Preparation, characterization and reactivities of chromium (III) complexes of a homologous series of Schiff-base ligands

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Abstract. Complexes of general formulation $[Cr(Schiff-base)(H_2O)_2]X$, where Schiff-base = 1, 2-*bis*(salicylideneamino)ethane (salen), 1, 3-*bis*(salicylideneamino) propane (salprn) and 1, 4-*bis*(salicylideneamino)butane (salbuen) and $X = ClO_4$ or Cl have been prepared and characterised. Single-crystal structure of the complex *trans*$[Cr(salprn)(H_2O)_2]Cl$ has been resolved. Evidence for less distorted coordination geometry around chromium in the salprn analogue as compared to that in *trans*-$[Cr(salen)(H_2O)_2]^+$ has been presented. The kinetics of the aqua ligand substitution in the complexes $Cr(Schiff-base)(H_2O)_2^+$ by thiocyanate have been investigated under pseudo-first order conditions with $[NCS^-] \gg [Cr(III)]$, $T = 10$–$50°C$, $[H^+] = 10^{-8}$–10^{-1} M, $I = 1·0$ M ($LiClO_4$). An attempt has been made to discuss the anomalous lability of *trans*-$[Cr(salen)(H_2O)_2]^+$ reported earlier in comparison to the reactivities of salprn and salbuen analogues. Bimolecular rate constants for the aqua ligand substitution by NCS^- in $[Cr(Schiff-base)(H_2O)_2]^+$ at 25°C vary by more than two orders of magnitude depending on the nature of the Schiff-base ligand. The reactivity order is discussed in terms of the possible steric strain imposed by the equatorially coordinated quadridentate ligand.

Keywords. Schiff base complex; chromium(III) complex; ligand substitution reactions; structure reactivity correlation.

1. Introduction

The factors controlling the reactivities of transition metal complexes have attracted general interest (Sisley and Jordan 1987, 1988, 1991; Wilkins 1991; Comba 1993; Hoss and Elias 1993; Crimp *et al* 1994; Dadci *et al* 1995). Although chromium(III) has been classified among inert metal ions, a relatively rapid rate of substitution of water ligand in the *trans*-diaqua-1,2-*bis*(salicylideneamino)ethanechromium(III) cation, *trans*-$[Cr(salen)(H_2O)_2]^+$ has been reported earlier (Prasad *et al* 1980, 1982; Gerdom *et al* 1981; Gerdom and Goff 1982; Lloret *et al* 1989). Probable causes for the anomalous reactivity of the complex *trans*-$[Cr(salen)(H_2O)_2]^+$ have roused further interest and remain puzzling. An interesting suggestion has been made that the labilization of the coordinated aqua ligands in *trans*-$[Cr(salen)(H_2O)_2]^+$ may originate from the

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conjugate base pathways arising from the coordination of salicylaldehydato "O" bases. (Swaddle 1983). An internal conjugate base mechanism has been advanced. Questions exist as to whether the lability arises from some peculiarity of the quadridentate ligand, salen. An attempt has now been made to examine the role of ring size in the quadridentate Schiff-base ligands, salen, salprn and salbuen on the substitutional lability of Cr(III) in a related homologous series of complexes. New diaqua complexes of the formulation $[Cr(Schiff\text{-}base)(H_2O)_2]X$ where $X = ClO_4$ or Cl and Schiff-base $=$ salprn or salbuen have now been prepared and their reactivities with NCS^- compared with that of *trans*-$[Cr(salen)(H_2O)_2]^+$.

2. Experimental section

2.1 *Materials and methods*

The Schiff-base ligands, salen, salprn, and salbuen, were prepared according to literature methods (Bouchler and Coe 1975; Borer *et al* 1983); The complex *trans*-$[Cr(salen)(H_2O)_2]ClO_4$ was prepared by the adaptation of the earlier procedures (Coggon *et al* 1970; Prasad *et al* 1981). Salicylaldehyde (SRL, Reagent Grade), 1,3-diaminopropane and 1,4-diaminobutane (both Aldrich) were employed in the synthesis of Schiff-base ligands without further purification. Other materials used were generally of reagent grade or better.

2.2 *Synthesis – trans-$[Cr(salprn)(H_2O)_2]ClO_4·H_2O$*

This complex was prepared employing a template procedure. Salicylaldehyde (SRL, Reagent Grade, 2·4 g) was dissolved in $100\,cm^3$ methanol. To this, 1,3-diamino propane (Aldrich, 0·74 g) was added. The resulting solution was purged with argon for 30 min. An aqueous solution of Cr(II) perchlorate (0·01 mol) (prepared by the Zn amalgam reduction of Cr(III) perchlorate employing known procedures) (Balahura and Johnston 1983) was transferred under anaerobic conditions into the mixture of salicylaldehyde and diamine. The resulting reaction mixture was oxidised by passing air through the solution for 5 min and then rotary-evaporated, until its total volume was reduced to $30\,cm^3$. When the concentrate was cooled to 5°C, a greenish yellow product crystallised out.

The crude product was dissolved in 0·05 M $HClO_4$ at 50°C and the slurry was filtered while hot. To the filtrate, concentrated perchloric acid was added dropwise until the solution turned cloudy. The mixture was then heated to 60°C when the precipitate redissolved. The clear solution thus obtained was allowed to cool slowly to room temperature and then to 5°C in an ice bath. The desired complex crystallised out as greenish brown needles. Analysis: Calcd. for $[Cr(C_{17}H_{16}N_2O_2)(H_2O)_2]ClO_4·H_2O$: C, 42·0; H, 4·54; N, 5·76; Cr, 10·7%. Found C, 41·6; H, 4·6; N, 5·45; Cr, 10·2%.

