1582 *J. Phys. Chem. A* **2004,** *108,* 1582−1588

Influence of Coligands on the EPR Hyperfine Coupling Constants of the Cu(I)−NO System − A Theoretical Study

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Received: August 7, 2003; In Final Form: November 10, 2003

EPR hyperfine coupling (hfc) constants were calculated for the isolated Cu(I)−NO system and various model complexes of this species with increasing number of oxygen-containing coligands. The influence of the basis sets, the computational level, and, especially, spin polarization effects on the isotropic and anisotropic hfc constants have been carefully explored. It turns out that it is rather difficult to obtain reliable Cu(I) hfc values for this system, in which a radical ligand is coordinated to a metal center with a formally closed-shell electron configuration. The spin density at the individual atomic centers is determined by two effects, the spin transfer from NO to unoccupied valence orbitals of Cu(I) and the spin polarization in formally doubly occupied orbitals of the system. A detailed analysis shows that both effects can yield large, but opposing contributions to the coupling constants. For copper, the anisotropic hfc constants are much more sensitive to the details of spin polarization than the isotropic one. For nitrogen, the situation is the opposite. It appears that it is difficult to describe the spin polarization quantitatively correctly by state-of-the-art density functional theory. For the type of systems under study, one has to conclude that experimentally obtained EPR parameters cannot be interpreted merely by the specific atomic contributions to the singly occupied molecular orbital. By considering model complexes with an increasing number of oxygen-containing coligands, we contribute to the interpretation of the EPR parameters that have been measured for the Cu(I)−NO species inside the ZSM-5 zeolite. Models with two or more oxygen neighbors rather well agree with the experiment. This is due to the additional charge transfer to the Cu(I) center caused by the coligands and the more realistic electrostatic potential around it.

1. Introduction

Electron paramagnetic resonance (EPR) spectroscopy is a powerful tool to explore the electronic and molecular structure of radicals and open-shell transition metal compounds. However, no direct information can be deduced from the experiments and the interpretation of EPR parameters often relies on empirical rules and simple models. On the other hand, modern quantum chemical methods allow us to calculate both isotropic and anisotropic hyperfine coupling (hfc) constants with acceptable accuracy (see, e.g., the review of Eriksson[1] and the references therein), thus providing valuable information for the analysis and interpretation of measured hfc parameters. But, quantum chemical methods, which explicitly take into account electron correlation (e.g., configuration interaction or coupled cluster techniques) are still restricted to comparably small compounds. For larger systems, especially transition metal complexes of chemically relevant size, effective procedures based on density functional theory (DFT) have been developed in the past decade. At this level of theory, the experimental metal hfc parameters can be reproduced rather well. Meanwhile, various aspects of the hyperfine coupling in transition metal complexes have been studied by several groups.[2−13] The results reveal, especially, that the spin density at metal centers with a formally open-shell electron configuration is, as expected, mainly determined by the unpaired electrons, but spin polarization in formally doubly occupied orbitals, especially in the core region, can change it remarkably.[6,10]

It has to be expected that it is much more difficult to calculate reliable hfc constants for a transition metal center with a formally closed-shell electron configuration. Such a situation appears, e. g., in the Cu(I)−NO system. In this case, the spin density at the copper center is determined, first, by the spin transfer from the NO radical to empty orbitals of the metal ion and, second, by the spin polarization in the [Ne]$d^{10}s^0$ core.

The isolated Cu(I)−NO system is a benchmark for the general case, in which a radical ligand is coordinated to a metal center with a formally closed-shell electron configuration. To our knowledge, a systematic theoretical study of such a small sample system has not been undertaken so far. The accuracy achieved for hfc parameters of open-shell transition metal centers cannot be expected. Therefore, detailed comparisons between the values obtained at various computational levels as well as with measured values are necessary. Unfortunately, it is extremely difficult to obtain trustworthy experimental data for such systems.

EPR data have not been measured up to now for the isolated Cu(I)−NO system, but for the Cu(I)−NO species inside the ZSM-5 zeolite.[14,15] Recently, isotropic as well as anisotropic hfc constants for copper and nitrogen were extracted from EPR powder spectra measured at various microwave frequencies (X-, Q- and, W-band).[15] The EPR data reveal the existence of two different Cu(I)−NO species in zeolite ZSM-5. The major species

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10.1021/jp0363388 CCC: $27.50

has an isotropic hfc constant of 168 × 10^{-4} cm^{-1} and the anisotropic ones are −38, −10, and +48 × 10^{-4} cm^{-1}. In the case of the minor species, the respective values are 177 × 10^{-4} cm^{-1} and −47, −19, and +65 × 10^{-4} cm^{-1}. Such data provide valuable information about Cu(I)−NO moieties formed on solid surfaces. These nitric oxide adsorption complexes are of special interest because the paramagnetic Cu(I)−NO species is an intermediate in the catalytic decomposition of nitric oxide into nitrogen and oxygen over CuZSM-5 zeolites.[16,17] Experimental data concerning the electronic and geometrical structure of the adsorption complexes as well as the sites where the Cu(I)−NO species are formed in the zeolites are key information for a deeper understanding of the catalytic activity of the CuZSM-5 materials.

