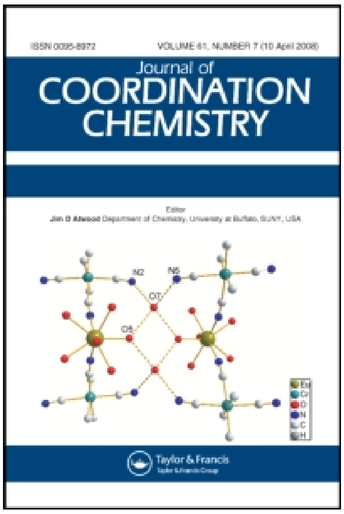

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

CRYSTAL AND MOLECULAR STRUCTURE OF CIS-DICHLORO(1,4,8,11-TETRAAZACYCLOTETRA-DECANE)RHODIUM(III) CHLORIDE, [Rh(cyclam)Cl_2]Cl

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To cite this Article Rosales, María J. , Sosa, Martha E. and Tobe, Martin L.(1987) 'CRYSTAL AND MOLECULAR STRUCTURE OF CIS-DICHLORO(1,4,8,11-TETRAAZACYCLOTETRA-DECANE)RHODIUM(III) CHLORIDE, [Rh(cyclam)Cl_2]Cl', Journal of Coordination Chemistry, 16: 1, 59 — 65

To link to this Article: DOI: 10.1080/00958978708079806

URL: http://dx.doi.org/10.1080/00958978708079806

J. Coord. Chem. 1987, Vol. 16 p. 59–65
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CRYSTAL AND MOLECULAR STRUCTURE OF CIS-DICHLORO(1,4,8,11-TETRAAZACYCLOTETRADECANE)RHODIUM(III) CHLORIDE, [Rh(cyclam)Cl_2]Cl.

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(Received July 14 1986; in final form October 10, 1986)

The crystal and molecular structure of the title compound has been determined from three-dimensional X-ray intensity data. The pale yellow crystals are monoclinic with space group $P2_1/c$, with $a = 7.563(2)$, $b = 14.408(3)$, $c = 14.666(3)$ Å, $\beta = 102.56(2)°$, $Z = 4$. The structure has been refined to $R = 0.023$ ($R_w = 0.025$). The metal is octahedrally coordinated with the angles between the adjacent coordination sites varying from 83.8(1)° to 95.1(1)° and the macrocyclic ligand is diagonally folded with the *R, R, R, R* (and *S, S, S, S*) configurations of the nitrogens, the centrosymmetric cell containing enantiomeric pairs of cations. The two coordinated chlorines occupy *cis* sites. Strong hydrogen bonding interactions between the amine protons *trans* to coordinated Cl and the chloride counter ions (N-H . . . Cl^- = 2.343 and 2.408 Å) are observed. These interactions, which have previously been deduced from a comparison of the ^1H n.m.r. spectra of the perchlorate and chloride salts in $^2H_6$ dimethyl sulphoxide are therefore also present in the solid state. There are no structural features to account for the very large difference in the exchange labilities of the protons on the nitrogens *trans* to Cl and those on the nitrogens *trans* to N.

Keywords: Rhodium, cyclam, chloride, structure, x-ray.

INTRODUCTION

The base catalysed substitution reactions of octahedral amine complexes are initiated by deprotonation and the rate constants for these reactions are therefore related to those for proton exchange.[1] As part of a general study of these relationships we have examined the kinetics of proton exchange of the various isomers of the complexes, $[M(cyclam)Cl_2]^+$ (*cyclam* = 1,4,8,11-tetraazacyclotetradecane; M = Co(III),[2] Cr(III),[3] Rh(III)[3] and Ru(III)[3]). Two isomers of the Rh(III) species had been identified as *cis* and *trans* respectively[4] and the ^1H n.m.r. spectrum of the perchlorate of the *cis* species contained two broad peaks of equal area assigned to the N-*H* protons (that of the *trans* isomer having only one N-*H* signal).[3] One of the two N-*H* peaks of the *cis* isomer in $^2H_6$-dimethyl sulphoxide is shifted by the addition of LiCl and, assuming that such a shift is due to ion-association which takes place as far as possible from the coordinated Cl and

