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Infrared Studies of Transition-Metal Nitrosyl (^{14}NO and ^{15}NO) Complexes—Nitrosylruthenium(III),[*1] Nitrosylchromium(II)[*1] and Nitrosylcobalt(II)[*1] Complexes

Eiichi Miki

Department of Chemistry, College of Science, St. Paul's (Rikkyo) University, Nishi-Ikebukuro, Tokyo

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For $K_2[RuX_5(NO)]$ (X=Cl and Br), $K_3[Cr(CN)_5(NO)]\cdot H_2O$, $[Cr(NH_3)_5(NO)]X_2$ (X=Cl and ClO_4) and black-$[Co(NH_3)_5(NO)]Cl_2$, it was attempted to determine the coordinating atom of the nitrosyl group to the metal atom and to assign the skeletal vibrations between the metal and the nitrosyl group by measuring the effect of the nitrogen isotope ^{15}N on infrared spectra. The isotopic shifts for the ^{15}NO-complex to the ^{14}NO-complex were calculated for two kinds of a linear three-body model, M–N–O and M–O–N (M=metal atom), and the calculated shifts were compared with the observed ones. For nitrosylruthenium and nitrosylchromium complexes, the M–N–O arrangement was found, and of the two absorption bands in the region 530—620 cm^{-1}, the higher wave number was assigned to the M–N stretching vibration and the lower one to the M–N–O bending vibration. For black-$[Co(NH_3)_5(NO)]Cl_2$, the Co–O–N arrangement was found.

It has been conventionally described that the nitrosyl group of the transition-metal nitrosyl compounds is bound to the metal atom through the nitrogen atom. There have been some studies on whether the nitrosyl group is coordinated to the metal atom through the nitrogen atom or through the oxygen atom. A neutron diffraction study of $Na_2[Ru(OH)(NO_2)_4(NO)]\cdot 2H_2O$[1] clearly showed that the nitrogen atom of the nitrosyl group is coordinated to the ruthenium atom, and that the Ru–N–O group is linear; infrared studies of black-$[Co(NH_3)_5(NO)]Cl_2$,[2] including an examination of its chemical properties, suggested the Co–N–O arrangement. On the other hand, visible-ultraviolet spectroscopic studies of the red-pentamminenitrosylcobalt(II) complex[3] have led to the Co–O–N arrangement. Moreover, an infrared study of $Co(NO)(CO)_3$ and its ^{15}NO-complex[4] determined the coordinating atom of the NO group to the cobalt atom, and led to the assignment of the absorption bands due to the Co–N stretching vibration and the Co–N–O bending vibration. The infrared study of $Na_2[Fe(CN)_5(NO)]\cdot 2H_2O$[5] in polarized light has enabled the assignment of the absorption bands due to the Fe–N stretching vibration and the Fe–N–O bending vibration.

This paper presents the determination of the coordinating atom of the NO group to the metal atom, and assignments of the skeletal vibrations between the metal and the NO group by measuring the effect of the nitrogen isotope ^{15}N on the infrared spectra for $K_2[RuX_5(NO)]$ (X=Cl and Br),[6] $K_3[Cr(CN)_5(NO)]\cdot H_2O$, $[Cr(NH_3)_5(NO)]X_2$ (X=Cl and ClO_4) and black-$[Co(NH_3)_5(NO)]Cl_2$.

Experimental

Preparations of Transition-metal Nitrosyl Compounds. ^{15}N enriched potassium nitrate, containing ^{15}N more than 92 atom %, used to prepare the ^{15}NO-complexes was obtained from the Institute of Physical and Chemical Research in Japan. The ^{15}NO-complexes were prepared on a semimicro scale. These preparations on a semimicro scale were thought to give the correct products because the prepared ^{14}NO-complex gave the same infrared spectrum as that prepared on an ordinary scale.

[*1] The oxidation number is given according to Rule 7323 of IUPAC Nomenclature of Inorganic Chemistry, because the oxidation state of the metal bound to the nitrosyl group can not be determined from the sole criterion unequivocally.

[1] S. H. Simonsen and M. H. Mueller, *J. Inorg. & Nucl. Chem.*, **27**, 309 (1965).

[2] W. P. Griffith, J. Lewis and G. Wilkinson, *ibid.*, **7**, 38 (1958).

[3] S. Yamada, H. Nishikawa and R. Tsuchida, *This Bulletin*, **33**, 930 (1960).

[4] R. S. McDowell, W. D. Horrocks and J. Yates, *J. Chem. Phys.*, **34**, 530 (1961).

[5] A. Sabatini, *Inorg. Chem.*, **6**, 4756 (1967).

[6] E. Miki, T. Ishimori, H. Yamatera and H. Okuno, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **87**, 703 (1966).

The infrared spectra of the ^{15}NO-complexes prepared showed that the NO group in the complexes retained almost the same ^{15}N-atom percentages as those of the starting ^{15}N-materials.

$K_2[RuX_5(NO)]$ (X=Cl and Br). Compounds with normal nitrogen isotopes were prepared by conventional methods.[7] The ^{15}N-labeled compound was prepared on a semimicro scale using a vacuum line. Nitrosylruthenium(III) solution could be prepared with a good yield by bringing an excess of ^{15}NO gas derived from 50—200 mg $K^{15}NO_3$ (^{15}N atom %=92 and 96.9) in contact with ruthenium halide (10—30 mg ruthenium) in hydrohalogenic acid solution, and then closing off the reaction vessel and allowing it to stand for 1—2 days at room temperature. A small excess of potassium halide was added to the nitrosylruthenium(III) solution and the solution evaporated to obtain the ^{15}NO-complex. The separation of ruthenium (III and IV) and nitrosylruthenium (III)*2 showed that ruthenium ion was converted to nitrosylruthenium ion almost completely (more then 99.9%) in this semimicro scale preparation.

