to combinations of modes whose direct product includes the t_{1u} and/or t_{2u} irreducible representations of the O_h group.[15] It is important to note that (i) in most vibronic interactions the effective combinations are those which are mixed with the totally symmetric mode transforming as A_{1g},[11,16,17] and that (ii) in general, the vibrational levels in the excited states differ from those of the ground state by approximately[18] ±10–20%. In the specific case of $Co(NH_3)_6^{3+}$, on the other hand, since the electronic transition is to an antibonding orbital, a decrease in the vibrational levels in the excited state is expected. (This point was brought to the author's attention by one of the referees.)

Thus, regarding the NH_3 ligand as one unit, the $Co(NH_3)_6^{3+}$ ion was treated as a seven-body problem. Using the assignments of Shimanouchi and Nakagawa[10] a normal coordinate analysis was performed with different "reasonable" sets of Urey–Bradley force constants.[19] Trends upon change of force constants were studied, and finally the most suitable set of force constants was adopted. (The adopted values were: $K = 1.34$ mdyn/Å, $H = 0.22$ mdyn/Å, and $F = 0.18$ mdyn/Å.) Then, *and only then*, were these used to calculate the frequencies of the isotopic species $Co(ND_3)_6^{3+}$. Table I gives the experimental as well as calculated values, and it can be seen that the agreement is rather good.

TABLE I

CALCULATED AND OBSERVED FREQUENCIES (IN CM^{-1})

Freq[a]	Vibrational mode	$Co(NH_3)_6^{3+}$	$Co(ND_3)_6^{3+}$	Absolute isotopic shifts
$\tilde{\nu}_1(a_{1g})$	Co–N str	454	418	36
$\tilde{\nu}_2(e_g)$	Co–N str	383	352	31
$\tilde{\nu}_3(t_{1u})$	Co–N str	504 (503)	482	22
$\tilde{\nu}_4(t_{1u})$	N–Co–N def	329 (325)	308 (310)	(15)
$\tilde{\nu}_5(t_{2g})$	N–Co–N def	357	329	28
$\tilde{\nu}_6(t_{2u})$	N–Co–N def	252	232	20

[a] Observed frequencies are given in parentheses.

Now, if one assumes that the 503- and 325-cm^{-1} bands in the ir spectrum *are* indeed the $\tilde{\nu}_3$ and $\tilde{\nu}_4$ modes, respectively, one would then expect a series of progressions in the low-temperature, polarized vibronic spectrum of $Co(NH_3)_6^{3+}$ due to: (i) the $\tilde{\nu}_3$ mode and separated approximately by 400–450 cm^{-1}, (ii) the $\tilde{\nu}_4$ mode and separated approximately by 260–290 cm^{-1}, (iii) the $\tilde{\nu}_6$ mode and separated approximately by 200–230 cm^{-1}, and/or (iv) a combination band with $\tilde{\nu}_1$, the value of the latter ranging from approximately 360 to 400 cm^{-1}.

The polarized crystal spectrum of $[Co(NH_3)_6][Co(CN)_6]$ at 80°K is reported by Wentworth[11] to exhibit *a uniquantal progression*[20] *of a* 420 ± 10 *vibration and its combination band with a* 390 ± 10 *vibration* (the italics are ours). It is obvious that at 80°K, vibronic transitions due to the $\tilde{\nu}_3$ and the $(\tilde{\nu}_1 + \tilde{\nu}_3)$ modes are becoming discernible. It is indeed gratifying to note that not only is the vibronic spectrum of $Co(NH_3)_6^{3+}$ explained by the Shimanouchi and Nakagawa[10] assignments but that the vibronic structure of $Co(ND_3)_6^{3+}$ *can* be calculated[21] and observed[11] as expected!

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[20] The vibrational quanta are superimposed on the band whose maximum is reported to be at 4720 Å.

