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Synthesis and Study of Some New Four-coordinated Nickel Nitro- and Nitrosyl-complexes. A New Ni(NO_2)–Ni(NO) Redox Couple

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Introduction

It is well known [1–4] that transition metal nitro-complexes undergo O-atom transfer reactions to inorganic substrates such as CO, NO and PR_3. These reactions can be made catalytic by reoxidation of the resulting nitrosyl complex using atmospheric oxygen as the oxidant. Very recently, Andrews and Kelly [5] reported some interesting new applications of the transition metal nitro–nitrosyl redox couples to the catalytic air oxidation of organic substrates such as olefins and isonitriles. Continuing our interest on the chemistry of nickel nitrosyl complexes [6], we report here our preliminary results concerning i) the synthesis and structural investigations of some new (tri-n-butylphosphine)(N-monoalkyldithiocarbamate)-(nitro)nickel(II) complexes of the general formula $Ni(NO_2)(S_2CNHR)(PBu^n_3)$ and ii) the study of the O-atom transfer reactions to CO, which these complexes undergo rapidly in mild conditions, yielding a new series of nickel nitrosyl complexes and CO_2. The nitrosyl complexes are easily reoxidized to the starting material by atmospheric oxygen at room temperature and atmospheric pressure. Due to the facile interconversion of the nitro- and nitrosyl nickel complexes, the $Ni(NO_2)$–Ni(NO) redox couple was found to be a potential homogeneous catalyst for the reaction between O_2 and CO.

Experimental

Physical Measurements

Infrared spectra were recorded in the region 4000–250 cm^{-1} on a Perkin-Elmer 467 spectrophotometer using KBr discs, or nujol mulls. ^1H n.m.r. spectra were recorded on a Varian A 60A (60Mc/s) instrument in $CDCl_3$ solutions using TMS as internal standard. Electronic spectra were obtained on a Perkin Elmer-Hitachi 200 spectrophotometer with freshly prepared acetone or methylene chloride solutions. Magnetic susceptibility measurements in solution were done by the Evans method using chloroform solutions 2% v/v in TMS.

The elemental analysis of carbon, nitrogen and hydrogen was performed on a Perkin-Elmer 240 Elemental Analyser.

Preparation of the Nitro Complexes

The nitro complexes of the general formula $Ni(NO_2)(S_2CNHR)(PBu^n_3)$ (where R = Me, Et, i-Pr and s-Bu) were prepared according to the following general method.

The complex $Ni(NO_2)_2(PBu^n_3)_2$ (0.55 g, 1.0 mmol), prepared according to a published method [7], was dissolved in acetone (30 ml) contained in a Schlenk tube and a solution of the $Ni(S_2CNHR)_2$ complex (1.0 mmol) in 30 ml of acetone was added slowly under continuous magnetic stirring. The mixture was stirred for 4 hr at room temperature and during that time the colour of the solution changed from greenish-yellow to deep red. The resulting solution was condensed to a small volume (*ca.* 10 ml) and 50 ml of petroleum ether were added in order to precipitate the desired complex. In some cases (R = i-Pr and s-Bu) the complexes were precipitated as oily products. In these cases a syringe was used to remove solvent from the oil formed, the latter was washed several times with small portions of petroleum ether and dried in a vacuum. Purification of the complexes was carried out by dissolving the crude products in a small amount of methylene chloride at room temperature, filtering the solution and diluting the filtrate with petroleum ether until no further precipitation of the complex was observed.

O-atom Transfer Reactions of the Nitro Complexes to CO

The complex $Ni(NO_2)(S_2CNHR)(PBu^n_3)$ (0.5 mmol) was placed with benzene (50 ml) in a Schlenk tube under nitrogen atmosphere. Carbon monoxide was bubbled through the solution under 1 atm pressure at room temperature. The deep red solution turned deep blue within 1 hr. The flow of CO was maintained for a further 30 min and the resulting blue solution was then evaporated to dryness. The oily products obtained were dried in vacuum and were kept under a dry oxygen-free nitrogen atmosphere. Elemental analysis and spectroscopic studies of these air-sensitive oily products showed that they are nitrosyl complexes of the general formula $Ni(NO)(S_2CNHR)(PBu^n_3)$.

