

Chromium(III) Complexes of Macrocyclic Ligands. II.

Preparation and Properties of Chromium(III) Complexes of *rac*-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane

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The reaction between anhydrous chromic chloride and the title amine, *cycb*, in non-aqueous solvents gives green insoluble *cis*-[Cr(*cycb*)Cl₂]Cl. This compound has been used as the starting material for a number of new *cis*-compounds all containing the Cr(*cycb*)-moiety, and all apparently having an identical *cycb*-ligand configuration. Visible absorption spectra and acid dissociation constants are given and are compared with and rationalized in relation to data for other more normally behaving *cis*-tetraaminechromium(III) systems.

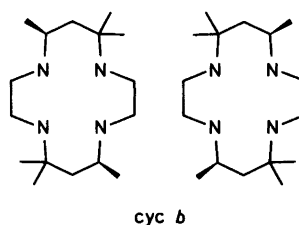


Fig. 1. *rac*-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane.

The title amine, Fig. 1, Table 1, is readily obtained by reduction of a condensation product between 1,2-ethanediamine and acetone.¹ This condensation reaction was first performed by dissolving tris(1,2-ethanediamine)nickel(II) salts in acetone^{2,3} but is now more easily carried out without nickel(II), but at a suitable pH.⁴ Many transition metal complexes of this amine have

been studied, and the present work extends these studies to include the preparation of a number of new chromium(III) complexes, with the particular intention to further study the influences from non-reacting ligands on the kinetic behaviour of metal complexes.

Table 1. List of ligand name abbreviations.

<i>cyc</i>	<i>meso</i> -5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane
<i>cycb</i>	<i>rac</i> -5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane
<i>cyclam</i>	1,4,8,11-tetraazacyclotetradecane
H(acac)	2,4-pentanedione
H ₂ (mal)	malonic acid
H ₂ (ox)	oxalic acid
en	1,2-ethanediamine
trien	1,4,7,10-tetraazadecane

RESULTS AND DISCUSSION

Solutions of anhydrous chromium(III) chloride react with *cycb* to give an insoluble green product. This reaction, which is complete after about two hours in boiling *N*-methylformamide, is significantly slower than the similar reactions with a number of other amines, such as 1,2-ethanediamine, 1,3-propanediamine, and *trans*-1,2-cyclohexanediamine.⁵ These latter reactions are all complete after 1 hour in *N,N*-dimethylformamide, DMF, or dimethylsulfoxide, DMSO, at 150 °C, whereas even after 8 hours in boiling DMF some unreacted *cycb* and Cr(III) is still present. In DMSO, at temperatures near the boiling point where the complex formation reaction is fast, amine decomposition apparently takes place in competition with complexation, and dark brown solutions result. The same green insoluble material analyzing as 1 Cr(III): 1 *cycb*: 3 Cl⁻ is obtained, however, in all three solvents. Further reactions of this material produce *cis*-tetraamine derivatives and the product is therefore most likely formulated as *cis*-[Cr(*cycb*)Cl₂]Cl, although a formulation as *fac*-[Cr(*cycb**)Cl₃], with the amine bound as a tridentate ligand cannot immediately be excluded, and is in better agreement with both colour and solubility characteristics of other chromium(III) complexes.

The green compound can be treated with hot aqueous hydroxide without loss of coordinated amine, which is an unusual robustness for a chromium(III) amine complex. This produces a blue solution from which blue-violet *cis*-[Cr(*cycb*)(OH)₂]ClO₄·2H₂O can be precipitated. The cation of this compound has the structure shown in Fig. 2⁶, and in aqueous solution it behaves as a divalent base. From potentiometric titrations the acid dissociation

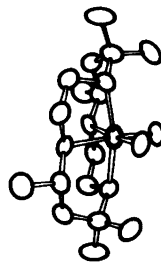


Fig. 2. Configuration of the *cis*-[Cr(*cycb*)(OH)₂]³⁺-cation, hydrogen atoms omitted, in *cis*-[Cr(*cycb*)(OH)₂]ClO₄·2 H₂O.⁶

constants have been determined, and in Table 2 it is seen that the *cis*-[Cr(*cycb*)(OH)₂]³⁺ cation is a significantly stronger acid than a number of other *cis*-tetraaminediaquachromium(III) cations. This marked difference is most plausibly associated with differences in cation-solvent interactions as the differences in solvation energies as function of charge are probably smaller for the less hydrated complexes with the more organic amine ligands, which will make these types of complexes stronger acids.

