

Reactions of Thiocyanatoruthenium(III)-ammine Complexes with Sodium Nitrite in Presence of Acid

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Reactions of thiocyanatoruthenium(III)-ammine complexes with sodium nitrite in presence of acid have been studied. The complexes, $[\text{Ru}_3(\text{NH}_3)_{11}(\text{SCN})(\text{NO})_2\text{Cl}_2]\text{Cl}_5$; $[\text{Ru}_2(\text{NH}_3)_7(\text{NO})_2(\text{SCN})\text{Cl}]\text{Cl}_4$; $[\text{Ru}_3(\text{NH}_3)_{11}(\text{NO})_2(\text{SCN})\text{Br}_2]\text{Br}_5$; $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})(\text{NCO})(\text{NO})]\text{Br}_2$; $[\text{Ru}(\text{NH}_3)_3(\text{NO})(\text{NCO})\text{H}_2\text{O}]\text{Br}(\text{NO}_2)$; $[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{NCS})](\text{NO}_2)_3$ and $[\text{Ru}(\text{NH}_3)_3(\text{H}_2\text{O})(\text{NO})\text{Cl}]\text{Cl}_2$, thus obtained have been characterised on the basis of elemental analyses, IR, electronic spectral and conductivity measurements. It has been observed that the nitrosyl group is present in NO^+ form in these complexes. When the reactions of the bromo complexes are carried out under refluxing conditions in the presence of HBr , the bonded NCS group in some cases transforms into NCO^- group. When the reaction with trinuclear species $[\text{Ru}_3(\text{NH}_3)_{13}(\text{NCS})\text{X}_2]^{6+}$ ($\text{X} = \text{Cl}^-, \text{Br}^-$) is performed at room temperature, the product obtained is found to be a trinuclear species $[\text{Ru}_3(\text{NH}_3)_{11}(\text{NO})_2(\text{NCS})\text{X}_2]^{5+}$ ($\text{X} = \text{Cl}^-, \text{Br}^-$) with ruthenium in +2 oxidation state, two NH_3 molecules being replaced by NO^+ group.

THERE have been several reviews¹⁻⁶ on the nitrosyl complexes of ruthenium. During our study of the reactions of $[\text{Ru}(\text{NH}_3)_5\text{X}]\text{X}_2$ ($\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$) with NH_4SCN , tri-, di- and mono-nuclear cationic and anionic species of $\text{Ru}(\text{III})$ having bridging thiocyanate and halide ions have been synthesized⁷. In view of the interesting results reported¹⁻⁵ on the reactions of nitrosyl moiety with monomeric ruthenium(III) ammine, it was of interest to study the reactions of these polynuclear thiocyanatoruthenium(III)-ammine complexes⁷ with the nitrosylating agent ($\text{NaNO}_2 + \text{acid}$). In this paper we report the results of these reactions.

Materials and Methods

All the chemicals used were of AR grade. $[\text{Ru}_3(\text{NH}_3)_{13}(\text{NCS})\text{X}_2]\text{X}_6$ ($\text{X} = \text{Cl}^-, \text{Br}^-$), $[\text{Ru}_2(\text{NH}_3)_8(\text{SCN})_3]\text{Br}_6$, $[\text{Ru}(\text{NH}_3)_4(\text{NCS})_2]\text{Br}_2$, $[\text{RuX}_3(\text{NCS})(\text{NH}_3)_2]^{+}$ ($\text{X} = \text{Cl}^-, \text{Br}^-$) were prepared according to the methods described elsewhere⁷.

Dowex 50 WX-8 (20-50 mesh) in Na^+ or H^+ form and Dowex-1-X8 (50-100 mesh) in Cl^- or NO_3^- form were used as the cation and anion exchange resins respectively.

