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Nitrosylrhenium(^{14}NO and ^{15}NO) Complexes

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The ^{15}NO-complexes for $M_2[ReX_5(NO)]$ (M=Rb, Cs, and pyH; X=Cl and Br) were prepared. The ^{15}N-isotopic shift for their N–O stretching vibrations, *ca.* 40 cm^{-1}, supports the view that the oxidation state of the NO group is I, while that of the rhenium atom is II. The Re–(NO) stretching and the Re–(NO) bending vibrations were observed in the 610—620 cm^{-1} region. A new compound, *cis*-(pyH)[$ReCl_4(NO)_2$], was prepared, the oxidation state of its rhenium atom being considered to be I, and that of the NO group, I.

The isotopic effects of ^{15}N-substitution in the NO group for several transition-metal nitrosyl complexes on the IR spectra have been measured.[1,2] From the comparison of the observed isotopic shifts with the calculated ones, a few rules were established: the isotopic shift of the metal–(NO) stretching vibration is smaller than that of the metal–(NO) bending vibration, independent of the metal–(NO) bond angle; the isotopic shifts of the N–O stretching vibrations observed on NO^+ complexes are almost equal to those calculated by assuming a linear arrangement of a metal–N–O, and are larger than those observed on NO^- complexes; the isotopic shifts of the N–O stretching vibrations decrease with the deviation of the metal–(NO) bond angle from linearity.

On the basis of these facts, the oxidation states of the rhenium atom and the NO group for $M_2[ReX_5(NO)]$ (M=Rb, Cs, and pyH; X=Cl and Br) were investigated. A new compound, *cis*-(pyH)[$ReCl_4$(NO$_2$], was prepared and characterized on the basis of spectroscopic evidence. This compound is the first one formulated containing a O–N–Re–N–O skeleton.

Experimental

Syntheses. $M_2[ReX_5(NO)]$ was prepared by means of a modification of Bandyopadhyay's procedure.[3] The starting materials, $Ag_2[ReCl_6]$ and $K_2[ReBr_6]$, were synthesized from $KReO_4$ by the method of Watt and Thompson.[4] The ^{15}NO-complexes were prepared in a vacuum line by the use of 5—6 mmol of ^{15}NO(^{15}N atom%=95 and 96.8) on the same scale as that used for preparing the ^{14}NO-complexes.

$Cs_2[ReCl_5(NO)]$: A 5-mmol portion of NO gas derived from KNO_3 was trapped in a reaction vessel containing 1.7 mmol of a finely-powdered $Ag_2[ReCl_6]$ by cooling with liquid nitrogen. A green product, $Cs_2[ReCl_5(NO)]$ (*ca.* 100 mg), was then obtained by the procedure shown in Ref. 3. The crude product thus obtained was then washed well with a cold 6 M hydrochloric acid solution to remove any impurities, then it was washed with ethanol and dried under a vacuum. Found: Cs, 39.5; Re, 28.5; N, 2.23; Cl, 26.61%. Calcd for $Cs_2[ReCl_5(NO)]$: Cs, 40.32; Re, 28.24; N, 2.12; Cl, 26.89%. $\mu_{eff.}$ (at 291 K)=1.62 B.M. *g*(at 296 K)=2.01.

