

Synthesis, Structure and Magnetic Properties of the Binuclear Chromium(III) Complex Di- μ -hydroxobis[(1,4,7,10-tetraazacyclododecane)chromium(III)] Dithionate Tetrahydrate, [(cyclen)CrOH]₂(S₂O₆)₂·4H₂O

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(Received May 8, 1986)

Abstract

The dark blue dimeric complex di- μ -hydroxobis[(1,4,7,10-tetraazacyclododecane)chromium(III)] dithionate tetrahydrate, [Cr(C₈H₂₀N₄)OH]₂(S₂O₆)₂·4H₂O or [Cr(cyclen)OH]₂(S₂O₆)₂·4H₂O, has been synthesized. The crystal structure of the complex has been determined from three-dimensional counter X-ray data. The complex crystallizes in space group *P*2₁/*n* of the monoclinic system with two dimeric formula units in a cell of dimensions *a* = 8.837(5), *b* = 14.472(8), *c* = 13.943(6) Å and β = 95.83(4)°. The structure has been refined by full-matrix least-squares methods to a final value of the weighted *R*-factor of 0.059 on the basis of 1774 independent intensities. The geometry of the cyclen macrocycle is unsymmetrical, the observed conformations being $\lambda\delta\delta\lambda$ and its enantiomer. The strained ligand conformation leads to significant deviations from octahedral geometry at the chromium centers, and to a bridged geometry in which the Cr–O–Cr angle ϕ and the Cr···Cr separation of 104.1(1)° and 3.086(2) Å are the largest observed in dimers of this kind. The magnetic susceptibility of the complex indicates antiferromagnetic coupling, with the ground state singlet lying 21.56(6) cm⁻¹ below the lowest lying triplet state. The structural parameters have been used to calculate the triplet energy by means of the Glerup–Hodgson–Pedersen (GHP) model, and the calculated value of 22.3 cm⁻¹ is very similar to the observed value.

Introduction

The investigation of the magnetic and spectroscopic properties of binuclear chromium(III) complexes has been an area of intense research activity [1, 2]. Our own interest has centered on the synthesis of di- μ -hydroxo and di- μ -alkoxo complexes [3–5], and on the understanding of the relationship between the structures of these complexes and their magnetic properties. Both we and others have noted the importance of the Cr–O–Cr bridging angle (ϕ) [6–9], the Cr–O bond length (*R*) [8, 9], and the dihedral angle (θ) between the O–H (or O–R) vector and the Cr₂O₂ bridging plane [10–15], and we have recently derived a quantitative relationship between the isotropic magnetic coupling constant (*J*) and these three structural parameters [16].

Although most of the dimers studied possess only *C*_i crystallographic symmetry, they approximate *C*_{2h} symmetry well; it should be noted that some complexes have *C*₁ symmetry and approximate *D*₂ geometry. The availability of a small symmetric, tetradentate macrocyclic ligand presents us with an opportunity to study a complex in which the symmetry of the complex is potentially similar to these but the distortions from octahedral geometry at the metal centers are very severe. The study of such a complex might allow us to determine the extent to which the local symmetry at each chromium center, rather than the symmetry of the bridging unit, plays a role in determining the magnetic exchange parameter.

We describe here, therefore, the synthesis and characterization of the 1,4,7,10-tetraazacyclododecane complex, [(cyclen)Cr(OH)]₂(S₂O₆)₂·4H₂O.

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Experimental

Synthesis

1,4,7,10-tetraazacyclododecane (cyclen)

Prepared according to Richman and Atkins [17]. The ^{13}C NMR spectrum shows that the product is at least 97% pure.

cis-Dichloro(1,4,7,10-tetraazacyclododecane)chromium(III) chloride

Cyclen (1.9 g, 0.011 mol) was dissolved in dry dimethylformamide (100 ml) and $\text{CrCl}_3(\text{THF})_3$ [18] (3.96 g, 0.01 mol) was added. The mixture was refluxed for 10 min, during which time the color changed to deep blue. The blue complex was precipitated by cooling to room temperature; yield 1.9 g (60%); *Anal. Calc.* for $\text{Cr}(\text{C}_8\text{H}_{20}\text{N}_4)\text{Cl}_3$: C, 29.06; H, 6.10; N, 16.95; Cl, 32.16. Found: C, 29.22; H, 6.07; N, 16.75; Cl, 32.00%.

cis-Aquahydroxo(1,4,7,10-tetraazacyclododecane)chromium(III) perchlorate

cis- $[\text{Cr}(\text{cyclen})\text{Cl}_2]\text{Cl}$ (0.33 g, 0.5 mmol) was dissolved in water (25 ml) and the solution was equilibrated for one day at room temperature. Chloride was replaced by perchlorate by addition of silver perchlorate (0.70 g, 3.1 mmol) and subsequent removal of the precipitated silver chloride by filtration. Saturated sodium perchlorate (1 ml) was added. After one day violet crystals precipitated. The precipitate was filtered and washed with 96% ethanol. Drying in air yielded 0.19 g (yield 42%).

