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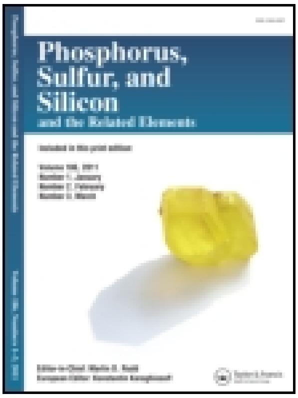

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Coordination Compounds of S- and Se-Containing Organic Ligands as Catalysts of Oxidation Reaction Under N_2O Action

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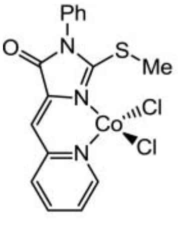
GRAPHICAL ABSTRACT



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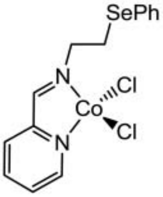

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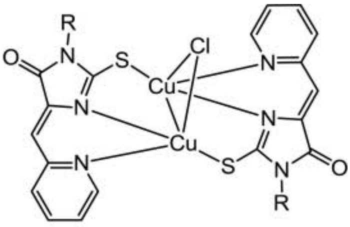

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Abstract *Nitrous oxide (N_2O) would be preferable to many other oxidants because in the reactions of N_2O with organic compounds the only byproduct is N_2, which is perfect from the point of view of "green" chemistry. We recently reported a series of new sulfur- and selenoorganic ligands, their coordination compound with Co(II) or Cu(I,II), and the possibility for these complexes to activate nitrous oxide in the oxidation reactions with phosphines and alkenes. The electrochemical data confirm the stability of reduced form of investigated complexes and the capacity of these complexes to associate with nitrous oxide.*

Keywords Nitrous oxide; oxidation; organic ligands; catalysis

INTRODUCTION

Nitrous oxide (N_2O) is an underutilized byproduct of chemical processes involving nitric acid. Because of the increased use of nitrate containing fertilizers in agriculture, a large amount of nitrous oxide is produced by denitrifying bacteria living in soil and seawater and subsequently released to the atmosphere. This way, nitrous oxide has become the second most important greenhouse gas (after CO_2). Hence, the properties of nitrous oxide and its reactivity are not only of interest for bioinorganic chemistry, but also of global importance.

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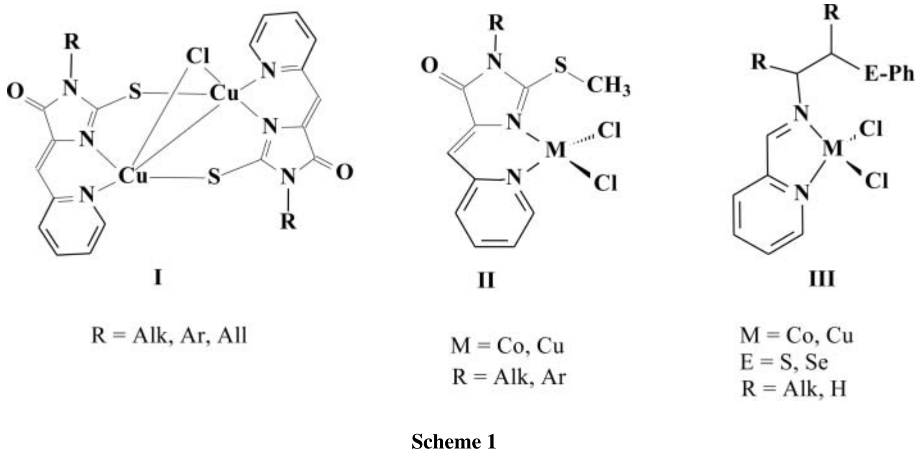
Although the reduction of N_2O to dinitrogen and water is highly exothermic ($\Delta G^{\circ}=-80$ kcal/mol), this gas is metastable and unreactive due to a kinetic barrier to its decomposition.[1] In nature, conversion of N_2O to N_2 and H_2O is catalyzed under ambient conditions during microbial dentrification by the metalloenzyme nitrous oxide reductase (N_2O-reductaze). N_2O reductase catalyzes the two-electron reduction of N_2O ($N_2O + 2H^+ + 2e- \rightarrow N_2 + H_2O$). X-ray crystallographic and spectroscopic studies have identified the active site of N_2OR as a μ-sulfido-tetracopper cluster with a distorted tetrahedral shape that cycles through tetracopper(I) and mixed-valent (with one copper(I) and three copper(II)) states during catalysis. A mechanism for N_2O reduction involves μ-1,3-coordination and bending of N_2O between two of the copper ions with the sulfide acting to facilitate electron delocalization during the redox process.[2]

