

# Structure, Magnetic Susceptibility and EPR Spectra of a Dimeric Macrocyclic Chromium(III) Complex Bridged by a Single Carbonate Ligand

E. Bang,<sup>a</sup> J. Eriksen,<sup>a</sup> J. Glerup,<sup>a,\*</sup> L. Mønsted,<sup>b</sup> O. Mønsted<sup>a</sup> and H. Weihe<sup>a</sup>

<sup>a</sup> Department of Inorganic Chemistry, H. C. Ørsted Institute, University of Copenhagen, Universitetsparken 5, DK-2100 København Ø and <sup>b</sup> Department of Chemistry, Royal Veterinary and Agricultural University, Thorvaldsensvej 40, DK-1871 Frederiksberg C, Denmark

Bang, E., Eriksen, J., Glerup, J., Mønsted, L., Mønsted, O. and Weihe, H., 1991. Structure, Magnetic Susceptibility and EPR Spectra of a Dimeric Macrocyclic Chromium(III) Complex Bridged by a Single Carbonate Ligand. – Acta Chem. Scand. 45: 367–372.

The orange dimeric carbonate bridged cation  $trans\text{-}[\text{Cr}(\text{NH}_3)(\text{cyclam})\text{O}]_2\text{CO}^{4+}$  [cyclam = 1,4,8,11-tetraazacyclotetradecane] has been isolated as the chloride salt from reaction mixtures of  $[\text{Cr}(\text{cyclam})\text{Cl}_2]\text{Cl}$  and liquid ammonia slightly contaminated with carbon dioxide. This dimeric cation is unusually robust and resists depolymerization even in hot 6 M hydrochloric acid. The iodide salt  $\{trans\text{-}[\text{Cr}(\text{NH}_3)(\text{cyclam})\text{O}]_2\text{CO}\}\text{I}_4 \cdot 2\text{H}_2\text{O}$  crystallizes in the space group  $P2_1/n$ , with  $a = 9.368(5)$ ,  $b = 21.977(5)$ ,  $c = 19.341(4)$  Å,  $\beta = 96.45(2)^\circ$  and  $Z = 4$ . Both independent 'cyclam' ligands are coordinated in the *trans* configuration with the RRSS chirality of the coordinated nitrogen atoms, and the five- and six-membered chelate rings in *gauche* and *chair* conformations, respectively.

The temperature dependence of the magnetic susceptibility is in agreement with an antiferromagnetic coupling between the two chromium(III) centres with  $J = 5.2(2)$   $\text{cm}^{-1}$ . The EPR spectra have been recorded on frozen glasses at temperatures down to 3.8 K. The dominant part of the spectrum is that of the quintet state, which has been computer-simulated using the mononuclear zero field splitting parameters  $D = 0.120(5)$   $\text{cm}^{-1}$  and  $E = -0.060(5)$   $\text{cm}^{-1}$ , and the dinuclear exchange parameters  $D_e = -0.0090(1)$   $\text{cm}^{-1}$  and  $E_e = -0.0038(1)$   $\text{cm}^{-1}$ .

The chemistry of complexes of chromium(III) coordinated by macrocyclic amine ligands has recently attracted considerable interest in a variety of contexts, and effective preparative procedures are mandatory for many applications.

Isomerically pure  $trans\text{-}[\text{Cr}(\text{cyclam})(\text{NH}_3)_2]^{3+}$  salts (cyclam = 1,4,8,11-tetraazacyclotetradecane) are conveniently prepared from crude  $cis/trans\text{-}[\text{Cr}(\text{cyclam})\text{Cl}_2]\text{Cl}$  mixtures and liquid ammonia at elevated temperatures. Occasionally such preparations contain orange impurities, and the  $trans\text{-}[\text{Cr}(\text{cyclam})(\text{OCONH}_2)_2]^+$  ion has previously been characterized as the perchlorate salt.<sup>1</sup> A more rigorous exclusion of carbon dioxide during the preparative procedure removed this impurity, but instead small amounts of another orange compound could sometimes be isolated by fractional crystallization from hot 6 M hydrochloric acid. Ion-exchange fractionation experiments suggested a 4+ charge in both acidic and basic solution, in agreement with uncharged spectral characteristics under these conditions. Elemental analyses suggested the presence of a carbonate ligand, but since the qualitative kinetic observations indicated an extreme robustness in strong acid which was not in agreement with the behaviour usually ascribed to a coordinated carbonate ligand, it was decided to characterize the cation further.