Di- μ -hydroxobis[(1,4,7,10-tetraazacyclododecane)chromium(III)] dithionate

cis- $[\text{Cr}(\text{cyclen})\text{Cl}_2]\text{Cl}$ (0.5 g, 0.76 mmol) was dissolved in water (15 ml). Within 10 min the color of the solution changed from blue to violet. Then pyridine (0.5 ml, 6.2 mmol) and lithium dithionate (1.6 g, 7.6 mmol) were added. The solution was kept at room temperature for two days during which time dark blue crystals of the di- μ -hydroxo complex were precipitated. The precipitate was filtered and washed with 96% ethanol and dried in air. Yield 0.48 g (70%). *Anal. Calc.* for $\text{C}_{16}\text{H}_{50}\text{N}_8\text{O}_{18}\text{S}_4\text{Cr}_2$: C, 21.96; H, 5.77; N, 12.81; S, 14.66. Found: C, 22.00; H, 5.49; N, 13.12; S, 14.76%.

Physical Measurements

All visible absorption spectra were measured on a Cary 219 spectrophotometer at room temperature. Magnetic susceptibility was measured by the Faraday method on equipment described earlier [10, 19]. The molar susceptibilities were corrected for ligand diamagnetism by Pascal's constants. C, H, N, Cl, S analyses were made by the microanalytical laboratory at the H.C. Ørsted Institute, Copenhagen, Denmark.

X-ray data collection

The data were collected and reduced as described elsewhere [20], using a blue, needle-shaped crystal mounted on a glass fiber and placed on an Enraf-Nonius CAD-4 automatic diffractometer. Cell constants and other data collection parameters are given in Table I.

TABLE I. Crystallographic and Data Collection Parameters

Formula:	$\text{Cr}_2\text{C}_{16}\text{H}_{50}\text{N}_8\text{S}_4\text{O}_{18}$
a	= 8.837(5) Å
b	= 14.472(8) Å
c	= 13.943(6) Å
β	= 95.83(4)°
V	= 1774(2) Å ³
Number observed	= 1700(>3 σ)
T	= 20 °C
D_o	= 1.644
Z	= 2
D_c	= 1.638
Space group:	$P2_1/n$
μ	= 9.50 cm ⁻¹
Data range:	2° < θ < 27°
Radiation:	Mo K α (λ = 0.71073 Å)
Data collected:	+ h , + k , $\pm l$

Structure solution and refinement

The location of the chromium atom was deduced from a three-dimensional Patterson function, and the remaining non-hydrogen atoms in the cation and anion were located in subsequent difference Fourier syntheses. Isotropic refinement of these 22 atoms plus two independent water oxygen atoms gave values of the conventional agreement parameters $R_1 = \Sigma \|F_o| - |F_c| \| / \Sigma |F_o|$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w(F_o)^2]^{1/2}$ of 0.108 and 0.116, respectively. Anisotropic refinement reduced these values to 0.089 and 0.100, respectively. Examination of a difference Fourier summation at this stage convinced us that the water molecules are disordered over three positions, the occupancy factors being approximately 85% in two positions and 30% in the third. The positions of the ligand hydrogen atoms and the hydrogen atom on the bridging hydroxo group were located in a difference Fourier map, but the former were placed in calculated positions on the basis of tetrahedral geometry; hydrogen atom parameters were not varied, and water hydrogen atoms could not be located. The final values of R_1 and R_2 were 0.062 and 0.059, respectively, with no parameter experiencing a shift of more than 0.180. A final difference Fourier was featureless, the highest peak being 0.26 e Å⁻³. All computer programs used were those provided by Enraf-Nonius in the CAD4/SDP package; atomic scattering factors were from ref. 21. The refined atomic positional parameters, along with their esti-