$M_2[ReBr_5(NO)]$ (M=Rb and Cs): A 6-mmol portion of NO gas was trapped in a reaction vessel containing 2 mmol of a finely-powdered $K_2[ReBr_6]$ and then heated at *ca.* 400 °C for 12 hr. A dark brown sublimate which was deposited on the wall of the vessel was dissolved in a hot 90% ethanol solution and then refluxed for 12 hr. The resulting brown filtrate was evaporated to dryness on a boiling-water bath. The solid residue thus obtained was dissolved in 25 ml of a hot 5 M hydrobromic acid solution and refluxed for 6 hr at 90 °C to give a greenish brown solution. An 8-mmol portion of rubidium bromide was added to the filtrate, and the mixture was condensed to *ca.* 10 ml on a boiling-water bath. The brown precipitate thus obtained, $Rb_2[ReBr_5(NO)]$, was filtered out, washed with cold concentrated hydrobromic acid, and dried in a vacuum. Yield, 220—500 mg. Found: Rb, 21.6; Re, 23.7; N, 1.69; Br, 50.61%. Calcd for $Rb_2[ReBr_5(NO)]$: Rb, 21.73; Re, 23.67; N, 1.78; Br, 50.79%. $\mu_{eff.}$ (at 291 K)=1.61 B.M. *g*(at 87 and 296 K)=2.06. $Cs_2[ReBr_5(NO)]$ was prepared by the same procedure; 5 mmol of NO gas, 1 mmol of $K_2[ReBr_6]$, and 8 mmol of caesium bromide were used. Yield, 250—270 mg. Found: Cs, 29.9; Re, 21.7; N, 1.72; Br, 44.97%. Calcd for $Cs_2[ReBr_5(NO)]$: Cs, 30.15; Re 21.12; N, 1.59; Br, 45.32%. μ_{eff}. (at 291 K)= 1.66 B.M. *g*(at 296 K)=2.08.

$(pyH)_2[ReCl_5(NO)]$ and cis-*(pyH)[$ReCl_4(NO)_2$]*: A mixture of 5 mmol of NO gas and 1.7 mmol of powdered $Ag_2[ReCl_6]$ was heated at *ca.* 320 °C for 5 hr. The brown sublimate thus obtained was dissolved in 100 ml of 99.5% hot ethanol, and the solution was refluxed for 6 hr. The greenish brown filtrate was evaporated to dryness on a water bath, dissolved in 30 ml of an 8 M hydrochloric acid solution, and refluxed for 21 hr at 95 °C to give a dark green solution. 5 mmol of pyridinium chloride in 5 ml of an 8 M hydrochloric acid solution was added to the filtrate, and the mixture was refluxed at 95 °C for 35 hr. The green solution thus obtained was evaporated on a boiling-water bath. The residue was then boiled with 20 ml of 99.5% ethanol for 1 min. The green extract was condensed in a vacuum line to *ca.* 10 ml with the aid of liquid nitrogen to precipitate olive green needles; (pyH)[$ReCl_4(NO)_2$]. Yield, 100 mg. Found: C, 13.49; H, 1.73; N, 8.87; Cl, 30.04%. Calcd for (pyH)[$ReCl_4(NO)_2$]: C, 12.83; H, 1.29; N, 8.98; Cl, 30.29%. χ_g(at 295 K)$=-0.06\times10^{-6}$(c.g.s.). After the olive green needles had been filtered out, a large excess of ether was added to the filtrate to give a green product, $(pyH)_2[ReCl_5(NO)]$. Yield, 50 mg. Found: C, 21.66; H, 2.28; N, 7.74; Cl, 30.44%. Calcd for $(pyH)_2[ReCl_5(NO)]$: C, 21.69; H, 2.18; N, 7.59; Cl, 32.02%. *g*(at 296 K)=2.02.

Apparatus. The IR spectra of the compounds as Nujol and hexachlorobutadiene mulls were recorded from 200—4000 cm^{-1} on JASCO DS-402G and JASCO model IR-F spectrophotometers. The wave numbers of the observed bands were calibrated with polystyrene film, 1,2,4-trichlorobenzene, and water vapour. The Raman spectra of the solid-state samples were measured from 100—700 cm^{-1} on a JASCO R-800 spectrometer equipped with an Ar ion laser, and on a Narumi 750Z-1200 double monochromator equipped with a He-Ne laser. The magnetic susceptibility was measured by the Gouy method at room temperature. Electron-spin resonance measurements were carried out in a pure powdered solid at room temperature and at the temperature of liquid nitrogen using a JEOL-ME3X spectrometer. The *G*-values were measured by shift from an external dilute manganese oxide in a magnesium oxide standard. The nuclear magnetic resonance spectra were measured on a