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is assisted by N-H . . . Cl$^-$ hydrogen bonding, the complex was assigned the *R, R, R, R* (*S, S, S, S*) configuration at the nitrogens. This configuration is adopted by the corresponding Co(III)[5] and Cr(III)[6,7] complexes. Since the proton exchange kinetics were followed by measuring the changing area under the peaks it was necessary to be sure of the assignment, and for this reason the structure of crystalline *cis*-[Rh(cyclam)Cl$_2$]Cl was studied. The results are reported in this paper.

EXPERIMENTAL

Preparations

1,4,8,11-tetraazacyclotetradecane (cyclam) was prepared by the method of Barefield *et al.*[7] *cis*-[Rh(cyclam)Cl$_2$]Cl was prepared by the method of Bounsall and Koprich.[4]

X-ray Structure Determination

Preliminary cell dimensions were obtained by Weissenberg photographic techniques (CuK_α radiation). The crystal, with dimensions 0.355 × 0.288 × 0.45 mm was then transferred to a Stoe four-circle diffractometer where accurate cell dimensions were obtained by least-squares refinement of 60 automatically centred reflections in the range $20° < 2\phi < 30.°$

Crystal data

$C_{10}H_{24}Cl_3N_4Rh$, $M = 410.58$, monoclinic space group $P2_1/c$ (No. 14), $a = 7.563(2)$, $b = 14.408(3)$, $c = 14.666(3)$ Å, $\beta = 102.56(2)°$, $V = 1559.9$ Å^3, $Z = 4$, $Dc = 1.748$ g cm^{-3}, Dm not measured, $F(000) = 752$, MoK_α radiation, $\lambda = 0.71069$ Å, $\mu(\text{Mo}K_\alpha) = 15.26$ cm^{-1}.

Data Collection and Processing

Intensity data were recorded using graphite monochromated MoK_α radiation, a ω-ϕ scan procedure; 24 steps, step width 0.05, variable scan speed from 0.10° s^{-1} to 0.25° s^{-1}, $5 \leqslant 2\phi \leqslant 50°$. Three check reflections were monitored every 50 measurements throughout the data collection and showed no significant variation, 6022 reflections were measured, a face indexing absorption correction was made (faces [100], [011]). Maximum and minimum transmission factors were 0.72 and 0.64 respectively. 2739 unique reflections with $F > 4\sigma(\text{Fo})$ were used in the calculations.

Structure Analysis and Refinements

The structure was solved by direct methods and subsequent electron-density difference synthesis. Refinement was by full-matrix least-squares methods with all non-hydrogen atoms assigned anisotropic thermal parameters. Methylene hydrogen atoms were placed in idealised positions and allowed to ride 1.08 A from the relevant carbon; these hydrogen atoms were assigned a common isotropic temperature factor. The hydrogen atoms bonded to N atoms were located in the difference map and assigned a common isotropic temperature factor in the remaining refinement cycle. Three reflections suffering from secondary extinction were omitted. Refinement of the structure continued until convergence was reached, $R = 0.023$, $R_w = 0.025$ [$R_w = (\Sigma w\Delta^2/$

TABLE I
Atomic Co-ordinates for Non-hydrogen Atoms (x10^4)

Atom	*x/a*	*y/b*	*z/c*
Rh(1)	7967(1)	2402(1)	9054(1)
Cl(1)	8851(1)	3652(1)	8202(1)
C1(2)	9926(1)	1431(1)	8424(1)
C1(3)	4341(1)	2920(1)	5851(1)
N(1)	5709(3)	2175(2)	7986(2)
N(2)	7313(3)	1274(1)	9795(1)
N(3)	10008(3)	2604(1)	10232(2)
N(4)	6271(3)	3308(2)	9545(2)
C(1)	5275(4)	1193(2)	7701(2)
C(2)	4990(4)	573(2)	8497(2)
C(3)	6690(4)	421(2)	9247(2)
C(4)	8943(4)	1069(2)	10539(2)
C(5)	9681(4)	1961(2)	10980(2)
C(6)	10322(4)	3569(2)	10585(2)
C(7)	8667(4)	4014(2)	10826(2)
C(8)	7099(4)	4170(2)	10004(2)
C(9)	4747(4)	3530(2)	8748(2)
C(10)	4128(4)	2644(2)	8239(2)