TABLE II. Positional Parameters for [(Cyclen)Cr(OH)]₂·(S₂O₆)₂·4H₂O

Atom	x	y	z
Cr	0.0294(1)	0.09269(9)	0.05335(9)
S(1)	0.4852(2)	0.0818(1)	0.8179(2)
S(2)	0.4695(3)	0.0306(2)	0.6746(2)
O(1)	-0.0994(5)	0.0351(3)	-0.0533(4)
O(2)	0.4146(7)	0.0153(4)	0.8732(4)
O(3)	0.4116(8)	0.1693(4)	0.8123(4)
O(4)	0.6450(6)	0.0896(5)	0.8420(5)
O(5)	0.5292(7)	0.1011(4)	0.6197(4)
O(6)	0.5524(10)	-0.0536(4)	0.6828(5)
O(7)	0.3090(8)	0.0166(7)	0.6501(5)
Ow(1)	0.0613(11)	0.1454(7)	0.7037(10)
Ow(2)	0.3222(11)	0.4627(9)	0.0540(7)
Ow(3)	0.0770(36)	0.0840(16)	0.5183(20)
N(1)	-0.1188(6)	0.0859(4)	0.1627(4)
N(4)	0.1862(6)	0.1267(4)	0.1669(4)
N(7)	0.1892(7)	0.1581(4)	-0.0270(5)
N(10)	-0.0695(6)	0.2201(4)	0.0358(5)
C(2)	-0.0229(9)	0.0842(6)	0.2551(5)
C(3)	0.1071(9)	0.1498(6)	0.2511(6)
C(5)	0.2934(8)	0.1974(6)	0.1371(6)
C(6)	0.3317(8)	0.1712(6)	0.0388(6)
C(8)	0.1259(10)	0.2487(6)	-0.0670(6)
C(9)	-0.0439(9)	0.2517(5)	-0.0618(6)
C(11)	-0.2303(8)	0.2095(6)	0.0584(6)
C(12)	-0.2251(8)	0.1670(6)	0.1567(6)

mated standard deviations, are collected in Table II. See also 'Supplementary Material'.

Results and Discussion

Solution Chemistry

The ligand cyclen was reacted with [Cr(THF)₃Cl₃] or [CrPy₃Cl₃] in dimethylformamide. This procedure normally gives violet *cis*-dichlorotetramine-

chromium(III) chloride complexes in high yield. In this case a sky blue complex analyzing as the expected *cis*-dichloro complex was formed. Apparently it is identical to the complex isolated by Blinn [22], but some of the spectral features differ. As noticed by Blinn and by other workers [23], this blue complex is unusually labile for a chromium(III) complex. The color immediately changes from blue to violet when the salt is dissolved in water. We have followed the Cl⁻ loss both by a Cl⁻ selective electrode and spectrophotometrically.

Within 15 min, 0.99 mol Cl⁻ is released per mol complex, at a rate of 2.80 × 10⁻³ s⁻¹ (20 °C, water). In contrast to the report of Blinn [22], we do not see a rapid loss of all three chlorides, but after 24 h, practically all Cl⁻ could be precipitated with silver perchlorate. From the solution we were able to isolate a red perchlorate salt with a first maximum (see Table III) at 518 nm in 0.1 M HClO₄ solution, not far from the value reported by Blinn [22]. We formulate the various species as Blinn did, but we cannot exclude a more complicated structure for these complexes.

The di- μ -hydroxocyclenchromium(III) complex was prepared directly from the blue chloride without isolating the intermediate hydrolysis complex. The procedure is the classical Pfeiffer method [24], which is a self assembly reaction run in a pyridine buffer between *cis*-aqua-hydroxocyclenchromium(III) ions. This method will only give a high yield if the product is only sparingly soluble, so therefore we chose the dithionate as the counter ion. The complex salt precipitated within two days in a yield of 70%. The salt is deep blue in coloration and only slightly soluble in water. The first ligand field transition in the electronic spectrum (Table III) is remarkably intense and strongly redshifted compared to other di- μ -hydroxo amine chromium(III) complexes. Aqueous solutions of the complex are extremely stable. No changes in the spectra were observed on