\* To whom correspondence should be addressed.

## Results and discussion

**Preparation.** Substitution of chloride ligands coordinated to a chromium(III) centre with ammonia ligands is conveniently performed under anhydrous conditions in liquid ammonia. When  $cis\text{-}[\text{Cr}(\text{cyclam})\text{Cl}_2]\text{Cl}$  is reacted under these conditions efficient isomerization to the *trans* series of complexes occurs simultaneously with ligand substitution, and  $cis\text{-}[\text{Cr}(\text{cyclam})(\text{NH}_3)_2]^{3+}$  has only been made by substitution of the significantly more labile nitrate ligands in  $cis\text{-}[\text{Cr}(\text{cyclam})(\text{ONO}_2)_2]^+$ .<sup>2</sup> Treatment of crude  $cis/trans\text{-}[\text{Cr}(\text{cyclam})\text{Cl}_2]\text{Cl}$  mixtures, easily prepared from anhydrous chromium(III) chloride and the cyclam ligand, with liquid ammonia is therefore an efficient route to the isomerically pure *trans* series of cyclam complexes. The yellow  $trans\text{-}[\text{Cr}(\text{cyclam})(\text{NH}_3)_2]^{3+}$  cation is easily purified by recrystallization as the chloride salt, but occasionally small amounts of an orange compound are also obtained. Elemental analyses, ion-exchange fractionation behaviour and the visible absorption spectrum (Fig. 1) suggested the presence of coordinated carbonate in a polymeric cation, but this is highly unexpected for a substance obtained by recrystallization from hot 6 M hydrochloric acid. The chloride salt proved unsuitable for a crystallographic investigation. Instead the iodide salt could be obtained as a dihydrate in a quality suitable for structure determination.

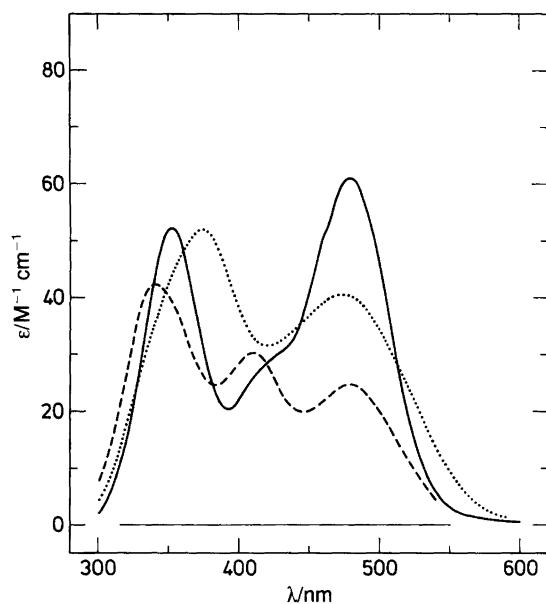


Fig. 1. Visible absorption spectra of (—)  $\{trans-[Cr(cyclam)(NH_3)O]_2CO\}^{4+}$  in 1 M HCl, (----)  $trans-[Cr(cyclam)(NH_3)(OH_2)]^{3+}$  in 1 M HClO<sub>4</sub> and (.....)  $trans-[Cr(cyclam)(NH_3)(OH)]^{2+}$  in 0.1 M NaOH + 0.9 M NaClO<sub>4</sub>. For comparative purposes the spectrum of the dimer is based upon mole chromium.

**Description of the structure.**  $\{trans-[Cr(cyclam)(NH_3)O]_2CO\}_2 \cdot 2H_2O$  crystallizes in the monoclinic space group  $P2_1/n$ , cf. the Experimental section. Two views of the dimeric cation are shown in Fig. 2, and selected bond distances and angles are given in Table 1. The distances and angles around the two independent chromium centres are very similar to each other, and also similar to those of the previously characterized  $trans-[Cr(cyclam)(OCONH_2)_2]^{2+}$ . In all cases the macrocyclic ligand is coordinated in the *trans* configuration, to give *R, R, S*, and *S* chiralities of the coordinated nitrogen atoms. This gives *gauche* and *chair* conformations to the five- and six-membered chelate rings. This conformation of the macrocyclic amine is that which from various semiempirical rationalizations is estimated to be the most stable for the present metal–nitrogen bond lengths. The bridging carbonate ligand is planar with normal bond lengths and angles. Hydrogen atoms on the two N1 atoms of the macrocyclic ligands at the two chromium centres form hydrogen bonds to the uncoordinated oxygen atom of the bridging carbonate ligand. The two macrocyclic ligands are parallel but rotated slightly around the chro-