Despite the biological and environmental significance of nitrous oxide, not much is known about the coordination chemistry of this molecule. Previously reported N_2O complexes formed with a redox active metal can be rapidly converted to N_2 and metal-oxidized species, $O{=}M^{n+2}$, N_2O complexes are usually detected only as transient species.[3] In fact, little metal complexes containing the N_2O ligand have been identified by X-ray diffraction. In $[Ru(NH_3)_5(N_2O)]\ X_2$, N_2O ligand has been found to coordinate to the Ru^{II} ion in a linear end-on mode through the terminal N atom.[4]

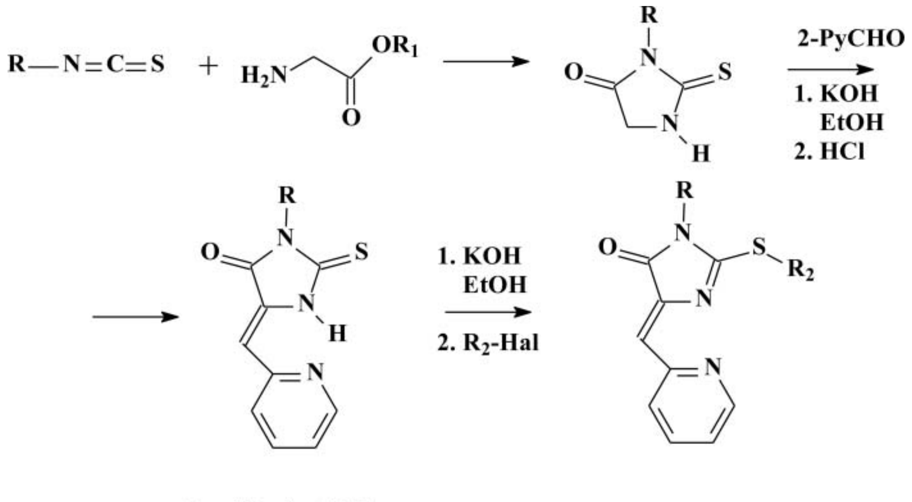
So, while a nitrous oxide has to be thermodynamically powerful oxidant, the oxidizing processes are very slow except at high temperatures. Alkenes can be oxidized by N_2O, but the reactions required temperatures of at least 300 °C.[5] Some small secondary alcohols were oxidized by N_2O at room temperature in the presence of platinum "black."[6] It describes the oxidation of phosphines by supercritical N_2O at 100 °C without catalyst.[7]

A few catalytic reactions of N_2O using metal-mediated catalysis had been found. The oxidation of Ph_3P into $Ph_3P{=}O$ by N_2O at room temperature was performed in the presence of phtalocyanyne complexes of Ru, but the yields of this reaction are not satisfactory.[8] Another example is the oxidation of olefins into corresponding epoxides by N_2O in the presence of manganese-substituted polyoxometalates.[9]

Our scientific group recently reported a series of new sulfur- and selenoorganic ligands and their coordination compounds with Co(II) or Cu(I,II), which can activate nitrous oxide in the oxidation reactions with phosphines and alkenes. The types of investigated complexes are given under Scheme 1.



Scheme 1



R = Alk, Ar, Allyl R_1 = H, Me, Et

R_2 = Me, CH_2COOEt, $(CH_2)_2COOEt$, $(CH_2)_3COOEt$

Scheme 2

Organic ligands in the complexes of types **I** and **II** are the 5-pyridylmethylene-substituted 2-thiohydantoins and 5-pyridylmethylene-3,5-dihydro-4H-imidazol-4-ones, respectively. Type **III** complexes have in the structure sulfur- or selenium-containing imino-pyridine ligands.