TABLE III. Spectral Data in Different Media at Room Temperature

Sample	Medium	First		Second		Reference
		λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}	
<i>meso</i> -[en ₂ Cr(OH) ₂ Cren ₂] ⁴⁺	1 M NaClO ₄ ^a	539	199	386	107	26
[(cyclen)Cr(OH) ₂ Cr(cyclen)] ⁴⁺	0.1 M HClO ₄	602	332	378	122	this work
<i>cis</i> -[Cr(cyclen)Cl ₂] ⁺	H ₂ O ^a	551	138	382	72	this work
<i>cis</i> -[Cr(cyclen)(OH) ₂] ⁺	0.1 M NaOH	627	103	362	78	this work
<i>cis</i> -[Cr(cyclen)(H ₂ O) ₂] ³⁺	1 M HClO ₄	518	173	359	66	this work
<i>cis</i> -[Cr(cycb)(OH) ₂] ⁺ ^b	1 M NaOH	609	111	380	73	28
<i>cis</i> -[Cr(cyclam)(H ₂ O) ₂] ^{3+ c}		483	126	370	38	29
<i>cis</i> -[Cr(cyclam)(OH) ₂] ⁺		547	84	370	66	29
[(cyclam)Cr(OH) ₂ Cr(cyclam)] ⁴⁺	a	558	365	392	170	30

^aExtrapolated back to time of dissolution.

^bcycb: *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane.

^ccyclam = 1,4,8,11-tetraazacyclotetradecane.

standing for weeks at room temperature. This observation is surprising considering our discovery [25] that an equilibrium is established relatively quickly in solution between di- μ -hydroxo and μ -hydroxo species in the case of the ethylenediamine chromium(III) systems [25, 26]. One explanation could of course be that the recorded spectrum actually represents an equilibrium mixture, where the ratio of di- μ -hydroxo to μ -hydroxo is large. However, this possibility was excluded by the observation that even in 0.1 M perchloric acid the complex was fairly stable. Although it is known that the protonation of the μ -hydroxo-aqua-hydroxo complex often requires quite acidic conditions, it is not plausible that the pK_{a1} value of the μ -hydroxodiaqua complex is much lower than 1, as required if an equilibrium is established rapidly. The spectrum of the acid solution, however, changes slowly ($t_{1/2} = 70$ hours at room temperature) to the spectrum of the diaqua monomer. This reaction exhibits a well defined isobestic point for at least 7 half lives, so an intermediate μ -hydroxo complex was not observed. On addition of strong base the di- μ -hydroxo complex is immediately changed to a new complex with a spectrum which is constant for hours in 0.01 M sodium hydroxide solution at room temperature. As the same spectrum is obtained by addition of base to the *cis*-di-aqua monomer, we suggest that the complex formed in both cases is the *cis*-dihydroxocyclen-chromium(III) complex (Table III). The low energy of the first spin-allowed ligand field transition of this complex (15.92 kK) is surprising, but on the other hand it is not far from what has been seen for *cis*-[Cr(cycb)(OH)₂]⁺ (cycb = *rac*-5,5,7,12,2,14-hexamethyl-1,4,8,11-tetraazacyclotetradodecane) (16.42 kK) [27]. In both cases the coordination geometry at the metal is far from octahedral, which may also explain the high intensity of the bands.

Description of the Structure

The structure consists of dimeric [(cyclen)Cr(OH)₂]⁴⁺ units, dithionate anions, and water molecules which are hydrogen bonded to each other. The geometry of one whole cation is shown in Fig. 1, and the coordination sphere around the chromium(III) centers is displayed in Fig. 2. The principal bond lengths and bond angles are listed in Tables IV and V, respectively.

The geometry about each chromium center is roughly octahedral. The *trans* angles at chromium fall in the range of 154.2(1) to 170.8(1)°, the greatest distortion from linearity occurring at the intraligand angle N(1)–Cr–N(7) defined by the two axial nitrogen atoms. The four chelate bond angles fall in the narrow range of 80.4(1) to 82.7(1)°, with an average value of 81.5(11)°. These angles are significantly smaller than the values of 84.3(2) to 85.4(2)° [average 84.8(6)°] and 85.2(8) to 86.8(10) [average

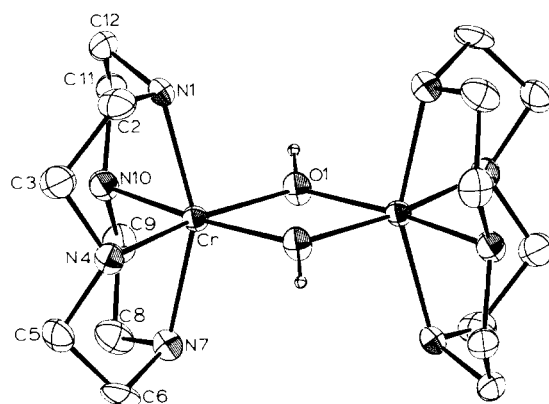


Fig. 1. View of the [Cr(cyclen)OH]₂⁴⁺ cation. Thermal ellipsoids are drawn at the 40% probability level, and hydrogen atoms are omitted for clarity.