[21] The observed separations of the progressions are of a 380 ± 10 cm^{-1} mode, and its combination band with a 340 ± 15 cm^{-1}, while the calculated values are 386–420 and 334–386 cm^{-1}, respectively.

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The Nature of the Intermediate in Unimolecular Octahedral Aquation

Sir:

Studies of the dependence of the rate of aquation of cobalt(III) complexes of the type $Co(en)_2ACl^{n+}$ (en = ethylenediamine) led Ašperger and Ingold[1] to postulate a duality of mechanism that depended upon the electron displacement properties of A. This proposal was later refined in the light of further evidence relating especially to the steric course[2] by postulating that (i) if A possessed an extra pair of electrons that could be donated to the metal to compensate for the loss of the departing ligand, a unimolecular mechanism was favored and (ii) in the absence of such assistance the mechanism was bimolecular. The stereochemical rules required that the intermediate must have a trigonal-bipyramidal form when A was originally *trans* to the leaving group which would therefore lead to steric change, whereas the bimolecular attack would be adjacent to the leaving group and therefore result in substitution with retention of configuration. These proposals extended a similar discussion by Basolo and Pearson some years earlier[3] where the π-bonding aspects of the process were stressed.

Later work involving the nonsolvolytic reactions of these complexes could provide no evidence in support of the bimolecular mechanism and any dependence of rate on the concentration of the entering nucleophile could be accounted for in terms of an equilibrium preassociation of the reagents. The rate of the subsequent interchange was rarely very sensitive to the nature of the entering group.[4]

It was suggested that all of these observations could be accounted for by an essentially dissociative mechanism in which the duality of response to the electron

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[1] S. Ašperger and C. K. Ingold, *J. Chem. Soc.*, 2862 (1956).

[2] C. K. Ingold, R. S. Nyholm, and M. L. Tobe, *Nature*, **187**, 477 (1960).

[3] F. Basolo and R. G. Pearson, *J. Am. Chem. Soc.*, **78**, 4878 (1956).

[4] M. L. Tobe, *Record Chem. Progr.* (Kresge-Hooker Sci., Lib.), **27**, 79 (1966), and references therein.

displacement properties of A in rates and steric course arose from the two possible shapes of the five-coordinate intermediate.[5] In an attempt to examine the validity of this suggestion we prepared complexes of the stereoretentive macrocyclic quadridentate 1,4,8,11-tetraazacyclotetradecane (cyclam) and examined the rates and steric courses of the reactions of *cis*- and *trans*-Co(cyclam)AX^{n+}.[6,7] As expected, aquation, anation, and base hydrolysis took place with complete retention of configuration, but no *systematic* change could be observed in the reactivity as a result of replacing ethylenediamine by the more stereorestrictive cyclam. Thus, *trans*-Co(cyclam)Cl_2^+ [6] and *trans*-Co(cyclam)NCSCl$^+$ [6a] aquate more slowly than the corresponding bis-ethylenediamine species whereas *trans*-Co(cyclam)OHCl$^+$ is more labile.[6b] The *cis*-Co(cyclam)Cl_2^+ cation aquates more rapidly than *cis*-Co(en)$_2$Cl$_2^+$.[7] Although these data do not indicate any obvious relationship, a new correlation emerges when the activation parameters are considered. A collection of published and unpublished data, recalculated where necessary from a plot of log (k/T) against $1/T$, is presented in Table I,[8–18] together with the steric course of the reaction. Only the aquation of complexes of the type *trans*-MLACl^{n+}, where M is a tervalent metal, L is either a pair of bidentate or one quadridentate amine ligand, and chloride is the leaving group, are considered. This is a reasonably exhaustive list of those reactions whose steric course *and* activation parameters are known with some measure of certainty and it will be seen that, *in every case*, steric change is associated with a higher entropy of activation than is retention of configuration.

