BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 3779—3784 (1973)

Infrared Spectra of Some Transition-metal (Fe, Co, Ru, and Ir) Nitrosyl (^{14}NO and ^{15}NO) Complexes

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(Received June 4, 1973)

Twelve ^{15}NO-complexes of iron, cobalt, ruthenium, and iridium were prepared. The correlations of the isotopic shifts of their IR spectra with a metal-(NO) bond angle were investigated. For several nitrosyl complexes, the absorption bands due to the skeletal vibrations between the metal and the NO group were clearly assigned. Of the two absorption bands in the region 250—650 cm^{-1}, the absorption band with a smaller isotopic shift could be assigned to the metal-(NO) stretching vibration and that with a larger isotopic shift to the metal-(NO) bending vibration.

Since an infrared study of $Co(NO)(CO)_3$ and its ^{15}N analogue led to definite assignments of the skeletal vibrations between the cobalt and the NO group,[1] the effect of the ^{15}N-substitution on infrared spectra has been measured on several nitrosyl complexes formulated as NO^+ complexes.[2-9] For the nitrosyl complexes of chromium, manganese and ruthenium, distinct assignments of the skeletal vibrations between the metal and the NO group, and determination of the coordinating atom of the NO group to the metal atom have been made from a comparison of the observed isotopic shifts with the calculated ones.[2-4] Recently,

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Table 1. Crystallographic data and preparative methods for nitrosyl complexes

Complex	M-N, Å	N-O, Å	M-N-O, deg.	Preparative Method
trans-$Na_2[Ru(OH)(NO_2)_4(NO)]\cdot 2H_2O$	1.75	1.13	180[a]	Ref. 16
trans-$K_2[Ru(OH)(NO_2)_4(NO)]$	1.79	1.12	171[b]	Ref. 17
$K_2[RuCl_5(NO)]$	1.88	1.09	171[c]	Ref. 3
$Ru(NO)(S_2CN(C_2H_5)_2)_3$	1.72	1.17	170[d]	l)
trans-$[Ru(OH)(NH_3)_4(NO)]Cl_2$	2.07	1.14	*ca.* 150[e]	Ref. 16
trans-$[RuCl(NH_3)_4(NO)]Cl_2$	no data			Ref. 16
$Ru(NO)(S_2CN(CH_3)_2)_3$	no data			l)
$Fe(NO)(S_2CN(CH_3)_2)_2$	1.71	1.02	173[f]	m)
$Co(NO)(S_2CN(CH_3)_2)_2$	1.75	1.03, 1.11	135, 136[g]	n)
$[Co(NH_3)_5(NO)]Cl_2$	1.87	1.15	119[h]	Ref. 3
$[Co(NO)en_2](ClO_4)_2$	no data			o)
$Ir(NO)(P(C_6H_5)_3)_3$	1.67	1.24	180[i]	p)
$[Ir(NO)_2(P(C_6H_5)_3)_2](ClO_4)$	1.77	1.21	164[j]	q)
$IrCl_2(NO)(P(C_6H_5)_3)_2$	1.94	1.03	123[k]	r)

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Sabatini[10] and Tosi[11-14] carried out polarized infrared studies on single crystals of some transition-metal nitrosyl compounds to assign the metal–(NO) skeletal vibrations. Their results are consistent with those obtained by the infrared isotopic shift method.

In this paper we describe infrared studies on the nitrosyl complexes of iron, cobalt, ruthenium, and iridium, and their ^{15}NO-complexes.

Experimental

The nitrosyl complexes were prepared according to the methods referred to in Table 1. Their ^{15}NO-complexes were prepared in a vacuum line with the use of ^{15}NO gas (1 mmol) derived from $K^{15}NO_3$ (^{15}N atom% = 95—99). All other reagents were of analytical grade. The infrared spectra and elementary analyses showed that the desired products were obtained.

Infrared spectra were measured in the region 200—4000 cm^{-1} by means of Nujol mull and hexachlorobutadiene mull techniques. JASCO DS-402G (700—4000 cm^{-1}) and JASCO model IR-F (200—700 cm^{-1}) infrared spectrophotometers were used. The wave numbers of the absorption bands were calibrated with 1,2,4-trichlorobenzene, polystyrene film and water vapor.