2.3 *$[Cr(salprn)(H_2O)_2]Cl$ for single-crystal X-ray structure determination*

A sample of the perchlorate salt, $[Cr(salprn)(H_2O)_2]ClO_4·H_2O$ (200 mg) was dissolved in aqueous methanol (1:1, $50\,cm^3$) at 50°C. Crystals of ammonium chloride (BDH, AnalaR) were added slowly until the solution turned cloudy. The mixture was then heated to 55°C and allowed to cool slowly. On cooling to room temperature, shiny crystals of the desired product, $[Cr(salprn)(H_2O)_2]Cl$ were obtained. The product thus obtained was recrystallised from 1:1 aqueous methanol. After examining the crystal under a microscope, a suitable crystal was chosen for X-ray structure determination.

2.4 [Cr(salbuen)(H₂O)₂]ClO₄

A solution of hexaaquachromium(II) perchlorate (0·1 mol, 50 cm³) was prepared employing previously known procedures (Balahura and Johnston 1983). A methanolic solution (100 cm³) of salbuen (0·01 mol) was prepared and deoxygenated. To the methanolic solution of salbuen was added an aqueous solution of Cr(II) (0·01 mol) under anaerobic conditions. The resulting mixture was then subjected to aerial oxidation to obtain the desired product. The green crude product was recrystallised from aqueous perchloric acid. Analysis: Calcd. for [Cr($C_{18}H_{18}N_2O_2$)(H_2O)₂]ClO₄: C, 44·8; H, 4·56; N, 5·82; Cr, 10·85%. Found C, 45·18; H, 4·85; N, 5·89; Cr, 11·1%. We could not crystallise the compound to the quality needed for single crystal X-ray diffraction study, and had to use other spectroscopic techniques to characterise the product.

2.5 *Estimation of acid–base dissociation constants in the* [Cr(Schiff base)(H₂O)₂]⁺ *complex cations*

The acid–base dissociation constants in the complex cations for the equilibration shown in (1) and (2) below have been estimated using potentiometric methods at $I = 0.025$ M, $T = 30$–50°C.

$$Cr(\text{Schiff base})(H_2O)_2^+ \rightleftharpoons Cr(\text{Schiff base})(H_2O)(OH) + H^+, \tag{1}$$

$$Cr(\text{Schiff base})(H_2O)(OH) \rightleftharpoons Cr(\text{Schiff base})(OH)_2 + H^+. \tag{2}$$
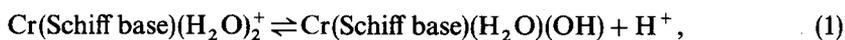
Standard software packages (Los Alamos Report 1959) implemented on an IBM PC/AT with 80486 co-processor were employed for the estimation of acid–base dissociation constants in the complex cations, [Cr(Salprn)(H_2O)₂]⁺ and [Cr(Salbuen) (H_2O)₂]⁺. The values estimated for [Cr(Salprn)(H_2O)₂]⁺ are $(5.0 \pm 0.8) \times 10^{-5}$ and $(1.0 \pm 0.1) \times 10^{-9}$ at 30°C, $(6.3 \pm 0.5) \times 10^{-5}$ and $(2.5 \pm 0.2) \times 10^{-9}$ M at 40°C and $(5.0 \pm 0.8) \times 10^{-5}$ and $(2.5 \pm 0.2) \times 10^{-9}$ M at 50°C. The value estimated for [Cr(salbuen)(H_2O)₂]⁺ ion is $(1.0 \pm 0.02) \times 10^{-7}$ M at 30°C. These values are in satisfactory agreement ($\pm 15\%$) with data obtained independently using spectrophotometric methods.

2.6 *Electrochemical studies*

Cyclic voltammetric investigations on the [Cr(Schiff base)(H_2O)₂]ClO₄ complexes, (where Schiff base = salen, salprn and salbuen) have been carried out in dimethyl sulphoxide employing tertiary butyl ammonium perchlorate (TBAP) as the supporting electrolyte. A Princeton Applied Research (PAR) Potentiostat interfaced to a Universal Programmer has been employed along with platinum working, platinum counter and standard calomel electrodes.

2.7 *Determination of structure using X-ray diffraction*

A crystal of the complex of the dimensions $0.15 \times 0.06 \times 0.03$ mm chosen under a microscope was mounted in a glass capillary. Cell constants and orientation matrices for the crystal were obtained from least squares refinement of 25 reflections data collected by setting angles in the range of $20 < 2\theta < 30°$. A Rigaku AFC-5R diffractometer and MoK$_a$ radiation ($1 = 0.71069$ Å) were employed. Intensities of standard reflections monitored after every 100 reflections showed no appreciable decay of the crystal occurred. The crystal data, intensity measurements and methods employed for

Table 1. The crystal data, intensity measurements and structure solution and refinement.

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Empirical formula	$CrClO_4N_2C_{17}H_{20}$
Formula weight	403·80
Crystal dimensions	$0.15 \times 0.06 \times 0.03$ mm
Crystal system	triclinic
Lattice type	Primitive
Lattice parameters	$a = 10.368(3)$ Å, $b = 13.779(4)$ Å, $c = 7.418(2)$Å,
	$\alpha = 96.24(5)°$, $\beta = 93.32(6)°$, $\gamma = 54.94(2)°$, $V = 862.3(5)$Å^3
Space group	$P^1 (\# 2)$
Z value	2
D_{calc}	1·555 g/cm^3
μ(MoKα)	8·43 cm^{-1}
B. *Intensity measurements*	
Diffractometer	Rigaku AFC5R
Radiation	MoK$\alpha(\lambda = 0.71069$ Å), Graphite monochromated
Temperature	20°C
Scan type	$\omega - 2\theta$
Scan width	$(1.20 + 0.50 \tan \theta)°$
Data collected	$\pm h, \pm k, +l$ ($2° < 2\theta < 46°$)
No. of reflections measured	Total: 2049; unique: 1863
C. *Structure solution and refinement*	
Structure solution	Direct methods (MULTAN)
Refinement	Full-matrix least-squares
Function minimized	$\Sigma \omega (|Fo|-|Fc|)^2$
Least squares weight	$\dfrac{1}{\sigma^2(Fo)} = \dfrac{4Fo2}{\sigma^2(Fo^2)}$
p-Factor	0·05
Anomalous dispersion	All non-hydrogen atoms
No. of observations (I > 2·50σ(I))	975
No. of variables	141
Reflection/parameter ratio	6·91
R(Rw)	0·075(0·084)
Goodness of fit indicator	1·68
Max-shift/error in final cycle	0·00
Maximum peak in final diff. map	0·62e$^-$/Å^3
Minimum peak in final diff. map	-0.44e$^-$/Å^3

