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## Chemistry and Optical Properties of 4d and 5d Transition Metals. III. Chemistry and Electronic Structures of Ruthenium Acidonitrosylamines, $[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{L})]^{q+}$ 1a

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Convenient new procedures were developed for preparing ten compounds, several of which have been known before, of general formula *trans*- $[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{L})]\text{X}_n$ , with  $\text{L} = \text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NCO}^-$ ,  $\text{N}_3^-$ ,  $\text{OH}^-$ ,  $\text{NH}_3$ , or  $\text{CH}_3\text{CO}_2^-$ ; counterions were  $\text{X}^- = \text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ , or  $\text{ClO}_4^-$ . Pertinent chemical observations are reported, and a number of properties of these compounds in their electronic ground and excited states are described. Electronic bands corresponding to "d-d," *i.e.*,  ${}^3\text{T}_1$ ,  ${}^3\text{T}_2$  and  ${}^1\text{T}_1$  states of " $t_2^3e^1$ ," charge transfer (" $t_{2g} \rightarrow \pi^*\text{NO}$ " and " $\pi\text{L} \rightarrow e_g$ "), and internal ( $\text{L} = \text{N}_3^-$ ) transition types were recognized. In the low-energy regions, the first band (lowest energy) arises from  ${}^1\text{A}_1 \rightarrow {}^3\text{T}_1 + \pi^*\text{NO}$ , and the second band is  ${}^1\text{A}_1 \rightarrow {}^1\text{T}_1$ . Interestingly this broad  $t_2 \rightarrow \pi^*\text{NO}$  charge-transfer band has low dipole strength, and it occurs at lower energy than  ${}^1\text{T}_1$ . These features resemble some 3d spectra of  $[\text{M}(\text{CN})_5(\text{NO})]^{q+}$ . Tetragonal components of  ${}^1\text{T}_1$  were observed only for  $[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{CH}_3\text{CO}_2)]^{2+}$  in both its electronic and MCD (24,500 G) spectra. However, the MCD spectrum of  $[\text{Ru}(\text{NH}_3)_4(\text{NO})\text{Cl}]\text{Cl}_2$  at 30,500 G uncovered both  ${}^1\text{T}_1$  components, whereas the electronic absorption spectrum shows only the low-energy component. It appears general that the *net* MCD rotation for  ${}^3\text{T}_1 + \pi^*\text{NO}$  is negative, whereas it is positive for  ${}^1\text{T}_1$ . In addition, both  $\text{C}_{4v}$  components ( ${}^1\text{E}$ ,  ${}^1\text{A}_2$ ) of  ${}^1\text{T}_1$  were positive, as observed for  $\text{L} = \text{CH}_3\text{CO}_2^-$  and  $\text{Cl}^-$ . There is no evidence of a MCD  $A$  term of  ${}^1\text{E}$  dominating the spectrum in the  ${}^1\text{T}_1$  regions of these compounds. The high-intensity electronic absorption bands at higher energy are assigned to  $(\pi\text{L} \text{ or } p\pi\text{L}) \rightarrow e\text{Ru}$  charge transfer or to ligand-ligand internal transitions. Using the vibrational frequency  $\nu(\text{NO})$  as an indicator the extension of an earlier vibrational trans-effect series now leads to the sequence  $\text{NH}_3 < \text{NCO}^- < \text{N}_3^- < \text{CH}_3\text{CO}_2^- < \text{Cl}^- < \text{Br}^-$ , with  $[\text{Ru}(\text{NH}_3)_4(\text{NH}_3)(\text{NO})]^{3+}$  having the highest value of  $\nu(\text{NO})$ . Finally, the MCD, infrared, and especially electronic absorption data rule out a previously suggested possibility that the intramolecular antiferromagnetic moiety  $[\text{Ru}^{\text{II}}-(\text{NO}^+)]$  exists in these compounds rather than  $[\text{Ru}^{\text{II}}-(\text{NO}^+)]$ .

### Introduction

Recent chemical literature reveals that transition metal nitrosyl compounds are being investigated by several groups in a vigorous manner reminiscent of metal carbonyl research initiated years earlier. The focus is most often on the (M-N-O) portions of compounds in their electronic ground states, *viz.*, the trans effect of L and NO in *trans*-(L-M-NO), the formal charge of bonded NO, and interatomic distances and angles of M-N-O. It is one of the most prominent features of ruthenium chemistry that there exist numerous compounds containing the  $\text{RuNO}^{3+}$  group. This paper deals with such compounds.

Following the preparation of *trans*- $[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{OH})]\text{Cl}_2$  by Werner,<sup>2</sup> the progress of ruthenium nitrosyl chemistry was slow for a number of years, *e.g.*,  $[\text{Ru}(\text{NH}_3)_5(\text{NO})]\text{Cl}_3 \cdot \text{H}_2\text{O}$  was not reported until 1952.<sup>3</sup> In recent years this area has been advanced more rapidly; *i.e.*, a number of definitive spectroscopic, X-ray, and chemical studies have appeared. For example, several X-ray investigations of  $\text{RuNO}$  compounds have been reported by Ibers<sup>4</sup> and Weaver<sup>5</sup> and their coworkers and by several others.<sup>6</sup> As another example, infrared spectra were investigated by Fairy<sup>7</sup> and Durig<sup>8</sup> and their coworkers. Electronic spectra of ruthenium

nitrosyl compounds have not appeared in the literature to the best of our knowledge, and the magneto-optical activity of ruthenium amines has also not been reported. However, Feltham and Nyholm<sup>9</sup> reported the electronic transitions of cobalt nitrosyls containing  $\text{Co}^{\text{III}}-(\text{NO}(\text{I}-))$ . Others were reported later by Feltham<sup>10</sup> and Gray<sup>11</sup> and their coworkers.

The present study includes new and convenient preparative procedures for the series of tetragonal amines,  $[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{L})]^{q+}$ . Some compounds were previously known and others are new. Their electronic absorption bands, *i.e.*, "d-d," "charge transfer," and ligand "internal" transitions, are reported along with several complementary MCD spectra. The latter data represent an initial study, and the spectra are used at this time primarily to provide additional resolution over electronic absorption spectra. All compounds are considered to contain  $\text{NO}^+$  (and therefore  $\text{Ru}(\text{II})$ ) in view of their high NO stretching frequencies ( $\sim 1870 \text{ cm}^{-1}$ ).

### Experimental Section

Electronic spectra were obtained using a Cary 14 spectrophotometer, and mid-infrared (KBr matrix) spectra were recorded on a Perkin-Elmer 521 instrument. Magnetic circular dichroism spectra were obtained using the following system. The magnetic field was generated using an Nb-Ti superconducting coil built into a 300°K-80°K-4°K dewar. Fields below *ca.* 42,000 G were employed until additional instrumental changes can be effected. The magnetic field was measured to within 1% accuracy using a rotating-coil type gaussmeter. The latter was calibrated against a more accurate Magnion G-502. The magnetic field and light directions are made to parallel each other in order to adhere to present convention. The circularly dichroic light of a Durrum Jasco Model ORD/UV/CD-5 was used. The xenon source was found not to require shielding in fields used

(1) (a) Presented in part at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970. (b) NDEA Predoctoral Fellow. (c) NSF Predoctoral Trainee.

(2) A. Werner, *Chem. Ber.*, **40**, 2614 (1907).

(3) K. Gieu and I. Budecker, *Z. Anorg. Allg. Chem.*, **269**, 202 (1952).

(4) (a) D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, **7**, 2345 (1968); (b) D. J. Hodgson and J. A. Ibers, *ibid.*, **8**, 1282 (1969), and references cited therein.

(5) D. A. Snyder and D. L. Weaver, *ibid.*, **9**, 2760 (1970).

(6) For example, see T. S. Khodashova, *J. Struct. Chem. (USSR)*, **6**, 678 (1965); P. T. Manoharan and W. C. Hamilton, *Inorg. Chem.*, **2**, 1043 (1963); D. A. Hall and A. A. Taggart, *J. Chem. Soc.*, 1359 (1965).

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

(8) J. R. Durig, E. E. Mercer, and W. A. McAllister, *Inorg. Chem.*, **5**, 1881 (1966), and references therein.

(9) R. D. Feltham and R. S. Nyholm, *ibid.*, **4**, 1334 (1965).

(10) R. D. Feltham, W. Silverthorn, and G. McPherson, *ibid.*, **8**, 344 (1969).

(11) P. T. Manoharan and H. B. Gray, *ibid.*, **5**, 823 (1966).

here, since results were identical with and without shielding foil. As the lamp arc lengthens with usage, it becomes more sensitive to the field, however. The end-on photomultiplier tube was removed, shielded, and housed outside the instrument. The instrument is still usable for absorption optical measurements, since the chopper drive cable was lengthened and repositioned by us. The instrument calibration was checked against the previously published MCD spectrum of  $K_3[Fe(CN)_6] \cdot 3H_2O$ .<sup>12</sup> The instrumental CD accuracy is adjusted by using camphor-sulfonic-*d*<sub>10</sub> acid as a standard. Whenever MCD and optical absorption spectra are shown together in a figure, they were both recorded on the Jasco, which uses prism optics. The data of Table I are based on Cary 14 spectra.