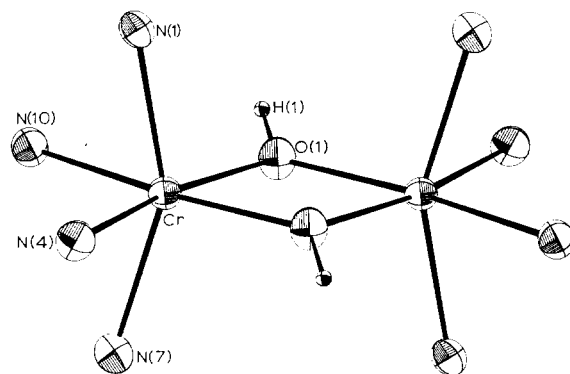


Fig. 2. View of the coordination around the chromium centers in [Cr(cyclen)OH]₂⁴⁺. Drawn as in the previous figure, but hydrogen atoms are shown as spheres of arbitrary size.

TABLE IV. Bond Lengths (Å) in [(cyclen)CrOH]₂(S₂O₆)₂ · 4H₂O

Atoms	Distance	Atoms	Distance
Cr–N(1)	2.111(4)	N(1)–C(2)	1.468(6)
Cr–N(4)	2.054(4)	N(1)–C(12)	1.500(6)
Cr–N(7)	2.114(4)	N(4)–C(3)	1.465(6)
Cr–N(10)	2.044(4)	N(4)–C(5)	1.482(6)
Cr–O(1)	1.964(3)	N(7)–C(6)	1.492(6)
Cr–O(1')	1.950(3)	N(7)–C(8)	1.510(6)
S(1)–S(2)	2.123(2)	N(10)–C(9)	1.476(6)
S(1)–O(2)	1.417(4)	N(10)–C(11)	1.494(5)
S(1)–O(3)	1.422(4)	C(2)–C(3)	1.495(7)
S(1)–O(4)	1.422(3)	C(5)–C(6)	1.495(7)
S(2)–O(5)	1.410(3)	C(8)–C(9)	1.510(7)
S(2)–O(6)	1.420(4)	C(11)–C(12)	1.499(7)
S(2)–O(7)	1.440(4)		

86.2(7)°] found in two six-coordinate cobalt(III) complexes of cyclen [30, 31]. The axial Cr–N bonds of 2.111(4) and 2.114(4) Å [average 2.113(2) Å] are

TABLE V. Bond Angles (deg) in [(cyclen)CrOH]₂(S₂O₆)₂·4H₂O

Atoms	Angle
N(1)–Cr–N(4)	82.7(1)
N(1)–Cr–N(7)	154.2(1)
N(1)–Cr–N(10)	80.7(1)
N(1)–Cr–O(1)	100.0(1)
N(1)–Cr–O(1')	100.2(1)
N(4)–Cr–N(7)	82.3(1)
N(4)–Cr–N(10)	97.0(1)
N(4)–Cr–O(1)	168.1(1)
N(4)–Cr–O(1')	92.2(1)
N(7)–Cr–N(10)	80.4(1)
N(7)–Cr–O(1)	99.0(1)
N(7)–Cr–O(1')	101.3(1)
N(10)–Cr–O(1)	94.9(1)
N(10)–Cr–O(1')	170.8(1)
O(1)–Cr–O(1')	75.9(1)
Cr–O(1)–Cr	104.1(1)
Cr–N(1)–C(2)	106.8(3)
Cr–N(1)–C(12)	110.7(3)
C(2)–N(1)–C(12)	111.4(4)
Cr–N(4)–C(3)	109.5(3)
Cr–N(4)–C(5)	110.5(3)
C(3)–N(4)–C(5)	115.9(4)
Cr–N(7)–C(6)	107.4(3)
Cr–N(7)–C(8)	110.0(3)
C(6)–N(7)–C(8)	112.0(4)
Cr–N(10)–C(9)	106.7(3)
Cr–N(10)–C(11)	106.6(3)
C(9)–N(10)–C(11)	117.6(4)
N(1)–C(2)–C(3)	109.5(4)
C(2)–C(3)–N(4)	108.4(4)
N(4)–C(5)–C(6)	107.0(4)
C(5)–C(6)–N(7)	109.9(4)
N(7)–C(8)–C(9)	110.0(4)
C(8)–C(9)–N(10)	106.3(4)
N(10)–C(11)–C(12)	107.0(4)
C(11)–C(12)–N(1)	109.4(4)
S(2)–S(1)–O(2)	106.5(1)
S(2)–S(1)–O(3)	105.9(2)
S(2)–S(1)–O(4)	102.6(2)
O(2)–S(1)–O(3)	114.3(2)
O(2)–S(1)–O(4)	114.0(3)
O(3)–S(1)–O(4)	112.3(3)
S(1)–S(2)–O(5)	105.4(2)
S(1)–S(2)–O(6)	103.9(2)
S(1)–S(2)–O(7)	104.0(2)
O(5)–S(2)–O(6)	116.5(3)
O(5)–S(2)–O(7)	112.7(3)
O(6)–S(2)–O(7)	112.7(4)