However, no direct information can be deduced from the experiments. A proper interpretation of the measured hfc parameters requires the help of theory. Originally, they have been analyzed in terms of the common restricted LCAO-MO approach by considering merely the spin-density distribution within the singly occupied molecular orbital (SOMO).[14,18] However, caution should be exercised because spin polarization effects in the formally doubly occupied orbitals may significantly influence the spin-density distribution leading possibly to a misinterpretation of the experimental data.[10] Thus, the potential of more elaborated quantum chemical methods has to be explored to check up, in particular, possible spin polarization effects and to provide, in that way, a more reliable basis for the interpretation of hfc parameters of formally closed-shell metal centers in paramagnetic complexes.

Very recently, two groups have calculated hfc coupling constants for the Cu(I)−NO species in the ZSM-5 zeolite for different pre-defined adsorption sites. Sojka et al.[19] as well as Nachtigall and Sauer[20] have shown that, depending on the site, the agreement between calculated and measured values is surprisingly good for some of the coupling constants whereas for others rather large deviations result.

In this paper, we present a systematic theoretical study of the isolated Cu(I)−NO system concerning the influence of the basis sets, the computational level and, especially, spin polarization effects on the isotropic and anisotropic hfc constants. Moreover, we consider complex moieties consisting of a Cu(I)−NO species and an increasing number of oxygen-containing coligands. This allows a stepwise modeling of the influence of the zeolite framework on the hfc coupling constants.

2. Computational Details

DFT calculations mainly adopting the B3LYP functional[21] were performed using the Gaussian98 program package.[22] Other density functionals were checked to study their influence on the coupling constants. After extensive preliminary calculations described in Section 3, the following basis set combinations were found to be suitable for our purposes. For copper, a relativistic effective core potential, replacing the 10 inner-core electrons, together with the corresponding valence basis set from the Stuttgart series[23] was used for the geometry optimizations, then replaced by Ahlrichs' TZV all-electron basis set[24] for the single-point calculations of the hfc coupling constants. For nitrogen and oxygen, the standard 6-311G* basis set[25] was used for the optimizations, replaced by the IGLO-III basis set[26] for the hfc calculations. Hydrogen, in the water models, was given a 6-31G basis. For the zeolite model, 6-311G* was used for aluminum and silicon, and 6-311G for oxygen.

TABLE 1: Isotropic Coupling Constants (in 10^{-4} cm^{-1}) for Cu(I)−NO in Dependence on the Copper Basis Set for a Fixed Structure (See text) and, in Italics, for the Optimized Structure (6-31G* Basis Set for NO)

	ref	Cu	N	O
6-31G*	29	590	13.9	−16.0
		505	*14.4*	*−16.3*
Wachters-Hay	27	513	13.1	−15.9
		515	*13.0*	*−15.9*
Ahlrichs TZV	24	519	13.0	−15.6
		535	*12.8*	*−15.6*
Ahlrichs VTZ	30	551	12.8	−15.5
		570	*12.9*	*−15.6*
DZVP2	31	530	13.7	−15.7
		542	*13.8*	*−15.8*
Roos Augmented TZ	32	492	13.0	−15.9
Partridge Uncontr. 3	33	505	12.8	−15.7

TABLE 2: Isotropic Coupling Constants (in 10^{-4} cm^{-1}) for Cu(I)−NO in Dependence on the NO Basis Set for a Fixed Structure (see text) and, in Italics, for the Optimized Structure (Wachters-Hay Basis Set for Cu)

	ref	Cu	N	O
6-31G*	25	513	13.1	−15.9
		515	*13.0*	*−15.9*
6-311+G*	25	507	10.4	−6.2
		513	*10.2*	*−6.1*
6-311++G(3df)	25	512	10.4	−6.9
		522	*10.3*	*−6.7*
IGLO−III	26	515	11.8	−9.8
		535	*11.7*	*−9.7*
Ahlrichs TZV	24	449	11.8	−7.7
		316	11.4	−8.1
Ahlrichs VTZ	30	445	13.1	−11.0
		313	12.8	−11.4
Partridge Uncontr. 3	33	448	12.9	−11.4

3. Results and Discussion for the Isolated Cu(I)−NO System

Influence of the Basis Sets on the Isotropic Coupling Constants. A large variety of different basis sets for copper as well as for NO was investigated concerning their influence on the resulting coupling parameters for the isolated Cu(I)−NO system. The copper basis set was varied using the standard 6-31G* basis set for NO. The basis set for NO was varied adopting the Wachters-Hay basis set for copper.[27] The results given for single-point calculations refer to a fixed geometrical structure (Cu−N = 195.4 pm, N−O = 114.2 pm, Cu−N−O = 132.94°) taken from a previous study.[28] Geometry optimizations show that the specific geometrical structure influences the calculated coupling constants less than the choice of the basis set.