Found: K, 20.1; Ru, 25.7; N, 3.66%. Calcd for $K_2[RuCl_5(NO)]$: K, 20.23; Ru, 26.15; N, 3.62%. Found: K, 12.7; Ru, 16.3; N, 2.38%. Calcd for $K_2[RuBr_5(NO)]$: K, 12.85; Ru, 16.60; N, 2.30%.

$K_3[Cr(CN)_5(NO)]\cdot H_2O$ and $[Cr(NH_3)_5(NO)]X_2$ (X=Cl and ClO_4). The pentacyano-and pentammine-nitrosylchromium(II) compounds with normal nitrogen isotopes were prepared by the methods of Griffith[8] and Mori,[9] respectively. The ^{15}NO-complexes were prepared on a scale 1/10—1/20 that of ordinary methods. $K_3[Cr(CN)_5(^{15}NO)]\cdot H_2O$ was obtained with ^{15}N-substituted hydroxylamine hydrochloride prepared according to the method of Ogata and Hirono,[10] who used sodium nitrite instead of potassium nitrate. $[Cr(NH_3)_5(^{15}NO)]X_2$ was prepared by Mori's method[9] using nitrogen-15 enriched potassium nitrate (^{15}N atom %=97.6) instead of sodium nitrite.

Found: K, 33.1; Cr, 15.0; C, 17.46; N, 24.74%. Calcd for $K_3[Cr(CN)_5(NO)]\cdot H_2O$: K, 33.77; Cr, 14.97; C, 17.29; N, 24.19%. Found: Cr, 21.5; N, 34.22; H, 6.00; Cl, 29.6%. Calcd for $[Cr(NH_3)_5(NO)]Cl_2$: Cr, 21.84; N, 35.30; H, 6.36; Cl, 29.78%. Found: Cr, 14.2; N, 22.76; H, 3.95%. Calcd for $[Cr(NH_3)_5(NO)](ClO_4)_2$: Cr, 14.20; N, 22.96; H, 4.13%.

Black-$[Co(NH_3)_5(NO)]Cl_2$. The black chloride with normal nitrogen isotopes was made according to the method of Moeller and King[11] and of Odell *et al.*,[12] but external cooling was not necessary in the reaction of Co(II)-ammoniacal solution with NO gas. The ^{15}NO-complex was prepared on a semimicro scale using ^{15}NO gas derived from about 1 g $K^{15}NO_3$ (^{15}N atom %=99.3 and 99.8). By cooling with liquid nitrogen, a slight excess of ^{15}NO gas was trapped in a reaction vessel containing an aqueous ammoniacal solution of cobalt(II) chloride freshly prepared, the concentration of ammonia in the solution of cobalt(II) chloride being about 10 mol/*l*. The reaction vessel was shaken in running water for about 20 min until the frozen solution was molten and the black chloride was formed as gray powder. The black chloride prepared by this procedure gave the same infrared spectra as those reported by several workers.[13,14] In the preparation of deuterated black chloride, deuterated aqueous ammonia obtained from magnesium nitride and deuterium oxide was used.

Found: Co, 24.1; N, 33.55; H, 6.01; Cl, 28.9%. Calcd for $[Co(NH_3)_5(NO)]Cl_2$: Co, 24.05; N, 34.30; H, 6.17; Cl, 28.94%.

Infrared Spectra. Infrared spectra were measured over 200—4000 cm^{-1} in Nujol mull, hexachlorobutadiene mull and a potassium bromide disk. The spectra were recorded on JASCO DS-301 (700—4000 cm^{-1}), DS-402 G (400—4000 cm^{-1}), DS-401 G (300—700 cm^{1-}) and Hitachi EPI-L type (200—700 cm^{-1}) infrared spectrophotometers. Reproducibility was about ± 1 cm^{-1} in the region 200—3000 cm^{-1}, and ± 10 cm^{-1} in the region 3000—4000 cm^{-1}.

Results

Assignments of Infrared Spectra. The assignments of the N-O stretching and the skeletal vibrations between the metal and the NO group were based first on the observation of isotopic shifts. As for the skeletal vibrations, a set of two absorption peaks in the range 530—620 cm^{-1} was selected and the assignment of each absorption was then determined so as to obtain agreement between the calculated isotopic shifts and the observed ones.

The assignments of vibrations other than those mentioned above were in accordance with the following references:

Ref. 15 for the stretching vibrations of Ru-X (X=Cl and Br),

Ref. 16 for the skeletal vibrations between the metal and the CN group,

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7) "Gmelins Handbuch," Ruthenium (1938), pp. 93, 99; J. M. Fletcher, I. L. Jenkins, F. M. Lever, F. S. Martin, A. R. Powell and R. Todd, *J. Inorg. & Nucl. Chem.*, **1**, 378 (1955).

*2 unpublished work.

8) W. P. Griffith, J. Lewis and G. Wilkinson, *J. Chem. Soc.*, **1959**, 872.

9) M. Mori, S. Ueshiba and S. Kawaguchi, This Bulletin, **36**, 796 (1963).

10) A. Ogata and S. Hirono, *Yakugaku Zasshi* (*J. Pharm. Soc. Japan*), **50**, 555 (1930).

11) T. Moeller and G. King, *Inorg. Syn.*, **4**, 168 (1953).

12) A. L. Odell, R. W. Olliff and A. A. Taggart, *J. Chem. Soc.*, **1965**, 6024.

13) E. P. Bertin, S. Mizushima, T. J. Lane and J. V. Quagliano, *J. Am. Chem. Soc.*, **81**, 3821 (1959).

14) J. B. Raynor, *J. Chem. Soc. Inorg. Phys. Theoret.*, **1966**, 997.

15) J. Hiraishi, I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **20**, 819 (1964).

16) I. Nakagawa and T. Shimanouchi, *ibid.*, **18**, 101 (1962).