Oxygenation of the Nitrosyl Complexes

The complex $Ni(NO)(S_2CNHR)(PBu^n_3)$ (0.5 mmol) was placed with petroleum ether (30 ml) in a Schlenk

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TABLE I. Analytical Data and Melting Points for the New Nickel Nitro- and Nitrosyl Complexes.

Compound	M.P. °C	%C	%N	%H
$Ni(NO_2)(S_2CNHCH_3)(PBu^n_3)$	85	40.28 (40.67)*	6.68 (6.77)	7.39 (7.50)
$Ni(NO_2)(S_2CNHC_2H_5)(PBu^n_3)$	96	41.82 (42.15)	6.38 (6.55)	7.70 (7.72)
$Ni(NO_2)[S_2CNH(i\text{-}C_3H_7)](PBu^n_3)$	oil	43.00 (43.53)	6.20 (6.34)	7.72 (7.93)
$Ni(NO_2)[S_2CNH(s\text{-}C_4H_9)](PBu^n_3)$	oil	44.65 (44.83)	6.08 (6.15)	8.06 (8.13)
$Ni(NO)(S_2CNHCH_3)(PBu^n_3)$	oil	42.20 (42.31)	7.00 (7.05)	7.69 (7.80)
$Ni(NO)(S_2CNHC_2H_5)(PBu^n_3)$	oil	43.60 (43.79)	6.80 (6.81)	7.95 (8.02)
$Ni(NO)[S_2CNH(i\text{-}C_3H_7)](PBu^n_3)$	oil	45.00 (45.17)	6.50 (6.58)	8.18 (8.23)
$Ni(NO)[S_2CNH(s\text{-}C_4H_9)](PBu^n_3)$	oil	46.15 (46.46)	6.20 (6.37)	8.40 (8.42)

*Figures in parentheses are the calculated values.

tube and air or oxygen was bubbled through the solution . The deep blue solution turned deep red within 1 hr, while a deep red oily product separated from the solution. After removing the solvent by means of a syringe, the products were dried in vacuum and were found to be the corresponding nitro complexes.

Catalytic Oxidation of CO by O_2 in the Presence of the $Ni(NO_2)$–$Ni(NO)$ Redox Couple

The complex $Ni(NO_2)(S_2CNHR)(PBu^n_3)$ (0.04 mmol) was placed with methylene chloride (25 ml) in a Schlenk tube and CO was bubbled through the solution. The progress of the reaction was followed by observing the colour changes of the solution (deep red → deep blue) and by taking samples of the mixture at appropriate reaction times and analysing them by UV–Vis spectroscopy. When all of the nitro complex was converted to the corresponding nitrosyl complex, oxygen was bubbled through the solution and the reaction was followed as before. After the conversion of the nitrosyl complex to the corresponding nitro complex we started a new cycle. These cycles can be repeated several times. The volatile material was found to be CO_2 by trapping it into a solution of $Ca(OH)_2$ and observing the precipitation of $CaCO_3$.

Results and Discussion

The new (tri-n-butylphosphine)(N-monoalkyldithiocarbamate)(nitro)nickel(II) complexes were prepared by the following general ligand exchange reaction:

$$Ni(NO_2)_2(PBu^n_3)_2 + Ni(S_2CNHR)_2 \rightarrow$$
$$\rightarrow 2\ Ni(NO_2)(S_2CNHR)(PBu^n_3)$$

where R = Me, Et, i-Pr and s-Bu.

These nitro complexes react, under mild conditions (room temperature) with carbon monoxide (1 atm pressure) in dry, oxygen-free methylene chloride or benzene solution, producing deep blue solutions, from which the corresponding nitrosyl complexes were isolated. This O-transfer reaction could be represented by the general scheme:

$$Ni(NO_2)(S_2CNHR)(PBu^n_3) + CO \rightarrow$$
$$\rightarrow Ni(NO)(S_2CNHR)(PBu^n_3) + CO_2$$

The nitro complexes, which were obtained in nearly quantitative yields were all reddish-brown in colour and, except for the complexes with R = Me or Et which were solids, all the compounds were isolated as oily products. They were remarkably stable in the atmosphere and were soluble in most of the common organic solvents, such as acetone, chloroform, methylene chloride and benzene, but were insoluble in petroleum ether and water.

