^{14}N NQR and the Molecular Charge Topology in Coordinated Ammonia *

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^{14}N NQR spectra of $[Co(NH_3)_6] \cdot 3\,Cl$, $[Co(NH_3)_5CO_3] \cdot NO_3$, $[Zn(NH_3)_4] \cdot 2\,Cl$, $[Zn(NH_3)_4] \cdot (BF_4)_2$, and $[Ag(NH_3)_4] \cdot NO_3$ were obtained at 77 K. The results, analyzed by means of the topology of the charge distribution obtained from *ab-initio* MO calculations of free and of a model of coordinated NH_3, showed that bonding to the metal-ion produces a strong decrease ($Co \gg Zn \approx Ag$) in the N nonbonded density ("lone pair") and an increase in the bonded maxima found in the N–H bond direction of the N valence shell.

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

Introduction

The nature of the metal-ligand bonding in transition-metal complexes can be determined from a knowledge of the molecular electron distribution [1] $\varrho(r)$. Such a charge distribution can be characterized by its external electric moments (total charge, dipole, quadrupole, octupole, etc.) and its internal moments such as the electric field gradient (EFG) at the position of the nuclei. In principle, these quantities can be measured experimentally and, in particular, the EFG can be obtained from the NQR frequencies [2]. The comparison of the EFGs present in the ligand before and after complexation provides important information about the changes occurring in $\varrho(r)$. NQR has been extensively used in the study of transition metal complexes and the measured EFGs have been interpreted by means of the Townes and Dailey (TD) theory [2]. In this theory, the EFG is given in terms of the populations of localized orbitals centered at the atom containing the quadrupolar nucleus. Nevertheless, the orbitals and their populations are not physical observables as defined by quantum mechanics because they are not invariant under unitary transformations [3]. Therefore, the "information" obtained by means of the TD theory is open to serious questions. More rigorous ways of interpreting the EFG are required in order to obtain reliable information about $\varrho(r)$ and the effects of metal-ion to ligand bonding. One way of doing this is to interpret the EFG directly in terms of $\varrho(r)$ or quantities that are directly related to the charge distribution. One of the main reasons behind this approach is that $\varrho(r)$ is a well defined physical observable and it is dependent of the orbital model used in its calculation [3].

Ammonia forms a large number of complexes with many different metal-ions [1]. This variety allows a comparison of the effects of different metal-ions on the same ligand. In order to obtain information about the changes introduced in the charge distribution of ammonia, a ^{14}N NQR study of several of its complexes with transition metal-ions was undertaken at 77 K. In order to interpret the NQR data, an *ab-initio* MO calculation of $\varrho(r)$ using a triple ζ basis set and a study of its topology was performed for free ammonia and a model of the coordinated NH_3. In this model, a point charge ($+0.2$, $+0.5$, and $+0.8$ e) was placed in the C_{3v} axis at different distances from the N "lone pair" and its effects on the N EFG and $\varrho(r)$ were calculated. Such a point charge mimics the metal-ion-ligand bonding and allows the estimation of the effects of dative bonding on the NH_3 charge distribution.

Experimental

The ^{14}N NQR spectra were obtained with a MATEC-NICOLET pulsed FT spectrometer at 77 K.

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The nuclear free induction decays obtained after the application of "90" degrees pulses were accumulated and later transformed (modulus FT) to record the absorption spectrum [4]. The samples were obtained following known procedures [5].

Computational Methods

The geometry optimization, *ab-initio* MO and EFG calculations were performed in an IBM RISC 6000 Model 530 computer using the HONDO 8 program [6] with a triple ξ basis set [7]. The topological properties of $\varrho(r)$ and its Laplacian in the free molecule and in the model of the coordinated ammonia were calculated with a locally modified version of the AIMPAC package [8].

Experimental Results

As ^{14}N has a spin $I = 1$, usually two NQR lines are observed per each crystallographically inequivalent N site [2]. The lines are $v^{\pm} = (3e^2qQ/4h)\ (1 \pm \eta/3)$, where e^2qQ/h is the nuclear quadrupole coupling constant ($eq = q_{zz}$ with $q_{ij} = \partial^2 V/\partial i\, \partial j$ where $V =$ electrostatic potential from external charges, $i, j = x, y$, and z), and $\eta = |(q_{yx} - q_{xx})/q_{zz}|$ is the asymmetry parameter of the EFG. The frequencies of the ^{14}N NQR lines of free ammonia and various complexes found at 77 K are shown in Table 1. The formation of the complex produces a strong decrease (30 to 50%) in e^2qQ/h of NH_3 and, in most cases, the appearance of a finite asymmetry parameter. Even if NH_3 is H bonded in the solid, and a noticeable decrease in e^2qQ/h is found between the gas and solid phase [2], the observed changes show a drastic variation in the ammonia charge distribution. The largest change is found in the octahedral complexes of Co, while the substitution of a NH_3 by a CO_3 group produces a relative increase in the coupling constant with regard to the $[Co(NH_3)_6]$ ion. In the CO_3 complex, two sets of lines of quite different intensities were found. The more intense set a lower average coupling constant and asymmetry parameter than the weaker set. In the Zn and Ag complexes, the NH_3 coupling constant showed a smaller decrease in e^2qQ/h than in the Co complexes and also smaller values were found for the asymmetry parameter.

