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

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The ^{15}NO-complexes for $K_3[Mn(CN)_5(NO)]\cdot 2H_2O$, $K_3[Mn(CN)_5(NO)]$ and $Ag_2[Mn(CN)_5(NO)]$ were prepared. By measuring and calculating the effect of the nitrogen isotope ^{15}N on the infrared spectra, the Mn–N–O arrangement was found in all the complexes, and the absorption bands due to the skeletal vibrations between the manganese and the NO group were clearly assigned.

X-Ray crystal structures have been determined for a number of transition-metal nitrosyl compounds. However, the X-ray method does not seem to be useful for distinguishing nitrogen from oxygen in the NO group.

Recently, for the nitrosylruthenium(III), nitrosylchromium(II) and nitrosylcobalt(II) complexes, the effect of the nitrogen isotope ^{15}N on the infrared spectra was measured, and the isotopic shifts were compared with those calculated by the simple three-body model of the metal and the NO group.[1,2] This method was found to be useful for determining the coordinating atom of the NO group to the metal atom, and for assigning the skeletal vibrations between the metal and the NO group.

In this paper are described infrared studies on $K_3[Mn(CN)_5(NO)]\cdot 2H_2O$, $K_3[Mn(CN)_5(NO)]$, $Ag_2[Mn(CN)_5(NO)]$ and their ^{15}NO-complexes.

Experimental

$K_3[Mn(CN)_5(NO)]\cdot 2H_2O$ with normal nitrogen isotopes was prepared by the method of Blanchard and Magnusson[3] who used NO gas, and was purified by the method of Cotton *et al.*[4] $K_3[Mn(CN)_5(NO)]$ and $Ag_2[Mn(CN)_5(NO)]$ were also prepared according to the same method. $K_3[Mn(CN)_5(NO)]\cdot 2D_2O$ was prepared by treating the unhydrated salt with D_2O in a vacuum line.

The ^{15}NO-complexes were prepared on about 1/10 the ordinary scale. $K_3[Mn(CN)_5(^{15}NO)]$ was prepared in a vacuum line; with the aid of liquid nitrogen, 3 mmol of ^{15}NO gas derived from $K^{15}NO_3$ (^{15}N atom% = 99) was trapped in a reaction vessel containing an outgassed pale-greenish slurry which was prepared by mixing 2 mmol of $Mn(C_2H_3O_2)_2\cdot 4H_2O$/(2.5 m*l* H_2O), 3 mmol of KOH/(2.5 m*l* H_2O), and 10 mmol of KCN/(2.5 m*l* H_2O) in succession. The reaction vessel was shaken under running water until the frozen solution was molten. The pale-greenish slurry was shaken for 5—6 hr at room temperature to give a clear violet solution containing $[Mn(CN)_5(^{15}NO)]^{3-}$. The yield of the purified $K_3[Mn(CN)_5(MO)]\cdot 2H_2O$ was about 50% based on $Mn(C_2H_3O_2)_2\cdot 4H_2O$. Preparation of the ^{15}NO-complexes on such a semi-micro scale was thought to give the correct products because the ^{14}NO-complexes prepared on the semi-micro scale gave the same infrared spectra as those prepared on an ordinary scale, and their elementary analyses showed the correct values.

Found: K, 31.9; Mn, 15.1; C, 16.5; N, 23.3; H_2O, 9.79%. Calcd for $K_3[Mn(CN)_5(NO)]\cdot 2H_2O$: K, 31.84; Mn, 14.9; C, 16.30; N, 22.82; H_2O, 9.78%. Found: C, 18.5; N, 25.2%. Calcd for $K_3[Mn(CN)_5(NO)]$: C, 18.07; N, 25.29%. Found: Ag, 49.4; Mn, 12.4; C, 14.1; N, 18.7%. Calcd for $Ag_2[Mn(CN)_5(NO)]$: Ag, 50.07; Mn, 12.75; C, 13.94; N, 19.51%.

