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In Situ Trapping of NO: Application of *S*-Nitroso Derivatives for Metal Nitrosyls Synthesis

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Several known nitrosyl complexes of Ru, Rh, and Co have been synthesized using *S*-nitroso organic compound (*S*-nitrosocysteine). Physicochemical methods such as IR, magnetic measurements, conductance measurements, and elemental analysis were used for characterization of the reaction products.

In situ trapping of NO as a synthetic procedure for metal-nitrosyls using *N*-nitroso derivatives ($^{R'}_{R}{>}$N-NO) has been exploited in our earlier work[1] and an attempt was made there to generalize the method and to reduce multistep process for nitrosyl synthesis to a single-step one. It was also pointed out that the reactivity of a particular *N*-nitroso derivatives is a function of the substituents R and R′.

Because of our continuing interest in finding new procedures for metal nitrosylation, we looked into the possibility of employing recently synthesized *S*-nitroso derivatives[2] as nitrosylating agents which undergo dissociation reaction (2 RS-NO$\rightarrow$R-S-S-R+2 NO) at varying temperatures depending upon the organic moiety linked to the sulfur. The temperature dependence of *S*-nitroso derivatives has further added an interest in us because for most of the cases the percentage yield of a particular metal nitrosyl using NO as a nitrosylating agent is temperature dependent. (Some metal nitrosyls can not be synthesized even at room temperature[3]). Thus there exists a possibility of choosing a S-nitroso derivative for a particular metal nitrosyl synthesis. The focus of this short note is to study the nitrosyl group transfer in solution from S-nitrosocysteine to metal centers (Ru, Rh, Co) in presence of other coligands.

Experimental

Chemically pure grade chemicals were used throughout. Microanalytical work has been carried out in the Microanalytical Lab. of the Indian Institute of Technology, Kanpur. Infrared spectra have been recorded on a Perkin-Elmer 580 Spectrophotometer in KBr discs. Magnetic measurements were made on a Guoy balance at room temperature. The results are given in Table 1.

Synthetic Reactions. Following are the procedures for the reactions of *S*-nitrosocysteine with the metal ions and their complexes. *S*-Nitrosocysteine was prepared by the literature method[4,5] (Cystine hereafter is referred as cys-cys).

(A) Reaction of $RuCl_3\cdot xH_2O$ with *S*-Nitrosocysteine in the Presence of Triphenylphosphine. 40 ml of a solution containing 25 ml of ethanolic solution of $RuCl_3\cdot xH_2O$ (0.5 mmol), triphenylphosphine (2 mmol), 15 ml of *S*-nitrosocysteine (0.48 mmol) in tris solution was heated under reflux for 40—45 min, whereupon shining yellow crystals of [Ru(cys-cys)$_2$Cl(NO)] were separated on cooling the solution. Crystals were filtered, washed with water, ethanol

Table 1.

Compound	Analysis: Calcd (Found)/%				
	C	H	N	X	S
[RuCl(NO)(cys-cys)$_2$]H$_2$O	21.6 (21.8)	3.6 (4.1)	10.5 (10.5)	5.4 (4.8)	19.2 (21.5)
[RuCl$_2$(NO)(PPh$_3$)$_2$(cys-cys)]	52.2 (53.9)	4.3 (4.1)	4.3 4.5)	7.1 (7.7)	6.4 (6.5)
[RuCl$_3$(NO)(PPh$_3$)$_2$]	56.9 (55.7)	4.1 (3.0)	2.0 (1.9)	14.3 (14.0)	— —
[RhCl$_2$(NO)(PPh$_3$)$_2$]	59.3 (58.7)	4.1 (3.8)	1.9 (2.3)	9.7 (10.4)	— —
[RhCl$_2$(NO)(cys-cys)(PPh$_3$)]	—	—	—	—	—
[CoCl(NO)(bpy)$_2$]ClO$_4$	44.8 (44.8)	3.0 (3.1)	13.0 (12.7)	12.8 (11.8)	— —
[Co(NO)(NO$_2$)(bpy)$_2$]ClO$_4$	42.7 (42.9)	2.8 (3.1)	14.9 (14.7)	6.2 6.3)	— —

and dried under vacuum.

