inversion without isomerization and averages trans sites *y* and *z*. The trigonal twist (Figure 1) is one physical conception of this permutation.[67]

Musher[66] has pointed out that permutation A_2, as well as A_6, is compatible with the pmr-averaging patterns of $Fe(R_1R_2dtc)_2(tfd)$[15] (**3**) and $Fe(R_1R_2dtc)_3$.[46] Pignolet[68] has recently obtained evidence that the LTP of the latter complexes proceeds with inversion of configuration, thereby revealing that A_2 is not a significant process. It has recently been suggested that the complexes **3** rearrange *via* a distorted hexagonal-planar structure.[50] If for the tropolonate complexes a similar transition state is entertained, rotation of the ligands through a coplanar arrangement to positions roughly perpendicular to the original ones gives as the net result A_5. If the rotation is continued, effectively a trigonal twist, the net result is A_2. Since neither A_2 nor A_5 is consistent with the averaging patterns of both types of tropolonate complexes, a planar transition state is not involved in the LTP of these complexes.

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(67) The product isomer, resulting from a permutation or permutation–inversion, can be drawn in 24 rotated forms. Comparison of the starting isomer with each of the orientations of the product can suggest ligand motions required to effect the observed site averaging. For A_6 physical mechanisms other than the trigonal twist appear to require greater ligand motion or highly selective bond rupture and formation and thus are considered less plausible than the trigonal twist.

(68) L. H. Pignolet, private communication.

Blue Chloroammine Complexes of Ruthenium

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Abstract: The preparation, characterization, and some reactions of the blue complex formed from $Ru(NH_3)_6Cl_2$ and HCl are described. The complex was identified as $Ru_2Cl_3(NH_3)_6{}^{2+}$, a mixed oxidation state complex, and is formed by the reaction $4Ru(NH_3)_6{}^{2+} + 14H^- + 6Cl^- \rightarrow 2Ru_2Cl_3(NH_3)_6{}^{2+} + H_2 + 12NH_4{}^+$. The blue cation decomposes to *cis*-$RuCl_3(NH_3)_3$ in the presence of oxygen. This, combined with spectral data, suggests that there is a triple chloride bridge between the two metal atoms.

The formation of intense blue solutions by the action of reducing agents on hydrochloric acid solutions of ruthenium has been the subject of considerable interest since first reported by Claus[1] in 1846. Recently we have identified the blue species in these solutions as ruthenium(II,III) dimers[2] which have the general formula $Ru_2Cl_{3+n}{}^{(2-n)+}$. In that study we noted that the formation of the blue complexes was always preceded by reduction of the metal to $Ru(H_2O)_6{}^{2+}$, followed by an oxidation to form the final product.

There have been several reports in the literature on the formation of blue solutions when hydrochloric acid is added to ruthenium(II) complexes containing nitrogen donor ligands. The simplest of these ligands is ammonia. Endicott and Taube[3] reported some qualitative observation on this reaction. Later Lever and Powell[4] isolated a blue solid. On the basis of chemical analysis they formulated the complex as $Ru(NH_3)_3Cl_2(H_2O)^+$, a ruthenium(III) complex. When our work was near completion, Bottomley and Tong[5] reported the characterization of a blue solid formed from the same reaction as $[Ru_2Cl_4(H_2O)(NH_3)_6]Cl$. In this report they have correctly identified this as a mixed oxidation state complex of ruthenium(II,III).

Experimental Section

Analyses. Ruthenium was determined spectrophotometrically[6] as $RuO_4{}^{2-}$.

Chloride determinations were made by two methods, both involving gravimetric determinations as AgCl. The first method has been reported previously.[2] In the second method, the chloride was separated from the ruthenium by distillation of HCl from a sulfuric acid solution of the compound. The distillate was collected in 2 *M* NaOH, and after acidification with nitric acid, the chloride was precipitated by addition of $AgNO_3$ solution.

Nitrogen was determined by either the Kjeldahl or Dumas method. Tin and zinc were measured polarographically. It was necessary to remove the ruthenium from solution by hydrogen reduction before the zinc determination was performed.

Reagents. Ruthenium chloride hydrate (~38% Ru) was obtained from Engelhard Industries. This was converted to $Ru(NH_3)_6Cl_2$ as reported by Allen and Senoff.[7] Ion exchange resins used were Dowex 50 × 8, 200–400 mesh (H^+ form), and Dowex 1 × 8, 100–200 mesh (Cl^- form). The cation resin was always washed with 6 *M* HCl to remove iron impurities, and washed free of acid with water prior to use.

