1. It strongly supports the suggested rationalization of the σ^p values, since deviations from the expected slope, $32\ \mu_B{}^2\mu_0/4\pi$, are within 10%. This finding is highly satisfactory in the sense that it is an independent demonstration of the nephelauxetic effect in transition-metal complexes. In fact, by calculating the circulation removing ratio from paramagnetic shielding on the basis of eq 1, we are able to gain insight into the nephelauxetic effect of complexes for which β_{35} is not known.

Registry No. $[V(CO)_6]^-$, 20644-87-5; $[Fe(CN)_6]^{4-}$, 13408-63-4; $[Co(OH_2)_6]^{3+}$, 15275-05-5; $[Co(NH_3)_6]^{3+}$, 14695-95-5; $[Co(CN)_6]^{3-}$, 14897-04-2; $[Rh(OH_2)_6]^{3+}$, 16920-31-3; $[RhCl_6]^{3-}$, 21412-00-0; $[RhBr_6]^{3-}$, 30211-18-8; $[PtF_6]^{2-}$, 16871-53-7; $[PtCl_6]^{2-}$, 16871-54-8.

Contribution from the Department of Chemistry,
University of Hong Kong, Pokfulam Road, Hong Kong

Ruthenium(III) Tertiary Amine Complexes

Chi-Ming Che,* Si-San Kwong, and Chung-Kwong Poon*

Received July 19, 1984

The chemistry of ruthenium(III) amine complexes has continued to be an active area of research in our laboratories.[1] Though the synthetic chemistry of ruthenium(III) complexes with primary and secondary amines has been well developed, their redox chemistry is usually complicated by oxidative dehydrogenation of the coordinated amines.[2] We have recently found that high-valent ruthenium(IV) and -(VI) oxo species could be prepared from complexes containing saturated tertiary amines.[3,4] Here, the synthesis and characterization of a class of ruthenium(III) complexes containing bidentate and macrocyclic tertiary amines are described. Our findings indicated that these tertiary amines, upon coordination to ruthenium, are particularly stable under drastic oxidizing conditions.

Experimental Section

Materials. $K_2[RuCl_5H_2O]$ (Johnson and Matthey) and 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (TMC) (Strem) were used as supplied. All solvents used were of analytical grade and *N,N,N′,N′*-tetramethyl-1,2-diaminoethane (TMEA) was distilled and stored over KOH before use.

***trans*-[Ru(TMC)Cl$_2$]Y (Y = Cl, ClO$_4$).** The chloride salt was prepared by suspending $K_2[RuCl_5H_2O]$ in absolute ethanol (1 g in 150 cm^3), and the suspension was heated under reflux and with vigorous stirring for about 15 min. An ethanolic solution of TMC (0.8 g in 200 cm^3) was added dropwise to the refluxing suspension, and the process took about 5 h for completion. After being further heated under reflux overnight, the solution was filtered while hot and the filtrate was evaporated to dryness. The residue was then dissolved in a minimum amount of hot HCl (3 mol dm^{-3}). Upon cooling, yellow crystals of *trans*-$[Ru(TMC)Cl_2]Cl$ deposited. As *trans*-$[Ru(TMC)Cl_2]^+$ has been found to be very substitutionally labile,[5] *trans*-$[Ru(TMC)Cl_2]ClO_4$ was obtained by the metathesis of *trans*-$[Ru(TMC)Cl_2]Cl$ with $NaClO_4$ in HCl (2 mol dm^{-3}), which helps to suppress the hydrolysis of the Cl^- ligands. Overall yield of the reaction ranges from 20% to 40%. Anal. Calcd for $[Ru(TMC)Cl_2]ClO_4$: C, 31.8; H, 6.1; N, 10.6; Cl, 20.2. Found: C, 31.7; H, 6.0; N, 10.3; Cl, 20.2. $E_f°$ (V vs. NHE) = 0.140 in HCl (2 mol dm^{-3}).

