conformational energy than **B**. In addition **D,** a C_{3v} structure (Fig. 7) was modeled and its ^{13}C NMR spectrum looks like that obtained for Compound **2** (See Table I). Based on these studies, the trigonal bipyramidal Structure **2** (Fig. 5) is proposed for the isolated compound, with three equatorial 2*H*-tetrazolato rings and one axial 5*H*-tetrazolato ring. This structure fits the experimental ^{13}C NMR spectrum; the signal at 145 ppm (20.6%) corresponds to the axial tetrazolato, and that at 177 ppm (100%), to the three equatorial tetrazolato rings. It is possible that the three bulky tetrazolato ligands do not allow any other such equatorial ligand to bind. We suggest **2** as the most likely structure.

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[2] HyperChem 5.1, Software for molecular modeling based on quantum chemistry.

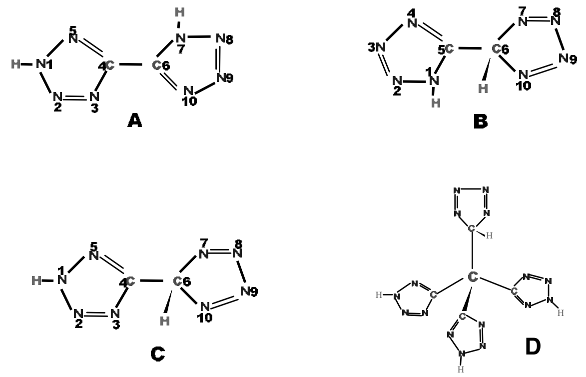

FIGURE 7 Model structures to confirm the ^{13}C NMR assignments.

TABLE I ^{13}C NMR chemical shifts for model structures

Structure	*CHn*	*No. of C tetrazolato signals*	δ
A (1*H*-, 2*H*-)	C	2	123 and 119
B (1*H*-, 5*H*-)	C and C–H	2	148 (25%) and 113 (100%)
C (2*H*-, 5*H*-)	C and C–H	2	146 (25%) and 114 (100%)
D	C and C–H	2	159 (86%), 121 (100%) and 82* (35%)
2	C and C–H	2	177 (100%) and 145 (20.69%)

*The central carbon on Structure **D**, Fig. 7.

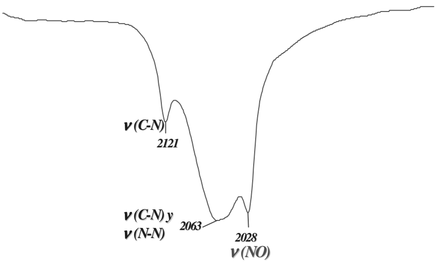

FIGURE 8 IR spectrum of Compound **3**.

The blue solid **3** isolated by treatment of **2** with stoichiometric amounts (1:2) of NO[SbCl$_6$] in ethanol at room temperature shows three intense IR bands which do not correspond to azide coordination. The elemental analysis suggests the formula Na[Fe(CN)$_4$(NO)(N$_2$)] in which coordinated dinitrogen could be formed by reaction of NO$^+$ on the N$_3^-$ group as proposed by Douglas *et al.* [5]. This attack also liberates N_3^- from the heterocycles [5]. The complex anion may have either the *trans*- or *cis*-geometry, as shown in Fig. 6. Group theory indicates that the *cis*-complex (C_s) should show four CN bands in the IR spectrum (3A$'$ and 1A$''$) whereas the *trans*-isomer (C_{4v}) should show only two (1A$_1$ and 1E). Also, the N–N and N–O bands should be in the same region. Figure 8 represents the IR spectrum between 2130 and 2000 cm^{-1}, where the bands assigned to ν(N$\equiv$O), ν(C$\equiv$N) and ν(N$\equiv$N) are shown. It is possible to predict which band should be assigned to NO by comparison with other NO complexes. Table II shows the IR bands for a series of pentacyanonitrosyl complexes with different

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TABLE II Signals (in cm^{-1}) for the nitrosyl ligand in different complexes

Compound	*Anion charge*	*ν(NO)*	*Oxidation states*	*ν(CN)*
$K_5[V(CN)_5NO]$	5−	1575	V(-I)	2095
$K_4[Cr(CN)_5NO]$	4−	1645	Cr(0)	2137, 2095
$K_3[Mn(CN)_5NO]$	3−	1725	Mn(I)	2100, 2060, 2138
$K_2[Fe(CN)_5NO]$	2−	1947	Fe(II)	2173, 2161, 2143
$K[Co(CN)_5NO]$	1−	>2000	Co(III)	–

TABLE III Chemical shifts in the ^{13}C-NMR Spectra

Compound	*No. of C signals*	*δ*	*Anion charge*
$Na[Fe(CN)_4(NO)(N_2)]$ (**3**)	1	109	1−
$Na_2[Fe(CN)_5(NO)] \cdot 2H_2O$ (**1**)	2	133 (100%) and 131 (30.5%)	2−
$Na_5[Fe(N_3)(CHN_4)_4] \cdot H_2O$ (**2**)	2	177 (100%) and 145 (20.69%)	5−

charge of the anions [20]. It is observed that the NO frequency increases when the negative charge of the anion decreases, due to $2\sigma^*$ back-donation M ← NO. On the other hand, the more negative the charge of the complex anion, the higher the NO π^* acceptance M→NO, and the lower the N–O vibration frequency (see above). It should then be expected to find this band in **3** (1-) (Fig. 6) at values higher than 1945 cm^{-1} where the band for **1** (2-) (Scheme 1) appears. Therefore the NO band in **3** should be that at 2028 cm^{-1}. The two sharp CN bands in the *trans*-isomer (Fig. 6) should have different intensities based on symmetry considerations, and 2063 and 2121 cm^{-1}could be assigned to these groups; the broad band at 2063 cm^{-1} could also contain the signal due to N≡N.

The *trans*-geometry is also supported by ^{13}C NMR in which the four equivalent CN groups should show only one signal which in effect is seen at 109 ppm. On the contrary, the *cis*-geometry should show three signals due to three inequivalent carbons. Table III lists the chemical shifts for **1**, **2**, and **3**.

The conductivity, 162 $S\,m^2\,mole^{-1}$ lies within the range expected for two ions, which also confirms the proposed structure of a hexacoordinated Fe(II) dinitrogen complex (Fig. 6, **3**), in which the preferred coordination number is reestablished due to the presence of less bulky ligands. Finally, Scheme 2 summarizes the compounds proposed in this work.

CONCLUSIONS

This work represents the first example of *in situ* formation of unsubstituted tetrazolato rings by cycloaddition of N_3^- on coordinated CN^- groups and may constitute a novel and useful method for the synthesis of these expensive reagents. The fact that these cycles decompose by action of NO^+ to regenerate CN^- groups is also noteworthy. Tetrazolato formation, as suggested in this article supports the mechanism proposed by Douglas *et al.* for the action of N_3^- on coordinated NO. These reactions might be important because they could represent basic steps in a homogeneous catalytic cycle. Obviously, a final confirmation of the results must await the X-ray diffraction studies of the proposed structures.

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Acknowledgments

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