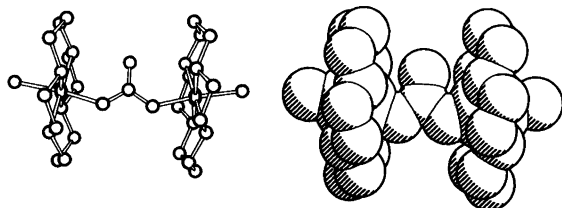


Fig. 2. Two views of the  $\{trans-[Cr(cyclam)(NH_3)O]_2CO\}^{4+}$  cation.

Table 1. Summary of structural data for  $\{trans-[Cr(cyclam)(NH_3)O]_2CO\}_2 \cdot 2H_2O$ .

	Range (std. dev.)
<b>Distances/Å</b>	
Cr–N (NH <sub>3</sub> )	2.128–2.131(8)
Cr–N (cyclam)	2.033–2.073(8)
Cr–O (carbonate)	1.946–1.950(8)
C–C	1.435–1.518(15)
C–N	1.455–1.516(15)
C=O	1.237(15)
C–O (–Cr)	1.294–1.306(15)
Cr–Cr	5.964(5)
<b>Angles/°</b>	
O=C–O (–Cr)	121.5–122.7(8)
N–Cr–N (NCCN-unit)	84.4–85.5(3)
N–Cr–N (NCCCN-unit)	93.9–95.8(3)

mium–chromium axis in relation to each other. This geometry seems to be adopted in an attempt to minimise the hydrogen–hydrogen repulsion. Similar hydrogen–hydrogen repulsion interactions may also be responsible for the fact that the bonds between the chromium centre and the nitrogen atom of the ammonia ligands are significantly longer than the average chromium–nitrogen bond lengths of about 2.06<sub>8</sub> Å as found for a number of hexaamminechromium (III) salts.<sup>1</sup> Alternatively, this bond lengthening may be caused by the influence of the carbonate ligand.

In Fig. 3 is shown a representation of the unit cell and the extensive net of hydrogen bonds between nitrogen-bound hydrogen atoms of the cations, water molecules and iodide ions. Except for the hydrogen at the N4a atom all hydrogens of water and coordinated nitrogen atoms are seen to

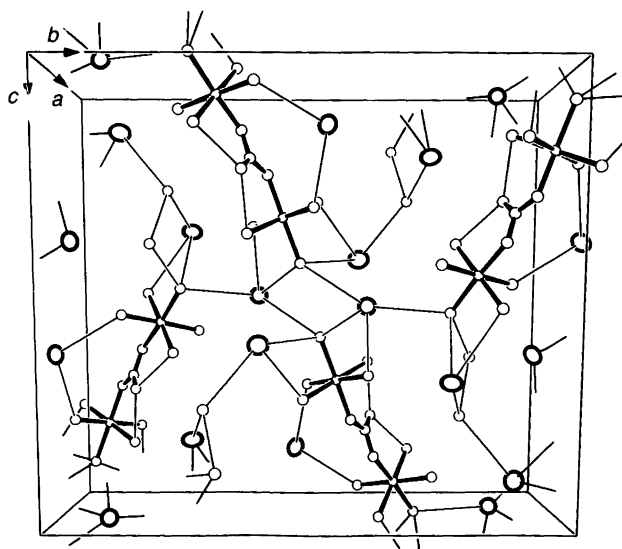


Fig. 3. Simplified cell packing and hydrogen bonds in  $\{trans-[Cr(cyclam)(NH_3)O]_2CO\}_2 \cdot 2H_2O$ . All carbon and hydrogen atoms are omitted. The remaining atoms are drawn as 35% probability ellipsoids.

Table 2. Interatomic bond distances<sup>a</sup> in {*trans*-[Cr(cyclam)(NH<sub>3</sub>)O]<sub>2</sub>}<sub>4</sub>·2H<sub>2</sub>O.

