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Single electron and H^+ coupled double electron transfer reductions of nitrosyl complexes: model reactions for key steps of the $NO_3^- \rightleftharpoons NH_3$ conversion in the nitrogen cycle

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Abstract

The individual redox steps of the biological nitrate ⇌ ammonia interconversion are catalyzed by metal enzymes. In order to find chemical model reactions demonstrating one of the key steps, leading from nitrogen monoxide to hydroxylamine, nitrosyl complexes having iron or molybdenum sulfur cores were synthesized and investigated. The single electron reduction of the 18 electron NO complex $[Fe(NO)('N_HS_4')]^+$ ($'N_HS_4'^{2-}$ = dianion of bis(2-(2-mercaptophenyl)thio)ethyl)-amine) gives the 19 electron species $[Fe(NO)('N_HS_4')]^0$ showing a strongly bent FeNO group and weakened $[Fe('N_HS_4')]$ core bonds. The reduction of $[Mo(NO)_2('S_4')]$ ($'S_4'^{2-}$ = dianion of 2,3,8,9-dibenzo-1,4,7,10-tetrahiadecane) by hydrazine, serving both as electron and proton source, yields $[Mo(NH_2O)(NO)('S_4')]$ having a side-on bound hydroxylaminyl ligand. By structural and spectroscopic investigations, this reduction is shown to be a ($2e^- + 2H^+$) reaction, which appears to be facilitated by the increase of the coordination number of the Mo center.

Introduction

The biological nitrogen cycle (Fig. 1) is one of the fundamental cycles of elements [1] and centers around N_2 being the source of all nitrogen chemistry. Major constituents of the cycle are N_2 fixation, nitrate ⇌ ammonia interconversion and so called denitrification reactions regenerating N_2.

All reactions are catalyzed by transition metal enzymes. The metals involved are mainly Fe, Mo and Cu which appear to prefer coordination spheres dominated by sulfur donors. This is taken for granted in the case of nitrogenases and nitrate reductase, and is assumed to be probable for many other relevant enzymes. Only a very few of these enzymes, however, have been isolated, and even more limited is the understanding of the enzymatic reactions on the molecular level. This is the reason, why the investigation of complexes of transition metals with sulfur ligands,

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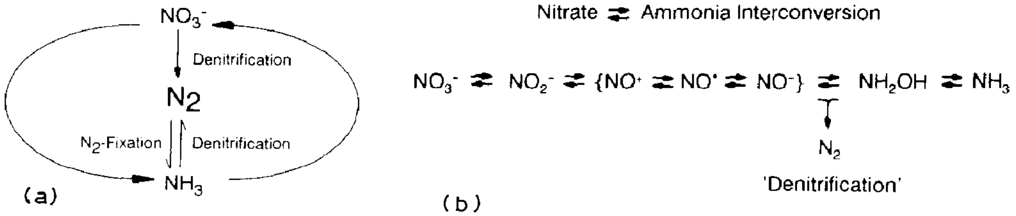


Fig. 1. (a) Major constituents of the biological nitrogen cycle and (b) intermediates of the nitrate ⇌ ammonia interconversion.

the binding of small molecules, as e.g. N_2, CO, N_2H_2, NH_3 or NO, to such complexes, and the reactivity of the resulting species is of fundamental importance for the understanding of many essential processes of life.

The nitrate ⇌ ammonia interconversion is an eight electron process. There is evidence that it takes place by two electron steps via the ions and molecules, respectively, shown in Fig. 1b, and since the species exist or form in the coordination sphere of the metals of metal enzymes, nitrate, nitrite, nitrosyl, hydroxylamine and ammonia complexes represent intermediates.