The standard deviation of an observation of unit weight was 1·68.

structure solution and refinement are listed in table 1. Intensities were corrected for polarization and Lorentz factors. No absorption correction was made since the linear absorption coefficient for Mok$_a$ radiation is small (8·4 cm^{-1}). A tiny crystal was used for the measurements.

The structure was solved by MULTAN and refined by a full matrix least squares method using the program of teXsan. No attempt was made to locate hydrogen atoms. The position of some hydrogen atoms could be detected by the Fourier map. Since the inclusion of hydrogen atoms would further reduce the reflection/parameter ratio, they were not included in the refinement. Anisotropic parameters were used for chromium, oxygen and nitrogen atoms and isotropic parameters were employed for carbon. The final R factor was 7·5 (unweighted) and 8·4% (weighted).

2.8 *Kinetic studies*

The kinetics of the thiocyanate equilibration of $[Cr(salprn)(H_2O)_2]^+$ and $[Cr(sal-buen)(H_2O)_2]^+$ have been investigated in the temperature range of $10-50°C$ under the conditions, $[NCS^-] \gg [Cr(III)]$; $[NCS^-] = 0.1 - 0.5\,M$, $[Cr(III)] = 1 \times 10^{-4}\,M$, $[H^+] = 4 \times 10^{-1}$ to $10^{-6}\,M$ and $I = 1.0\,M$ (LiClO$_4$). Pseudo first-order rate constants for the equilibration, k_{eq}, have now been measured at different temperatures.

$$Cr(\text{Schiff base})(H_2O)_2^+ + NCS^- \overset{k_{eq}}{\rightleftharpoons} Cr(\text{Schiff base})(NCS)(H_2O) + H_2O.$$

(3)
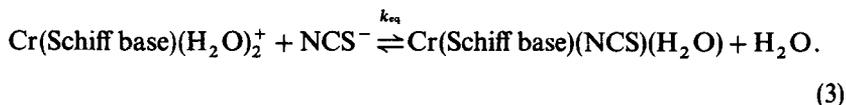
The pseudo first-order plots for the NCS$^-$ equilibration with the complex were linear to $> 93\%$ of the reaction.

2.9 *Product analysis*

The complex cation, $Cr(salprn)(H_2O)_2^+$, affords dithiocyanato product, $[Cr(salprn)(NCS)_2]^-$, on reaction with thiocyanate under preparative conditions which include a reaction time of 3 h at 55°C. It is necessary to examine the nature of the primary product of equilibration of NCS$^-$ with the complexes $Cr(\text{Schiff base})(H_2O)_2^+$ under kinetic conditions. Optical changes occurring in the spectral range of 650–400 nm were monitored as a function of reaction time under kinetic conditions in the case of NCS$^-$ equilibration with $Cr(salprn)(H_2O)_2^+$ at $[NCS^-] = 0.4\,M$ and $[H^+] = 0.1\,M$. The electronic spectra of authentic samples of the $Cr(salprn)(H_2O)_2^+$ and its dithio-cyanato $Cr(salprn)(NCS)_2^-$ derivative were also examined for any isosbestic point at the same $[H^+]$ conditions as the reaction mixture. Comparisons were made between isosbestic point observed for the equilibration under kinetic conditions employed for studies with that observed from the known spectra of the diaqua and dithiocyanato products.

2.10 *Instruments employed*

For the characterization of the Schiff-base ligands and their Cr(III) complexes made in this study, a Nicolet 20 DXB Fourier Transform Infra Red, and Shimadzu 160 A or Cary 219 UV-visible spectrophotometers as well as Bruker CXP 90 FT-NMR were employed.

3. Results and discussions

Elemental analysis data of the complexes investigated in this study are consistent with the general formulation, $[Cr(\text{Schiff base})(H_2O)_2]ClO_4$. The uv-visible spectral data on the $Cr(\text{Schiff-base})(H_2O)_2]ClO_4$ complexes where Schiff-base = salen, salprn, salbuen and acacen in the spectral range of 220–600 nm are presented in table 2. The electronic spectra of the Schiff-base complexes investigated are dominated by ligand centred and charge transfer type transitions in the spectral range of 220–440 nm. The absorption maxima observed for the diaqua complexes at 485, 580 and 545 nm for the salen, salprn and salbuen complexes respectively are assigned to *d-d* type transitions. For *trans*-complexes of Cr(III) with D_{4h} point group, four *d-d* bands are expected. (Perumareddi 1969). However, in the case of compounds where charge transfer transitions are

Table 2. UV-visible spectral data for Cr(Schiff-base) $(H_2O)_2^+$ complexes, where Schiff base = salen, salprn, salbuen and acacen in the spectral range 220–600 nm.

Cr(salen)(H₂O)₂⁺ [a]					
λ_{max}(nm)	220	235	277	381	485
ε_{max}(M⁻¹cm⁻¹)	40000	18800	20000	4800	275
Cr(salprn)(H₂O)₂⁺					
λ_{max}(nm)	220	271	366	485	580
ε_{max}(M⁻¹cm⁻¹)	36900	18800	4710	115	52·5
Cr(salbuen)(H₂O)₂⁺					
λ^{max}(nm)	225	277	388	545	
ε_{max}(M⁻¹cm⁻¹)	43700	23300	5200	135	
Cr(acacen)(H₂O)₂⁺ [a]					
λ_{max}(nm)	252	324	390	330	585
ε_{max}(M⁻¹cm⁻¹)	5012	6918	138	2760	57

[a] Prasad *et al* (1981)

sufficiently low in energy, some of the expected *d-d* transitions may not be well resolved. This appears to be the case for some of the $[Cr(\text{Schiff base})(H_2O)_2]^+$ complexes investigated.