$\Sigma w F_o^2)^{1/2}]$*. Complex neutral scattering factors[9] were employed throughout the structure solution and refinement. All computations were performed on the University of Cambridge IBM 3081 computer using programmes written by Professor G.M. Sheldrick.[10] The final atomic coordinates are listed in Table I. The molecular plot was drawn using the ORTEP programme.[11]

RESULTS AND DISCUSSION

Figure 1 shows a perspective view of the structure of the cationic complex together with the numbering scheme adopted. Bond lengths and angles are listed in Table II.

The structure consists of discrete [Rh(cyclam)Cl$_2$]$^+$ cations and Cl$^-$ anions. As predicted,[3] the complex cation displays octahedral coordination with the macrocyclic ligand folded diagonally at N(1) and N(3), coordinating to four adjacent sites of the Rh atom, the two chloride ligands occupying the remaining *cis* sites. Angles between adjacent coordination sites of the Rh atom vary from 83.1(1)° to 95.1(1)°. It is therefore a compound with very little distortion from octahedral geometry.

The values of the bond distances and angles within the chelate rings correspond closely to the same parameters in the *trans* Ru(III)[12] and *cis* Cr(III)[6,7] complexes and are similar to those found in the structure of [cyclam H$_2$] (ClO$_4$)$_2$.[13] Based on the sequence rule priority, H < CH$_2$CH$_2$CH$_2$ < CH$_2$CH$_2$NH < Rh, the enantiomeric forms in the unit cell have the *RRRR* and *SSSS* configurations and in the former the '*en*' rings adopt the δ conformation while the '*tn*' rings adopt the chair form. In this respect the structure is the same as that of the resolved $(-)_{589}$-*cis*-$\delta\delta cc$-$\Lambda_{en}, \Delta_{tn}$-(*RRRR*)-CrCl$_2$(cyclam)$^+$ cation, the structure of whose perchlorate has been reported[6] and virtually identical to that of the racemic chloride.[7]

Two points of considerable interest arise when we look for relationships between the solution properties of these complexes, in particular their amine proton exchange labilities and ion-association, and the structures of the crystalline solids. In the Rh(III)

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*The weighting scheme used was $w = 6.196/[\sigma^2(F_o) + 0.000101|F_o|^2]$.

