repeated attempts were made to grow larger ones. Crystallographic data from single-crystal studies are given in Table II for those compounds for which suitable crystals could be grown. From these data it is seen that no higher symmetry for the chelated Eu than S_2 or C_2 is required by any of these crystal structures, although a higher symmetry is not ruled out. The important question of whether the water and/or the DMF is involved in the coordination sphere of the Eu ion or is just a "lattice" molecule must await crystal structure determinations.

In summary, our results show that the differences in the fluorescence spectra can be attributed to the different crystal structures and presumably different Eu environments caused by the presence of H_2O or DMF and that it is not necessary to assume the existence of stereoisomers. They also serve to emphasize the point made by previous authors regarding the necessity of careful chemical identification of the species from which interpretations of the spectra are to be made.

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Syntheses of *cis*- and *trans*-Tetraamminebis(pyridine)ruthenium(II). High Stereospecificity in Ruthenium(II) Substitution Reactions

By Peter C. Ford[1] and Chris Sutton

Recent efforts in this laboratory have been directed toward elucidation of substitution mechanisms in ruthenium(II)–ammine complexes. In the course of this work, it became necessary to distinguish between the stereochemical isomers of tetraammineruthenium complexes, $Ru^{II}(NH_3)_4X_2$ (A), where X is either H_2O or Cl^-. Reaction of either *cis*-A or *trans*-A with excess pyridine gives a single isomer of $Ru(NH_3)_4(py)_2{}^{2+}$ in each case, presumably identical in stereochemistry with the initial complex. The two ions $Ru(NH_3)_4(py)_2{}^{2+}$ thus prepared are distinguished by differences in their cation-exchange elution behavior and by differences in the position, shape, and intensity of absorption bands in the visible spectrum.

Experimental Section

All reactions were carried out at ambient temperature unless otherwise noted.

trans- and *cis*-[Ru(NH₃)₄(py)₂][ClO₄]₂.—Synthesis was accomplished from the respective dichlorotetraammineruthenium(III) salt by a procedure analogous to one used to prepare pentaammineruthenium(II) complexes of aromatic heterocycles from [Ru(NH₃)₅Cl]Cl₂.[2] *trans*-[Ru(NH₃)₄Cl₂]Cl[3] (0.063 g, 2.3×10^{-4}

(1) Author to whom inquiries should be addressed.
(2) P. Ford, De F. P. Rudd, R. Gaunder, and H. Taube, *J. Am. Chem. Soc.*, **90**, 1187 (1968).
(3) K. Gleu and W. Breuel, *Z. Anorg. Allgem. Chem.*, **237**, 197 (1938).

mol) was dissolved in 5 ml of pyridine hydrochloride buffer ([py] $\approx$ 1 M) and deaerated with a stream of purified argon. Granular amalgamated zinc (0.5 g) was added, and after stirring for 20 min, the resulting yellow solution was filtered. Addition of sodium perchlorate gave 0.099 g (82% crude yield) of [Ru(NH₃)₄-(py)₂][ClO₄]₂. Recrystallization from aqueous methanol gave 0.067 g (56% over-all yield) of the yellow salt. *Anal.* Calcd for RuC₁₀H₂₂O₈N₆Cl₂: C, 22.8; H, 4.2; N, 16.0. Found: C, 22.9; H, 4.5; N, 16.2.

A similar procedure starting with *cis*-[Ru(NH₃)₄Cl₂]Cl[3] (0.103 g, 3.7×10^{-4} mol) gave the crystalline yellow solid *cis*-[Ru(NH₃)₄-(py)₂][ClO₄]₂ (0.065 g, 33% yield when recrystallized). *Anal.* Calcd for RuC₁₀H₂₂O₈N₆Cl₂: C, 22.8; H, 4.2; N, 16.0. Found: C, 22.5; H, 4.4; N, 16.6. Analyses of this compound gave poor reproducibility owing to consistent detonation during combustion.