The nitrosyl complexes which were also obtained in quantitative yields were deep-blue oily products,

TABLE II. Relevant I.r. Frequencies (cm^{-1}) of the Studied Nitro- and Nitrosyl Complexes of Nickel with their Assignments.

Compound	ν(N–H)	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$	ν_{sym} (NO$_2$)	ν_{asym} (NO$_2$)	δ(NO$_2$)	ν(NO)
$Ni(NO_2)(S_2CNHCH_3)(PBu^n_3)$	3170m,br	1560vs,br	1370s,br	1310s,br	823m	–
$Ni(NO_2)(S_2CNHC_2H_5)(PBu^n_3)$	3170m,br	1540vs,br	1375s,br	1332s,br	820m	–
$Ni(NO_2)[S_2CNH(i\text{-}C_3H_7)](PBu^n_3)$	3170m,br	1535vs,br	1375s,br	1320s,br	817m	–
$Ni(NO_2)[S_2CNH(s\text{-}C_4H_9)](PBu^n_3)$	3170m,br	1535vs,br	1375s,br	1322s,br	818m	–
$Ni(NO)(S_2CNHCH_3)(PBu^n_3)$	3260m,br	1514vs,br	–	–	–	1712vs,br
$Ni(NO)(S_2CNHC_2H_5)(PBu^n_3)$	3260m,br	1506vs,br	–	–	–	1708vs,br
$Ni(NO)[S_2CNH(i\text{-}C_3H_7)](PBu^n_3)$	3260m,br	1500vs,br	–	–	–	1705vs,br
$Ni(NO)[S_2CNH(s\text{-}C_4H_9)](PBu^n_3)$	3250m,br	1501vs,br	–	–	–	1700vs,br

very sensitive to the atmospheric oxygen, both in the solid state or in solution. They were soluble in all of the common organic solvents, but insoluble in water.

The analytical data for the new compounds are shown in Table I.

The structures of the new complexes were established by spectroscopic methods as well as by magnetic susceptibility measurements. Table II lists some of the most important infrared absorption bands of the complexes studied, along with their assignments.

All the nitro complexes studied exhibit in the infrared spectra the three non-degenerate infrared-active vibrational modes of the NO$_2$ ligand (local symmetry C_{2v}), *e.g.* the symmetric N–O stretch (ν_{sym}), the asymmetric N–O stretch (ν_{asym}) and the NO$_2$ deformation (δ). It is well known [8–11] that the coordination of the NO$_2$ ligand via nitrogen causes an increase of the frequencies of both ν_{sym}(NO$_2$) and ν_{asym}(NO$_2$) relative to the free ion values of 1328 and 1260 cm^{-1}, respectively. On the other hand, coordination via oxygen raises the frequency of the ν_{sym}(NO$_2$) and lowers that of the ν_{asym}(NO$_2$) relative to those of the free ion. The values of ν_{sym}(NO$_2$) and ν_{asym}(NO$_2$) shown in Table II are in accord with the presence of coordinated nitrite ions via nitrogen as a nitro ligand. In addition, the nitro complexes exhibit the NO$_2$ rocking mode near 600 cm^{-1}, which is absent in the nitrito complexes [12].

The NO ligand of the nitrosyl complexes showed in the infrared spectra a very strong, broad band in the region of 1700–1720 cm^{-1}. The position of this band strongly suggests [13–15] the existence of a bending Ni–N–O moiety in the studied nitrosyl complexes. By comparing the position of the ν(NO) band of the complexes in question with that of the previously reported [6] (triphenylphosphine)(nitrosyl)(O-alkyldithiocarbonate)nickel complexes it is evident that the Ni–N–O moiety is more bending in the present complexes. This could be explained on the basis of the stronger electron donating ability of both the N-monoalkyldithiocarbamato and tri-n-butylphosphino ligands relative to the O-alkyldithiocarbonato and triphenylphosphino ligands, respectively. Thus, the accumulation of more electron density on the central atom of the studied nitrosyl complexes favors the π-back bonding between the central atom and the nitrosyl ligand and consequently the bending of the Ni–N–O moiety increases.