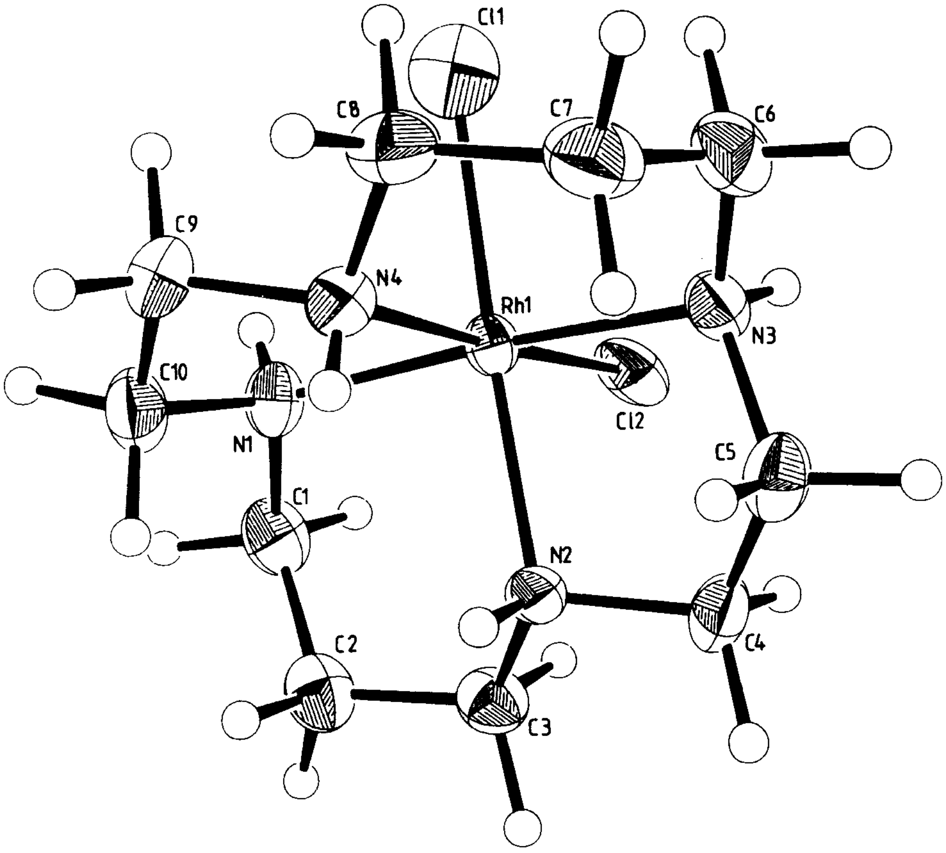

FIGURE 1 View of the complex cation

complex, the rate constant for the exchange of the proton on the nitrogen *trans* to Cl (9.9×10^5 dm^3 mol^{-1} s^{-1}; 20°C), is very much greater than that for exchange of the protons on the mutually *trans* nitrogens (4.5 dm^3 mol^{-1} s^{-1}; 20°C).[3] This is quantitatively much greater than the effect in analogous Co(III) systems where the dependence of amine proton lability on the nature and position of the other ligands in the complex has been more thoroughly studied. It has been suggested that there is a very marked *trans* effect in which the weakest σ donor produces the greatest labilisation.[14] The nitrogen *trans* to such a ligand is able to develop its bond to the metal with least competition and its protons are thereby labilised. There is no indication in the structure of the *cis*-$[Rh(cyclam)Cl_2]^+$ cation of any measurable difference in the *trans* influences of NHR_2 and Cl and, although two of the N-H bonds are longer than the others, one is *trans* to Cl and the other *trans* to NHR_2. The proton exchange labilities of the $[Cr(cyclam)Cl_2]^+$ cations [k_1 (*trans* to Cl in the *RRRR(SSSS)-cis* complex) = 8.2×10^3 dm^3 mol^{-1} s^{-1}; 0°C; (*trans* to NHR_2 in the *RSSR-trans* complex) = 9.8 dm^3 mol^{-1} s^{-1}, 0°C[3,15]] are smaller and less sensitive to the nature of the *trans* ligand. In the crystalline solids, the Cr-N bond distances are more sensitive to the nature of the counter ion than to the nature of the *trans* ligand. Thus, in *RRRR(SSSS)-cis*-$[Cr(cyclam)Cl_2]Cl$, Cr-N = 2.097 Å (*trans* to N) and 2.013 Å (*trans* to Cl)[7] while in *RRRR-cis*-$[Cr(cyclam)Cl_2]ClO_4$, Cr-N = 2.084 Å (*trans* to N) and 2.076 Å (*trans* to Cl).[6] Unless one can show that bond

TABLE II

Bond Lengths (Å) and Interbond Angles (°) for the Complex.