Results

Assignments of Infrared Spectra. The assignments of the N–O stretching vibrations and the skeletal vibrations between the metal and the NO group were made on the basis of observation of the ^{15}N-isotopic shifts. The ^{15}N-isotopic shifts of the skeletal vibrations observed in the limited region *ca.* 450—650 cm^{-1} were carefully measured[1-17] in order to obtain distinct assignments for the skeletal vibrations. The isotopic shifts observed were compared with those calculated with a three-body model of the metal and the NO group.[3] The assignments of the absorptions due to metal–(NO) skeletal vibrations, and the observed and calculated isotopic shifts are shown in Table 2. A number of absorption bands due to the ligands except for NO group were assigned according to Adams.[18]

trans-$Na_2[Ru(OH)(NO_2)_4(NO)]\cdot 2H_2O$: The skeletal vibrations between the ruthenium and the NO group could not be clearly assigned. The skeletal vibrations, the Ru–OH stretching vibration and the wagging vibration of NO_2 group are observed in the region 550—640 cm^{-1}. These four bands shifted upon ^{15}N-substitution. Deuteration of this complex was carried out for assigning the four bands.

The absorption bands in the region 550—640 cm^{-1} lacked sharpness. This is considered to be due to the overlap with the broad and strong absorption band of

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the libration of water of crystallization. The dehydrated salts of the ^{14}NO- and ^{15}NO-complexes were prepared in order to measure the isotopic shifts more exactly. The spectral figure of $Na_2[Ru(OH)(NO_2)_4(NO)]$ is quite similar to that of its dihydrate.

The N–O stretching vibration of $Na_2[Ru(OH)(NO_2)_4(NO)]\cdot 2H_2O$ shifted from 1898 (vs)[19] to 1862 cm^{-1} (vs) upon ^{15}NO-substitution. The 584 cm^{-1} band (m) of $Na_2[Ru(OH)(NO_2)_4(^{14}NO)]$ shifted to 568 cm^{-1} (sh) upon deuterium substitution, but not the bands at 634, 612, and 555 cm^{-1}. Therefore, the band at 584 cm^{-1} (m) could be assigned to the Ru–OH stretching vibration. The 634 (m), 612 (vs), and 555 cm^{-1} (vs) bands of $Na_2[Ru(OH)(NO_2)_4(^{14}NO)]$ shifted downwards by *ca.* 9, 5, and 4 cm^{-1}, respectively, upon ^{15}NO-substitution. From the values of the isotopic shift the 634 cm^{-1} band could be assigned to a skeletal vibration between the ruthenium and the NO group. The 612 and the 555 cm^{-1} bands are considered to be due to another skeletal vibration and the wagging vibration of NO_2 group. The 612 cm^{-1} band may be assigned to the wagging vibration of NO_2 group in view of the following. A neutron diffraction study on $Na_2[Ru(OH)(NO_2)_4(NO)]\cdot 2H_2O$ shows that the $O(H_2O)$–$N(NO_2)$ distances are 2.9—3.3 Å, and the $O(H_2O)$–O(OH) and the $O(H_2O)$–O(NO) distances are 3.5 Å and 3.9 Å, respectively.[20] Thus we see that the water of crystallization affects the wagging vibration of NO_2 groups to a greater extent than the Ru–OH stretching vibration and the skeletal vibrations, and the NO_2 wagging vibration is more influenced by the dehydration of the water of crystallization than the Ru–OH stretching vibration and the skeletal vibrations. The 635 (s), 583 (w), and 557 cm^{-1} (vs) bands hardly shift on the dehydration of water of crystallization, while only the 602 cm^{-1} band (vs, b) shifts to 612 cm^{-1}. The 635 and the 557 cm^{-1} bands of $Na_2[Ru(OH)(NO_2)_4(^{14}NO)]\cdot 2H_2O$ could be assigned to the skeletal vibrations between the ruthenium and the NO group. The 583 and 602 cm^{-1} bands were assigned to the Ru–OH stretching vibration and the wagging vibration of NO_2 group, respectively.

trans-$K_2[Ru(OH)(NO_2)_4(NO)]$: The N–O stretching vibration shifted from 1887 cm^{-1} (vs) to 1848 cm^{-1} (vs) upon ^{15}NO-substitution. In the region 550—640 cm^{-1}, four absorption bands at 623 (vs, b), 580 (s), 573 (s), and 565 cm^{-1} (sh) were also observed as in the case of the sodium salt. Their isotopic shifts upon ^{15}NO- and deuterium substitutions were complicated, making it impossible to assign the four bands unambiguously.

