BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 3007—3008 (1969)

The Effects of Outer Sphere Cations and Halide Ions on Infrared Spectra of Pentahalogenonitrosylruthenium(III) Complexes

Eiichi MIKI, Tatsujiro ISHIMORI, Hideo YAMATERA* and Hisateru OKUNO

Department of Chemistry, College of Science, St. Paul's (Rikkyo) University, Nishi-Ikebukuro, Toshima-ku, Tokyo
**Department of Chemistry, Faculty of Science, The University of Nagoya, Chikusa-ku, Nagoya*

(Received March 20, 1969)

On the infrared spectra of alkali metal salts of nitrosylruthenium(III) complex anions, studies have been made on the effects of outer sphere cations and coordinated halide ions. The wave number of the N–O stretching vibration decreases in the order of K^+, NH_4^+, Rb^+ and Cs^+ for $M_2[RuCl_5(NO)]$ (M=K, NH_4, Rb and Cs)[1] and in the order of NH_3, Cl^-, Br^- and OH^- for $[RuX(NH_3)_4(NO)]^{n+}$ ion (X=NH_3, Cl, Br and OH *trans* to NO group).[2] Sinitsyn and Petrov have reported that, for $M_2[RuX_5(NO)]$ (M=Na, K, Rb and Cs; X=Cl, Br and I), the wave number of the Ru–N stretching as well as the N–O stretching vibration increases in the order of I, Br and Cl for a given alkali metal salt.[3] However, a distinction between the two skeletal vibrations of the RuNO group does not seem to have been fully made. Recently, we have made a clear assignment on the skeletal vibrations of the RuNO group of $K_2[RuX_5(NO)]$ (X=Cl and Br).[4,5]

We studied the infrared spectra of $M_2[RuX_5(NO)]$ (M=K, Rb and Cs; X=Cl, Br and I) and measured the wave numbers of the N–O stretching, Ru–N stretching, RuNO bending and Ru–X stretching vibrations. This report presents interesting observations on the shifts of the wave numbers of the vibrations by the replacement of the outer sphere cations and the halide ions.

In Table 1 are shown the wave numbers of the vibrations measured for $M_2[RuX_5(NO)]$.

For these compounds, the effects caused by the replacement of the outer sphere cations were observed on the Ru–N stretching and especially on the Ru–X (X *cis* to NO) stretching vibrations as well as on the N–O stretching vibration, but hardly any on the RuNO bending vibration. The wave

TABLE 1. INFRARED SPECTRA OF $M_2[RuX_5(NO)]$ (M=K, Rb and Cs; X=Cl, Br and I)

Compounds	N–O str. (A_1)		Ru–N str. (A_1)	RuNO bend. (E)	Ru–X str. (E)		Ru–X str. (A_1)
$K_2[RuCl_5(NO)]$	1915 vs	1904 vs	606 w	588 s	336 vs	327 vs	286 vs
$K_2[RuBr_5(NO)]$	1888 vs	1880 vs	606 w	573 s	260 vs	252 vs	221 vs
$K_2[RuI_5(NO)]$	1865 sh	1854 vs	600 m	554 s	214 vs		174 vs
$Rb_2[RuCl_5(NO)]$	1900 sh	1888 vs	600 w	587 s	326 vs		281 vs
$Rb_2[RuBr_5(NO)]$	1872 vs		602 m	579 m	260 vs	250 vs	218 vs
$Rb_2[RuI_5(NO)]$	1840 vs		600 w	556 s	210 vs		—
$Cs_2[RuCl_5(NO)]$	1873 vs		596 w	588 s	320 vs		277 vs
$Cs_2[RuBr_5(NO)]$	1855 vs		597 m	576 s	250 vs		220 vs
$Cs_2[RuI_5(NO)]$	1824 vs		594 m	557 s	205 vs		—

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

1) N. M. Sinitsyn and O. E. Zvyagintsev, *Zh. Neorg. Khim.*, **8**, 234 (1963).
2) N. M. Sinitsyn and O. E. Zvyagintsev, *Dokl. Acad. Nauk SSSR*, **145**, 109 (1962).
3) N. M. Sinitsyn and K. I. Petrov, *Zh. Struk. Khim.*, **9**, 45 (1968).
4) E. Miki, T. Ishimori, H. Yamatera and H. Okuno, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **87**, 703 (1966).
5) E. Miki, This Bulletin, **41**, 1835 (1968).

numbers of the N–O, the Ru–N and the Ru–X (X *cis* to NO) stretching vibrations decreased regularly in the order of M=K, Rb and Cs.

On the other hand, the shifts caused by the replacement of the halide ions were observed on the N–O stretching and especially on the RuNO bending vibrations, but hardly any on the Ru–N stretching vibration; replacing Cl^- with Br^- and I^-, the wave numbers of the N–O stretching and the RuNO bending vibrations decreased regularly in the order of X=Cl, Br and I. Although the N–O stretching and the RuNO bending vibrations shifted, the wave numbers of the Ru–N stretching vibration hardly changed at all by the replacement of the halide ions. This seems to be due to the fact that the RuNO bending vibration (E) is nearer the Ru–X (X *cis* to NO) stretching vibration (E) than the Ru–N stretching vibration (A_1) is to the Ru–X (X *trans* to NO) stretching vibration (A_1).

The effect on the vibrations caused by the replacement of the outer sphere cations and the halide ions can be qualitatively explained by the difference in electronegativities of the outer sphere cations and halide ions as suggested by Sinitsyn *et al.*[1-3] Although the positions of the cations in the crystals have not been determined yet, it should be noted that the outer sphere cations have an appreciable effect on the N–O, the Ru–N and the Ru–X (*cis* to NO) stretching vibrations.