The position of the $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ band strongly suggests the bidentate character of the dithiocarbamato ligand [16]. Therefore, from the examination of the infrared spectra we conclude that the complexes studied are four-coordinated complexes of nickel and their structures should be either square-planar or tetrahedral. Magnetic measurements by ^{1}H n.m.r. spectroscopy using the Evans method indicated that the complexes are diamagnetic.

The diamagnetism in the case of the nickel(II) nitro complexes is consistent with a square-planar structure. The square-planar structure of the nitro complexes is further supported from their electronic spectra. The electronic spectra of the nitro complexes in the ultraviolet region contained intense bands at 41 kK ($\epsilon \cong$ 10.000–12.000), 34 kK ($\epsilon \cong$ 7.000–9.000), 31.5 kK ($\epsilon \cong$ 7.000–9.000) and 26.7 kK ($\epsilon \cong$ 1.000), which can be assigned to intraligand transitions ($\pi^* \leftarrow \pi$ and $\pi^* \leftarrow n$). In the visible region of the spectra low intensity bands occur at 23.6 kK ($\epsilon \cong$ 300–500), 21.0 kK ($\epsilon \cong$ 400–500) and 15.8 kK ($\epsilon \cong$ 7). All these bands are characteristic bands for square-planar nickel(II) complexes [17] and could be assigned to $^1E_g \leftarrow {}^1A_{1g}$, $^1B_{2g} \leftarrow {}^1A_{1g}$ and $^1B_{1g} \leftarrow {}^1A_{1g}$ transitions, respectively.

On the other hand, in the case of the nitrosyl complexes their diamagnetic nature could not be used to distinguish the two possible structures, since both structures correspond to diamagnetic complexes (in the tetrahedral structure they correspond to the $\{NiNO\}^{10}$ complexes which contain Ni^0 and the NO$^+$ ligand, while in the square-planar structure they correspond to the {NiNO}^{8} complexes which contain Ni^{2+} and the NO$^-$ ligand). The square-planar structure for the nitrosyl-complexes can be excluded, since no i.r. absorption bands characteristic of the coordinated NO$^-$ group in the region of *ca.* 1100 cm^{-1} [13–16] were observed. Hence, the most probable structure for the nitrosyl complexes is the tetrahedral one. However, it is well known [18] that the tetrahedral {MNO}^{10} complexes contain a linear M–N–O group, which can be bent if the symmetry of the complexes is lowered. The bending Ni–N–O group in our new nitrosyl complexes indicates a low symmetry for the complexes and therefore their structure must be pseudo-tetrahedral. It must be noted that the analogous nickel nitrosyl complexes $\mathrm{Ni(NO)(N_3)(PPh_3)_2}$ and $\mathrm{Ni(NO)[(S_2COCH(CH_2)_4]}$-$\mathrm{(PPh_3)}$, whose structures were determined by X-ray crystallography [19, 20], were found to adopt a pseudo-tetrahedral geometry. The pseudo-tetrahedral structure of the new nitrosyl complexes is further supported from their electronic spectra. In the ultraviolet region of the electronic spectra of the nitrosyl complexes the same intraligand transitions occur as in the case of the corresponding nitro complexes. However, the pattern of the bands occuring in the visible region of the spectra is quite different. Thus, the nitrosyl complexes gave low intensity bands at 23.6 kK ($\epsilon \cong 300$–500) and 18.0 kK ($\epsilon \cong 500$–800), as well as a shoulder at 21.5 kK ($\epsilon \cong 400$–500) The high extinction coefficient of the band at 18.0 kK is characteristic for tetrahedral complexes. On the basis of the proposed structures for the nitrosyl- and nitro complexes under question, we can also explain the observed lower values of the $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ stretching frequencies in the nitrosyl-complexes. In the pseudo-tetrahedral nitrosyl complexes of the zerovalent nickel (d^{10}) the central atom is a weaker electron density acceptor than the central atom of the square-planar nitro complexes of the divalent nickel (d^8). Hence the flow of electron density from the N-monoalkyldithiocarbamato ligand to the central atom is less in the nitrosyl- than in the nitro complexes. This has as a result a bond order of the $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ bond in the dithiocarbamato ligand lower in the nitrosyl- than in the nitro complexes, and consequently the $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ stretching frequencies are lowered in the nitrosyl complexes.