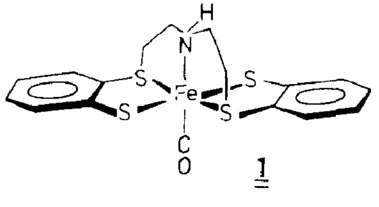
Little is known of the interconversion of these intermediates, in particular of the step leading from the nitrogen monoxide to the hydroxylamine stage (see Fig. 1b). This is a key step, because NO is surprisingly difficult to reduce, in industry as well as in the laboratory. On the other hand, the energetically favored dinitrogen lies in between the two oxidation states of NO and NH_2OH, and many bacteria use the production of dinitrogen from either nitrate or ammonia in order to meet their requirements of energy. This may explain why a chemical equivalent demonstrating the reduction of a nitrosyl to a hydroxylamine complex was unknown yet and this paper wants to address two points: (1) The possibility of reducing a nitrosyl to a hydroxylamine complex. (2) Changes on the molecular level, which a nitrosyl complex undergoes if it is reduced by either one electron or, if possible, by two electrons.

There are many redox processes in nature being formulated to take place via two electron steps, on the other hand, evidence is increasing that redox reactions favorably occur by single electron rather than two electron transfer processes. Thus, an answer to the questions above would yield not only a better insight into a biological process of major importance but also to general reaction mechanisms.

Synthesis and single electron reduction of $[\mathrm{Fe(NO)('N_HS_4')}]^+$

A single electron reduction of a nitrosyl complex was observed with $[\mathrm{Fe(NO)('N_HS_4')}]\mathrm{BF_4}$ ($\mathrm{N_HS_4'^{2-}}$ = dianion of bis(2-((2-mercaptophenyl)thio)ethyl)-amine) which was obtained from the corresponding carbonyl complex $[\mathrm{Fe(CO)('N_HS_4')}]$ (**1**) [2] according to eq. 1:

$$\mathrm{FeCl_2} + \mathrm{Li_2}\text{-}'\mathrm{N_HS_4'} + \mathrm{CO} \xrightarrow[\mathrm{THF}/-2\mathrm{LiCl}]{1\ \mathrm{bar}/20\,^\circ\mathrm{C}}$$



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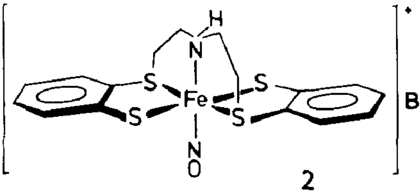
(1)

1 is a diamagnetic 18 electron carbonyl complex, in which the two $C_6H_4S_2$ units are connected by the $NH(C_2H_4)_2$ bridge such that the thioether S atoms occupy *trans* positions. Reacting this CO complex with $NOBF_4$ according to eq. 2, gives the

$$1 + NOBF_4 \xrightarrow[-CO]{20\,°C/CH_2Cl_2} \qquad (2)$$



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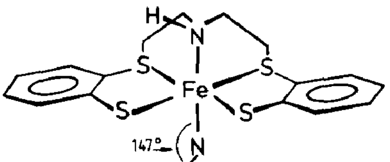
isoelectronic and, according to the ^{13}C NMR spectrum, also isostructural NO complex $[Fe(NO)('N_HS_4')]BF_4$ (**2**) [2]. The very mild reaction conditions and the retention of configuration indicate that the CO substitution takes place via the indirect way of a 'thionitrosylation' [3]. NO^+ primarily adds to a thiolato S donor, then the CO is released, and simultaneously the NO shifts to the vacant iron site, thus avoiding a coordinatively unsaturated intermediate which could isomerize by the well known square pyramidal ⇌ trigonal bipyramidal equilibrium of five coordinate metal complexes.