TABLE I

OPTICAL BANDS AND PARAMETERS<sup>a</sup> OF RUTHENIUM(II) NITROSONIUM AMMINE COMPLEXES<sup>b</sup> IN AQUEOUS SOLUTION<sup>c</sup> { $[Ru(NH_3)_4(NO)L]^{2+}$  ( $q = 3$  IF  $L = NH_3$ ;  $q = 2$  FOR OTHER  $L$ )}

L	Counter-ion	$\nu_{max}$ , K	$\epsilon_{max}$ , $M^{-1} cm^{-1}$	$D, D^2$	$f$	Assignment
NH <sub>3</sub>	Cl <sup>-</sup>	22,000	15	...	...	I <sup>e-h</sup>
		32,800	56	0.0979	0.00150	II
OAc <sup>-</sup>	ClO <sub>4</sub> <sup>-</sup>	23,000	22	...	...	I
		30,500	131	0.189	0.00289	IIB
		33,400	162	0.133	0.00203	III
		44,600	4970	9.12	0.191	IV
Cl <sup>-</sup>	Cl <sup>-</sup>	22,700	17	...	...	I
		30,300	264	0.283	0.00404	II
		41,200	4220	7.29	0.136	IV
OH <sup>-</sup>	Cl <sup>-</sup>	23,300	25	...	...	I
		29,900	211	0.319	0.00448	II
		43,900	5750	10.6	0.220	IV
NCO <sup>-</sup>	ClO <sub>4</sub> <sup>-</sup>	22,200	31	...	...	I
		29,100	427	0.568	0.00777	II
		43,900	6460	10.1	0.192	IV
N <sub>3</sub> <sup>-</sup>	ClO <sub>4</sub> <sup>-</sup>	21,300	54	...	...	I
		27,700	740	1.59	0.0208	II
		34,400	4810	6.74	0.109	IV
		40,400	5380	7.56	0.144	V
Br <sup>-</sup>	ClO <sub>4</sub> <sup>-</sup>	21,100	17	...	...	I
		26,900	87	0.124	0.00160	II
		36,500	3700	5.98	0.103	IV

<sup>a</sup> Except for the bands of the nitrosylpentaammineruthenium(II) complex and the spin-forbidden transitions of each compound, the parameters are for separated components of overlapping bands. Parameters are given as three significant figures. The variance of the parameters was not determined. <sup>b</sup> Symbols:  $\nu$ , frequency ( $1 K = 1 cm^{-1}$ ) of band maximum;  $\epsilon_{max}$ , molar extinction coefficient defined by absorbance =  $\epsilon \times$  path length (cm)  $\times$  molarity;  $D$ , dipole strength ( $D^2$ );  $f = (8\pi^2 m c \nu) / 3 h e^3$  ( $f$  is the oscillator strength). <sup>c</sup> Band I is  ${}^1A_1 \rightarrow {}^3T_1$ ,  ${}^3T_2$  and  $t_{2g} \rightarrow \pi^*NO$ . <sup>d</sup> Transition II is  ${}^1A_1 \rightarrow {}^1T_1$ . <sup>e</sup> Transition IIB is  ${}^1E$  or  ${}^1A_2$  of  ${}^1T_1$ . <sup>f</sup> Transition III is the same as IIB. <sup>g</sup> Transition IV is  $\pi\pi^*$  ( $x^2 - y^2, z^2$ )  $Ru$ . <sup>h</sup> Transition V is  $\pi L \rightarrow \pi^*L$ . <sup>i</sup>  $H_2O$  was deaerated prior to use.

**Preparations of Compounds. General Data.**—Commercial " $RuCl_3 \cdot nH_2O$ " (1 g) (Engelhardt Industries) was ground with concentrated HCl (10 ml) and evaporated to dryness on a steam bath. This step was repeated with the intention of obtaining ruthenium in the form of  $Ru(III)$ .<sup>13</sup> Carbon, chlorine, hydrogen, nitrogen, and iodine analyses were done by Galbraith Laboratories, Inc., Knoxville, Tenn., to confirm the identities of compounds initially concluded from infrared spectra. The preparations of these compounds are described in some detail here because most previously existing literature is very brief on this subject.

**Chloronitrosyltetraammineruthenium(II) Chloride. Procedure A.**—Hydrated ruthenium trichloride (1 g) was added to a reaction flask containing aqueous ammonia (25 ml, 8 *M*), and flushing with  $N_2$  was begun. Following the addition of zinc dust (3 g), the mixture was stirred, and the reaction was continued 24 hr, during which time the original red-violet solution turned deep yellow. This solution containing  $[Ru(NH_3)_6]^{2+}$  was filtered free of excess zinc.<sup>14</sup> The deep yellow filtrate was

treated with gaseous  $Cl_2$  (ca. 0.25  $cm^3/sec$ ) until the solution became acidic. At this point concentrated  $NH_4OH$  (20 ml) was added, and the solution was boiled (20 min). After addition of HCl (20 ml, 6 *M*), refluxing (2 hr), and cooling ( $0^\circ$ ), a deep orange-yellow precipitate formed. Following recrystallization (0.1 *M* HCl), 0.7 g (60% yield) of the orange-red, crystalline compound was obtained. It was identified as *trans*- $[Ru(NH_3)_4(NO)Cl]Cl_2$  from its infrared spectrum.<sup>8</sup> This is a convenient new preparative procedure.

**Procedure B.**—By this new method *trans*- $[Ru(NH_3)_4(NO)Cl]Cl_2$  was prepared from  $[Ru(NH_3)_6]Cl_2$ . The latter compound (0.5 g) was dissolved in aqueous ammonia (25 ml, 8 *M*) by warming. The solution was chlorinated (ca. 0.25  $cm^3/sec$ ) until it was slightly acidic; more concentrated ammonia solution (20 ml) was added. After the addition of HCl (20 ml, 6 *M*) the mixture was refluxed (2 hr). The deep orange-yellow compound that precipitated (0.3 g) was retained on a filter and washed (ice water, ethanol, ether). The pure compound, *trans*- $[Ru(NH_3)_4(NO)Cl]Cl_2$ , was obtained after recrystallization as described in part A above.

**Procedure C.**—By this new method *trans*- $[Ru(NH_3)_4(NO)Cl]Cl_2$  was prepared from  $[Ru(NH_3)_6]Cl_3$ . The latter compound (0.5 g) was dissolved in  $NH_4OH$  (40 ml, 8 *M*) by warming. The solution was chlorinated (ca. 0.25  $cm^3/sec$ ) until it was acidic. Additional aqueous ammonia (20 ml, concentrated) was added to the solution, and it was boiled (20 min). HCl (20 ml, 6 *M*) was then added to the hot solution. The mixture was refluxed (2 hr) and cooled ( $0^\circ$ ), after which the deep orange-yellow complex precipitated (0.25 g). The fine crystals were retained on a filter and washed (ice water, ethanol, ether). Infrared evidence confirmed the presence of mainly *trans*- $[Ru(NH_3)_4(NO)Cl]Cl_2$  with  $[Ru(NH_3)_6]Cl_2$  as contaminant.<sup>15</sup> Pure chloronitrosyltetraammineruthenium(II) chloride was obtained by the method described in procedure A.

**Azidonitrosyltetraammineruthenium(II) Iodide and Perchlorate.**—Chloronitrosyltetraammineruthenium(II) chloride (0.2 g) was added to hot water (20 ml,  $75^\circ$ ). Following the addition of  $NaN_3$  (0.5 g), the solution was acidified with potassium hydrogen phthalate solution (0.1 *M*) and heated ( $75^\circ$ , 25 min). This solution turned orange from its original light yellow color, and it was kept acidic. The acidity is necessary because in basic medium the light yellow *trans*- $[Ru(NH_3)_4(NO)(OH)]^{2+}$  was the major product. The hot solution was filtered into cold potassium iodide solution (2 *M*, 5 ml). An orange precipitate formed immediately. The orange complex was retained on a filter and was washed (ice water, ethanol, ether). The compound was redissolved in cold water (40 ml), and the solution was filtered into KI solution (2 *M*, 5 ml), from which the orange compound precipitated. It was retained on a filter and washed (ice water, ethanol, ether). This orange compound (0.15 g, 45% yield) was identified as  $[Ru(NH_3)_4(NO)N_3]I_2$ . *Anal.* Calcd: N, 22.50; I, 51.55. Found: N, 21.20; I, 50.08.

$[Ru(NH_3)_4(NO)N_3](ClO_4)_2$  was prepared by filtering the solution of  $[Ru(NH_3)_4(NO)N_3]I_2$  into saturated  $NaClO_4$  solution. The light orange complex precipitated and was retained on a filter and washed (ice water, ethanol, ether).

**Acetonitrosyltetraammineruthenium(II) Perchlorate and Iodide.**—*trans*- $[Ru(NH_3)_4(NO)Cl]Cl_2$  (0.2 g) was dissolved in hot water (20 ml,  $90^\circ$ ). Sodium acetate (1 g) was added, and the solution was acidified with acetic acid and heated ( $90^\circ$ , 30 min). The yellow, hot solution was filtered into 5 ml of saturated  $NaClO_4$  solution, and the mixture was cooled ( $0^\circ$ , 30 min). A yellow precipitate formed; it was retained on a filter and was washed (ethanol, ether), redissolved in cold water (15 ml), and filtered into 5 ml of saturated  $NaClO_4$  solution. The mixture was cooled ( $0^\circ$ , 30 min), yellow precipitate formed, and the latter was retained on a filter and washed with ethyl alcohol (20 ml) and ether. The yellow compound (0.10 g, 33% yield) was identified from its infrared spectrum (as the iodide salt) as  $[Ru(NH_3)_4(NO)(OAc)](ClO_4)_2$ . *Anal.* Calcd: N, 15.28; C, 5.23; H, 3.27. Found: N, 15.06; C, 4.77; H, 3.93.

**Isocyanatonitrosyltetraammineruthenium(II) Perchlorate and Iodide.**—*trans*- $[Ru(NH_3)_4(NO)Cl]Cl_2$  (0.2 g) was added to an aqueous solution of KOCN (0.5 g in 20 ml). The mixture was heated ( $90^\circ$ ) until most of the solid dissolved; it was then acidified with acetic acid. This acidic solution was heated ( $90^\circ$ , 30 min), and the acidity of the solution was checked every 5 min. If it is basic, one obtains  $[Ru(NH_3)_4(NO)(OH)]^{2+}$  as the major

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(14) F. M. Lever and A. R. Powell, *Chem. Soc., Spec. Publ.*, **No. 13**, 135 (1959).

(15) Unpublished results of this laboratory; also see ref 8.

product. The solution gradually changed color from light yellow to orange during the course of the reaction. The hot, orange solution was filtered into KI solution (2 M, 5 ml). The deep orange  $[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{NCO})]_2\text{I}_2$  precipitated immediately. It was retained on a filter and washed (ice water). The compound was redissolved in cold water (60 ml) and filtered into KI solution (2 M, 5 ml). The resulting orange precipitate was isolated and washed (ice water, ethanol, ether), and it was identified from its infrared spectrum.<sup>8</sup> The purified product weighed 0.10 g (32% yield). *Anal.* Calcd: N, 16.95; I, 51.20. Found: N, 16.84; I, 50.32.

