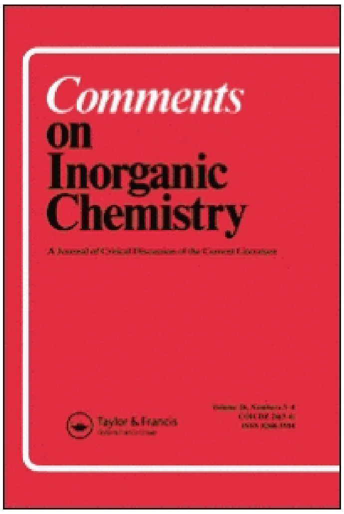

Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

First Steps Towards an Interchange Mechanism Scale for Substitution in Octahedral Transition Metal Am(m)ine Complexes

Donald A. House[a]
[a] Chemistry Department, University of Canterbury, Christchurch, New Zealand

To cite this Article House, Donald A.(1994) 'First Steps Towards an Interchange Mechanism Scale for Substitution in Octahedral Transition Metal Am(m)ine Complexes', Comments on Inorganic Chemistry, 16: 4, 229 — 242

To link to this Article: DOI: 10.1080/02603599408035861

URL: http://dx.doi.org/10.1080/02603599408035861

First Steps Towards an Interchange Mechanism Scale for Substitution in Octahedral Transition Metal Am(m)ine Complexes

DONALD A. HOUSE
Chemistry Department,
University of Canterbury,
Christchurch, New Zealand

Received March 29, 1994

If the activation entropies (ΔS^{*}) for a series of thermal or Hg^{2+}-assisted chloride release aquation rates from chloroam(m)ine complexes are ranked, orders for the effect of the non-replaced ligands are obtained. These orders are within reasonable expectation for the extent of interchange that takes place as the reaction proceeds.

Key Words: *octahedral substitution, interchange mechanism, chloroam(m)ine complexes*

Abbreviations Used: *n*PrNH$_2$ = *n*-propylamine, *n*BuNH$_2$ = *n*-butylamine, py = pyridine, en = $NH_2(CH_2)_2NH_2$, pn = $NH_2CH(CH_3)CH_2NH_2$, ibn = $NH_2C(CH_3)_2CH_2NH_2$, N*n*Pren = $CH_3CH_2CH_2NH(CH_2)_2NH_2$, NEten = $CH_3CH_2NH(CH_2)_2NH_2$, NMeen = $CH_3NH(CH_2)_2NH_2$, tn = $NH_2(CH_2)_3NH_2$, Me$_2$tn = $NH_2CH_2C(CH_3)_2CH_2NH_2$, NMetn = $CH_3NH(CH_2)_3NH_2$, bn = $NH_2(CH_2)_4NH_2$, ampy = 2-aminomethylpyridine, tacn = 1,4,7-triazacyclononane, dien = $NH_2(CH_2)_2NH(CH_2)_2NH_2$, 2,3-tri = $NH_2(CH_2)_2NH(CH_2)_3NH_2$, dpt = $NH_2(CH_2)_3NH(CH_2)_3NH_2$, Medpt = $NH_2(CH_2)_3N(CH_3)(CH_2)_3NH_2$, 2,3,2-tet = $NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$, 3,2,3-tet = $NH_2(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$, 3,3,3-tet = $NH_2(CH_2)_3NH(CH_2)_3NH(CH_2)_3NH_2$, cyclam = 1,4,8,11-tetraazacyclotetradecane, tet*a* = *meso*-5,7,7,12,14,14-Me$_6$cyclam.

Comments Inorg. Chem.
1994, Vol. 16, No. 4, pp. 229–242
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in Malaysia

1. INTRODUCTION

Current thinking[1-4] with regard to the mechanism of substitution at octahedral transition-metal centers suggests that emphasis on the assignment of D (dissociative) or A (associative) labels is counterproductive. It is thus proposed that all substitution processes are interchange mechanisms covering a continuum without demarcation.[4] The question addressed here is how to rank substitution processes within such a mechanistic continuum.

For the present purposes, our treatment will be restricted to the well studied reactions of the type

$$[MCl(N)_5]^{2+} + H_2O \xrightarrow{H+} [M(N)_5(OH_2)]^{3+} + Cl^-, \qquad (1)$$

$$\textit{trans}\text{-}[MCl_2(N)_4]^+ + H_2O \xrightarrow{H+} [MCl(N)_4(OH_2)]^{2+} + Cl^-, \qquad (2)$$

$$[MCl(N)_5]^{2+} + Hg^{2+} + H_2O \xrightarrow{H+} [M(N)_5(OH_2)]^{3+} + HgCl^+ \qquad (3)$$

which the chloro ligand as the constant leaving group.