All other chemicals were reagent grade and were used without further purification.

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(1) C. Claus, *Justus Liebigs Ann. Chem.*, **59**, 283 (1846).

(2) E. E. Mercer and P. E. Dumas, *Inorg. Chem.*, **10**, 2755 (1971).

(3) J. F. Endicott and H. Taube, *ibid.*, **4**, 437 (1965).

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(5) F. Bottomley and S. B. Tong, *Can. J. Chem.*, **49**, 3739 (1971).

(6) J. L. Woodhead and J. M. Fletcher, *J. Chem. Soc.*, 5037 (1961).

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Table I. Analytical Data

Compound	% Ru		% N		% Cl		% M	
	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd
$Ru_2(Cl_3)(NH_3)_6Cl_2 \cdot 2H_2O$	39.05	38.96	16.23	16.27	34.25	33.81		
$Ru_2(Cl)_3(NH_3)_6Cl_2$	41.97	41.90	17.45	16.97	36.81	37.58		
$Ru_2(Cl)_3(NH_3)_6(SnCl_3)_2$	23.48	24.00	9.76	10.53	37.07	36.36	27.58	28.00
$Ru_2(Cl)_3(NH_3)_6ZnCl_4$	32.72	32.50	13.60		40.17	39.40	10.58	10.60
$Ru_2(Cl)_3(NH_3)_6HgCl_4$	26.84	26.80	11.16		32.95	32.90	26.64	
$Ru_2(Cl)_3(NH_3)_6CdCl_4$	30.40	30.42	12.64		37.32	37.30	16.91	16.90

Equipment. All ultraviolet and visible spectra were recorded on a Cary 14 spectrophotometer using quartz cells. Infrared spectra were recorded on a Perkin-Elmer 621 instrument as KBr or CsI pellets and Nujol mulls. Polarograms were obtained using a Sargent Model XV polarograph. A dme was used where possible. In more positive regions both rotating platinum and carbon paste[8] electrodes were employed. A saturated calomel electrode was used as a reference in all cases. Magnetic susceptibility was measured at room temperature by the Gouy method. The apparatus consists of a Varian 4 in. electromagnet with a Mettler H-16 balance. Trisethylenediaminenickel(II) thiosulfate was used as a standard. Mass spectra were recorded on a Hitachi-Perkin-Elmer Model RMU-6 mass spectrometer.

Preparation of the Blue Compounds. $[Ru_2Cl_3(NH_3)_6]Cl_2 \cdot 2H_2O$. Hydrazine hydrate (85%, 5 ml) was added slowly to 0.65 g of ruthenium chloride hydrate dissolved in 5 ml of water. Following the initial vigorous reaction the solution was refluxed for 90 min under an atmosphere of nitrogen. The resulting solution was filtered by gravity and cooled to 0°; 10 ml of 8 *M* HCl was added and the solution was allowed to stand for 30 min under nitrogen at ice temperature. Addition of 20 ml of ethanol precipitated the blue solid. After filtration the solid was washed with 95% ethanol and acetone and air dried.

$[Ru_2Cl_3(NH_3)_6]Cl_2$. An anhydrous chloride was formed by placing the dihydrate under vacuum at room temperature for 4–6 hr.

$[Ru_2Cl_3(NH_3)_6](SnCl_3)_2$. Addition of an excess of $SnCl_2$ dissolved in 4 *M* HCl to a solution of the blue chloride in 4 *M* HCl resulted in the formation of a dark blue solid. The precipitate was filtered, washed with water, and dried under vacuum.

$[Ru_2Cl_3(NH_3)_6][MCl_4]$, M = Hg(II), Zn(II), Cd(II). These were prepared in the same way as the chlorostannate(II) salt, by using the appropriate metal chloride.

Results

Table I summarizes the analyses performed on the several salts of the blue cation. For all of these solids the calculated and observed compositions are in satisfactory agreement with our formulation of the blue cation as $Ru_2Cl_3(NH_3)_6^{2+}$. Furthermore, all of these compounds exhibit the same electronic spectrum when dissolved in acidic media. This spectrum is shown in Figure 1. Unless extreme precautions were exercised in removing all dissolved oxygen from the solvent some decomposition was observed. This decomposition could be slowed considerably by cooling to 0°. Very pure samples of the blue cation in solution were prepared by eluting it from a cation exchange column with 1 *M* H^+ at 0°.