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-402G (700—4000 cm^{-1}), JASCO model IR-F, and Hitachi EPI-L type (200—700 cm^{-1}) infrared spectrophotometers. The wave numbers of the observed absorption bands were calibrated with 1,2,4-trichlorobenzene, polystyrene film and water vapour. 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. Assignments of the N–O stretching and the skeletal vibrations between the manganese and the NO group were made on the

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[1] E. Miki, T. Ishimori, H. Yamatera, and H. Okuno, *Nippon Kagaku Zasshi*, **87**, 703 (1966).

[2] E. Miki, This Bulletin, **41**, 1835 (1968).

[3] A. A. Blanchard and R. R. Magnusson, *J. Amer. Chem. Soc.*, **63**, 2236 (1941).

[4] F. A. Cotton, R. R. Monchamp, R. J. M. Henry, and R. C. Young, *J. Inorg. Nucl. Chem.*, **10**, 28 (1959).

Table 1. Wave numbers and assignment of infrared absorption bands in $K_3[Mn(CN)_5(NO)]\cdot 2H_2O$, $K_3[Mn(CN)_5(NO)]\cdot 2D_2O$, $K_3[Mn(CN)_5(NO)]$, and $Ag_2[Mn(CN)_5(NO)]$

$K_3[Mn(CN)_5(NO)]\cdot 2H_2O$ and $K_3[Mn(CN)_5(NO)]\cdot 2D_2O$

^{14}NO-complex		^{15}NO-complex	Assignment
3600 m	(2653 m)[a]	3610 m	O-H str.
3410 m, b	(2496 m, b)	3420 m, b	
3250 w	(2405 w)	3250 w	
2129 w	(2128 w)	2129 w	C-N str.
2095 vs	(2095 vs)	2095 vs	
2054 sh	(2054 sh)	2054 sh	
1741 vs	(1736 vs)	1704 vs	N-O str.
1733 vs	(1728 vs)	1694 vs	
1657 w	(1220 sh)	1658 w	O-H bend.
1638 m	(1208 m)	1639 m	
663 m	(663 m)		Mn-^{14}N str. + Mn-^{14}N-O bend.
		660 w	Mn-^{15}N str.
653 w	(653 w)		Mn-^{14}N-O bend.
		651 w	Mn-^{15}N-O bend.
		646 m	Mn-^{15}N-O bend.
494 m	(490 m, b)	493 m	Mn-C str. + Mn-C-N bend.
470 sh		470 sh	
451 vs[b]	(455 vs)	451 s	
435 sh		435 sh	
423 m	(421 sh)	423 m	
405 s	(405 s)	404 s	
365 s	(365 s, b)	364 s	
	(330 m, b)[c]		
318 m	(315 m, b)	317 m	

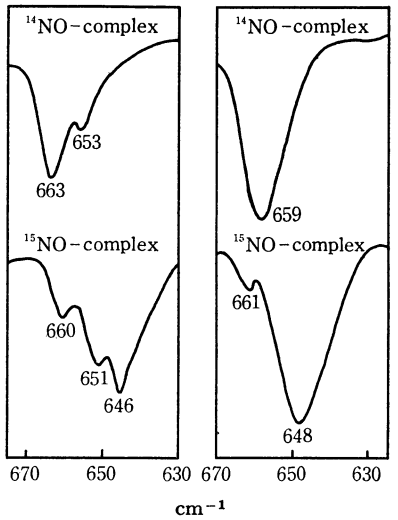
$K_3[Mn(CN)_5(NO)]$

^{14}NO-complex	^{15}NO-complex	Assignment
3610 vw, b	3620 vw, b	
3420 vw, b	3300 vw, b	
2129 w	2125 w	C-N str.
2103 vs	2103 vs	
2065 sh	2064 sh	
1711 vs	1675 vs	N-O str.
1695 vs	1663 vs	
659 s		Mn-^{14}N str. + Mn-^{14}N-O bend.
	661 w	Mn-^{15}N str.
	648 s	Mn-^{15}N-O bend.
490 w	487 w	Mn-C str. + Mn-C-N bend.
455 m	454 m	
447 m	446 m	
405 s	404 s	
368 s, b	368 s, b	
315 w	314 w	