TABLE 1. FREQUENCY (cm^{-1}) AND ASSIGNMENT OF INFRARED ABSORPTION BANDS IN $K_2[RuX_5(NO)]$ (X=Cl and Br)

$K_2[RuCl_5(NO)]$		$K_2[RuBr_5(NO)]$		Assignment
^{14}NO-complex	^{15}NO-complex	^{14}NO-complex	^{15}NO-complex	
1915 vs.	1874 vs.	1888 vs.	1850 vs.	NO str. (A_1)
1904 vs.	1865 vs.	1880 vs.	1843 vs.	
606 w.	600 w.	606 w.	605 w.	RuN str. (A_1)
588 s.	588 w.	573 s.	572 w.	RuNO bend. (E)
	572 s.		557 s.	
336 vs.		257 vs.		RuX str. (E)
327 vs.				
286 vs.		221 vs.		RuX str. (A_1)

Abbreviations: str.=stretching; bend.=bending; vs.=very strong; s.=strong; m.=medium; w.=weak; vw.=very weak; sh.=shoulder; b.=broad; deg.=degenerate; def.=deformation; sym.=symmetric; rock.=rocking.

Ref. 17 for the characteristic absorption bands on ammine complexes and
Ref. 18 for perchlorate ion.

The infrared bands and their assignments for $K_2[RuX_5(NO)]$ (X=Cl and Br) are shown in Table 1. The two very strong absorption peaks in the region 1840—1920 cm^{-1} correspond to the N-O stretching vibration reported by Lewis *et al.*[19] The two absorption bands in the region 550—610 cm^{-1} are thought to be skeletal vibrations between the ruthenium atom and the NO group as reported by Gans[20] and Cleare.[21] The weak absorption bands at 588 cm^{-1} for $K_2[RuCl_5(^{15}NO)]$ and at 572 cm^{-1} for $K_2[RuBr_5(^{15}NO)]$ are thought to be due to the presence of a small amount of the corresponding ^{14}NO-complex.

The assignment of the infrared spectra of $K_2[RuBr_5(NO)]$ can be carried out in a similar manner.

The absorption band of the N-O stretching vibration split into two peaks for $K_2[RuX_5(NO)]$, and the wave number of the stronger peak was used to calculate the isotopic shifts.

The infrared bands and their assignments for $K_3[Cr(CN)_5(NO)]\cdot H_2O$ are given in Table 2. The strong band of the ^{14}NO-complex at 1643 cm^{-1} was assigned to the N-O stretching vibration[8]; this band shifted to 1610 cm^{-1} for the ^{15}NO-complex. The absorption bands at 620 cm^{-1} and 610 cm^{-1} (shoulder) seem to correspond to skeletal vibrations between the chromium and the NO group[20]; these absorption shifted and appeared separately as two peaks at 617 and 600 cm^{-1} upon ^{15}NO-substitution.

TABLE 2. FREQUENCY (cm^{-1}) AND ASSIGNMENT OF INFRARED ABSORPTION BANDS IN $K_3[Cr(CN)_5(NO)]\cdot H_2O$

^{14}NO-complex	^{15}NO-complex	Assignment
3600–3200 w.	3600–3200 w.	H_2O
2121 vs.	2121 vs.	CN str.
2092 vw.	2092 vw.	
2078 vw.	2078 vw.	
1643 vs.	1610 vs.	NO str.
1635 sh.	1590 sh.	
620 s.	617 s.	Cr–NO str.
610 sh.	600 w.	Cr–N–O bend.
428 s.	426 s.	CrC str.
417 sh.	415 sh.	
398 s.	397 s.	
360 sh.	360 sh.	CrCN bend.
345 s.	345 s.	
330 sh.	330 sh.	
304 vw.	303 vw.	?
291 w.	290 w.	?

Table 3 shows the infrared bands and their assignments for $[Cr(NH_3)_5(NO)]X_2$ (X=Cl and ClO_4). For the chloride, the absorptions due to the N-O stretching and the skeletal vibrations were assigned according to Cleare and Griffith.[21] For the perchlorate, similar assignments could be made. The strong band at 626 cm^{-1} due to perchlorate ion[18] did not disturb the weak absorptions (577 cm^{-1} for ^{14}NO-complex and 574 cm^{-1} for ^{15}NO-complex) due to one of the skeletal vibrations.

Table 4 and Fig. 1 show the infrared bands and their assignments for black-$[Co(NH_3)_5(NO)]Cl_2$. Absorptions caused by impurities were found as reported by Bertin[13] and Raynor.[14] These impurities are discussed later. Griffith *et al.*[2] assigned the absorption

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17) L. Sacconi, A. Sabatini and P. Gans, *Inorg. Chem.*, **3**, 1772 (1964); T. Shimanouchi and I. Nakagawa, *ibid.*, **3**, 1805 (1964).

18) H. Cohn, *J. Chem. Soc.*, **1952**, 4282.

19) J. Lewis, R. J. Irving and G. Wilkinson, *J. Inorg. & Nucl. Chem.*, **7**, 32 (1958).

20) P. Gans, A. Sabatini and L. Sacconi, *Inorg. Chem.*, **5**, 1877 (1966).

21) M. J. Cleare and W. P. Griffith, *J. Chem. Soc. Inorg. Phys. Theoret.*, **1967**, 1144.

TABLE 3. FREQUENCY (cm^{-1}) AND ASSIGNMENT OF INFRARED ABSORPTION BANDS IN $[Cr(NH_3)_5(NO)]X_2$ (X=Cl and ClO_4)

$[Cr(NH_3)_5(NO)]Cl_2$

^{14}NO-complex	^{15}NO-complex	Assignment
3290 vs.	3290 vs.	NH str.
3230 sh.	3230 sh.	
3170 sh.	3170 sh.	
1685 s.	1649 s.	NO str.
1612 m. b.	1615 m. b.	NH_3 deg. def.
1298 m. b.	1300 sh.	NH_3 sym. def.
1281 s.	1281 s.	
1244 w.	1244 w.	
791 sh.	786 sh.	NH_3 rock.
776 m. b.	774 m. b.	
734 m.	736 sh.	
573 s.	570 s.	Cr–NO str.
535 m.	526 m.	CrNO bend.
464 w.	464 w.	Cr–NH_3 str.
455 sh.	455 sh.	
440 vs.	438 vs.	
359 w.	359 w.	?
306 s.	306 s.	H_3N–Cr–NH_3 bend.
264 vs. b.	264 vs. b.	