Spectrophotometric titration of the blue cation with Ce(IV) required 0.50 equiv of oxidant per ruthenium atom. The spectrum of the yellow product of this oxidation is also shown in Figure 1. This behavior is entirely analogous to $Ru_2Cl_3(H_2O)_6^{2+}$ which was studied previously. Further evidence on the oxidation state of the ruthenium in this complex was obtained by studying its formation from $Ru(NH_3)_6^{2+}$. The reaction of $Ru(NH_3)_6Cl_2$ with 4, 6, and 8 *M* HCl was carried out in a closed system and the volume of gas evolved was measured. This gas was shown to be hydrogen by mass spectrometry. The results of these experiments are presented in Table II and are clearly in accord with the stoichiometry of eq 1. This stoichiometry

$$4Ru(NH_3)_6^{2+} + 14H^+ + 6Cl^- \longrightarrow 2Ru_2Cl_3(NH_3)_6^{2+} + 12NH_4^+ + H_2 \quad (1)$$

etry shows clearly that the blue complex contains ruthenium(II,III) and the product obtained by oxidation with Ce(IV) contains ruthenium(III). Upon standing the ruthenium(III) solution deposits a red solid identical with that identified by Bottomley and Tong[5] as *cis*-$RuCl_3(NH_3)_3$.

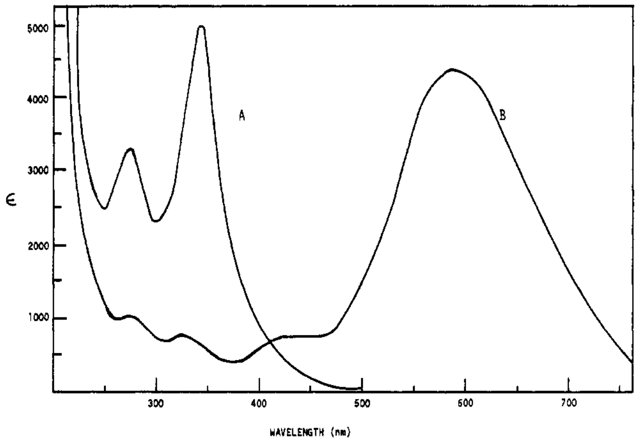

Figure 1. The ultraviolet visible spectra of $Ru_2Cl_3(NH_3)_6^{2+}$ (curve B) and $Ru_2Cl_3(NH_3)_6^{3+}$ (curve A) in 0.5 *M* H_2SO_4.

Table II. Hydrogen Ion Oxidation of $Ru(NH_3)_6Cl_2$

Sample no.	1	2	3
Sample, mg	170.6	271.7	240.6
Ru, mmol	0.662	0.991	0.878
HCl concn, *M*	4	6	8
H_2 evolved, ml (corrected to STP)	3.56	5.65	5.35
H_2 evolved, mmol	0.142	0.230	0.217
H^+ consumed per g-atom of Ru oxidized, mol	0.457	0.464	0.495

While the composition of the solids isolated suggests the presence of three coordinated chlorides in the blue cation, this was further substantiated by ion exchange experiments. An aliquot of a water solution of $[Ru_2Cl_3(NH_3)_6]Cl_2$ was loaded on a cation exchange column in the H^+ form. The column was washed with 0.05 *M* H_2SO_4 until no free chloride was present in the column effluent. The effluent was then titrated with standard silver nitrate solution and the ionic chloride in the compound was calculated. In other experiments the

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(8) C. Olson and R. N. Adams, *Anal. Chim. Acta*, **22**, 582 (1960).

Table III. Charge per Ruthenium Atom Determination

Ru, μg-atoms	Cl^-, μm	H^+, μm	Charge per Ru atom
5.17	5.10		0.987
6.65	6.64		0.998
5.52		5.49	0.995
6 25		6.20	0.992

column was washed with distilled water and the H^+ displaced from the resin was titrated with base. Table III summarizes the results and clearly shows that the complex has a charge of +1 for each metal atom present. Thus there are only three coordinated chlorides for each two metal atoms.

