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Six-Coordinate Halogen Complexes of Rhodium(III) and Iridium(III) with 2,2′,2″-Triammoniotriethylamine, $N(CH_2CH_2NH_3)_3^{3+}$ as the Cation

S. G. ZIPP and S. K. MADAN*
Department of Chemistry, State University of New York at Binghamton, Binghamton, N.Y. 13901, U.S.A.
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Several new hexahalo complexes of the formulas $[N(CH_2CH_2NH_3)_3][MX_6]$ *(M = Rh, Ir; X = Cl, Br) and* $[N(CH_2CH_2NH_3)_3][RhCl_3Y_3]$ *(Y = Br, I) were prepared. The complexes were characterized by elemental analysis, infrared and electronic spectra.*

Introduction

Although hexachloro and hexabromo complexes of Rh(III) and Ir(III) are known[1,2], much of the research in the area was carried out many years ago or was done in solution, where hydrolysis is now known to occur, even in concentrated acid[3,4]. A recent report[5] of the isolation of some hexahalo Ru(III) compounds with the counterion $N(CH_2CH_2NH_3)_3^{3+}$ or $[trenH_3]^{3+}$ prompted us to see whether this cation could also be used in the isolation of similar Rh(III) or Ir(III) anionic species, since the properties of the tripodal amine tren, $N(CH_2CH_2NH_2)_3$, have long been of interest in this laboratory[6]. We wish to report here the isolation of several such species, including the novel mixed halo complexes $[N(CH_2CH_2NH_3)_3][RhCl_3Br_3]\cdot H_2O$ and $[N(CH_2CH_2NH_3)_3][RhCl_3I_3]\cdot H_2O$.

Experimental

Infrared spectra were recorded on a Beckman IR-12 Spectrophotometer as Nujol mulls between CsBr (4000–300 cm^{-1}) and polyethylene (300–200 cm^{-1}). The infrared measurements were made under anhydrous conditions by purging the sample compartment of the instrument with dry air. Electronic spectra were obtained on a Cary-14 Spectrophotometer as Nujol mulls C, H and N analyses were performed by Weiler and Strauss, Oxford, England. Halogen analyses were done by a potentiometric method using standardized silver nitrate solution. Complexes were decomposed by boiling with 6*M* NaOH solution and then were acidified with HNO_3 for determination of halogen.

Materials

$RhCl_3\cdot 3H_2O$ and $IrCl_3\cdot 3H_2O$ were purchased from Englehart Industries, N.J. $N(CH_2CH_2NH_3)_3Cl_3$ was isolated[7] from an 85% tren–15% trien mixture donated by the Dow Chem. Co. All other chemicals used were reagent grade. Hydrated $K_3Rh(C_2O_4)_3$ and $K_3Ir(C_2O_4)_3$ were prepared by mixing concentrated solutions of $RhCl_3\cdot 3H_2O$ or $IrCl_3\cdot 3H_2O$ and $K_2C_2O_4$ in a 1 : 3 mole ratio, heating on a steam bath for 30 minutes and evaporating to dryness.

$[N(CH_2CH_2NH_3)_3][RhCl_6]\cdot H_2O$.

$RhCl_3\cdot 3H_2O$ [0.0087 mol, 0.23 g] were added to 10 ml of 6*M* HCl and the mixture was warmed on a steam bath until dissolution occured. When $N(CH_2CH_2NH_3)_3Cl_3$ (0.27 g; 0.0106 mol) was added, a red-brown precipitate was formed immediately. After cooling, the product was washed successively with ice H_2O, absolute ethanol and ether, and dried *in vacuo*.

$[N(CH_2CH_2NH_3)_3][RhCl_3Br_3]\cdot H_2O$; $[N(CH_2CH_2NH_3)_3][RhCl_3I_3]\cdot H_2O$; $[N(CH_2CH_2NH_3)_3][IrCl_6]\cdot 3H_2O$.

These complexes were prepared with the appropriate acid or metal halide as starting material, in a manner similar to that used for the hexachloro complex.