The increased acidity of these types of complexes compared to more traditional ones, is also demonstrated by the *cis*-[Cr(*cycb*)(mal)]⁺ cation, which in strongly basic solution shows the variation of visible absorption spectra exhibited in Fig. 3. In view of a greatly increased intensity of the second absorption band, this spectral change probably reflects the equilibrium shown on the Fig. Interpretation of the data using this model gives $K \sim 1.76 \pm 0.04 \text{ M}^{-1}$, which using $K_w \sim 10^{-13.80} \text{ M}^2$ ⁸ yields the acidity constant $K_A \sim 10^{-13.55} \text{ M}$ at 25 °C, which is unusually acid for a malonato ligand in aqueous solution.

The spectral characteristics of *cis*-[Cr(*cycb*)(OH)₂]⁺ and its protonation products are

Table 2. Acid dissociation constants for some *cis*-tetraaminediaquachromium(III) complexes at 25.0 °C in 1.00 M sodium perchlorate solution.

Complex ^a	-log K ₁ ^b	-log K ₂ ^b
<i>cis</i> -[Cr(NH ₃) ₄ (OH) ₂] ³⁺	4.961±0.015	7.53±0.03
<i>cis</i> -[Cr(en) ₂ (OH) ₂] ³⁺	4.75±0.03	7.35±0.05
<i>cis</i> -[Cr(trien)(OH) ₂] ³⁺	4.47±0.03	7.14±0.05
<i>cis</i> -[Cr(cyclam)(OH) ₂] ³⁺	4.212±0.013	7.25±0.03
<i>cis</i> -[Cr(<i>cycb</i>)(OH) ₂] ³⁺	3.331±0.012	7.019±0.014

^a Ref. 7 and this work. ^b The *K*'s are measured in mol l⁻¹.

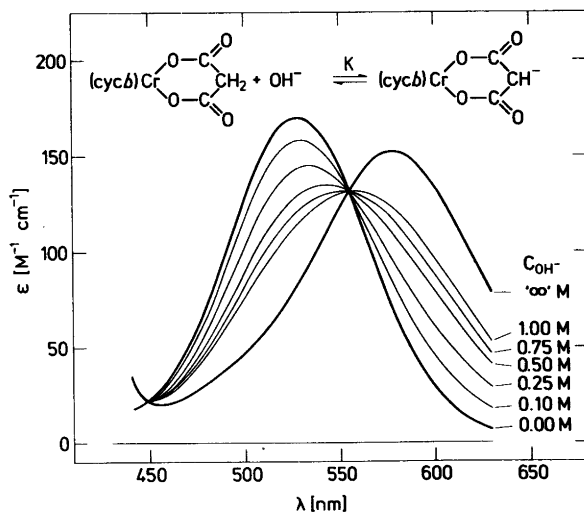
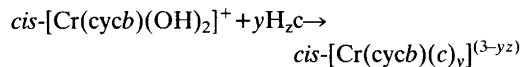


Fig. 3. Spectral changes of $\text{cis-}[\text{Cr}(\text{cycb})(\text{mal})]^+$ in 1.00 M $\text{Na}(\text{ClO}_4, \text{OH})$. The absorption spectrum of the deprotonated species is calculated from the series of spectra given in the figure assuming the equilibrium shown.

summarized in Fig. 4 A. All three spectra are characterized by an increased intensity and a red-shift of the absorption bands compared to other *cis*-tetraaminechromium(III) complexes such as those of both ammonia and 1,2-ethanediamine, and also of the macrocyclic *cis*-(1,4,8,11-tetraazacyclotetradecane)chromium(III) derivatives, as shown in Fig. 4 B. Both these effects may qualitatively be accounted for with reference to Fig. 2 which shows a pronounced tetrahedral distortion of the CrN_2O_2 -plane apparently induced by the two methyl groups above and below this plane.