Cation-Exchange Analysis of Reaction Mixtures.—Reaction mixtures containing $Ru(NH_3)_4(py)_2{}^{2+}$ and other species generated by one of the procedures described below were quenched with acidic hydrogen peroxide and then were eluted from a cation-exchange resin column (11.5-cm length, Biorad AG5OW-X2), with acidic sodium chloride solution (pH 1). Sodium ion concentration in the eluent was gradually increased from an initial 0.3 M to a final 3.3 M. Aliquots of 10 ml each were collected and their uv spectra were recorded. This procedure was tested with a solution of the known ion $Ru(NH_3)_5py^{2+}$. Oxidation with acidic H_2O_2 followed by cation exchange leads to separation of an elution band containing a quantitative yield of the known Ru(III) analog,[2] $Ru(NH_3)_5py^{3+}$. The ions *cis*- and *trans*-$Ru(NH_3)_4$-$py_2{}^{3+}$ were the only +3 ruthenium species detected in mixtures from methods A and B. These eluted at the approximate sodium ion concentrations 2.2 and 2.5 M, respectively, and were cleanly separated on the column from other reaction components and from each other. The separation of $Ru(NH_3)_5py^{3+}$ from *cis*-$Ru(NH_3)_4(py)_2{}^{3+}$ in the elution of products from method C is poor. However, an estimate of the percentage of each can be made because of spectra differences.

The three methods used to generate $Ru(NH_3)_4(py)_2{}^{2+}$ solutions for analysis by ion exchange follow. (A) A 3.2-mg (1.2×10^{-5} mol) sample of either *cis*- or *trans*-[Ru(NH₃)₄Cl₂]Cl was dissolved in 10 ml of pyridine hydrochloride buffer solution ([py] ≈ 1 M) and the solution was deaerated with purified argon. Amalgamated zinc (0.5 g) was added, and the reaction mixture was stirred in the dark for 30 min and then quenched. (B) A 3.2-mg (1.2×10^{-5} mol) sample of either *cis*- or *trans*-[Ru(NH₃)₄Cl₂]Cl was dissolved in 10 ml of the pyridine buffer and the solution was deaerated. To this solution was added *via* syringe techniques 1.0 ml of Cr(II) solution ([Cr(II)] = 0.019 M), and the reaction mixture was stirred in the dark for 30 min and then quenched. (C) A 5.3-mg sample of [Ru(NH₃)₅py][ClO₄]₂ was dissolved in 10 ml of the pyridine buffer solution and deaerated. Zinc (0.5 g) was added, and the solution was stirred in the dark for 2.5 hr at 60° and then quenched.

Results and Discussion

Amalgamated zinc reduction of *trans*-[Ru(NH₃)₄-Cl₂]Cl in pyridine buffer gives a bright yellow solution from which can be isolated [Ru(NH₃)₄(py)₂][ClO₄]₂. The solution spectrum of this material has an intense absorption band centered at 423 nm. Similar treatment of *cis*-[Ru(NH₃)₄Cl₂]Cl gives a solid with the correct analysis for [Ru(NH₃)₄(py)₂][ClO₄]₂ but with a different spectrum (λ_{max} 410 nm, shoulder at 375 nm; see Table I). Oxidation of either product followed by elution from a cation-exchange column gave a single ruthenium(III) component. An equal mixture of the two submitted to the same treatment elutes as two cleanly separated bands suggesting that the products of the syntheses are stereochemically pure and have

TABLE I

SPECTRA OF TETRAAMMINEBIS(PYRIDINE)RUTHENIUM COMPLEX IONS[a]

Complex ion	λ_{max}, nm (log ϵ)
cis-Ru(NH$_3$)$_4$(py)$_2^{2+}$	410 (3.90), 375 sh (3.81), 245 (3.86)
cis-Ru(NH$_3$)$_4$(py)$_2^{3+}$	261 (3.84), 254 (3.86), 250 (3.86)
trans-Ru(NH$_3$)$_4$(py)$_2^{2+}$	423 (4.22), 245 (3.93)
trans-Ru(NH$_3$)$_4$(py)$_2^{3+}$	267 (3.94), 261 (3.98), 256 (3.97)

[a] Ru(III) spectra were obtained from elution aliquots. Reproducible ϵ's were determined by reduction to the Ru(II) analog followed by comparison of absorption band intensities between the initial Ru(III) species and the Ru(II) species for which ϵ's were determined by direct techniques.