$[\text{Ru}_3(\text{NH}_3)_{11}(\text{SCN})(\text{NO})_2\text{Cl}_2]\text{Cl}_5$ (1) — Sodium nitrite (0.4 g) was added to an aqueous solution (20 ml) of $[\text{Ru}_3(\text{NH}_3)_{13}(\text{SCN})\text{Cl}_2]\text{Cl}_6$ (0.1 g) followed by the addition of conc. HCl dropwise until the evolution of brown NO_2 gas ceased. The reaction mixture was stirred for 5 min. at room temperature whereby a rose-red coloured complex precipitated out. It was filtered, washed twice with 50% ethyl alcohol and finally with 95% ethyl alcohol and ether. It was dried *in vacuo* (yield, 63%). The compound was recrystallized by dissolving it in minimum volume of water and adding conc. HCl dropwise.

$[\text{Ru}_2(\text{NH}_3)_7(\text{NO})_2(\text{SCN})\text{Cl}]\text{Cl}_4$ (2) — The compound was prepared by the method similar to that given above, except that the reaction mixture obtained after adding conc. HCl was refluxed for 30 min., whereby, the colour of the solution changed from red to yellow. On cooling to 0°C , a yellow powder separated out which was filtered and washed several times with cold water, 50% EtOH and finally with 95% ethyl alcohol and ether. It was dried in vacuum desiccator (yield, 40%).

$[\text{Ru}_3(\text{NH}_3)_{11}(\text{NO})_2(\text{SCN})\text{Br}_2]\text{Br}_5$ (3) — $[\text{Ru}_3(\text{NH}_3)_{13}(\text{NCS})\text{Br}_2]\text{Br}_6$ (0.2 g) was dissolved in water (25 ml) and sodium nitrite (0.7 g) added to it followed by conc. HBr (48%) dropwise until the evolution of NO_2 gas ceased. The reaction mixture was stirred at room temperature for 15 min, whereby a dark red coloured compound separated out. It was filtered, washed with 50% ethyl alcohol several times, and finally with 95% ethyl alcohol and ether. It was dried *in vacuo* and recrystallised by dissolving the product in minimum quantity of water and adding HBr to the solution. This procedure was repeated 2-3 times (yield, 30%).

$[\text{Ru}(\text{NH}_3)_3(\text{H}_2\text{O})(\text{NCO})(\text{NO})]\text{Br}_2$ (4) — $[\text{Ru}_3(\text{NH}_3)_{13}(\text{NCS})\text{Br}_2]\text{Br}_6$ (0.15 g) was dissolved in water (15 ml), NaNO_2 (0.5 g) added to it followed by conc. HBr dropwise until the NO_2 gas evolution ceased. The reaction mixture was refluxed on a water-bath for 30 min., whereby the colour of the solution changed from red to yellow. On cooling it at 0°C , yellow powder precipitated out which was filtered, washed and dried as described for 3 above (yield, 33%).

$[\text{Ru}(\text{NH}_3)_3(\text{NO})(\text{NCO})\text{H}_2\text{O}]\text{Br}(\text{NO}_2)$ (5) — The method of preparation of this compound was similar to that described for 4, except that $[\text{Ru}_2(\text{NH}_3)_8(\text{SCN})_3]\text{Br}_6$ was used instead of $[\text{Ru}_3(\text{NH}_3)_{13}(\text{NCS})\text{Br}_2]\text{Br}_6$.

(SCN)₃[RuBr₆](0.2 g) was used instead of [Ru₃(NH₃)₁₃(NCS)Br₂]Br₆. The amount of sodium nitrite used was 2g.

[Ru(NH₃)₄(NO)(NCS)](NO₃)₂ (6) — Ru(NH₃)₄(NCS)₂[Ru(NH₃)₂X₃(NCS)] (X = Cl⁻, Br⁻) (0.1 g) was dissolved in the minimum quantity of water and NaNO₂ (1g) added to it followed by glacial acidic acid in large excess. The mixture was refluxed on a water-bath until the colour of the solution changed from deep red to light yellow. The solution was concentrated to half its volume and cooled, whereby light brown coloured crystals separated out. These were filtered, washed with 50% EtOH several times and finally with 95% EtOH and ether. The same compound was also obtained when the reaction was carried out using the cation [Ru(NH₃)₄(NCS)₂]⁺ as the starting material (The cation in its NO₃⁻ form was separated by using NO₃⁻ form of anion exchange resin).