The perchlorate salt,  $[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{NCO})](\text{ClO}_4)_2$ , was prepared by rapidly dissolving  $[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{NCO})]_2\text{I}_2$  (0.10 g) in hot water (60°, 30 ml) and adding it to 5 ml of saturated sodium perchlorate solution. The yellow perchlorate precipitated immediately and was isolated and washed (ice water, ethanol, ether).

**Bromonitrosyltetraammineruthenium(II) Perchlorate and Bromide.** Procedure A.—“ $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ ” (1 g) was added to a reaction flask containing aqueous ammonia (35 ml, 8 M) and  $\text{N}_2$ -flushing was begun. Following the addition of zinc dust (3 g), the mixture was stirred and the reaction continued 24 hr. The solution containing  $[\text{Ru}(\text{NH}_3)_6]^{2+}$  was filtered free of excess zinc. The deep yellow filtrate was treated with gaseous  $\text{Cl}_2$  (ca. 0.25 cm<sup>3</sup>/sec) until the solution became slightly acidic. At this point concentrated aqueous ammonia (20 ml) was added; the solution was boiled (20 min) and then acidified with concentrated hydrobromic acid (48%, 15 ml). This solution was heated (90°, 1 hr) during which time the orange  $[\text{Ru}(\text{NH}_3)_4(\text{NO})\text{Br}]_2\text{Br}_2$  precipitated. The mixture was cooled and the compound was isolated on a filter and washed (ice water, ethanol, ether). It (0.7 g, 42% yield) was identified from its infrared spectrum.<sup>8</sup>

*trans*- $[\text{Ru}(\text{NH}_3)_4(\text{NO})\text{Br}](\text{ClO}_4)_2$  was prepared by dissolving  $[\text{Ru}(\text{NH}_3)_4(\text{NO})\text{Br}]_2\text{Br}_2$  in cold water and the solution was filtered into a saturated  $\text{NaClO}_4$  solution. The orange perchlorate precipitated and was retained on a filter and washed (ice water, ethanol, ether).

Procedure B.—By this method *trans*- $[\text{Ru}(\text{NH}_3)_4(\text{NO})\text{Br}]_2\text{Br}_2$  was prepared from *trans*- $[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{OH})\text{Cl}]_2$  as described in the literature.<sup>9</sup> A hot solution of the latter compound was treated with concentrated hydrobromic acid, giving *trans*- $[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{H}_2\text{O})]^{3+}$  as an intermediate in solution.  $\text{H}_2\text{O}$  was replaced from the latter by  $\text{Br}^-$  to give *trans*- $[\text{Ru}(\text{NH}_3)_4(\text{NO})\text{Br}]_2\text{Br}_2$  (70% yield).

**Hydroxonitrosyltetraammineruthenium(II) Chloride.** Procedure A.—“ $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ ” (1 g) was added to a reaction flask containing aqueous ammonia (25 ml, 8 M), and flushing with  $\text{N}_2$  was begun. Following the addition of zinc dust (3 g), the mixture was stirred, and the reaction was continued 24 hr. The solution containing  $[\text{Ru}(\text{NH}_3)_6]^{2+}$  was filtered free of excess zinc. The deep yellow filtrate was treated with gaseous  $\text{Cl}_2$  (ca. 0.25 cm<sup>3</sup>/sec) until the solution became slightly acidic. At this point concentrated aqueous ammonia (20 ml) was added, and the solution was boiled (20 min). It was then evaporated (70°) down to 20 ml and neutralized with dilute  $\text{HCl}$  (0.5 M). The filtrate (20 ml) was evaporated (70°) down to 15 ml. After addition of concentrated aqueous ammonia (0.2 ml) the yellow concentrated solution of  $[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{OH})]^{2+}$  was kept in a desiccator 4 days. Orange crystals of the chloride formed; they were isolated and washed (ethanol, ether), and the compound (0.4 g, 37% yield) was identified from its infrared spectrum.<sup>8</sup> The yield was improved by precipitating the perchlorate, which is less soluble than the chloride salt.

Procedure B.—By this method the complex was prepared from *trans*- $[\text{Ru}(\text{NH}_3)_4(\text{NO})\text{Cl}]_2\text{Cl}_2$  as described in the literature.<sup>2</sup> A hot solution of the latter compound was treated with concentrated ammonia solution. The  $\text{Cl}^-$  in *trans*- $[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{OH})\text{Cl}]_2$  was isolated from the chloride solution (60% yield).

**Nitrosylpentaammineruthenium(II) Chloride Hydrate,  $[\text{Ru}(\text{NH}_3)_5(\text{NO})\text{Cl}]_2 \cdot \text{H}_2\text{O}$ .**—The compound was prepared according to qualitative directions previously reported.<sup>3</sup>

Molar conductance measurements were carried out on three of the new compounds,  $[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{OAc})](\text{ClO}_4)_2$  and  $[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{L})]_2$  (L =  $\text{N}_3^-$  and  $\text{NCO}^-$ ) (Table II). The results are consistent with 2:1 type compounds.

## Results and Discussion

**A. Preparative Chemistry.**—The hydrated ruthenium nitrosyl chloride  $\text{Ru}(\text{NO})\text{Cl}_3 \cdot 3\text{H}_2\text{O}$  has historically

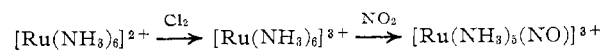
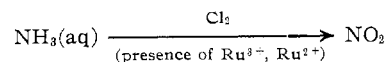
L <sup>-</sup>	X <sup>-</sup>	Concn, M	$\Omega, \text{ohm}^{-1}$	Type compd
$\text{CH}_3\text{CO}_2^-$	$\text{ClO}_4^-$	0.000508	222	2:1
$\text{N}_3^-$	$\text{I}^-$	0.000545	253	2:1
$\text{NCO}^-$	$\text{I}^-$	0.000420	250	2:1

<sup>a</sup> Aqueous solution. <sup>b</sup>  $\Omega$  is the molar conductance.

been used as starting material<sup>16</sup> for preparing a number of previously known nitrosyl ammine compounds using multistep procedures, *e.g.*, by making the intermediate  $[\text{Ru}(\text{NO})\text{Cl}_5]^{2-}$ . The present study leads directly to  $[\text{Ru}(\text{NH}_3)_4(\text{NO})\text{Cl}]\text{Cl}_2$  from  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ , thus eliminating a number of intermediate isolation steps. The tetraammine,  $[\text{Ru}(\text{NH}_3)_4(\text{NO})\text{Cl}]\text{Cl}_2$ , was usable as the precursor of other compounds of general formula  $[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{L})]\text{X}_2$ .

The controlled chlorination of an ammoniacal solution of freshly generated  $[\text{Ru}(\text{NH}_3)_6]^{2+}$  (from  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ ) led to *trans*- $[\text{Ru}(\text{NH}_3)_4(\text{NO})\text{Cl}]^{2+}$ . The preparation of the hexaammine was qualitatively described by Lever and Powell, *i.e.*, reduction of ruthenium trichloride with zinc dust in an ammoniacal solution containing  $\text{NH}_4\text{Cl}$  in a nitrogen atmosphere.<sup>14</sup> However, hexaammineruthenium(II) undergoes rapid, complex oxidation reactions in air, resulting in the formation of a dimer and a number of unidentified products.<sup>14</sup> For these reasons it is not advisable to isolate crystalline  $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_2$  as an intermediate for preparative work. Instead, the latter compound was freshly generated and kept under nitrogen atmosphere prior to its use for reactions. It was already stated above that one product is the nitrosylpentaammine  $[\text{Ru}(\text{NH}_3)_5(\text{NO})]^{3+}$  when  $[\text{Ru}(\text{NH}_3)_6]^{2+}$  is chlorinated in aqueous ammonia solution. In addition, chloronitrosyltetraammineruthenium(II), *trans*- $[\text{Ru}(\text{NH}_3)_4(\text{NO})\text{Cl}]^{2+}$ , is a major product when the chlorination is carried out in the presence of higher chloride ion concentration and in acid medium. The latter condition prevents rapid base hydrolysis which leads to breakage of the Ru-Cl bond and formation of  $[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{OH})]^{2+}$ .

This introduction of NO into the coordination sphere of ruthenium is probably rather complex when one considers possible reactions of  $\text{Cl}_2$  with the components ( $\text{NH}_4\text{OH}$ ,  $\text{H}_2\text{O}$ ,  $[\text{Ru}(\text{NH}_3)_6]^{2+}$ ) of the solution. For example,  $\text{Cl}_2$  probably oxidizes  $[\text{Ru}(\text{NH}_3)_6]^{2+}$  to the ruthenium(III) hexaammine. Further, brown  $\text{NO}_2$  was observed escaping from solution. Since the latter is suspect of forming the  $\text{RuNO}^{3+}$  group,<sup>13</sup> the following reactions may take place leading to  $[\text{Ru}(\text{NH}_3)_5(\text{NO})]^{3+}$



Mechanistic studies need to be carried out, however.<sup>17</sup>

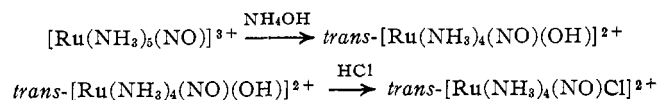
One of several *trans*-influence studies of NO in ruthenium compounds was reported by Zvjagintsev and co-workers,<sup>18</sup> who found that NO in  $[\text{Ru}(\text{NH}_3)_5(\text{NO})]^{3+}$  has a stronger *trans* influence than  $\text{NH}_3$ ; *i.e.*, in warm

(16) M. B. Fairy and R. J. Irving, *J. Chem. Soc. A*, 475 (1966).

(17) It has also been documented that  $\text{N}_2\text{O}_4$  in acid solution ( $\text{H}_2\text{SO}_4$ ) disproportionates directly to  $\text{NO}^+$  and  $\text{NO}_2^-$  (see ref 13):  $\text{N}_2\text{O}_4 + 3\text{H}_2\text{SO}_4 = \text{NO}^+ + \text{NO}_2^- + 3\text{HSO}_4^- + \text{H}_3\text{O}^+$ . This might be the source of  $\text{NO}^+$  in  $\text{RuNO}^{3+}$  rather than  $\text{NO}_2$  or NO attacking Ru(III).

