CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF GUELPH, GUELPH, ONTARIO, CANADA

The Stabilization of Hexachlororuthenate(III) and Hexabromoruthenate(III) Anions by 2,2′,2′′-Triammoniotriethylamine, $N(CH_2CH_2NH_3)_3{}^{3+}$

BY J. R. GAYLOR AND C. V. SENOFF*

Received December 17, 1971

Simple hexahaloruthenate(III) salts have been known for some time.[1,2] Recently the anions $[RuCl_6]^{3-}$ and $[RuBr_6]^{3-}$ have been isolated as $[Al(H_2O)_6][RuCl_6]\cdot H_2O$[3] and anilinium salts of empirical formula, $(C_6H_8N)_6RuX_9$ (X = Cl, Br).[4] Diffraction experiments have unambiguously established the presence of $[RuCl_6]^{3-}$ and $[RuBr_6]^{3-}$ in $[Al(H_2O)_6][RuCl_6]\cdot H_2O$ and $(C_6H_8N)_6RuBr_9$, respectively.[3,4] During the course of investigating the coordinating properties of the tetradentate ligand 2,2′,2′′-triaminotriethylamine (tren) toward heavier transition metals, we have observed that $[RuCl_6]^{3-}$ and $[RuBr_6]^{3-}$ are stabilized by the "bulky" cation 2,2′,2′′-triammoniotriethylamine, $N(CH_2CH_2NH_3)_3{}^{3+}$. In the solid state these salts are characterized by the presence of one molecule of HX acid (X = Cl or Br). The purpose of this Note is to report the preparation and characterization of these particular salts.

Results and Discussion

A warm aqueous solution of $K_3[Ru(C_2O_4)_3]$ readily reacts with $[N(CH_2CH_2NH_3)_3]Cl_3$ in the presence of excess concentrated HX (X = Cl or Br) to form $[RuX_6]^{3-}$ in solution which is precipitated from solution by $N(CH_2CH_2NH_3)_3{}^{3+}$. This reaction may be regarded to proceed *via* eq 1. It is interesting to note that the

$$Ru(C_2O_4)_3{}^{3-} + 6H_3O^+ + 6X^- \longrightarrow RuX_6{}^{3-} + 3C_2O_4H_2 + 6H_2O \tag{1}$$

linear isomeric ligand, triethylenetetramine, trien, *coordinates* to ruthenium(III) under essentially the same experimental conditions to form *cis*-$[Ru(trien)X_2]^+$ (X = Cl, Br).[5,6] Analytical data and infrared spectral data for the salts produced from reaction 1 indicate that they are best formulated as $[N(CH_2CH_2NH_3)_3][RuCl_6]\cdot HCl\cdot 2H_2O$ (**1**) and $[N(CH_2CH_2NH_3)_3][RuBr_6]\cdot HBr$ (**2**). The infrared spectrum of **1** in addition to exhibiting absorption bands due to the cation, $N(CH_2CH_2NH_3)_3{}^{3+}$, showed additional bands at 3600 (s), 3490 (s), and 1635 (m) cm^{-1} which are characteristic of water of crystallization.[7] These particular bands are absent in the infrared spectrum of **2**. The far-infrared spectra of these complex salts are also quite diagnostic. Strong, sharp bands were observed at 313 and 240 cm^{-1} for **1** and **2**, respectively which may readily be assigned to the infrared active F_{1u} modes, ν_{Ru-Cl} and ν_{Ru-Br}, respectively, and confirm that the halide ligands are octahedrally coordinated to ruthenium(III).[8] A molecule of acid of solvation (HX) must be included in the formulation of **1** and **2** in order to account for the observed high halogen content. The presence of HX of solvation was confirmed by pH measurements at room tempeature and by titration with standardized aqueous NaOH. The pH data are presented in Table I and indicate that aqueous solutions of **1** and **2** contain 1 mol of HX per mole of complex. The acidic hydrogens associated with the cation make a negligible contribution to the observed pH.[9] Four equivalents of base was consumed when aqueous solutions of **1** and **2** were titrated with NaOH confirming the presence of $N(CH_2CH_2NH_3)_3{}^{3+}$ and HX of solvation. The complexes **1** and **2** are paramagnetic with μ_{eff} = 1.95 BM and 2.01 BM, respectively, at 299°K. These magnetic moments are consistent with those reported for other octahedral ruthenium(III) salts.[4-10] The electronic spectra of **1** and **2** were measured in concentrated acid solution in order to suppress hydrolysis to aquo species which was observed in less acidic solutions. These spectral data are given in Table II; representative spectra are shown in Figure 1.