$[N(CH_2CH_2NH_3)_3][RhBr_6]\cdot 3H_2O$ *and* $[N(CH_2CH_2NH_3)_3][IrBr_6]\cdot H_2O$.

These were prepared by adding the appropriate amount of $N(CH_2CH_2NH_3)_3Cl_3$ to a solution of $K_3Rh(C_2O_4)_3$(hyd) or $K_3Ir(C_2O_4)_3$(hyd) in 9*M* HBr. The precipitate was washed as above.

Results and Discussion

The elemental analyses of these compounds are given in Table I. Potentiometric titrations on the hexachloro and hexabromo complexes indicated the expected amount of halogen, but, although those performed on the mixed halide complexes always indicated the presence of two halogens, coprecipitation of chloride

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* Author to whom correspondence should be addressed.

TABLE I. Elemental Analyses and Other Properties.

Complex	%C		%H		%N		%Halogen		Color	Thermal Stability
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found		
$[N(CH_2CH_2NH_3)_3][RhCl_6]\cdot H_2O$	14.90	15.50	4.76	4.74	11.60	12.05	44.0	43.9	rose-red	stable beyond 300° C
$[N(CH_2CH_2NH_3)_3][RhCl_3Br_3]\cdot H_2O$	11.68	12.00	3.74	3.50	9.09	9.33	55.7	56.0	light green	stable beyond 300° C
$[N(CH_2CH_2NH_3)_3][RhCl_3I_3]\cdot H_2O$	9.51	9.60	3.04	2.89	7.39	6.85	[a]	[a]	deep-brown	stable beyond 300° C
$[N(CH_2CH_2NH_3)_3][RhBr_6]\cdot 3H_2O$	9.16	9.04	3.44	3.51	7.14	6.91	61.0	61.5	red-brown	stable beyond 300° C
$[N(CH_2CH_2NH_3)_3][IrCl_6]\cdot 3H_2O$	11.85	12.15	3.96	4.01	9.22	9.08	35.2	35.8	light green	stable beyond 300° C
$[N(CH_2CH_2NH_3)_3][IrBr_6]\cdot H_2O$	8.58	8.03	2.84	3.08	6.68	6.12	57.2	57.4	lime green	stable beyond 300° C

[a] Solid solution formation and separation difficulties precluded accurate halogen analysis.

led to high values for the precent of bromide or iodide and low values for the precent of chloride.

The mixed halogeno species $[trenH_3][RhCl_3Br_3]\cdot H_2O$ and $[tren\ H_3][RhCl_3I_3]\cdot H_2O$, which were prepared by reacting $RhCl_3\cdot 3H_2O$ with HBr or HI, respectively, have not been reported previously. When an attempt was made to prepare an analogous iridium complex by the reaction of $IrCl_3\cdot 3H_2O$ with HBr, the complex $[trenH_3][IrBr_6]\cdot H_2O$ was precipitated. Since the ionic radii of Rh^{3+} and Ir^{3+} are very similar, 0.67 Å and 0.73 Å, respectively, it is unclear whether this phenomenon is due to the size or the metal cation.

Infrared Spectral Studies

The rather complicated infrared spectra of these compounds were examined in detail for four main features: (a) lattice water vibrations [3400–3500 and ~1630 cm^{-1}]; (b) N–H stretching vibrations [2950–3100 cm^{-1}]; (c) N–H antisymmetric bending vibrations [~1550–1650 cm^{-1}]; (d) M–X stretching vibrations [<400 cm^{-1}; X = Cl, Br], as listed in Table II.

(a) Water of crystallization is present in these compounds as indicated by the elemental analyses and by characteristic absorptions in the 3350–3550 cm^{-1} range[8], which remained after the compounds were dried at 110° C. Weak absorptions were seen near 1630 cm^{-1} (HOH bending)[8] in the spectra of the hexahalo complexes, but this region was obscured by N–H absorptions in the two mixed halo complexes.