(18) O. E. Zvjagintsev, N. M. Sinitsyn, and V. N. Pitchov, *Proc. Int. Conf. Coord. Chem.*, **8**, 142 (1964).

basic solutions of this complex ion, one obtains *trans*-[Ru(NH<sub>3</sub>)<sub>4</sub>(NO)(OH)]<sup>2+</sup> (also see above preparation section). Furthermore, we find that reaction of Cl<sup>-</sup> with *trans*-[Ru(NH<sub>3</sub>)<sub>4</sub>(NO)(OH)]<sup>2+</sup> leads to the chloronitrosyltetraammineruthenium cation in concentrated HCl solution.



The coordinated chloride ion in *trans*-[Ru(NH<sub>3</sub>)<sub>4</sub>(NO)Cl]Cl<sub>2</sub> was found in this study to be replaceable by the nitrogen-containing ligands N<sub>3</sub><sup>-</sup> and NCO<sup>-</sup> and by acetate (OAc<sup>-</sup>), in hot acidic solutions. It was necessary to carry out these reactions in acidic media, since *trans*-[Ru(NH<sub>3</sub>)<sub>4</sub>(NO)(OH)]<sup>2+</sup> would be the major product otherwise. One contributing factor for this is that these anions (X<sup>-</sup> = N<sub>3</sub><sup>-</sup>, NCO<sup>-</sup>, OAc<sup>-</sup>) of weak acids hydrolyze and produce basic solutions. In turn OH<sup>-</sup> replaces L in *trans*-[Ru(NH<sub>3</sub>)<sub>4</sub>(NO)L]<sup>2+</sup> and forms the hydroxonitrosyltetraammine.

These compounds containing RuNO<sup>3+</sup> appear to be very stable.<sup>19</sup> For example, no change was detected when *trans*-[Ru(NH<sub>3</sub>)<sub>4</sub>(NO)Cl]Cl<sub>2</sub> was refluxed in HCl (6 M) for 12 hr. A plausible cause for the stability of Ru(II) is the presence of unfilled low-lying π\*NO orbitals which are of proper symmetry (e in C<sub>4v</sub>) to combine with occupied ruthenium *xz* and *yz* orbitals, making possible electron density migration from the region of Ru(II) (t<sub>2g</sub><sup>6</sup>) to π\*NO. The electron density distribution over the three atoms in Ru-NO is not experimentally known. The isoelectronic Ru<sup>II</sup>-N<sub>2</sub> bond in [Ru(NH<sub>3</sub>)<sub>5</sub>N<sub>2</sub>]<sup>2+</sup> is much less stable, however.<sup>20</sup>

**B. Electronic Transitions. General Data.**—"Charge transfer," "d-d" transitions, and ligand "internal" transitions are of interest here. Band assignments were made on the basis of intensities, energies, and comparisons of these quantities between related compounds. Overlapping bands of electronic spectra were decomposed into individual components assuming gaussian forms (Table I). The magneto-optical activities of several compounds are also shown and discussed. It was initially considered possible that tetragonal excited states <sup>1</sup>E of <sup>1</sup>T<sub>1</sub>(t<sub>2g</sub><sup>5</sup>e<sub>g</sub><sup>1</sup>) parentage might have sufficient orbital angular momentum to produce a dominating *A* term in each MCD spectrum. Furthermore, additional bands can sometimes be uncovered using MCD if neighboring bands have alternating positive and negative magneto-optical activity or quite different intensity ratios compared to bands of electronic absorption spectra. We include the MCD data for these reasons.

Regarding the structure of RuNO<sup>3+</sup>, the NO<sup>+</sup> stretching frequencies in nitrosonium salts are in the range 2222–2300 cm<sup>-1</sup>, while the stretching frequencies of complexed NO<sup>+</sup> occur in the range 1700–1900 cm<sup>-1</sup>.<sup>19</sup> The frequencies shown in Table III are between 1834 cm<sup>-1</sup> (*trans*-[Ru(NH<sub>3</sub>)<sub>4</sub>(NO)(OH)]Cl<sub>2</sub>) and 1903 cm<sup>-1</sup> ([Ru(NH<sub>3</sub>)<sub>5</sub>(NO)]Cl<sub>3</sub>). Therefore, it is considered that we have [Ru<sup>II</sup>-(NO<sup>+</sup>)] rather than [Ru<sup>III</sup>-(NO)]

TABLE III  
STRETCHING FREQUENCIES ν(N-O) AND  
ν(Ru-NO), AND δ(RuNO)

Complex	ν(Ru-NO) or δ(Ru-NO), K	ν(N-O), K
[Ru(NH <sub>3</sub> ) <sub>5</sub> (NO)]Cl <sub>3</sub> ·H <sub>2</sub> O	602	1903 <sup>a</sup>
[Ru(NH <sub>3</sub> ) <sub>4</sub> (NO)(NCO)]I <sub>2</sub>	615	1890
[Ru(NH <sub>3</sub> ) <sub>4</sub> (NO)N <sub>3</sub> ]I <sub>2</sub>	595	1884
[Ru(NH <sub>3</sub> ) <sub>4</sub> (NO)(OAc)]I <sub>2</sub>	595	1882
[Ru(NH <sub>3</sub> ) <sub>4</sub> (NO)Cl]Cl <sub>2</sub>	608	1880 <sup>a</sup>
[Ru(NH <sub>3</sub> ) <sub>4</sub> (NO)Br]Br <sub>2</sub>	591	1870 <sup>a</sup>
[Ru(NH <sub>3</sub> ) <sub>4</sub> (NO)(OH)]Cl <sub>2</sub>	628	1834 <sup>a</sup>

<sup>a</sup> Present work and ref 8. See J. R. Durig and D. W. Wertz, *Appl. Spectrosc.*, **22**, 627 (1968), regarding comments about assignments of ν(Ru-NO) and δ(RuNO).

or [Ru<sup>IV</sup>-(NO<sup>-</sup>)] and the presence of intramolecular antiferromagnetism, possible in principle for [Ru<sup>III</sup>-(NO)], appears unreasonable.<sup>21</sup>

There are two other arguments against this antiferromagnetism. First, in compounds known to contain Ru(III) on the basis of magnetism we find that the MCD activity of d-d bands<sup>22</sup> is at least ten times larger than in these RuNO compounds. For example, |θ<sub>max</sub>/ε<sub>max</sub>| ≅ 7.5 × 10<sup>-3</sup> deg cm<sup>2</sup>/(dmol G ε) for [Ru(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>3</sub>, whereas this ratio is only about 3 × 10<sup>-4</sup>, at the most, for RuNO compounds.<sup>22</sup> Also, the first band (lowest energy) of all [Ru(NH<sub>3</sub>)<sub>5</sub>L]<sup>2+</sup> of Ru(III) compounds (L = N<sub>3</sub><sup>-</sup>, NCO<sup>-</sup>, NCS<sup>-</sup>, NCSe<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup>) is the intense π<sup>\*</sup>L → t<sub>2g</sub><sup>5</sup> charge-transfer band. If these nitrosyl compounds contained the t<sub>2g</sub><sup>5</sup> entity Ru<sup>III</sup>-NO, then we would expect band I of [Ru(NH<sub>3</sub>)<sub>4</sub>(NO)Cl]<sup>2+</sup> to have ε<sub>max</sub> ~1700 as observed in [Ru(NH<sub>3</sub>)<sub>5</sub>Cl]<sup>2+</sup>.<sup>23</sup> This parallelism is not found to occur in any of our compounds. Therefore, we conclude that they contain Ru<sup>II</sup>-(NO<sup>+</sup>) and not Ru<sup>III</sup>-(NO<sup>0</sup>).

Finally, the formation of numerous compounds containing coordinated NO<sup>+</sup> appears to be in part due to the fact that the ionization potential of NO is ~39,000 cm<sup>-1</sup> less than that of CO,<sup>19</sup> making it relatively easy to remove an electron from NO.

Figure 1 is a partial, simplified MO energy level diagram showing possible relative locations of a number of orbital types in *trans*-[Ru(NH<sub>3</sub>)<sub>4</sub>(NO)L]<sup>2+</sup>, and Figure 1B is most likely correct. Some octahedral d-d states of t<sub>2g</sub><sup>6</sup> and t<sub>2g</sub><sup>5</sup>e<sub>g</sub><sup>1</sup> are shown in their familiar Tanabe-Sugano sequence in Figure 2. The C<sub>4v</sub> components of states are given under the assumption that the axial ligands have a larger net antibonding than bonding influence on the t<sub>2</sub> metal orbitals.<sup>24</sup> (However, with π\*NO between e<sub>g</sub> and t<sub>2g</sub>, the separation of tetragonal components might not be large and could possibly reverse. We are continuing to investigate this possibility using polarized crystal spectra.) One might also expect to observe charge-transfer transitions of either type (*xy*, *yz*, *xz*)Ru → π\*NO or pπL → (z<sup>2</sup>, x<sup>2</sup> - y<sup>2</sup>)Ru, where pπL symbolizes pπ ligand electrons or nonbonding p electrons. These possibilities will be discussed.

**1. d-d Transitions.**—The d-d spectra of [Ru(NH<sub>3</sub>)<sub>6</sub>]<sup>2+</sup> and amines [Ru(AA)<sub>3</sub>]<sup>2+</sup> were reported

(19) B. F. G. Johnson and J. A. McCleverty, *Progr. Inorg. Chem.*, **7**, 277 (1966).

(20) S. W. Lin and A. F. Schreiner, *Inorg. Nucl. Chem. Lett.*, **6**, 561 (1970); A. D. Allen, F. Bottomley, V. P. Reinsalu, and C. V. Senoff, *J. Amer. Chem. Soc.*, **89**, 5595 (1967); D. F. E. Harrison, E. Weissberger, and H. Taube, *Science*, **159**, 320 (1968).

(21) C. K. Jørgensen, "Oxidation Numbers," Springer-Verlag, New York N. Y., 1969.

(22) A. F. Schreiner and S. W. Lin, MCD data of Ru(III) compounds to be published.

(23) S. W. Lin and A. F. Schreiner, *Inorg. Chim. Acta*, **5**, 290 (1971).

(24) H. Yamatera, *Bull. Chem. Soc. Jap.*, **31**, 95 (1958).

