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EPR Characteristics of the $[(NC)_5M(NO)]^{3-}$ Ions ($M = Fe, Ru, Os$). Experimental and DFT Study Establishing NO$^{\bullet}$ as a Ligand

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Introduction

The transition-metal chemistry of the nitrosyl ligand[1] has seen a tremendous revival since the discovery[2] 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 $[(NC)_5Fe(NO)]^{2-}$, which serve as directly active hypotensive agents (vasodilators).[3]

NO is a typical noninnocent ligand[1] which can act as diamagnetic, strongly π accepting NO^+, as the equally diamagnetic NO^- (isoelectronic with O_2), or as the paramagnetic, neutral $NO^{\bullet}$. Although the free nitric oxide radical does not exhibit an EPR spectrum under standard conditions,[4] its attachment to a solid support[5] 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 $[(NC)_5Fe(NO)]^{3-}$ derived from the classical nitroprusside has been experimentally analyzed in terms of the facile cyanide dissociation $[(NC)_5Fe(NO)]^{3-} \rightleftharpoons CN^- + [(NC)_4Fe(NO)]^{2-}$ by EPR[9] 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 $[(NC)_5M(NO)]^{3-}$ ($M = Fe, Ru, Os$) on the basis of experimental and theoretical results.

Experimental Section

Materials. The compounds $K_2[(NC)_5M(NO)]$ ($M = Ru, Os$) were obtained in analogy to the sodium salts,[11] using KNO_2 instead of $NaNO_2$.[13] Ion exchange K^+/nBu_4N^+ ($M = Os$) was performed at a Dowex 50 WX2 column as described.[13]

$K_2[(NC)_5Ru(NO)]\cdot 2H_2O$. A solution of 1.00 g (2.22 mmol) of $K_4[Ru(CN)_6]\cdot 2H_2O$ and 1.13 g (13.36 mmol) of KNO_2 in 200 mL of H_2O was acidified to pH 3 using about 3 mL of CF_3COOH. Irradiation with a mercury lamp for 14 h gave an orange solution from which the solvent was removed. The resulting oily residue was chromatographed over Sephadex G25 to yield, after drying over P_2O_5, 150 mg (75%) of orange microcrystals. Anal. Calcd for $C_5H_4K_2N_6O_3Ru$ (mol wt 375.3): C, 15.99; H, 1.07; N, 22.39. Found: C, 15.26; H, 1.07; N, 22.30.

$(NEt_4)_2[(NC)_5Ru(NO)]$. A solution of 67 mg (0.18 mmol) of $K_2[(NC)_5Ru(NO)]\cdot 2H_2O$ in 3 mL of H_2O was run through a Dowex 50 WX2 ion exchange column, charged with the tetraethylammonium cation. Condensation of the water from the eluate at a N_2(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 $C_{21}H_{44}N_8O_3Ru$ (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 cell[14] were recorded in the X band on a Bruker System ESP 300 equipped with a Bruker ER035 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 $[(NC)_5M(NO)]^{n-}$ complex ions have been done using density-functional theory (DFT) methods, specifically the ADF2000.02[15,16] and Gaussian 98[17] 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−

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2p for Fe, 1s−3d for Ru, and 1s−4d for Os were kept frozen); basis II also includes core electrons. The following density functionals were used within ADF: the local density approximation (LDA) with VWN parametrization of electron gas data or the functional including Becke's gradient correction[18] to the local exchange expression in conjunction with Perdew's gradient correction[19] to the LDA expression (ADF/BP). The scalar relativistic (SR) zero order regular approximation (ZORA) was used within the geometry optimization. The **g** tensor was obtained from a spin-nonpolarized wave function after incorporating the spin−orbit (SO) coupling. **A** tensors were obtained from spin-unrestricted wave functions. **A** tensors and the **g** tensor were obtained by first-order perturbation theory from the ZORA Hamiltonian in the presence of a time-independent magnetic field.[20,21]

Within Gaussian-98 Dunning's polarized valence double-ζ basis sets[22] were used for the C, N, and O atoms; quasi-relativistic effective core pseudopotentials and the corresponding optimized set of basis functions[23] were used for Fe, Ru, and Os. The hybrid Becke three-parameter functional with the Lee, Yang, and Parr correlation functional (B3LYP)[24] was used in the Gaussian 98 calculations (G98/B3LYP).

