EPR Characteristics of the [(NC)5M(NO)]3− Ions (M = Fe, Ru, Os). Experimental and DFT Study Establishing NO+ as a Ligand

Matthias Wanner, Thomas Scheiring, and Wolfgang Kaim*

Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70550 Stuttgart, Germany

Leonardo D. Slep, Luis M. Baraldo, and José A. Olabe
Departamento de Química Inorgánica, Analítica y Química Física (Inquimae), Facultad de Ciencias Exactas y Naturales, UBA, Pabellón 2, Ciudad Universitaria, C1428EH Buenos Aires, Republic of Argentina

Stanislav Záliš
J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, CZ-18223 Prague, Czech Republic

Evert Jan Baerends
Afdeling Theoretische Chemie, Vrije Universiteit, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

Received April 30, 2001

Introduction

The transition-metal chemistry of the nitrosyl ligand1 has seen a tremendous revival since the discovery2 of nitric oxide as an essential biological molecule.3 Not only physiological NO synthesis and receptor sites but also synthetic NO acceptor and delivery systems are thus of great importance for the understanding and possible treatment of various diseases. Among the oldest such therapeutic compounds have been salts of the nitroprusside dianion [(NC)2Fe(NO)]2−, which serve as directly active hypotensive agents (vasodilators).3

NO is a typical noninnocent ligand1 which can act as diamagnetic, strongly π accepting NO+, as the equally diamagnetic NO− (isoelectronic with O2), or as the paramagnetic, neutral NO+. Although the free nitric oxide radical does not exhibit an EPR spectrum under standard conditions,4 its attachment to a solid support5 or fixation in a coordination compound usually gives rise to EPR signals which allow for an analysis of the electronic structure.6−9 Whereas the paramagnetic [(NC)2Fe(NO)]2− derived from the classical nitroprusside has been experimentally analyzed in terms of the facile cyanide dissociation [(NC)2Fe(NO)]2− ⇌ CN− + [(NC)2Fe(NO)]2− by EPR7 and spectroelectrochemical techniques,10 there has not yet been a consistent EPR investigation of the analogous complexes with the two heavier homologues.11 Recently, it was shown that the zero-order regular approximation is a powerful tool to calculate the g and hyperfine tensors of systems containing transition metals.12 Extending and modifying our earlier work,13 we now present a comprehensive EPR picture for the ions [(NC)3M(NO)]3− (M = Fe, Ru, Os) on the basis of experimental and theoretical results.

Experimental Section

Materials. The compounds K2[(NC)3M(NO)] (M = Ru, Os) were obtained in analogy to the sodium salts,11 using KNO2 instead of NaN02.13 Ion exchange K+/nBu4N+ (M = Os) was performed at a Dowex 50 WX2 column as described.11

K3[(NC)3Ru(NO)2]2H2O. A solution of 67 mg (0.18 mmol) of K3[(NC)3Ru(NO)2]2H2O in 3 mL of H2O was run through a Dowex 50 WX2 ion exchange column, charged with the tetraethylammonium cation. Condensation of the water from the eluate at a N2 (liq)-cooled (77 K) condenser gave an orange solid which was washed with diethyl ether to yield 95 mg (94%) of the product. Anal. Calcd for C21H44N8O3−Ru (mol wt 557.7): C, 45.23; H, 7.95; N, 20.09. Found: C, 45.09; H, 7.93; N, 19.91.

EPR Spectroscopy. EPR spectra of electrolyzed solutions in a two-electrode cell14 were recorded in the X band on a Bruker ER305 M gaussmeter and a HP 5350B microwave counter. An Oxford Instruments cryostat ESR 900 was used for measurements at liquid He temperatures.

DFT Calculations. Ground-state electronic structure calculations on [(NC)3M(NO)]3− complex ions have been done using density-functional theory (DFT) methods, specifically the ADF2000.0215,16 and Gaussian 9817 program packages.

Within the ADF program, Slater type orbital (STO) basis sets of triple-ζ quality with polarization functions were employed. Basis I was represented by a frozen-core approximation (1s for C, N, and O, 1s−


Results and Discussion

EPR Measurements. For dissolution in the aprotic electrolyte acetonitrile/0.1 M Bu4NPF6, the precursor ions \([\text{NC})_5 \text{M(NO)}_3\] were prepared as tetraalkylammonium salts (Et4N+) were used for the C, N, and O atoms; quasi-relativistic effective core pseudopotentials and the corresponding optimized set of basis functions were used for Fe, Ru, and Os. The hybrid Becke three-parameter functional with the Lee, Yang, and Parr correlation functional (B3LYP) was used in the Gaussian 98 calculations (G98/B3LYP).