In the experimental section results are given for a number of preparative experiments of the general type:



The preference for ligands which can be expected not to interact significantly with the methyl groups above and below the CrN_2O_2 -plane should be noted. For coordinated ammonia and 1,2-ethanediamine, models indicate that hydrogen atoms of these ligands will point in directions towards these methyl groups, and it is therefore noteworthy that several attempts to coordinate these two ligands to the $\text{Cr}(\text{cycb})$ -moiety were unsuccessful. For cobalt(III) a *cis*-

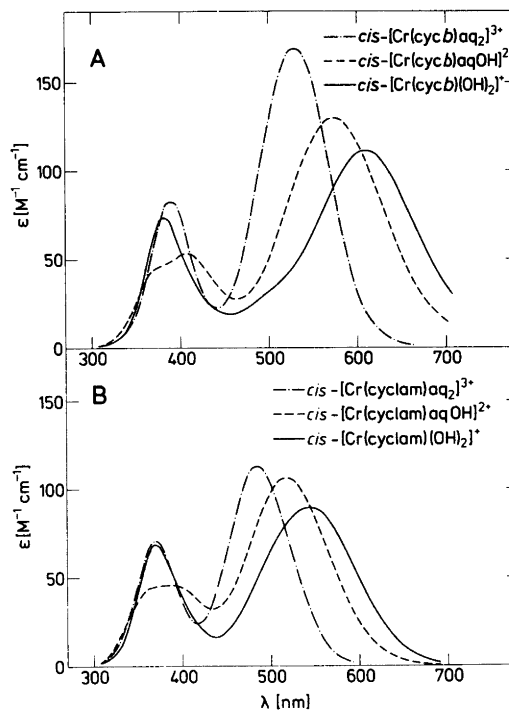


Fig. 4. Visible absorption spectra of diaqua-cycb- and -cyclam-Cr(III) complexes and their deprotonation products. Further details of the solutions for the cycb complexes are given in Table 3. The cyclam complexes are measured in 0.5 M $\text{HClO}_4 + 0.5$ M NaClO_4 , 1 M NaCl with $\log[\text{H}^+] \sim \frac{1}{2}(\log K_1 + \log K_2)$ cf. Table 2, and 0.95 M $\text{NaCl} + 0.05$ M NaOH , respectively.

$[\text{Co}(\text{cycb})(\text{en})]^{3+}$ cation has been reported,⁹ which is a manifestation of the differences between the cobalt(III)- and the chromium(III)-*cycb* complexes, which is also apparent when the relatively easy transformation between a *trans* isomer and several *cis* isomers in the cobalt(III) system¹⁰ is contrasted to the presence, so far at least, of only one geometric ligand arrangement in the $\text{Cr}(\text{cycb})$ -moiety, as demonstrated both by the structural studies of the $[\text{Cr}(\text{cycb})(\text{OH})_2]^+$ - and $[\text{Cr}(\text{cycb})(\text{O}_2\text{CO})]^+$ -cations⁶ and the inability so far to detect more than one isomer in any of the compounds from the preparative studies.

EXPERIMENTAL

Chemicals. *rac*-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane hydrate: *cycb*· H_2O , was prepared and separated from the corresponding *meso*-isomer dihydrate: *cycb*· $2\text{H}_2\text{O}$ according to a literature method.⁴ *cis*- $[\text{Cr}(\text{cyclam})\text{Cl}_2]\text{Cl}$ was prepared directly from CrCl_3 and cyclam by a modification of a literature method.¹¹ All other chemicals were commercial products.

Preparations. The following compounds were all made with kinetic and thermodynamic investigations in solution in mind. Whenever possible fairly soluble compounds were therefore made, and greater yields than reported can therefore normally be obtained by precipitation with other anions. For the 1+ cations the solubility decreases fairly regularly along the series: $\text{Cl}^- > \text{Br}^- > \text{ClO}_4^-$. This provides an opportunity for recovery of the *cis*- $\text{Cr}(\text{cycb})$ -moiety even from fairly dilute solutions by precipitation of either *cis*- $[\text{Cr}(\text{cycb})\text{Cl}_2](\text{ClO}_4, \text{Cl})$ in acid or *cis*- $[\text{Cr}(\text{cycb})(\text{O}_2\text{CO})]\text{ClO}_4$ in base.