It is appropriate to compare the energies for the lowest spin allowed *d-d* transitions of the $[Cr(\text{Schiff base})(H_2O)_2]^+$ complexes investigated with those of other related chromium(III) complexes with the CrN_2O_4 chromophore. The lowest energy *d-d* bands in the complexes $[Cr(\text{salprn})(H_2O)_2]^+$ and $[Cr(\text{salbuen})(H_2O)_2]^+$ observed at 17240 and 17095 cm^{-1}, respectively are lower when compared to the corresponding transitions in $Cr(\text{en})(H_2O)_4^+$ (19530 cm^{-1}), or $Cr(NH_3)_2(H_2O)_4^{3+}$ (19190 cm^{-1}) (Perumareddi 1969). In other words, the average ligand field stabilization energy of the Schiff bases, salprn and salbuen, appears to be lower than that expected for the N_2O_2 core structure associated with the tetradentate. A marginally higher ligand field stabilization energy is predicted for salen compared to salprn and salbuen on the basis of the electronic spectral data of these complexes.

The FT-IR spectra of $[Cr(\text{salen})(H_2O)_2]ClO_4$, $[Cr(\text{salprn})(H_2O)_2]ClO_4$ and $[Cr(\text{salbuen})(H_2O)_2]ClO_4$ complexes have been recorded using the KBr mull technique. Additional $\delta(CH_2)$ bands are observed in the FT-IR spectra at 1410 cm^{-1} in $[Cr(\text{salprn})(H_2O)_2]^+$ and 1432 and 1401 cm^{-1} in $[Cr(\text{salbuen})(H_2O)_2]^+$ when compared to that of $[Cr(\text{salen})(H_2O)_2]^+$. This is as expected. The number of $\rho(CH_2)$ bands in the IR spectra of the macrocyclic complexes of Cr(III) has been advantageously used for distinguishing *cis-* and *trans*-isomers previously (Poon and Pun 1980; Nair *et al* 1986). Higher numbers (4 to 5) of bands in the $\rho(CH_2)$ region have been reported for *cis*-compounds with a lower symmetry compared to those in corresponding *trans*-isomers of D_{4h} point group. In the case of the cation, $[Cr(\text{salen})(H_2O)_2]^+$, X-ray structure data reveal a *trans*-diaqua arrangement. In the complexes $[Cr(\text{salen}) (H_2O)_2]^+$ as well as $[Cr(\text{salprn})(H_2O)_2]^+$, only two bands are observed in the region 700–900 cm^{-1}. This supports the assignment of *trans*-diaqua structure to the complex $[Cr(\text{salprn})(H_2O)_2]^+$. On the other hand, a total of five bands are observed in the FT-IR spectrum of $[Cr(\text{salbuen})(H_2O)_2]^+$ in the range 740–910 cm^{-1}. These data suggest that a *cis*-$[Cr(\text{salbuen})(H_2O)_2]^+$ structural arrangement is not unlikely.

Resolved FT-NMR spectra could be observed for $[Cr(salen)(H_2O)_2]^+$ as well as $[Cr(salprn)(H_2O)_2]^+$ complexes. A triplet (centred at 2·98, 2·90, 2·81 ppm) and a quintuplet (centred at 1·85 ppm) are observed in the NMR spectrum of the salprn derivatives, whereas in the salen analogue only a singlet at 3·16 ppm is seen. This is in accordance with the structure of coordinated salen and salprn ligands.

Electrochemical investigations have been made to ascertain whether the quadridentate ligands, salen, salprn and salbuen afford significantly different reorganisational barriers for the Cr(III)–Cr(II) exchange reactions. The cyclic voltammograms of the $[Cr(Schiff-base)(H_2O)_2]^+$ complexes investigated reveal quasi-reversible electrochemical behaviour with anodic-cathodic peak separations being less than 72 mV and ratios of anodic to cathodic currents around $1·0 \pm 0·02$. The observed half wave potentials for the complexes are $-1·34$, $-1·31$ and $-1·41$ V against SCE for salen, salprn and salbuen derivatives of Cr(III) respectively. The observed differences in the electrochemical potentials are small and do not seem to warrant elaborate discussions based on the available structural data for the Cr(III) derivatives. The observed quasireversibility of the electrochemical behavior for Cr(III)/Cr(II) couple, however, indicates that the reorganisation involved in the Cr(III)/(II) exchange, may well be smaller than in $Cr(H_2O)_6^{3+,2+}$ couples. Meaningful discussions have to await an analysis of heterogeneous electron transfer rates.