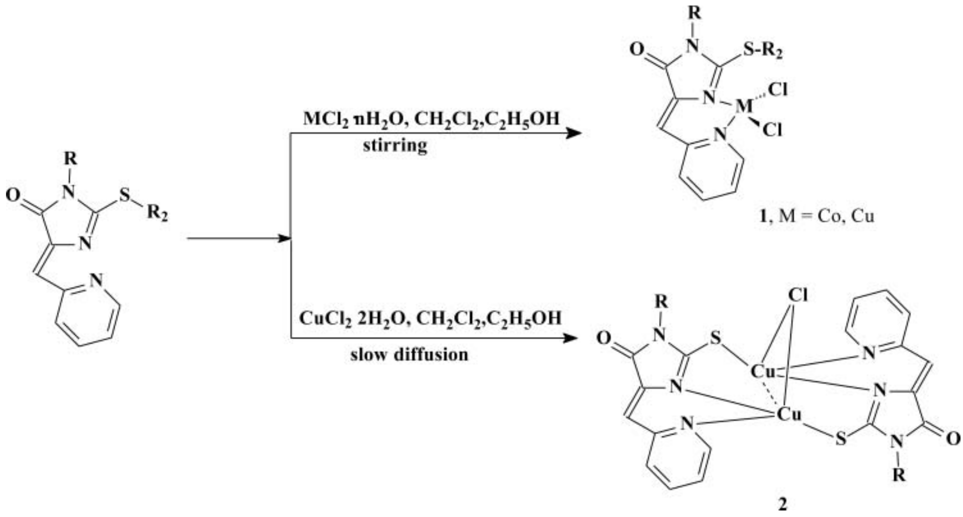
The synthesis of the thiohydantoin derivatives is outlined in the Scheme 2.[10] The initial 3-substituted 2-thiohydantoins were prepared by the reaction of isothiocyanate with amino acid ester with the yields to 85%. 5-Pyridylmethylene-substituted derivatives were prepared by Knoevenagel condensation between heteroaromatic aldehydes and the thiohydantoin core under basic catalyses. The key step in the formation of the dihydro-imidazolone backbone was achieved by S-alkylation reactions under basic conditions.

To obtain the target coordination compounds, the method of slow diffusion of ligand solution in CH_2Cl_2 to the cobalt or copper chloride solution in EtOH or CH_3CN was used. In the case of cobalt salt, the isolated coordination compounds have the composition $LCoCl_2$ (Scheme 3).[11]

As a result of the reaction of dihydro-imidazolone ligands with copper(II) chloride, surprisingly, different types of complexes were isolated, depending on the character of substituent at sulfur atom and the reaction condition (Scheme 3). In the reaction with S-methylated derivatives, the complexes, analogous to these with $CoCl_2$, were obtained.[12]

However, in the case of carbethoxy-substituted ligand, we have obtained two different types of complexes: if the complexation reaction was carried out under stirring of ligand with copper chloride, the fast precipitation of dark-brown solid of complex **1** with the composition of $LCuCl_2$ took place. However, if we obtained the complex by slow diffusion of ligand solution to the copper chloride solution, we have isolated the different coordination compound.

X-Ray analysis indicated the formation of unexpected mixed-valence thiolate copper complexes **2** in which the anionic ligand behaves as tridentate bridge between two copper centers. Both copper atoms in complexes **2** have the same coordination sphere geometry,



Scheme 3

namely, a tetragonal pyramidal. Such coordination geometry suggests that this complex has a delocalized mixed-valence form with a [$Cu^{+1.5}Cu^{+1.5}$] redox state. Thus, in the case of ligands of this type, S-desalkylation and reduction of copper atom occur during the complex formation. The reducing agent is probably ethyl alcohol.

Complexes **2**, containing Cu(I) and Cu(II) ions, may be regarded as a low molecular model of N_2O-reductase. Both natural enzyme and synthesized complexes contain copper(I) and copper(II) atoms, nitrogen and bridged sulfur donors, and the distances between copper atoms are practically identical for the N_2O-reductase and complex **2**.