(B) Reaction of $[RuCl_2(PPh_3)_3]$ with *S*-Nitrosocysteine. 15 ml of an aqueous solution of *S*-nitrosocysteine (0.48 mmol) was added to 10 ml ethanolic solution of $[RuCl_2(PPh_3)_3]$ (0.05 mmol) and the reaction mixture was heated to reflux for 40—45 min whereby a yellowish orange colored compound $[Ru(NO)Cl_2(cys\text{-}cys)(PPh_3)_2]$ was separated. It was filtered and washed as in (A) and dried in vacuum.

(C) Reaction of $[RuCl_2(PPh_3)_3]$ with S-Nitrosocysteine in Presence of $HgCl_2$. The procedure for carrying out the reaction was the same as that given in "B" except that 0.05 g of $HgCl_2$ was added to the reaction mixture. It resulted in the formation of a compound which was analyzed as $[Ru(NO)Cl_3(PPh_3)_2]$.

(D) Reaction of $[RuCl_2(PPh_3)_4]$ with *S*-Nitrosocysteine. 5 ml of an aqueous solution of *S*-nitrosocysteine was allowed to react with 10 ml of an ethanolic solution of $[RuCl_2(PPh_3)_4]$ by the procedure given in "B" whereupon $[Ru(NO)Cl_2(cys\text{-}cys)(PPh_3)]$ was precipitated out.

(E) Reaction of $[RhCl(PPh_3)_3]$ with *S*-Nitrosocysteine. A solution of $[RhCl(PPh_3)_3]$ (0.1 mmol) in 15 ml of ethanol was allowed to react with 15 ml of an aqueous solution of *S*-nitrosocysteine (0.5 mmol), according to the procedure given in "B" whereby $[Rh(NO)Cl_2(PPh_3)]$cys-cys was separated

The same reaction when carried out in presence of $HgCl_2$ yielded $[Rh(NO)Cl_2(PPh_3)_2]$.

(F) Reaction of $CoCl_2\cdot 6H_2O$ with *S*-Nitrosocysteine in Presence of $LiClO_4$ and 2,2′-Bipyridyl. $CoCl_2\cdot 6H_2O$ (0.25 g) and $LiClO_4$ (0.2 g) were dissolved in 20 ml of absolute ethanol and the solution was deaerated by flushing with nitrogen. A solution of 2,2′-bipyridyl (0.37 g) dissolved in hot ethanol (10 ml) was slowly added to the $CoCl_2$ solution under nitrogen, followed by the addition of *S*-nitrosocysteine (0.25 g) in 15 ml water. The resulting solution was stirred at room temperature for 30 minutes, whereby brown microcrystalline compound $[Co(bpy)_2Cl(NO)]ClO_4$ was separated. It was filtered, washed with ethanol, ether and dried under vacuum.

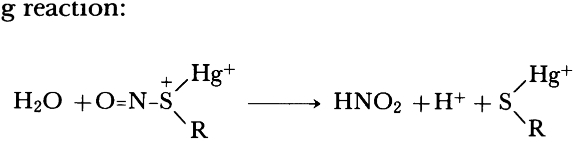
(G) Reaction of $CoCl_2\cdot 6H_2O$ with *S*-Nitrosocysteine in the Presence of $LiClO_4$, $NaNO_2$, and 2,2′-Bipyridyl. 0.15 g 2,2′-bipyridyl, 0.5 g $LiClO_4$, and 0.04 g $NaNO_2$ were mixed in 10 ml of ethanolic solution of $CoCl_2\cdot 6H_2O$ (0.15 g) and deaerated with N_2 gas, followed by the addition of 15 ml of *S*-nitrosocysteine solution in water. The color of the solution turned brown and finally a yellowish brown solid was separated out. It was filtered, washed with ethanol and ether and dried under vacuum. The compound was analyzed for $[Co(bpy)_2(NO)(NO_2)]ClO_4$.