$[Cr(NH_3)_5(NO)](ClO_4)_2$

^{14}NO-complex	^{15}NO-complex	Assignment
3360 vs.	3330 vs.	NH str.
3270 s.	3270 s.	
3200 sh.	3190 sh.	
1727 s.	1723 vw.	^{14}NO str.
	1692 s.	^{15}NO str.
1616 m. b.	1622 m. b.	NH_3 deg. def.
1299 s.	1300 s.	NH_3 sym. def.
1092 vs.	1092 vs.	ClO_4 str.
764 sh.	758 sh.	NH_3 rock.
732 m.	733 m.	
700 sh.		
626 vs.	626 vs.	ClO_4 bend.
577 vw.	574 vw.	Cr–NO str.
531 s.	521 s.	Cr–N–O bend.
462 m.	462 m.	Cr–NH_3 str.
421 s.	418 s.	
347 w.	350 w.	?
315 sh.	315 sh.	H_3N–Cr–NH_3 bend.
264 vs.	263 vs.	
255 vs.	256 vs.	
230 sh.	230 sh.	

TABLE 4. FREQUENCY (cm^{-1}) AND ASSIGNMENT OF INFRARED ABSORPTION BANDS IN BLACK-$[Co(NH_3)_5(NO)]Cl_2$

^{14}NO-complex	^{15}NO-complex	Assignment
3260 vs.	3270 vs.	NH str.
3170 vs.	3170 vs.	
1614 vs.	1589 vs.	NO str.+NH_3 deg. def.
1425 vw.	1453 vw.	?
1362 vw.	1397 vw.	?
1293 vs.	1292 vs.	NH_3 sym. def.
	1257 w.	?
1172 vs.	1173 m.	NH_3 sym. def. of Co(II)-ammine complex
	1025 w.	?
	854 sh.	NH_3 rock.
818 vs.	820 s.	
638 vs.	640 vs.	NH_3 rock. of Co(II)-ammine complex
581 vs.	579 vs.	Co-ON bend. ?
564 vs.	558 vs.	Co-ON str. ?
	494 w.	?
470 w.	467 w.	Co-NH_3 str.
444 s.	445 s.	
403 w.	405 w.	?
	340 sh.	H_3N–Co–NH_3 bend.
295 s.	295 s.	
250 sh.	250 sh.	

TABLE 5. FREQUENCY (cm^{-1}) AND ASSIGNMENT OF INFRARED ABSORPTION BANDS IN BLACK-$[Co(ND_3)_5(NO)]Cl_2$

^{14}NO-complex	^{15}NO-complex	Assignment
2450 vs.	2460 vs.	ND str.
2360 s.		
2310 vs.	2310 vs.	
1613 vs.	1589 vs.	NO str.
1495 w.		
1427 w.	1451 m.	?
1344 w.	1393 vw.	
1302 w.		
1260 vw.	1278 w.	
1166 w. b.	1167 w. b.	ND_3 deg. def.
1068 w.	1070 w.	?
	1015 sh.	?
991 s.	996 m.	ND_3 sym. def.
899 m.	901 m.	ND_3 sym. def. of Co(II)-ammine complex
829 w.	820 w.	?
	785 w.	?
	669 m.	?
637 v.	637 v.	ND_3 rock.
572 m.	561 m.	Co-ON str. ?
	490 sh.	?
454 vs.	455 vs.	ND_3 rock. of Co(II)-ammine complex

at 1172 cm^{-1} to the N–O stretching vibration. However, the absorption bands at 1172 cm^{-1} for the ^{14}NO-complex and 1173 cm^{-1} for the ^{15}NO-complex were shifted by deuterium substitution to 899 cm^{-1} and 901 cm^{-1}, respectively, as shown in Table 5. On the other hand, Bertin[13)] and Raynor[14)] assigned the absorption band at *ca.* 1600 cm^{-1} to the N–O stretching vibration. Isotopic shift of the absorption at 1614 to 1589 cm^{-1} was observed upon ^{15}NO-substitution, as reported by Mercer *et al.*[22)] The absorptions in the region 1630—1700 cm^{-1} for the other nitrosylcobalt complexes have been assigned to the N–O stretch-

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[22)] E. E. Mercer, W. A. McAllister and J. R. Durig, *Inorg. Chem.*, **6**, 1816 (1967).

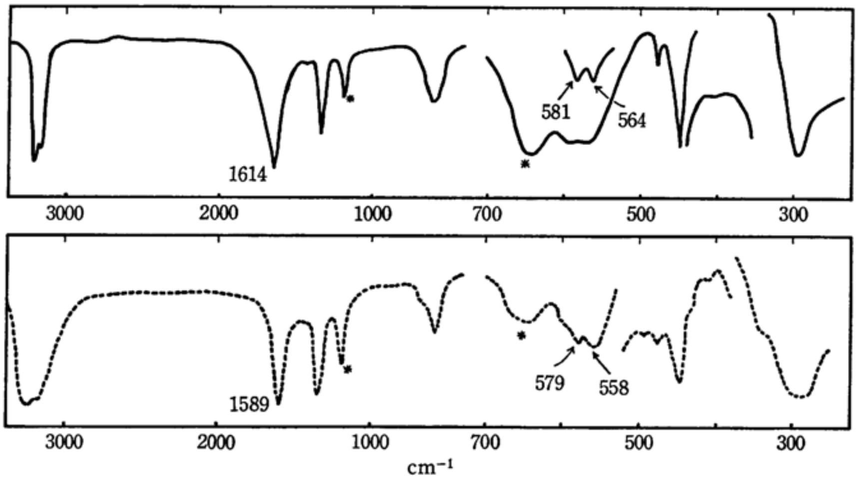

Fig. 1. Infrared spectra of black-[$Co(NH_3)_5(NO)$]Cl_2.
—— : ^{14}NO-complex.
- - - : ^{15}NO-complex (^{15}N atom %=99.3 and 99.8).
* : Co(II)-ammine impurities in black chloride.