1. *cis*- $[\text{Cr}(\text{cycb})\text{Cl}_2]\text{Cl}$. 10 g CrCl_3 is warmed with about 10 mg Zn-powder in 50 ml *N*-methylformamide until it dissolves. 18 g *cycb*, dried in vacuum over conc H_2SO_4 , is added and the resulting solution refluxed for 2 h. During this treatment a bluish-green precipitate slowly forms. The resulting mixture is cooled in ice after which the precipitate is filtered off and washed twice with cold water* and then with ethanol.

* *cycb* is the most common impurity in *cycb* preparations. The primary reaction products between the two amines: *cycb* and *cycb* and CrCl_3 have, however, such different solubilities in water that small amounts of soluble *trans*- $[\text{Cr}(\text{cycb})\text{Cl}_2]\text{Cl}$ are easily removed from insoluble *cis*- $[\text{Cr}(\text{cycb})\text{Cl}_2]\text{Cl}$ by washing the crude product with water.

The yield is 25 g (89 %). Analyses: Cr, Cl, N, C, H.

2. *cis*- $[\text{Cr}(\text{cycb})(\text{OH})_2]^+$ -solution. 10 g *cis*- $[\text{Cr}(\text{cycb})\text{Cl}_2]\text{Cl}$, preparation no. 1, is dissolved in a solution of 4 g NaOH in 100 ml water at 100 °C. The resulting blue solution is cooled to room temperature and filtered to remove traces of undissolved material. This solution is the starting material for the following preparations.

3. *cis*- $[\text{Cr}(\text{cycb})(\text{OH})_2]\text{ClO}_4 \cdot 2\text{H}_2\text{O}$. 20 ml saturated NaClO_4 (aq)-solution is slowly added to 100 ml *cis*- $[\text{Cr}(\text{cycb})(\text{OH})_2]^+$ -solution, preparation no. 2. The mixture is cooled in ice, and the bluish-black crystals are filtered off and washed quickly twice with ice-cold acetone in which it is somewhat soluble. Yield 10 g corresponding to 88 %. Analyses: Cr, Cl, N, C, H. This material is analytically pure but can be recrystallized by dissolving it in 250 ml 0.1 M NaOH(aq) at 80 °C and slowly adding 40 ml saturated NaClO_4 (aq)-solution while cooling to 0 °C. Yield 6.0 g (53 %).

4. *cis*- $[\text{Cr}(\text{cycb})(\text{OH})_2]\text{Br}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$. 100 ml *cis*- $[\text{Cr}(\text{cycb})(\text{OH})_2]^+$ -solution, preparation no. 2, is cooled in ice and made strongly acid by the slow addition of 100 ml 63 % HBr(aq). The temperature should be kept below 10 °C. A reddish-violet precipitate is formed, and after standing at 0 °C for 30 min it is filtered off and washed twice with ice-cold acetone. The yield is about 12 g of impure material containing varying amounts of chloride ions. It is purified by dissolution in 80 ml 0.5 M NaOH(aq) solution at 80 °C and reprecipitating the bromide salt by the addition of 50 ml 63 % HBr(aq) in the cold, as described above. The yield of recrystallized material is about 10 g (65 %). Analyses: Cr, Br, (Cl), N, C, H.

5. *cis*- $[\text{Cr}(\text{cycb})(\text{OH})_2]\text{Cl}(\text{ClO}_4)_2 \cdot x\text{aq} \cdot y\text{HClO}_4$. 15 ml *cis*- $[\text{Cr}(\text{cycb})(\text{OH})_2]^+$ -solution, preparation no. 2, is acidified with 5 ml 70 % HClO_4 (aq) at room temperature and left for some weeks. A violet precipitate is slowly formed. This is filtered off and washed twice with diethylether. Yield 2.5 g. This product is recrystallized by dissolving it in 65 ml 0.1 M HCl(aq), and reprecipitating the perchlorate by the slow addition of 8 ml saturated NaClO_4 (aq) solution. Yield 1.25 g, which is 56 % based upon a formulation as *cis*- $[\text{Cr}(\text{cycb})(\text{OH})_2]\text{Cl}(\text{ClO}_4)_2 \cdot 0.4 \text{HClO}_4 \cdot 3 \text{H}_2\text{O}$ suggested by Cr, Cl, Cl^- , N, C, H analyses.