Table 1. ^{14}N NQR frequencies in some ammonia complexes.

Compound	v^+ [kHz]	v^- [kHz]	e^2qQ/h [kHz]	η
NH_3[a]	2370.6	–	3161	0.000
$[Co(NH_3)_6] \cdot 3Cl$	933.2	931.3	1243	0.003
$[Co(NH_3)_5CO_3] \cdot NO_3$	1194	1070	1478	0.166
	1178	1043		
	1137	1027		
	1359*	1156*	1633*	0.252*
	1296*	1087*		
$[Zn(NH_3)_4] \cdot 2Cl$	1564.6	1545.5	2073	0.018
$[Zn(NH_3)_4] \cdot (BF_4)_2$	1661.6	–	2215	0.000
	1638.5	1613.9	2168	0.023
	1605.2	1580.4	2124	0.023
$[Ag(NH_3)_4] \cdot NO_3$	1506.8	1414.1	1947	0.095

[a] S. S. Lehrer and C. O'Konski, J. Chem. Phys. **43,** 1941 (1965). * Weaker lines.

Discussion

In order to understand the N EFG and its changes upon complex formation, it is necessary to determine the topology of $\varrho(r)$ and, in particular, that of the valence shell of the N atom. The latter shell produces large contributions [9] to the EFG, so a knowledge of its topology will help in the understanding of the changes produced by the N coordination.

The regions where the electronic shells are located cannot be determined directly from [3] $\varrho(r)$. An efficient method of locating the local extremes in $\varrho(r)$ involves the use of the Laplacian $\nabla^2\varrho(r)$ distribution [3]. The Laplacian of $\varrho(r)$ readily identifies the atomic regions wherein the charge is locally concentrated ($\nabla^2\varrho(r) < 0$) or depleted ($\nabla^2\varrho(r) > 0$) thus providing an enhanced view of the local form [3] of $\varrho(r)$. The $\nabla^2\varrho(r)$ distribution shows that the valence shell in a free atom is a sphere on whose surface $\varrho(r)$ is maximal [3] and (for atoms without large nuclear quadrupole moment) uniform. The formation of ionic or covalent bonds produces a number of small local extremes in the valence shells that are a function of the number and type of the intervening atoms [3]. These extremes were found to be the important sources of the EFG in one- and two-coordinated N atoms [9–11].

Considering the $\nabla^2\varrho(r)$ distribution in a plane that contains one of the N–H bonds of NH_3, one finds four maxima in the $\nabla^2\varrho(r)$ distribution of the N valence shell in ammonia, three of them correspond to a bonded concentration along each of the N–H "single bonds" M_1, while the remaining nonbonded maxi-

Table 2. Maxima in the Laplacian of the N valence shell in free and complexed NH_3. All quantities are in atomic units.

N nonbonded maximum (M_{nb})			N–H bonded maximum (M_i)		
Molecule	Max. $\nabla^2\varrho(r)$	Distance	Max. $\nabla^2\varrho(r)$	Angle	Distance
NH_3	2.816	0.737	2.072	110.2	0.834
NH_3^+ e(+0.2)	2.715	0.748	2.110	111.8	0.830
NH_3^+ e(+0.5)	2.522	0.755	2.168	113.3	0.825
NH_3^+ e(+0.8)	2.308	0.764	2.223	114.6	0.821

Table 3. Total energy, geometry and EFG for different point charges and distances. All quantities are in atomic units.

r_{NH}	θ_{HNH}	Dist. N–$e^{(+)}$	Energy	Charge $e^{(+)}$	q_{xx}	q_{zz}
0.998	109.8	–	56.216623	–	0.512	−1.024
1.002	106.74	3.5	56.234857	0.2	0.438	−0.877
1.007	104.31	3.5	56.266889	0.5	0.329	−0.658
1.014	101.71	3.5	56.304521	0.8	0.212	−0.424
1.002	107.27	2.5	56.244622	0.2	0.421	−0.842
1.006	105.43	2.5	56.295740	0.5	0.284	−0.570
1.013	103.38	2.5	56.357780	0.8	0.141	−0.282
0.997	110.31	2.0	56.243698	0.2	0.456	−0.912
0.999	110.21	2.0	56.298965	0.5	0.333	−0.663
1.004	109.11	2.0	56.371359	0.8	0.186	−0.373

Table 4. Atomic contributions to the N EFG. All quantities are in atomic units.