The calculations on \([\text{NC})_5 \text{M(NO)}_3]^-\) ions were performed in C4v-constrained symmetry with the z axis coincident with the C4 symmetry axis. The geometries of the \([\text{NC})_5 \text{M(NO)}_3]^-\) complexes were optimized without any symmetry restrictions using the spin-unrestricted open shell Kohn–Sham (UKS) approach. All results discussed correspond to the optimized geometries.

Table 1. Comparison of Experimental and Calculated g Values and \(^{14}N\) Hyperfine Constants \(a (\text{mT})\) for \([\text{NC})_5 \text{M(NO)}_3]^-\) Complexes (Optimized Geometries, cf. Table 2)

<table>
<thead>
<tr>
<th></th>
<th>([\text{NC})_5 \text{Fe(NO)}_3]^-)</th>
<th>([\text{NC})_5 \text{Ru(NO)}_3]^-)</th>
<th>([\text{NC})_5 \text{Os(NO)}_3]^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(g_1)</td>
<td>(g_2)</td>
<td>(g_3)</td>
</tr>
<tr>
<td>(g_{\text{av}})</td>
<td>1.99</td>
<td>1.995</td>
<td>2.002</td>
</tr>
<tr>
<td>(g_{14})</td>
<td>1.967</td>
<td>1.968</td>
<td>1.959</td>
</tr>
<tr>
<td>(A_1)</td>
<td>n.a.</td>
<td>0.73</td>
<td>n.o.</td>
</tr>
<tr>
<td>(A_2)</td>
<td>2.8</td>
<td>3.16</td>
<td>3.8</td>
</tr>
<tr>
<td>(A_3)</td>
<td>n.a.</td>
<td>0.65</td>
<td>n.o.</td>
</tr>
</tbody>
</table>

Notes


9. (a) M = Os. The newly reported EPR spectrum should be unambiguously assigned to \([\text{NC})_5 \text{M(NO)}_3]^+\) by the comparison with literature data. Strongly suggest the identification of the paramagnetic species as \([\text{NC})_5 \text{M}^4\text{II(NO)}_3]^+\). We performed high-level DFT calculations (ADP/BP and G98/B3LYP) for all three systems (M = Fe, Ru, Os) for the following reasons.

(a) M = Os. The newly reported EPR spectrum should be unambiguously assigned to \([\text{NC})_5 \text{M(NO)}_3]^+\). In addition, the considerable deviation of \(g\) components from \(g\) (electron) = 2.0023 for osmium compounds has been attributed to the very high spin–orbit coupling constant of osmium(II) at \(\xi = 3000\) cm\(^{-1}\) vs 1200 cm\(^{-1}\) for ruthenium(II) or 440 cm\(^{-1}\) for iron-
(II). A quantitative reproduction of the EPR parameters in line with the experiment confirms the identity of the \([\text{NC}_5\text{Os(NO)}]^{3-}\) species and certifies the validity of the computational method.

(b) \(M = \text{Ru}\). Although described as “rare”\(^8\), there are a number of ruthenium(II) complexes binding NO\(^2\).\(^{8,27}\) A recent review, EPR investigation, and spin Hamiltonian treatment by McGarvey et al.\(^8\) and a computational study by Gomez and Guenzburger\(^28\) have dealt with such systems in detail. The latter work using DVM-DFT methodology with M–N bond length and M–N–O angle variation made some predictions concerning the geometry and the EPR hyperfine features of \([\text{NC}_5\text{Ru(NO)}]^{3-}\).

The \(g\) tensor values were not calculated by this study.\(^28\)

(c) \(M = \text{Fe}\). The facile loss of cyanide from one-electron-reduced nitroprusside has led to a number of EPR studies involving isotope labeling\(^9\) and to continued efforts of calculations.\(^8\) Having proved the reliability of the ADF/BP procedure through successful treatment of the ruthenium and osmium examples, we can now eventually confirm the \(g\) anisotropy through successful treatment of the ruthenium and osmium examples, we can now eventually confirm the \(g\) anisotropy with the experiment confirms the identity of the \([\text{NC}_5\text{Os(NO)}]^{3-}\) species and certifies the validity of the computational method.

The geometries of the precursor ions \([\text{NC}_5\text{M(NO)}]^{2-}\) (\(M = \text{Fe}, \text{Ru}\))\(^{11a}\) are well reproduced by the ADF/BP procedure (Table 2). The G98/B3LYP approach gives very similar results. As previously calculated,\(^28,30\) the addition of one electron causes the most pronounced changes in the M–NO and N–O bond lengths and in the M–N–O angle. The increase of the metal–nitrosyl bond distance is fairly uniform for all three systems (“reductive labilization”), and the lengthening of the N–O bond is obvious from distinctly lowered stretching frequencies following IR spectroelectrochemistry.\(^10,13\) In agreement with simple electron repulsion concepts (Scheme 1) the linear arrangement in the NO\(^1\)-containing precursors changes to a bent situation in the NO radical-binding complexes.