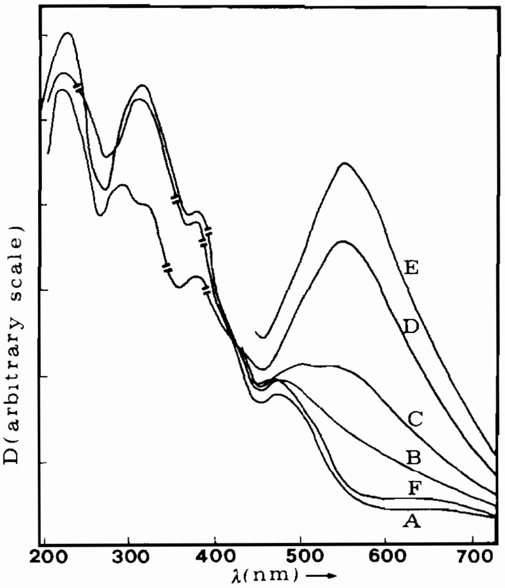

Fig. 1. Electronic spectra of the $\mathrm{Ni(NO_2)[(S_2CNH(i\text{-}C_3H_7)]}$-$\mathrm{(PBu^n_3)}$–$\mathrm{Ni(NO)[S_2CNH(i\text{-}C_3H_7)](PBu^n_3)}$ redox couple, formed during the catalytic oxidation of CO in $\mathrm{CH_2Cl_2}$ solution at certain reaction times A) The starting nitro complex. B) After 10 min. C) After 20 min. D) After 30 min. E) At the end of the reaction (pure nitrosyl complex). F) After 1 hr reaction of the nitrosyl complex with atmospheric oxygen.

Keeping the deep blue solution of the nitrosyl complexes in air for a few hr results in the formation of a deep red solution, from which the corresponding nitro complex was isolated and identified. The easy reversibility of the $\mathrm{Ni(NO_2)}$–Ni(NO) redox couple in the presence of CO and $\mathrm{O_2}$ prompted us to study the catalytic activity of this couple in the oxidation of CO with atmospheric oxygen. The catalytic process was followed qualitatively by electronic spectroscopy. In Fig. 1 are shown the electronic spectra of a representative $\mathrm{Ni(NO_2)}$–Ni(NO) redox couple formed during the oxidation of CO with $\mathrm{O_2}$. The changes observed in the electronic spectra clearly show the interconversion of the $\mathrm{Ni(NO_2)}$–Ni(NO) redox couple during the course of the reaction. Thus as CO passes through the solution of the nitro complex the band at 18.0 kK which is characteristic of the {NiNO}^{10} complexes appears, while the band at 21.5 kK which is characteristic for the nitro complexes gradually disappears. After the disappearance of the band at 21.5 kK oxygen passes through the solution, which has as a result the disappearance of the band at 18.0 kK and the gradual increase in the intensity of the band at 21.5 kK. This reaction cycle can be repeated several times giving $\mathrm{CO_2}$ which is trapped into a $\mathrm{Ca(OH)_2}$ or KOH solution. Thus, we can conclude that the $\mathrm{Ni(NO_2)}$–Ni(NO) redox couple is a very efficient homogeneous catalyst for the oxidation of CO with atmospheric oxygen. The mechanism of this catalytic reaction, as well as the relation between the structures of the nitro- and nitrosyl complexes of the $\mathrm{Ni(NO_2)}$–Ni(NO) redox couples and their catalytic activity, are at present under investigation and the results will be published soon.

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