The $\nu(NO)$ band of **2** appears in the KBr-IR spectrum at 1880 cm^{-1}, indicating a linear FeNO entity. NO complexes with $\nu(NO) > 1860$ cm^{-1} are usually suited for nucleophilic addition reactions at the NO group [4], but such a reaction could not be observed so far. Instead, with hydrazine as well as azide ions, a reduction takes place already at low temperatures yielding the neutral 19 electron species $[Fe(NO)('N_HS_4')]$ (**3**) [5] (eq. 3), which is one of the rare 19 electron nitrosyl

$$2 \xrightarrow[-20\,°C/CH_2Cl_2]{+N_2H_4(\text{or } N_3^-)} \qquad + \text{other products} \qquad (3)$$



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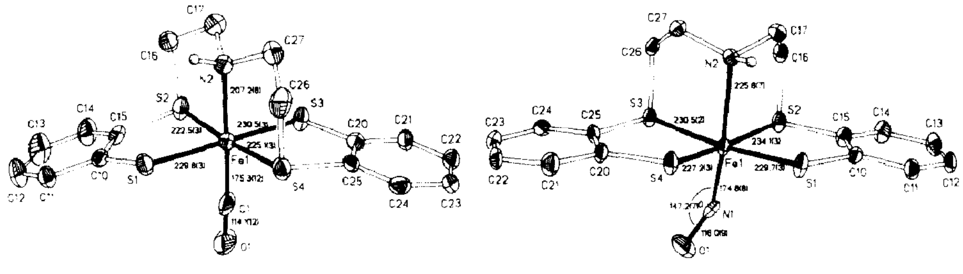
complexes [6] and to our knowledge, apart from $[CpW(NO)_2P(OPh_3)]$ [7], it is the only structurally characterized 19 electron nitrosyl complex which was obtained by reduction of a 18 electron species.

The major consequences of the addition of a nineteenth electron are: (1) The neutral NO complex is paramagnetic and has one unpaired electron (μ_{eff} 2.13 BM, 295 K). (2) During the reduction, an isomerization takes place leading to a *trans* → *cis* rearrangement of the thioether S donors. (3) The $\nu(NO)$ frequency decreases more than 250 wavenumbers from 1880 cm^{-1} down to 1620 cm^{-1}. (4) As X-ray structure analysis shows the FeNO group becomes bent with an angle of 147.2(7)°.

Decrease of the $\nu(NO)$ as well as the bending of the FeNO entity indicate that the odd electron resides in an orbital possessing mainly NO π^* character [4], and the metal bound nitrogen in the FeNO entity obtains a hybridization just halfway



	[pm]	[pm]
$\bar{d}_{\text{Fe-S(Thioether)}}$	223.5	232.8
$\bar{d}_{\text{Fe-S(Thiolato)}}$	230.1	228.4
$d_{\text{Fe-N(Amine)}}$	207.2(8)	225.8(7)

Fig. 2. Molecular structures and comparison of selected bond distances of (a) 18 electron $[Fe(CO)('N_HS_4')]$ and (b) 19 electron $[Fe(NO)('N_HS_4')]$.

between the 180° of *sp* and the 120° of sp^2 hybridization. **3** yields a relatively well resolved ^1H NMR spectrum with signals which are only little shifted isotropically, and an EPR spectrum for determining more exactly the localization of the odd electron could not be obtained yet. The X-ray structure analysis, however, shows clearly that the orbital, in which the odd electron is localized, does not have only π^*(NO) character, but must be anti-bonding also with respect to the metal sulfur ligand bonds. This follows from a comparison of the distances in the 18 electron CO complex **1** [2] and the 19 electron NO complex **3** [5]. (No single crystals of $[Fe(NO)('N_HS_4')]^+$ salts could be obtained yet). Figure 2 shows the molecular structures of **1** and **3** and lists the average distances of the bonds in the $[Fe('N_HS_4')]$ cores. The Fe–S(thiolato) distances stay almost unchanged, when going from **1** to **3**, but the Fe–S(thioether) distances increase quite noticeably, and most remarkable is the lengthening of the Fe–N_H distance by more than 18 pm.