ing vibrations.[23,24] Hence, the absorption of the ^{14}NO-complex at 1614 cm^{-1} was assigned to the N-O stretching vibration. The frequencies of the nitrosyl stretching vibration for the deuterated ^{14}NO- and ^{15}NO-complexes were also measured to eliminate interfering absorptions due to the NH_3 degenerate deformation in the 1600 cm^{-1} region. This degenerate deformation was found to have no effect on the observed frequency value for the N-O stretching vibration as shown in Table 5.

Mercer *et al.*[22] assigned the absorptions at 578 and 644 cm^{-1} to the Co-N-O bending and Co-N stretching vibrations, respectively. In the present measurement, no definite absorption peak was observed at 644 cm^{-1}, instead the peak at 578 cm^{-1} was quite definitely split into two peaks at 581 and 564 cm^{-1}, which were shifted to 579 and 558 cm^{-1}, respectively, for the ^{15}NO-complex (Table 4 and Fig. 1).

On the other hand, for the deuterated complexes only one absorption was found in the region 560—580 cm^{-1}; the absorption at 572 cm^{-1} for the ^{14}NO-complex shifted to 561 cm^{-1} for the ^{15}NO-complex as shown in Table 5 and Fig. 2.

To assign the observed peaks and calculate the isotopic shifts, the following cases are considered: Case-1. For the NH_3-complex, the two peaks in the region 560—580 cm^{-1} are due to skeletal vibrations, while for the ND_3-complex these two peaks happen to overlap. Case-2. One of the two peaks observed with the NH_3-complex is due to an impurity. The absorption intensity of an other skeletal vibration is very weak, and this absorption is assumed to be in the 570 cm^{-1} region because two skeletal vibrations between the metal and the NO group are within the limited region observed for the nitrosyl complexes examined.

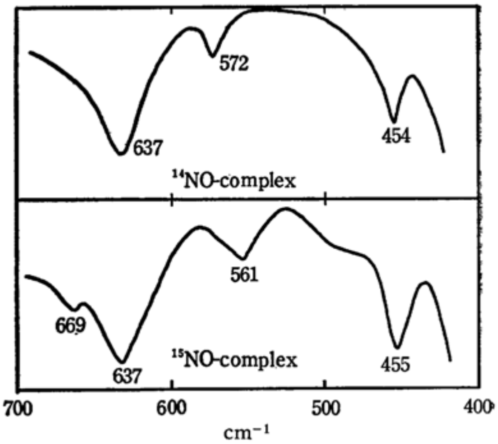

Fig. 2. Infrared spectra of black-[$Co(ND_3)_5$-(NO)]Cl_2 in the region 400—700 cm^{-1}.

Impurities in Black-[$Co(NH_3)_5(NO)$]Cl_2. Bertin[13] and Raynor[14] reported that the absorption band at *ca.* 1170 cm^{-1} for the black chloride is due to the NH_3 symmetric deformation of hexamminecobalt(II) impurity in the black chloride. However, a recent magnetic study by Asumussen *et al.*[25] has shown that carefully prepared black chloride gives $\chi_g=+0.17\times10^{-6}$ cgs units at room tempera-

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[23] R. D. Feltham and R. S. Nyholm, *ibid.*, **4**, 1334 (1965).

[24] T. B. Jackson, M. J. Baker, J. O. Edwards and D. Tutus, *ibid.*, **5**, 2046 (1966).

[25] R. W. Asumussen, Ole Bostrup and J. P. Jensen, *Acta Chim. Scand.*, **12**, 24 (1958).

ture; that is, the black chloride is essentially diamagnetic. Examples of magnetic susceptibilities of black chlorides used in this study are $\chi_g = 1.25$ (288°K), 1.58 (237°K), 2.16 (173 °K) and 3.05×10^{-6} (115°K) cgs units. These show the temperature dependence, and also that the chloride is paramagnetic. So the black chloride may be contaminated by strong paramagnetic compounds (Co(II)-ammine complexes such as $[Co(NH_3)_6]Cl_2$). Magnetic data reveal the presence of as much as 25% $[Co(NH_3)_6]Cl_2$ in the black salt, assuming that the black chloride is essentially diamagnetic and the impurity is only $[Co(NH_3)_6]Cl_2$.