[Ru(NH₃)₃(H₂O)(NO)Cl]Cl₂ (7) — An aq. solution of [Ru(NH₃)₄(NCS)₂][RuX₃(NCS)(NH₃)₂] (X = Cl⁻, Br⁻) (0.1g) in water (20-30 ml) was passed through the NO₃⁻, Cl⁻ form of anion exchange resin. It was eluted with water and to the cation [Ru(NH₃)₄(NCS)₂]⁺ in the eluent, excess of NaNO₂ was added followed by conc. HCl dropwise, until the NO₂ gas evolution ceased. Conc. HCl (1ml) was then added and the mixture refluxed for 30-40 min, whereby the colour of the solution changed from red to yellow. It was cooled at 0°C for 30 min., and the yellow powder obtained was filtered, washed with 50% EtOH and finally with ether. The compound was recrystallized by dissolving in it the minimum quantity of water and adding conc. HCl to it.

Physicochemical measurements: Analyses — Total sulphur in the sample was analysed by oxidizing the

NCS group with ether aquaregia or by a mixture of Na₂O₂ and KNO₃ in a Parr bomb and estimating sulphur as BaSO₄. Total halide was analysed by decomposing the compound with NaOH in Parr bomb and analysing the halogen gravimetrically as silver halide. Sulphur and halide in the complexes were analysed in the cation and anion exchangers, eluting the column by water, until the eluent did not show any trace of the cation or anion, followed by the gravimetric determination of halide, sulphur by the standard methods in the eluent. The gravimetric determination was carried out by concentrating the eluent and decomposing the anion or cation (as the case may be) by the method as described in the foregoing paragraph.

Conductivity measurements — These were carried out in conductivity water using an Elico conductivity bridge type CM82T. Extensive conductance measurements at various concentrations have been carried out in the range 10⁻²—10⁻² eq/litre, and the plots of (λ₀—λ_e) versus √C were obtained to confirm the charge type on the different cationic species.

Results and Discussion

The analytical results of the complexes are given in Table 1. All the compounds formed are highly soluble in water indicating them to be ionic in nature. They are practically insoluble in common organic solvents. They have been crystallized from the acidic solution by dissolving them in minimum quantity of the dilute (2N) acid and concentrating on water-bath and then cooling at low temperature.

All the complexes are diamagnetic at room temperature indicating the presence of Ru in +2 oxidation state having as pin paired *d*⁶ configuration in the octahedral environment.

TABLE 1 — ANALYTICAL AND CONDUCTIVITY DATA OF THE VARIOUS COMPLEXES

Complex	Found (%) (Calc.)						Conductivity data	
	C	H	N	S	X _{total} ⁻ (Cl ⁻ or Br ⁻)	X _{total} ⁻	λ ₀ ohm ⁻¹ cm ² eq ⁻¹	Slopes*
[Ru ₃ (NH ₃) ₁₁ (SCN)(NO) ₂ Cl ₂]Cl ₅ (1)	1.6 (1.4)	3.2 (3.8)	24.8 (22.9)	2.5 (3.7)	29.0 (29.0)	19.1 (20.8)	510	2050
[Ru ₂ (NH ₃) ₇ (NO) ₂ (NCS)Cl]Cl ₄ (2)	2.0 (1.9)	3.5 (3.4)	24.1 (22.6)	5.0 (5.2)	30.0 (28.8)	22.5 (23.1)	337.5	1725
[Ru ₃ (NH ₃) ₁₁ (NO) ₂ (NCS)Br ₂]Br ₅ (3)	0.8 (1.0)	3.2 (2.8)	17.0 (16.3)	2.5 (2.6)	47.0 (46.7)	35.0 (33.4)	550	1975
[Ru(NH ₃) ₃ (H ₂ O)(NCO)NO]Br ₂ (4)	3.0 (3.0)	2.5 (2.7)	17.5 (17.5)	—	42.0 (40.0)	42.0 (40.0)	194	1000
[Ru(NH ₃) ₃ (NO)(NCO)(H ₂ O)]Br(NO ₂) (5)	3.1 (3.1)	2.7 (2.9)	23.0 (21.9)	—	22.2 (20.9)	22.1 (20.9)	210	950
[Ru(NH ₃) ₄ (NO)(NCS)](NO ₂) ₂ (6)	3.6 (3.2)	3.5 (3.2)	32.3 (29.4)	7.5 (8.4)	—	—	—	—
[Ru(NH ₃) ₃ (H ₂ O)(NO)Cl]Cl ₂ (7)	—	3.0 (3.6)	17.8 (18.3)	—	33.8 (34.8)	24.5 (23.2)	206	1250
[Ru(bipy) ₃](PF ₆) ₂ **	—	—	—	—	—	—	193	667
[(bipy) ₃ (py)Ru] ₂ (4,4'-bipy)](PF ₆) ₄ **	—	—	—	—	—	—	364	2967
[(NH ₃) ₅ Ru-O-Ru(NH ₃) ₅](PF ₆) ₄ **	—	—	—	—	—	—	344	3309