The calculations on $[(NC)_5M(NO)]^{2-}$ ions were performed in C_{4v}-constrained symmetry with the z axis coincident with the C_4 symmetry axis. The geometries of the $[(NC)_5M(NO)]^{3-}$ 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.

Results and Discussion

EPR Measurements. For dissolution in the aprotic electrolyte acetonitrile/0.1 M Bu_4NPF_6 the precursor ions $[(NC)_5M(NO)]^{2-}$ were prepared as tetraalkylammonium salts (Et_4N^+ for M = Ru, $n$$Bu_4N^+$ for M = Os).[13] Reversible one-electron reduction[10c,13] produces paramagnetic $[(NC)_5M(NO)]^{3-}$ ions, which had previously been characterized by IR spectroelectrochemistry.[10c,13] In contrast to previous experiments[10c] we were now able to obtain an EPR response from $[(NC)_5Ru(NO)]^{3-}$ by studying a frozen solution of the in situ generated species at low temperatures. No EPR signal was observable in fluid solution at room temperature. Figure 1 shows an almost axial spectrum ($g_{1,2} \approx 2.00$, $g_3 < 2.00$) with one ^{14}N hyperfine coupling constant at A_2 = 3.8 mT being observable. As will be discussed below, these features agree with other reports on coordinated $NO^{\bullet}$, including ruthenium complexes.[5,6,8,9a] The EPR data are summarized together with calculation results in Table 1.

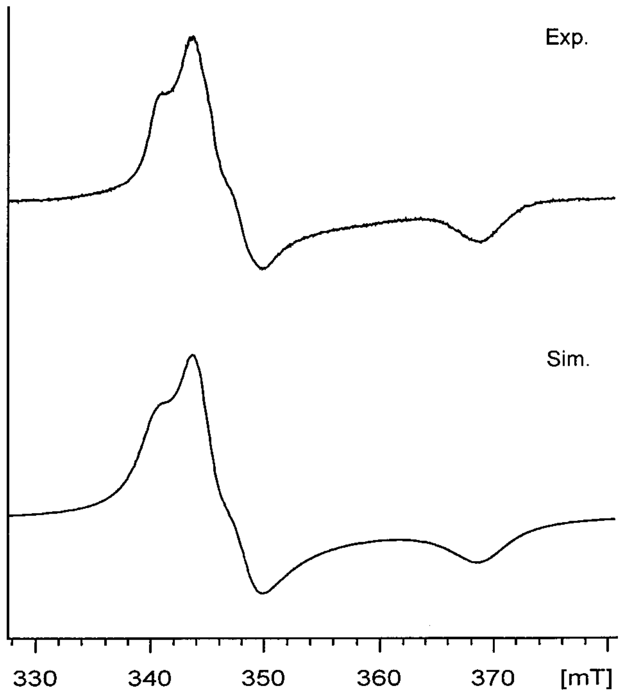

Figure 1. (top) EPR spectrum of electrogenerated $[(NC)_5Ru(NO)]^{3-}$ in CH_3CN/0.1 M Bu_4NPF_6 at 3.5 K and (bottom) computer-simulated spectrum with the parameters listed in Table 1.

Table 1. Comparison of Experimental and Calculated g Values[a] and ^{14}N Hyperfine Constants a (mT)[b] for $[(NC)_5M(NO)]^{3-}$ Complexes (Optimized Geometries, cf. Table 2)

	$[(NC)_5Fe(NO)]^{3-}$		$[(NC)_5Ru(NO)]^{3-}$		$[(NC)_5Os(NO)]^{3-}$	
	exptl[c]	calcd	exptl[d]	calcd	exptl[d]	calcd
g_1	1.99	2.015	2.004	2.000	1.959	2.002
g_2	1.99	1.995	2.002	1.991	1.931	1.940
g_3	1.92	1.893	1.870	1.803	1.634	1.583
$g_1 - g_3$	0.07	0.122	0.134	0.197	0.325	0.419
g_{av}[e]	1.967	1.968	1.959	1.932	1.847	1.824
A_1	n.a.	0.73	n.o.	0.51	n.o.	0.58
A_2	2.8[f]	3.16	3.8	3.23	3.5	3.28
A_3	n.a.	0.65	n.o.	0.36	n.o.	0.44

[a] Spin-restricted calculations, including spin−orbit coupling. [b] Calculations using scalar relativistic UKS-ZORA approach. [c] From ref 9a, in aqueous solution, EPR measurements at 77 K. [d] From electrolysis in CH_3CN/0.1 M Bu_4NPF_6, EPR measurements at 3.5 K. [e] Calculated from $g_{av} = [(g_1^2 + g_2^2 + g_3^2)/3]^{1/2}$. [f] Extracted from Figure 1 of ref 9a (not explicitly stated in that reference).