significantly larger than the equatorial values of 2.054(4) and 2.044(4) [average 2.049(7) Å]. In the four 1,2-diaminoethane (ethylenediamine) analogues which have been characterized, the Cr–N bond lengths fall in the range 2.068(4) to 2.096(1) Å,

with an average value of 2.083(7) Å [32, 34]. Thus, it would appear that in the present complex the axial bonds are elongated and the equatorial bonds are compressed. The significance of this distortion is discussed later.

The Cr–O bonds in the bridging unit are slightly asymmetric, but the values of 1.950(3) and 1.964(3) Å fall within the range found in earlier studies [2]. The bridging unit is strictly planar, the Cr–O–Cr' bridging angle ϕ being 104.1(1)^o and the Cr–Cr' separation (R) being 3.086(2) Å. These values of ϕ and R are the largest yet reported for a di- μ -hydroxochromium(III) complex, and are both significantly larger than the maximum values of 103.4(1)^o and 3.059(2) Å, respectively, reported previously [2, 32]. The hydrogen atoms on the bridging hydroxyl groups lie out of the Cr₂O₂ plane, the calculated dihedral angle (θ) being 13.2^o. Since the hydrogen atom positional parameters were not refined, this estimate of θ is necessarily imprecise.

The geometry of the twelve-membered macrocyclic ligand is of great interest. In principle, three different configurations are possible for a cyclen group which is coordinated to a metal center; these three structures are depicted in Fig. 3. One of these structures (Fig. 3a), in which three of the N–H hydrogen atoms lie on the same side of the macrocycle (*cis* to the OH groups) and one N–H hydrogen lies on the other side (*trans* to OH), has approx-

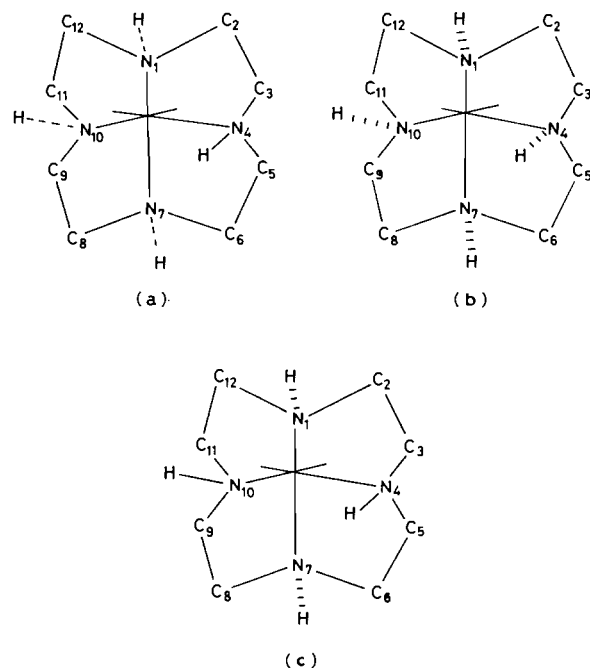


Fig. 3. Schematic drawings of the three reasonable configurations for a coordinated cyclen moiety. (a) The unsymmetrical (approximately C_3) form. (b) The symmetrical, all *cis* (approximately C_{2v}) form. (c) The symmetrical, *cis-trans* (approximately C_{2v}) form.