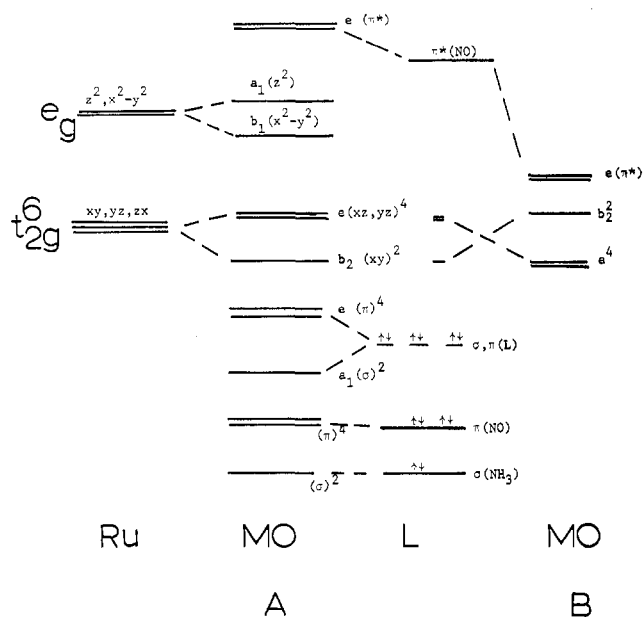


Figure 1.—Partial, simplified one-electron MO energy level diagram of  $trans\text{-}[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{L})]^{2+}$  in  $C_{4v}$  symmetry: A, NO and L more antibonding than NO is bonding; B,  $\pi^*\text{NO}$  more bonding on  $t_{2g}$  than the antibonding of  $\pi\text{L}$  and  $\pi^*\text{NO}$  orbitals on  $t_{2g}$ .

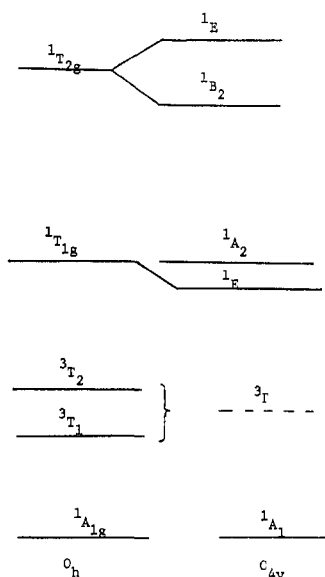


Figure 2.—Several d-d states of  $[\text{Ru}^{\text{II}}(\text{NH}_3)_4(\text{NO})(\text{L})]^{2+}$  (see text and ref 24). Some state orders may reverse if Figure 1B is accepted.

some time ago.<sup>25-27</sup> In contrast, spectra of a number of benzonitrilepentaammineruthenium(II) compounds exhibit only  $d \rightarrow \pi^*\text{L}$  and  $\pi\text{L} \rightarrow \pi^*\text{L}$  transitions, with d-d transitions masked.<sup>28</sup> The nitrosyltetraammine spectra studied here contain additional information, since d-d, charge-transfer, and ligand internal bands were observed. A representative spectrum is discussed next for which Table I contains the numerical results.

- (25) H. H. Schmidtke and D. Garthoff, *Helv. Chim. Acta*, **49**, 2042 (1966).  
 (26) T. J. Meyer and H. Taube, *Inorg. Chem.*, **7**, 2369 (1968).  
 (27) J. F. Endicott and H. Taube, *ibid.*, **4**, 437 (1965); *J. Amer. Chem. Soc.*, **84**, 4984 (1962); **86**, 1686 (1964).  
 (28) P. C. Ford, DeF. P. Rudd, R. Gaunder, and H. Taube, *ibid.*, **90**, 1187 (1968).

**Typical Electronic Absorption Spectrum.**  $trans\text{-}[\text{Ru}(\text{NH}_3)_4(\text{NO})\text{Cl}]\text{Cl}_2$ .—The spectrum of  $trans\text{-}[\text{Ru}(\text{NH}_3)_4(\text{NO})\text{Cl}]^{2+}$  is shown in Figure 3 and is typical of the

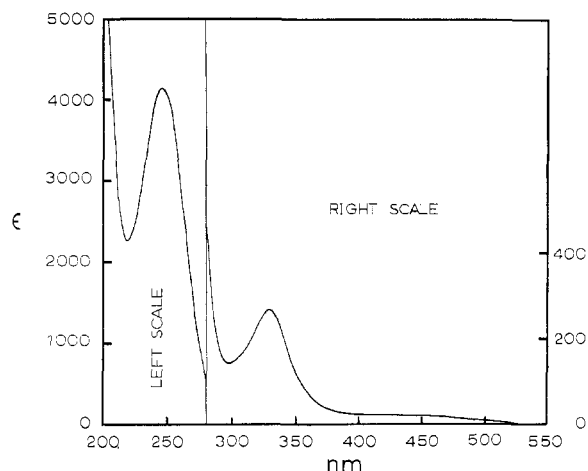


Figure 3.—Typical solution electronic spectrum of a  $trans\text{-}[\text{Ru}(\text{NH}_3)_4(\text{NO})\text{Cl}]\text{Cl}_2$ .

other tetraammines of this series (Table I). There is a broad band of very low intensity ( $\epsilon$  17) at 22.7 kK (440 nm). This intensity is characteristic of interconfigurational spin-forbidden transitions in 4d and 5d compounds. For example, the  $[\text{Rh}(\text{NH}_3)_5\text{Br}]^{2+}$  ion has a spin-forbidden d-d band with  $\epsilon$  25 at 424 nm.<sup>29</sup> Very important also is that the energies of these first bands in the collection of these compounds follows the positions of  ${}^1\text{T}_1$  (Figure 4),

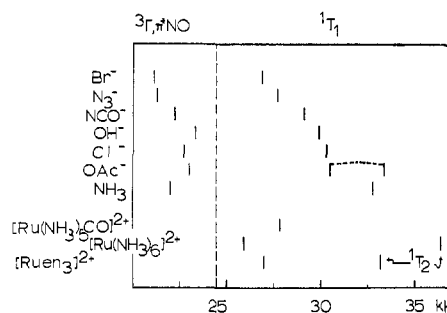


Figure 4.—Location of band I and  ${}^1\text{T}_1$  of  $[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{L})]^{2+}$

as expected if the bands were of  ${}^3\Gamma({}^3\text{T}_1, {}^3\text{T}_2)$  d-d origin. However, the large MCD and electronic absorption half-widths, absence of a pronounced internal heavy-atom effect (as  $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$  and  $\text{Rh}(\text{NH}_3)_5\text{Br}^{2+}$  demonstrate so well), and other experimental reasons given below, as well as semiempirical LCAO-MO results, lead us to conclude that band I also contains  $t_{2g} \rightarrow \pi^*\text{NO}$ . The second band is of medium intensity ( $\epsilon$  264) and appears at 30.3 kK (330 nm). This band height is characteristic of spin-allowed d-d transitions. A third band was observed at 41.2 kK (243 nm). It is very intense ( $\epsilon$  4220) and is assigned to an electric dipole allowed, charge-transfer band. The more detailed nature of these bands will be discussed by starting with the spectrum of the air-unstable parent hexaammine,  $[\text{Ru}(\text{NH}_3)_6]^{2+}$ .

$[\text{Ru}(\text{NH}_3)_6]^{2+}$ .—Solution spectra of the hexaammine

- (29) C. K. Jørgensen, *Acta Chem. Scand.*, **10**, 501 (1965).

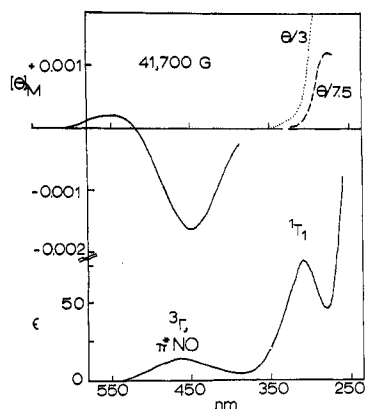


Figure 5.—MCD and electronic absorption spectra of  $[\text{Ru}(\text{NH}_3)_5(\text{NO})]\text{Cl}_3$ .  $[\theta]_M$  is the molar ellipticity per gauss ( $\text{deg cm}^2 \text{ dmol}^{-1} \text{ G}^{-1}$  or  $\text{deg dl dm}^{-1} \text{ mol}^{-1} \text{ G}^{-1}$ ).

were reported by three groups.<sup>25-27,30</sup> On the basis of work done by Meyer and Taube,<sup>26</sup> who investigated  $[\text{Ru}(\text{en})_3]^{2+}$  and  $[\text{Ru}(\text{NH}_3)_6]^{2+}$ , it is most reasonable to assign the bands of  $[\text{Ru}(\text{NH}_3)_6]^{2+}$  at *ca.* 25 kK (400 nm;  $\epsilon \approx 30$ ) and 36.4 kK (275 nm;  $\epsilon$  624) to spin-allowed  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  and  ${}^1A_{1g} \rightarrow {}^1T_{2g}$  transitions, respectively. Also,  $[\text{Ru}(\text{en})_3]^{2+}$  has  ${}^1T_1$  at 27.0 kK (370 nm;  $\epsilon \approx 30$ ) and  ${}^1T_2$  at 33.3 kK (302 nm;  $\epsilon \approx 1020$ ). Locations of  ${}^3T$  were not reported.

If one  $\text{NH}_3$  molecule were replaced from  $[\text{Ru}(\text{NH}_3)_6]^{2+}$  by  $\text{NO}^+$  or  $\text{CO}$  to form  $[\text{Ru}(\text{NH}_3)_5(\text{XY})]^{2+}$  ( $\text{XY} = \text{NO}^+$  or  $\text{CO}$ ), d-d bands would shift to higher energy. The spectrum<sup>30</sup> of  $[\text{Ru}(\text{NH}_3)_5(\text{CO})]^{2+}$  reflects this expectation; *i.e.*, the band at 27.8 kK (360 nm) was assigned to  ${}^1T_1$ . Strictly speaking one ought to discuss transitions to  $C_{4v}$  components  ${}^1E$  and  ${}^1A_2$  of  ${}^1T_1$ . However, doublet structure was observed only in the MCD spectrum of  $[\text{Ru}(\text{NH}_3)_4(\text{NO})\text{Cl}]\text{Cl}_2$  and in both MCD and electronic spectra of  $[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{OAc})]^{2+}$ . For this reason octahedral notation is employed.