The results for the isotropic coupling constants are presented in Tables 1 and 2. For copper, values in the range of 400 to 600 × 10^{-4} cm^{-1} result. We remark, first, that these values are much higher than the respective values measured for the Cu(I)−NO species inside the ZSM5-zeolite (see the Introduction). Obviously, the zeolite framework has a huge influence on the isotropic copper coupling constant. Second, we remark that the values are much lower than those observed[34] and calculated[4] for Cu(0)−CO (about 4000 × 10^{-4} cm^{-1}). The latter system is, in a certain sense, the counterpart of the system considered here. Both have the same number of electrons, but in Cu(0)−CO the unpaired electron is located at copper instead of the ligand.

For nitrogen and oxygen, values in the range of 10 to 14, and −6 to −16 × 10^{-4} cm^{-1}, respectively, result. We will show later that these values are only slightly influenced by additional

TABLE 3: Anisotropic Coupling Constants (in 10^{-4} cm^{-1}) for Cu(I)−NO in Dependence on the Copper Basis Set for a Fixed Structure (see text) and, in Italics, for the Optimized Structure (6-31G* Basis Set for NO)

	Cu			N		
6-31G*	−11.3	−2.7	14.1	−7.6	−7.5	15.1
	−9.6	*−6.4*	*16.0*	*−7.7*	*−7.6*	*15.4*
Wachters-Hay	−6.3	−4.1	10.5	−8.4	−8.2	16.6
	−6.2	*−4.0*	*10.2*	*−8.4*	*−8.1*	*16.5*
Ahlrichs TZV	−5.8	−3.3	9.1	−8.4	−8.2	16.6
	−5.7	*−3.4*	*9.1*	*−8.3*	*−8.1*	*16.4*
Ahlrichs VTZ	−4.7	−2.5	7.3	−8.3	−8.1	16.4
	−5.0	*−2.7*	*7.7*	*−8.2*	*−8.0*	*16.3*
DZVP2	−5.3	−3.7	9.0	−8.2	−8.0	16.1
	−5.7	*−3.9*	*9.7*	*−8.2*	*−7.9*	*16.1*
Roos Augmented TZ	−6.9	−4.7	11.6	−8.4	−8.2	16.6
Partridge Uncontr. 3	−6.7	−4.5	11.2	−8.5	−8.2	16.8

TABLE 4: Anisotropic Coupling Constants (in 10^{-4} cm^{-1}) for Cu(I)−NO in Dependence on the NO Basis Set for a Fixed Structure (see text) and, in Italics, for the Optimized Structure (Wachters-Hay Basis Set for Cu)

	Cu			N		
6-31G*	−6.3	−4.1	10.5	−8.4	−8.2	16.6
	−6.2	*−4.0*	*10.2*	*−8.4*	*−8.1*	*16.5*
6-311+G*	−6.6	−4.2	10.8	−9.1	−8.9	18.0
	−6.3	*−4.1*	*10.3*	*−9.0*	*−8.8*	*17.9*
6-311++G(3df)	−6.5	−4.1	10.7	−9.3	−9.1	18.4
	−6.3	*−4.1*	*10.4*	*−9.2*	*−9.1*	*18.3*
IGLO−III	−6.5	−4.2	10.7	−9.3	−9.1	18.5
	−6.2	*−4.1*	*10.4*	*−9.2*	*−9.0*	*18.3*
Ahlrichs TZV	−7.0	−4.0	11.0	−9.3	−9.1	18.4
	−8.8	*−3.7*	*12.5*	*−9.8*	*−9.7*	*19.5*
Ahlrichs VTZ	−7.0	−4.0	10.9	−9.3	−9.1	18.4
	−8.6	*−3.7*	*12.3*	*−9.8*	*−9.7*	*19.5*
Partridge Uncontr. 3	−7.0	−4.0	11.0	−9.5	−9.4	18.9

TABLE 5: Isotropic and Anisotropic Coupling Constants (in 10^{-4} cm^{-1}) for Cu(I)−NO in Dependence on the Computational Procedure

	LSDA	PW91[35]	B3LYP[21]	B3PW91	BHandH[22]	HF	QCISD
%HF	0	0	20	20	50	100	−
%LDA	100	100	80	80	50	0	−
%ΔGGA	0	100	72	72	0	0	−
Cu iso	894	846	534	514	300	135	289
N iso	12.7	12.4	11.8	10.2	11.9	20.6	13.5
O iso	−1.0	−3.6	−9.7	−7.9	−15.1	−21.9	−10.3
Cu aniso	−8.0	−7.5	−6.3	−7.5	−7.6	−9.3	−7.0
	−0.9	−2.0	−3.8	−4.4	−6.3	−7.8	−6.1
	8.9	9.5	10.1	11.9	13.8	17.1	13.1
N aniso	−7.0	−7.3	−9.2	−9.8	−10.3	−14.8	−11.7
	−6.9	−7.3	−9.1	−9.8	−10.2	−7.7	−7.3
	13.9	14.6	18.3	19.6	20.6	22.4	19.0

coligands modeling the zeolite framework. This is expected because NO interacts only via the copper center with other groups.

The copper basis set influences the nitrogen and oxygen values only little (N) or insignificantly (O), whereas the NO basis set has a remarkable influence on the copper value. This behavior indicates that the isotropic nitrogen and oxygen coupling constants are dominated by the spin distribution inside the NO unit which is not strongly altered by the bonding to Cu(I). The spin density at the Cu(I) center, however, depends on both the intra-NO spin distribution and the NO-to-Cu(I) spin transfer. Therefore, the copper value is sensitive to changes in both basis sets.