The single crystal X-ray structure of the complex $[Cr(salprn)(H_2O)_2]Cl$ has now been resolved. The ORTEP plot of the complex cation is as shown in figure 1. The positional parameters of non-hydrogen atoms are listed in table 3. For comparison, bond distances and angles in the complex cations $[Cr(salen)(H_2O)_2]^+$ and $[Cr(salprn)(H_2O)_2]^+$ of interest to discussions in this study are included in table 4. It is evident from the data given in table 4 that the expansion of [12]-membered intraligand cavity size in salen to the [13]-membered ring in salprn relaxes the coordination geometry towards a more regular octahedron in $[Cr(salprn)(H_2O)_2]^+$ (compared to the salen analogue). Typically the angles subtended by the ligand donor atoms in salen derivative vary in the range of 81–95·7°, whereas in the salprn analogue the corresponding range is only 85–92·3°. Further, the two metal–water ligand bond lengths in the salen complex vary significantly viz. 2·085 and 1·923 Å whereas in the salprn analogue the two metal–water ligand bond distances, 2·03 and 2·00 Å, are more similar. The metal–salicylaldehydato oxygen donor atom distances are nearly equal in both
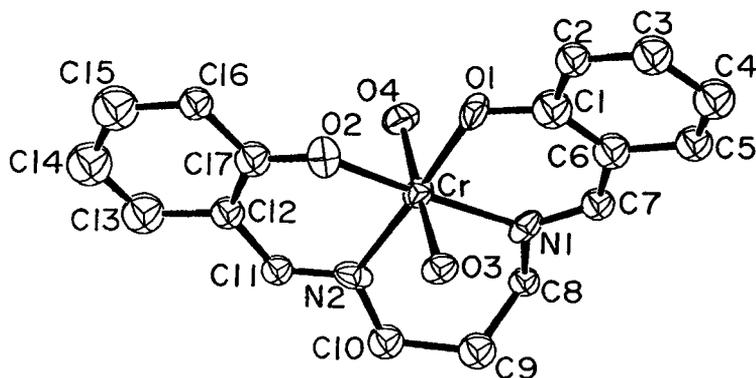

Figure 1. ORTEP-diagram of $[Cr(salprn)(H_2O)_2]^+$.

Table 3. Atomic position parameters and β_{iso}/β_{eq} values for non-hydrogen atoms in *trans*-Cr(salprn)(H$_2$O)$_2$Cl.

Atom	X	Y	Z	β_{eq}/β_{iso}^a
Cr1	0·1986(3)	0·4395(3)	0·2543(4)	2·08(7)
Cl1	0·4838(5)	0·2692(4)	0·7477(7)	3·7(1)
O1	0·004(1)	0·5926(9)	0·244(1)	2·4(3)
O2	0·067(1)	0·3840(9)	0·279(1)	2·7(3)
O3	0·206(1)	0·4677(9)	0·528(1)	2·7(3)
O4	0·200(1)	0·4096(9)	−0·016(1)	3·0(3)
N1	0·322(1)	0·513(1)	0·228(2)	2·4(4)
N2	0·399(1)	0·267(1)	0·259(2)	2·4(3)
C1	−0·023(2)	0·700(1)	0·291(2)	2·5(4)
C2	−0·177(2)	0·797(1)	0·337(2)	3·2(4)
C3	−0·212(2)	0·912(2)	0·388(2)	4·1(4)
C4	−0·088(2)	0·929(2)	0·386(2)	4·1(4)
C5	0·063(2)	0·834(1)	0·336(2)	3·3(4)
C6	0·096(2)	0·718(1)	0·292(2)	3·1(4)
C7	0·260(2)	0·628(2)	0·252(2)	2·3(3)
C8	0·495(2)	0·434(1)	0·192(2)	2·6(4)
C9	0·574(2)	0·340(1)	0·332(2)	3·4(4)
C10	0·564(2)	0·235(1)	0·283(2)	3·3(4)
C11	0·396(2)	0·174(1)	0·224(2)	2·5(4)
C12	0·256(2)	0·177(1)	0·196(2)	2·1(3)
C13	0·282(2)	0·062(2)	0·144(2)	4·4(5)
C14	0·158(2)	0·052(2)	0·121(2)	4·3(4)
C15	−0·003(2)	0·154(2)	0·140(3)	4·9(5)
C16	−0·030(2)	0·269(1)	0·190(2)	2·6(4)
C17	0·100(2)	0·279(1)	0·222(2)	2·3(3)

[a]For carbon atoms isotropic parameters, β_{iso}, and for other atoms β_{eq} are listed. The values of β_{eq} are given by
$$B_{eq} = 8/3\,\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha$$

Table 4. Important bond distances (Å) and bond angles (deg.) in Cr(salen)(H$_2$O)$_2^{+a}$ and Cr(salprn)(H$_2$O)$_2^+$ complexes.

	salen	salprn
Bond distances		
Cr–O1	1·951(8)	1·91(1)
Cr–O2	1·916(8)	1·94(1)
Cr–O3	2·085(9)	2·03(1)
Cr–O4	1·923(10)	2·01(1)
Cr–N1	1·997(8)	2·07(1)
Cr–N2	2·005(9)	2·07(1)
Bond angles		
O1–Cr–O2	95·1(0·3)	85·0(4)
O1–Cr–O3	87·7(0·3)	91·0(4)
O1–Cr–O4	91·0(0·4)	90·5(5)
O2–Cr–O3	89·4(0·3)	90·6(4)
O2–Cr–O4	92·0(0·3)	91·2(5)
O1–Cr–N1	91·7(0·4)	90·1(5)
O2–Cr–N2	91·2(0·4)	90·6(5)
O3–Cr–N1	88·2(0·4)	89·2(4)
O3–Cr–N2	85·5(0·4)	90·8(5)
O4–Cr–N1	90·5(0·4)	89·1(5)
O4–Cr–N2	95·7(0·4)	87·9(5)
N1–Cr–N2	81·6(0·4)	94·3(5)

