^{14}N NQR in 1,10-Phenanthroline and Dicyano bis(1,10-phenanthroline)iron(III)*

Juan Murgich, Yosslen Aray**, Edgar Ospina Rico***, and Ismardo Bonalde
Centro de Química, IVIC, Apartado 21827, Caracas 1020A, Venezuela

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^{14}N NQR spectra of 1,10-phenanthroline and of dicyano bis(1,10-phenanthroline)iron(III) were obtained at room temperature. An analysis based on the shifts of the NQR frequencies and in the topology of the charge distribution in a model (pyridine) showed that the complex formation produces a strong decrease in the N valence shell nonbonded maximum and an increase in the bonded density along each of the N–H bond directions. The NQR spectrum showed that the complex formation produces only small changes in the charge distribution of the cyanide groups.

Key words: ^{14}N NQR, Phenanthroline, Complex, Charge distribution, Topology.

Introduction

Aromatic polyimines form complexes with metal atoms in a great range of oxidation states [1]. In particular, 1,10-phenanthroline (Phen) forms a stable chelated complex with the $Fe(CN)_6^{3-}$ ion. In this complex, two Phen molecules are coordinated to the Fe(III) through their N atoms [1]. The two ligand molecules displace four cyanide groups of the complex ion and the nitrogens of Phen form dative bonds with the Fe(III) ion. In order to study the effect of the metal coordination on the ligand charge distribution, a ^{14}N NQR study of Phen and dicyano bis(1,10-phenanthroline)iron(III) (PhenIron) was undertaken at room temperature.

Previously, Phen complexes of Pd(II) were studied and the data interpreted in terms of the Townes-Dailey (TD) theory [2]. There, the EFG is interpreted in terms of the population of orbitals centered at the atom containing the quadrupolar nucleus [2, 3]. Nevertheless, the orbital populations are not *invariant* under unitary transformations, so they do not constitute physical observables as defined by quantum mechanics [4]. Therefore, the information obtained through the TD theory is open to serious question. Ideally, one should connect the EFG directly with a physical observable such as the molecular charge density $\varrho(r)$. Nevertheless, it is known that from $\varrho(r)$, one can not determine directly the regions where the electronic shells are located [4]. An efficient method of identifying the local maxima and minima involves the use of the Laplacian $\nabla^2\varrho(r)$ distribution [4]. This distribution shows that the valence shell in a free atom is a sphere on whose surface $\varrho(r)$ is maximal and, in atoms without a nucleus with a large quadrupole moment, uniform. Formation of covalent bonds produces a number of small maxima and minima in each valence shell with characteristics that are a function of the type and number of intervening atoms [4]. As the EFG reflects mainly the asymmetry in the charge distribution of the shells, a connection between the extremes in the Laplacian distribution of the N valence shell and the components of the EFG tensor was found in nitriles [5], imines [6], di-imides [6] and monocyclic azines [7]. In order to interpret the NQR data in free and complexed Phen, an *ab initio* MO calculation and a study of the topology of the resulting $\varrho(r)$ were performed for a model system formed by free and coordinated pyridine. The effects of coordination on the N EFG and $\varrho(r)$ were modeled by placing a point charge (+0.2, +0.5 and +0.8 e) in the plane containing the nuclei and at fixed distance from the N "lone pair".

Experimental

The ^{14}N NQR spectra were obtained with a MATEC-NICOLET pulsed FT spectrometer [8]. The samples were obtained from commercial sources and studied without further purification. The sample of

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[**] On leave from the Dep. de Química, Univ. del Zulia, Maracaibo, Venezuela.

[***] On leave from the Dep. de Química, Universidad Nacional de Colombia, Bogotá, Colombia.

Reprint requests to Dr. J. Murgich, Centro de Química, IVIC, Apartado 21827, Caracas 1020A, Venezuela.

free Phen was kept under dry N_2 gas to avoid any further hydratation.

Computational Methods

The geometry optimization, *ab initio* MO and EFG calculations of the free and coordinated pyridine were performd in an IBM RISC 6000 Model 530 computer using the HONDO 8 program [9] with a doubly polarized triple ξ basis set [10]. The topological properties of $\varrho(r)$ and its Laplacian in the pyridines were calculated with a locally modified version of the AIMPAC package [11].

Results

As ^{14}N has a spin $I=1$, usually two NQR lines are observed for each crystallographically inequivalent N site [3]. The lines are $\nu^{\pm}=(3e^2qQ/4h)(1\pm\eta/3)$, where e^2qQ/h is the nuclear quadrupole coupling constant ($eq=q_{zz}$ with $q_{ij}=\partial^2V/\partial i\,\partial j$ where V = electrostatic potential from charges outside the nucleus and $i,j=x,y,z$) and $\eta=|(q_{yy}-q_{xx})/q_{zz}|$ is the asymmetry parameter of the electric field gradient (EFG). The frequencies of the NQR lines found in Phen, PhenIron and $K_3Fe(CN)_6$ KFR are shown in Table 1. In Phen, six ^{14}N lines of unequal intensity were found at room temperature. The x-ray structure [12] shows that two molecules of Phen form the asymmetric unit of the crystal. One of the molecules occupies a special position with twofold symmetry, and consequently its two nitrogens are equivalent. The NQR spectrum of Phen obtained in this work is in accordance with the published crystal structure, as two of the lines were stronger than the other four lines. Only four resonances were previously reported [13] for the Phen, at slightly different frequencies than those found here. This discrepancy may be caused by a) the use of a hydrate of Phen instead of the pure compound or b) the use of a previously unknown phase [13]. With regard to the hypothesis a), we found that the monohydrate of Phen is piezoelectric, so it gives "resonance lines" that may be easily confused with NQR lines.