Extensive tabulations of kinetic parameters have been reported[9,24] and the data used in the present analysis are listed in Tables I–IX.

2. RATIONALE

Reaction rate theory[5] allows modification of the empirical Arrhenius equation

$$k = Ae^{-Ea/RT} \qquad (4)$$

by collision theory or absolute reaction rate theory. In the former, the pre-exponential function (A) in (4) is partitioned into encounter frequency (Z) and orientation (steric) factor (P) components

$$A = PZ \qquad (5)$$

TABLE I

Kinetic parameters for the thermal acid hydrolysis of some $[CoCl(N)_5]^{2+}$ complexes (25°C) (Eq. (1)).[a]

N_5	$10^6\ k_H$ (s^{-1})	ΔH^* (kJ mol^{-1})	ΔS^* ($JK^{-1}\ mol^{-1}$)
sfac-(dien)(en)	0.094	111	−7
usfac-(dien)(en)	25.6	108	−8
sfac-(dien)(tn)	0.216	108	−10
$(NH_2CH_3)_5$	39.6	95	−10
cis-$(tn)_2(NH_3)$	6.5	98	−14
usfac-(dien)(bn)	7730	95	−15
sfac-(dien)$(NNH_3)_2$	0.316	107	−20
cis-$(en)_2(py)$	0.62	98	−21
(tacn)(ampy)	0.343	103	−22
mer-(dien)(en)	17.8	102	−31
mer-(dien)(tn)	565	92.2	−36
cis-$(en)_2(NH_3)$	0.42	98	−39
(tacn)(en)	1.63	93	−44
$(NH_3)_5$	1.77	93	−44
usf-(dien)$(NH_3)_2$	192	95	−44
(tacn)(tn)	1.86	92	−47

[a] Data from: D. A. House and R. van Eldik, Aust. J. Chem. **46**, 1775 (1993).

and in the latter into a quasi-thermodynamic[6] "entropy of activation" (ΔS^*) term

$$A = \frac{kT}{h} e^{\Delta S^*/R}. \tag{6}$$

Combination of (5) and (6)[5] gives

$$\ln PZ = \ln\left(\frac{kT}{h}\right) + \Delta S^*/R. \tag{7}$$

Entropy of activation data (along with enthalpy of activation, ΔH^*) are routinely calculated from the variation of rate constant with temperature using either modified Arrhenius[7] or Eyring[8] equations. The relative accuracy of these parameters has been discussed by Edwards *et al.*,[9] and the problem of obtaining meaningful mechanistic information from ΔS^* data in terms of "change in randomness" has been discussed by Swaddle.[6]

TABLE II

Kinetic parameters for the thermal acid hydrolysis of some $[CrCl(N)_5]^{2+}$ complexes (25°C) (Eq. (1)).

N_5	$10^7\,k_H$ (s^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ ($JK^{-1}\,mol^{-1}$)	Ref.
$(NH_2CH_3)_5$	2.48	111	−2	*a*
mer-(tn)(Medpt)	0.29	114 ± 5	−5 ± 10	*b*
mer-(tn)(2,3-tri)	0.306	110 ± 4	−20 ± 8	*b*
mer-(ampy)(2,3-tri)	0.21	109 ± 2.7	−25 ± 7	*f*
mer-(ampy)(dpt)	3.16	101 ± 2.3	−32 ± 6	*f*
sfac-(tn)(dien)	218	88.6	−37	*c*
mer-(en)(dpt)	5.34	96.8	−40	*d*
sfac-(en)(dien)	224	86.8	−43	*c*
mer-(ibn)(dpt)	3.95	96.9 ± 5	−43 ± 10	*b*
ufac-(NMetn)(dien)	37	91.6	−45	*e*
$(NH_3)_5$	95	86.9	−50	*a*
mer-(Me_2tn)(dpt)	2.07	93.3 ± 6	−59 ± 12	*b*
mer-(en)(Medpt)	1.24	94.1 ± 5	−62 ± 10	*b*
mer-(en)(2,3-tri)	2.87	88.5	−73	*d*
mer-(tn)(dpt)	5.04	80.4	−96	*d*

[a] D. A. House, Coord. Chem. Rev. **23**, 223 (1977).