[a]Data for *trans* Cr(salen)(H$_2$O)$_2^+$ taken from Coggon *et al* (1970)
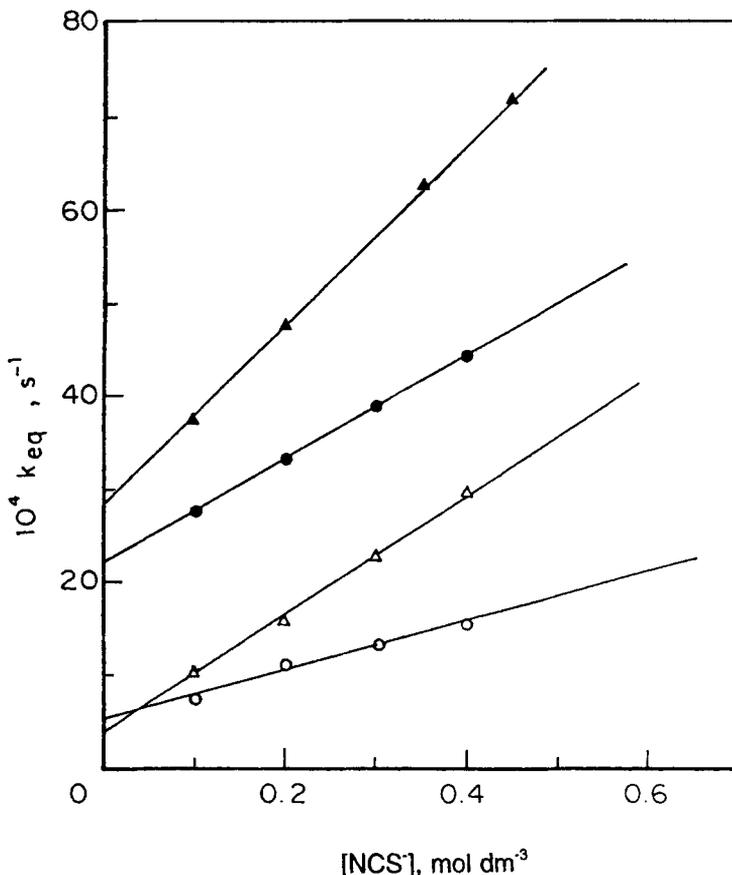
Figure 2. The [NCS⁻] dependence of k_{eq} for the reaction of $CrL(H_2O)_2^+$ with thiocyanate, where L = salen, [H⁺] = 0·001 M, $T = 40°C$ (O), [H⁺] = 0·001 M $T = 50°C$ (●) and L = salbuen, [H⁺] = 0·0004 M, $T = 10°C$ (Δ), [H⁺] = 0·0004 M, $T = 20°C$ (▲).

salen and salprn complexes (viz. 1·916 and 1·951 Å and 1·91 and 1·94 Å) respectively, as shown in table 4. The electronic effects of salicylaldehydato O⁻ bases at the metal centre may be expected to be similar in both salen and salprn complexes. Further expansion of the ring size of the quadridentate ligand to 14 in salbuen, seems to promote the folding of the macrocycle and lead to the formation of a *cis*- rather than *trans*-Cr(salbuen)$(H_2O)_2^+$. In spite of repeated efforts, crystals of appropriate quality for single crystal X-ray structure determination could not be obtained.

The approach to the equilibration between NCS⁻ and *trans*-Cr(salprn)$(H_2O)_2^+$ is attended by the maintenance of an isosbestic point at 650 nm. On the basis of the available evidence, the primary reaction product of the equilibration of NCS⁻ with Cr(salprn)$(H_2O)_2^+$ is assigned as Cr(salprn)(NCS)(H_2O). Plots of k_{eq} against [NCS⁻] shown in figure 2 for some selected reaction conditions are linear with positive intercepts indicating approach to an equilibrium. From the linear least squares fit of k_{eq} to [NCS⁻], the bimolecular rate constants for the forward step k_f and first-order rate constants for reverse reaction k_r, can be easily obtained using standard methods (Los Alamos Report 1959). The values of k_f (in $M^{-1} s^{-1}$) and k_r (in s^{-1}) obtained in

Table 5. Rate constants for the forward reaction, k_f, and reverse reaction, k_r, in the equilibration of NCS$^-$ with *trans*-Cr(Schiff-base)(H$_2$O)$_2^+$ at various [H$^+$], temperatures and $I = 1.0$ (LiClO$_4$).
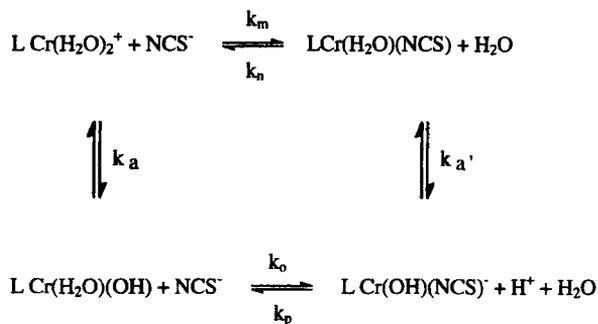
(Schiff base)	Temp. (°C)	pH	$10^3 k_f a$ (M^{-1}s^{-1})	$10^4 k_r$ (s^{-1})
salprn	30	1.0	0.70 ± 0.03	1.3 ± 0.1
		3.0	0.77 ± 0.04	1.6 ± 0.1
		3.3	0.75 ± 0.02	1.8 ± 0.15
		3.6	0.78 ± 0.02	2.0 ± 0.2
		4.1	1.15 ± 0.05	2.6 ± 0.2
		6.0	2.20 ± 0.1	19 ± 2
	40	1.1	1.5 ± 0.05	6.0 ± 0.5
		1.5	1.5 ± 0.07	6.2 ± 0.4
		3.0	2.3 ± 0.07	6.6 ± 0.5
		3.3	2.4 ± 0.09	7.6 ± 1
		4.0	2.6 ± 0.10	10 ± 1
		4.3	3.5 ± 0.10	18 ± 2
		4.6	4.9 ± 0.15	30 ± 4
		5.0	6.0 ± 0.25	45 ± 3
		5.3	6.6 ± 0.25	51 ± 3
		6.0	7.5 ± 0.30	56 ± 4
	50	1.5	5.5 ± 0.3	17 ± 2
		3.0	7.4 ± 0.3	14 ± 1
		3.3	8.3 ± 0.3	14 ± 1
		3.5	9.2 ± 0.4	15 ± 1
		4.0	11 ± 0.4	20 ± 2
		6.0	20 ± 1	75 ± 5
salbuen	10	3.4	66 ± 3	4 ± 0.5
	15	3.4	84 ± 5	9 ± 0.8
	20	3.4	122 ± 9	27 ± 1.2
		4.6	120 ± 9	24 ± 1.5
		5.5	128 ± 10	26 ± 1.5
	25	3.4	173 ± 11	31 ± 2.0

[a] At $pH = 8$, $10^3 k_f$ values obtained were (2.5 ± 0.3) and (9.2 ± 0.4) at 30° and 40°C respectively. These values were not used for computation because there were changes in pH of about $0.15 - 0.2$ units during the course of reaction.

this investigation are given in table 5. The observed kinetic data for the NCS$^-$ equilibration with the two new [Cr(Schiff-base)(H$_2$O)$_2$]$^+$ complexes (where Schiff base = salprn and salbuen) can be fitted to the same general reaction (scheme 1) employed previously for the [Cr(salen)(H$_2$O)$_2$]$^+$ cation (Prasad *et al* 1980, 1982).