trans-$[Ru(OH)(NH_3)_4(NO)]Cl_2$: The absorption bands at 1841 (vs), 630 (m), and 589 cm^{-1} (m) shifted to 1807, 613, and 585 cm^{-1}, respectively, upon ^{15}NO-substitution. On the other hand, the 564 cm^{-1} band (vs, b) did not shift upon ^{15}NO-substitution and was assigned to the Ru–OH stretching vibration. Ru–NH_3 stretching vibrations were observed at 476 cm^{-1} (m) and 497 cm^{-1} (vw).

trans-$[RuCl(NH_3)_4(NO)]Cl_2$: The 1880 cm^{-1} band (vs) shifted to 1844 cm^{-1}, the 603 cm^{-1} band (s) to 586 cm^{-1}, and the 562 cm^{-1} band (m) to 560 cm^{-1} upon ^{15}NO-substitution. The Ru–NH_3 stretching vibration was observed at 486 cm^{-1} (vs).

$Ru(NO)(S_2CNR_2)_3$ ($R=CH_3$ and C_2H_5) and $Fe(NO)(S_2CN(CH_3)_2)_2$: The absorption bands due to dialkyldithiocarbamate ion[21,22] (the C–S stretching, the C–N–C bending, the metal–S stretching and the ring deformation vibrations) overlapped with the skeletal vibrations between the metal and the NO group. Thus, the isotopic shifts upon the ^{15}NO-substitution could not be measured exactly.

The bands at 1827 (vs), 1808 (vs), and 544 cm^{-1} (sh) for $Ru(NO)(S_2CN(CH_3)_2)_3$ shifted upon ^{15}NO-substitution to 1790, 1771, and 540 cm^{-1} (s), respectively. The bands at 1806 (vs), 572 (s, b), and 554 cm^{-1} (sh) for $Ru(NO)(S_2CN(C_2H_5)_2)_3$ shifted to 1774, 560 (s, b), and 540 cm^{-1} (s), respectively.

The N–O stretching vibration for $Fe(NO)(S_2CN(CH_3)_2)_2$ shifted from 1691 to 1656 cm^{-1}, and the band at 560 cm^{-1} (m) shifted to 556 cm^{-1} (m) upon ^{15}NO-substitution.

$Co(NO)(S_2CN(CH_3)_2)_2$: The N–O stretching vibration shifted from 1624 cm^{-1} (vs) to 1596 cm^{-1} upon ^{15}NO-substitution. Three absorption bands (576 cm^{-1} (w), 555 cm^{-1} (sh) and 551 cm^{-1} (w)) observed in the region where the skeletal vibrations between the metal and the NO group would have been observed did not shift upon ^{15}NO-substitution. These absorption bands could be assigned to the C–S stretching vibration, the Co–S stretching vibration and the ring deformation due to the coordinated dimethyldithiocarbamate.[21,22] On the other hand, the broad bands at 317 cm^{-1} (m) and 259 cm^{-1} (m) shifted by ^{15}NO-substitution to 311 cm^{-1} and 256 cm^{-1}, respectively. These bands observed at rather extraordinarily low frequencies are assigned to the skeletal vibrations between the cobalt and the NO group. An X-ray diffraction study of $Co(NO)(S_2CN(CH_3)_2)_2$ shows that the bond angle of the Co–N–O is 135°, and the oxygen atom of the NO group alternately lies above two of the Co–S bonds of the same dimethyldithiocarbamate ligand.[23] The skeletal vibrations between the cobalt and the NO group are considered to reflect the structure. However, another possibility of overlapping of CoNO skeletal vibrations with the vibrations due to the coordinated dimethyldithiocarbamate ligands can not be excluded.

$[Co(NO)en_2](ClO_4)_2$: The N–O stretching vibration shifted from 1661 (vs) to 1632 cm^{-1} and the bands at 560 (sh) and 490 cm^{-1} (m) shifted to 550 (b, w) and 486 cm^{-1} (m), respectively. These absorption bands seem to be due to the Co–(NO) skeleton.

$Ir(NO)(P(C_6H_5)_3)_3$, $[Ir(NO)_2(P(C_6H_5)_3)_2]ClO_4$, and $Ir(NO)Cl_2(P(C_6H_5)_3)_2$: The N–O stretching vibrations and the skeletal vibrations between the iridium

19) The sign in parentheses presents the abbreviations of the absorption strength and shape; vs=very strong, s=strong, m=medium, w=weak, vw=very weak, sh=shoulder, b=broad.