[b] D. A. House, unpublished research.

[c] B. S. Dawson and D. A. House, Inorg. Chem. **16**, 1354 (1977).

[d] D. A. House and W. T. Robinson, Inorg. Chim. Acta **141**, 211 (1988).

[e] D. A. House, Inorg. Chim. Acta **121**, 223 (1986).

[f] D. A. House, S. Schaffner, R. van Eldik, A. McAuley and M. Zhender, Inorg. Chim. Acta, submitted for publication.

TABLE III

Kinetic parameters for the thermal acid hydrolysis of some $[MCl(NH_3)_5]^{2+}$ complexes (25°C) (Eq. (1)).[a]

M	$10^8\,k_H$ (s^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ ($JK^{-1}\,mol^{-1}$)
Co	177	93.0	−44
Ru	71	94.4	−45
Cr	950	86.9	−50
Rh	4.83	99.5	−51
Ir	0.11	93.6	−101

[a] Data from: J. O. Edwards, F. Monacelli and G. Ortaggi, Inorg. Chim. Acta **11**, 47 (1974).

TABLE IV

Kinetic parameters for the first step in the thermal acid hydrolysis of some *trans*-$[CoCl_2(N)_4]^+$ complexes (25°C) (Eq. (2)).[a]

$(N)_4$	$10^5\ k_H$ (s^{-1})	$\Delta H^{\neq}$ ($kJ\ mol^{-1}$)	$\Delta S^{\neq}$ ($JK^{-1}\ mol^{-1}$)
$(pn)_2$	6.2	117	+58
$(N\mathit{n}Pren)_2$	7.25	113	+55
(tet*a*)	93	107	+54
t,t-$(ibn)_2$	99.4	106	+45
$(en)_2$	3.2	112	+44
$(NMeen)_2$	1.59	113	+36
$(tn)_2$	5530	87	+29
(3,2,3-tet)	5.6	106	+29
$(Me_2tn)_2$	557	94	+28
(en)(tn)	43.3	99	+21
c,t-$(ibn)_2$	307	93.6	+13
(2,3,2-tet)	1.2	104	+8
$(NEten)_2$	8.12	94.5	−6
$(NH_3)_4$	224	86.6	−6
cyclam	0.14	76.5	−25

[a] Data from: G. Daffner, D. A. Palmer and H. Kelm, Inorg. Chim. Acta **61**, 57 (1982) and M. Harnett, D. A. House and W. T. Robinson, Inorg. Chim. Acta **102**, 87 (1985).

Following the ideas of classical collision theory, an interchange mechanism for reaction (1) will be characterized by the following:

(i) approach of the water molecule (presumably from the second coordination sphere[10,11]),
(ii) stretching of the M−Cl bond,
(iii) reorganization of the bonds to the non-replaced ligands,
(iv) loss of the leaving group into the second coordination sphere and formation of the $M{-}OH_2$ bond, and
(v) relaxation to products.

According to the calculations of Connick and Alder,[11] the exchange pathway involves a highly correlated collective motion of many vibrations so that steps (ii)–(iv) are taking place synchronously.

Nevertheless, step (i) is probably associated with the classical "encounter frequency" (*Z*) and steps (ii)–(v) with the "steric factor" (*P*). For reactions characterized by Eq. (1), the major influ-

TABLE V

Kinetic parameters for the first step in the thermal acid hydrolysis of some *trans*-$[CrCl_2(N)_4]^+$ complexes (25°C) (Eq. (2)).

N_4	$10^5\ k_H$ (s^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ ($JK^{-1}\ mol^{-1}$)	Ref.
$(Me_2tn)_2$	2.25	101	+5	*a*
$(tn)_2$	2.08	100	+1	*b*
(2,3,2-tet)	0.323	107	0	*c*
(3,3,3-tet)	0.74	102	−2	*d*
cyclam	0.002	116	−8	*e*
(tn)(en)	1.93	95	−15	*f*
$(en)_2$	2.25	95	−17	*g*
$(NH_3)_4$	4.5	91	−29	*h*
(tet*a*)	1.26	93	−37	*i*
(3,2,3-tet)	0.106	95	−50	*j*

[a] D. A. House, Inorg. Chem. **25**, 1671 (1986).

[b] M. C. Couldwell and D. A. House, Inorg. Chem. **11**, 2024 (1972).