TABLE I

pH MEASUREMENTS

Concentration, *M*	$[H]^+$, *M*	$[H]^+/[\text{complex}]$
	(a) $[N(CH_2CH_2NH_3)_3][RuCl_6]\cdot HCl\cdot 2H_2O$	
6.61×10^{-5}	6.46×10^{-5}	0.98
1.82×10^{-4}	1.91×10^{-4}	1.05
7.15×10^{-4}	6.46×10^{-4}	0.90
7.20×10^{-4}	9.12×10^{-4}	1.26
9.86×10^{-4}	12.6×10^{-4}	1.27
	Av	1.09 ± 0.15
	(b) $[N(CH_2CH_2NH_3)_3][RuBr_6]\cdot HBr$	
1.14×10^{-4}	1.26×10^{-4}	1.10
1.30×10^{-4}	1.51×10^{-4}	1.17
1.52×10^{-4}	1.26×10^{-4}	0.83
9.00×10^{-4}	1.00×10^{-3}	1.11
	Av	1.05 ± 0.09

TABLE II

ELECTRONIC SPECTRAL DATA[a]

$\bar{\nu}$, cm^{-1}	ϵ, cm^{-1} M^{-1}	$\bar{\nu}$, cm^{-1}	ϵ, cm^{-1} M^{-1}
	(a) $[RuCl_6]^{3-}$		
42,600	16,410	(25,400)	2150
32,300	2,400	(21,900)	780
28,500	3,980		
	(b) $[RuBr_6]^{3-}$		
37,000	24,900	22,000	2690
(32,900)	15,100	(21,400)	2320
27,800	2,900	(19,200)	810
25,200	2,310	(16,500)	104
(22,900)	2,370		

[a] Parentheses indicate a band which was not well resolved.

The band positions and corresponding molar extinction coefficients agree reasonably well with those reported by Jorgensen for $[RuCl_6]^{3-}$ and $[RuBr_6]^{3-}$ generated *in*

---

(1) E. Wedekind, *Z. Angew. Chem.*, **41**, 771 (1928).

(2) R. Charronat, *Ann. Chim.* (*Paris*), **16**, 235 (1931).

(3) T. E. Hopkins, A. Zalkin, D. H. Templeton, and M. G. Adamson, *Inorg. Chem.*, **8**, 2421 (1969).

(4) M. G. B. Drew, D. A. Rice, and C. W. Timewell, *Inorg. Nucl. Chem. Lett.*, **7**, 59 (1971).

(5) J. A. Broomhead and L. A. P. Kane-Maguire, *J. Chem. Soc. A*, 546 (1967).

(6) R. O. Harris and B. A. Wright, *Can. J. Chem.*, **48**, 1815 (1970).

(7) K. Nakamoto, "Infrared Spectra of Inorganic & Coordination Compounds," Wiley, New York, N. Y., p 156.

(8) A. D. Allen and C. V. Senoff, *Can. J. Chem.*, **45**, 1337 (1967).

(9) J. E. Prue and G. Schwarzenbach, *Helv. Chim. Acta*, **33**, 963 (1950).

(10) B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 37 (1964).