The observed k_{eq} data have been fitted to [H$^+$] and [NCS$^-$] at each temperature using a standard nonlinear least squares software package written by Newton and Moore and implemented on an IBM PC/AT with 80406 co-processor (Los Alamos Report 1959). The rate law employed for the fit is –

$$k_{eq} = \frac{(k_m[\text{H}^+] + k_o K_a)[\text{NCS}^-]}{([\text{H}^+] + K_a)} + \frac{(k_n[\text{H}^+] + k_p K_a')}{([\text{H}^+] + K_a')} = k_f[\text{NCS}^-] + k_r .$$

(4)

$$L\ Cr(H_2O)_2^+ + NCS^- \xrightleftharpoons[k_n]{k_m} LCr(H_2O)(NCS) + H_2O$$

$$\Big\updownarrow k_a \qquad\qquad\qquad\qquad \Big\updownarrow k_{a'}$$

$$L\ Cr(H_2O)(OH) + NCS^- \xrightleftharpoons[k_p]{k_o} L\ Cr(OH)(NCS)^- + H^+ + H_2O$$
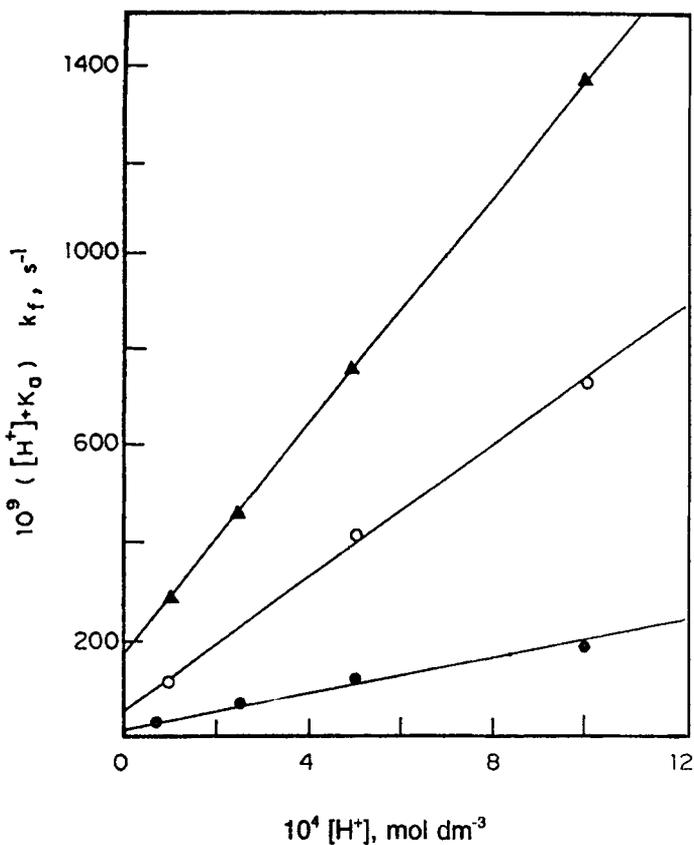
where L = Deprotonated Schiff base = salen, salprn and salbuen.

Scheme 1.

Figure 3. Plot of $([H^+] + K_a)k_f$ against $[H^+]$ for the thiocyanate anation of $Cr(salprn)(H_2O)_2^+$, When $I = 1{\cdot}0\,M$, $(LiClO_4)$, $[Cr(III)] = 1 \times 10^{-4}\,M$, $T = 30^{\circ}C$ (●), $40^{\circ}C$ (○) and $50^{\circ}C$ (▲).

The values of k_f computed from this study have been analyzed using

$$k_f = \frac{(k_m[H^+] + k_o K_a)}{[H^+] + K_a}, \tag{5}$$

and

$$k_f([H^+] + K_a) = k_m[H^+] + k_o K_a. \tag{6}$$

When the potentiometrically determined values of K_a are employed for the computation, plots of $k_f([H^+] + K_a)$ against $[H^+]$ are linear as shown in figure 3. The rate constants for the NCS$^-$ anation into the conjugate acid forms [Cr(Schiff-base)(H$_2$O)$_2$]$^+$, where Schiff-base = salen, salprn and salbuen, k_m, have been obtained. The values of k_m computed for the NCS$^-$ reaction with the diaqua complexes [Cr(salprn)(H$_2$O)$_2$]$^+$ and [Cr(salbuen)(H$_2$O)$_2$]$^+$ at each temperature have been listed in table 6. From the Arrehenius fit of k_m data to temperature, activation energies $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the anation into the diaqua species have been computed. The $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values estimated are 87 ± 5 kJ mol^{-1} and -27 ± 13 JK mol^{-1} for [Cr(salprn) (H$_2$O)$_2$]$^+$ and 100 ± 8 kJ mol^{-1} and 62 ± 25 JK^{-1} mol^{-1} for [Cr(salbuen)(H$_2$O)$_2^+$, respectively. These values are to be compared to 64 ± 7 kJ mol^{-1} and -42 ± 24 JK^{-1} mol^{-1} reported for the analogous reaction step of [Cr(salen)(H$_2$O$_2$)]$^+$ (Prasad *et al* 1980, 1982).