imate C_s symmetry while the others (Figs. 3b, 3c) have approximate C_{2v} symmetry; in Fig. 3b the N–H hydrogen atoms all lie on the same side (*cis*), while in Fig. 3c two hydrogen atoms are up and the others are down. In the present complex we observe the unsymmetrical (C_s) structure of Fig. 3a, in which the hydrogen atoms at N(1), N(4), and N(7) lie on the *cis* side (relative to OH) and the hydrogen atom at N(10) sits on the *trans* side. This configuration has been observed [30, 31] in two other six-coordinate complexes, $[\text{Co}(\text{cyclen})(\text{NO}_2)_2]^+$ and $[\text{Co}(\text{cyclen})(\text{CO}_3)]^+$, and appears to be the least strained configuration for octahedral geometry. It is noteworthy, however, that the symmetric structure of Fig. 3b has been observed [35] in a five-coordinate complex, $[\text{Cu}(\text{cyclen})(\text{NO}_3)]^+$. To our knowledge, the structure depicted in Fig. 3c has not been observed.

An examination of the bond angles at nitrogen (Table V) suggests that the greatest strain in the macrocycle is at the equatorial nitrogen atoms N(4) and N(10). Thus, the C(3)–N(4)–C(5) and C(9)–N(10)–C(11) bond angles of $115.9(3)^\circ$ and $117.6(4)^\circ$, respectively, are significantly distorted from tetrahedral geometry, while the corresponding values of $111.4(4)^\circ$ and $112.0(4)^\circ$ at N(1) and N(7), respectively, show very little distortion. This flattening at the equatorial nitrogen atoms is alleviated by the adoption of a geometry in which the axial Cr–N lengths are longer than the equatorial Cr–N distances. This concept was first discussed by Sargeson and coworkers [36–38] in connection with the classic β -trien complexes (trien = triethylenetetramine), and was also noted by Kimura and coworkers [30] in the structure of $[\text{Co}(\text{cyclen})(\text{NO}_2)_2]^+$.

The conformations of the four chelate rings in the macrocycle show the same pattern in the present structure as those in the previous six-coordinate structures [30, 31]. Thus, two adjacent rings [N(1)–N(4) and N(4)–N(7)] are enantiomeric and have the unsymmetrical *gauche* conformation, while the other two rings are more nearly flattened into envelope conformations and are again enantiomeric. Thus, if we designate the ring involving C(2)–C(3) as A, that involving C(5)–C(6) as B, etc, we have the conformation $\lambda\delta\delta\lambda$ with the A and B rings *gauche* and the C and D rings flattened; necessarily, in these centrosymmetric dimers the conformation at the other chromium center is $\delta\lambda\lambda\delta$. The torsion angles in the rings are compared with those reported in the other six-coordinate cyclen structures in Table VI. As is apparent from an examination of this Table, the conformations of the macrocycles in these three structures are all very similar. In the five-coordinate complex, $[\text{Cu}(\text{cyclen})(\text{NO}_3)]^+$, which exhibits the symmetric structure of Fig. 3b, all four rings are approximately equally flattened and all have the

TABLE VI. Torsion Angles in the Ligand Rings in 6-Coordinate cyclen Complexes

Atoms	Angle		
	A ^a	B ^b	C ^c
M–N(1)–C(2)–C(3)	40.3	–40.8	36.9
N(1)–C(2)–C(3)–N(4)	–54.1	54.8	–51.6
C(2)–C(3)–N(4)–M	39.6	–44.0	42.4
M–N(4)–C(5)–C(6)	–41.4	44.6	–45.3
N(4)–C(5)–C(6)–N(7)	53.2	–55.5	54.6
C(5)–C(6)–N(7)–M	–38.7	40.8	–38.7
M–N(7)–C(8)–C(9)	–16.0	10.6	–19.8
N(7)–C(8)–C(9)–N(10)	46.6	–36.1	48.6
C(8)–C(9)–N(10)–M	–55.9	46.2	–53.1
M–N(10)–C(11)–C(12)	54.2	–45.3	49.3
N(10)–C(11)–C(12)–N(1)	–47.5	34.9	–44.2
C(11)–C(12)–N(1)–M	19.0	–9.6	19.4

^a $[\text{Cr}(\text{cyclen})\text{OH}]_2^{4+}$, this work. ^b $[\text{Co}(\text{cyclen})(\text{NO}_2)_2]^+$, ref. 30. ^c $[\text{Co}(\text{cyclen})(\text{CO}_3)]^+$; calculated from the data in ref. 31.

same chirality, the structure observed being the $\delta\delta\delta\delta$ complex [35].