For the subject under study, the basis sets have to fulfill two requirements. First, their valence parts have to be sufficiently flexible to provide a proper spin-density distribution between the atomic centers of the molecule. Second, they have to be sufficiently flexible in the core region to allow a proper description of the core spin polarization. Both is certainly not the case for unflexible basis sets, which explains their poor performance. In fact, one has to look at both regions when the flexibility of a certain basis set is discussed. Remark (see Table 2) that the N and O values are almost equal for the 6-311+G* and 6-311++G(3df) basis sets, indicating that the former is sufficiently flexible. The additional diffuse and polarization functions in the latter are not required. On the other hand, one can show that a higher flexibility in the core region influences the resulting values. For that reason, we have extended the 6-311+G(3df) basis set for NO by an increasing number of very steep s-Gaussians. This shifts the N and O coupling constants to significantly higher (absolute) values. It turns out that by involving around five additional functions, results are obtained which agree well with those for the uncontracted basis set in Table 2.

Thus, the most reliable results should be those obtained with strongly extended or completely uncontracted basis sets. One has to recognize that the use of less flexible basis sets, which is often required because of the computational effort, leads to a certain systematic error, the amount of which can be estimated by inspecting Tables 2.

Influence of the Basis Set on the Anisotropic Coupling Constants. The basis set variation described above leads, for the anisotropic copper and nitrogen hfc coupling constants, to the results given in Tables 3 and 4. It can be clearly seen that the variation of the NO basis set hardly influences the nitrogen values (Table 4), in agreement with the usual assumption that anisotropic coupling constants are generally less basis-set dependent than isotropic ones because they result from an integration over space instead from the spin density of a single space point, i.e., the nucleus. Thus, we conclude that the experimental anisotropic nitrogen hfc constants, which are not observed up to now, should lie very near to the calculated values, i.e., near to −9.5, −9.5 and 19 × 10^{-4} cm^{-1}.

Concerning the anisotropic copper coupling constants, we find a rather strong influence of the copper basis set on the absolute magnitude of the three components as well as on the ratios between them. This is due to spin polarization effects, the amount of which strongly depends on the basis set. Spin polarization in transition metal complexes has been investigated in great detail by Munzarova et al.[10] For the present system, we discuss it somewhat later in this section.

Influence of the Density Functional. Previous investigations on transition metal compounds concerning the suitability of certain hybrid density functionals have shown a systematic dependence of the calculated hfc constants on the percentage of Hartree−Fock (HF) exchange.[9] This results in an overall uncertainty of about 10−15% for complexes with a dominant SOMO contribution, while no general picture appears for other cases. In Table 5, we collect single-point calculations (fixed geometric structure as before) with various density functionals for the isolated Cu(I)−NO system. For comparison, conventional Hartree−Fock and QCISD results are included. QCISD is considered to be comparable to the CCSD level.[36] The latter is assumed to give good results for this type of calculation.[9] The MP2 and CISD methods have been found to be not well suited for the calculation of EPR parameters.[1]

The isotropic coupling constants of copper and oxygen show a strong dependence on the percentage of HF exchange, while nitrogen is less influenced. Overall, an increasing amount of HF exchange lowers the values for copper and oxygen. The changes do not indicate an interatomic spin transfer, but rather

TABLE 6: Decomposition of the Non-zero Coupling Constants for Cu(I)−NO (with *xy* Symmetry Plane) into Orbital Contributions (in percent of the final value, the dominant character of the orbitals or orbital groups being given in the top line)

	Cu 2p	Cu 3p	Cu 3d (a′)	Cu 3d (a″)	N 1s	O 1s	N/O 2s	NO σ/π	SOMO	sum
Cu iso	0	0	−3	0	0	0	−1	−1	+104	99
N iso	0	0	−5	0	−78	0	+178	−39	45	101
O iso	0	0	0	0	0	−227	+330	−5	+2	100
Cu *xx*	−32	+228	−269	−60	0	0	−12	−18	+274	111
Cu *yy*	−13	+83	−200	+5	0	0	−6	−26	+259	102
Cu *zz*	−8	+42	−180	+23	0	0	−4	−27	+255	101
Cu *xy*	−9	+44	−27	+11	0	0	0	+7	+70	96
N *xx*	0	0	+11	0	0	0	+1	+12	+77	101
N *yy*	0	0	+23	+1	0	0	+9	+21	+43	100
N *zz*	0	0	+7	+1	0	0	−1	+9	+88	100
N *xy*	0	0	+7	0	0	0	+3	+2	+90	102

an intraatomic spin redistribution related to changes in the core polarization. Remarkable changes are obtained also for the anisotropic values. Again, this refers not only to the magnitude of the components but also to the ratios between them. Compared to the QCISD results, all DFT procedures underestimate the difference between the two small components for nitrogen and overestimate it for copper.