6. *cis*- $[\text{Cr}(\text{cycb})\text{Cl}_2]\text{Cl} \cdot \text{H}_2\text{O}$. 100 ml *cis*- $[\text{Cr}(\text{cycb})(\text{OH})_2]^+$ -solution, preparation nr. 2, is acidified with 100 ml concentrated HCl(aq), and the resulting solution boiled to precipitate the green chloride until the solution is almost colourless. This takes about 5 min. After cooling the mixture to room temperature the precipitate is filtered off and washed twice with cold water and

then with ethanol. Yield 8.8 g (86 %). Analyses: Cr, Cl, N, C, H.

7. *cis*-[Cr(cycb)F₂]ClO₄. 50 ml *cis*-[Cr(cycb)(OH)₂]⁺-solution, preparation no 2, is acidified with 40 % HF(aq). 4 g NaF is dissolved in this solution which is then kept at 80 °C for 10 min. A violet precipitate forms, and after cooling the mixture to room temperature it is filtered off and washed twice with cold acetone. Yield 3.6 g. More material is obtained by adding 3 ml saturated NaClO₄(aq) to the mother liquor. Yield 2.3 g. The two fractions were reprecipitated from the minimum amount of water at 80 °C by the slow addition of saturated NaClO₄(aq) solution. Yield 2.2 and 1.5 g, respectively, which is a total of 68 %. Analyses: Cr, Cl, N, C, H. The two fractions have identical analyses, visible absorption spectra in both acid and basic solution, and powder diffraction patterns, and are also, by the same criteria, identical to the compound which can be prepared in lower yield from *trans*-[Cr(py)₄F₂]ClO₄ and *cycb* in *N*-methylformamide.

8. *cis*-[Cr(cycb)O₂CO]Cl · H₂O. 5 g of solid NH₄Cl is dissolved in 100 ml *cis*-[Cr(cycb)(OH)₂]⁺-solution, preparation no. 2, which is then saturated with CO₂ at 0 °C. The red-violet precipitate is filtered off and washed twice with ethanol. Yield 8.0 g corresponding to 78 %. The compound is recrystallized by dissolving it in 120 ml water at 80 °C. This solution is saturated with CO₂ and then reduced in volume to about 20 ml by vacuum evaporation of solvent. Yield 6.0 g of recrystallized material (59 %). Analyses: Cr, Cl, N, C, H.

9. *cis*-[Cr(cycb)(ox)]Cl · 2H₂O. 50 ml *cis*-[Cr(cycb)(OH)₂]⁺-solution, preparation no. 2, is acidified with a solution of 10 g (COOH)₂ · 2H₂O

in 60 ml of water. The resulting solution is kept at 100 °C for 5 min and then cooled to 0 °C. The precipitate is filtered off and washed twice with acetone. Yield 8.2 g of crude material which contains excess oxalic acid. It is purified by dissolution in about 200 ml of water at 90 °C and precipitated by the slow addition of 50 ml saturated NaCl solution and cooling to 0 °C. Yield 4.1 g (74 %). Analyses: Cr, Cl, N, C, H.

10. *cis*-[Cr(cycb)(mal)]ClO₄. 50 ml *cis*-[Cr(cycb)(OH)₂]⁺-solution, preparation no. 2, is acidified with a solution of 10 g malonic acid in 20 ml of water. 20 ml of a saturated NaClO₄(aq) solution is added, and the resulting mixture kept at 100 °C for 2 minutes and then cooled to 0 °C. The violet precipitate is filtered off and washed twice with acetone. Yield 4.5 g. The compound is recrystallized by extraction with 100 °C warm water on the filter, slow addition of 1/10 vol saturated NaClO₄(aq) solution and cooling to 0 °C. Yield 3.6 g (59 %). Analyses: Cr, Cl, N, C, H.