*Values of the linear plots of (λ₀—λ_e) versus √C; **Values taken from ref. 17.

Electronic spectra — The electronic spectra of the complexes† are typical of the $\text{Ru}^{\text{II}}\text{NO}^+$, d^6 system, in an octahedral environment^{8,9}. The lower energy band in these complexes in the range 470-495 nm is assigned to d-d transition, the medium energy band (300-400 nm), to $d\pi(\text{Ru}) \rightarrow \pi^*(\text{NO})$ charge transfer and the higher energy bands (250-300 nm), to intra-ligand or ligand (Cl^- , Br^- , NCS^- , NCO^- etc.) to metal charge transfer ones^{8,9}. However, Schreiner and coworkers^{10,11} assigned the low energy band to $d\pi(\text{Ru}) \rightarrow \pi^*(\text{NO})$, and the medium intensity band to d-d transitions.

In the monomeric compounds $[\text{Ru}(\text{NH}_3)_3(\text{H}_2\text{O})(\text{NCO})(\text{NO})]\text{XY}$ ($\text{X}=\text{Y}=\text{Br}$ and $\text{X}=\text{Br}$, $\text{Y}=\text{NO}_3^-$), the presence of two distinct low intensity bands around 470 and 350 nm, suggests that the NCO group is *cis* to the linear NO group^{10a,b}. On similar grounds Cl^- is assumed to be *cis* to the NO in $[\text{Ru}(\text{NH}_3)_3(\text{H}_2\text{O})\text{NOCl}]\text{Cl}_2$. $[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{NCS})]\text{X}_2$ ($\text{X}=\text{NO}_3^-$) shows the corresponding bands around 490 ($\epsilon=35$) and 305 nm ($\epsilon=130$), typical of the *cis*-configuration of the NCS^- ligand to the nitrosyl group^{10b}. The trinuclear compounds $[\text{Ru}_3(\text{NH}_3)_{11}(\text{NO})_2(\text{CSN})\text{X}_2]\text{X}_5$ show a more complex pattern of the bands in the 340-500 nm region. $[\text{Ru}_2(\text{NH}_3)_7(\text{NO})_2(\text{SCN})\text{Cl}]\text{Cl}_4^{4+}$ shows, however, only one band at 330 nm ($\epsilon=1100$).

The presence of NCO^- group in the cation $[\text{Ru}(\text{NH}_3)_3(\text{H}_2\text{O})(\text{NCO})\text{NO}]^{2+}$ is substantiated by the presence of a band around 340-350 ($\epsilon=80-100$) region although the intensity of the band is weak¹². It is further corroborated by the IR spectral studies.