Sojka et al. have found a better agreement between calculated and experimental copper hfc parameters with the BPW91 functional compared to the B3LYP one.[19] We conclude from Table 5 that, indeed, the B3LYP functional seems to be not the optimal one with respect to the copper values. Compared to the QCISD results, the half-and-half functional BHandH with just 50% HF exchange yields almost identical copper values, isotropic as well as anisotropic ones. Otherwise, the B3LYP value of the isotropic oxygen hfc constant seems to be the better one, whereas for the isotropic and anisotropic nitrogen parameters, both functionals yield comparable results.

Because no unique preference of a certain density functional appears, we decided to use the commonly accepted B3LYP functional throughout this investigation.

Influence of the Spin Polarization. The spin density at the copper center is determined by both the spin transfer from the NO radical to the Cu(I) ion and the spin polarization within the Cu(I) core. Information about the amount of spin polarization is usually extracted from the difference between the total spin distribution and that described by the SOMO. However, applying molecular orbital methods, the spin polarization can be analyzed in more detail, taking into account that the spin density at a certain center is obtained by summing up the individual orbital contributions. Consequently, it is possible to split up a calculated hfc constant into orbital contributions, i.e., to separate the direct contribution of the SOMO from contributions originating from the spin polarization within formally doubly occupied orbitals. This strategy has been successfully used by other authors.[6,10]

In Table 6, the results of our respective analysis for the isolated Cu(I)−NO system are presented. The relative contributions of various orbitals or orbital groups to the calculated total hfc coupling constants are given. The first three lines refer to the isotropic coupling constants, the remaining ones to the nonvanishing components of the anisotropic coupling tensor (the *xz* and *yz* components vanish because of the *xy* mirror plane). Each column refers to one specific orbital or orbital group, the determining character of which is indicated in the head line. The table entries are the relative contributions (in percent of the final value) of the specific orbitals to the respective coupling constant. Orbitals with individual contributions of less than 5% to any of the hfc parameters are not included. They are indeed unimportant, because the contributions of the considered orbitals sum up to almost exactly 100% (last column).

The isotropic coupling constant of copper is exclusively determined by the SOMO, and core spin polarization does not play any role. This agrees with the results of Munzarova et al., who have found that the core spin polarization is proportional to the spin population of the valence d orbitals.[10] The latter is close to zero in the formal [Ne]$d^{10}s^0$ configuration. For nitrogen and oxygen, on the contrary, the core polarization described by the 1s and 2s orbitals is crucial. Both orbitals give large but opposing contributions to the coupling constants. The SOMO plays no or only a minor role. This is to be expected, because the formally spin-bearing N−O π^*-orbital has a nodal plane at the position of the two nuclei. Only as a consequence of the bending coordination mode, a small s-orbital contribution appears in the SOMO.

For the anisotropic coupling constants of copper we obtain the notable result that both the SOMO and the core spin polarization yield large, but opposing contributions. The copper core polarization itself involves several orbital pairs with different sign. This effect has already been observed and discussed by Munzarova et al.[10] Finally, for the anisotropic coupling constants of nitrogen, spin polarization only enhances the direct SOMO contribution, mainly by σ/π-polarization and the spin transfer from the copper d-orbitals discussed above.

We summarize that for copper the anisotropic coupling constants are much more sensitive to the details of spin polarization than the isotropic one. For nitrogen and oxygen, the situation is the opposite, the isotropic coupling constants depend strongly on the spin polarization while the anisotropic ones are less affected. This confirms the conclusion of other authors[10] that it is rather problematic to use the conventional LCAO-MO analysis of the hfc parameters, in which the MO coefficients of the metal d-orbitals contributing to the SOMO are evaluated from the anisotropic copper hfc constants not taking into account any spin polarization effects. The application of the usual LCAO-MO approach may produce misleading results concerning the geometric and electronic structure of formally closed-shell transition metal centers in paramagnetic complexes such as Cu(I)−NO.

4. Results and Discussion for the Coordinated Cu(I)−NO System

Influence of the Coordination Number. The copper hfc constants obtained for the isolated Cu(I)−NO system do not match the values measured[14,15] and calculated[19,20] for the Cu(I)−NO moiety in the ZSM-5 zeolite (see the Introduction). The values are strongly influenced by the zeolite framework. Most striking is the huge reduction of the isotropic constant.

To analyze this specific influence and to contribute, on this way, to an understanding of the EPR parameters that have been found for the Cu(I)−NO moiety in the ZSM-5 zeolite, we have considered model complexes with increasing number of oxygen-containing coligands. Cationic species of the structure $[(H_2O)_n\text{-}Cu(NO)]^+$ and neutral complexes $[(OH)(H_2O)_{n-1}Cu(NO)]$ with increasing number of water ligands were taken into account. Additionally, the cluster-type model $[(HO)_2Al(\mu\text{-}OH)_2Cu(NO)]$ (Scheme 1) was included, which constitutes a more realistic model of the surrounding of the copper center in the zeolite.