[c] D. A. House and D. Yang, Inorg. Chim. Acta **74**, 179 (1983); C. Kutal and A. W. Adamson, Inorg. Chem. **12**, 1990 (1973).

[d] D. A. House, J. Erikson and O. Mønsted, Acta Chem. Scand. **41A**, 335 (1987).

[e] E. Campi, J. Ferguson and M. L. Tobe, Inorg. Chem. **9**, 1781 (1970).

[f] M. C. Couldwell, D. A. House and H. K. J. Powell, Inorg. Chem. **12**, 627 (1973).

[g] C. S. Garner and D. A. House, Trans. Met. Chem. **6**, 59 (1970).

[h] L. Mønsted and O. Mønsted, Acta Chem. Scand. **32A**, 917 (1978).

[i] D. Yang and D. A. House, Inorg. Chim. Acta Letters **64**, L167 (1982).

[j] D. Yang and D. A. House, Inorg. Chem. **21**, 2999 (1982).

ence of N_5 will be in process (i)–(iii) and hence the non-bonded ligands will influence the position of any particular complex within the mechanistic spectrum. Thus the size, rigidity, and stereochemistry of N_5, as well as the length of the M–Cl bond in the ground state, may all influence the motion of the encounter complex on its passage along the reaction coordinate. Such parameters (apart from bond length, which is perhaps the least important[4]) are difficult to quantify, but all will contribute to changes in the pre-exponential factor (*PZ*) (and hence $\Delta S^{\#}$) within a related series.

With these concepts in mind, we have ordered the complexes in Tables I–IX with respect to measured $\Delta S^{\#}$ values (ln *PZ* values give the same order) to see if such a ranking would correlate with the general concepts of steric size[12] and ease of distortion[13–15] that have previously been qualitatively applied in discussions of the reaction mechanism.

TABLE VI

Kinetic parameters for the Hg^{2+}-assisted chloride release from some $[CoCl(N)_5]^{2+}$ complexes (25°C, I = 1.0 M)[a] (Eq. (3)).

N_5	$10^3\,k_{Hg}$ ($M^{-1}\,s^{-1}$)	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ ($JK^{-1}\,mol^{-1}$)
(tacn)(tn)	54.0	76.7	−13
mer-(dien)(phen)	0.113	90.0	−15
mer-(dien)(en)	5.21	79.0	−23
usfac-(dien)(bn)	2170	66	−26
(tacn)(ampy)	10.2	75.6	−30
(tacn)(en)	11.0	74.7	−32
$(NH_3)_5$	131	67.0	−37
sfac-(dien)(en)	4.95	72.7	−45
usfac-(dien)$(NH_3)_2$	77.6	62.8	−55
usfac-(dien)(tn)	126	64	−56
usfac-(dien)(phen)	10.7	63.4	−66
usfac-(dien)(en)	14.9	55.5	−93

[a] Data from: D. A. House and R. van Eldik, Aust. J. Chem. **46**, 1775 (1993).

TABLE VII

Kinetic parameters for the Hg^{2+}-assisted chloride release from some $[CrCl(N)_5]^{2+}$ complexes (25°C, I = 1.0 M)[a] (Eq. (3)).

N_5	$10^4\,k_{Hg}$ ($M^{-1}\,s^{-1}$)	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ ($JK^{-1}\,mol^{-1}$)
mer-(tn)(Medpt)	9.14	89.3 ± 2	+26 ± 4
mer-(ampy)(dpt)	0.572	102 ± 0.4	+16 ± 1
$(NH_2CH_3)_5$	21.5	93.2 ± 0.6	+16 ± 1
mer-(ampy)(2,3-tri)	0.044	106 ± 1	+9 ± 3
mer-(tn)(2,3-tri)	2.66	95 ± 3	+5 ± 6
mer-(tn)(dpt)	29.1	87 ± 6	−1 ± 10
mer-(ibn)(dpt)	5.81	89.5 ± 1.5	−6 ± 3
mer-(Me_2tn)(dpt)	22.2	84.9 ± 4	−11 ± 8
mer-(en)(Medpt)	0.417	94.6 ± 5	−11 ± 10
mer-(en)(2,3-tri)	1.94	87.0 ± 8	−24 ± 16
mer-(en)(dpt)	6.44	75.5 ± 3	−53 ± 6
$(NH_3)_5$	984	64.6 ± 1.6	−27 ± 3

[a] Data from: D. A. House and R. van Eldik, Inorg. Chim. Acta, submitted, and J. Wang and D. A. House, unpublished.