This increase of bond distances certainly indicates a weakening of the respective bonds, and indeed, **3** is a highly reactive species [8]. With respect to the influence of the nineteenth electron upon distances and angles, **3** contrasts with $[C_5H_5W(NO)_2P(OPh)_3]$ [7]. A comparison of the structural parameters of $[CpW(NO)_2P(OPh_3]$ and the 18 electron species $[C_5H_5W(NO)_2Cl]$ shows that the nineteenth electron in this case does not markedly change the WNO angles nor (C_5H_5)–W distances, and the only major differences are an increase in the NWN angle and the N–O distances.

Thus one may summarize: If the metal coordination sphere is dominated by sulfur donors, it is possible to trap single electron reduction products of 18 electron nitrosyl complexes. The additional odd electron causes a strong bending of the MNO entity as well as a weakening of the metal ligand bonds.

H^+ coupled two electron reduction of $[Mo(NO)_2('S_4')]$

The reduction of $[Fe(NO)('N_HS_4')]^+$ stops after the transfer of one electron, a two electron reduction could not be achieved. This, however, was possible with the dinitrosyl complex $[Mo(NO)_2('S_4')]$ (**4**) ($'S_4'^{2-}$ = dianion of 2,3,8,9-dibenzo-

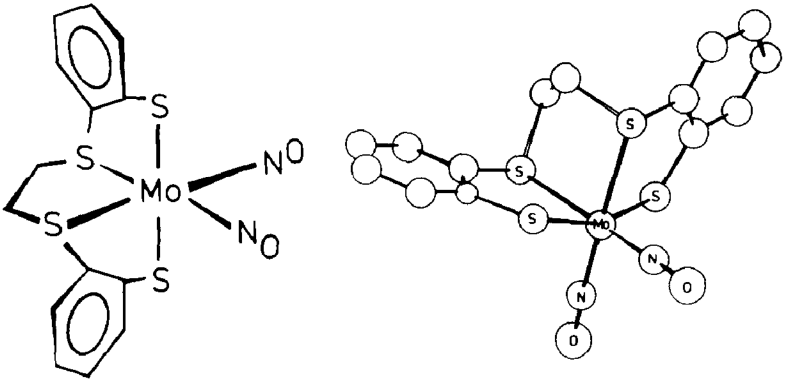


Fig. 3. Schematic drawing and molecular structure of $[\mathrm{Mo(NO)_2({}'S_4')}]$ (**4**).

1,4,7,10-tetrathiadecane) (Fig. 3). **4**, too, is a 18 electron complex with linear metal nitrosyl groups (176.8° average), its $\nu(\mathrm{NO})$ bands, however, appear at relatively low frequencies at 1765 and 1660 $\mathrm{cm^{-1}}$ [9]. Such NO complexes are not expected to be susceptible to nucleophilic attack at the NO groups or to reduction [4]. Contrary to these expectations, **4**, does react with a large variety of nucleophiles, and e.g. with phosphines, it yields the phosphineiminato complexes $[\mathrm{Mo(NO)(NPR_3)({}'S_4')}]$ [9b]. **4** reacts also with the nucleophile hydrazine, in this case, however, hydrazine acts as reducing agent, and in a stochiometric reaction according to eq. 4, $[\mathrm{Mo(NO)_2({}'S_4')}]$ is converted into $[\mathrm{Mo(NH_2O)(NO)({}'S_4')}]$ (**5**) [10].

$$[\mathrm{Mo(NO)_2({}'S_4')}] + \tfrac{1}{2}\mathrm{N_2H_2} \xrightarrow{\mathrm{THF}/20\,^{\circ}\mathrm{C}} \underset{\textbf{(5)}}{[\mathrm{Mo(NH_2O)(NO)({}'S_4')}]} + \tfrac{1}{2}\mathrm{N_2} \qquad (4)$$

The starting material and product differ by two hydrogen atoms only, and **5** is a neutral and diamagnetic complex. Since the addition of two hydrogen atoms is equivalent to adding two electrons plus two protons, reaction 4 is a proton coupled two electron reduction of **4** and represents the first chemical equivalent for the two electron reduction step leading from the NO to the hydroxylamine stage in the biological nitrate ⇌ ammonia interconversion.