The folded, strained conformation of the cyclen ligand leads to several relatively short intraligand H \cdots H contacts. Thus, the folding about the apical N(1)–Cr–N(7) axis leads to HC(2)' \cdots HC(12)' and HC(6)' \cdots HC(8) interactions of 2.30 and 2.32 Å, respectively. The most severe interaction, however, is an HC(3)' \cdots HC(12)' interaction of 2.21 Å; a similar, but less severe interaction of 2.32 Å was observed [30] between these same atoms in $[\text{Co}(\text{cyclen})(\text{NO}_2)_2]^+$. Similarly, several ligand hydrogen atoms approach closely to the hydrogen atom [H(1)] on the bridging hydroxo group, the closest contacts being separations of 2.27 and 2.34 Å between H(1) and HC(11) and HC(9), respectively. The large Cr \cdots Cr separation in the dimer may reflect in part an attempt to reduce the interligand interactions between the HN(1) atoms on each chromium center and the HN(7) atoms on the other; these separations are 2.53 Å.

A complete analysis of the hydrogen bonding in the crystals is precluded by our inability to locate the hydrogen atoms on the water molecules. Since the dimeric cation presumably acts exclusively as a donor, however, we can examine the hydrogen bonding involving that moiety. Ligand nitrogen atoms N(1) and N(10) act as hydrogen bonding donors to the dithionate anions, with N(1) \cdots O(2), HN(1) \cdots O(2) and N(1)–HN(1) \cdots O(2) metrical parameters of 2.994(6) Å, 2.23 Å, and 143° and N(10) \cdots O(5), HN(10) \cdots O(5) and N(10)–HN(10) \cdots O(5) values of 2.935(6) Å, 2.10 Å, and 158° . In addition, the bridging hydroxo group also forms a hydrogen bond to the dithionate ion, with O(1) \cdots O(4) and

H(1)···O(4) separations of 2.681(5) and 1.71 Å, and an O(1)–H(1)···O(4) angle of 166°.

The geometry of the dithionate anion is consistent with that found in previous determinations [7, 15, 33, 39, 40]. The S–S bond length of 2.123(2) Å is normal. The geometry at each sulfur atom is distorted tetrahedral, with S–S–O angles in the range 102.6(2) to 106.5(1)° [average 104.7(15)°] and O–S–O angles from 112.3(3) to 116.5(3)° [average 113.8(15)°]. The conformation is staggered, with approximate *D*_{3d} symmetry. Thus, the torsion angles involving 'trans' atoms [e.g. O(2)–S(1)–S(2)–O(5)] are 175.4° to 176.7°, with an average of 176.2(6)°; in idealized *D*_{3h} symmetry, these angles would be 180°.

Magnetic Properties

The magnetic susceptibility data in the temperature range 4–300 K for the complex were fitted to the usual expression

$$\chi_A' = -\frac{N}{H} \frac{\sum_i \left(\frac{\partial E_i}{\partial H} \right) \exp(-E_i/kT)}{\sum_i \exp(-E_i/kT)}$$

where the E_i are the energies of the sixteen components of the ground-state manifold. The fitting was accomplished using the simple Van Vleck Hamiltonian

$$\mathcal{H} = JS_1 \cdot S_2 + g\beta M_S'$$

where $S' = S_1 + S_2$ and the only exchange variable is J and the triplet, quintet, and septet energies are J , $3J$, and $6J$, respectively. The fitting leads to a value for J of 21.56(6) cm⁻¹. This result can be compared with those that we have obtained for other dimeric species of this type. Using the values of $R = 1.957$ Å, $\phi = 104.1^\circ$, and $\theta = 13.2^\circ$ we calculate by means of the GHP model which we have described elsewhere [16] a value for J of 22.3 cm⁻¹. This calculated value of J is, of course, very similar to the observed value of 21.56 cm⁻¹, and suggests that the model is valid even in systems in which the geometry at the metal center is highly distorted.

Supplementary Material

Tables of hydrogen atom coordinates, anisotropic thermal parameters, and observed and calculated structure amplitudes (16 pages).

Acknowledgements

This research was supported by the Scientific Affairs Division, North Atlantic Treaty Organization

(NATO) through grant RG85/0790 (to D.J.H. and E.P.) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society through grant number 17363-AC3-C (to D.J.H.). A gift of a sample of cyclen(H₂SO₄)₂, from Dr. Johan Springborg, The Agricultural University of Copenhagen, is gratefully acknowledged. We also thank Dr. Springborg for allowing us to quote the spectral data of [cyclamCrOH]₂(ClO₄)₄ prior to publication.

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