(b) The N–H symmetrical stretching vibrations near 3100 cm^{-1} were broad, and only ranges of absorption are given in Table II. Although broadness makes quantitative comparison difficult, it can be seen that this absorption band is approximately 100 cm^{-1} lower in $N(CH_2CH_2NH_3)_3Cl_3$ than in the complexes which were studied here. Similar lowerings occur in amines and in compounds of the type $Co(NH_3)_6X_3$ [X = Cl, Br, I][9,10]. In the latter compounds, the N–H stretching frequency is lowered to the greatest extent when the strongest hydrogen bond is formed, with X = Cl. Much weaker hydrogen bonds are formed between the primary amine hydrogens and the halogens in the complexes than are formed in $N(CH_2CH_2NH_3)_3Cl_3$, and therefore the frequency is less for the complexes than for the amine hydrochloride.

(c) The N–H degenerate deformation bands for these complexes (Table II) fall within the range 1560–1650 cm^{-1} reported for some octahedral cobalt–haloammine complexes[11] and for some ruthenium(III)–ethylenediamine species[12]. It is interesting that this N–H deformation frequency occurs near 1600 cm^{-1} in the chloro–bromo and chloro–iodo complexes as it does in $N(CH_2CH_2NH_3)_3Cl_3$, while in the hexahalo complexes it is approximately 30–85 cm^{-1} lower. It is possible that the lower symmetry of the mixed chloro–halo complex anions may affect the wavelengths of the N–H deformation in $N(CH_2CH_2NH_3)^{3+}$, but little is known about such effects.

(d) Octahedral complexes of the type MX_6^{3-} are expected to have an F_{1u} infrared active metal–halogen stretching vibration[13], and the sharp bands seen below 350 cm^{-1} in the infrared spectra of the four hexahalo complexes were assigned to this mode, in good agreement with results reported from other sources[13,14,15].

Complexes of the type $MCl_3X_3^{3-}$ may occur in the *cis* configuration, (C_{3v} symmetry) or the *trans* configuration, with C_{2v} symmetry[8], and would be expected to exhibit two or three Rh–Cl stretching vibrations, respectively. Both $[trenH_3][RhCl_3Br_3]\cdot H_2O$ and $[trenH_3][RhCl_3I_3]\cdot H_2O$ have absorptions at 355(360), 335 and 295 cm^{-1}, corresponding very closely to the frequencies reported for Rh–Cl vibrations in *trans*-$[RhCl_3py_3]$[16] (355, 225, 295 cm^{-1}) and thus suggesting that these complexes have the *trans* configuration.

TABLE II. Infrared Spectral Band Assignments (cm^{-1}).[a]

Complex	Lattice Water	N–H Sym. Stretch	N–H Asym. Deformation	Metal–Halogen Stretch
$[N(CH_2CH_2NH_3)_3][RhCl_6]\cdot H_2O$	3510 3380 1610–20 br wk	3060– 3160 br	1570 1580 sh	330 s
$[N(CH_2CH_2NH_3)_3][RhCl_3Br_3]\cdot H_2O$	3510 3380	3110– 3140 br	1595 1605 sh	355 335 295
$[N(CH_2CH_2NH_3)_3][RhCl_3I_3]\cdot H_2O$	3520 3360	3060– 3140 br	1595 1605	360 335 295
$[N(CH_2CH_2NH_3)_3][RhBr_6]\cdot 3H_2O$	3500 3400 1620 wk	3100– 3170 br	1550 1570	260 s
$[N(CH_2CH_2NH_3)_3][IrCl_6]\cdot 3H_2O$	3500 3380 1680	3120– 3160 br	1570 1560 sh	305 s
$[N(CH_2CH_2NH_3)_3][IrBr_6]\cdot H_2O$	3500 3380	3080– 3120 br	1550 1560	220 s
$N(CH_2CH_2NH_2)_3\cdot 3HCl$		2940 3080 multiplet br	1595 1605	–
$N(CH_2CH_2NH_2)_3$ (neat)		3360 3280 3180 sh	1600	–
$[RhN(CH_2CH_2NH_2)_3Cl_2]Cl\cdot H_2O$	3400 3490 1630 wk	3100– 3210 br	1595 1585 sh	295 s

[a] s = sharp; sh = shoulder; wk = weak; br = broad.