***trans*-[Ru(TMEA)$_2$Cl$_2$]Y (Y = Cl, ClO$_4$).** These complexes were prepared by essentially the same method as that described for *trans*-$[Ru(TMC)Cl_2]ClO_4$ except that TMEA and methanol were used instead. After the methanolic suspension of $K_2[RuCl_5H_2O]$ was refluxed with TMEA overnight, a bluish green solution was obtained. This was filtered, and the filtrate was evaporated to dryness. The crude solid obtained was dissolved in boiling HCl (2 mol dm^{-3}), filtered, and purified through chromatography on a Sephadex C-25 column with HCl (2 mol dm^{-3}) as the eluent. The first band (yellow) was identified as *trans*-$[Ru(TMEA)Cl_2]^+$ by measuring its UV–vis absorption spectrum. The second and third bands were dark blue and red, respectively. No further attempts were made to characterize these species. The first band was collected, and the solution was then rotary evaporated down to ~10 cm^3. On cooling, yellow crystals of *trans*-$[Ru(TMEA)Cl_2]Cl$ deposited. The perchlorate salt was obtained by the metathesis of *trans*-$[Ru(TMEA)Cl_2]Cl$ with $NaClO_4$ in HCl (2 mol dm^{-3}). Overall yield of the reaction ranges from 20% to 30%. Anal. Calcd for $[Ru(TMEA)Cl_2]ClO_4$: C, 28.6; H, 6.3; N, 11.1; Cl, 21.2. Found: C, 28.7; H, 6.0; N, 11.0; Cl, 21.4. $E_f°$ (V vs. NHE) = 0.14 in $NaClO_4$ solution (0.1 mol dm^{-3}).

Table I. Infrared Spectra in the Regions 3500–1300 and 100–600 cm^{-1} of Ruthenium(III) Tertiary Amine Complexes[a]

complex	absorption bands, cm^{-1}
trans-$[Ru(TMC)Cl_2]ClO_4$	990 (m), 970 (w), 960 (s), 945 (w), 910–920 (br, m), 840 (m), 830 (m), 810 (m), 790 (m), 750 (br, m), 720 (w)
trans-$[Ru(TMC)(NCO)_2]ClO_4$	3520 (m), 2240 (vs, br),[b] 1340 (s),[b] 990 (m), 970 (w), 960 (s), 945 (w), 925 (w), 916 (m), 840 (m), 830 (m), 810 (m), 790 (m), 750 (m), 720 (w)
trans-$[Ru(TMC)(NCS)_2]ClO_4$	2020 (vs, br),[c] 985 (m), 970 (w), 960 (s), 940 (w), 915 (m), 860 (w), 840 (m), 810 (m), 790 (m), 750 (m), 740 (w), 720 (w)
trans-$[Ru(TMC)(NCS)Cl]ClO_4$	2020 (vs, br),[c] 985 (m), 960 (br, s), 940 (w), 915 (br, w), 845 (m), 810 (m), 790 (m), 720 (w)
trans-$[Ru(TMEA)_2Cl_2]ClO_4$	946 (s), 915 (w), 800 (m), 770 (m)

[a] Abbreviations: vs, very strong; s, strong; m, medium; w, weak; br, broad. [b] $\nu_{as}(NCO) = 1340\ cm^{-1}$, $\nu_s(NCO) = 2240\ cm^{-1}$. [c] $\nu(C{\equiv}N) = 2020\ cm^{-1}$.

***trans*-[Ru(TMC)(NCS)$_2$]Y (Y = NCS, ClO$_4$).** This was prepared by heating an aqueous solution (50 cm^3) of *trans*-$[Ru(TMC)Cl_2]Cl$ (0.4 g) and NaNCS (4 g) on a steam bath for $^1/_2$ h. A blue-violet crystalline solid of *trans*-$[Ru(TMC)(NCS)_2]NCS$ came out on cooling. *trans*-$[Ru(TMC)(NCS)_2]ClO_4$ was obtained by metathesis of *trans*-$[Ru(TMC)(NCS)_2]NCS$ with $NaClO_4$ in water; overall yield >70%. Anal. Calcd for $[Ru(TMC)(NCS)_2]NCS$: C, 38.4; H, 6.0; N, 18.4; S, 18.1. Found: C, 38.5; H, 6.2; N, 18.2; S, 18.4. IR: $\nu(C{\equiv}N)$ 2020 cm^{-1} (Nujol mull). $E_f°$ (V vs. NHE) = 0.42 in $HClO_4$ (0.1 mol dm^{-3}).

