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Infrared Spectra of Nitrosylplatinum (^{14}NO and ^{15}NO) Complexes

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The ^{15}NO-complexes for *trans*-$[PtCl(NH_3)_4(NO)]Cl_2$, *trans*-$K_2[PtCl(NO_2)_4(NO)]$ and $M_2[PtX_5(NO)]$ (M=K and Cs, X=Cl and Br) were prepared. The effect of ^{15}N-substitution on infrared spectra indicated that the weak absorption band at *ca.* 290 cm^{-1} is assigned to the Pt-(NO) stretching vibration and the absorptoin band in the region 530—570 cm^{-1} to the Pt-(NO) bending vibration.

For transition-metal nitrosyl compounds, the isotopic effects of ^{15}N in the NO group on infrared spectra were measured. The isotopic shifts observed were compared with those calculated by a three-body model of the metal and the NO group. This method is found to be useful for assigning the skeletal vibrations between the metal and the NO group; the isotopic shift of the metal–(NO) stretching vibration is smaller than that of the metal–(NO) bending vibration.[1]

We have measured the isotopic shifts for ^{15}NO-substitution in *trans*-$[PtCl(NH_3)_4(NO)]Cl_2$, *trans*-$[PtCl(ND_3)_4(NO)]Cl_2$, *trans*-$K_2[PtCl(NO_2)_4(NO)]$ and $M_2[PtX_5(NO)]$ (M=K and Cs, X=Cl and Br). The Pt-(NO) binding states are discussed on the basis of the following: comparison of the infrared spectra with those for ammine- and chloro-complexes of Pt(II) and Pt(IV), the approximate force constant for the Pt-(NO) stretching vibration and the isotopic shift of the N–O stretching vibration upon ^{15}NO-substitution.

Experimental

Preparation of Nitrosylplatinum Compounds. The complexes were prepared by the method of Griffith *et al.*[2] Their ^{15}NO-complexes were prepared in a vacuum line with the use of ^{15}NO, ^{15}NO–^{15}NO$_2$, or ^{15}NOCl derived from 3—10 mmol of $K^{15}NO_3$ (^{15}N atom %=95–99.7). Nitrosyl chloride was prepared from nitric oxide and potassium chloride by the method of Ratcliffe.[3] The elementary analyses and IR spectra showed that the desired products were obtained.

trans-*$[PtCl(NH_3)_4(NO)]Cl_2$*: (A) By cooling with liquid nitrogen, 3 mmol of NO gas was trapped into a reaction vessel containing 0.3 mmol of $[Pt(NH_3)_4]Cl_2\cdot H_2O$ in 10 ml of 6M hydrochloric acid. The reaction vessel was shaken in running water until the frozen solution was molten. Air was then introduced into the reaction vessel to instantly give green precipitates with shaking. The products were filtered out and dried under vacuum. $\chi_g=-0.27\times10^{-6}$ (c.g.s.). Found: Pt, 48.9; N, 17.5; H, 4.3; Cl, 25.2%. Calcd for $[PtCl(NH_3)_4(NO)]Cl_2$: Pt, 48.82; N, 17.53; H, 3.03; Cl, 26.62%. (B) Finely powdered $[Pt(NH_3)_4]Cl_2\cdot H_2O$ (0.3 mmol) was stirred with 5 mmol of NOCl in 5 ml of freshly distilled chloroform for 70 hr at about 0 °C. Found: Pt, 49.5; N, 16.3; H, 2.9; Cl, 26.9%.

trans-*$[PtCl(ND_3)_4(NO)]Cl_2$*: 3 mmol of NO gas was trapped into a reaction vessel containing a solution prepared by adding 5 ml of concentrated hydrochloric acid to 0.3 mmol of $[Pt(NH_3)_4]Cl_2\cdot H_2O$ in 5 ml of D_2O. Green products were obtained by the same produre as for *trans*-$[PtCl(NH_3)_4(NO)]Cl_2$. The IR spectra showed that deuteration was accomplished by hydrogen exchange with D_2O.

trans-*$K_2[PtCl(NO_2)_4(NO)]$*: This compound was synthesized with NOCl in a similar procedure to that for $[PtCl(NH_3)_4(NO)]Cl_2$. Found: K, 14.3; Pt, 36.7; N, 11.0%. Calcd for $K_2[PtCl(NO_2)_4(NO)]$: K, 14.96; Pt, 37.32; N, 13.40%.