The bimolecular rate constants k_m for the aqua ligand substitution in Cr(Schiff base)(H$_2$O)$_2$]$^+$ complexes at $T = 25°C$ and $I = 1·0$ M (LiClO$_4$) have been calculated. They are $1·5 \times 10^{-1}$, $4·0 \times 10^{-4}$ and $1·7 \times 10^{-2}$ M^{-1} s^{-1} for salen, salprn and salbuen complexes of Cr(III), respectively. Single crystal X-ray structure data show unambiguously a *trans*-diaqua structure for the salen and salprn analogues.

All the three Schiff-base ligands investigated in this study are derived from salicylaldehydato O$^-$ bases. However, significant differences are observed in the kinetic and activation parameters for the aqua ligand substitution by NCS$^-$ in the complex cation [Cr(Schiff-base)(H$_2$O)$_2$]$^+$. A *cis*-structure appears feasible on the basis of FT-IR evidence and molecular mechanics calculations for the cation [Cr(salbuen)(H$_2$O)$_2$]$^+$. Since reliable X-ray structural data for the salbuen derivative could not be obtained due to experimental difficulties, discussions have to be limited to the substitutional reactions of complexes, *trans*-[Cr(Schiff-base)(H$_2$O)$_2$]$^+$, where Schiff-base = salen and salprn at this stage.

Crystal structures of salen and salprn analogues of [Cr(Schiff-base)(H$_2$O)$_2$]$^+$ show that in the salprn derivative, the coordination geometry is relaxed towards a more regular octahedral arrangement. The M-OH$_2$ bond lengths of relevance to substitution

Table 6. The values of k_m for the reaction of Cr(Schiff-base)(H$_2$O)$_2^+$ with NCS$^-$ where Schiff base = salprn and salbuen at different temperatures.

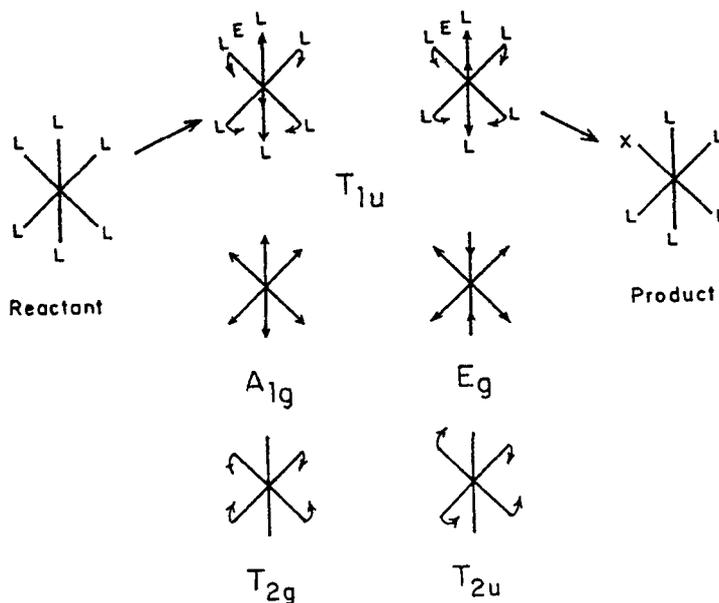| Schiff base	Temp. (°C)	$10^3 k_m$ (M^{-1}s^{-1})
salprn	30	0·68 ± 0·03
	40	1·8 ± 0·2
	50	6·3 ± 0·5
salbuen	10	2·2 ± 0·2
	20	12·2 ± 1
	25	17 ± 1
	30	42 ± 2

Figure 4. Normal coordinate analysis for heterolytic substitutions in complexes of O_h symmetry favouring T_{1u} over other modes as promoting vibrational pathways where E and L represent entering and leaving ligands.

are 2·085 Å and 2·03 Å in salen and salprn respectively. Although $\Delta H^{\ddagger}$ values estimated in this study are associated with significant errors due to the nature of the system, there is sufficient ground to suggest that one of the $Cr-OH_2$ bonds in the salen derivative is weaker as compared to those in the salprn analogue. Based on the longer and weaker $Cr-OH_2$ bond, the aqua ligand substitution in salen is expected to be more facile compared to that in salprn. There are significant differences in the $\Delta S^{\ddagger}$ values for the NCS^- anation of the Schiff-base complexes investigated in this study. In other words, the solvational characteristics of the complexes seem to be influenced markedly by the nature of the Schiff bases, which are non-leaving ligands in the reaction of interest in this study.

It may be appropriate to consider the various normal modes of vibrations for octahedral symmetry in preparing a reactant along the (heterolytic) substitutional reaction coordinate (as in figure 4). Among the different vibrational modes T_{1u} type distortions seem more relevant to heterolytic substitution than other promoting vibrations regardless of whether the reaction follows an associative or dissociative mode of mechanistic pathways. It is noteworthy that vibrational promotions along T_{1u} type modes implicate also the nuclear displacements of non-leaving ligand environment away from the equatorial plane of an octahedron. It is of interest that in *trans*-[Cr(salen)(H₂O)₂]⁺, the metal ion is displaced away from the plane of the ring donor atoms of salen (although only by 0·077 Å) in the ground state. In other words, ground state distortion towards the geometry of a possible transition state is likely in the salen derivative. On the other hand, on adding a CH_2 unit in the macrocycle as in salprn, deviations from octahedron towards T_{1u} type distortion are minimized and the aqua ligand lability diminished markedly. In the absence of precise X-ray structural

information on $[Cr(salbuen)(H_2O)_2]^+$, the observed lability of the complex needs to be discussed in terms of possible changes in the geometry of the aqua ligand from *trans*-to *cis*-configuration. The steric strain arising from the coordination of the quadridentate ligands may seem to influence the relative aqua ligand substitutional lability in a homologous series of $[Cr(salen)(H_2O)_2]^+$ type complexes.

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