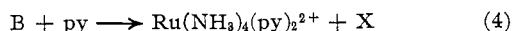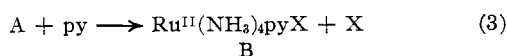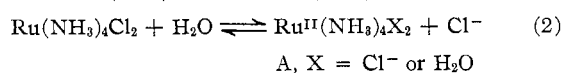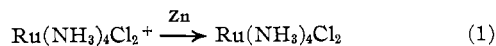configurations identical with those of the starting materials.

Yields of the perchlorate salts in neither case were quantitative, and a small percentage of the other isomer, if produced in the synthesis, could have been removed by recrystallization. To explore this possibility, the entire reaction mixture from the zinc reduction of each dichloro isomer in pyridine buffer was analyzed by cation exchange. High yields of the corresponding tetraamminebispyridine complexes were the rule, and these proved to be stereochemically pure in each case (Table II). On the basis of ion-exchange experiments involving isomer mixtures, we estimate that no more than 2% of one would go undetected in the elution of a mixture largely of the other. The only other ruthenium species identified in the elution were traces of the monopyridine complex Ru(NH$_3$)$_4$pyCl^{2+} and of starting material Ru(NH$_3$)$_4$Cl$_2^+$.

TABLE II

Ru(NH$_3$)$_4$(py)$_2^{2+}$ STEREOCHEMISTRY IN SYNTHESIS MIXTURE

Starting material	Method[a]	Yield,[b] %	% *cis*[c]	% *trans*[c]
cis-[Ru(NH$_3$)$_4$Cl$_2$]Cl	A	95	>98	...
trans-[Ru(NH$_3$)$_4$Cl$_2$]Cl	A	85	...	>98
cis-[Ru(NH$_3$)$_4$Cl$_2$]Cl	B	95	>98	...
trans-[Ru(NH$_3$)$_4$Cl$_2$]Cl	B	86	...	>98
[Ru(NH$_3$)$_5$py][ClO$_4$]$_2$	C	~80	~70	~30

[a] See Experimental Section. [b] Total Ru(NH$_3$)$_4$(py)$_2^{3+}$ separated by ion exchange. [c] Per cent of total Ru(NH$_3$)$_4$(py)$_2^{2+}$ analyzed by ion exchange.

The synthesis might be envisioned to involve the reactions

$$\text{Ru(NH}_3)_4\text{Cl}_2^+ \xrightarrow{\text{Zn}} \text{Ru(NH}_3)_4\text{Cl}_2 \qquad (1)$$

$$\text{Ru(NH}_3)_4\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{Ru}^{II}(\text{NH}_3)_4\text{X}_2 + \text{Cl}^- \qquad (2)$$
$$\text{A, X} = \text{Cl}^- \text{ or H}_2\text{O}$$

$$\text{A} + \text{py} \longrightarrow \underset{\text{B}}{\text{Ru}^{II}(\text{NH}_3)_4\text{pyX}} + \text{X} \qquad (3)$$

$$\text{B} + \text{py} \longrightarrow \text{Ru(NH}_3)_4(\text{py})_2^{2+} + \text{X} \qquad (4)$$

Unlike chloride ligands in chloroammineruthenium(III) complexes, chloro- and aquoruthenium(II) ligands are quite labile as demonstrated by rapid formation of Ru(NH$_3$)$_5$py^{2+} on addition of pyridine to a solution of Ru(NH$_3$)$_5$H$_2$O^{2+} (generated by Ru(NH$_3$)$_5$Cl^{2+} reduction).[2] Given the high stereospecificity of the Ru(NH$_3$)$_4$(py)$_2^{2+}$ syntheses, both reactions 3 and 4 as well as

any prior equilibrium (eq 2) must take place with retention of configuration.