Table 1. Wave numbers, observed isotopic shifts, and assignments of IR and Raman bands due to the ReNO group

Compound	N–O str ($\Delta\nu_{obsd}$)	Skeletal vibrations between Re and NO ($\Delta\nu_{obsd}$)
$Cs_2[ReCl_5(NO)]$	1720 vs (42)	611 s (7), 610(4)$^{a)}$
$(pyH)_2[ReCl_5(NO)]$	1736 vs (44)	608 s (3)$^{b)}$
$Rb_2[ReBr_5(NO)]$	1728 vs (38)	617 s (9), 619(4)$^{a)}$
$Cs_2[ReBr_5(NO)]$	1720 vs (37)	612 s (9), 615(7)$^{a)}$

a) Raman band. b) Overlapped with the absorption band due to the pyridinium ion; $\Delta\nu_{obsd}=\nu^{14}$NO-complex(obsd) $-\nu^{15}$NO-complex(obsd); Abbreviations: str=stretching; vs=very strong; s=strong.

Hitachi Perkin-Elmer R-20A High Resolution NMR spectrometer, using tetramethylsilane as the internal standard.

Results and Discussion

$M_2[ReX_5(NO)]$ (M=Rb, Cs, and pyH; X=Cl and Br). The wave numbers, isotopic shifts, and assignments of the IR and the Raman bands due to the ReNO group for the mononitrosyl complexes are shown in Table 1. The N–O stretching vibrations were observed in the 1720—1740 cm^{-1} region. The isotopic shifts upon ^{15}NO-substitution are 37—44 cm^{-1}, and are almost equal to those for the NO$^+$ complexes which were studied in Ref. 1.

Of the IR and Raman bands in the 100—700 cm^{-1} region, only the strong ones in the 610—620 cm^{-1} region shifted downwards by 3—9 cm^{-1} upon ^{15}NO-substitution for all the compounds. These bands are considered to be due to the skeletal vibrations between the rhenium atom and the NO group. The isotopic shifts observed on the IR spectra were found to be larger than those observed on the Raman spectra.

The ^{15}*N*-isotopic shifts of the N–O stretching, the Re–(NO) stretching, and the Re–(NO) bending vibrations were calculated from the wave numbers of the ^{14}NO-complexes by assuming a linear arrangement of Re–N–O and using a Valence Force Field. For the NO$^+$ complexes, the calculation of the isotopic shifts by means of the three-body model of the metal and the NO group is useful for assigning distinctly the skeletal vibrations when the metal and the ligands other than the NO group are much heavier than nitrogen and oxygen.[1,2] The calculated isotopic shifts of the N–O stretching, Re–(NO) stretching, and Re–(NO) bending vibrations are 40, 5, and 14 cm^{-1} respectively, while their calculated force constants are 11, 6.9, and 0.4 mdyn/Å respectively. The good agreement of the observed isotopic shift for the N–O stretching vibration with the calculated one is considered to support the theory that the oxidation state of the NO group is I, and that, therefore, that of the rhenium atom is II.

The isotopic shift observed on the 610—620 cm^{-1} band(3—9 cm^{-1}) is smaller than that calculated for the Re–(NO) bending vibration (14 cm^{-1}). The isotopic shift observed on the Raman bands is almost equal to that calculated for the Re–(NO) stretching vibration, while the isotopic shift observed on the IR bands is larger than that calculated for the Re–(NO) stretching vibration. These suggest the possibilities that the band due to the Re–(NO) stretching vibration accidentally overlaps with that due to the Re–(NO) bending one, and that the relative intensity of the Re–(NO) stretching band to the Re–(NO) bending one observed on the IR spectra is smaller than that observed on the Raman ones. However, another possibility, that the intensity of one of the skeletal vibrations is too weak to be observed, can not be excluded.