11. *cis*-[Cr(cycb)(acac)]Br₂ · 3H₂O. A mixture of 25 ml *cis*-[Cr(cycb)(OH)₂]⁺-solution, preparation no. 2, and 5 ml acetylacetone is left at room temperature overnight. The resulting solution is precipitated with 10 ml saturated NaBr(aq)-solution and cooled to 0 °C. The precipitate is filtered off and washed twice with acetone. Yield 2.1 g. The compound is recrystallized by dissolving it in 25 ml of water at 80 °C, and precipitated by the addition of 3 ml saturated NH₄Br-solution and cooling to 0 °C. Yield 1.6 g (43 %). Analyses: Cr, Br, N, C, H.

Analyses, spectra and potentiometric measurements. Microanalyses were performed by the analytical sections of the Chemistry Departments I and II of the Institute: I: Cr and II: C, H, N, Cl,

Table 3. Summary of spectral characteristics of some *cis*-*cycb*-Cr(III) complexes in aqueous solution.

Complex	Medium	$\lambda_{1,\max}$ [nm]	$\epsilon_{1,\max}$ [M ⁻¹ cm ⁻¹]	$\lambda_{2,\max}$ [nm]	$\epsilon_{2,\max}$ [M ⁻¹ cm ⁻¹]
<i>cis</i> -[Cr(cycb)(OH) ₂] ⁺	1 M NaOH	609	111	380	73
<i>cis</i> -[Cr(cycb)(OH)(OH ₂) ²⁺] ^a	~1 M NaCl	572	130	407	53
<i>cis</i> -[Cr(cycb)(OH ₂) ₂] ³⁺	1 M HClO ₄ , 0.1 M HClO ₄ +0.9 M NaClO ₄	529	169	388	82
<i>cis</i> -[Cr(cycb)(OH ₂)Cl] ²⁺	1 M HCl	554	173	405	105
<i>cis</i> -[Cr(cycb)F ₂] ⁺	1 M HCl, 1 M NaOH	541	145	379	58
<i>cis</i> -[Cr(cycb)(O ₂ CO)] ⁺	0.1 M NaOH+0.9 M NaCl	521	145	382	106
<i>cis</i> -[Cr(cycb)(ox)] ⁺	Water, 1 M NaOH	516	157	384	102
<i>cis</i> -[Cr(cycb)(mal)] ⁺	1 M HCl, 0.01 M NaOH+0.99 M NaCl	527	167	387	82
<i>cis</i> -[Cr(cycb)(acac)] ²⁺	1 M HCl, 1 M NaOH	535	161	390	256

^a *cis*-[Cr(cycb)(OH)₂]⁺ solution titrated to $\log[H^+] \sim \frac{1}{2}(\log K_1 + \log K_2)$.

Br. Samples were further tested for impurities by acid-base titrations and cation exchange chromatography on Sephadex SP-C-25.

Visible absorption spectra were measured on a Cary 118C spectrophotometer at room temperature (20–25 °C), *cf.* Table 3.

Potentiometric measurements and the processing of these measurements to give acid dissociation constants for the *cis*-[Cr(cyclam)aq₂]³⁺– and *cis*-[Cr(cycb)aq₂]³⁺-cations were performed as previously described.⁷ *Cis*-[Cr(cycb)aq₂]³⁺-solutions were prepared by dissolving *cis*-[Cr(cycb)(OH)₂]ClO₄ · 2 H₂O in acid perchlorate solution. Solutions of *cis*-[Cr(cyclam)aq₂]³⁺ were prepared as follows: 25 mg of recrystallized *cis*-[Cr(cyclam)Cl₂]Cl was heated to boiling with 2 ml 0.25 M NaOH-solution. The resulting solution was cooled to room temperature and made slightly acid, pH~3, by the addition of perchloric acid. This solution was charged onto a 2×15 cm Sephadex SP-C-25 filled column, and the *cis*-[Cr(cyclam)aq₂]³⁺-cation eluted by 1.0 M NaClO₄ or 1.0 M NaCl.

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