Retention also appears to be the rule for aquation of the rhodium(III) complexes,[4] RhA$_4$Y$_2^+$, and the ruthenium(III) complexes,[5] RuA$_4$Y$_2^+$ (A = NH$_3$ or (en)$_{0.5}$; Y$^-$ = Cl$^-$, Br$^-$, or I$^-$). In the only ruthenium(II) case for which stereochemical information has been previously reported,[6] anion substitution for pyridine in the complex ion *cis*-Ru(phen)$_2$(py)$_2^{2+}$ (phen = 1,10-*o*-phenanthroline) gives *cis*-Ru(phen)$_2$pyY$^+$. However, in contrast to the present case, none of these reactions is rapid at room temperature.

Retention of configuration in octahedral substitutions is consistent either with a dissociative pathway *via* an intermediate maintaining the other ligands in a square pyramid[7] or with associative or interchange mechanisms occurring by *cis* attack.[4] Dissociation leading to trigonal-bipyramidal intermediates is expected to result in isomerization for at least one of the isomers and therefore appears less likely.

The chromous reduction of Ru(NH$_3$)$_5$Cl^{2+} occurs by an inner-sphere path leading to the formation of CrCl^{2+}-(aq) and Ru(NH$_3$)$_5$H$_2$O^{2+}.[8,9] The favored inner-sphere path would give intermediate C (eq 5) on Cr(II) reduc-

$$\text{Cr(aq)}^{2+} + \text{Ru(NH}_3)_4\text{Cl}_2^+ \longrightarrow$$
$$\underset{\text{C}}{[(\text{H}_2\text{O})_5\text{CrCl-Ru(NH}_3)_4\text{Cl}]^{3+}} \qquad (5)$$

tion of Ru(NH$_3$)$_4$Cl$_2^+$. The analogous intermediate from chromous reduction of Ru(NH$_3$)$_5$Cl^{2+} decomposes too rapidly to be observed by flow techniques.[9] Consequently, loss of Cr(H$_2$O)$_5$Cl^{2+} from a Ru(II) coordination site in C should be fast and might be expected to generate a pentacoordinate Ru(II) intermediate as the bulk of this leaving group makes concerted *cis* attack improbable. Nonetheless, the Cu(II) reduction of neither *cis*- nor *trans*-Ru(NH$_3$)$_4$Cl$_2^+$ in pyridine buffer is accompanied by any rearrangement as determined from isomer ratios of the Ru(NH$_3$)$_4$(py)$_2^{2+}$ products (Table II).

The complex ion Ru(NH$_3$)$_4$(py)$_2^{2+}$ has been prepared previously; however, no spectral or stereochemical information has been published. Allen and coworkers[10] obtained Ru(NH$_3$)$_4$(py)$_2$I$_2$ by heating the nitrogen complex [Ru(NH$_3$)$_5$N$_2$]I$_2$ in an aqueous pyridine solution. Rudd[11] has isolated [Ru(NH$_3$)$_4$(py)$_2$][ClO$_4$]$_2$ from the reaction of [Ru(NH$_3$)$_5$Cl][CF$_3$CO$_2$]$_2$, pyridine, and zinc in refluxing methanol for 4 hr. Duplication of Rudd's procedure in this laboratory gave a mixture of both isomers. Since it is probable that both syntheses occur by initial formation of Ru(NH$_3$)$_5$py^{2+}, we have analyzed the products of the thermal reaction between Ru(NH$_3$)$_5$-py^{2+} and pyridine (method C, Experimental Section).

(4) S. A. Johnson, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 1741 (1963).

(5) J. A. Broomhead and L. Kane-Maguire, *Inorg. Chem.*, **7**, 2519 (1968).

(6) B. Bosnich and F. P. Dwyer, *Australian J. Chem.*, **19**, 2235 (1966).