The extent of this bending is calculated at similar values of about 145\(^°\)\(^\text{a}\) using either the ADF/BP or the G98/B3LYP optimization; it is further connected with the loss of \(C_2\) symmetry and thus with nonequal CN\(_{eq}\) ligands. The calculations confirm the addition of the electron to the \(\varepsilon\) MO of \([\text{NC}_5\text{M(NO)}]^{2-}\), resulting in the described symmetry lowering (removal of degeneracy) and in the occupation of one \(\pi^*\) MO (singly occupied MO, SOMO) of the nitrosyl ligand.\(^{33}\) The splitting of the \(\varepsilon(\pi^*)\) level is smallest for the ruthenium compound; the larger splitting for the other two analogues is due to stronger metal–ligand interaction (Os) or closer lying orbitals (Fe). According to a general rule,\(^33\) the closeness of the other \(\pi^*\) orbital (LUMO) of the previous \(\varepsilon\) set causes a shift to lower \(g\) values in the NO\(^1\) complexes; the calculated energy differences to fully occupied MOs are much larger. The reverse is observed for metal complexes\(^33\) of \(\text{O}_2\)\(^-\) where the occupation of the former \(\varepsilon(\pi^*)\) level with three electrons causes a particular closeness of SOMO and HOMO and, consequently, \(g\) components typically larger than 2.\(^{34}\) The optimized geometry of the \(3\)-complexes has no symmetry, but the M–N–O fragment is close to the plane forming the bisector of the two NC–M–CN axes.

The calculated SOMO composition of the three ions \([\text{NC}_5\text{M(NO)}]^{1-}\) is rather invariant and summarized in Table 3. As the spin density representation for \([\text{NC}_5\text{Os(NO)}]^{1-}\) in Figure 3 illustrates, the spin density is not only confined to the nitrosyl part of the molecule (with about two-thirds share on


The effect is most pronounced for the osmium system, where the differences are only marginal and corroborate the previously noted leveling effect of five cyanide coligands on the three complexes. This partial covalency is well-known from nitrosyl-ruthenium(II) complexes. The metal contribution of about 25% decreases slightly for the heavier homologues, representing a somewhat stronger stabilization of the metal(II) = low-spin d6 configuration in the resonance formulation (eq 1). However, the differences are only marginal and corroborate the previously noted leveling effect of five cyanide coligands on the three elements of the group 8 triad. Both the significant metal contribution and the closeness of the LUMO to the SOMO appear to cause rapid relaxation, as is evident from the failure to observe EPR signals of the ruthenium and osmium systems at room temperature. The restricted DFT calculations including spin–orbit coupling gave SOMO–LUMO gap values of 0.65, 0.55, and 0.54 eV for the Fe, Ru, and Os species, respectively.

While a comparison with EPR data for NO+ bound to solid supports, copper, or other ruthenium complex fragments confirms the predominantly ligand centered spin, the effect of the strongly increasing spin–orbit coupling is clearly evident from both the experimental and calculated g data (Table 1). The effect is most pronounced for the osmium system, where g3 and the calculated isotropic value gav are lowest and the total g anisotropy g1 – g3 is largest. The decrease of g2 and g3 on going from Fe to Os is due to the joint effects of the M–N–O bent character and the spin–orbit coupling from the metal ion. Neither the slightly diminishing metal contribution to the SOMO (Table 3) nor the marginal structural differences (Table 2) can account for this effect. The symmetry as well as the individual g components and the derived values are well-reproduced by both kinds of DFT calculations. We are thus confident that the originally reported g factor values (species I in ref 9a) for [(NC)3Fe(NO)]3− are correct, as incorporated in Table 1.

Calculations of the nitrosyl14N hyperfine components show one such large value, A2 > 3 mT, which agrees with the data obtained for the ruthenium and osmium complex (Table 1) and with previous experimental results for bound NO.5,8

In summation, with this combined experimental and theoretical study of all three species [(NC)3M(NO)]3− (M = Fe, Ru, Os), we could contribute to a clarification of literature reports.9,13,28 Although ruthenium(II)–nitrosyl complexes were treated recently,8,28 the EPR analysis of the simple pentacyano species is described here for the first time. Using advanced DFT methodology, we could show that the geometry changes and the NO labilization effects on reduction are rather comparable for all three homologues; in addition, the g factor calculations turned out to be fairly reliable, even for heavy-element systems where the effects of spin–orbit coupling are dominant.

Acknowledgment. This collaborative work was supported through grants from the Volkswagenstiftung, the Deutsche Forschungsgemeinschaft, and the COST D14 program. W.K. also thanks the Fonds der Chemischen Industrie for support.