In an extension of our earlier studies[13] of the osmium analogue, we could now establish that the previously reported poorly resolved EPR signal with $g > 2$ is not due to $[(NC)_5Os(NO)]^{3-}$ but to a trace species with less negative reduction potential. Continued electrolysis produces an EPR spectrum of $[(NC)_5Os(NO)]^{3-}$ for which all g components lie well below 2 (Figure 2, Table 1), with qualitatively similar features as for the ruthenium analogue.

DFT Calculations. Although the qualitative correspondence between Ru and Os species and the comparison with literature data[5,6,8] strongly suggest the identification of the paramagnetic species as $[(NC)_5M^{II}(NO^{\bullet})]^{3-}$, we performed high-level DFT calculations (ADF/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 $[(NC)_5Os(NO)]^{3-}$. In addition, the considerable deviation of g components from g(electron) = 2.0023 for osmium compounds[25] has been attributed to the very high spin−orbit coupling constant of osmium(II) at ξ = 3000 cm^{-1} vs 1200 cm^{-1} for ruthenium(II) or 440 cm^{-1} for iron-

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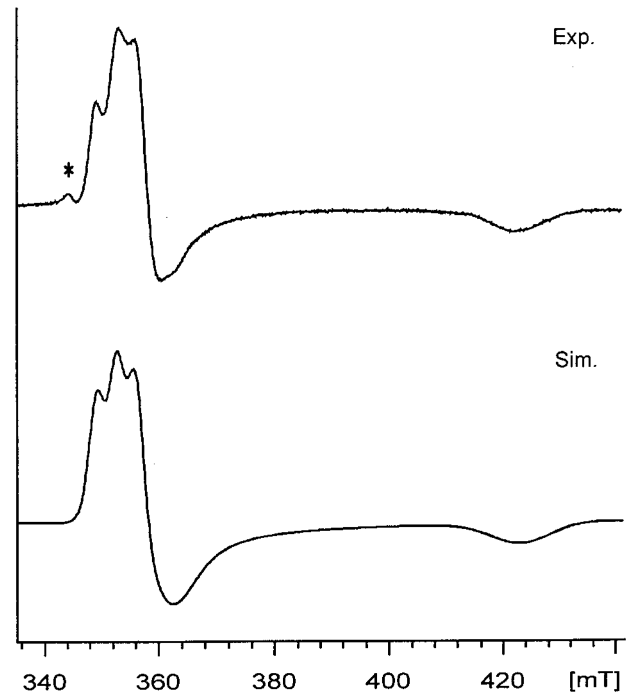


Figure 2. (top) EPR spectrum of electrogenerated $[(NC)_5Os(NO)]^{3-}$ in CH_3CN/0.1 M Bu_4NPF_6 at 3.5 K (the asterisk denotes a low-field impurity; see text) and (bottom) computer-simulated spectrum with the parameters listed in Table 1.

(II).[26] A quantitative reproduction of the EPR parameters in line with the experiment confirms the identity of the $[(NC)_5Os(NO)]^{3-}$ species and certifies the validity of the computational method.

(b) M = Ru. Although described as "rare",[8] there are a number of ruthenium(II) complexes binding $NO^{\bullet}$.[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 $[(NC)_5Ru(NO)]^{3-}$. The **g** tensor values were not calculated by this study.[28]

(c) M = 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.[28] 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 results presented in 1966 by van Voorst and Hemmerich[9a] for $[(NC)_5Fe(NO)]^{3-}$ and even identify the perceptible but not explicitly mentioned[9a] hyperfine coupling as A_2 (Table 1).

The geometries of the precursor ions $[(NC)_5M(NO)]^{2-}$ (M = Fe,[29] 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

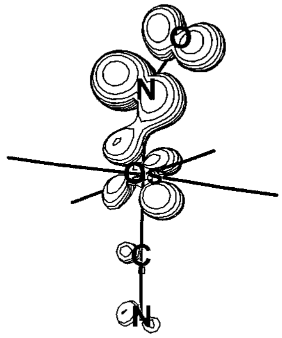
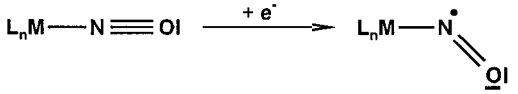


Figure 3. Spin density distribution within $[(NC)_5Os(NO)]^{3-}$.