***trans*-[Ru(TMC)(NCS)Cl]Y (Y = PF$_6$, ClO$_4$).** This was prepared by heating an ethanolic solution of *trans*-$[Ru(TMC)Cl_2]Cl$ (0.3 g in 50 cm^3) and NaNCS (2 g) on a steam bath. The course of the reaction was followed by monitoring the UV–vis spectral changes. When the peak at 370 nm disappeared and the peak at ~520 nm developed,[6] excess $LiClO_4$ was added to the solution mixture. The violet-red precipitate obtained was filtered off and was purified by chromatography on a Sephadex C-25 column with HCl (0.1 mol dm^{-3}) as the eluent. Three bands were observed. The first and the last band were *trans*-$[Ru(TMC)(NCS)_2]^+$ and *trans*-$[Ru(TMC)Cl_2]^+$, respectively, whereas the middle one (major portion) was *trans*-$[Ru(TMC)(NCS)Cl]^+$. The middle portion was preconcentrated down to ~15 cm^3, and upon addition of $NaClO_4$, *trans*-$[Ru(TMC)(NCS)Cl]ClO_4$ was precipitated out. This was purified by rechromatography on a Sephadex C-25 column; yield ~60%. The PF_6^- salt was obtained by metathesis of *trans*-$[Ru(TMC)(NCS)Cl]ClO_4$ and $NaPF_6$ in HCl (0.1 mol dm^{-3}). Anal. Calcd for $[Ru(TMC)(NCS)Cl]PF_6$: C, 30.2; H, 5.4; N, 11.8; Cl, 6.0. Found: C, 30.1; H, 5.4; N, 11.9; Cl, 6.2. IR: $\nu(C{\equiv}N)$ 2020 cm^{-1} (Nujol mull). $E_f°$ (V vs. NHE) = 0.24 in $HClO_4$ (0.1 mol dm^{-3}).

***trans*-[Ru(TMC)(NCO)$_2$]ClO$_4$.** *trans*-$[Ru(TMC)(NCS)_2]NCS$ (0.4 g) and 30% H_2O_2 (2 cm^3) in H_2O (50 ml) was heated on a steam bath with continuous stirring. When the color of the solution changed from blue to yellow, the solution was ice cooled and filtered, if necessary. Upon addition of excess $NaClO_4$, yellow solid of *trans*-$[Ru(TMC)(NCO)_2]ClO_4$ was precipitated out. This was filtered off, washed with ice-cooled water, and dried under vacuum at room temperature; overall yield >70%. Anal. Calcd for $[Ru(TMC)(NCO)_2]ClO_4$: C, 35.5; H, 5.9; N, 15.5; Cl,

---

(1) Poon, C. K.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1980**, 756–762.
(2) Poon, C. K.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1981**, 1919–1923.
(3) Che, C. M.; Tang, T. W.; Poon, C. K. *J. Chem. Soc., Chem. Commun.* **1984**, 641–642.
(4) Che, C. M.; Wong, K. Y.; Poon, C. K., results to be submitted for publication.
(5) Kwong, S. S., unpublished work.
(6) The ratio of the absorbance at 520 nm to that at 370 nm is 3:1.

0020-1669/85/1324-1601$01.50/0

Table II. UV-Vis Absorption Spectra of Some Ruthenium(III) Amine Complexes

complex	solvent (concn, mol dm^{-3})	λ_{max}, nm (ϵ_{max}, cm^{-1} dm^3 mol^{-1})[a]
trans-[Ru(TMEA)Cl_2]ClO_4	HCl (1)	367 (3100), 308 (1540)
trans-[Ru(en)$_2Cl_2$]ClO_4[b]	HCl (0.1)	343 (3850), 292 (br) (800), 272 (br) (900)
trans-[Ru(cyclam)Cl_2]Cl[b]	HCl (0.1)	357 (2260), 312 (1250)
trans-[Ru(TMC)Cl_2]ClO_4	HCl (0.1)	370 (2340), 315 (805)
trans-[Ru(TMC)(NCS)$_2$]NCS	H_2O	594 (124 000), 488 (b sh) (1130)
trans-[Ru(TMC)(NCS)Cl]PF_6	HCl (0.1)	510 (3900), 360 (br) (1300)
trans-[Ru(TMC)(NCO)$_2$]ClO_4	H_2O	384 (7040), ~350 (b sh) (2740), 272 (br) (900)
trans-[Ru(cyclam)(NCS)$_2$]$ClO_4\cdot H_2O$[c]	Me_2SO	558 (7350), ~485 (sh) (940), 378 (br) (2310), ~340 (br) (1700)
trans-[Ru(en)$_2$(NCS)$_2$]ClO_4[c]	H_2O	529 (10 933), 446 (sh) (1470), 328 (920)
cis-[Ru(en)$_2Cl_2$]Cl[d]	HCl (1)	354 (1750), 314 (1420), 269 (900)
cis-[Ru(cyclam)Cl_2]Cl[e]	HCl (1)	380 (br) (1070), 336 (1480), 276 (br) (950)