5 crystallizes from DMF as **5** · DMF, the molecular structure of which is shown in Fig. 4. The X-ray structure determination shows that the reduction of **4** leads to an even stronger bending of one NO ligand such that it becomes side-on bound, the two protons added simultaneously being bound to the N atom. The distances in the three membered [MoON] ring system indicate single bonds between the atoms (d(Mo1–O1) 205.3(3) pm, d(O1–N1) 137.5(5), d(Mo1–N1) 210.3(3) pm), the MoN and NO distances of the remaining MoNO group indicate an increased backbonding in relation to $[\mathrm{Mo(NO)_2({}'S_4')}]$ (176.1(3) and 119.3(4) pm vs. 183.7 and 114.5 pm average). The two NH protons were located by difference Fourier synthesis; the formation of NH (instead of OH) bonds follows also from position of the DMF solvate molecule which is connected with **5** via a hydrogen bridge (d(N–H...O) 184.5 pm), as well as from IR ($\nu(\mathrm{NH})$ 3240 $\mathrm{cm^{-1}}$) and NMR spectra.

In the reduction according to eq. 4, two configurational isomers are formed. The one shown in Fig. 4 was characterized by X-structure analysis, that a second isomer forms in equal amounts is revealed by NMR spectroscopy: The ^{13}C NMR spectrum

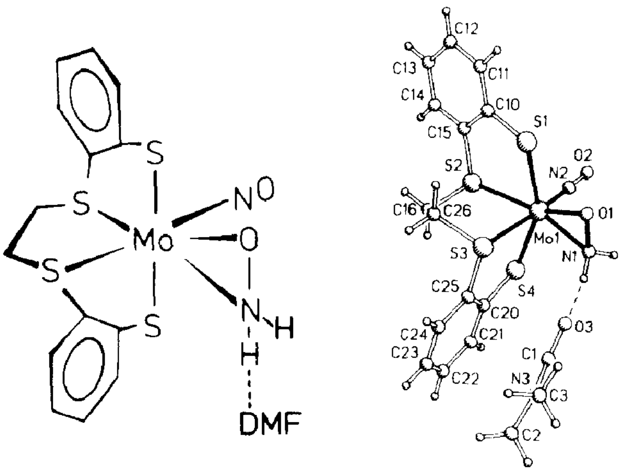


Fig. 4. Schematic drawing and molecular structure of [Mo(NH$_2$O(NO)('S$_4'$)]·DMF, **5**·DMF.

(67.940) MHz does not show fourteen signals, as expected for the fourteen magnetically inequivalent C atoms of the ('S$_4'$) ligand, instead, two sets of fourteen signals are observed. These two sets of fourteen signals each are also found at higher temperatures. Since the ^{13}C NMR spectrum does not change up to 75 °C in DMSO-d_6, the two isomers must be configurationally quite stable. The ^{1}H NMR spectrum (Fig. 5), too, is in agreement only with the presence of two isomers: four lines, arising from two different AB systems, are observed for the NH$_2$ protons. These NMR signals are temperature dependent giving rise to two signals only at +60 °C and one broad signal at +120 °C. This indicates that the NH$_2$ protons can exchange and eventually shift to the O atom. The NO atoms of the NH$_2$O ligand, however, stay in their original position as indicated by the ^{13}C NMR spectra.

The question concerning the structure of the second configurational isomer could be further settled by the ^{95}Mo NMR spectrum (17.061 MHz), which exhibits only a broad ^{95}Mo signal at δ −395 ppm (rel. (NH$_4$)$_6$Mo$_7$O$_{24}$) with a half-width of 760 Hz. On the one hand, the half-width presumably prevents resolution of the expected two Mo signals, on the other, it shows that the two Mo centers have very similar chemical environments and differ only in the position of the NH$_2$O ligand in relation to the [Mo(NO)('S$_4'$)] fragment.