If this correlation is significant, then it must be concluded that *the grosser aspects of the steric course of aquation are determined in the rate-determining transition state.* This is fully in agreement with the Ašperger–Ingold postulate of a duality of mechanism,[1] but then it would be necessary to explain why the replacement of two ethylenediamines by one cyclam causes the mechanism to change from S$_N$1 to S$_N$2 with an increase of reactivity when A = OH. It would also be necessary to explain why inversion of the configuration of one of the secondary nitrogens in the quadridentate, 2,3,2-tet, was sufficient to change the mechanism of aquation of the *trans*-dichloro complex. It would also be necessary to accept that most of the *cis* isomers (see Table II) aquated bimolecularly.

TABLE I

ACTIVATION PARAMETERS AND STERIC COURSES OF THE REACTIONS[a]

$$trans\text{-MLACl}^{n+} + H_2O \longrightarrow \text{MLAH}_2O^{(n+1)+} + Cl^-$$

M	L	A	$\Delta H^{\ddagger}$, kcal mole^{-1}	$\Delta S^{\ddagger}$, cal deg^{-1} mole^{-1}	% steric change	Ref
Co	(en)$_2$	OH	25.9	+20	75	8
Co	(en)$_2$	Cl	26.2	+14	35	8, 9
Co	(en)$_2$	Br	24.9	+3	50	10
Co	(en)$_2$	N$_3$	22.5	0	20	11
Co	(en)$_2$	NCS	30.2	+9	60 ± 10	12, 13
Co	*SS*-trien[b]	Cl	25.5	+16	100	14
Co	*RR*,*SS*-2,3,2-tet[b]	Cl	25.1	+9	>95	15
Co	(en)$_2$	NH$_3$	23.2	−11	0	16
Co	(en)$_2$	CN	22.5	−2	0	17
Co	(en)$_2$	NO$_2$	20.9	−2	0	1
Co	cyclam	OH	18.1	−7	0	6b
Co	cyclam	Cl	24.6	−3	0	6b
Co	*RS*-2,3,2-tet	Cl	23.7	−1	0	15
Rh	en$_2$	Cl	24.7	−9	0	18
Rh	en$_2$	Br	23.2	−12	0	18
Rh	en$_2$	I	21.1	−7	0	18

[a] The enthalpies of activation quoted in this table and in Table II are generally reliable to better than ±0.5 kcal mole^{-1} and the $\Delta S^{\ddagger}$ values to better than ±1.5 cal deg^{-1} mole^{-1}. [b] trien = 1,4,7,10-tetraazadecane (triethylenetetramine); 2,3,2-tet = 1,4,8,11-tetraazaundecane; the *RR* and *RS* designations refer to the configurations of the secondary nitrogens when coordinated.

TABLE II

ACTIVATION PARAMETERS AND STERIC COURSES OF THE REACTIONS

$$cis\text{-CoLACl}^{n+} + H_2O \longrightarrow \text{CoLAH}_2O^{(n++1)+} + Cl^-$$

L	A	$\Delta H^{\ddagger}$, kcal/mole^{-1}	$\Delta S^{\ddagger}$, cal deg^{-1} mole^{-1}	% steric change	Ref
(en)$_2$	OH	23.0	+10	0	8
(en)$_2$	Cl	21.5	−5	0	20
(en)$_2$	Br	23.5	+5	0	10
(en)$_2$	NCS	20.1	−14	0	13
(en)$_2$	N$_3$	21.3	−4	0	11
(en)$_2$	NH$_3$	22.9[a]	−11	0	21
(en)$_2$	NH$_3$	24.5[b]	−6	0	21
(en)$_2$	HONH$_2$	19.7	−17	0	22
(en)$_2$	CH$_3$NH$_2$	25.9	−2	0	23
(en)$_2$	CH$_3$CH$_2$NH$_2$	25.5	−4	0	23
(en)$_2$	CH$_3$CH$_2$CH$_2$NH$_2$	24.1	−8	0	24
(en)$_2$	(CH$_3$)$_2$CHNH$_2$	24.3	−4	0	24
(en)$_2$	CH$_3$CH=CHNH$_2$	25.6	−4	0	25
(en)$_2$	CH$_3$C=CHNH$_2$	25.0	−5	0	25
(en)$_2$	ClCH$_2$CH$_2$NH$_2$	25.7	−5	0	26
(en)$_2$	CH$_3$CH(Cl)CH$_2$NH$_2$	25.6	−5	0	26
(en)$_2$	ClCH$_2$CH$_2$CH$_2$NH$_2$	25.9	−3	0	26
(en)$_2$	NO$_2$	21.8	−3	0	1
(+)α-trien	Cl	21.0	−6	0	14
β-*SS*-trien	Cl	20.3	−3	0	14
trien[c]	NH$_3$	23.7	−10	0	21
cyclam	Cl	18.3	−6	0	7
β-*RR*,*SS*-2,3,2-tet	Cl			0	15