$[\text{Ru}(\text{NH}_3)_5(\text{NO})]^{3+}$ .—It is advantageous to discuss the transitions of  $[\text{Ru}(\text{NH}_3)_5(\text{NO})]^{3+}$  next before assigning bands of other *trans*- $[\text{Ru}(\text{NH}_3)_4(\text{NO})\text{L}]^{2+}$ . Two maxima were observed in the electronic spectrum of the pentaammine, one low-intensity band at 22.0 kK (455 nm;  $\epsilon$  15) and the other at 32.8 kK (305 nm;  $\epsilon$  56,  $f = 0.0015$ ) (Table I). The first band at 22.0 kK is broad and cannot be the  ${}^1A_1 \rightarrow {}^1T_1$  transition because it is of lower energy than the analogous transition of the hexaammine at 25 kK and of  $[\text{Ru}(\text{en})_3]^{2+}$  at 27.0 kK. This 22.0-kK band (band I) is for this reason considered to contain the manifold of bands composed of the eight spin-orbit components of  ${}^3T_1$  and  ${}^3T_2$ . Three other reasons were given above. In addition the band also contains  $t_2 \rightarrow \pi^*\text{NO}$  for reasons to be given below. The second band (32.8 kK) corresponds to excited state  ${}^1T_1$  (band II) and is above  ${}^1T_1$  of  $[\text{Ru}(\text{en})_3]^{2+}$  and the hexaammine, as expected. The transition is also of higher energy than in  $[\text{Ru}(\text{NH}_3)_5(\text{CO})]^{2+}$  (27.8 kK). This difference, however, is reasonable on the basis of vibrational data, *viz.*, the carbonylpentaammine has  $\nu(\text{CO}) = 1955 \text{ K}$ , which is 188 K lower than that for the free ligand, whereas the nitrosylpentaammine has  $\nu(\text{NO}) = 1903 \text{ K}$ , which is at least 300 K lower than that for the free ligand. This leads one to conclude that  $\text{NO}^+$  penetrates the 4d shell more severely than the isoelec-

tronic  $\text{CO}$ .<sup>30,31</sup> {An initial crystal spectrum<sup>32</sup> of  $[\text{Ru}(\text{NH}_3)_5(\text{NO})]\text{Cl}_3 \cdot \text{H}_2\text{O}$  actually reveals two bands, one at 29 kK (weaker) and the other at 32.5 kK (stronger). Therefore,  ${}^1T_1$  is only perhaps 3 kK above the analogous band of  $[\text{Ru}(\text{NH}_3)_5(\text{CO})]^{2+}$ .}

The 41.7-kG MCD spectrum of  $[\text{Ru}(\text{NH}_3)_5(\text{NO})]\text{Cl}_3$  is shown in Figure 5. The region of band I at *ca.* 450 nm has large net negative rotational strength, whereas  ${}^1T_1$  is positive and small. The high MCD activity of band I is in large part expected due to the small energy separations of spin-orbit components of  ${}^3T_1$  and  ${}^3T_2$ . This will favor large *B*-term activity according to the Buckingham-Stephens interpretation, *i.e.*, for each component *j*

$$B(a \rightarrow j) \cong 3 \sum_j \text{Im} \left\{ \sum_{k \neq j} \frac{\langle j | \hat{z} | k \rangle}{\Delta E(k-j)} [\langle a | \hat{m} | j \rangle \langle k | \hat{m} | a \rangle] \right\}$$

where  $a \equiv {}^1A_1$ ,  $j \equiv {}^3T$ ,  $k \equiv$  all spin-orbit states within  ${}^3T_1$  and  ${}^3T_2$  except state *j*, and  $\hat{z}$  and  $\hat{m}$  are magnetic dipole and electric dipole operators.<sup>33</sup> We find similar high intensity in the  ${}^3T_1, {}^3T_2$  region of  $[\text{Rh}(\text{NH}_3)_5\text{X}]^{2+}$  compounds.<sup>32</sup> It is clear that the MCD spectrum also uncovers a second band in the region labeled  ${}^3T, \pi^*\text{NO}$  (Figure 5). In addition, we have subsequently obtained an 80°K absorption spectrum of the orthorhombic crystals of  $[\text{Ru}(\text{NH}_3)_5(\text{NO})]\text{Cl}_3 \cdot \text{H}_2\text{O}$ . Analogous to the MCD spectrum, two bands were found in the region of band I. The major MCD activity of  ${}^1T_1$  appears to reside in the positive band at *ca.* 285 nm.

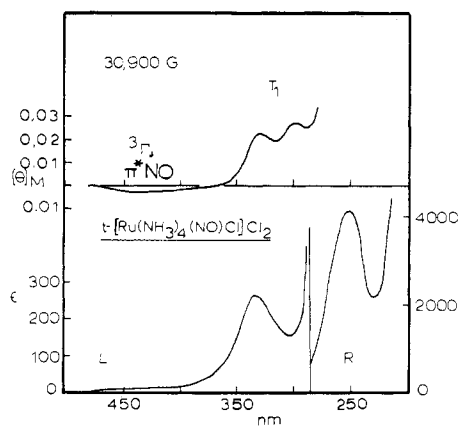


Figure 6.—MCD and electronic absorption spectra of  $[\text{Ru}(\text{NH}_3)_4(\text{NO})\text{Cl}]\text{Cl}_2$ . See caption of Figure 5.

$[\text{Ru}(\text{NH}_3)_4(\text{NO})\text{Cl}]^{2+}$ .—The  ${}^1A_1 \rightarrow {}^1T_1$  transition of *trans*- $[\text{Ru}(\text{NH}_3)_4(\text{NO})\text{Cl}]^{2+}$  is expected at lower energy than that of  $[\text{Ru}(\text{NH}_3)_5(\text{NO})]^{3+}$  as was indeed observed; *i.e.*, they were at 30.3 kK (330 nm) and 32.8 kK (305 nm), respectively (Table I). The band is more intense ( $\epsilon$  264) than  ${}^1T_1$  of  $[\text{Ru}(\text{NH}_3)_5(\text{NO})]^{3+}$  ( $\epsilon$  56). The 22.7-kK band is weakest ( $\epsilon$  17), is near band I (22.0 kK) of nitrosylpentaammine, and is probably of similar spin-triplet and  $t_2 \rightarrow \pi^*$  origin, since both bands also have quite similar intensities ( $\epsilon$  15 and 17).

The MCD spectrum of the chloride salt of this compound is very useful (Figure 6). The spin-triplet region

(30) J. A. Stanko and T. M. Starrinshak, *Inorg. Chem.*, **8**, 2156 (1969).

(31) D. J. Darensbourg and C. L. Hyde, *ibid.*, **10**, 431 (1971).

(32) Observations of this laboratory.

(33) A. D. Buckingham and D. J. Stephens, *Ann. Rev. Phys. Chem.*, **17**, 399 (1966).

of the 30.90-kG spectrum is of negative rotational strength and its intensity is about  $[\theta]_M = 0.004 \text{ deg dl dm}^{-1} \text{ mol}^{-1} \text{ G}^{-1}$ . These features are similar to  $[\text{Ru}(\text{NH}_3)_5(\text{NO})]\text{Cl}_3$ . However, the  ${}^1\text{T}_1$  region in the vicinity of 340–300 nm is very interesting. First, the activity is two to three times that of the pentaammine and, second, the MCD spectrum reveals another band at 300 nm which was not evident from the electronic spectrum. We assign these two bands, separated by about 1.8 kK, to tetragonal  ${}^1\text{E}$  and  ${}^1\text{A}_2$  components of  ${}^1\text{T}_1$ . The magnitude of this splitting is much less, as expected, than the  ${}^1\text{T}_1$ – ${}^1\text{T}_2$  separations<sup>25</sup> of all known ruthenium(II) ammines, for which reason we rule out the possibility of assigning the 300-nm band to  ${}^1\text{T}_2$ . The higher component is probably not  ${}^1\text{T}_2$  because then  $B = (33-30)/16 \approx 200 \text{ cm}^{-1}$  only. These two components (30 and 33 kK) are also at about the same positions and of similar separations as the two  ${}^1\text{T}_1$  components (2.9 kK) of  $[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{Ac})]^{2+}$  (*vide infra*).

$[\text{Ru}(\text{NH}_3)_4(\text{NO})\text{Br}]^{2+}$ .—The d–d bands for *trans*- $[\text{Ru}(\text{NH}_3)_4(\text{NO})\text{Br}]^{2+}$  are expected to occur at lower energy than *trans*- $[\text{Ru}(\text{NH}_3)_4(\text{NO})\text{Cl}]^{2+}$  on the basis of any spectrochemical series. This was indeed observed here for both band I and  ${}^1\text{T}_1$ ; and  ${}^1\text{T}_1$  of the bromo compound has only about 50% of the dipole strength of  ${}^1\text{T}_1$  of the chloro complex. However, the spin-forbidden and  $t_2 \rightarrow \pi^*$  transitions are of about the same intensity ( $\epsilon$  17), which is *contrary to an expected pronounced internal heavy-atom effect* (Table I) as in  $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$  and  $\text{Rh}(\text{NH}_3)_5\text{Br}^{2+}$ .  ${}^1\text{T}_1$  was observed at 26.9 kK (371 nm;  $f = 0.0016$ ) and showed no appearance of splitting in its electronic spectrum, but the proximity of the charge-transfer band is largely responsible for this. The MCD spectrum of the perchlorate,  $[\text{Ru}(\text{NH}_3)_4(\text{NO})\text{Br}](\text{ClO}_4)_2$ , had the characteristic negative rotation (42.2 kG) for band I at 21.5 kK (465 nm) and positive rotation (Figure 7) for  ${}^1\text{T}_1$  at  $\sim 26.7$  kK (375 nm).