The magnetic susceptibility of $[Ru_2Cl_3(NH_3)_6](SnCl_3)_2$ was measured. At room temperature the molar susceptibility is $(1420 \pm 40) \times 10^{-6}$ esu, quite a reasonable value for a complex containing one unpaired electron.

The bands observed in the infrared spectrum of $[Ru_2Cl_3(NH_3)_6]Cl_2$ are listed with their assignments in Table IV.

Table IV. Infrared Spectral Data

Complex				
$Ru_2(Cl)_3(NH_3)_6Cl_2 \cdot 2H_2O$		$Ru_2(Cl)_3(NH_3)_6Cl_2$		
cm^{-1}	Intensity	cm^{-1}	Intensity	Assignment
3430 br	m			H_2O stretching
3290	s	3290	s	NH_3 stretching
3220	s	3220	s	NH_3 stretching
3160	s	3175	s	NH_3 stretching
1620	s			H_2O bending
1610	s	1610	s	NH_3 antisymmetric deformation
1320 sh	m	1300 sh	m	NH_3 symmetric deformation
1300	s	1295	s	NH_3 symmetric deformation
800	m	800	m	NH_3 rocking
475	m	475	m	Ru–NH_3 stretching
270	m	270	m	Ru–Cl–Ru stretching
240	m	240	m	H_3N–Ru–NH_3 stretching

Polarograms of the blue complex were obtained in 1 *M* HCl, 1 *M* KCl, and 1 *N* H_2SO_4. An oxidation wave was observed in all of these supporting electrolytes at $E_{1/2} = +0.32 \pm 0.01$ V *vs.* sce at both platinum and carbon paste electrodes. Polarograms recorded on mixtures of the blue complex and its yellow oxidation product showed a single wave at the same potential, proving the reversibility of the electrode reaction and identifying the product of the electrode reaction. Plots of E *vs.* log $(i - i_a)/(i_c - i)$ for these polarograms all had slopes of 59 ± 2 mV. A reduction wave at −0.28 V *vs.* sce was observed when the solvent was not thoroughly deoxygenated before dissolving the blue compound. This wave dissappeared when the solution was loaded on a cation column and eluted with 1 *N* electrolyte. No reduction wave was observed in 1 *M* HCl solutions of the purified complex, but the hydrogen discharge occurs at a somewhat less negative potential than normal. In both KCl and H_2SO_4, however, a one electron reduction wave is observed at −0.61 V *vs.* sce, followed closely by catalytic hydrogen evolution.

Discussion

All of our data are consistent with the formulation of the blue cation as tri-μ-chloro-hexaamminediruthenium(II,III). The location of the only Ru–Cl stretching frequency at 270 cm^{-1} strongly suggests these ligands occupy bridging positions. In monomeric ruthenium complexes this vibrational mode occurs in the range 290–340 cm^{-1}.[9] The lower frequency observed here would be expected if the chlorides occupied bridging positions. Furthermore, only one Ru–Cl stretching mode is infrared active for our proposed structure. There are several known ruthenium complexes which contain triple halogen bridges, and at least two of these are supported by X-ray crystal structure determinations.[10,11] Finally this structure for the complex is consistent with the observation that acid solutions decompose in the presence of oxygen to produce *cis*-$Ru(NH_3)_3Cl_3$ in high yield, since the ammonia is all cis in the starting material.

From all of our measurements it appears that the blue species isolated by Bottomley and Tong[5] is the same as ours. The ultraviolet and visible spectra are essentially identical. They used the conductivity in dimethylformamide to identity the compound as a 1:1 electrolyte. Our more direct ion exchange experiments show that there are two ionic chlorides present for each dimeric cation. This suggests that the interpretation of the conductivity data used by Bottomley and Tong was inadequate for this system. If the conductivity data of ref 5 are plotted as $\Lambda_0 - \Lambda$ *vs.* $\sqrt{c}$, both the blue chloride and bromide complexes lie on the same straight line, with a much steeper slope than the conductance of $(C_2H_5)_4NBr$. It has been suggested by Feltham[12] that this is a more reliable way to identify charge type from conductivity data. We have shown that the reduction wave at −0.28 V *vs.* sce which they report is probably due to partial oxidation of the complex and the actual reduction of the blue species would not be observable in the supporting electrolyte which they used.