An infrared study has shown that the black salt contains cobalt atoms in the +3 oxidation state.[13] The wave numbers of the NH_3 rocking vibration in ammine complexes are characteristic of the oxidation state of the central atom.[26] Moreover, the wave numbers of the NH_3 symmetric deformation for cobalt-ammine complexes seem to be characteristic of the oxidation state of the cobalt atom. Infrared absorptions of $[Co(NH_3)_6]Cl_3$ and $[Co(NH_3)_6]Cl_2$ are listed in Table 6 as representative of cobalt(III)-ammine and cobalt(II)-ammine complexes, respectively. If most of the impurities are hexamminecobalt(II) or cobalt(II)-ammine complexes, assignment of infrared spectra for the black chloride can be reasonably made by comparing the infrared spectra for the black chloride (Tables 4 and 5) with those for hexamminecobalt(III) and hexamminecobalt(II) chlorides (Table 6). The absorption bands at 1166 and 1167 cm^{-1} for the deuterated ^{14}NO-complex and ^{15}NO-complex in Table 5 were assigned to the ND_3 degenerate deformation due to the deuterated black chloride and cobalt(II)-ammine complex impurities. The absorption bands at 1293 cm^{-1} for the ^{14}NO-complex and at 1292 cm^{-1} for the ^{15}NO-complex were shifted by deuterium substitution to 991 and 996 cm^{-1}, respectively, which were assigned to the NH_3 symmetric deformation of the black chloride; the absorptions at 1172 cm^{-1} for the ^{14}NO-complex and at 1173 cm^{-1} for the ^{15}NO-complex were shifted by deuterium substitution to 899 and 901 cm^{-1}, respectively. These bands were assigned to the NH_3 symmetric deformation of the cobalt(II)-ammine complex impurities in the black chloride. The absorption bands at *ca.* 820 cm^{-1} for the ^{14}NO- and ^{15}NO-complexes were shifted by deuterium substitution to 637 cm^{-1}. These bands are due to the NH_3 rocking vibration for the black chloride. The absorptions at *ca.* 640 cm^{-1} for the ^{14}NO- and ^{15}NO-complexes were shifted by deuterium substitution to *ca.* 455 cm^{-1}. These bands are due to the NH_3 rocking vibration of cobalt (II)-ammine complex in the black chloride. These magnetic and infrared data lead to the conclusion that the black chloride used in this study may be contaminated by cobalt(II)-ammine complexes.

TABLE 6. INFRARED SPECTRA OF HEXAMMINE-COBALT(II) AND HEXAMMINECOBALT(III) CHLORIDE

Compound	$\delta(NH_3)_d$	$\delta(NH_3)_s$	$\delta(NH_3)_r$
$[Co(NH_3)_6]Cl_3$	1613	1330	830
$[Co(ND_3)_6]Cl_3$*	1155	1016	665
$[Co(NH_3)_6]Cl_2$	1598	1160	634
$[Co(ND_3)_6]Cl_2$ (calc.)	1170	884	464

$\delta(NH_3)_d$: NH_3 degenerate deformation.
$\delta(NH_3)_s$: NH_3 symmetric deformation.
$\delta(NH_3)_r$: NH_3 rocking vibration.
* From Ref. 17.

Calculation of Isotopic Shifts. Crystal X-ray studies of $K_2[RuCl_5(NO)]$,[27] $K_3[Cr(CN)_5(NO)]$,[28] black-$[Co(NH_3)_5(NO)]Cl_2$[29] and electron spin resonance studies of $[Cr(NH_3)_5(NO)]^{2+}$ and $[Cr(CN)_5(NO)]^{3-}$[30] have shown an approximately linear arrangement of the metal and the NO group, although crystallographic X-ray studies are not now thought to be able to distinguish nitrogen from oxygen. Hence, the two linear three-body models, M–N–O and M–O–N were used to calculate the isotopic shifts for all of the nitrosyl complexes examined here. For the skeletal vibrations between the metal and the NO group, two assignments are possible. Assignment 1 is that, of the two absorptions assumed due to skeletal vibrations, the higher wave number is assigned to the stretching vibration between the metal and the NO group, and the lower one to the bending vibration. Assignment 2 is the reverse of Assignment 1. Then, by the Valence Force Field method, the calculation of the isotopic shifts for absorptions due to the N–O stretching, the metal-nitrosyl stretching and the metal-nitrosyl bending vibrations was carried out for the four cases corresponding to the two models (M–N–O and M–O–N) and the two possible assignments (Assignment 1 and

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[28] N. Vannerbeg, *Acta Chem. Scand.*, **20**, 1571 (1966).

[29] D. Hall and A. A. Taggart, *J. Chem. Soc.*, **1965**, 1359; D. Dale and D. C. Hodgkin, *ibid.*, **1965**, 1364.

[30] I. Bernel, *Chem. Commun.*, **1965**, 571.

TABLE 7. OBSERVED AND CALCULATED ISOTOPIC SHIFTS ($\Delta\nu_{obs.}$ AND $\Delta\nu_{calc.}$ IN cm^{-1}) OF $K_2[RuX_5(NO)]$ (X=Cl and Br), $K_3[Cr(CN)_5(NO)]\cdot H_2O$, $[Cr(NH_3)_5(NO)]X_2$ (X=Cl AND ClO_4) AND BLACK-$[Co(NH_3)_5(NO)]Cl_2$

$K_2[RuCl_5(NO)]$

^{14}NO-complex wave number (cm^{-1})	$\Delta\nu_{obs.}$	$\Delta\nu_{calc.}$ Assignment 1		Assignment 2	
		model RuNO	RuON	RuNO	RuON
1904 (νNO)	39	40	28	40	29
606	6	6	9	16	4
588	16	16	4	5	9

$K_2[RuBr_5(NO)]$

^{14}NO-complex wave number (cm^{-1})	$\Delta\nu_{obs.}$	$\Delta\nu_{calc.}$ Assignment 1		Assignment 2	
		model RuNO	RuON	RuNO	RuON
1880 (νNO)	37	40	27	39	28
606	1	5	10	16	4
573	16	16	4	5	9

$K_3[Cr(CN)_5(NO)]\cdot H_2O$

^{14}NO-complex wave number (cm^{-1})	$\Delta\nu_{obs.}$	$\Delta\nu_{calc.}$ Assignment 1		Assignment 2	
		model CrNO	CrON	CrNO	CrON
1643 (νNO)	33	36	23	36	23
620	3	4	9	16	4
610	10	16	4	4	8

$[Cr(NH_3)_5(NO)]Cl_2$

^{14}NO-complex wave number (cm^{-1})	$\Delta\nu_{obs.}$	$\Delta\nu_{calc.}$ Assignment 1		Assignment 2	
		model CrNO	CrON	CrNO	CrON
1685 (νNO)	36	36	25	35	26
573	3	4	8	15	4
535	9	14	4	4	7