Bond Lengths			
C1(1)-Rh(1)	2.371(1)	C1()-Rh(1)	2.367(1)
N(1)-Rh(1)	2.077(2)	N(2)-Rh(1)	2.074(2)
N(3)-Rh(1)	2.071(2)	N(4)-Rh(1)	2.066(2)
C(1)-N(1)	1.491(3)	C(10)-N(1)	1.490(4)
N(1)-H(1N)	0.731(33)	N(2)-H(2N)	0.871(28)
C(3)-N(2)	1.489(3)	C(4)-N(2)	1.487(3)
H(3N)-N(3)	0.871(33)	C(5)-N(3)	1.497(3)
C(6)-N(3)	1.485(3)	H(4N)-N(4)	0.785(28)
C(8)-N(4)	1.485(3)	C(9)-N(4)	1.487(3)
C(2)-C(1)	1.522(4)	C(3)-C(2)	1.515(4)
C(5)-C(4)	1.491(4)	C(7)-C(6)	1.514(4)
C(8)-C(7)	1.514(4)	C(10)-C(9)	1.502(4)
Bond Angles			
Cl(2)-Rh(1)-Cl(1)	88.3(1)	N(1)-Rh(1)-C1(1)	90.1(1)
N(1)-Rh(1)-Cl(2)	95.4(1)	N(2)-Rh(1)-C1(1)	177.1(1)
N(2)-Rh(1)-C1(2)	89.0(1)	N(2)-Rh(1)-N(1)	91.2(1)
N(3)-Rh(1)-C1(1)	95.1(1)	N(3)-Rh(1)-C1(2)	89.6(1)
N(3)-Rh(1)-N(1)	173.0(1)	N(3)-Rh(1)-N(2)	83.8(1)
N(4)-Rh(1)-C1(1)	88.4(1)	N(4)-Rh(1)-C1(2)	176.6(1)
N(4)-Rh(1)-N(1)	83.8(1)	N(4)-Rh(1)-N(2)	94.3(1)
N(4)-Rh(1)-N(3)	91.6(1)	H(1N)-N(1)-Rh(1)	106.0(28)
C(1)-N(1)-Rh(1)	117.1(2)	C(1)-N(1)-H(1N)	108.7(23)
C(10)-N(1)-Rh(1)	108.2(2)	C(10)-N(1)-H(1N)	104.8(26)
C(10)-N(1)-C(1)	111.1(2)	H(2N)-N(2)-Rh(1)	106.3(19)
C(3)-N(2)-Rh(1)	116.6(2)	C(4)-N(2)-H(2N)	109.3(18)
C(4)-N92)-Rh(1)	106.6(2)	C(4)-N(2)-H(2N)	107.4(18)
C(4)-N(2)-C(3)	110.3(2)	H(3N)-N(3)-Rh(1)	102.0(21)
C(5)-N(3)-Rh(1)	108.2(2)	C(5)-N(3)-H(3N)	107.8(19)
C(6)-N(3)-Rh(1)	117.1(2)	C(6)-N(3)-H(3N)	109.7(18)
C(6)-N(3)-C(5)	111.3(2)	H(4N)-N(4)-Rh(1)	111.5(22)
C(8)-N(4)-Rh(1)	117.0(2)	C(8)-N(4)-H(4N)	107.7(21)
C(9)-N(4)-Rh(1)	107.2(2)	C(9)-N(4)-H(4N)	101.5(21)
C(9)-N(4)-C(8)	110.7(2)	C(2)-C(1)-N(1)	113.7(2)
C(3)-C(2)-C(1)	113.7(2)	C(2)-C(3)-N(2)	113.1(2)
C(5)-C(4)-N(2)	108.6(2)	C(4)-C(5)-N(3)	108.8(2)
C(7)-C(6)-N(3)	113.6(2)	C(8)-C(7)-C(6)	114.9(2)
C(7)-C(8)-N(4)	114.6(2)	C(10)-C(9)-N(4)	108.2(2)
C(9)-C(10)-N(1)	109.2(2)		

distances are too insensitive a probe of *trans* influence it will be necessary to seek an alternative explanation of the *trans* effect on amine proton labilisation.