$K_2[PtCl_5(NO)]$: $K_2[PtCl_4]$ (0.3 mmol) was stirred with 5 mmol of NOCl in 5 ml of freshly distilled chloroform for 50 hr at about 0 °C to convert it into olive green products. The products were washed with chloroform and dried under vacuum. Found: K, 16.3; Pt, 41.1; Cl, 38.5; N, 2.7%. Calcd for $K_2[PtCl_5(NO)]$: K, 16.57; Pt, 40.45; Cl, 36.75; N, 2.91%.

$Cs_2[PtCl_5(NO)]$: An aqueous solution of $K_2[PtCl_4]$ (1 mmol in 5 ml) was passed through a 5 cm column (1 cm diameter) of cation exchange resin, Diaion SK#1, in hydrogen form. CsCl (2 mmol) in 5 ml of H_2O was added to the effluent. NO–NO$_2$ gas was bubbled into the solution to give dark brown products. $\chi_g=-0.08\times10^{-6}$ (c.g.s.). To prepare the ^{15}NO-complex, 0.5 mmol of $K_2[PtCl_4]$ and 3 mmol of ^{15}NO–^{15}NO$_2$ gas were used. Found: Cs, 39.9; Pt, 29.3; N, 2.1; Cl, 26.4%. Calcd for $Cs_2[PtCl_5(NO)]$: Cs, 39.78; Pt, 29.20; N, 2.10; Cl, 26.53%.

$K_2[PtBr_5(NO)]$ (contaminated with a large amount of $K_2[PtBr_6]$): 5 mmol of NO gas was trapped with liquid nitrogen into a reaction vessel containing 1 mmol of $K_2[PtBr_4]\cdot 2H_2O$ in 3 ml of 1M hydrobromic acid. After the frozen solution was melted in running water, the solution was stirred for *ca.* 6 hr. $K_2[PtBr_6]$ formed was removed by filtration and the filtrate was added to 25 ml of ice-cooled ethyl alcohol to give dark brown powder. The product was washed with ether and dried in air. Stirring of NO with $K_2[PtBr_4]\cdot 2H_2O$ in hydrobromic acid over a long period gave only $K_2[PtBr_6]$. Found: N, 1.3; Br, 57.8%. Calcd for $K_2[PtBr_5(NO)]$: N, 1.99; Br, 56.85%.

The synthetic procedure for the complexes shows the possibility that nitro-complex contaminates the nitrosyl complex. However, infrared spectra showed no characteristic absorption bands of nitro-complex.

Apparatus. Infrared spectra were measured in the region 200—4000 cm^{-1} as Nujol mull and hexachlorobutadiene mull in sodium chloride and in polyethylene plates. The spectra at room temperature were recorded on JASCO DS-402G and JASCO model IR-F infrared spectrophotometers. The spectra of *trans*-$[PtCl(NH_3)_4(NO)]Cl_2$ and $K_2[PtCl_5(NO)]$ at liquid nitrogen temperature were measured *in vacuo* as Nujol mull on KRS-5 plates in the range *ca.* 300—600 cm^{-1} on a Hitachi EPI-L infrared spectrophotometer. The wave numbers of the observed bands were calibrated with polystyrene film, 1,2,4-trichlorobenzene and water vapour. The magnetic susceptibility was measured by the Gouy method.