Infrared spectra — In all the complexes‡ the band due to νNO appears in the region 1850-1920 cm^{-1} , suggesting the presence of linear Ru-N-O linkage^{13,14}. In addition, all the compounds show characteristic bands due to NH_3 , H_2O etc. in 3200, 1600, 1400, 800 and 477 cm^{-1} regions. The IR spectra of $[\text{Ru}_3(\text{NO})_2(\text{NH}_3)_{11}(\text{SCN})\text{X}_2]\text{X}_5$ ($\text{X}=\text{Cl}^-$, Br^-), $[\text{Ru}_2(\text{NH}_3)_7(\text{NO})_2(\text{SCN})\text{Cl}]\text{Cl}_4$ and $[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{NCS})](\text{NO}_3)_2$, exhibit broad ($\Delta_{1/2}$, 100 cm^{-1}) and sharp medium intensity bands having maximum around 2065 cm^{-1} , which is assigned to νCN of the bridging (in trinuclear and dinuclear species) and terminal N bonded (in mononuclear) thiocyanate group respectively. The presence of bands around 317s, 302sh, 287sh and 270s cm^{-1} in the trinuclear and dinuclear species suggests that one of the two halide ions is bonded as terminal ($\nu\text{M-Cl}$, 317 cm^{-1}). In the monomeric complex $[\text{Ru}(\text{NH}_3)_4(\text{NCS})\text{NO}](\text{NO}_3)_2$, the presence of another band due to νCS around 800 cm^{-1} as shoulder indicates that thiocyanate group is $-\text{N}$ bonded¹⁵. The $\nu\text{M-NO}$ in all the complexes appears in the region 595-610 cm^{-1} .

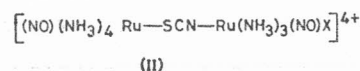
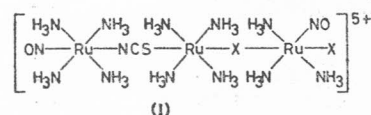
The interesting feature of the work is the formation of the NCO group in the reaction of $[\text{Ru}_3(\text{NH}_3)_{13}(\text{SCN})\text{Br}_2]\text{Br}_6$ and $[\text{Ru}_2(\text{NH}_3)_8(\text{SCN})_3][\text{RuBr}_6]$ with NaNO_2 in the presence of only HBr under refluxing conditions. The presence of NCO in these cation

is suggested by the appearance of the bands due to νCN at 2245 cm^{-1} (sharp and intense) and that due to νCO at 1277 cm^{-1} , suggesting the presence of N-bonded cyanate group. The products obtained by reacting the polymeric species with NO in the presence of other acids except HBr do not show bands at 2245 and 1277 cm^{-1} . It is not possible to reason out at this stage the formation of NCO from NCS .

Conductivity measurements — The values of the molar conductance for the compounds (Table 1) $[\text{Ru}_3(\text{NH}_3)_{11}(\text{NO})_2(\text{NCS})\text{X}_2]\text{X}_5$ ($\text{X}=\text{Cl}^-$, Br^-) are higher than those for other ruthenium ammine complexes. Feltham and Hayter¹⁶ have recently employed the conductance measurements over a concentration range to distinguish between mononuclear and polynuclear species. The conductivity measurements of the compounds have therefore, been carried out in the concentration range 10^{-2} – 10^{-4} eq/litre and λ_0 determined by extrapolating the linear plots to zero concentration (equivalent weights of the compounds have been determined by the method reported by Feltham¹⁶).