(7) D. A. Buckingham, I. I. Olsen, A. M. Sargeson, and H. Satropa, *Inorg. Chem.*, **6**, 1027 (1967); D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *Australian J. Chem.*, **20**, 597 (1967).

(8) J. F. Endicott and H. Taube, *Inorg. Chem.*, **4**, 437 (1965).

(9) J. Stritar, Ph.D. Thesis, Stanford University, 1967.

(10) A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalau, and C. V. Senoff, *J. Am. Chem. Soc.*, **89**, 5595 (1967).

(11) De F. P. Rudd, private communication.

Ion exchange shows that the resulting $Ru(NH_3)_4(py)_2{}^{2+}$ is about 70% *cis*. However, column separation of the *cis* isomer and starting material was incomplete, and further interpretation of this result should await data refinement.

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The Effect of Steric Hindrance on the Bonding Mode of the Cyanate Ion in Palladium(II) Complexes

BY JOHN L. BURMEISTER AND NICHOLAS J. DESTEFANO

The sensitivity of the bonding modes of the thiocyanate and selenocyanate ions to the steric hindrance created by both coordinated and noncoordinated groups has recently been demonstrated.[1-5] The X- → N-bonded isomerization observed[2-5] for solutions of $[Pd(Et_4dien)XCN]^+$ (Et_4dien = 1,1,7,7-tetraethyl-diethylenetriamine; X = S, Se) has been explained in terms of the decreased interaction between the XCN^- ions and the ethyl groups of the triamine resulting from the switch to the smaller nitrogen donor atom and, concurrently, the switch from a nonlinear Pd–XCN to a linear Pd–NCX linkage. It should be noted that the parent $Pd(XCN)_4{}^{2-}$ and the sterically unhindered $Pd(dien)XCN^+$ complexes are stable X-bonded species. The N- → X-bonded reisomerization observed[4,5] in the solid state when the $Pd(Et_4dien)NCX^+$ ions are precipitated using a large counterion, *i.e.*, $B(C_6H_5)_4{}^-$, has been rationalized in terms of the steric interaction between the large X atoms and the counterion since $[Pd(Et_4dien)NCS]SCN$ is stable[2] with respect to isomerization in the solid state. It was therefore of considerable interest to ascertain whether the bonding mode of the cyanate ion (X = O) would prove to be sensitive to either of these effects, since, in this case, the angular requirements of the Pd–OCN and Pd–NCO linkages would also be expected to be different, whereas the radii of the two donor atoms are comparable.

Experimental Section

Preparation of Compounds. $[Pd(Et_4dien)NCO][B(C_6H_5)_4]$. Method A.—To a slurry of 5.0 mmol (0.89 g) of palladium(II)

(1) F. Basolo, W. H. Baddley, and J. L. Burmeister, *Inorg. Chem.*, **3**, 1202 (1964).

(2) F. Basolo, W. H. Baddley, and K. J. Weidenbaum, *J. Am. Chem. Soc.*, **88**, 1576 (1966).

(3) J. L. Burmeister and H. J. Gysling, *Chem. Commun.*, 543 (1967).

(4) J. L. Burmeister and J. C. Lim, *ibid.*, 1346 (1968).

(5) J. L. Burmeister, H. J. Gysling, and J. C. Lim, *J. Am. Chem. Soc.*, **91**, (1969).

chloride in 200 ml of Spectrograde methanol was added 10 mmol each of silver cyanate (1.5 g) and sodium cyanate (0.65 g). The resulting mixture was stirred for 1.5 hr at room temperature and then filtered to remove the precipitated silver chloride and any unreacted solids. Three milliliters of 1,1,7,7-tetraethyl-diethylenetriamine (Et_4dien) was added to the blood red filtrate, and the resulting solution was stirred for 1 hr at room temperature and then filtered into a solution of 5 mmol (1.75 g) of sodium tetraphenylborate dissolved in a minimum amount of methanol. The solution became cloudy after stirring for 15 min, and an off-white solid, identified as silver tetraphenylborate, was removed by filtration. *Anal.* Calcd for $AgBC_{24}H_{20}$: C, 67.4; H, 4.72; N, 0.00. Found: C, 66.93; H, 5.04; N, 0.06. The orange filtrate was allowed to stand overnight at 0°, but no crystallization of the product occurred. The volume of the solution was then reduced under a stream of dry nitrogen until a light yellow solid began to form. The solution was cooled to 0° and the product was isolated by filtration and dried *in vacuo* over calcium chloride. Several additional fractions were collected in this manner, but some were contaminated with silver tetraphenylborate. As a result, only the initial precipitate was further characterized; yield 26%; mp 154–157° dec. *Anal.* Calcd for $BC_{37}H_{49}N_4OPd$: C, 65.00; H, 7.17; N, 8.19. Found: C, 65.09; H, 7.36; N, 8.29.