$[Cr(NH_3)_5(NO)](ClO_4)_2$

^{14}NO-complex wave number (cm^{-1})	$\Delta\nu_{obs.}$	$\Delta\nu_{calc.}$ Assignment 1		Assignment 2	
		model CrNO	CrON	CrNO	CrON
1727 (νNO)	35	36	26	35	27
577	3	4	8	15	4
531	10	14	4	4	7

$[Co(NH_3)_5(NO)]Cl_2$

^{14}NO-complex wave number (cm^{-1})	$\Delta\nu_{obs.}$	$\Delta\nu_{calc.}$ Assignment 1		Assignment 2	
		model CoNO	CoON	CoNO	CoON
1614 (νNO)	25	35	23	35	23
581	2	4	8	15	4
564	6	15	4	4	8

Assignment 1: Of the two wave numbers in the region 530—620 cm^{-1}, the higher wave number is assigned to the stretching vibration between the metal and the NO group and the lower one to the bending virbation.

Assignment 2: The reverse of Assignment 1.

$\Delta\nu_{obs.} = \nu^{14}$NO-complex (obs.) $-\nu^{15}$NO-complex (obs.). $\Delta\nu_{calc.} = \nu^{14}$NO-complex (obs.) $-\nu^{15}$NO-complex (calc.).

(νNO): The N–O stretching vibration.

2). The secular equation for the calculation of isotopic shifts was set up in accordance with Wilson's procedure.[31] The calculated shifts were compared with the observed ones.

Table 7 shows the observed and calculated isotopic shifts for $K_2[RuX_5(NO)]$ (X=Cl and Br), $K_3[Cr(CN)_5(NO)]\cdot H_2O$, $[Cr(NH_3)_5(NO)]X_2$ (X=Cl and ClO_4) and black-$[Co(NH_3)_5(NO)]Cl_2$. For black-pentammine-nitrosylcobalt complex, the isotopic shifts for the NH_3-complex calculated by assuming Case-1 are compared with the observed isotopic shifts.

The calculated isotopic shifts in Table 7 were calculated neglecting off-diagonal interaction constants. Calculations were also performed with off-diagonal interaction constants of 0.4 mdyn/Å and 0.2 mdyn/Å for $K_2[RuCl_5(NO)]$ and $[Cr(NH_3)_5(NO)]Cl_2$, respectively. However, these latter calculated isotopic shifts differed only negligibly from those in Table 7.

The electron spin resonance study of $K_3[Cr(CN)_5(NO)]\cdot H_2O$ by McGarvey and Pealman[32] has shown that the Cr-N-O or Cr-O-N bond is bent slightly. Calculation of the isotopic shifts was made over a bond angle ranging from 170—180°. However, in this angle range, the range of shifts was very small.

Arrangement and Assignment. Comparison of observed isotopic shifts with calculated ones shows that the calculated isotopic shifts in the case of the M-N-O arrangement with Assignment 1 are in agreement with the observed ones for both the nitrosylruthenium(III) and nitrosylchromium(II) complexes. For black-$[Co(NH_3)_5(NO)]Cl_2$, the following conclusions were obtained. For the NH_3-complex is Case-1, the calculated isotopic shifts for the Co-O-N arrangement with Assignment 2 are in agreement with observed values. For the ND_3-complex in Case-1, the Co-O-N arrangement is found and only one absorption in the region 560—580 cm^{-1} is thought mainly attributable to the Co-O stretching vibration. In Case-2, the Co-O-N arrengement is also found but the distinction between skeletal vibrations cannot be made. However, the calculated isotopic shifts in all cases of possible assignments supported the Co-O-N arrangement for the black-pentam-minenitrosylcobalt complex.

Discussion

The agreement between the observed isotopic shifts and calculated ones is excellent for the nitrosylruthenium(III) complexes with the Ru-N-O arrangement and Assignment 1, but less so for the nitrosylchromium(II) complexes with the Cr-N-O arrangement and Assignment 1 and for black-$[Co(NH_3)_5(NO)]Cl_2$ with the Co-O-N arrangement. In the latter cases, however, the poorer agreement is attributable to the use of the three-body model in calculating the isotopic shifts.

The wave numbers of the normal vibrations calculated for the ^{15}NO-complexes from the observed wave numbers for the ^{14}NO-complexes by the three-body model are expected to

TABLE 8. OBSERVED AND CALCULATED ISOTOPIC SHIFTS ($\Delta\nu_{obs.}$ AND $\Delta\nu_{calc.}$ IN cm^{-1}) OF $K_2[RuCl_5(NO)]$ AND $Co(NO)(CO)_3$

$K_2[RuCl_5(NO)]$

Assignment	Observed			Calculated (1)[a]			Calculated (2)[b]		
	^{14}NO-complex	^{15}NO-complex	$\Delta\nu_{obs.}$	^{14}NO-complex	^{15}NO-complex	$\Delta\nu_{calc.}$	^{14}NO-complex	^{15}NO-complex	$\Delta\nu_{calc.}$
NO str.	1904	1865	39	1909	1869	40	1904	1864	40
RuN str.	606	600	6	607	602	5	606	600	6
RuNO bend.	588	572	16	589	574	15	588	572	16

$Co(NO)(CO)_3$

Assignment	Observed[c]			Calculated (1)[c]			Calculated (2)[b]		
	^{14}NO-complex	^{15}NO-complex	$\Delta\nu_{obs.}$	^{14}NO-complex	^{15}NO-complex	$\Delta\nu_{calc.}$	^{14}NO-complex	^{15}NO-complex	$\Delta\nu_{calc.}$
NO str.	1822	1786	36	1860	1822	38	1822	1784	38
CoN str.	594	591	3	588	585	3	594	589	5
CoNO bend.	565	555	10	600	591	9	565	550	15

a) Calculated by Dr. Jiro Hiraishi (Department of Chemistry, Faculty of Science, The University of Tokyo) using the eight-body model.
b) Calculated by the author using the three-body model.
c) Taken from Ref. 4.