Results

Assignments of Infrared Spectra. The IR spectra and isotopic shifts upon ^{15}NO-substitution for *trans*-

TABLE 1. WAVE NUMBERS, OBSERVED ISOTOPIC SHIFTS AND ASSIGNMENTS OF INFRARED ABSORPTION BANDS DUE TO THE PtNO GROUP

Compound	NO str. ($\Delta\nu_{obsd}$)	Pt–(NO) bend. ($\Delta\nu_{obsd}$)	Pt–(NO) str. ($\Delta\nu_{obsd}$)
trans-$[PtCl(NH_3)_4(NO)]Cl_2$	1684 vs. (23)	569 s. (11)	not observed
trans-$[PtCl(ND_3)_4(NO)]Cl_2$	1685 vs. (23)	564 s. (13)	not observed
trans-$K_2[PtCl(NO_2)_4(NO)]$	1729 vs. (20)	552 m. (3)	
		540 sh. (11)	not observed
$K_2[PtCl_5(NO)]$	1728 vs. (30) 1712 vs. (30)	558 s. (12)	291 w. (2)
$Cs_2[PtCl_5(NO)]$	1723 vs. (29) 1709 vs. (30)	559 s. (13)	283 w. (4)
$K_2[PtBr_5(NO)]$	1681 vs. (43)	544 s. (10)	287 w. (3)

$\Delta\nu_{obsd} = \nu$ ^{14}NO-complex (obsd) $-$ ν ^{15}NO-complex (obsd)

Abbreviations: str. = stretching; bend. = bending; vs. = very strong; s. = strong; *m.* = medium; w. = weak; sh. = shoulder.

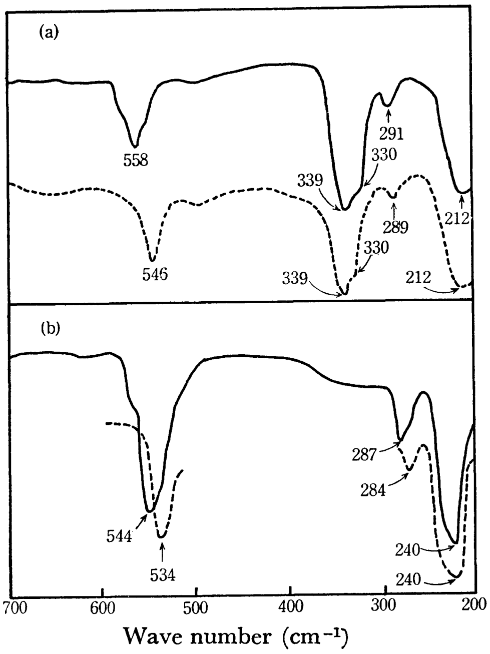

Fig. 1. Infrared spectra of $K_2[PtCl_5(NO)]$ (a) and $K_2[PtBr_5(NO)]$ (b) in the region 200—700 cm^{-1}. ^{14}NO-complex, ——; ^{15}NO-complex, ------.

$[PtCl(NH_3)_4(NO)]Cl_2$ prepared with the use of NO–NO_2 gas were almost the same as those prepared with NOCl.

Pt–NH_3 stretching vibration was expected in the region where the skeletal vibrations between the metal atom and the NO group are usually observed. This absorption band for *trans*-$[PtCl(NH_3)_4(NO)]Cl_2$ was ascertained on the basis of considerable isotopic shifts upon deuterium substitution and no isotopic shifts upon ^{15}NO-substitution. It was found that the band did not overlap with the bands due to the PtNO skeleton.

The wave numbers, isotopic shifts and assignments of infrared absorption bands due to the PtNO group of the examined complexes are shown in Table 1. The N–O stretching vibrations were observed in the region 1680—1730 cm^{-1}, the isotopic shifts upon ^{15}NO-substitution being 20—40 cm^{-1}.

Of the absorption bands in the region 200—700 cm^{-1}, only strong ones in the region 530—570 cm^{-1} shifted downwards by 10—15 cm^{-1} upon ^{15}NO-substitution for all the compounds. For $K_2[PtCl(NO_2)_4(NO)]$, the absorption bands in this region were broad and the isotopic shifts could not be measured exactly.