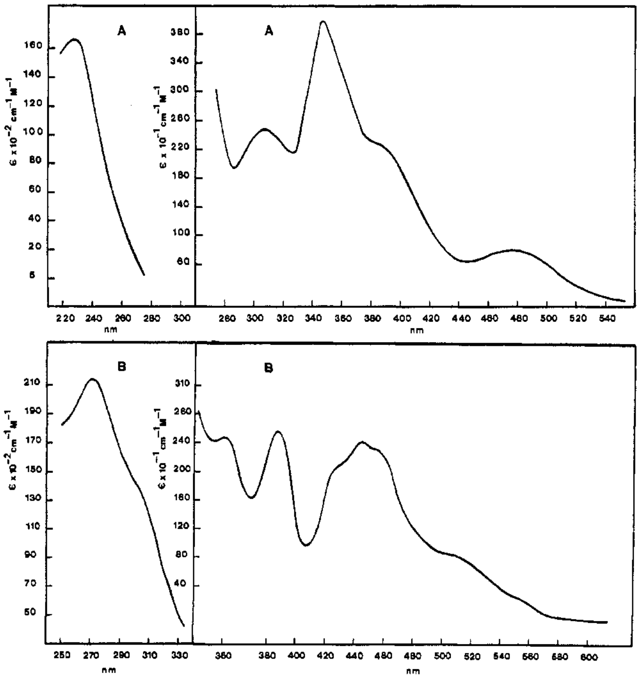

Figure 1.—A, electronic spectrum of $[RuCl_6]^{3-}$ in 12 *M* HCl; B, electronic spectrum of $[RuBr_6]^{3-}$ in 9 *M* HBr.

situ[11,12] and by Hartmann and Buschbeck[13] for K_3RuCl_6. No attempt was made in this study to assign the observed absorption bands since detailed assignments have been given considerable attention by Jorgensen.[11,12]

There is no supporting evidence for the presence of $H_5O_2^+$ in **1** although Gillard and Wilkinson[14] have reported that this ion is present in a number of rhodium(III) complexes. It may then be concluded that $[RuCl_6]^{3-}$ and $[RuBr_6]^{3-}$ are stabilized by $N(CH_2CH_2NH_3)_3{}^{3+}$ and that crystal packing considerations probably require one molecule of HX to be present in the solid. This situation would be similar to that observed for the anilinium salts, $(C_6H_8N)_6RuX_9$.[4] Attempts to stabilize $[RuF_6]^{3-}$ and $[RuI_6]^{3-}$ by $N(CH_2CH_2NH_3)_3{}^{3+}$ by the general method presented herein were unsuccessful.

Experimental Section

Infrared spectra were recorded on a Beckman IR-12 spectrophotometer as Nujol mulls between CsI plates. Electronic spectra were obtained with a Cary-14 spectrophotometer. Beer's law was obeyed over the concentration range $\sim 1 \times 10^{-5}$–1×10^{-4} *M*. A Radiometer pH meter model 28 was used to measure the pH of aqueous solutions. Microanalyses were performed by A. B. Gygli, Toronto or by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Ruthenium was determined by reduction to the metal in an atmosphere of hydrogen at 700°. Halogen analyses were determined by potentiometric titration with silver nitrate solution. Magnetic susceptibility measurements were carried out using a Gouy balance at room temperature.

Materials.—Ruthenium trichloride was purchased from Engelhard Industries, N. J. Potassium tris(oxalato)ruthenate(III) tetrahydrate was prepared according to the method of Witschy and Beattie.[15] Other chemicals used were reagent grade. The ligand, $[N(CH_2CH_2NH_3)_3]Cl_3$, was purchased from Strem Chemicals, Inc., Danvers, Mass.

$[N(CH_2CH_2NH_3)_3][RuCl_6] \cdot HCl \cdot 2H_2O$.—To an acidic solution (pH <3) made from 5.0 ml of concentrated HCl and 5 ml of water was added $K_3[Ru(ox)_3] \cdot 4H_2O$ (0.5 g) and $[N(CH_2CH_2NH_3)_3]Cl_3$ (0.5 g). The resulting mixture was heated on a steam bath for 15–20 min during which time the solution changed from dark green to red-brown in color. After cooling the solution the product was filtered and washed successively with cold water, methanol, and ether. The crude product was recrystallized by dissolving it in the minimum volume of hot water followed by filtration of the hot solution into an equal volume of concentrated HCl. The reddish brown powder was washed as before and dried *in vacuo* over boiling H_2O. *Anal.* Calcd for $C_6H_{26}Cl_7N_4O_2$: C, 13.46; H, 4.86; N, 10.47; Cl, 46.36; Ru, 18.88. Found: C, 13.41; H, 4.40; N, 10.60; Cl, 46.64; Ru, 19.51.