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[31] E. S. Wilson, Jr., *J. Chem. Phys.*, **7**, 1047 (1939); **9**, 76 (1941).

[32] B. R. McGarvey and J. Pearlman, *ibid.*, **46**, 4992 (1967).

be smaller than those calculated by a complete treatment because of interactions of vibrations neglected in the three-body model. Thus, the shifts calculated with the three-body model ($\nu_{obs.}$(^{14}NO-complex) $- \nu_{calc.}$(^{15}NO-complex)) would be larger than the observed shifts.

In the case of $K_2[RuX_5(NO)]$ (X=Cl and Br), the central metal atom and ligands other than the NO group are much heavier than nitrogen and oxygen. The three-body model can be expected to be a good approximation, and good agreement is actually obtained between the calculated and observed shifts. In Table 8, the calculated isotopic shifts using the three-body model for $K_2[RuCl_5(NO)]$ are compared with those obtained using the eight-body model,*[3] and good agreement is found also between these. However, for the Ru-N stretching and the Ru-N-O bending vibration the isotopic shifts obtained using the three-body model are slightly larger than those obtained with the eight-body model. Since the three-body model is a good approximation for pentachloronitrosylruthenium(III) ion, the results based on the three-body model for $K_2[RuX_5(NO)]$ lead to the conclusion that the complexes have a Ru-N-O arrangement and, of the two absorptions in the region 570—610 cm^{-1}, the higher wave number is assigned to the Ru-N stretching vibration and the lower one to the Ru-N-O bending vibration.

On the other hand, the central metal atom and ligands other than the NO group in $K_3[Cr(CN)_5(NO)]\cdot H_2O$, $[Cr(NH_3)_5(NO)]X_2$ (X =Cl and ClO_4) and black-$[Co(NH_3)_5(NO)]Cl_2$ are lighter than ruthenium and halide ion in $K_2[RuX_5(NO)]$. So, for the chromium and the cobalt complexes examined, the difference between the calculated isotopic shifts obtained using the three-body model and the observed shifts can be expected to be greater than the difference for the ruthenium complexes.

McDowell *et al.*[4] have determined the Co-N-O arragement and assigned the skeletal vibrations between the cobalt and the NO group by comparing the calculated isotopic shifts using the nine-body model with the observed ones for $Co(NO)(CO)_3$ and its ^{15}N-substituted compound. In order to demonstrate the relation between the results obtained with the three-body model and a more complete model, the present author calculated the isotopic shifts with the three-body model using McDowell's data for $Co(NO)(CO)_3$. In Table 8, these calculated isotopic shifts are compared with the observed ones and with the calculated ones of McDowell. The calculated isotopic shifts of McDowell are nearly equal to the observed ones, and for the Co-N stretching and Co-N-O bending vibrations, are slightly smaller then the isotopic shifts calculated by the author. The N-O stretching vibration would be less affected by the other vibrations than the two skeletal vibrations between the metal and the NO group would be. Thus, the isotopic shifts calculated with the three-body model are greater than the observed ones, especially for the skeletal vibrations between the metal and the NO group. These considerations support the following conclusions: the nitrosylchromium(II) complexes examined in this study have a Cr-N-O arrangement and of their two absorptions in the region 530—620 cm^{-1}, the higher wave number is assigned to the Cr-NO stretching vibration and the lower one to the Cr-N-O bending vibration; black-$[Co(NH_3)_5(NO)]Cl_2$ has a Co-O-N arrangement.

For black-$[Co(NH_3)_5(NO)]Cl_2$, the very strong absorption at about 640 cm^{-1} due to hexamminecobalt(II) impurity interfered considerably with the skeletal vibrations between the cobalt and the NO group, as the absorption at 637 cm^{-1} due to the ND_3 rocking vibration of the deuterated complex did for black-$[Co(ND_3)_5(NO)]Cl_2$; there may be some uncertainty concerning values of the wave numbers for the skeletal vibrations. However, this uncertainty is not thought to be great enough to change the conclusion on arrangement.

The Ru-N-O arrangement found for pentahalogenonitrosylruthenium(III) complexes is in agreement with the result of a neutron diffraction study.[1] The Cr-N-O arrangement for the nitrosylchromium(II) complexes examined is very interesting when the great affinity of Cr(III) for oxygen is considered. The nitrosyl group of black-$[Co(NH_3)_5(NO)]Cl_2$ is found to coordinate to the cobalt atom through the oxygen atom. The Co-O-N arrangement is not in agreement with the assumption by Griffith[2] and Mercer *et al.*[22] The present result is the first to establish the Co-O-N arrangement for black-$[Co(NH_3)_5(NO)]Cl_2$.

The assignments of the skeletal vibrations between the metal and the NO group for the nitrosyl complexes examined have been reported by several workers.[20-22,33-35] However,

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*[3] The calculated isotopic shifts by the eight-body model were kindly provided by Dr. Jiro Hiraishi (Department of Chemistry, Faculty of Science, The University of Tokyo).

33) M. B. Fairey and R. J. Irving, *Spectrochim. Acta.*, **22**, 359 (1966).

their assignments have been tentative, or a distinction between the two skeletal vibrations has not been made. Clear assignments of the skeletal vibrations for the compounds examined, except for the black chloride, are established by this study.

For metal-nitrosyl complexes, calculation of the ^{15}N-isotopic shifts using the three-body model of the metal and nitrosyl group is a useful method for the determination of the coordinating atom of the NO group, and a clear assignment of the skeletal vibrations between the metal atom and the NO group.

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35) B. Jeżowska-Trzebiatoska and J. Ziołkoski, *Bull. Acad. Polon. Sci. Ser. Sci. Chim.*, **12**, 503 (1964).