The infrared spectra at liquid nitrogen temperature showed that the bands in the region 530—570 cm^{-1} shifted downwards but did not split; the band at 575 cm^{-1} shifted to 565 cm^{-1} for $[PtCl(NH_3)_4(NO)]Cl_2$, that at 570 to 555 cm^{-1} for $[PtCl(ND_3)_4(NO)]Cl_2$, and that at 565 to 552 cm^{-1} for $K_2[PtCl_5(NO)]$. In the region other than 530—570 cm^{-1}, no isotopic shifts could be observed for $[PtCl(NH_3)_4(NO)]Cl_2$, $[PtCl(ND_3)_4(NO)]Cl_2$, and $K_2[PtCl(NO_2)_4(NO)]$. On the other hand, for $M_2[PtX_5(NO)]$ (M=K and Cs, X=Cl and Br) the weak absorption bands at about 290 cm^{-1} shifted downwards by 2—4 cm^{-1} (Table 1 and Fig. 1). Such absorption bands for the examined complexes except for $M_2[PtX_5(NO)]$ could not be observed because of the overlapping with the strong absorption bands due to the H_3N–Pt–NH_3 bending and the NO_2 rocking vibrations.

The IR study on $[MCl_5(NO)]^{n-}$ anion (M=Ru, Os, and Ir) by Cleare *et al.*[4] has shown that two or three M–Cl stretching, two or three Cl–M–Cl bending and (ON)–M–Cl bending vibrations are observed in the regions 280—340 cm^{-1}, 120—185 cm^{-1}, and 70—90 cm^{-1}, respectively. For $[MBr_5(NO)]^{n-}$ anion (M=Ru, Os, and Ir), M–Br stretching, Br–M–Br bending and (ON)–M–Br bending vibrations are observed in the regions 180—260 cm^{-1}, 120—140 cm^{-1}, and 60—90 cm^{-1}, respectively. No isotopic shifts upon ^{15}NO-substitution are shown for all of the absorption bands. The possibility of assigning the *ca.* 290 cm^{-1} bands to the (ON)–Pt–halogen bending vibrations can be excluded. Thus the weak bands at *ca.* 290 cm^{-1} and the strong bands at 530—570 cm^{-1} are considered to be assigned to the skeletal vibrations between the platinum and the NO group. The strong absorption band at 339 cm^{-1} with a shoulder at *ca.* 330 cm^{-1} and the broad 212 cm^{-1} band for $K_2[PtCl_5(NO)]$ can be assigned to the Pt–Cl stretching and the Cl–Pt–Cl bending vibrations, respectively. The 240 cm^{-1} band for $K_2[PtBr_5(NO)]$ can be assigned to the Pt–Br stretching vibration.

Table 2. Observed and calculated isotopic shifts ($\Delta\nu_{\text{obsd}}$ and $\Delta\nu_{\text{calcd}}$ in cm^{-1}), and force constants of $K_2[PtCl_5(NO)]$

Assignment	Observed		Calculated		$\Delta\nu_{\text{obsd}}$	$\Delta\nu_{\text{calcd}}$	Force constants (mdyn/Å)
	^{14}NO-complex	^{15}NO-complex	^{14}NO-complex	^{15}NO-complex			
Pt–N–O arrangement							
NO str.	1712	1682	1712	1682	30	30	$f_{11}=12.9$, $f_{12}=0.2$
PtNO bend.	558	546	559	546	12	13	$f_{13}=0.2$, $f_{22}=1.3$
PtN str.	291	289	291	288	2	3	$f_{23}=0.3$, $f_{33}=0.6$
Pt–O–N arrangement							
NO str.	1712	1682	1712	1682	30	30	$f_{11}=12.8$, $f_{12}=0.2$
PtON bend.	558	546	558	546	12	12	$f_{13}=0.2$, $f_{22}=1.6$
PtO str.	291	289	291	289	2	2	$f_{23}=0.8$, $f_{33}=0.8$

$\Delta\nu_{\text{obsd}}=\nu^{14}$NO-complex (obsd) $-$ ν^{15}NO-complex (obsd). $\Delta\nu_{\text{calcd}}=\nu^{14}$NO-complex (calcd) $-$ ν^{15}NO-complex (calcd). Abbreviations: str.=stretching; bend.=bending; f_{11}=force constant of N–O stretching vibration; f_{22}=force constant of Pt–(NO) stretching vibration; f_{33}=force constant of Pt–(NO) bending vibration; f_{12}=force constant associated with N–O stretching and Pt–(NO) stretching vibrations (assumed to be 0.2 mdyn/Å); f_{13}=force constant associated with N–O stretching and Pt–(NO) bending vibrations (assumed to be 0.2 mdyn/Å); f_{23}=force constant associated with Pt–(NO) stretching and Pt–(NO) bending vibrations.