These rankings would assign systems with the most negative $\Delta S^{\#}$ values to the more associative end of the mechanistic spectrum, as would be expected from the previously cited[6] analysis.

TABLE VIII

Kinetic parameters for the first step in the Hg^{2+}-assisted chloride release from some *trans*-$[CrCl_2(N)_4]^+$ complexes (25°C).[a]

N_4	$10^2\ k_{Hg}$ ($M^{-1}\ s^{-1}$)	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ ($JK^{-1}\ mol^{-1}$)
$(NH_3)_4$	203	74.3 ± 3.2	+10 ± 6
$(n\text{BuNH}_2)_4$	2.73	77.2 ± 2.3	−16 ± 5
(3,3,3-tet)	3.05	76.5 ± 1.0	−17 ± 2
(tet*a*)	4.04	74.9 ± 1.5	−20 ± 3
$(Me_2tn)_2$	10.1	70.9 ± 1.5	−26 ± 3
(2,3,2-tet)	1.34	74.0 ± 1.5	−32 ± 3
$(tn)_2$	35.4	63.8 ± 4.1	−39 ± 8
$(n\text{PrNH}_2)_4$	3.01	69.8 ± 2.0	−40 ± 4
(3,2,3-tet)	0.357	74.1 ± 1.5	−43 ± 5
$(en)_2$	18.0	63.5 ± 3.0	−46 ± 6
(tn)(en)	28.2	60.0 ± 2.2	−54 ± 5

[a] In 50:50 dmf:aqueous $HClO_4$, I = 0.5 M. D. A. House, unpublished data.

TABLE IX

Kinetic parameters for the Hg^{2+}-assisted chloride release from some $[CrCl(RNH_2)_5]^{2+}$ complexes (25°C)[a] (Eq. (3)).

R	$10^3\ k_{Hg}$ ($M^{-1}\ s^{-1}$)	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ ($JK^{-1}\ mol^{-1}$)
nBu	0.530	98.0 ± 5	+21 ± 10
nPr	0.706	96.3 ± 6	+17 ± 12
Et	1.19	86.8 ± 8	−9 ± 16
Me	1.78	79.0 ± 6	−32 ± 12
H	54.5	74.7 ± 4	−18 ± 8

[a] In 50:50 dioxane:aqueous $HClO_4$, I = 0.5 M: J. Wang and D. A. House, unpublished.

3. COMPARISON OF THE ENTROPY ORDERING WITH EXPECTATION

In the acid hydrolysis of $[MCl(N)_5]^{2+}$ and *trans*-$[MCl_2(N)_4]^+$ complexes we have a constant set of ligating atoms with the chloro ligand as the leaving group and a water molecule as the entering group (Eqs. (1) and (2)). Similarly for the Hg^{2+}-assisted equation, the leaving group is $HgCl^+$ and again a water molecule enters in an interchange process (Eq. (3)). However, it is not legitimate to expect direct comparisons of the absolute $\Delta S^{\neq}$ values for the two types of reaction, as the appropriate rate constants have different units. Nevertheless, relative order patterns should follow if our entropy ranking has any significance.

For both series of reactions (thermal or Hg^{2+}-assisted) there will be non-replaced ligand dependent steric effects that restrict or facilitate the entry of the water molecule. These are perhaps best reflected in the $[MCl(RNH_2)_5]^{2+}$ systems where the change in R = H to R = Me has the greatest effect. In all cases (Tables I, II, VII, IX) our entropy ordering would place this steric change as associatively restricting.

The only anomaly may be in Table VIII where the entropy data would reverse the expectation (i.e., $(NH_3)_4$ more dissociative than $(n PrNH_2)_4$). However, relative steric congestion in a *trans*-$[MCl_2(N)_4]^+$ (N = NH_3 vs. $n PrNH_2$) complex may be less dominant than in the $[MCl(N)_5]^{2+}$ situation. In the solid state structures of both *trans*-$[CrCl_2(NH_3)_4]I$[16] and *trans*-$[CrCl_2(n PrNH_2)_4]BF_4 \cdot H_2O$,[17] there appear to be readily available open faces adjacent to the (Hg^{2+}-assisted) chloro leaving group.

The concept that increasing steric bulk of the non-replaced ligands is associatively restricting for Cr(III) *and* Co(III) allows that there will be an associative contribution in the aquation of $[CoCl(NH_3)_5]^{2+}$ rather than the previous proposals of "dissociative" (NH_3) and "more dissociative" (RNH_2).

