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The Infrared Spectra of Some *Cis*- and *Trans*- Isomers of Octahedral Cobalt(III) Complexes with a Cyclic Quadridentate Secondary Amine*

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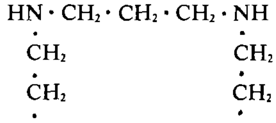
Received December 7, 1970

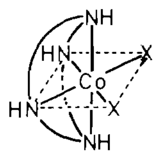
The infrared spectra of 22 different complex cations with a variety of anions of mononuclear cobalt(III) and binuclear peroxo-bridge cobalt(III) complexes with 1,4,8,11–tetraazacyclotetradecane (cyclam) have been examined. Consistent differences between the spectra of cis– *and* trans– *isomers have been found in the region 800-910 cm^{-1}. Deuteration studies suggest that the vibrational modes of both the secondary amine and methylene groups which occur in this region are useful in differentiating between the two geometric isomers of cobalt(III) cyclam complexes.*

Introduction

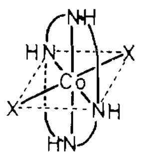
As a continued program to examine the structural and mechanistic behaviour of octahedral cobalt(III) complexes containing a macrocyclic ligand, 1,4,8,11–tetraazacyclotetradecane (cyclam) it is desirable to investigate the various physical techniques for differentiating between *cis*- and *trans*- isomers of new complexes. Visible and magnetic resonance spectra have been used with varying degrees of success.[1-3] The method of comparing the visible absorption spectra of cyclam complexes with the spectra of the *cis*- and *trans*- isomers of the corresponding bis(ethylenediamine) cobalt(III) complexes is reliable only when the spectra of the two geometric isomers are distinctly different, *e.g.* in the dihalo, diaquo and diazido complexes.[1,3] This method is much less decisive for [Cocyclam(NO_2)$_2$]$^+$ and [Cocyclam(NCS)$_2$]$^+$ where the spectral difference between the *cis*- and *trans*- isomers is small. The presence of two isomers of the same compound, however, still enables a comparision to be made. The method becomes totally inapplicable when a compound has very similar *cis*- and *trans*- spectra and when only one isomer of the compound is available, *e.g.* [CocyclamNO_2Cl]$^+$. The NMR method proves very useful for disubstituted mononuclear complexes. Unfortunately, this method requires too much compound for a single determination and there is also a solubility problem. It is, therefore, urgently needed to search for another physical method. This paper describes the applicability of infrared spectroscopy for differentiating between *cis*- and *trans*- isomers of new cobalt(III) cyclam complexes.



(cyclam)



Cis-configuration



Trans-configuration

Experimental Section

Preparation of the Compounds. Most of the compounds examined here are prepared by standard methods published elsewhere,[1-4] except *trans*–[Cocyclam(CN)$_2$]Cl and *trans*–[CocyclamNH_3Cl]Cl_2 which are prepared by the methods of Mok[5] and *trans*–[CocyclamNO_2Br]Br which is prepared by the method of Lui.[6]

Deuteration of the Compounds. Deuterated *trans*–[CocyclamCl_2]Cl was prepared by dissolving the protic compound in a minimum amount of deuterium oxide (99.7%) at 80° and the solution was maintained at this temperature for one hour. On cooling the solution in an ice bath, the deuterated *trans*–[CocyclamCl_2]Cl crystallised out which was filtered off and washed with acetone and ether and was air dried. The purity of the compound was checked by comparing its visible absorption spectrum in water with the known spectrum of *trans*–[CocyclamCl_2]Cl.[1]

The partially deuterated *cis*–[Cocyclam(NO_2)$_2$]NO_3 was prepared and checekd in a similar manner.

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* Work performed in part at the University College, London, under the supervision of Dr. M.L. Tobe.

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(4) K.S. Mok and C.K. Poon, *Inorg. Chem.*, *10*, 225 (1971).
(5) K.S. Mok and C.K. Poon, unpublished results.
(6) C.K. Lui and C.K. Poon, in press.