Calculation of Isotopic Shifts. No structural study on monomeric nitrosylplatinum complex has been reported. IR studies for the examined complexes show that the oxidation state of the platinum atom is considered to be IV and that of the NO group $-$I. X-ray diffraction studies on several nitrosyl complexes formulated as NO$^-$ complexes have shown that the metal–(NO) bond angle is almost equal to 120° and the N–O bond distance is 1.1—1.2 Å.[5] The Pt–(NO) bond distance is considered to be 1.9—2.0 Å.[6]

Calculation of the ^{15}N-isotopic shifts by means of the three-body model of the metal atom and the NO group is useful for determining the coordination atom of the NO group and for assigning distinctly the skeletal vibrations between the metal and the NO group, when the metal atom and the ligands other than the NO group are much heavier than nitrogen and oxygen.[1] Thus the calculation is considered to be useful in the case of $K_2[PtCl_5(NO)]$ as well as $K_2[RuCl_5(NO)]$. The isotopic shifts were calculated with two angular three-body models, Pt–N–O and Pt–O–N (the metal–(NO) bond angle is 120°) and by assuming that the N–O distance is 1.1 Å and the Pt–(NO) distance 2.0 Å. The force constants f_{12} and f_{13} were assumed to be 0.2 mdyn/Å[1] (Table 2). The calculation was carried out with a Hitachi 5020E at the Computer Centre of the University of Tokyo.

The observed isotopic shifts, calculated ones and the force constants for $K_2[PtCl_5(NO)]$ are shown in Table 2. The wave numbers and isotopic shifts calculated from the bent Pt–N–O model were almost the same as those from the bent Pt–O–N one. Application of ^{15}NO-substitution to determine the coordinating atom of the NO group in the case of the NO$^-$ complexes seems to be useless even though metal and ligands are much heavier than nitrogen and oxygen. From a comparison of the observed isotopic shifts with the calculated ones, the absorption bands observed in the region 530—570 cm^{-1} can be assigned to the Pt–(NO) bending vibration, and the *ca.* 290 cm^{-1} bands which could be observed on $M_2[PtX_5(NO)]$ (M=K and Cs, X=Cl and Br) to the Pt–(NO) stretching vibration. The *ca.* 290 cm^{-1} band is in the same region as that of the 259 cm^{-1} band which was assigned to the Co–(NO) stretching vibration for $Co(NO)(S_2CN(CH_3)_2)_2$.[1] The calculation shows that the isotopic shift for the Pt–(NO) stretching vibration is smaller than that of the Pt–(NO) bending vibration for the nitrosylplatinum complexes as observed on other nitrosyl complexes.[1]

Discussion

IR studies on ammine- and chloro-complexes have shown that the NH$_3$ rocking and the Pt–Cl stretching vibrations are sensitive to the oxidation state of the metal atom.[7,8] The NH$_3$ rocking vibrations of Pt(II)- and Pt(IV)-ammine complexes are observed in the region 810—840 cm^{-1} and *ca.* 940 cm^{-1}, respectively. The Pt–Cl stretching vibrations of Pt(II)– and Pt(IV)–chloro complexes are observed at *ca.* 320 and 340 cm^{-1}, respectively. For *trans*-$[PtCl(NH_3)_4(NO)]Cl_2$, the NH$_3$ rocking vibration and the Pt–Cl stretching vibration were observed at 918 and 350 cm^{-1}, respectively. The Pt–Cl stretching vibration of $K_2[PtCl_5(NO)]$ was observed at 339 cm^{-1}. This seems to support the view that the oxidation state of the platinum atom is IV and that of the NO group $-$I.