On the basis of IR and Raman studies of the $[MX_5(NO)]^{n-}$ anion (M=Ru, Os, and Ir; X=Cl, Br, and I),[5] the IR bands at 308(vs, b)[6] with a shoulder at 297 cm^{-1}, and 278 cm^{-1}(m) for $Cs_2[ReCl_5(NO)]$ can be assigned to the Re–Cl stretching E mode, ν_{10}, and the A_1 one, ν_4, respectively, and the IR band at 331 cm^{-1}(m) and the Raman one at 329 cm^{-1}, to the Re–Cl stretching A_1 mode, ν_3. The two Raman bands at 166 and 142 cm^{-1} are assigned to the Re–Cl deformation vibrations. The three IR bands at 330(m), 300(vs, b), and 275 cm^{-1}(m) for $(pyH)_2[ReCl_5(NO)]$ are assigned to the Re–Cl stretching vibrations, ν_3, ν_{10}, and ν_4 respectively, for the Cs-salt, while the IR bands at 250(m) and *ca.* 230 cm^{-1}(w) are considered to be due to the pyridinium ion. The Raman band at 212 cm^{-1} for $Rb_2[ReBr_5(NO)]$ and that at 207 cm^{-1} for $Cs_2[ReBr_5(NO)]$ can be assigned to the Re–Br stretching A_1 mode, ν_3, and the IR band at 221 cm^{-1}(vs) for the Rb-salt and that at 218 cm^{-1}(vs) for the Cs-salt, to the Re–Br stretching E one, ν_{10}.

cis-*(pyH)[ReCl$_4$(NO)$_2$]*. The IR bands at 1896 (vs), 1795(vs, b), and 1760 cm^{-1}(m) (the N–O stretching vibrations) shifted to 1859, 1756, and 1726 cm^{-1} respectively. The four IR bands in the 490—610 cm^{-1} region shifted upon ^{15}NO-substitution (from 610(s),

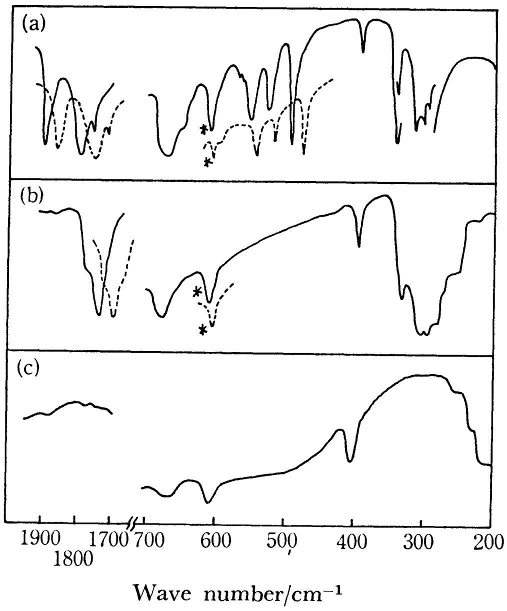

Fig. 1. IR spectra of *cis*-(pyH)[ReCl$_4$(NO)$_2$] (a), $(pyH)_2[ReCl_5(NO)]$ (b), and pyHCl (c). ^{14}NO-complex, ——; ^{15}NO-complex(^{15}N atom%=95), ----; in (a) and (b). *; overlapped with the band due to the pyridinium ion.

550(s), 526(s), and 491 cm^{-1}(vs) to 608, 542, 521, and 477 cm^{-1} respectively), as is shown in Fig. 1. The two very strong N–O stretching bands at 1896 and 1795 cm^{-1} suggest the presence of two NO groups in this compound, in a *cis* position to each other. The observed isotopic shifts for the N–O stretching vibrations are about 40 cm^{-1}; hence, the oxidation state of two of the NO groups may be considered to be I.

The ^{15}N-isotopic shifts for the six IR bands in the 490—1900 cm^{-1} region can reasonably be explained on the basis of an O–N–Re–N–O skeleton. If this skeleton belongs to the C_{2v} point group, the number of IR-active bands should be eight. The bands at 1896 and 1795 (and 1760) cm^{-1} can be assigned to the N–O antisymmetric and symmetric stretching vibrations respectively, and the four bands in the 490—610 cm^{-1} region, to the Re–(NO) stretching, its bending, and the N–Re–N bending vibrations. Such a phenomenon was also observed on $[Ir(NO)_2(P(C_6H_5)_3)_2]ClO_4$[1], in which the O–N–Ir–N–O skeleton belongs to the C_{2v} point group.