We have investigated the possibility of the reaction of complex **2a** (**2**; R = Ph) with nitrous oxide. First, we have studied the electrochemical behavior of this complex itself and in the presence of N_2O. At scanning potential in cathodic region, three one-electronic reversible peaks were observed on cyclic voltammetry (CVA) curve of a complex **2a**. These peaks are probably due to three consecutive reduction processes (Scheme 4):

In the presence of N_2O, the first reduction peak does not change position and remains reversible, thus pointing to the fact that substrates are not bonded by initial complex. However, at the potential of second cathodic peak ($E^{\text{Red}} = -1.13$ V), the increase of the current and the decrease of next wave current were observed. It means that initial complex **2a** does not take part in catalytic cycle, as also the natural N_2O-reductaze, a catalytic active form of which is the reduced "all-copper(I)" form. The current increase is consistent with an electrocatalytic process at this potential. We suppose that intermediate **B** can coordinate N_2O as additional ligand at a vacant coordination position.

$$\begin{array}{ccccccc} & E_{pc}/E_{pa} = 0{,}05/0{,}11\ \text{B} & & E_{pc}/E_{pa} = -1{,}13/-1{,}08\ \text{B} & & E_{pc}/E_{pa} = -1{,}26/-1{,}18\ \text{B} & \\ \mathrm{Cu^{1,5}Cu^{1,5}} & \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} & \mathrm{Cu^{1}Cu^{1}} & \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} & \mathrm{Cu^{0,5}Cu^{0,5}} & \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} & \mathrm{Cu^{0}Cu^{0}} \\ \mathbf{A} & & \mathbf{B} & & \mathbf{C} & & \mathbf{D} \end{array}$$

Scheme 4

Apparently, only N_2 (not NH_3) forms under catalytic N_2O reduction because the NH_3 re-oxidation peak under $E_{pa} \sim 1.0$ B is not observed at CVA reverse scan in the anodic region after carrying of cathodic potential $E_{pc} = -1.0$ V.

Note that in the absence of a complex **2a**, the electrochemical reduction of N_2O occurs only at very negative potentials (−2.12 V).

We have investigated the catalytic activity of compound **2a** in the model reaction of triphenylphosphine oxidation by N_2O. The reactions were carried out both in the presence of complex **2a** and without it, and also in the presence of inorganic salts of copper(I) or copper(II). Triphenylphosphine oxide was obtained with quantitative yield only in the presence of complex **2a**.

Thus, complex **2a** can be regarded as actual catalyst of phosphines oxidation. This catalysis mimics the behavior of the N_2ORs enzymes, which reduce nitrous oxide by two electrons, yielding dinitrogen and water.

We have also investigated by CVA the interaction of cobalt complex **1a** (**1**; R = Ph, M = Co) with N_2O.[13] Complex **1a** itself reduces on first two-electron stage "to metal" giving the complex zero-valent cobalt. At slow scan rate (20 mV/s), the potential of first reduction peak in the presence of N_2O shifts to less negative potential, whereas the potential of second reduction peak shifts to more negative potential.[13] These facts confirm the interaction of both initial and reduced form of complex **1a** with N_2O. At one time, increase in first wave current and decrease in next wave current were observed. The increase in current is consistent with an electrocatalytic process at the potential of the Co(II)/Co(0) redox couple.

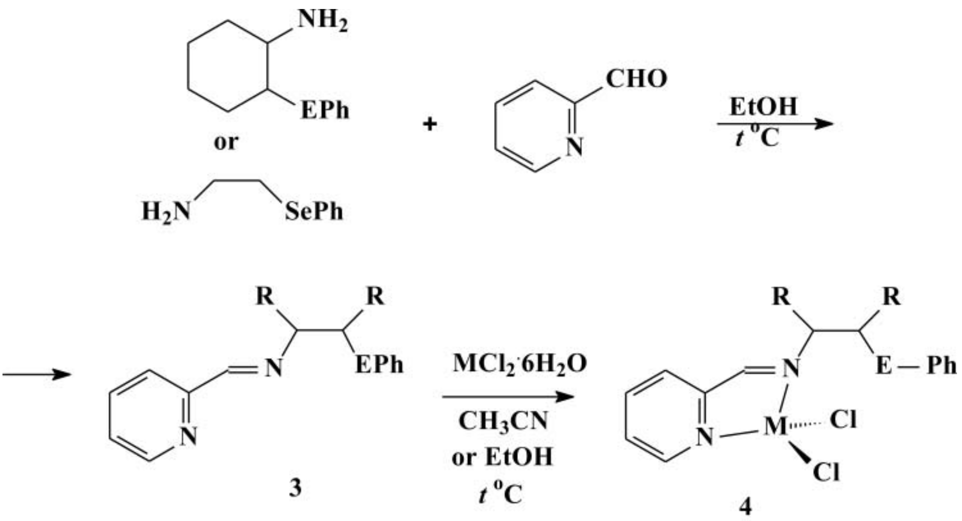
The presumable mechanism of the N_2O interactions with **1a** in the electrochemical cell involves two parallel processes:[13] (a) the initial reduction of complex **1a** followed by complexation with N_2O and regeneration of **1a** accompanied by N_2 deliberation, and (b) the complexation of **1a** with N_2O at first followed by reduction of N_2O-containing complex with N_2 evolution.