Method B.—To a solution of 8.0 mmol (3.5 g) of tetraphenylarsonium cyanate dihydrate, prepared according to the method of Norbury and Sinha,[6] in 125 ml of Spectrograde acetone was added 1.0 mmol (0.18 g) of palladium(II) chloride. The mixture was stirred for 6 hr at room temperature and 2 hr at reflux temperature. After cooling the mixture to room temperature, it was filtered to remove any unreacted starting material and decomposition products. To the golden yellow filtrate was added 8.0 mmol (2.75 g) of sodium tetraphenylborate, dissolved in a minimum amount of acetone. The mixed precipitate of $[(C_6H_5)_4As][B(C_6H_5)_4]$, $NaNCO$, and $NaCl$ which formed was removed by filtration. To the filtrate was added 0.6 ml of Et_4dien and, after the solution had been stirred for 15 min, 1 mmol (0.34 g) of sodium tetraphenylborate. The solution was filtered to remove the sodium cyanate precipitate, and the volume of the filtrate was reduced to *ca.* 10 ml under a stream of dry nitrogen. The yellow crystals which formed were isolated by filtration, washed with ethyl ether, and dried *in vacuo* over calcium sulfate; yield 60%; mp 155–157° dec. *Anal.* Found: C, 65.47; H, 7.25; N, 8.06.

Method C.—A solution of 2.1 mmol (0.35 g) of silver nitrate in 5 ml of water was added, with vigorous stirring, to a suspension of 1.0 mmol (0.39 g) of $[Pd(Et_4dien)Cl]Cl$, prepared according to the method of Baddley and Basolo,[7] in 50 ml of water. A white precipitate formed immediately. The solution was maintained at 40–50° for 1 hr, with continued stirring, and then cooled to 0° and filtered. A solution of 1.1 mmol (0.071 g) of sodium cyanate in 5 ml of water was added to the pale yellow filtrate, and the resulting solution was stirred for 45 min. Half of the solution was filtered into a solution containing 0.5 mmol of sodium tetraphenylborate in 10 ml of acetone. A heavy, cream-colored precipitate formed immediately which, on stirring, became more flocculent. A light yellow solid was isolated by filtration, washed with ethyl ether, and dried *in vacuo* over calcium sulfate; yield 88%; mp 154–157° dec. *Anal.* Found: C, 64.91; H, 7.39; N, 7.82.

The remaining half of the reaction mixture was treated in an identical manner, except for the fact that the sodium tetraphenylborate was dissolved in 20 ml of 50% (v/v) acetone–water. A larger yield of 98% resulted; mp 156–158° dec. *Anal.* Found: C, 65.24; H, 7.35; N, 7.77.

$[Pd(dien)NCO][B(C_6H_5)_4]$.—A solution of 4.1 mmol (0.69 g) of silver nitrate in 5 ml of water was added, with stirring, to a suspension of 2.0 mmol (0.93 g) of $[Pd(dien)I]I$ (dien = diethylenetriamine), prepared according to the method of Basolo,

(6) A. H. Norbury and A. I. P. Sinha, *J. Chem. Soc., A*, 1598 (1968).

(7) W. H. Baddley and F. Basolo, *J. Am. Chem. Soc.*, **88**, 2944 (1966).