20) Reference (a) in Table 1.

21) G. Durgaprasad, D. N. Sathyanarayana, and C. C. Patel, *Can. J. Chem.*, **47**, 631 (1969).

22) I. Ojima, T. Ohnishi, T. Iwamoto, N. Iwamoto, and K. Tamaru, *Inorg. Nucl. Chem. Letters*, **6**, 65 (1970).

23) Reference (g) in Table 1.

and the NO group overlapped with the absorption bands due to triphenylphosphine. From a comparison of the absorption strength of free triphenylphosphine with that of $Ir(NO)(P(C_6H_5)_3)_3$ and $Ir(NO)Cl_2(P(C_6H_5)_3)_2$, it was considered that the 617 cm^{-1} band assigned to a skeletal vibration might overlap with the band due to triphenylphosphine.

For $Ir(NO)(P(C_6H_5)_3)_3$, the N–O stretching vibrations at 1601 (vs) and 1582 cm^{-1} (m) shifted to 1557 and 1541 cm^{-1}, respectively, upon ^{15}NO-substitution. The bands at 617 (m) and 533 cm^{-1} (w) shifted to 610 (m) and 522 cm^{-1}, respectively.

For $[Ir(NO)_2(P(C_6H_5)_3)_2]ClO_4$, the bands at 1759 (m) and 1707 cm^{-1} (vs) (the N–O stretching vibrations) shifted to 1725 and 1674 cm^{-1}, respectively. Five absorption bands in the region 370—590 cm^{-1} shifted upon ^{15}NO-substitution (from 584 (m), 553 (m), 539 (m), 527 (m), and 381 cm^{-1} (m) to 570 (w), 545 (w), 533 (w), 524 (w), and 373 cm^{-1} (m), respectively). An X-ray diffraction study shows that the O–N–Ir–N–O skeleton belongs to the point group C_{2v}.[24] The seven absorption bands could be attributed to the skeletal vibrations due to the O–N–Ir–N–O group.

For $IrCl_2(NO)(P(C_6H_5)_3)_2$, the bands at 1628 (vs) and 1558 cm^{-1} (vs) shifted to 1599 and 1533 cm^{-1}, respectively, upon ^{15}NO-substitution. The 1558 cm^{-1} band has already been assigned to the N–O stretching vibration.[25] The 1628 cm^{-1} band can also be assigned to it. It is not clear why the splitting of the N–O stretching vibration is extraordinarily large. The skeletal vibrations were observed at 617 (m) and 589 cm^{-1} (w), and shifted to 598 (w) and 576 cm^{-1} (w), respectively.

Calculation of Isotopic Shifts and Definite Assignments of Skeletal Vibrations. In previous reports, the

Table 2. Observed isotopic shifts, calculated ones ($\Delta\nu_{obsd}$ and $\Delta\nu_{calcd}$ in cm^{-1}) and force constants of some transition-metal nitrosyl compounds