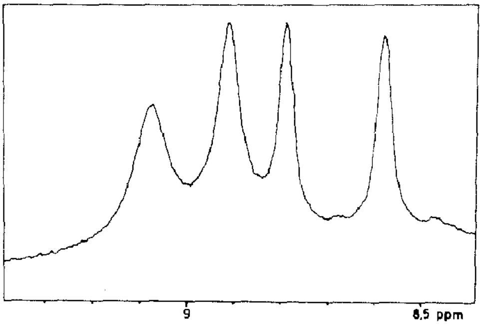
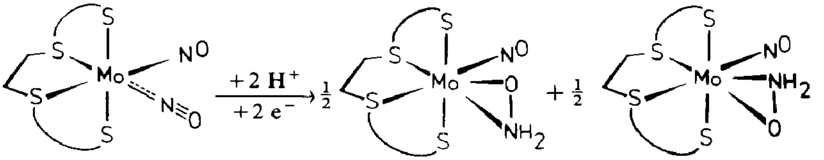


Fig. 5. NH region of the ^{1}H NMR spectrum (270 MHz) of **5** (in DMSO-d_6, 20 °C) (bulk product obtained according to eq. 4).

The 1/1 ratio of the two isomers is understandable in terms of the route of formation of $[Mo(NO)(NH_2O)('S'_4')]$: the reduction (eq. 4) is a proton-coupled two electron reduction, hydrazine serving as both proton and electron source (eq. 5).

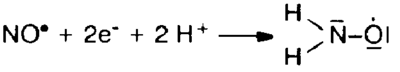
$$N_2H_4 \rightarrow N_2 + 4\,H^+ + 4e \qquad (5)$$

Upon reduction of **4** the bending of one of the two NO ligands can occur with equal probability 'upwards' or 'downwards' resulting in the formation of **5a** or **5b** (eq. 6) [15*].

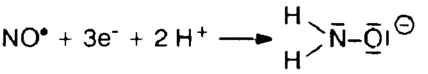


(4) **(5a)** **(5b)** (6)

Critical for understanding the mechanism of reduction, for describing the NH_2O ligand as well as for the electron balance, is the question whether electrons of the metal are involved in the $NO \rightarrow NH_2O$ reduction, i.e, whether the $NO \rightarrow NH_2O$ reduction is a true 2 electron reduction leading to a hydroxylaminyl ligand (eq. 7a) or whether it is a 3 electron reduction yielding a hydroxylamido(1 −) ligand (eq. 7b), since the Mo center is contributing one electron, e.g. according to eq. 7c.



$$NO^{\bullet} + 2e^- + 2\,H^+ \longrightarrow H_2\bar{N}{-}\overset{\cdot}{\underline{\bar{O}}}| \quad \text{Hydroxylaminyl} \qquad (7a)$$



$$NO^{\bullet} + 3e^- + 2\,H^+ \longrightarrow H_2\bar{N}{-}\underline{\bar{O}}|^{\ominus} \quad \text{Hydroxylamido(-1)} \qquad (7b)$$

$$Mo^{II} \longrightarrow Mo^{III} + 1e^- \qquad (7c)$$

The only very small difference in the ^{95}Mo shifts of **4** (δ −512) and **5** (δ −395) indicates that the reaction according to equation 4 does not lead to a change in the oxidation state of the Mo centers. ^{95}Mo resonances cover a shift range of 10000 ppm, and even for Mo^{II} complexes, a range of more than 2000 ppm is observed [11]. Therefore, the only marginal ^{95}Mo shift difference between **4** and **5** allows to regard both complexes as Mo^{II} species. Accordingly, the NH_2O species must be a neutral hydroxylaminyl ligand, and the 15 electron fragment $[Mo(NO)('S'_4')]$ is stabilized in **4** by the 3 electron donor $|\dot{N}{\equiv}O|$ and in **5**, isoelectronically, by the 3 electron donor $|NH_2{-}\dot{O}|$ (Scheme 1).