The structures of the model systems were optimized using the basis sets described in Section 2. Selected structural parameters are reported in Table 7. The Cu−N bond distance decreases by 10 pm when going from the water-free complex

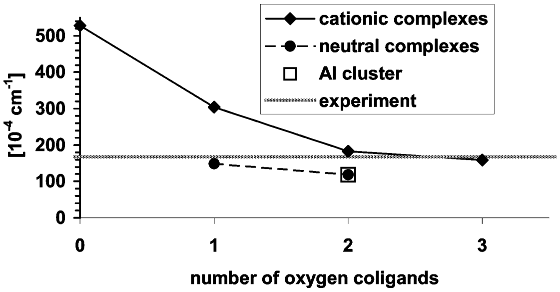

Figure 1. Dependence of the isotropic copper hfc coupling constant (in 10^{-4} cm^{-1}) on the coordination number of the model complexes. The horizontal line denotes the value measured for the major Cu(I)−NO species in the zeolite.

SCHEME 1: The $[(HO)_2Al(\mu\text{-}OH)_2Cu(NO)]$ Cluster Model

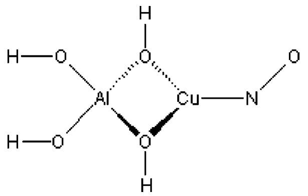

TABLE 7: Optimized Structural Parameters (in picometers and degrees), Mulliken Charge of the Cu(I)−NO Unit, and Spin Population of the Cu(I) Center for the Model Complexes $[(H_2O)_nCu(NO)]^+$

n	0	1	2	3
d(Cu−N)	195	186	185	186
d(N−O)	113.2	114.0	114.8	115.2
∠(Cu−N−O)	133	139	143	142
$d(Cu-O_{H_2O})$		191	203	208−221
q(CuNO)	1.00	0.83	0.79	0.76
s(Cu)	0.14	0.08	0.05	0.05

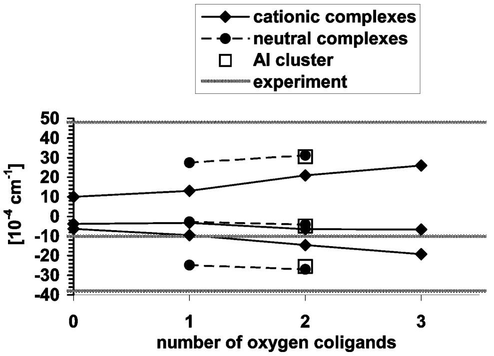

Figure 2. Dependence of the anisotropic copper hfc coupling constants (in 10^{-4} cm^{-1}) on the coordination number of the model complexes. The horizontal lines denote the values measured for the major Cu(I)−NO species in the zeolite.

to the coordinated ones, whereas the number of coligand has no influence. The N−O bond distance gradually increases when water ligands are added. It is to be concluded that the presence of coligands strengthens the Cu−N bond and weakens the N−O bond by a back-donation into the N−O π*-orbitals. The same conclusion has been drawn by Sojka et al.,[19] who found for the NO unit within the zeolite a lengthening of the N−O bond and a weakening of the respective stretching vibration in comparison with the free NO molecule.

In Table 8, we present the calculated coupling constants for the considered model complexes in comparison with the values measured for the Cu(I)−NO species in the zeolite. For the cationic systems $[(H_2O)_nCu(NO)]^+$, the most striking feature is the distinct stepwise decrease of the isotropic copper coupling constant from more than 500 × 10^{-4} cm^{-1} for the isolated Cu(I)−NO system to about 160 × 10^{-4} cm^{-1} with 3-fold oxygen coordination. Contrary, the absolute values of the anisotropic copper coupling constants increase significantly. The nitrogen values, on the other hand, change less.

By replacing one water molecule by a hydroxide ion, the positive charge of the model systems can be avoided. For the neutral complexes $[(OH)(H_2O)_{n-1}Cu(NO)]$, the copper values are stronger shifted. This behavior is visualized in Figures 1 and 2. The effect of the coordination number becomes smaller if an OH^- group is involved. Obviously, an OH^- group with its relatively short Cu−O bond has a stronger influence on the copper hfc constants than the more distant water ligands.

We have checked whether this characteristic ligand influence is dominated by orbital interactions between the coordinating oxygen atoms and the copper ion or by the electrostatic field originating from the partially negative oxygen atoms. To this end, the water molecules and—in the case of the neutral

TABLE 8: Isotropic and Anisotropic Coupling Constants (in 10^{-4} cm^{-1}) Calculated for the Model Complexes $[XCu(NO)]^+$ in Comparison with the Values Measured for the Cu(I)−NO Major Species in the Zeolite[15] (in italics, the values for the point-charge models are given, see text)