Here the solution was only warmed up to 60° for 30 min. and concentrated nitric acid was added to the cooled D_2O solution to crystallize out the product. Complete deuteration of the compound was complicated by the isomerization reaction.

Physical Measurement. The infrared spectra of nujol mulls between KBr windows were measured with a Perkin-Elmer 337 spectrophotometer.

Results and Discussion

The use of infrared spectroscopy as a proble to differentiate between *cis-* and *trans-* isomers of the closely related bis(ethylenediamine)cobalt(III) complexes have been extensively studied.[7-12] It has been found that in each of the following three regions of absorption, *viz.* ~1600, ~1120-1150, and ~870-900 cm^{-1}, to which the NH_2 asymmetric deformation, the symmetric deformation and the CH_2 rocking modes have been assigned respectively, most complexes with a *cis-* configuration show two bands, while those with a *trans-* configuration show one. In particular, the bands in the CH_2 rocking region, which are insensitive to changes in the ligands or anions,[10] have been widely used with success. The infrared spectra in the 510-600 cm^{-1} region where CO–N stretching modes occur has also been used. It was claimed that in this region no *trans-* complex had more than three bands, while all *cis-* complexes had at least four bands.[11,12]

When the infrared spectra of the four known *cis*–*trans*– pairs of $[CocyclamCl_2]Cl$, $[Cocyclam(N_3)_2]NO_3$, $[Cocyclam(NO_2)_2](PtCl_6)_{1/2}$ and $[Cocyclam(NCS)_2](PtCl_6)_{1/2}$, which were characterized by visible

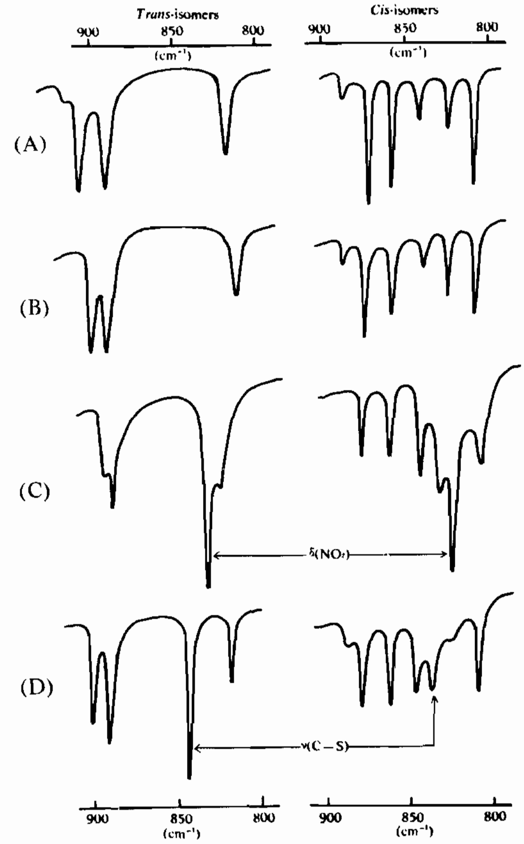

Figure 1. Infrared Spectra in the 800-910 cm^{-1} region of some *cis-* and *trans-* cobalt(III) cyclam complexes.
(A) $[Cocyclam\ Cl_2]Cl$
(B) $[Cocyclam(N_3)_2]NO_3$
(C) $[CoCyclam(NO_2)_2](PtCl_6)_{1/2}$
(D) $[Cocyclam(NCS)_2](PtCl_6)_{1/2}$

Table I. Infrared spectra in the 800-910 cm^{-1} region of some cobalt(III) cyclam complexes