[a] Abbreviations: br, broad; sh, shoulder; b sh, broad shoulder. [b] Poon, C. K.; Che, C. M. *J. Chem. Soc., Dalton Trans.* 1980, 756–762. Abbreviations: en, 1,2-diaminoethane; cyclam, 1,4,8,11-tetraazacyclotetradecane. [c] Che, C. M. Ph.D. Thesis, University of Hong Kong, 1982. [d] Broomhead, J. A.; Kane-Maguire, L. A. P. *J. Chem. Soc. A* 1967, 546–553. [e] Poon, C. K.; Che, C. M. *J. Chem. Soc., Dalton Trans.* 1981, 1336–1341.

6.6, S, 0.0. Found: C, 35.4; H, 6.0; N, 15.3; Cl, 6.6; S, <1.0. IR: ν_a(NCO) 2240, ν_s(NCO) 1340 cm^{-1} (Nujol mull). $E_f°$ (V vs. NHE) = 0.085 in *p*-toluenesulfonic acid (0.1 mol dm^{-3}).

Physical Measurements. Elemental analyses of the newly prepared compounds were performed by Australian Microanalytical Service Unit. Infrared spectra were measured in Nujol mulls on a Perkin-Elmer 577 spectrophotometer (4000–200 cm^{-1}), and the results were tabulated in Table I. Electronic absorption spectra of freshly prepared solutions were measured with a Beckman Acta CIII spectrophotometer, and the results were tabulated in Table II. Formal redox potentials, $E_f°$, were obtained by cyclic voltammetry with Princeton Applied Research (PAR) instruments: Model 175 Universal Programmer and Model 173 potentiostat-galvanostat. A pyrolytic graphite electrode was used as the working electrode.

Results and Discussion

The controlled dropwise addition method[1] that has previously been employed for the synthesis of ruthenium(III) primary and secondary amine species is also applicable here, though the yield of the reaction is comparatively low. It is quite likely that tertiary amine ligands, being more basic than primary or secondary amines, might enhance the base hydrolysis of $K_2[RuCl_5H_2O]$ and complicate the synthesis of ruthenium(III) amine species.[1] Attempts to prepare *cis*- and *trans*-$[RuA_4Cl_2]^+$ species (A = monodentate tertiary amine) from the reactions of A with $K_2[RuCl_5H_2O]$ or $Ru(ox)_3^{3-1}$ (ox = $C_2O_4^{2-}$) were unsuccessful. It has been found that $Ru(ox)_3^{3-}$ is unreactive toward TMEA or TMC.

All the prepared ruthenium(III) complexes exhibited one band upon chromatography on a Sephadex C-25 column with HCl (0.1 mol dm^{-3}) as the eluent. Although Isied has reported that reaction of $K_2[RuCl_5H_2O]$ with cyclam (1,4,8,11-tetraazacyclotetradecane) may produce cis ruthenium(III) tetraamine species,[7] we found no evidence for the formation of any cis complexes from the reaction of $K_2[RuCl_5H_2O]$ with TMC or TMEA. The similarities of UV–vis absorption spectra of *trans*-$[Ru(TMC)Cl_2]^+$ and *trans*-$[Ru(TMEA)_2Cl_2]^+$ complexes with that of the previously reported *trans*-dihalotetraamineruthenium(III) species[8] suggest a trans configuration for these newly prepared ruthenium(III) tertiary amine species. The assignment has further been supported by the finding that a structurally characterized *trans*-$[Ru^{IV}(TMC)O(CH_3CN)][PF_6]_2$[9] has been synthesized in high yield utilizing *trans*-$[Ru(TMC)Cl_2]^+$ as the starting material. A direct comparison of the UV–vis absorption spectrum of *trans*-$[Ru(TMC)Cl_2]^+$ (or *trans*-$[Ru(TMEA)_2Cl_2]^+$) with that of *trans*-$[Ru(cyclam)Cl_2]^+$ (or *trans*-$[Ru(en)_2Cl_2]^+$) (see Table II) reveals a much larger splitting of the $p_\pi(Cl) \rightarrow d_\pi^*$ transition in the former species. Whether this is due to the tertiary amine nature of the ligands or the expected larger steric repulsive interaction between the p_π(Cl) orbitals and the $-CH_3$ groups of TMC (or TMEA) is still uncertain. It is also not possible to give an exact description about the orientation of the *N*-CH_3 groups in *trans*-$[Ru(TMC)Cl_2]^+$. Perhaps one important aspect in this work is that *trans*-$[Ru^{II}(TMC)Cl_2]^0$ and *trans*-$[Ru(TMC)Cl_2]^+$ have been found to be substitutionally more labile than *trans*-$[Ru^{II}(NH_3)_4Cl_2]^0$ and *trans*-$[Ru(NH_3)_4Cl_2]^+$, respectively,[5] but yet the TMC species have substantially higher redox potentials (~300 mV) than the tetraammine ones. Previously, Taube and his co-workers[11] suggested that for any possible application of mononuclear ruthenium complexes as catalysts for oxygen electrodes the required species must be substitutionally labile (to favor an inner-sphere mechanism) and have a high reduction potential. However, raising the potential simply by replacing ammonia with π acids (as in the previously reported work[12]) will lead to a reduction in the substitutional lability of the ruthenium amine complexes.[12] It is therefore important here to point out that the increasing of steric effects on macrocycles may be important in the future design of ruthenium macrocyclic amine species for oxygen reduction.