It is interesting to compare the properties of this ammonia complex to those of $Ru_2Cl_3(H_2O)_6^{2+}$. These complexes appear to be very similar to each other in most respects. Both may be oxidized to moderately stable ruthenium(III) dimers without any change in coordination. The ammonia complex is somewhat

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[9] W. A. McAllister, Ph.D. Thesis, University of South Carolina, Columbia, S. C., 1967.

[10] G. Chioccola and J. J. Daly, *J. Chem. Soc. A*, 1981 (1968).

[11] N. W. Alcock and K. A. Raspin, *ibid.*, 2108 (1968).

[12] R. D. Feltham, *Inorg. Chem.*, 3, 1038 (1964).

more easily (+0.32 V compared to +0.55 V) and rapidly oxidized than the corresponding aquo complex. The band which causes the blue color is at shorter wavelength for the ammine (585 nm compared to 605 nm). Incomplete studies of a series of blue ruthenium chloride complexes suggest that there is a good correlation between the basicity of the terminal ligands and the wavelength of the maximum of this band. The nature of this transition is not known, but this correlation suggests that it may involve the d electrons which are of π symmetry in octahedral complexes. In the dimeric complexes these electrons are very likely to be involved in metal–metal bonding.

With both the ammine and aquo complexes, oxidation beyond the ruthenium(III) state apparently results in disruption of the coordination sphere. The most striking difference in the two complexes occurs in the reaction leading to their formation. When HCl is added to $Ru(H_2O)_6^{2+}$ no hydrogen is evolved. However, after a few hours a ruthenium mirror is deposited on the walls of the reaction vessel. Apparently this reaction proceeds by a disproportionation, while hydrogen ion is the oxidizing agent in producing $Ru_2Cl_3(NH_3)_6^{2+}$ from hexaammineruthenium(II).

Acknowledgments. The authors express their thanks to the U. S. Atomic Energy Commission for financial support which made this study possible. We also thank Dr. T. J. Meyer for suggesting that the blue chloroammines may be related to the aquo complexes which we were studying.

Asymmetric Catalytic Reduction with Transition Metal Complexes. I. A Catalytic System of Rhodium(I) with (−)-2,3-*O*-Isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane, a New Chiral Diphosphine

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Abstract: The catalytic system (−)-(diop)–Rh(I) (diop = 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (**7**)) is described and is used for an extensive study of the hydrogenation of various precursors of alanine, phenylalanine, tyrosine, Dopa, and leucine. Optical yields in the range of 70–80% are obtained in the reduction of β-substituted α-acetamidoacrylic acids. The presence of a carboxyl group is found not to be absolutely necessary for good optical yield. The favorable effect of the enamide function on the catalytic process is deduced from comparisons of the rates of hydrogenation of atropic and acetamidocinnamic acids, from the optical yields obtained in the reduction of different precursors of phenylalanine, and from the high optical yield (78%) obtained in the hydrogenation of the enamide **12**, a compound having no carboxyl groups.

The use of asymmetric catalytic systems for the preparation of optically active compounds is a promising method, enabling one to avoid the manipulation of large quantities of optically active material (as resolving agents or chiral reactants). Several reports of asymmetric heterogeneous catalysis have appeared in the literature.[1,2] The best optical yield, about 50%, was obtained in the reduction of ethyl acetoacetate using Raney Nickel modified by (+)-2-metyltartaric acid; the results, however, are difficult to reproduce.[2]

A more rational approach to the problem of asymmetric synthesis consists in the use of transition-metal complexes as homogeneous catalysts, for steric and electronic effects can be introduced by modification of the ligands in the complex. Our requirements for a catalyst system applicable to a wide range of substrates and having a fairly well-known mechanism lead us to investigate the homogeneous catalytic reduction of olefins using rhodium complexes with phosphines as ligands.[3–5] Wilkinson has extensively studied this system, using the catalyst precursor $[P(C_6H_5)_3]_3RhCl$, and has proposed[3] a mechanism involving the catalytic species **1** (L = $P(C_6H_5)_3$). Internal hydrogen transfer onto the olefinic double bond gives rise to the alkane. The transfer is stereospecific (cis addition) but is a stepwise mechanism passing through an alkyl–rhodium complex.[6,7]

One can make the observation that the rhodium atom is asymmetric in **1**, **1a** and **1b** being enantiomers. In the general case where ligands around the rhodium atom are achiral, there is necessarily hydrogen transfer

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