$Ag_2[Mn(CN)_5(NO)]$

^{14}NO-complex	^{15}NO-complex	Assignment
2166 m	2166 m	C-N str.
1888 vs	1850 vs	N-O str.
628 m, b	620 m, b	Mn-N str. + Mn-N-O bend.
468 vs, b	482 vs, b	Mn-C str. + Mn-C-N bend.
417 vs	417 vs	
346 s	345 s	
310 m	310 m	

a) The wave numbers of the bands in parentheses are for the deuterated complex.
b) The 450 cm^{-1} band includes H_2O libration mode.
c) The 330 cm^{-1} band includes D_2O libration mode.
Abbreviations: str. = stretching; bend. = bending; vs = very strong; s = strong; m = medium; w = weak; vw = very weak; sh = shoulder; b = broad.



$K_3[Mn(CN)_5(NO)]\cdot 2H_2O$ $K_3[Mn(CN)_5(NO)]$

Fig. 1. Infrared spectra of $K_3[Mn(CN)_5(NO)]\cdot 2H_2O$ and $K_3[Mn(CN)_5(NO)]$ in the region 630—670 cm^{-1}.

basis of the ^{15}N-isotopic shifts. The observed frequencies and their assignments for $K_3[Mn(CN)_5(NO)]\cdot 2H_2O$, $K_3[Mn(CN)_5(NO)]$ and $Ag_2[Mn(CN)_5(NO)]$ are shown in Table 1. The two very strong absorption bands in the region 1700—1740 cm^{-1} of $K_3[Mn(CN)_5(^{14}NO)]\cdot 2H_2O$ and its unhydrate correspond to the N–O stretching vibrations since these bands shift upon ^{15}N-substitution. The wave number of the stronger peak was used to calculate the isotopic shifts. For the hydrate, the absorption bands at 663 and 653 cm^{-1} shifted and split to 660, 651 and 646 cm^{-1} upon ^{15}N-substitution as shown in Fig. 1. These bands can be assigned to the skeletal vibrations between the manganese and the NO group because the wave numbers for the deuterate hydrate were the same as those for the normal hydrate. For $K_3[Mn(CN)_5(NO)]$, on the other hand, the single absorption band at 659 cm^{-1} split into two peaks at 661 and 648 cm^{-1} upon ^{15}NO-substitution as shown in Fig. 1. For $Ag_2[Mn(CN)_5(NO)]$, a strong band of the ^{14}NO-complex at 1888 cm^{-1} was assigned to the N–O strethcing vibration; this band shifted to 1850 cm^{-1} upon ^{15}NO-substitution. A broad absorption at 628 cm^{-1} shifted to 620 cm^{-1} upon ^{15}NO-substitution, but did not split. This band seems to be due to the skeletal vibrations between the manganese and the NO group.

A number of absorption bands observed in a region lower than 620 cm^{-1} could be assigned to the skeletal vibrations between the manganese and the CN group.[5] For $K_3[Mn(CN)_5(NO)]\cdot 2H_2O$, such bands were observed on the background of a very broad absorption band centered at about 450 cm^{-1}. This broad band seems to be due to the libration of the crystal water because the absorption shifted to about 330 cm^{-1} upon deuterium substitution.

Calculation of Isotopic Shifts. An X-ray study of $K_3[Mn(CN)_5(NO)]\cdot 2H_2O$ has shown an approximately linear arrangement of the manganese and the

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5) D. M. Adams, "Metal-Ligand and Related Vibrations," Edward Arnold Publishers Ltd., London (1967), p. 169—173.