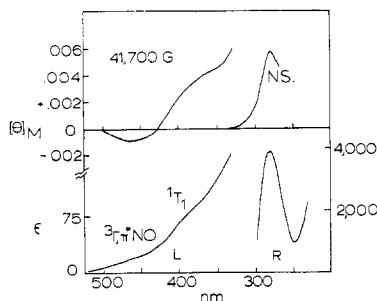


Figure 7.—MCD and electronic absorption spectra of  $[\text{Ru}(\text{NH}_3)_4(\text{NO})\text{Br}](\text{ClO}_4)_2$ . L and R refer to left scale and right scale. See caption of Figure 5.

$[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{L})]^{2+}$  ( $\text{L} = \text{OAc}^-$  and  $\text{OH}^-$ ).—Two tetraammines were studied with ligand L having oxygen in the coordination sphere, *i.e.*,  $\text{OH}^-$  and  $\text{CH}_3\text{CO}_2^-$  ( $\text{OAc}^-$ ). As expected, transition energies for  ${}^1\text{A}_1 \rightarrow {}^1\text{T}_1$  and  ${}^1\text{A}_1 \rightarrow {}^3\text{T}_1$ ,  $\pi^*\text{NO}$ , separated by *ca.* 6.5 kK similar to other Ru(II) compounds, were observed to occur at about the same energies for both compounds (Table I). *trans*- $[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{OH})]^{2+}$  had bands at 29.9 kK (335 nm;  $\epsilon$  211) and 23.3 kK (429 nm;  $\epsilon$  25) which correspond to  ${}^1\text{T}_1$  and to  ${}^3\text{T}_1$  plus  $\pi^*\text{NO}$ . The dipole strength ( $0.319 \text{ D}^2$ ) of  ${}^1\text{T}_1$  and its transition energy differ only little from the chlorotetraammine (Table I).

The MCD spectrum of  $[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{OH})]\text{Cl}_2$  was obtained in aqueous solution using a 42.2-kG field (Figure 8).  ${}^1\text{T}_1$  is broad and rotates positively as usual. There is no evidence of any splitting.

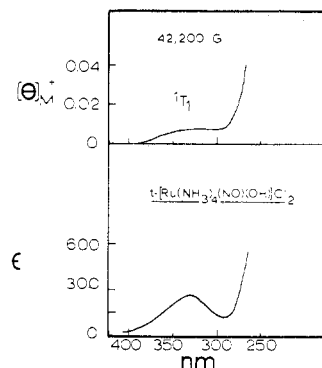


Figure 8.—MCD and electronic absorption spectra of  $[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{OH})]\text{Cl}_2$ . See caption of Figure 5.

Band I and two spin-allowed transitions were assigned for *trans*- $[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{OAc})]^{2+}$ . These bands were at 23.0 kK (435 nm;  $\epsilon$  22), 30.5 kK (328 nm;  $\epsilon$  131) and 33.4 kK (299 nm;  $\epsilon$  162) in the electronic spectrum. The first of these is  ${}^3\text{T}_1$ ,  $\pi^*\text{NO}$  and the last two belong to  ${}^1\text{T}_1$ . Under  $\text{C}_{4v}$  microsymmetry about Ru and with the assumption that NO plus  $\text{OAc}^-$  are most and  $\text{NH}_3$  is least antibonding on  $t_{2g}$ , the 30.5 kK-band maximum is tentatively assigned to  ${}^1\text{E}({}^1\text{T}_1)$  and the 33.4-kK one to  ${}^1\text{A}_2({}^1\text{T}_1)$ . (See Figure 1. The order may actually be reversed,  $\text{E} > \text{A}_2$ . This is under further study.) This 2.9-kK splitting can be compared with the 2.6-kK splitting in  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ <sup>34</sup> and with the  $\sim 3$ -kK splitting of  ${}^1\text{T}_1$  of  $[\text{Ru}(\text{NH}_3)_4(\text{NO})\text{Cl}]^{2+}$  (*vide supra*). It is also interesting to note that the sum of dipole strengths of these two  ${}^1\text{T}_1$  components is about equal to the dipole strength ( $0.320 \text{ D}^2$ ) of  ${}^1\text{T}_1$  of *trans*- $[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{OH})]^{2+}$ .

The MCD activity of  ${}^1\text{T}_1$  at 24.5 kG is shown in Figure 9. The maximum activity appears at about

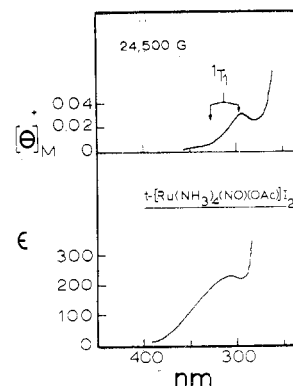


Figure 9.—MCD and electronic absorption spectra of  $[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{OAc})]\text{I}_2$ . See caption of Figure 5.

295 nm and is positive again. The rotational strength is about 3 times the  ${}^1\text{T}_1$  maximum activity of hydroxynitrosyltetraammine but similar to that of the chloronitrosyltetraammine. In addition, the splitting of

${}^1T_1$  is clearly evident in the MCD spectrum. However, this splitting was also present in the electronic absorption spectrum.

$[\text{Ru}(\text{NH}_3)_4(\text{NO})\text{L}]^{2+}$  ( $\text{L} = \text{NCO}^-$  and  $\text{N}_3^-$ ).—The spectra of two tetraammines were studied in which L of  $\text{trans-}[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{L})]^{2+}$  coordinates to Ru through a nitrogen atom, *i.e.*,  $\text{L} = \text{NCO}^-$  or  $\text{N}_3^-$ . The data of Table I show the azide ion has a somewhat weaker ligand field strength than cyanate. However, the band intensities in the azide complex are higher perhaps due to the expected nonlinearity of Ru–N–N–N. For the azidotetraammine,  ${}^1T_1$  was found at 27.7 kK and  ${}^3T_1, \pi^*\text{NO}$  at 21.3 kK. The analogous transitions were observed at 29.1 kK ( ${}^1T_1$ ) and 22.2 kK ( ${}^3T_1, \pi^*\text{NO}$ ) for  $\text{trans-}[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{NCO})]^{2+}$ .

The MCD activity of  $[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{NCO})](\text{ClO}_4)_2$  is shown in Figure 10. The spectrum of this aqueous

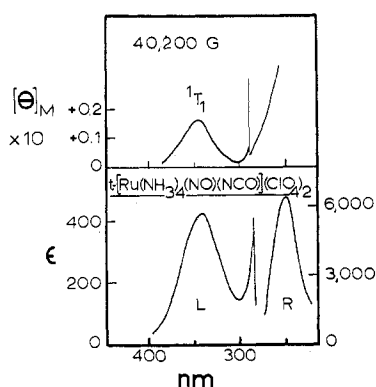


Figure 10.—MCD and electronic absorption spectra of  $[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{NCO})](\text{ClO}_4)_2$ . L and R refer to left scale and right scale. See caption of Figure 5.

solution was recorded at 40.2 kG.  ${}^1T_1$  does not appear to be split.

Regarding the MCD spectra in d–d regions, it can be summarized that the net rotational strengths in the  ${}^3T_1, \pi^*\text{NO}$  and  ${}^1T_1$  regions are negative and positive, respectively.

**2. Charge Transfer and Internal Transitions.**— $\text{trans-}[\text{Ru}(\text{NH}_3)_4(\text{NO})\text{Cl}]^{2+}$  has an intense electronic absorption band at 41.2 kK (243 nm) with oscillator strength 0.136 (Figures 3 and 5 and Table I) and  $\epsilon$  4220. The band shifts to 36.5 kK (274 nm) in the bromo analog,  $\text{trans-}[\text{Ru}(\text{NH}_3)_4(\text{NO})\text{Br}]^{2+}$ , and becomes somewhat less intense ( $f = 0.103$ ). Because of their relative positions ( $\text{Br} < \text{Cl}$ ), these bands are assigned to  $p\pi(\text{Cl or Br}) \rightarrow e_g\text{Ru}$ . Regardless of whether the electron's fate is the  $4x^2 - y^2$  or  $4z^2$  molecular orbital, the excited state will be  ${}^1E[(p\pi)^3(4x^2 - y^2 \text{ or } 4z^2)^1]$ . The MCD dispersion at 42.2 kG (Figure 7) of  $[\text{Ru}(\text{NH}_3)_4(\text{NO})\text{Br}](\text{ClO}_4)_2$  through this intense band is positive, but the maxima of electronic and MCD bands coincide. This leads one to conclude that there is very little if any orbital angular momentum in this  ${}^1E$  state and the intensity is primarily due to the  $B$  term. It is clear, however, that the Faraday operators efficiently mix other nearby excited states with  ${}^1E$ , as the rotation is high.

The intense band of  $\text{trans-}[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{OH})]^{2+}$  is at higher energy (43.9 kK) by 2700 K than the similar band of  $\text{trans-}[\text{Ru}(\text{NH}_3)_4(\text{NO})\text{Cl}]^{2+}$  and its intensity ( $f = 0.22$ ) is greater. If the transition were of type

$t_2\text{Ru} \rightarrow \pi^*\text{NO}$ , its energy would be expected to be nearly the same in these two chromophores. This is contrary to observations, and the band is assigned to charge-transfer transition  $p\pi\text{OH} \rightarrow e_g\text{Ru}$ . The band was not accessible to us in the MCD.

The charge-transfer band in  $\text{trans-}[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{OAc})]^{2+}$  was, as expected for  $p\pi\text{OAc} \rightarrow e_g\text{Ru}$ , nearly of the same energy (44.5 kK) as the hydroxo compound (43.9 kK), and their oscillator strengths (0.191 ( $\text{OAc}^-$ ) and 0.220 ( $\text{OH}^-$ )) are also similar.