[a] 50–80°. [b] 20–50° [c] Stated by the author to be the α-*cis* isomer, but probably the β-*cis* form.

These difficulties do not arise if the Langford explanation is adopted. It is proposed, therefore, that in this group of complexes where the leaving group is always the same and where there are always four amine groups *cis* to the leaving group the higher entropies of activation are diagnostic of an incipient trigonal-bipyramidal intermediate and the lower values are diagnostic of an incipient tetragonal pyramid.

Many implications arise from this conclusion. (i) Whether or not the trigonal-bipyramidal form of the intermediate will develop is determined in the transi-

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tion state and *not by subsequent rearrangement of a square pyramid.* Even if the mechanism is not truly dissociative but is better represented as a solvent-assisted dissociation, the critical stretching of the metal–chlorine bond must be accompanied by the rearrangement of the rest of the complex toward trigonal-bipyramidal symmetry when steric change is subsequently observed. (ii) In these cobalt(III) amine complexes, the energetic difference between the square pyramid and the trigonal bipyramid cannot be large because a stereoretentive ligand, such as cyclam, can tip the balance in favor of the tetragonal form without any marked systematic effect upon the rate of reaction. Were the attainment of the trigonal-bipyramidal form a vital condition for the full development of the labilizing power of a π donor, such as –OH or –Cl, one would expect to find that the *trans*-Co(cyclam)Cl_2^+ and *trans*-Co(cyclam)$OHCl^+$ cations were far less labile than their bis-ethylenediamine analogs. As it is, one is less labile and the other more labile. It is, of course, possible that the labilizing power of the *trans*-hydroxo group is the consequence of an internal proton transfer that generates an amido group *cis* to the leaving group.[19]

These considerations can also be applied to the activation parameters for the aquation of the corresponding *cis*-$MLACl^{n+}$ complexes, although the proximity of A to the leaving group should cause the entropy of activation to be more sensitive to the nature of A. In Table II[20–26] the entropies and enthalpies of activation and the steric courses are reported. All of these complexes aquate (under noncatalyzed conditions) with complete retention of configuration, and, with two exceptions, all have somewhat negative entropies of activation. One might conclude that these *cis* complexes all generated tetragonal-pyramidal intermediates in the course of their aquation, but substitution reactions of *cis*-Co(en)$_2$$Cl_2^+$ in nonaqueous solution and the Hg^{2+}-catalyzed aquation in water take place with stereochemical change: this has been taken as evidence for a trigonal-bpyramidal intermediate.[27,28] However, if the difference between the energies of the two geometries is not large, it is quite possible that a suitable change of solvent or a modification of the leaving group might be sufficient to tip the balance.

It is therefore concluded that the aquation of these octahedral complexes is essentially dissociative and that, when the central ion is Co(III), the duality of the kinetic and stereochemical response represents the interplay of the electron-displacing and steric properties of the nonparticipating ligands in deciding whether the trigonal-bipyramidal or the energetically similar tetragonal-pyramidal intermediate is generated.

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