Assignment	Observed		Calculated		$\Delta\nu_{obsd}$	$\Delta\nu_{calcd}$	force constants (mdyn/Å)		
	^{14}NO-complex	^{15}NO-complex	^{14}NO-complex	^{15}NO-complex					
			trans-$Na_2[Ru(OH)(NO_2)_4(NO)]\cdot 2H_2O$						
NO str.	1898	1862	1899	1861	36	38	$f_{11}=14.7$,	$f_{12}=0.2$,	
RuNO bend.	635	625	638	622	10	16		$f_{22}=4.6$	
RuN str.	557	553	558	552	4	6			$f_{33}=0.6$
			$K_2[RuCl_5(NO)]$						
NO str.	1904	1865	1904	1865	39	39	$f_{11}=14.5$,	$f_{12}=0.2$,	$f_{13}=0.2$
RuN str.	606	600	608	602	6	6		$f_{22}=5.6$,	$f_{23}=0.3$
RuNO bend.	588	572	585	571	16	14			$f_{33}=0.5$
			trans-$[Ru(OH)(NH_3)_4(NO)]Cl_2$						
NO str.	1841	1807	1848	1810	34	38	$f_{11}=13.9$,	$f_{12}=0.2$,	$f_{13}=0.2$
RuNO bend.	630	613	628	612	17	16		$f_{22}=5.2$,	$f_{23}=0.7$
RuN str.	589	585	591	586	4	5			$f_{33}=0.7$
			$[Co(NH_3)_5(NO)]Cl_2$ (Co-N-O arrangement)						
NO str.	1614	1589	1617	1586	25	31	$f_{11}=11.1$,	$f_{12}=0.2$,	$f_{13}=0.2$
CoN str.	581	579	584	576	2	8		$f_{22}=3.9$,	$f_{23}=1.1$
CoNO bend.	564	558	567	555	6	12			$f_{33}=0.9$
			$[Co(NH_3)_5(NO)]Cl_2$ (Co-O-N arrangement)						
NO str.	1614	1589	1615	1588	25	27	$f_{11}=11.2$,	$f_{12}=0.2$,	$f_{13}=0.2$
CoON bend.	581	579	583	578	2	5		$f_{22}=3.7$,	$f_{23}=0.9$
CoO str.	564	558	565	556	6	9			$f_{33}=0.9$
			$Ir(NO)(P(C_6H_5)_3)_3$						
NO str.	1601	1557	1598	1560	44	38	$f_{11}=9.0$,	$f_{12}=0.2$	
IrN str.	617	610	615	611	7	4		$f_{22}=7.3$	
IrNO bend.	533	522	534	521	11	13			$f_{33}=0.4$
			$IrCl_2(NO)(P(C_6H_5)_3)_2$						
NO str.	1558	1533	1561	1530	25	31	$f_{11}=10.0$,	$f_{12}=0.2$,	$f_{13}=0.2$
IrNO bend.	617	598	614	601	19	13		$f_{22}=5.4$,	$f_{23}=1.4$
IrN str.	589	576	586	579	13	7			$f_{33}=1.0$

$\Delta\nu_{obsd}=\nu_{^{14}NO\text{-complex(obsd)}}-\nu_{^{15}NO\text{-complex(obsd)}}$; $\Delta\nu_{calcd}=\nu_{^{14}NO\text{-complex(calcd)}}-\nu_{^{15}NO\text{-complex(calcd)}}$; f_{11}, force constant of NO str.; f_{12}, force constant associated with metal-N str. and NO str. (assumed to 0.2 mdyn/Å); f_{13}, force constant associated with metal-NO bend. and NO str. (assumed to 0.2 mdyn/Å in the case of the compounds which contain an angulary coordinated NO group); f_{22}, force constant of metal-N str.; f_{23}, force constant associated with metal-N str. and metal-NO bend.; f_{33}, force constant of metal-NO bend; str., stretching; bend., bending.

24) Reference (j) in Table 1.

25) C. A. Reed and W. P. Roper, *J. Chem. Soc. A*, **1970**, 3054.

isotopic shifts observed upon ^{15}NO-substitution were compared with those calculated by the simple three-body model of the metal and the NO group. For the complexes formulated as NO^+ complexes, it has been found that this method is useful for a definite assignment of the skeletal vibrations between the metal and the NO group.[3,6,7]

We have calculated the isotopic shifts for the following six compounds: *trans*-$Na_2[Ru(OH)(NO_2)_4(NO)]\cdot 2H_2O$, $K_2[RuCl_5(NO)]$, *trans*-$[Ru(OH)(NH_3)_4(NO)]Cl_2$, $[Co(NH_3)_5(NO)]Cl_2$, $Ir(NO)(P(C_6H_5)_3)_3$, and $IrCl_2(NO)(P(C_6H_5)_3)_2$.

The isotopic shifts of the N–O stretching vibration and the skeletal vibrations could be measured exactly. When the N–O stretching absorption band splitted into two peaks, the wave number of the stronger peak was used in the calculation.

The isotopic shifts of $K_2[RuCl_5(NO)]$ and $[Co(NH_3)_5(NO)]Cl_2$ were calculated on the assumption that the metal–N–O are linearly arranged.[3] For $K_2[RuCl_5(NO)]$, the bond angle of the Ru–N–O is 171°. The isotopic shifts were therefore recalculated by using the wave numbers already reported and this bond angle. For $[Co(NH_3)_5(NO)]Cl_2$, if the NO group coordinated linearly to the Co atom as revealed by X-ray diffraction studies,[26] a comparison of the observed isotopic shifts with the calculated ones leads to the result that the NO group coordinates to the cobalt atom through the oxygen atom rather than through the nitrogen atom.[3] However, a recent X-ray diffraction study from three-dimensional data has shown that the bond angle of Co–(NO) is 119° (see Table 1). Therefore, the isotopic shifts of the Co–N–O and the Co–O–N arrangements were calculated by using of the wave numbers already reported and this bond angle.