The $[MCl(RNH_2)_5]^{2+}$ system is a good model to probe "approach trajectories" as the effects of the coupled N_5 distortion and M–Cl stretch are likely to be similar throughout. Most other complexes in the tables will have variable contributions from all three processes and it will be necessary to make the assumption that contributions to two of these [approach path and M–Cl (or M–ClHg) stretch] are constant.

Rather similar, but less well formulated, ideas have previously been proposed; for example, the driving force towards spontaneous thermal aquation of $[CoCl(N)_5]^{2+}$ complexes is a function of the degree of distortion allowed by the N_5 ligand set.[13–15] This has led to predictable structure-reactivity patterns; for example, labilization is induced by increasing chelate ring size or by the incorporation of C-methyl substituents.[18] Also the reaction rate can be correlated with a bidentate ligand reactivity order phen <

ampy < en < $(NH_3)_2$ < tn < bn.[19] These concepts are structure-reactivity correlations, i.e., they pertain to the effect of the structure on the *rate constant.*

Here we wish to see if these effects are manifest in the entropy patterns, i.e., whether the non-replaced bidentate ligands can be placed in a "dissociatively activating" series. Of course, the comparison must be made against a background of constant, remaining N donor sites, and stereochemistry.

In view of the experimental uncertainty in $\Delta S^{\#}$ values, we would be surprised if a consistent pattern of data developed uniformally across all systems; nevertheless it appears from the trends in Table X that steric bulk is a dominant dissociatively activating (or associatively restricting) influence. This is particularly marked in the unexpected position of ampy (2-aminomethylpyridine), and to a lesser extent phen (and py) as more dissociatively activating than, say, en (and NH_3).

Following this line, the pattern of entropy changes in the order $(NH_3)_2$ < en < tn < bn with increasing ring size are reflecting associatively restricting steric bulk rather than concepts such as release of steric strain in a dissociative process.[20]

Methyl substituents (both C and N) are also believed to increase the steric bulk of the ligand[18] and these are sometimes reflected in more positive $\Delta S^{\#}$ values (associatively restricting) than the unsubstituted parent. Favorable cases are Medpt vs. dpt in Table VII and tet*a* vs. cyclam in Table IV (see, however, the reverse in Table V). More ambiguous are the N-substituted ethylenediamine systems in Table IV, and the $\Delta S^{\#}$ values show little discrimination between Me_2tn and tn.

The data in Table III (acid hydrolysis for $[MCl(NH_3)_5]^{2+}$ systems) suggest that these complexes are all [except Ir(III)] in about the same position in the interchange spectrum. This leads to the perhaps not unreasonable conclusion that the water molecule has the same approach trajectory to all $[MCl(NH_3)_5]^{2+}$ independent of M(III). The entropy trends in this series have previously been discussed in terms of electrostriction due to changes in the size of the $[MCl(NH_3)_5]^{2+}$ ions. Constant $\Delta S^{\#}$ and variable ion size suggest the degree of association increases in the order Co(III) < Cr(III) < Rh(III) < Ru(III) < Ir(III), but all could be at the dissociative end of the mechanistic spectrum.[2] Our entropy ranking

TABLE X

Summary of dissociatively activating non-replaced bidentate ligand effects.