However, because of the weakness of these low frequency bands and also because of the possibility of interference from bands from the $trenH_3^{3+}$ cation[17], the assignment of the *trans* configuration is tentative at the present time. No attempt was made to look for Rh–Br or Rh–I absorptions in the mixed halo complexes, the latter being certainly out of the range of the instrument used.

Electronic Spectral Studies

The visible absorption spectra of Rh(III) and Ir(III) complexes have the same explanation as do those of Co(III) complexes. The anions $[MX_6]^{3-}$ (M = Rh; X = Cl or Br) and $[MX_3Y_3]^{3-}$ (M = Rh; X = Cl; Y = Br and I) exhibit two bands towards the blue end of the visible region, which together with any additional absorption in the blue resulting from charge-transfer (CT) transition, are responsible for the characteristic orange, red, yellow or brown colors of rhodium(III) complexes. Thus, the bands shown in Table III are assigned as transitions from the $^1A_{1g}$ ground state to the $^1T_{1g}$ and $^1T_{2g}$ higher states, these assignments are in accordance with the energy level diagram for Fe(II) and Co(III). A similar interpretation is given for the spectra of Ir(III) complexes (Table III).

However, in the case of $[N(CH_2CH_2NH_3)_3[[RhCl_3I_3]\cdot H_2O$ (Table III) only one band (instead of the usual three bands) was observed in the charge-transfer region. This may be attributed to the fact that the complex appears to undergo some photochemical change or a change in composition as it is been ground in Nujol to make a mull.

TABLE III. Electronic Spectral Bands.

Complex	$10^3\nu_{max}$ (cm^{-1})	Band Assignment
$[N(CH_2CH_2NH_3)_3][RhCl_6]\cdot H_2O$	19.2	$^1A_{1g}\rightarrow {}^1T_{1g}$
	23.9 sh	$\rightarrow {}^1T_{1g}$
	35.7	L→M (CT) Transition
$[N(CH_2CH_2NH_3)_3][RhCl_3Br_3]\cdot H_2O$	18.5	$^1A_{1g}\rightarrow {}^1T_{1g}$
	21.9 sh	$\rightarrow {}^1T_{1g}$
	33.0	L→M (CT) Transition
$[N(CH_2CH_2NH_3)_3][RhCl_3I_3]\cdot H_2O$	30.1	?
$[N(CH_2CH_2NH_3)_3][RhBr_6]+3H_2O$	17.8	$^1A_{1g}\rightarrow {}^1T_{1g}$
	22.7 sh	$\rightarrow {}^1T_{1g}$
	29.4	L→M (CT) Transition
$[N(CH_2CH_2NH_3)_3][IrCl_6]\cdot 3H_2O$	19.6	$^1A_{1g}\rightarrow {}^1T_{1g}$
	23.2	$\rightarrow {}^1T_{1g}$
	40.7	L→M (CT) Transition
$[N(CH_2CH_2NH_3)_3][IrBr_6]\cdot H_2O$	17.5	$^1A_{1g}\rightarrow {}^1T_{1g}$
	22.7 sh	$\rightarrow {}^1T_{1g}$
	37.00	L→M (CT) Transition

Conclusion

It is interesting that tren can react with Rh(III) in two different ways depending on the acidity of the reaction mixture. In neutral solution, it coordinates to the Rh(III) ion producing $[Rh(tren)Cl_2]Cl$[18, 6d], while in acid solution, the $trenH_3^+$ cation acts as a very efficient precipitation agent for anionic Rh(III) and Ir(III) halogens species. The ready and, in fact, almost exclusive formation of the triply-charged species $N(CH_2CH_2NH_3)_3^{3+}$ (an aid to precipitation of triply-charged anions), rather than ions of other charges, is no doubt due to the large separation and resulting low electrostatic attraction between the primary amine functions in tren[19].

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