The secular equations for calculating the isotopic shifts were set up in accordance with Wilson's ***GF*** matrix method.[27] The calculations were carried out at the Computation Centre of the University of Tokyo, with a Hitachi 5020E, the programs being set up in the laboratory of Prof. T. Shimanouchi.

Table 2 shows the observed isotopic shifts ($\Delta\nu_{obsd.}$ in cm^{-1}), calculated isotopic shifts ($\Delta\nu_{calcd.}$ in cm^{-1}) and the force constants for the above six compounds. For the compounds which contain a linearly coordinated NO group, the wave numbers, isotopic shifts and force constants were calculated assuming the force constant f_{12} associated with metal–(NO) stretching and N–O stretching vibration to be 0.2 mdyn/Å. For the compounds which contain an angularly coordinated NO group, both f_{12} and f_{13} were presumed to be 0.2 mydn/Å.

Detailed infrared studies on transition-metal cyano complexes have shown that the force constants associated with the C–N stretching and the metal–(CN) stretching vibrations are 0.2—0.4 mdyn/Å.[28,29] The metal–NO bonding state of the nitrosyl complex formulated as NO^+ complex are similar to the metal–CN bonding state. Hence, it is considered to be reasonable as a first approximation that f_{12} and f_{13} are presumed to be 0.2 mydn/Å.

Assignments of the skeletal vibrations between the metal and the NO group were performed by calculating potential energy distribution. The results show that definite assignments of the skeletal vibrations exclusively depend on the extent of the isotopic shifts but not on the relative positions and strength of the absorption bands. Of the two absorption bands in the region 400—650 cm^{-1} where the isotopic shifts are observed, the absorption band which caused a smaller isotopic shift was assigned to the metal-(NO) stretching vibration and another band which caused a larger isotopic shift to the metal–(NO) bending vibration. The same assignments will be also expected for other compounds examined. For *trans*-$[RuCl(NH_3)_4(NO)]Cl_2$, the 603 cm^{-1} band ($\Delta\nu_{obsd.}=17$ cm^{-1}) can be assigned to the Ru–(NO) bending vibration and the 562 cm^{-1} band ($\Delta\nu_{obsd.}=2$ cm^{-1}) to the Ru–(NO) stretching vibration. For $Co(NO)(S_2CN(CH_3)_2)_2$, the 317 cm^{-1} band ($\Delta\nu_{obsd.}=6$ cm^{-1}) may be assigned to the Co–(NO) bending vibration and the 259 cm^{-1} band ($\Delta\nu_{obsd.}=3$ cm^{-1}) to the Co–(NO) stretching vibration. For $[Co(NO)en_2](ClO_4)_2$, the 560 cm^{-1} band ($\Delta\nu_{obsd.}=10$ cm^{-1}) may be assigned to the Co–(NO) bending vibration and the 490 cm^{-1} band ($\Delta\nu_{obsd}=4$ cm^{-1}) to the Co–(NO) stretching vibration. The 544 cm^{-1} band ($\Delta\nu_{obsd}=4$ cm^{-1}) for $Fe(NO)(S_2CN(CH_3)_2)_2$ may be assigned to the Fe–(NO) stretching vibration from the value of the observed isotopic shifts. For $Ru(NO)(S_2CN(C_2H_5)_2)_3$, the isotopic shifts upon the ^{15}NO-substitution were observed but definite as-