Complexes	Frequencies of absorption bands (cm^{-1}) [a]									
cis-$[Co\ cyclam\ CO_3]Cl$		890(w)	877(w)	860(w)	845(w)	833(m) [b]	828(m)			810(m)
cis-$[Co\ cyclam\ Cl_2]Cl$		890(w)	872(s)	859(s)	841(w)		824(w)			808(s)
cis-$[Co\ cyclam\ (N_3)_2]NO_3$		888(w)	874(m)	859(m)	840(w)		825(m)			808(m)
cis-$[Co\ cyclam\ (N_3)_2](PtCl_6)_{1/2}$		889(w)	875(m)	859(w)	844(w)		818(w)			808(m)
cis-$[Co\ cyclam\ (NCS)_2](PtCl_6)_{1/2}$		890(wsh)	876(m)	860(m)	846(m)	836(m) [c]	822(wsh)			807(m)
cis-$[Co\ cyclam\ (NO_2)_2]NO_3$			874(m)	860(m)	840(w)		828(m)		820(s) [d]	802(w)
cis-$[Co\ cyclam\ (NO_2)_2](PtCl_6)_{1/2}$			877(m)	860(m)	842(m)		832(m)		822(s) [d]	805(m)
trans-$[Co\ cyclam\ Cl_2]Cl$	906(s)	888(s)								818(s)
trans-$[Co\ cyclam\ Cl_2]NO_3$	905(s)	888(s)								818(s)
trans-$[Co\ cyclam\ Cl_2]ClO_4$	903(s)	890(s)								818(s)
trans-$[Co\ cyclam\ Br_2]Br$	900(m)	888(m)								812(m)
trans-$[Co\ cyclam\ (N_3)_2]NO_3$	900(m)	890(m)								812(m)
trans-$[Co\ cyclam\ (N_3)_2](PtCl_6)_{1/2}$	902(m)	890(m)								814(m)
trans-$[Co\ cyclam\ (NCS)_2]NCS$	902(m)	890(m)				852(m) [c]				822(w)
trans-$[Co\ cyclam\ (NCS)_2](PtCl_6)_{1/2}$	902(m)	890(m)				842(s) [c]				816(m)
trans-$[Co\ cyclam\ (NO_2)_2](PtCl_6)_{1/2}$	892(msh)	887(m)							830(s) [d]	820(msh)
trans-$[Co\ cyclam\ (CN)_2]Cl$	903(m)	893(m)								822(m)
trans-$[Co\ cyclam\ NO_2Cl]Cl$	899(m)	889(m)							828(s) [d]	812(m)
trans-$[Co\ cyclam\ NO_2Cl]NO_3$	898(m)	885(m)							829(s) [d]	820(msh)
trans-$[Co\ cyclam\ NO_2Br]Br$	898(m)	888(m)							825(s) [d]	810(m)
trans-$[Co\ cyclam\ NCSCl]ClO_4$	900(m)	890(m)				845(w) [c]				818(m)
trans-$[Co\ cyclam\ NH_3Cl]Cl_2$	902(m)	890(m)								813(m)
trans-$[Co\ cyclam\ CNCl]Cl$	905(m)	893(m)								814(m)
trans-$[Co\ cyclam\ CNCl]NO_3$	903(m)	891(m)								825(m)
trans-$[Co\ cyclam\ SO_3CN]$	903(m)	885(m)								824(m)
trans-$[Co\ cyclam\ SO_3Cl]$	895(msh)	891(m)								815(m)
trans-$[Cl\ Co\ cyclam.O_2.Co\ cyclamCl](ClO_4)_2$	895(m)	887(m)								812(m)
trans-$[N_3\ Co\ cyclam.O_2.Co\ cyclamN_3](ClO_4)_2$	900(m)	888(m)								810(m)
trans-$[SCN\ Co\ cyclam.O_2.Co\ cyclam\ NCS](NCS)_2$	899(m)	883(m)				835(m) [c]				809(m)
trans-$[O_2N\ Co\ cyclam.O_2Co\ cyclam\ NO_2]Br_2$	896(m)	889(m)						828(msh) [d]	824(s) [d]	812(msh)
trans-$[O_2N\ Co\ cyclam.O_2.Co\ cyclam\ NO_2](ClO_4)_2$	900(m)	892(m)							822(s) [d]	812(m)

[a] Abbreviations: s, strong; m, medium; w, weak; sh, shoulder. [b] This band arises from $\pi(CO_3)$; ref. 15. [c] This band arises from ν(C-S); ref. 15. [d] This band arises from $\delta(NO_2)$; ref. 15.