Table	Reaction	Entropy Ranking	Comments
I	$[\mathrm{CoCl(N)_5}]^{2+} + \mathrm{H^+}$	$(\mathrm{NH_3})_2 <$ bn ~ tn ~ en $<$ ampy	various dien config.
I	$[\mathrm{CoCl(en)_2(N)}]^{2+} + \mathrm{H^+}$	$\mathrm{NH_3} <$ py	
I	$[\mathrm{CoCl(N)_4(NH_3)}]^{2+} + \mathrm{H^+}$	en $<$ tn	
IV	*t*-$[\mathrm{CoCl_2(N)_4}]^{+} + \mathrm{H^+}$	$(\mathrm{NH_3})_2 < \mathrm{Me_2}$tn $<$ tn $<$ en $<$ pn	
VI	$[\mathrm{CoCl(N)_5}]^{2+} + \mathrm{Hg^{2+}}$	en $<$ phen $<$ tn $< (\mathrm{NH_3})_2 <$ bn	*usf*-dien
		en $<$ ampy $<$ tn	tacn
		en $<$ phen	*mer*-dien
II	$[\mathrm{CrCl(N_5)}]^{2+} + \mathrm{H^+}$	tn $< \mathrm{Me_2}$tn $<$ ibn $<$ en $<$ ampy	*mer*-dpt
		en $<$ ampy $<$ tn	2,3-tri
		en $<$ tn	Medpt
V	*t*-$[\mathrm{CrCl_2(N_4)}]^{+} + \mathrm{H^+}$	$(\mathrm{NH_3})_2 <$ en $<$ tn ~ $\mathrm{Me_2}$tn	
VII	$[\mathrm{CrCl(N)_5}]^{2+} + \mathrm{Hg^{2+}}$	en $< \mathrm{Me_2}$tn $<$ ibn $<$ tn $<$ ampy	*mer*-dpt
		en $<$ tn $<$ ampy	2,3-tri
		en $<$ tn	Medpt
VIII	*t*-$[\mathrm{CrCl_2(N)_4}]^{+} + \mathrm{Hg^{2+}}$	en $< (n\mathrm{PrNH_2})_2 <$ tn $< (n\mathrm{BuNH_2})_2 < (\mathrm{NH_3})_2$	

would put these complexes more to the middle of the mechanistic spectrum insofar as the measured $\Delta S^{\#}$ are quite negative.

If, as we argue, there is a constant approach trajectory for the water molecule towards these $[MCl(NH_3)_5]^{2+}$ complexes, then variation in the observed rate constant will be controlled by steps (ii) and (iii), but the M–Cl bond energy will be more important than the M–N bond energy, as complete dissociation of M–Cl rather than M–N stretching is required.

While we are examining entropy as a mechanistic probe, it should be remembered that many years ago M. L. Tobe[21] commented on the observation that steric change in the aquation of *trans*-$[MCl_2(N)_4]^+$ systems was associated with a positive $\Delta S^{\#}$ value. Almost all the Co(III) complexes listed in Table IV show some steric change on aquation (except perhaps cyclam), whereas the Cr(III) complexes listed in Table V are generally stereoretentive (negative $\Delta S^{\#}$). Our ordering would put the *trans*-$[CoCl_2(N_4)]^+$ systems that show steric change towards the dissociatively activating end of the mechanistic spectrum, that is, where bond distortions have a greater influence than approach of the water molecule. Conversely, the *trans*-$[CrCl_2(N)_4]^+$ are in the associatively enhanced region where the approach of the water molecule is more important.

We now believe it is unwise to associate rate constant comparisons directly with mechanism. The rate constant is a function of both $\Delta H^{\#}$ and $\Delta S^{\#}$. It is possible that relative reactivities can change with temperature (unless $\Delta H^{\#}$ is constant for the two reactions being compared), but more important is the fact that relatively modest changes in $\Delta H^{\#}$ can cause considerable changes in the rate constant. For example, *trans*-$[CoCl_2(tn)_2]^+$ aquates about 1000 times faster than *trans*-$[CoCl_2(3,2,3\text{-tet})]^+$ due to a $\Delta H^{\#}$ difference of about 19 kJ mol^{-1}, whereas our entropy ranking would have these complexes (with reasonably similar ring conformations) in identical positions on the interchange mechanism spectrum.

4. CONCLUSIONS

In this "first steps" approach we proposed that chemically similar substitution processes in octahedral chloroam(m)ine complexes can be ranked in an interchange mechanistic continuum on the basis of the observed entropy of activation. Our conclusion from this ranking is that non-replaced ligand steric effects are much more important in these ligand exchange reactions [Cl^-(or $HgCl^+$) for H_2O] than has previously been appreciated. We have considered reaction series resulting mainly from our own work, but there are other examples in the literature, e.g., acid hydrolysis of [$CoBr(RNH_2)_5]^{2+}$ [23] where the entropy trends exactly parallel the present proposals. Interesting data for the thermal acid hydrolysis of *trans*-[$RhCl_2(N)_4]^+$ are also available.[22] Curiously, activation entropy data for the acid hydrolysis of the *cis*-[$CoCl(en)_2(NH_2R)]^{2+}$ series[24] is approximately constant (given a large experimental error), indicating a sterically independent water approach path, a proposal that is quite reasonable in view of the molecular structure.

There are reaction series (especially Table IV) where, for example, $MCl(N)_4$ bond motion is thought to contribute significantly along the approach to the transition region,[22] but for most of the other data, the influence of steric effects on the approach of the water molecule appears to control the activation entropy order.