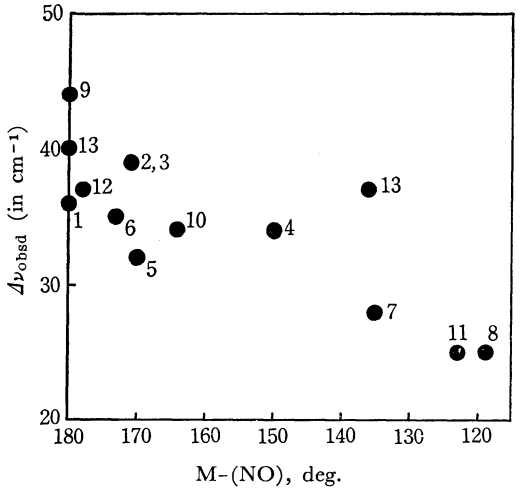

Fig. 1. Correlation of ^{15}N-isotopic shift for N–O stretching vibration with metal-(NO) bond angle.
1: *trans*-$Na_2[Ru(OH)(NO_2)_4(NO)]\cdot 2H_2O$, 2: *trans*-$K_2[Ru(OH)(NO_2)_4(NO)]$, 3: $K_2[RuCl_5(NO)]$, 4: *trans*-$[Ru(OH)(NH_3)_4NO)]Cl_2$, 5: $Ru(NO)(S_2CN(C_2H_5)_2)_3$, 6: $Fe(NO)(S_2CN(CH_3)_2)_2$, 7: $Co(NO)(S_2CN(CH_3)_2)_2$, 8: $[Co(NH_3)_5(NO)]Cl_2$, 9: $Ir(NO)(P(C_6H_5)_3)_3$, 10: $[Ir(NO)_2(P(C_6H_5)_3)_2](ClO_4)$, 11: $IrCl_2(NO)(P(C_6H_5)_3)_2$, 12: $Na_2[Fe(CN)_5(NO)]\cdot 2H_2O$(Ref. 6), 13: $[RuCl(NO)_2(P(C_6H_5)_3)_2][PF_6]$(Ref. 28)
1～11 present work

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signments of the skeletal vibrations could not be made from the values of the observed isotopic shifts.

The correlations of the ^{15}N-isotopic shifts observed for the N–O stretching vibrations with a metal–(NO) bond angles are shown in Fig. 1. The isotopic shifts for the N–O stretching vibrations decreased with deviation of metal–(NO) bond angle from linearity.

The force constants calculated from a simple three-body model are also summarized in Table 2. The force constants of the N–O stretching vibrations are 9—15 mdyn/Å, those of the metal–(NO) stretching vibrations 4—6 mdyn/Å and those of the metal–(NO) bending vibrations 0.4—1 mdyn/Å. The force constants (f_{23}) associated with a metal–(NO) stretching and the metal–(NO) bending vibrations are 0.3—1.5 mdyn/Å. The values were found to agree with those already reported.[1,5,30-33]

Discussion

Deviation of the metal-(NO) bond angle from linearity causes a decrease in the isotopic shifts of the N–O stretching vibration. The decrease might be explained as follows; the smaller the metal-(NO) bond angle, the greater the effect on N–O stretching vibration by the skeletal vibrations between the metal and the NO group. Such a phenomenon has been reported on $[RuCl(NO)_2(P(C_6H_5)_3)_2][PF_6]$ on which an X-ray diffraction study has shown that both the linear and the bent nitrosyl groups coordinate to the ruthenium atom, the corresponding bond angles being 179.5° and 136.0°, respectively.[34] The N–O stretching vibrations of the linear and the bent NO groups are observed at 1850 and 1687 cm^{-1}, these bands shifting upon the ^{15}NO-substitution downwards by 40 and 37 cm^{-1}, respectively.[35] This shows that the bond angle significantly influences the value of the isotopic shift.

For $[Co(NH_3)_5(NO)]Cl_2$, a comparison of the observed isotopic shifts with the calculated ones showed that the NO group coordinated to the cobalt atom through the oxygen atom rather than through the nitrogen atom. However, when the bond angle deviates from 180° the criterion based on the isotopic shift becomes less useful; in the case of $[Co(NH_3)_5(NO)]Cl_2$ where Co–(NO) bond angle is 119°, it cannot be concluded whether the coordinated atom is oxygen or nitrogen (Fig. 1).

Calculation of the ^{15}NO-isotopic shifts with the use of the three-body model of the metal and the NO group is useful for assigning distinctly 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 independent of the metal–(NO) bond angle. This method is considered to be useful for estimating the oxidation state of NO group since the isotopic shifts of the N–O stretching vibrations for the complexes formulated as NO^+ complexes are almost equal to those calculated by assuming a linear arrangement of a metal–N–O, and are larger than those for the NO^- complexes where metal–(NO) bond angle is approximetely 120°. The three-body model can be considered to be a good approximation when the central metal atom and ligands other than the NO group are much heavier than nitrogen and oxygen. Hence, of the complexes examined, the best approximation was given by $K_2[RuCl_5(NO)]$.

The authors are indebted to Professor Ichiro Nakagawa, Tohoku University and Mr. Hiroshi Saito, Rikkyo University, for their valuable suggestions concerning calculations of normal vibrations.

The present work was supported in part by a Grant for Scientific Research from the Ministry of Education.

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