We have attempted to use complex **1a** for activation of nitrous oxide in chemical reactions. We have found that if N_2O is bubbled to a solution of complex and Ph_3P at room temperature, catalytic oxidation to O=PPh_3 takes place.[13] Second, we have found that norbornene reacts with nitrous oxide in the presence of complex **1a** at room temperature forming 3-oxatricyclo[3.2.1.0^{2,4}]oct-6-ene **with** yields upto 25%.[13] In conclusion, complex **1a** is capable of catalyzing norbornene and Ph_3P oxidation by nitrous oxide under ambient conditions.

It is unlikely that the oxygen source was anything other than N_2O. The reactions of norbornene with air in the presence of **1a** or with N_2O in the presence of $CoCl_2$ at the same conditions gave 0% oxidation products. The N_2 byproduct is assumed but not experimentally confirmed.

The final type of studied complexes was the sulfur- or selenium-containing pyridylimines. The target ligands **3** were obtained by the reactions of 2-chalcogen-substituted amines with 2-pyridine carboxaldehyde at almost quantitative yield.[14] Metal complexes **4** precipitated after boiling of ligands with equimolar amount of cobalt(II) or copper(II) chloride[14] (Scheme 5). Metal atoms in these complexes have a distorted tetrahedral ligand environment; they are coordinated by two chloride anions and two nitrogen atoms of pyridine and imine fragments; selenium or sulfur atoms do not participate in metal coordination.

Ligands and complexes of this type were studied by CVA.[14] For example, ligand **3a** (**3**; E=Se, M=Co, R,R=(CH2)4) undergoes a two-step reduction at substantially negative potentials. The additional quasi-reversible peak on complexes **4a** (**4**; E=Se, M=Co, R,R=$(CH_2)_4$) CVA curves corresponds to two-electron reduction at metal.



E = S, Se; **M** = Co, Cu; **R** = H or **R,R** = $(CH_2)_4$

Scheme 5

Under the reduction of complex **4a** in the presence N_2O at the slow scan rates, the intensity of first cathodic peak increases, along with a concomitant loss of reversibility. At the same time, the following peaks became low intensive. These facts are related to an electrocatalytic process at the formal potential of Co^{II}/Co^0 reduction. Thus, complex **5** is capable of catalyzing the reduction of nitrous oxide to N_2 under mild conditions at a moderate potential ($E_{pc} < -1.0$ B).

During tests on selenium-containing complexes **4a, 4b** (**4**; E = Se, M = Co, R = H) for activation of nitrous oxide in chemical reactions, we found that norbornene reacts with nitrous oxide in the presence of complexes under normal pressure at room temperature forming 3-oxatricyclo[3.2.1.$0^{2,4}$]oct-6-ene **with** yields up to 90%.

Also, it has been found that if N_2O is bubbled to a solution of the complex and Ph_3P at room temperature, catalytic oxidation to $OPPh_3$ takes place.

It may be specially noted that sulfur-containing analogs of complex **4a,b**, based on CVA data and model oxidation reaction results neither react with nitrous oxide nor catalyze phosphine oxidation under N_2O action.

In summary, all types of investigated complexes, namely, complexes with 5-pyridylmethylene-substituted thiohydantoins, pyridylmethylene-dihydro-imidazolones, and selenium-containing imino-pyridines, are capable of catalyzing oxidation reactions of norbornene and Ph_3P by nitrous oxide under ambient conditions. The best results for norbornene oxidation were demonstrated by selenium-containing cobalt complexes, for phosphine oxidation - by the mixed-valence copper thiohydantoin complex.

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