The values of $(\lambda_0 - \lambda_e)$ as a function of $\sqrt{C}$ [cf. Onsagar equation $(\lambda_0 - \lambda_e) = a\lambda_0 + b\sqrt{C} = A\sqrt{C}$] have been plotted and slopes of the linear plots calculated from these plots (Table 1). It is clear that the slope value increases with the charge type on the electrolyte, in conformity with the literature data¹⁷. The values of λ_0 and slopes from the literature for the sake of comparison are given in Table 1. It has been further observed that at lower concentrations ($<10^{-4}$ eq/litre) the plots between $(\lambda_0 - \lambda_e)$ and $\sqrt{C}$ are non-linear. This could be either due to solvolysis process or the change of species at very low concentration. The compounds $[\text{Ru}(\text{NH}_3)_3(\text{NCO})(\text{H}_2\text{O})\text{NO}]\text{XY}$ ($\text{X}, \text{Y}=\text{Br}$; $\text{X}=\text{Br}$, $\text{Y}=\text{NO}_3^-$) and $[\text{Ru}(\text{NH}_3)_4(\text{NO})(\text{NCS})](\text{NO}_3)_2$ and $[\text{Ru}(\text{NH}_3)_3(\text{H}_2\text{O})(\text{NO})\text{Cl}]\text{Cl}_2$ have λ_0 values in the range 200 $\text{ohm}^{-1}\text{cm}^2\text{eq}^{-1}$ which is typical of 1:2 electrolyte¹⁷ and other dimer and trimeric compounds have higher value in the range 350 and 500 $\text{ohm}^{-1}\text{cm}^2\text{eq}^{-1}$ respectively suggesting them to be of higher charge type.

Ion exchange studies — The high value of charge on the trimer, dimer and the various monomeric species was established by passing an aqueous solution of the compound through ion exchanger and estimating the halide and/or sulphur in cation and anion separately. These studies provide further support to the data obtained by conductivity measurements. Hence on the basis of the above results the following tentative structures (I) and (II) may be proposed for the trinuclear and dinuclear complexes :



†The detailed electronic spectral data of the complexes can be had from the authors on request.

‡Detailed IR data of the complexes can be had from the authors on request.

References

1. JOHNSON, B. F. G. & McLEVERTY, J. A., *Progr. Inorg. Chem.*, **7** (1966), 277.
2. CONNELLY, N. G., *Inorg. chim. Acta Rev.*, **6** (1972), 48.
3. MCGINNETY, J. A., *M.T.P. Int. Rev. Ser. I.*, **5** (1972), 229.
4. COULTON, K. G., *Coord. chem. Rev.*, **14** (1972), 317.
5. BOTTOMLEY, F., *Coord. chem. Rev.*, **26** (1978), 7-29.
6. GRIFFITH, W. P., *The chemistry of rarer platinum metals* (Interscience, London), 1967, 174.
7. PARASHAD, R., YADAV, S. K. S. & AGARWALA, U., *J. inorg. nucl. Chem.*, 1980 (in press).
8. SIZOVA, O. B., ANTOMOV, N. G., NIKOL'SKII, A. B. & BARANOVSKII, V. I., *Soviet J. coord. Chem.*, **2** (1976), 853.
9. NIKOLSKII, A. B., POPOV, A. M. & VASILEVSKII, I. V., *Soviet J. coord. Chem.*, **2** (1976), 508.
10. (a) SCHREINER, A. F., LIN, S. W., HAUSER, P. J., HOPCUS, E. A., HANM, D. J. & GUNTER, J. D., *Inorg. Chem.*, **11** (1972), 880.
- (b) PELL STEVEN & ARMOR JOHN, N., *Inorg. Chem.*, **12** (1973), 873.
11. GUENZBURGER, D. GARNIER, A. & DANON, J., *Inorg. chim. Acta*, **21** (1977), 119.
12. ABBAS, A., AWADY, E. L. & BASOLO, F., *Inorg. chim. Acta Lett.*, **31** (1978), L363-L366.
13. HAYMORE, B. L. & IBERS, J. A., *Inorg. Chem.*, **14** (1975), 3060.
14. GAUGHAN, A. P., HAYMORE, B. L., IBERS, J. A., MYERS, W. H., NAPIER, T. F. & MEEK, D. W., *J. Am. chem. Soc.*, **95** (1973), 6859.
15. NORBURY, A. H., *Advanced inorganic chemistry & radiochemistry*, **17** (1975), 253.
16. FELTHAM, R. D. & HAYTER, R. G., *J. chem. Soc.*, (1968), 4587.
17. BAUMANN JOHN, A. & MEYER, T. J., *Inorg. Chem.*, **19** (1980), 345.