X	isolated	H_2O	$(H_2O)_2$	$(H_2O)_3$	(OH^-)	$(H_2O)(OH^-)$	$(HO)_2Al(OH)_2$	exp
Cu iso	528	304	183	159	149	118	119	168
		397	*267*	*247*	*191*	*180*		
N iso	11.9	11.7	9.6	8.9	10.1	9.2	8.9	
		12.0	*10.5*	*9.7*	*10.2*	*9.8*		
O iso	−9.7	−10.4	−10.5	−10.3	−11.5	−11.2	−11.3	
		−10.2	*−10.4*	*−10.3*	*−10.4*	*−10.5*		
Cu aniso	−6.3	−9.6	−14.5	−19.2	−24.8	−26.9	−25.5	−38
		−9.2	*−14.3*	*−18.9*	*−23.2*	*−25.0*		
	−3.8	−3.3	−6.5	−6.7	−2.7	−4.2	−4.9	−10
		−3.2	*−5.1*	*−3.6*	*0.0*	*−1.8*		
	10.1	13.0	21.0	25.9	27.5	31.1	30.4	48
		12.4	*19.5*	*22.5*	*23.2*	*26.8*		
N aniso	−9.2	−10.1	−10.5	−10.6	−11.3	−11.2	−11.2	
		−9.8	*−10.2*	*−10.3*	*−10.6*	*−10.7*		
	−9.1	−10.0	−10.3	−10.4	−9.2	−9.4	−9.6	
		−9.7	*−10.2*	*−10.1*	*−10.3*	*−10.2*		
	18.3	20.1	20.8	21.0	20.5	20.6	20.8	
		19.5	*20.4*	*20.4*	*21.0*	*20.9*		
N total	2.7	1.6	−0.9	−1.7	−1.2	−2.0	−2.3	
(iso + aniso)	2.8	1.7	−0.7	−1.5	0.9	−0.2	−0.7	
	30.2	31.8	30.4	29.9	30.6	29.8	29.7	29

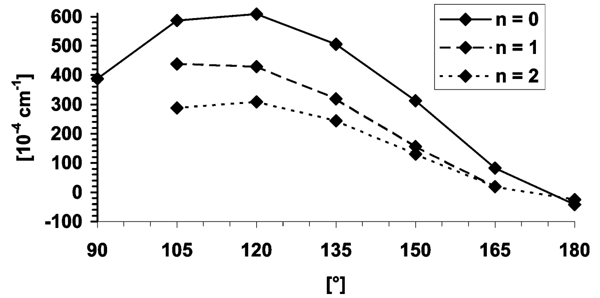

Figure 3. Dependence of the isotropic copper hfc coupling constant (in 10^{-4} cm^{-1}) on the Cu−N−O bond angle for $[(H_2O)_nCu(NO)]^+$.

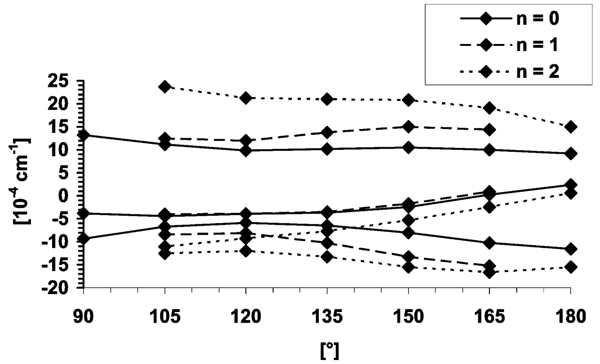

Figure 4. Dependence of the anisotropic copper hfc coupling constants (in 10^{-4} cm^{-1}) on the Cu−N−O bond angle for $[(H_2O)_nCu(NO)]^+$.

complexes—the hydroxide ion were replaced by point charges at the atomic positions with charge values derived from a natural population analysis (NPA) following the DFT calculations. The hfc values resulting from these point-charge models (included in Table 8) agree—with one exception—rather well with those obtained from the primary calculations. This indicates that in these cases electrostatic effects play the determining role. Remarkable deviations occur, however, for the isotropic copper constant. In this case, the values resulting for the point-charge models are systematically too high. Obviously, a significant influence arises from the coordinative oxygen-to-copper bond. In fact, the increasing charge transfer to the Cu(I)−NO unit due to the increasing number of donor ligands hinders the spin transfer from the NO radical to the copper center (see Table 7).

Influence of the Cu−N−O Bond Angle. The question arises whether the decrease of the spin density at the copper center with increasing number of donating coligands is indeed originated directly by the increased charge density at the copper center which hinders the spin transfer from NO. The increasing Cu−N−O bond angle upon coordination (compare Table 8) as well reduces the spin transfer from NO to Cu(I) due to the diminished overlap between the spin-bearing in-plane π^*-orbital of NO and the copper s-orbitals. This latter effect is independent of the charge density at the copper center.

We have investigated the influences of these two effects on the resulting hfc coupling constants for the isolated Cu(I)−NO system and the water complexes by a systematic variation of the Cu−N−O bond angle followed by the relaxation of all the other structural parameters by partial optimization. The results are displayed in Figures 3 and 4. The most striking feature is the strong decrease of the isotropic copper constant with increasing bond angle (Figure 3), which is expected as discussed above. Only s-symmetric spin density contributes to the isotropic coupling constants, but the spin is originated in a π^*-orbital of NO that does not mix with the copper s-orbitals in a linear bonding mode. Consequently, the spin density at the copper center decreases with increasing bond angle reaching a value of around zero for the linear arrangement.

It turns out that the anisotropic copper coupling constants (Figure 4) as well as the nitrogen hfc values, both isotropic and anisotropic, are hardly influenced by the Cu−N−O bond angle.