Molecule	$q_{xx}=q_{yy}$		q_{zz}	
	N	3H	N	3H
NH_3	0.421	0.092	−0.844	−0.181
NH_3^+ 0.2 e	0.363	0.075	−0.727	−0.150
NH_3^+ 0.5 e	0.273	0.057	−0.547	−0.111
NH_3^+ 0.8 e	0.176	0.036	−0.352	−0.072

mum M_{nb}, corresponds to the classical N "lone pair". The position and values of $\nabla^2\varrho(r)$ at the maxima in the N valence shell are shown in Table 2 for the free and coordinated NH_3.

The relationship of the maximum component of the N EFG q_{zz} with $\varrho(r)$ may be explored by relating q_{zz} with the extremes of the Laplacian $\nabla^2\varrho(r)$ distribution of the N valence shell [9–11]. In Table 3 are shown the values of the q_{xx} and q_{zz} components of the EFG tensor. As the positive charge is located along the C_{3v} axis in the model of the coordinated NH_3, the asymmetry parameter is zero and $q_{xx}=q_{yy}$. We see from Tables 2 and 3 that as a positive charge approaches ammonia, it produces a decrease in M_{nb}, an increase in the M_is and also a small shift of their positions. An increase in the positive charge kept at a fixed distance induces, in all cases, a decrease in the q_{zz} value. If this distance is increased and the charge is kept fixed, a minimum in q_{zz} is found. The calculated changes in q_{zz} are such that they correlate very well with the variation of the maximum of the Laplacian at the "lone pair" (i.e. $\Delta q_{zz}=-2.276+1.167\,\Delta M_{nb}$ with $r=0.999$ for the fixed position case).

The changes in the bonded maximum ΔM_i in the $\nabla^2\varrho(r)$ of the N valence shell show a trend opposite to that found for the "lone pair". Nevertheless, it also correlates very well with the changes in q_{zz} (i.e. $\Delta q_{zz}=9.221-3.955\,\Delta M_i$ again with $r=0.999$ for the same case mentioned above). The results indicate that the polarization of the N "lone pair" by the point charge (or metal-ion) produces a back-polarization [3] of the rest of the valence shell that increases M_i. This back-polarization produced in the valence shell achieves a balance between the forces acting on the N nucleus [3]. As a result of this, the changes observed in q_{zz} also are connected to the variations in the N–H bond charge distribution and not only to the changes in the "lone pair" as was assumed before, in similar cases.

In Table 4 are shown the atomic contributions to the EFG components obtained for different values of the point charge kept at a fixed distance (1.890 Å). The atomic volumes used in this calculation are enclosed by zero flux surfaces [3] defined by $\nabla\varrho(r)\cdot n(r)=0$, where n is the normal unit vector. In q_{zz}, the contribution from the electronic part of the *N* is much larger than that produced by the remaining three H atoms. A similar trend is found for q_{xx} although the difference between the electronic and atomic contributions is smaller than in q_{zz}. For both components, an increase in the point charge produces a decrease in their values, showing that the presence of the point charge polarizes the charge distribution towards a tetrahedral set of bonds. Such an arrangement has high symmetry and the resulting EFG at the N nucleus consequently tends to zero.

It is clear that the changes in $\varrho(r)$ upon complexation and their effects on the EFG are easily analyzed if the topology of the charge distribution are employed. This approach has the advantage of only using physical observables as defined by quantum mechanics or quantities that are derived from them. In this way, one is sure that the analysis reflects the true changes produced in the charge distribution at the molecular level.

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[1] F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 4th. Ed., John Wiley, New York 1980.
[2] E. A. C. Lucken, Nuclear Quadrupole Coupling Constants, Academic, New York 1969 and J. A. S. Smith, Chem. Soc. Rev. **15,** 225 (1986).
[3] R. F. W. Bader, Atoms in Molecules: a Quantum Theory, Oxford University Press, Oxford, U.K., 1990.
[4] J. Murgich, J. A. Abanero, M. Santana, and R. and M. V. Capparelli, J. Chem. Phys. **85,** 6047 (1986).
[5] G. Brauer, Handbook of Preparative Inorganic Chemistry, Vol. 2, Academic, New York 1965.
[6] HONDO 8, MOTEC^{TM} package, IBM Corporation Center for Scientific and Engineering Computations, Kingston, N.Y. 12401, USA.
[7] T. H. Dunning, J. Chem. Phys. **3,** 2223 (1970).
[8] F. W. Biegler-König, R. F. W. Bader, and T. T. Nguyen-Dang, J. Comp. Chem. **3,** 317 (1982).
[9] Y. Aray and J. Murgich, J. Chem. Phys. **91,** 293 (1989).
[10] Y. Aray and J. Murgich, IX International Symposium on NQR Spectroscopy, London (1991).
[11] Y. Aray, H. Soscun, and J. Murgich, International Journal of Quantum Chemistry (to be published, 1991).