Two chemical formulae, *cis*-(pyH)$[ReCl_4(NO)_2]$, in which the oxidation state of the rhenium atom is I, and *cis*-$[ReCl_3py(NO)_2]Cl$, in which it is II, are possible, judging from the elementary analyses. However, the latter can be excluded on the basis of the IR spectra. An IR study of pyridine complexes and pyridinium salts has shown that the bands at about 1530—1540 and 1280—1330 cm^{-1} are observed on the pyridinium salts, but not on the pyridine complexes; these are assigned to the N–H deformation vibration and the combination bands involving the N–H deformation.[7] These bands were observed at 1528(s) and 1328(m) for (pyH)$[ReCl_4(NO)_2]$, at 1538(vs) and 1318(m) for pyHCl, and at 1530(s) and 1322 cm^{-1}(m) for $(pyH)_2[ReCl_5(NO)]$. The bands at 393(m) and *ca.* 670 cm^{-1} (vs, b) can be assigned to the ring deformations due to the pyridinium ion, and the other deformation vibration band may overlap with the 610 cm^{-1} band assigned to the skeletal vibrations between the rhenium atom and the NO group.[8] On the basis of the ^{15}N-isotopic shift of the N–O stretching vibrations for *cis*-(pyH)$[ReCl_4(NO)_2]$, the oxidation state of the NO group is considered to be I, —that of the rhenium atom I. The IR spectra for pyHCl, $(pyH)_2[ReCl_5(NO)]$, and *cis*-(pyH)$[ReCl_4(NO)_2]$ are shown in Fig. 1. The bands at 342(s), 311(vs), 300(vs), and 298 cm^{-1}(vs) can be assigned to the Re–Cl stretching vibrations.

The NMR studies of pyHCl and *cis*-(pyH)$[ReCl_4(NO)_2]$ were carried out in $CDCl_3$ and DMSO-d_6, using tetramethylsilane as the internal standard. According to a study of pyHX(X=Cl, Br, and I) by Kotowycz *et al.*,[9] the triplet at δ 8.1—8.3, the triplet at δ 8.6—8.8, and the doublet at δ 8.9—9.1 for (pyH)$[ReCl_4(NO)_2]$ are considered to be due to the C–H protons in the *meta-*, *para-*, and *ortho-*positions respectively. The C–H proton shifts were not so much affected, but the N–H proton shift was sensitive to the counterions, the solvents used, and a trace of water, as is shown in Ref. 9. For pyHCl, the singlet at δ *ca.* 13 in DMSO-d_6 may be assigned to the N–H proton; this peak shifted to a higher magnetic field upon the addition of water to the solvent. The singlet at δ 7.8 for (pyH)$[ReCl_4(NO)_2]$ in DMSO-d_6 may be due to the N–H proton; it shifted to a higher magnetic field upon the addition of water, as was observed on the N–H proton for pyHCl. The integration of the spectra of (pyH)$[ReCl_4(NO)_2]$ and pyHCl in DMSO gives a ratio of the C–H protons to the N–H proton of 5 : 1. The NMR data also suggest the presence of the pyridinium ion in (pyH)$[ReCl_4(NO)_2]$.

The nitrosyl complexes of rhenium so far investigated are not so numerous,[10–12] and the oxidation states of rhenium atoms are 0, I, and II. *cis*-(pyH)$[ReCl_4(NO)_2]$ is the first compound containing an O–N–Re–N–O skeleton in which the oxidation state of the rhenium atom is I.

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6) The signs in parentheses indicate the abbreviations of the strength and shape of the absorption band; vs=very strong, s=strong, m=medium, w=weak, b=broad.

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