Scheme 1



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 stetching frequencies following IR spectroelectrochemistry.[10c,13] In agreement with simple electron repulsion concepts (Scheme 1) the linear arrangement in the NO^+-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°[31] using either the ADF/BP or the G98/B3LYP optimization; it is further connected with the loss of C_{4v} symmetry and thus with nonequal CN_{eq} ligands. The calculations confirm the addition of the electron to the e MO of $[(NC)_5M(NO)]^{2-}$, resulting in the described symmetry lowering (removal of degeneracy) and in the occupation of one π^* MO (singly occupied MO, SOMO) of the nitrosyl ligand.[32] The splitting of the e(π^*) 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 π^* orbital (LUMO) of the previous e set causes a shift to lower g values in the $NO^{\bullet}$ complexes; the calculated energy differences to fully occupied MOs are much larger. The reverse is observed for metal complexes[34] of $O_2^{\bullet -}$ where the occupation of the former e(π^*) 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 $[(NC)_5M(NO)]^{3-}$ is rather invariant and summarized in Table 3.

As the spin density representation for $[(NC)_5Os(NO)]^{3-}$ in Figure 3 illustrates, the spin density is not only confined to the nitrosyl part of the molecule (with about two-thirds share on

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Table 2. Selected ADF/BP-Calculated Bond Lengths (Å) and Angles (deg) within $[(NC)_5M(NO)]^{n-}$ Complexes

	M−C$_{ax}$	M−C$_{eq}$	M−N	C$_{ax}$−N	C$_{eq}$−N	N−O	M−N−O
$[(NC)_5Fe(NO)]^{2-}$	1.944	1.947	1.633	1.173	1.175	1.170	180.0
$[(NC)_5Fe(NO)]^{3-}$	2.003	1.946−1.979	1.754	1.180	1.182	1.219	143.9
$[(NC)_5Ru(NO)]^{2-}$	2.003	2.079	1.770	1.174	1.176	1.176	180.0
$[(NC)_5Ru(NO)]^{3-}$	2.093	2.067−2.092	1.893	1.181	1.182	1.221	144.9
$[(NC)_5Os(NO)]^{2-}$	2.095	2.087	1.785	1.171	1.173	1.183	180.0
$[(NC)_5Os(NO)]^{3-}$	2.085	2.067−2.086	1.904	1.180	1.181	1.227	145.8

Table 3. ADF/BP-Calculated Composition (in Percent) of the SOMO in $[(NC)_5M(NO)]^{3-}$ Complexes as Expressed in Terms of Individual Fragments

	M	(CN)$_{ax}$	(CN)$_{eq}$	NO (O)
$[(NC)_5Fe((NO)]^{3-}$	29	4	4	62 (22)
$[(NC)_5Ru(NO)]^{3-}$	26	3	4	66 (24)
$[(NC)_5Os(NO)]^{3-}$	24	2	4	69 (25)

the nitrogen atom), the SOMO also has a sizable metal contribution. Similar figures were obtained for Ru and Fe complexes. This partial covalency is well-known from nitrosylruthenium(II) complexes.[35] The metal contribution of about 25% decreases slightly for the heavier homologues, representing a somewhat stronger stabilization of the metal(II) = low-spin d^6 configuration in the resonance formulation (eq 1). However,

$$[(NC)_5M^{II}(NO^{\bullet})]^{3-} \leftrightarrow [(NC)_5M^{I}(NO^{+})]^{3-} \qquad (1)$$

the differences are only marginal and corroborate the previously noted[36] 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 $NO^{\bullet}$ bound to solid supports,[5] copper,[6] or other ruthenium complex fragments[8] 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 g_3 and the calculated isotropic value g_{av} are lowest and the total g anisotropy $g_1 - g_3$ is largest. The decrease of g_2 and g_3 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 $[(NC)_5Fe(NO)]^{3-}$ are correct, as incorporated in Table 1.

Calculations of the nitrosyl ^{14}N hyperfine components show one such large value, $A_2 > 3$ mT, which agrees with the data obtained for the ruthenium and osmium complex (Table 1) and with previous experimental results for bound $NO^{\bullet}$.[5,6,8]

In summation, with this combined experimental and theoretical study of all three species $[(NC)_5M(NO)]^{3-}$ (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.

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