Unlike the case of the ruthenium(III) primary and secondary amine complexes, tertiary amines, upon coordination to ruthenium, remain intact under oxidizing conditions. Formation of *trans*-$[Ru(TMC)(NCO)_2]^+$ through H_2O_2 oxidation of *trans*-$[Ru(TMC)(NCS)_2]^+$ indicates that the latter species is a N-bonded thiocyanate species. The *trans*-$[Ru(TMC)(NCO)_2]ClO_4$ species has also been characterized by its IR absorption bands at 2240 and 1340 cm^{-1}, assignable to ν_a(NCO) and ν_s(NCO), as a N-bonded –NCO complex.[13] The UV–vis absorption spectrum of *trans*-$[Ru(TMC)(NCO)_2]^+$ is also very similar to that of the previously reported $Ru(NH_3)_5NCO^{2+}$ species[14] ($p_\pi(NCO) \rightarrow d_\pi^*$ transition, ~340–370 nm). However, unlike $Ru(NH_3)_5NCO^{2+}$, *trans*-$[Ru(TMC)(NCO)_2]^+$ has been found to be very stable in strong acid media. No hydrolysis of the coordinated –NCO group to NH_3 has been detected.

trans-$[Ru(TMC)(NCS)Cl]^+$ has been found to be a versatile reagent for the generation of *trans*-$[Ru(TMC)(NCS)H_2O]^+$. Controlled-potential electrolysis of *trans*-$[Ru(TMC)(NCS)Cl]^+$ at $E_f°$ = –0.1 V vs. NHE in *p*-toluenesulfonic acid (0.1 mol dm^{-3}) would lead to nearly quantitative formation of *trans*-$[Ru^{II}(TMC)(NCS)H_2O]^+$.[15] Work in utilizing this species as an effective reagent for binding to π-aromatic nitrogen heterocycles is now in active progress in our laboratories.

Acknowledgment. We thank the Committee on Research and Conference Grants of the University of Hong Kong for support. Helpful discussions with Dr. T. C. Lau are also gratefully acknowledged.

---

(7) Isied, S. S. *Inorg. Chem.* **1980**, *19*, 911–914.

(8) Poon, C. K.; Lau, T. C.; Che, C. M. *Inorg. Chem.* **1983**, *22*, 3893–3898.

(9) *trans*-$[Ru^{IV}(TMC)O(CH_3CN)][PF_6]_2$ has been characterized by X-ray crystallography: Che, C. M.; Mak, T. C. W. results to be submitted for publication.

(10) Poon, C. K.; Che, C. M. *J. Chem Soc., Dalton Trans.* **1981**, 1336–1341.

(11) Tweedle, M. F.; Taube, H. *Inorg. Chem.* **1982**, *21*, 3361–3371.

(12) Isied, S. S.; Taube, H. *Inorg. Chem.* **1976**, *15*, 3070–3075.

(13) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley: New York, 1978.

(14) Ford, P. C. *Inorg. Chem.* **1971**, *10*, 2153–2158.

(15) Che, C. M.; Wong, K. Y., unpublished work.