In PhenIron, six lines were detected, although at much lower frequencies than in pure Phen. The frequencies of free Phen are typical of a two-coordinated N atom present in cyclic azines such as uncomplexed quinoline [14]. A comparison of the N NQR frequencies measured [15] in $K_3Fe(CN)_6$, in coordinated pyridine [13] and Phen [16] showed that the high frequency doublet found in PhenIron could be assigned to the cyanide groups while the remaining low frequency lines to the N atoms of the coordinated Phen. This assignment shows that there is only one type of cyanide group and a Phen molecule in the asymmetric unit of the PhenIron unit cell.

KFR [kHz]	Phen [kHz]	PhenIron [kHz]
2811.9	3810.1	2738.7
2808.6	3721.2	2625.0
2757.8	3712.9	2380.2
2746.6	3093.8	2362.2
2740.3	3081.7	2056.2
2694.6	3048.7	2046.1

Table 1. ^{14}N NQR frequencies found at room temperature.

Discussion

As seen in Table 1, the complex formation produces a reduction of 35% in the N coupling constant and of 30% in the asymmetry parameter in Phen, while in the cyanides only minor changes were observed upon complex formation. In order to understand these changes in terms of $\varrho(r)$, it is necessary to use a model system because a full MO *ab initio* calculation of the $\varrho(r)$ for PhenIron in the solid state is beyond today's computational capabilities. Therefore, a simplified model of the azine coordination should be used to understand the changes in its charge distribution. In the case of Phen, pyridine is a suitable molecular model as the N containing rings of phenanthroline are involved in the coordination. The dative bond is expected to decrease the charge of the N atom, and this may be simulated by placing a suitable positive point charge near its "lone pair". The choice of the position and value of the point charge are rather arbitrary, but as we are interested only in trends, values ranging from +0.2 to +0.8 e were used for the point charge kept at a fixed distance (1.890 Å) from the N atom in pyridine.

The topology of the N valence charge distribution in pyridine shows a nonbonding maximum M_{nb} in the "lone pair" position and another of the bonded type M_{b} in each of the C−N bond directions (see Table 2). An analysis of the two coordinated N atoms has shown that the N coupling constant is determined essentially by its M_{nb} charge concentration [6, 7].

Table 2. Total energy, EFG and topology of the N valence shell in free and coordinated pyridine.

Charge	−Energy	q_{zz}	q_{yy}	q_{xx}	M_{nb} $\nabla^2\varrho(r)$	M_b $\nabla^2\varrho(r)$
0	246.767490	−1.211	0.309	0.901	3.272	2.173
+0.2	246.783047	−1.090	0.293	0.797	3.120	2.174
+0.5	246.813882	−0.873	0.256	0.618	2.837	2.223
+0.8	246.855329	−0.600	0.196	0.404	2.474	2.267

Therefore, the experimental result shows that the N M_{nb} density in Phen is drastically reduced by the complex formation. From Table 2, we see that an increase in the positive charge generates a strong decrease in q_{zz} but a strong increase in the other two components. The changes in the q_{zz} component show an excellent correlation with the variations in M_{nb} ($\Delta q_{zz} = -1.293 + 0.764\,\Delta M_{nb}$ with $r = 0.999$). From Table 2, we see that the coordination of Phen depletes the N "lone pair" but also increases the maximum found in the N−C bond direction as a result of the polarization of the valence shell by the point charge. This charge rearrangement is produced in order to balance the forces acting on the N nucleus and shows that the complex formation perturbs the entire valence shell.

The analysis of η is more complicated because all the diagonal components are included in its definition [3]. Nevertheless, in the analysis of the two-coordinated N atoms it was found [6, 7] that η has contributions from other parts of the molecule beside that of the N valence shell. The observed reduction in the asymmetry parameter contains then contributions from the Phen molecule itself and from other atoms of the complex ion that are very difficult to estimate. Then, until an *ab initio* calculation of $\varrho(r)$ for the solid PhenIron becomes available, the analysis of η can not proceed further.

The shifts observed in the NQR spectrum of the cyanides are similar to those found in solid $M_3Fe(CN)_6$ when the M is changed [17] from K to Na, Rb, NH_4, etc. Therefore, it seems that the coordination of the Phen molecules does not change the metal-ion to cyanide bond significantly and consequently does not change the charge distribution of the CN group. The small shifts observed are due to the expected changes in the crystal field contributions to the EFG produced by the differences in the structure of the unit cell [3].

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