For $Ir(NO)Cl_2(P(C_6H_5)_3)_2$ and $[Co(NO)(NH_3)_5]Cl_2$ formulated as NO$^-$ complexes, two skeletal vibrations between the metal and the NO group were observed in the region 560—620 cm^{-1}.[1] The Pt–(NO) bending vibration was observed in this region but the Pt–(NO) stretching vibration was observed at extraordinarily low wave numbers. An X-ray diffraction study on nitrosyl complexes by Mingos and Ibers[5] has shown that the N–O bond distance for nitrosyl complex formulated as NO$^-$ complex is almost equal to that formulated as NO$^+$ complex, a multiple bond character existing in the NO group of the NO$^-$ complex. This might reflect the suggestion that the Pt–(NO) bending vibration is left behind in the region 530—570 cm^{-1} where the skeletal vibrations between the metal and the NO group would have been observed even though the Pt–(NO) stretching vibration shifts to *ca.* 290 cm^{-1}. The same phenomenon has been observed on octahedral cyanides. IR studies on $[M(CN)_6]^{n-}$ and $[M(CN)_5L]^{m-}$ have shown that bands at *ca.* 460—590 cm^{-1} and at *ca.* 340—420 cm^{-1} are assigned to metal–(CN) bending and metal–(CN) stretching vibrations, respectively, and that the stretching vibrations are in a lower region than the bending vibrations by *ca.* 50—150 cm^{-1}.8)

If another possibility of overlapping of the Pt–(NO) stretching vibration with the strong absorption band assigned to the Pt–(NO) bending vibration exists, the *ca.* 290 cm^{-1} band might be assigned to one of the Pt–Cl stretching vibrations for $[PtCl_5(NO)]^{2-}$ anion, but a reasonable explanation cannot be given to the *ca.* 290 cm^{-1} band for $[PtBr_5(NO)]^{2-}$ anion.

Our recent study has shown that the isotopic shifts observed on the N–O stretching vibration for the NO$^-$ complexes are smaller than those for the NO$^+$ complexes which are almost equal to those calculated by assuming the linear metal–N–O model.1) Thus the extent of isotopic shift for N–O stretching vibration might be used as a measure for determining the oxidation state of the NO group. The isotopic shifts of the N–O stretching vibrations observed on the examined complexes are in the region 20—30 cm^{-1}, and the shift calculated by assuming a linear Pt–N–O model is 38 cm^{-1}. This seems to suggest a bent Pt–N–O linkage. The isotopic shift observed on $K_2[PtBr_5(NO)]$ was 43 cm^{-1}. The abnormally large value may be attributed to the change of Pt–(NO) bond angle due to the great size of the bromide ion in $[PtBr_5(NO)]^{2-}$ anion. However, no details can be given.

The force constants of the metal–(NO) stretching vibrations calculated by means of the three-body model are in the region 4—7 mdyn/Å. The approximate force constant of the Pt–(NO) stretching vibration for $K_2[PtCl_5(NO)]$ was calculated to be 1.3 mdyn/Å. This is considered to reflect the suggestion that the metal–(NO) bond distances for the NO$^-$ complexes are generally longer than those for the NO$^+$ complexes.5) The force constant for the Pt–(NO) stretching vibration is considered to be comparable to the force constants for the Pt–NH$_3$ stretching vibrations; for the Pt(II) and the Pt(IV)-ammine complexes, the force constants of the Pt–NH$_3$ stretching vibrations have been reported to be 1.92 and 2.13 mdyn/Å, respectively.9)

For $M_2[PtX_5(NO)]$ (M=K and Cs, X=Cl and Br), the effects of outer sphere cations and halide ions on IR spectra were observed on the absorption bands due to the Pt–(NO) skeleton. The wave numbers of the N–O stretching, Pt–(NO) bending and Pt–(NO) stretching vibrations increase in the order Br and Cl for the potassium salts, and the wave numbers of the N–O stretching and Pt–(NO) stretching vibrations increase in the order Cs and K for the chloro-complexes. These tendencies were similar to those observed on the absorption bands due to the Ru–(NO) skeleton for $M_2[RuX_5(NO)]$ (M=K, Rb, and Cs; X=Cl, Br, and I).10)

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