TABLE 2. OBSERVED AND CALCULATED ISOTOPIC SHIFTS ($\Delta\nu_{obsd}$ AND $\Delta\nu_{calcd}$ IN cm^{-1}) OF $K_3[Mn(CN)_5(NO)]$ AND $Ag_2[Mn(CN)_5(NO)]$

$K_3[Mn(CN)_5(NO)]$

^{15}NO-compex wave number (cm^{-1})	$\Delta\nu_{obsd}$	$\Delta\nu_{calcd}$			
		Assignment 1		Assignment 2	
		model MnNO	MnON	MnNO	MnON
1663	32	38	22	38	23
661	(−2)*	4	10	17	6
648	11	17	6	4	10

$Ag_2[Mn(CN)_5(NO)]$

^{15}NO-complex wave number (cm^{-1})	Assignment	$\Delta\nu_{obsd}$	$\Delta\nu_{calcd}$	
			model MnNO	MnON
1850	a	38	40	28
620	b	(8)**	5	8
620	c	(8)**	16	6

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

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

Assignment 1: Of the two wave numbers in the region 630—670 cm^{-1}, the higher wave number is assigned to the stretching vibration between the manganese and the NO group and the lower one to the bending vibration.

Assignment 2: The reverse of Assignment 1.

a: The N–O stretching vibration.

b: The stretching vibration between the manganese and the NO group.

c: The bending vibration between the manganese and the NO group.

*: This observed isotopic shift($\Delta\nu_{obsd}$) is explained by Ref. 8.

**: These observed isotopic shifts are very rough values since the two skeletal vibrations appear to be adjacent to each other.

NO group.[6] The isotopic shifts were calculated for $K_3[Mn(CN)_5(NO)]\cdot 2H_2O$, its unhydrate[7] and $Ag_2[Mn(CN)_5(NO)]$[7] by the use of the two linear three-body models, Mn–N–O and Mn–O–N as described previously.[1,2] A probable assignment of the skeletal vibrations and determination of the arrangement were based on a comparison of the calculated isotopic shifts with the observed ones. Table 2 shows the observed and the calculated isotopic shifts for $K_3[Mn(CN)_5(NO)]$ and $Ag_2[Mn(CN)_5(NO)]$.

Arrangement and Assignment. The calculated isotopic shifts in the case of the Mn–N–O arrangement with Assignment 1 for the unhydrate (see Table 2) are in agreement with the observed ones. The Mn–N stretching and the Mn–N–O bending vibrations seem to overlap accidentally at 659 cm^{-1}. They shifted and split into the 661 cm^{-1} (the Mn–N stretching vibration) and 648 cm^{-1} (the Mn–N–O bending vibration) bands upon ^{15}NO-substitution.[8] Both the hydrate and $Ag_2[Mn(CN)_5(NO)]$ were found to show the Mn–N–O arrangement from the observed isotopic shifts for the N–O stretching vibrations upon ^{15}NO-substitution.

For $K_3[Mn(CN)_5(NO)]\cdot 2H_2O$, three absorption bands were observed in the region 640—670 cm^{-1} on the ^{15}NO-complex, and two on the ^{14}NO-complex. They are caused by the skeletal vibrations of the Mn–NO group. The doubly degenerate Mn–N–O bending vibrations of the free complex ion can be assumed to split into two absorption bands in the crystalline state. For the isotopic shifts of the absorption bands, the following assignments may be most probable. Two absorption bands due to the Mn–N stretching and one of the Mn–N–O bending vibrations overlap at 663 cm^{-1} for the ^{14}NO-complex. They shift and split into two bands at 660 cm^{-1} (the Mn–^{15}N stretching vibration) and 651 cm^{-1} (the Mn–^{15}N–O bending vibration), while another Mn–^{14}N–O bending vibration (653 cm^{-1}) shifts to 646 cm^{-1} upon ^{15}NO-substitution (Fig. 1).