Unfortunately, steric bulk, while a conceptually simple parameter, is not readily quantified. We are currently exploring the possibility of correlating measured[25] or calculated[26–28] partial molar volumes with activation entropy. Even these data may not show sufficient resolution, as it is the site specific entry position where the effect of changes in steric bulk will be most pronounced, rather than the bulk volume.

One consequence of the interchange mechanistic spectrum is that the concept of an "intermediate" along the reaction coordinate may have less validity than previously proposed. Dissociative 5-coordinate intermediates with a finite lifetime would only be manifest at the D end of the spectrum—all interchange processes would involve synchronous bond-making and bond-breaking with transient 7-coordination. Consequently, the search for "5-coordinate intermediates" in a substitution process of the type under consideration may prove elusive.

In the above discussion, we have concentrated primarily on the effects of the approach of the water molecule during the substitution process. We have not yet addressed the problem of what specific entry sites are available for H_2O-M bond formation during step (iv). Are these adjacent to the leaving group? Are these controlled by the stereochemistry of the non-replaced ligands? Can we design complex ions where preferred entry sites are blocked or open?

We hope that both experiment and calculation can provide answers to these questions.

References

1. L. Mønsted and O. Mønsted, Coord. Chem. Rev. **94**, 190 (1989).
2. P. Lay, Comments Inorg. Chem. **11**, 235 (1991).
3. P. Lay, Coord. Chem. Rev. **110**, 213 (1991).
4. T. W. Swaddle, Comments Inorg. Chem. **12**, 237 (1991).
5. S. Glasstone, *Textbook of Physical Chemistry* (MacMillan and Co., London, 1947), 2nd Ed., p. 1087.
6. T. W. Swaddle, Coord. Chem. Rev. **14**, 217 (1974).
7. A. J. Cunningham, D. A. House and H. K. J. Powell, J. Inorg. Nucl. Chem. **33**, 572 (1971).
8. P. W. Atkins, *Physical Chemistry* (OUP, Oxford, U.K., 1982), 2nd Ed., p. 982.
9. J. O. Edwards, F. Monacelli and G. Ortaggi, Inorg. Chim. Acta **11**, 47 (1974).
10. D. A. House, in *Mechanisms of Inorganic and Organometallic Reactions*, ed M. V. Twigg (Plenum Press, New York, 1994), Vol. 9.
11. R. E. Connick and B. J. Alder, J. Phys. Chem. **87**, 2764 (1983).
12. G. Guastalla and T. W. Swaddle, Canad. J. Chem. **51**, 821 (1973).
13. B. J. Cameron, D. A. House and A. McAuley, J. Chem. Soc. Dalton Trans. 1019 (1993).
14. D. A. House and M. L. Tobe, Pure and Appl. Chem. **60**, 1197 (1988).
15. D. A. House and M. L. Tobe, J. Chem. Soc. Dalton Trans. 853 (1989).
16. J. V. Brencic, I. Leban and J. Zule, Z. Anorg. Allgem. Chem. **521**, 199 (1986).
17. D. A. House and M. Nieuwenhuyzen, to be published.
18. M. D. Alexander, Inorg. Chem. **5**, 2084 (1966).
19. D. A. House and R. van Eldik, Aust. J. Chem. **46**, 1775 (1993).
20. R. G. Pearson, C. R. Boston and F. Basolo, J. Am. Chem. Soc. **75**, 3083 (1953).
21. M. L. Tobe, Inorg. Chem. **7**, 1260 (1968).
22. M. L. Tobe, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson (Pergamon Press, 1987), Vol. 1, p. 281.
23. L. F. Book, K. Y. Hui, O. W. Lau and Wai-Kee Li, Z. Anorg. Allgem. Chem. **426**, 215 (1976).
24. D. A. House, Coord. Chem. Rev. **23**, 223 (1977).
25. D. A. House, K. Bal Reddy and R. van Eldik, Inorg. Chim. Acta **186**, 5 (1991).
26. D. Tran, J. P. Hunt and S. Wherland, Inorg. Chem. **31**, 2460 (1992).
27. D. M. P. Mingos, A. L. Rohl and J. Burgess, J. Chem. Soc. Dalton Trans. 423 (1993).
28. W. J. Spillane, G. G. Birch, M. G. B. Drew and I. Bartolo, J. Chem. Soc. Perkin II 497 (1992).