$\text{trans-}[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{NCO})]^{2+}$  has a very intense band ( $f = 0.192$ ) at 43.9 kK. Since the highest occupied MO in  $\text{NCO}^-$  is  $\pi$  bonding, the transition is assigned to  $\pi\text{NCO} \rightarrow e_g\text{Ru}$ . It is excluded as an internal  $\text{NCO}^-$  transition because it would require about 9 kK more energy than the analogous  $\text{NCS}^-$  internal transition. But, this transition is usually observed at 42 kK in  $\text{NCS}^-$ , *e.g.*,  $[\text{Rh}(\text{NH}_3)_5(\text{NCS})]^{2+}$ .<sup>29</sup>

Two intense bands in  $[\text{Ru}(\text{NH}_3)_4(\text{NO})\text{N}_3]^{2+}$  were observed at 34.4 kK ( $f = 0.110$ ) and 40.4 kK ( $f = 0.144$ ) (Table I). The first of these is too low in energy to be assigned as internal in character, *i.e.*, the latter occurs at *ca.* 40 kK in  $[\text{Rh}(\text{NH}_3)_5\text{N}_3]^{2+}$ .<sup>29</sup> The 34.4-kK band is therefore assigned to  $\pi\text{N}_3^- \rightarrow e_g\text{Ru}$ . The second transition (40.4 kK,  $\epsilon$  5380), however, is probably an azide internal transition. Its energy and extinction coefficient are similar to the analogous band (39.9 kK,  $\epsilon$  5200) in  $[\text{Rh}(\text{NH}_3)_5\text{N}_3]^{2+}$ .<sup>29</sup>

In conclusion we summarize the data which are consistent with believing that the first absorption band (band I) of each compound contains the  ${}^3T_1$  manifold. (1) Band I of  $[\text{Ru}(\text{NH}_3)_5(\text{NO})]^{3+}$  is at lower energy than  ${}^1T_1$  of  $[\text{Ru}(\text{NH}_3)_6]^{2+}$  and  $[\text{Ru}(\text{en})_3]^{2+}$ . (2a) Bands I of compounds  $[\text{Ru}(\text{NH}_3)_4(\text{NO})\text{L}]^{2+}$  have approximately the intensity of d–d spin-forbidden transitions of some rhodium(III) ammines. (2b)  ${}^3T_1({}^3T_1, {}^3T_2)$  of rhodium(III) ammines are also intense in the MCD.<sup>32</sup> (3) The positions of bands I vary approximately as the positions of the more intense  ${}^1T_1$  (Figure 4). (4) At least  ${}^3T_1(t_2^5e^1)$  is expected to appear at lower energy than  ${}^1T_1(t_2^5e^1)$ . (5) Positions of bands I are expected to vary less than the observed 2.2 kK, if the band origin were  $t_2^6 \rightarrow t_2^5(\pi^*\text{NO})^1$  alone. (6) If the intensity were only of the  $t_2 \rightarrow \pi^*\text{NO}$  origin, then band I of  $[\text{Ru}(\text{NH}_3)_5(\text{NO})]^{3+}$  should be at higher energy than all the other compounds. This expectation was not confirmed.

One reason for considering the possible origin of band I as  $t_2^6 \rightarrow t_2^5(\pi^*\text{NO})^1$  is that Manoharan and Gray<sup>11</sup> on studying  $[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$  found that their two lowest energy bands at *ca.* 20.1 and 25.4 kK, which were very small ( $\epsilon$  8 and 25), were independent of temperature and showed  $\perp$  and  $\parallel$  polarizations. While these intensities are too large for spin-forbidden transitions of d–d type and the temperature independence need not infer that they are electric dipole charge-transfer types (molecule is  $C_{4v}$ ), assigning these two bands to  $t_2 \rightarrow \pi^*\text{NO}$  is no doubt correct by a process of elimination. This proposed level ordering ( $xz, yz$ )  $<$   $xy$   $<$   $\pi^*\text{NO}$   $<$   $x^2 - y^2$   $<$   $z^2$  was challenged by McNeil, Raynor, and Symons<sup>35</sup> on the basis of their esr interpretations of  $[\text{Fe}(\text{CN})_5(\text{NO})]^{3-}$ . However, addition of an electron into a  $\pi^*\text{NO}$  molecular orbital

(35) D. A. C. McNeil, J. B. Raynor, and M. C. R. Symons, *Proc. Chem. Soc., London*, 364 (1964).



of  $[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$  may raise the orbital energy above those of  $x^2 - y^2$  and  $z^2$ . Nevertheless, there are several pieces of our data which support that  $t_2\text{Ru} \rightarrow \pi^*\text{NO}$  is also present in the 22-kK region in addition to  ${}^3\Gamma$  described above. Reasons for believing this include the absence of an expected pronounced internal heavy-atom effect on bands I of  $[\text{Ru}(\text{NH}_3)_4(\text{NO})\text{Cl}]^{2+}$  and  $[\text{Ru}(\text{NH}_3)_4(\text{NO})\text{Br}]^{2+}$ , band I of  $[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{N}_3)]^{2+}$  has the large height of  $\epsilon \sim 50$ , intensities of bands I of  $[\text{Ru}(\text{NH}_3)_4(\text{NO})\text{L}]^{q+}$  are all larger than d-d spin-forbidden transitions of similar rhodium(III) amines whereas  $\zeta_{4d}\text{Ru}(\text{II}) < \zeta_{4d}\text{Rh}(\text{III})$ , and results of our Wolfsberg-Helmholz LCAO-MO calculation on the similar molecule ion,  $[\text{RuCl}_5(\text{NO})]^{2-}$ , indicate the energy level ordering— $(xz, yz)^4 < (xy)^2 < (\pi^*\text{NO}) < (x^2 - y^2) < (z^2)$ —over a wide range of ruthenium basis functions and energies. Furthermore, our large metal ( $xz, yz$ ) character in  $\pi^*\text{NO}$  may account for a low intensity of transition  $t_2 \rightarrow \pi^*\text{NO}$ , and preliminary intensity calculations are consistent with this.<sup>36</sup> Polarized crystal work now in progress may further corroborate or negate some of these last deductions. As a final note we add that, of the spin-orbit states, the  $\Gamma_4$  of  ${}^3\text{T}_1$  and  ${}^3\text{T}_2$  are expected to derive highest intensity from  ${}^1\text{T}_1$  since  $\bar{\text{L}} \cdot \bar{\text{S}} \approx \text{A}_1$ . However, the crudely calculated intensity (we acknowledge one of the reviewers for the source of this information) is an order of magnitude too small. This offers additional evidence that band I contains  $t_{2g} \rightarrow \pi^*\text{NO}$ .

**The Trans Effect in  $[\text{Ru}(\text{NH}_3)_4(\text{NO})\text{L}]^{q+}$ .**—A number of trans-effect studies have been made of transition metal carbonyl compounds using the CO stretching frequency as a probe. The widely accepted interpretation of the effect for groups *trans*-(L-M-CO) is that the CO stretching frequency decreases (due to increasing  $\pi^*\text{CO}$  population) as the  $\pi$ -acceptor ability of L decreases. It is assumed that the group *trans*-(L-Ru-NO) can be looked at in like manner.

Table III summarizes observed stretching frequencies  $\nu(\text{N-O})$ . With the exception of the very low value of  $\nu(\text{N-O})$  in hydroxotetraammine, the deviation of which is suspected of being the result of an intermolecular interaction,<sup>8</sup> one concludes the following extended order of increasing  $\pi$ -electron donor ability:  $\text{NH}_3 < \text{NCO}^- < \text{N}_3^- < \text{CH}_3\text{CO}_2^- < \text{Cl}^- < \text{Br}^-$ . It is assumed that the variation of ruthenium-ligand

(36) J. A. Stanko, private communication.

$\sigma$  bonding is much smaller than the change in  $\pi$  bonding as in (L-M-CO) systems.

For monotonically increasing series of  $\nu(\text{N-O})$  values one might expect a corresponding series of decreasing Ru-NO stretching frequencies, if the sum of Ru-N and N-O bond orders are constant. We find that the variations of  $\nu(\text{Ru-NO})$  values (Table III) are not related in any obvious way to the N-O stretching frequencies. However, there is still some doubt regarding the assignments of  $\nu(\text{Ru-NO})$  and  $\delta(\text{Ru-NO})$ .<sup>8, 37, 38</sup>

### Summary

A number of new nitrosonium-ruthenium(II) compounds were prepared, and these procedures are reported in detail. They are convenient since the starting material is hydrated  $\text{RuCl}_3$  in each case. The presence of  $\text{NO}^+$  (and  $\text{Ru}(\text{II})$ ) in the coordination sphere is concluded from the high N-O stretching frequencies, MCD, and electronic absorption data. The antiferromagnetic  $\text{Ru}^{\text{III}}(\text{NO}^0)$  is ruled out. The highest value of  $\nu(\text{N-O})$  was found for  $[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{NH}_3)]^{3+}$ , and the frequency of this stretching band decreased in the order  $\text{NH}_3 > \text{NCO}^- > \text{N}_3^- > \text{CH}_3\text{CO}_2^- > \text{Cl}^- > \text{Br}^-$  for *trans*- $[\text{Ru}(\text{NH}_3)_4(\text{NO})\text{L}]^{q+}$ . Regarding the electronic absorption bands of these compounds,  ${}^1\text{A}_1 \rightarrow {}^3\Gamma({}^3\text{T}_1, {}^3\text{T}_2)$ ,  $\pi^*\text{NO}^*$  and  ${}^1\text{A}_1 \rightarrow {}^1\text{T}_1$  transitions were observed. Tetragonal splitting of  ${}^1\text{T}_1$  showed up in the electronic absorption spectrum of  $[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{OAc})]^{2+}$ . Intense ligand-to-metal charge-transfer bands  $p\pi\text{L} \rightarrow e_g(4d)$  were observed in the ultraviolet region for  $\text{L} = \text{OAc}^-, \text{Cl}^-, \text{OH}^-, \text{NCO}^-, \text{N}_3^-$ , and  $\text{Br}^-$ , but not for  $[\text{Ru}(\text{NH}_3)_5(\text{NO})]^{3+}$ . Only for the azidotetraammine was a ligand internal transition observed. Initial MCD spectra in the d-d regions of these compounds were included due to primarily the method's potentially higher resolution than electronic absorption spectra. The general features which emerged were that the transition  ${}^1\text{A}_1 \rightarrow {}^3\Gamma$ ,  $\pi^*\text{NO}$  has a net negative rotational strength and  ${}^1\text{T}_1$  has a positive net activity. Furthermore, the  ${}^1\text{T}_1$  splitting of  $[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{OAc})]^{2+}$  became more distinct in the MCD, and both components of  ${}^1\text{T}_1$  became apparent for  $[\text{Ru}(\text{NH}_3)_4(\text{NO})\text{Cl}]^{2+}$ .

(37) J. R. Durig and D. W. Wertz, *Appl. Spectrosc.*, **22**, 627 (1968).

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