Discussion

The Mn–N–O arrangement was found in the pentacyanonitrosylmanganese complexes as conventionally described for metal nitrosyl complexes. In $K_2[RuX_5(NO)]$ (X=Cl and Br), the overtone band of the Ru–N–O linear bending vibration is observed in the frequency region near twice the value of the fundamental frequency of the Ru–N–O bending vibration.[9] $K_3[Mn(CN)_5(NO)]\cdot 2H_2O$ and its unhydrate show bands at 1325 and 1313 cm^{-1}; these frequencies are nearly

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[6] A. Tullberg and N. Vannerberg, *Acta Chem. Scand.*, **21**, 1462 (1967).

[7] For $K_3[Mn(CN)_5(NO)]$ and $Ag_2[Mn(CN)_5(NO)]$, the linear three-body model was assumed although a crystal X-ray study was not carried out.

[8] The absorption intensity of the Mn–N stretching vibration would be very weak as compared with that of the Mn–N–O bending vibration. If the two absorptions are adjacent to each other, the wave number of the overlapping bands will be approximately equal to that of the Mn–N–O bending vibration and roughly to that of the stretching vibration. The Mn–^{14}N stretching vibration can be estimated to appear at about 665 cm^{-1} by calculation of the isotopic shift as shown in Table 2.

[9] J. Hiraishi, Ph. D. Thesis, The University of Tokyo (1956).

the same as twice the 663 and 659 cm^{-1} bands ($663\times 2=1326$ and $659\times 2=1318$). From this observation, the 663 and 659 cm^{-1} bands can be assigned to the Mn–N–O linear bending vibrations. This is in agreement with the assignment by the comparison of the observed isotopic shifts with the calculated ones. For $Ag_2[Mn(CN)_5(NO)]$, the overtone band of the Mn–N–O bending vibration was not observed.

One Mn–N stretching and two Mn–N–O bending vibrations were observed in $K_3[Mn(CN)_5(NO)]\cdot 2H_2O$. This can be explained as follows. The $[Mn(CN)_5(NO)]^{3-}$ ion belongs to the point-group symmetry C_{4v} and the reduced representation can be shown as $8A_1+A_2+4B_1+2B_2+9E$. The A_1 and the E species are infrared active, and the N–O and the Mn–N stretching vibrations belong to the A_1 species and the Mn–N–O bending vibration to the E species. $K_3[Mn(CN)_5(NO)]\cdot 2H_2O$ crystallizes in the space group No. 9 *Cc*,$^{6)}$ where E species is expected to split into infrared active A' and A'' species, but not A_1 species. Thus, one Mn–N stretching and two Mn–N–O bending vibrations are expected to be observed in crystalline state.

The wave numbers of the N–O stretching vibrations increase in the order of $K_3[Mn(CN)_5(NO)]$, $K_3[Mn(CN)_5(NO)]\cdot 2D_2O$ and $K_3[Mn(CN)_5(NO)]\cdot 2H_2O$ (see Table 1). The changes suggest that hydrogen bonds are formed between the NO group and the crystal waters as revealed by X-ray study of $K_3[Mn(CN)_5(NO)]\cdot 2H_2O$.$^{6)}$ The changes were observed in the N–O stretching vibrations but hardly at all in C–N stretching vibrations.

The wave numbers of the N–O and the C–N stretching vibrations for $Ag_2[Mn(CN)_5(NO)]$ are higher than those for $K_3[Mn(CN)_5(NO)]\cdot 2H_2O$ and its unhydrate, while the reverse is observed for the skeletal vibrations between the manganese and the NO group. This can be explained from the difference of oxidation states of the manganese atom; the oxidation state of the manganese atom for the K-salts and the Ag-salt are II and III, respectively.

The assignment of the skeletal vibrations between the manganese and the NO group for the examined complexes is tentative, and no distinction between the skeletal vibrations was made.$^{10)}$ However, a probable assignment of the skeletal vibrations for $K_3[Mn(CN)_5(NO)]\cdot 2H_2O$ and its unhydrate is thought to have been established.

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