Results and Discussion

The empirical formulae of the compounds resulting by the interaction of *S*-nitrosocysteine with metal ions are enlisted in Table 1. The bright yellow diamagnetic Ru(II) complex $[RuCl(NO)(cys\text{-}cys)_2]$ exhibited in its IR spectrum a band at 1870 cm^{-1} corresponding to $\nu(NO)$ besides the characteristic bands of cystine. The positions of all cystine bands (3500, 2900, 2565, 1742, 1577, 1521, 1231, 1216, and 876 cm^{-1}) except one around 1700 cm^{-1} (assigned to $\nu(CO)$ of COO^- group) remained constant. The lowering of 1700 cm^{-1} band position suggested bonding of ruthenium through COO^- moiety. Presuming ruthenium in +2 oxidation state with a formal charge of +1 on NO [$\nu(NO)$, 1870 cm^{-1}] the charge balance required cystine to be bonded with ruthenium as uninegative ion (Dipositive ruthenium in the complex is also suggested by its diamagnetic nature). It is therefore, assumed that the binding of cystine with ruthenium occurs through COOH group after deprotonation. Further six being the preferred coordination number of Ru(II) in its complexes[6] each cystine anion should provide two bonding sites to the metal center which could be either another oxygen, sulfur or nitrogen atom. Although it is difficult to decide the second donor site, but since the positions of other IR bands assigned to cystine remained practically unaltered, we tentatively assume oxygen atom of the COO^- group to be another bonding site. It is, however, only tentative.

An orange yellow complex having an empirical formula $[RuCl_2(NO)(PPh_3)_2(cys\text{-}cys)]$ has been obtained by the reaction of $[RuCl_2(PPh_3)_3]$ with *S*-nitrosocysteine. The IR spectrum exhibited the characteristic bands of PPh_3 and cystine. The position of $\nu(CO)$ of cystine also shifted to lower wave number suggesting the bonding of ruthenium with carboxyl group after deprotonation because of the charge balance as discussed in the preceding paragraph.

It appears that in both Ru(II) complexes sites above cystine formed during the decomposition of *S*-nitrosocysteine also coordinated to ruthenium along with NO group. In order to inhibit the cystine coordination during the reaction, a strategy of removing the cystine from the reaction site formed after decomposition of *S*-nitroso compound was thought. If the reaction is performed in presence of $HgCl_2$, the latter will not only catalyze the decomposition of *S*-nitroso compound[7] but will also pickup preferentially the formed organothio radical leaving NO radical for coordination with the metal ion in accordance with the following reaction:



$$H_2O + O{=}N\text{-}\overset{+}{S}(Hg^+)(R) \longrightarrow HNO_2 + H^+ + S(Hg^+)(R)$$

Thus, the reaction when carried out in the presence of excess $HgCl_2$ yielded pure $[RuCl_3(NO)(PPh_3)_2]$ in our reactions.

Similar to ruthenium complexes the reaction of $[RhCl(PPh_3)_3]$ with *S*-nitrosocysteine yielded a mixture of $[RhCl_2(NO)(PPh_3)(cys\text{–}cys)]$ and $[RhCl_2(NO)(PPh_3)_2]$. However, the same reaction in presence of $HgCl_2$ yielded pure literature known compound $[RhCl_2(NO)(PPh_3)_2]$.

The reaction of Co(II) salts with the *S*-nitroso compound did not yield a complex having bonded cystine even under varying reaction conditions. These reactions, however, yielded pure literature known complexes (Table 1). Possibly Co(II), being 'a' class metal ions may not bind preferentially with sulfur-containing cystine in presence of a better base, viz 2,2′-bipyridyl. The literature known complexes viz. $[RuCl_3(NO)(PPh_3)_2]$,[8] $[RhCl_2(NO)(PPh_3)_2]$,[9] $[CoCl(NO)(bipy)_2]ClO_4$,[10] $[Co(NO_2)(NO)(bpy)_2]ClO_4$[10] were identified by comparing their mp mixed mp spectral (IR, UV, and visible) and magnetic properties with the authenticated samples prepared by the literature methods.

It is evident from the above discussion that there exists a definite possibility of applying successfully *S*-nitrosococysteine, in particular, and *S*-nitroso derivatives, in general, for metal nitrosylation reactions. It is also obvious that the competitive reaction of the generated organothio radical to link with the metal ion (particularly b-class) along with its dimerization can be inhibited by adding excess $HgCl_2$ which not only assists in removing the thio radical from the reaction but also catalyzes the decomposition of S-nitroso compounds. Further work in this direction is in progress where the application of the method will be utilized for the nitrosylation of other metal ions with other *S*-nitroso derivatives, especially those having stability at low temperature. The latter reactions will be carried out with those metal ions where nitrosyls are obtained only at low temperature.

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