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Table II. Frequencies (cm^{-1}) of the amine vibrations in undeuterated and deuterated *trans*-[CocyclamCl$_2$]Cl and *trans*-[Coen$_2$Cl$_2$]Cl.

Undeuterated- *trans*-[CocyclamCl$_2$]Cl	Deuterated- *trans*-[CocyclamCl$_2$]Cl	N-H / N-D	Undeuterated- *trans*-[Coen$_2$Cl$_2$]Cl[a]	N-H / N-D[a]
			3250	1.33
3160	2380	1.33	3165	1.31
			3077	1.35
1325	1175	1.13	1591	1.35
1137	1092	1.04	1120	1.17
1041	955	1.09	1110	1.18
1029	938	1.10		
906	796	1.13	1004	1.19
888	780	1.14	994	1.22

[a] Data were taken from ref. 10.

absorption spectroscopy, are compared,[1,3] it was found that the most consistent variations are in the 800-910 cm^{-1} region (Table I). Here complexes with a *trans*-configuration show two bands near 900 cm^{-1} and one band near 810 cm^{-1} while those with a *cis*-configuration have at least five bands spread fairly evenly between 800 and 910 cm^{-1}. These spectra are shown in Figure 1.

Deuteration of *trans*–[CocyclamCl$_2$]Cl, shifts the doublet near 900 cm^{-1} but does not affect the band near 810 cm^{-1} (Table II). This observation suggests that the former doublet arise predominantly from the secondary amine vibration while the latter singlet arises from the methylene vibration. When the infrared spectra of *trans*–[CocyclamCl$_2$]Cl and *trans*–[Coen$_2$Cl$_2$]Cl are compared (Table II), it is clear that the corresponding amine vibrations of the cyclam complex occur in lower frequency regions and that these vibrations show smaller isotope shifts. These are consistent with the replacement of one amine-proton by a much heavier alkyl group in the cyclam complex. On partial deuteration* of *cis*–[Cocyclam(NO$_2$)$_2$]NO$_3$ it was found that the intensities of the bands at 840, 860, and 874 cm^{-1} are seriously reduced with respect to other bands at 802, 820 (δ NO$_2$) and 828 cm^{-1}, which are not affected. Thus it can be concluded that on going from a *trans*- to a less symmetrical *cis*-isomer, the amine vibration doublet at ~900 cm^{-1} split into at least three bands while the methylene vibration singlet at ~800 cm^{-1} splits into two.

The above differentiation is supported by the spectrum of *cis*–[CocyclamCO$_3$]Cl (Table I). Here the bidentate carbonato group ensures a *cis*- disposition of the cyclic ligand. This method proves especially useful for complexes where only one isomeric form has been isolated. It is well known in cobalt(III) cyclam chemistry that all substitution reactions proceed with complete retention of configuration and that *trans*- isomers are thermodynamically much more stable with respect to their *cis*- counterparts except probably for complexes with suitable bidentate ligands.[3,4,13,14] Thus starting with a *trans*- substrate it would be expected that only *trans*- products would be formed. In fact, no more than one geometric isomer has ever been isolated in all preparations starting with *trans*-[CocyclamCl$_2$]Cl. The assignment of a *trans*- configuration to these substituted products[1-6,13,14] is now confirmed by their infrared spectra as shown in Table I. From the same table, it is clear that the method is independent of the nature of other ligands and anions present. It is also clear that the method is found true even for binuclear peroxo-bridge complexes, to which the previous *trans*- configuration assignment[2] is now confirmed.

Acknowledgment. This research is supported by the Committee on Higher Degrees and Research Grants of the University of Hong Kong.

(*) Complete deuteration of the compound was complicated by the isomerization reaction.

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