Keeping in mind that the optimized Cu−N−O bond angle varies between 133° and 143° (compare Table 7), we can derive from Figures 3 and 4, even for the isotropic copper case, that the influence of additional coligands independent of the bond angle is significantly stronger than the value of the bond angle independent of the coordination number. Thus, the strong decrease of the isotropic copper coupling constant with increasing number of coligands is, indeed, mainly determined by an increasing charge transfer to the Cu(I) center which hinders the spin transfer from NO.

Comparison with the Experiment. In addition to the cationic species $[(H_2O)_nCu(NO)]^+$ and the neutral complexes $[(OH)(H_2O)_{n-1}Cu(NO)]$, the cluster-type model $[(HO)_2Al(\mu\text{-}OH)_2Cu(NO)]$ (denoted by Al cluster in the figures) was involved (Scheme 1). The latter should somewhat better model the zeolite framework. Thus, we provide further information concerning the specific Cu(I) coordination sites in the ZSM-5 zeolite. This problem has been investigated in several theoretical studies.[19,20,37−44]

In Figures 1 and 2, the calculated values of the copper isotropic and anisotropic hfc coupling constants are collected and compared to those measured for the Cu(I)−NO species (major species) in the zeolite. It is found that the isotropic coupling constants can be reasonably well reproduced with all three model types if at least two oxygen atoms in the neighborhood of copper are considered. An even larger coordination number could be concluded from the comparison of the calculated values of the anisotropic coupling constants with the experimental ones. From the present investigation, we can, however, not derive a preference of a certain adsorption site in comparison to alternative ones as has been done by Nachtigall and Sauer.[20] There are too large uncertainties with respect to the chosen density functional, the Cu−N−O bond angle, and the type of coligands

In the powder spectra experiment, the isotropic and anisotropic hyperfine coupling constants cannot be determined independently. In fact, a total hfc coupling constant, i.e., the sum of the isotropic value and one anisotropic component, is measured. For nitrogen, only the hyperfine splitting along the symmetry axis of the spin-bearing N−O π^*-orbital has been observed with a total hfc value of 29×10^{-4} cm^{-1}. There is no experimental possibility to split up this value into an isotropic and an anisotropic contribution. This can be achieved only by theoretical analyses. From our calculations, it turns out that the nitrogen coupling constants do not depend very much on the coordination number (see Table 8), i.e., on the coordinative surrounding of the Cu(I) center. Looking, for instance, at the cluster-type model (Scheme 1), we have values of 8.9×10^{-4} cm^{-1} for the isotropic coupling constant and of −11.2, −9.6, and $+20.8 \times 10^{-4}$ cm^{-1} for the anisotropic ones (see Table 8). This would lead to total hfc values of −2.3, −0.7, and 29.7. These values are only slightly changed (less than 1×10^{-4} cm^{-1} for the observable value) for the other model systems and fit very well the experimental findings with only one observed value of 29.[15] The other two values are obviously too small to be observed in the experiment. It follows that the nitrogen hfc parameters derived from the powder spectra experiment cannot provide information about the specifics of the adsorption sites of the Cu(I)−NO species in the zeolite.

5. Conclusions

It appears to be rather difficult to calculate reliable EPR hyperfine coupling constants for metal centers with a formally closed-shell electron configuration inside a paramagnetic compound applying state-of-the-art quantum chemical methods such as density functional theory. The Cu(I)−NO system may serve as a benchmark for such investigations. The spin density at the individual atomic centers is determined by two effects, the coordinative spin transfer from NO to unoccupied valence orbitals of Cu(I) and the spin polarization in formally doubly occupied orbitals of the system. A detailed analysis has shown that both effects can yield large, but opposing contributions to the coupling constants. For copper, the anisotropic coupling constants are much more sensitive to the details of spin polarization than the isotropic one. For nitrogen, the situation is the opposite. It turned out that it is difficult to describe the spin polarization quantitatively correctly by density functional theory. This leads to a rather large uncertainty of the calculated anisotropic copper hfc constants, whereas the calculated nitrogen values appear to be quite reliable.

The comparison of the calculated values of the copper hfc constants for the isolated Cu(I)−NO system with the measured values for the Cu(I)−NO species in the zeolite shows that the copper hfc parameters are strongly influenced by the zeolite framework. However, modeling of the latter by certain coligands improves significantly the agreement with the experiment. This is due to the additional charge transfer to the Cu(I) center caused by the coligands and the more realistic electrostatic potential around it. On the basis of our analysis, we conclude that the isotropic copper hfc parameter provides more reliable information about the complex geometry and the number of oxygen atoms coordinated to the Cu(I) ion than the anisotropic copper hfc parameters because the former displays a pronounced dependence on both the number of coligands and the Cu−N−O bond angle. Furthermore, the isotropic copper hfc is much less subjected to spin polarization effects. Models with two or more oxygen neighbors agree rather well with the experiment, but the remaining uncertainty of the calculated values, mainly caused by the computational procedure, does not favor one of these models. Thus, it appears to be a very difficult task to distinguish reliably between different adsorption sites in the zeolite. From the nitrogen hfc parameters, no information concerning this problem can be derived. They are hardly influenced by the zeolite framework.

Acknowledgment. We thank the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft, Priority Program 1051, for financial support.

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