It has been shown that, in $^2H_6$ dimethylsulphoxide solution, the ^1H n.m.r. spectrum of *cis*-[Rh(cyclam)Cl$_2$]ClO$_4$ (broad peaks assigned to NH at δ 6.16 and δ 6.52) is sensitive to the addition of LiCl, the peak at δ 6.16 shifting with increasing [LiCl] to δ 8.1.[3] This was also observed for the Co(III) complex[2] and has previously been discussed in terms of ion-association and hydrogen bonding with the protons on nitrogens remote from the coordinated acido group.[16] This effect has been used to assign the amine proton signals in the study of proton exchange.[2,3,17] The hydrogen bonding between the amine protons and the chloride counter ion is carried over into the structure of the crystalline solid and is evident in the packing. There are short, non-bonding contacts between the four amine protons and the non-coordinating chloride ions that surround the cation in the unit cell. The hydrogen atoms bound to the nitrogen were located directly in a difference Fourier map and their position parameters were successfully refined in the last cycles of the least-squares refinement. The packing diagram, Figure 2, shows the proximity of these protons to the chloride ions. These contacts are all shorter than the sum of the Van der Walls radii (3.0 - 3.3 Å[18]) but it is those involving H2N and H4N that

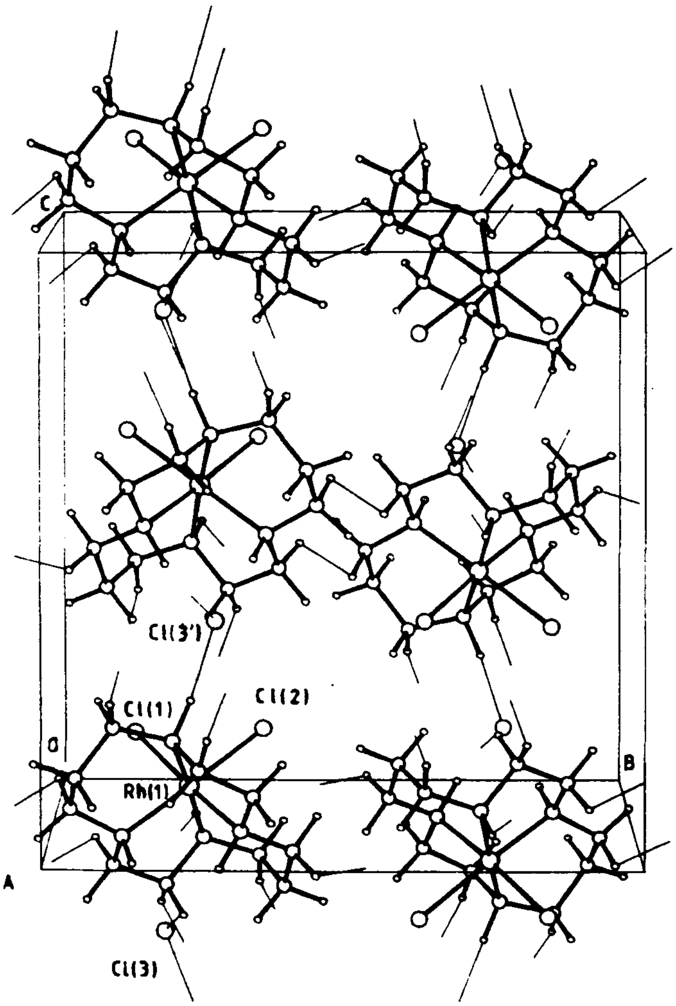

Figure 2 View of the crystal packing down the *a* axis.

are the shorter. These protons, which are bound to the nitrogen atoms *trans* to the coordinated chlorines, are found at 2.343 and 2.408 Å from a chloride. H1N and H3N, which lie *trans* to each other in the complex, form slightly longer contacts from two different chloride anions at 2.645 and 2.617 Å. This effect has recently been observed in the very similar structure of the corresponding Cr(III) complex *cis-RRRR(SSSS)*-[Cr(cyclam)Cl_2]Cl[7] and is absent of the structure of the *RRRR* perchlorate where hydrogen bonding between the perchlorate anion and the amine protons is not observed but is replaced by slight intermolecular hydrogen bonding interactions between the coordinated chloride and the amine protons on adjacent cation groups (N-H. . .Cl = *ca* 3.28 Å).[6,7]

ACKNOWLEDGEMENTS

We wish to thank Dr. P. Raithby for his assistance.

SUPPLEMENTARY MATERIAL AVAILABLE

Lists of anisotropic thermal parameters, hydrogen positions and observed and calculated structure factors have been deposited with the Editor and are available upon request.

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