5 is by no means the first complex with a NH_2O ligand. Numerous other complexes with such a ligand [12] and even complexes containing the closely related HNO species were described, where the HNO may be regarded as either anionic hydroxylamido(2 −) or neutral nitroxyl ligand [12]. As it appears, however, none of these

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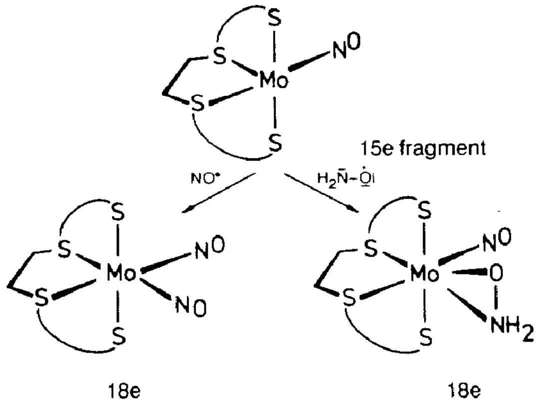
* Reference number with asterisk indicates a note in the list of references.

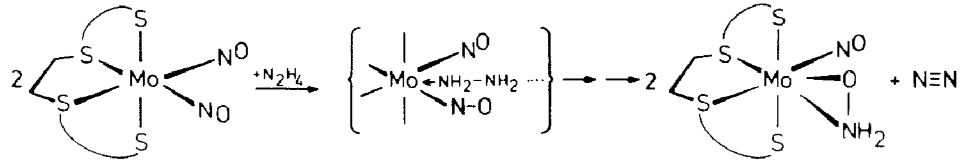


Scheme 1.

complexes was obtained by a genuine reduction of a nitrosyl complex via intermolecular transfer of electrons. NH_2O and NHO complexes were also suggested in order to explain the electrochemical redox reactions of $[Ru(NO_2)(tpy)(bpy)]^+$ (tpy = 2,2′,2″-terpyridine; bpy = 2,2′bipyridine), these species, however, were not isolable [14].

Why does a one electron reduction occur in the case of the iron complex, in the case of the molybdenum complex, however, a two electron reduction? In both cases, sulfur donors dominate the coordination sphere of the metals, eventually stabilizing unstable 19 electron intermediates. Considering the differences, e.g. charge, denticity of the ligands, metal center of the two complexes, the decisive difference could be that the molybdenum center can increase its coordination number from six to seven. This is not found with iron complexes and may favor the rapid transfer of the second electron in the molybdenum case, since the doubly reduced NO ligand can bind side-on.

The facile change of molybdenum(II) complexes between the coordination number six and seven allows also to suggest a mechanism for the reduction (eq. 4),



(8)

according to eq. 8. In the primary step, the hydrazine coordinates to the Mo center yielding a seven coordinate species having one bent MoNO group. Then, the electron as well as proton transfer processes take place leading to N_2 which is released such that the vacant site can be filled by the NH_2O ligand.

Conclusion

The results show that under certain circumstances the reduction of ligating NO to the hydroxylamine stage by intermolecular electron transfer reactions is easily achieved. If the coordination sphere of the metal center is dominated by sulfur donor atoms, 19 electron complexes are stabilized, if the metal center can increase its coordination number, a proton coupled double electron transfer takes place leading to side-on bound hydroxyl aminyl species. It will be interesting to see which structures and reaction mechanisms will be found for the active centers of nitrous oxide reductases.

Acknowledgement

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15 One referee suggested that isomer **5a** should easily transform into isomer **5b** by a "rocking" motion of the η^2-NH_2O ligand. As revealed by NMR spectroscopy, such a transformation does obviously not take place, and in this respect, the η^2-NH_2O ligand being bound via two σ-bonds to the Mo center differs noticeably from olefin ligands or related species. **5a** and **5b** are diastereometric, but they could not be separated by chromatography.