$[N(CH_2CH_2NH_3)_3][RuBr_6] \cdot HBr$.—This dark brown complex salt was prepared in a manner similar to that used for the $[RuCl_6]^{3-}$ salt except that HBr (9 *M*) was used instead of HCl. *Anal.* Calcd for $C_6H_{22}Br_7N_4Ru$: C, 8.89; H, 2.71; N, 6.91; Br, 69.01; Ru, 12.47. Found: C, 8.80; H, 2.90; N, 6.89; Br, 68.11; Ru, 13.81.

Acknowledgment.—The authors thank the National Research Council of Canada for financial support in the form of an operating grant to C. V. S.

---

[11] C. K. Jorgensen, *Acta Chem. Scand.*, **10**, 518 (1956).

[12] C. K. Jorgensen, *Mol. Phys.*, **2**, 309 (1959).

[13] H. Hartmann and C. Buschbeck, *Z. Phys. Chem.* (*Frankfurt am Main*), **11**, 120 (1957).

[14] R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 1640 (1964).

[15] J. K. Witschy and J. K. Beattie, *Inorg. Nucl. Chem. Lett.*, **5**, 969 (1969).

CONTRIBUTION FROM THE BELL LABORATORIES,
MURRAY HILL, NEW JERSEY 07974

The Identity of So-Called "Cupric Iodate Monohydrate" and Bellingerite, $3Cu(IO_3)_2 \cdot 2H_2O$

BY K. NASSAU* AND J. W. SHIEVER

Received February 2, 1972

Despite some early confusion,[1] the product of the metathetic reaction between copper salts and iodic acid or alkali iodates has long been considered to be the cupric iodate hydrate $Cu(IO_3)_2 \cdot H_2O$.[1-5] At the same time the mineral bellingerite, found in Chuquicamata, Chile, was reported by Berman and Wolfe[6] to have the formula $3Cu(IO_3) \cdot 2H_2O$, *i.e.*, only two-thirds of the water content of the synthetic product; they also found this formula to apply to one of the previously reported products (that of Granger and de Schulten[4,5]).

A variety of physical data, including thermodynamic,[7-9] infrared,[10] and magnetic[11] properties, have nevertheless been reported under the designation $Cu(IO_3)_2 \cdot H_2O$. The differences in analysis expected from these two formulations are quite small (the water has frequently been determined by difference, and direct water determinations are easily vitiated by in-

---

[1] J. W. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. 2, Longmans, Green and Co., New York, N. Y., 1922, p 343.

[2] For example, J. F. Spencer, *Z. Phys. Chem.*, **83**, 290 (1913).

[3] J. Martinez-Cros and L. Le Boucher, *An. Soc. Espan. Fis. Quim.*, **33**, 229 (1935).

[4] A. Granger and A. de Schulten, *Bull. Soc. Fr. Mineral.*, **27**, 137 (1904).

[5] A Granger and A. de Schulten, *Bull. Soc. Chim. Fr.*, **31**, 1027 (1904).

[6] H. Berman and C. W. Wolfe, *Amer. Mineral.*, **25**, 505 (1940).

[7] B. H. Peterson and E. L. Meyers, *J. Amer. Chem. Soc.*, **52**, 4853 (1930).

[8] P. and H. Lumme, *Suom. Kemistilehti B*, **35**, 129 (1962).

[9] L. M. Gedansky, P. J. Pearce, and L. G. Hepler, *Can. J. Chem.*, **48**, 1770 (1970).

[10] C. Rocchicciole, *C. R. Acad. Sci.*, **250**, 1232 (1960).

[11] P. Escoffier and J. Gauthier, *ibid.*, **252**, 271 (1961).