Hydrogen atom donor	Distance [Acceptor]/Å		
<b>NH<sub>3</sub></b>			
N0 a	3.622 [11]	3.654 [14]	2.987 [O2 w]
N0 b	3.748 [11]	3.796 [11]	3.679 [13]
<b>Cyclam</b>			
N1 a	2.751 [Oc]		
N8 a	3.674 [14]		
N11 a	3.522 [12]		
N1 b	2.810 [Oc]		
N4 b	3.568 [11]		
N8 b	3.582 [13]		
N11 b	3.615 [12]		
<b>Water</b>			
O1 w	3.584 [13]	3.616 [14]	
O2 w	3.536 [13]	2.824 [O1 w]	

<sup>a</sup>All standard deviations are in the range 0.005–0.010 Å.

take part in the net of hydrogen bonds. This is further described in Table 2.

**Reactivity.** The bond lengths described in Table 1 give no immediate clues to the extreme robustness of the coordinated carbonate ligand. The mechanism generally accepted for aquation of a bidentate carbonate ligand involves a protonation equilibrium followed by a metal–oxygen bond-breaking reaction and introduction of solvent water into the metal coordination sphere.<sup>3</sup> This mechanism may suggest a reason for the observed kinetic inertness. Firstly, diffusion away by the leaving ligand will probably be hindered by hydrophobic interactions between the two cyclam rings, and secondly entry of solvent water at the partly vacated coordination position will be severely sterically hindered. The ‘associative’ character of chromium(III) substitution reactions has been rationalized in terms of the absence of equilibration between the reactive intermediate and the second coordination sphere.<sup>4</sup> The limited lifetime of the reactive intermediate implied by this intimate mechanism, in combination with the suggested effects, will effectively prevent the depolymerization reaction.

**Magnetic susceptibility.** The temperature dependence of the magnetic susceptibility of the iodide salt of the dimeric complex was measured in the range 4–296 K, as shown in Fig. 4. The susceptibility shows a maximum at 10 K, and the effective magnetic moment at room temperature is approximately  $5.3\mu_B$ , which should be compared with the theoretical value for  $g = 2$  of  $5.48\mu_B$  for a non-interacting chromium(III) dimer. These features are characteristic for a weak anti-ferromagnetic coupling.

The susceptibility data were analyzed using the isotropic

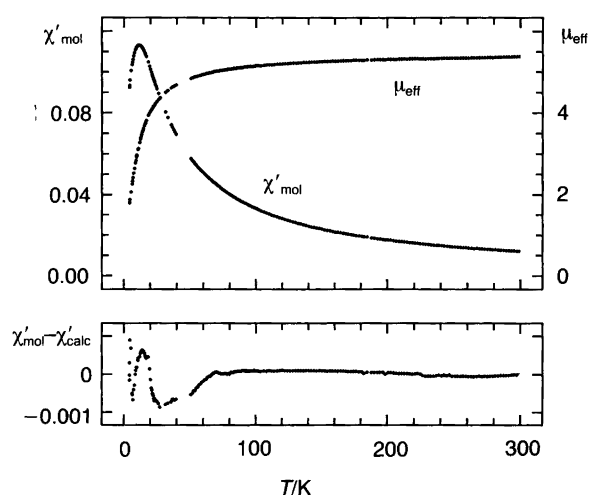


Fig. 4. The magnetic susceptibility (in c.g.s. units) and the effective magnetic moment of {*trans*-[Cr(cyclam)(NH<sub>3</sub>)O]<sub>2</sub>CO}<sub>4</sub>·2H<sub>2</sub>O as a function of temperature. The lower graph gives the difference between the calculated and the measured susceptibilities.

spin Hamiltonian for two equivalent metal centres, eqn. (1), where  $a$  and  $b$  refer to the two metal atoms, respec-

$$\hat{H} = g\mu_B\hat{S}_a\cdot\hat{H} + g\mu_B\hat{S}_b\cdot\hat{H} + J\hat{S}_a\cdot\hat{S}_b \quad (1)$$

tively. This gave  $J = 5.2(2) \text{ cm}^{-1}$  and  $g = 1.96(1)$ .

This  $J$  value is relatively high considering not only the distance of  $5.964 \text{ \AA}$  between the two chromium atoms but also that the  $\pi$ -interaction has to extend over four bonds, in comparison with two bonds in the  $\mu$ -hydroxochromium(III) complexes,<sup>5–7</sup> where the  $J$ -values are in the range  $21\text{--}35 \text{ cm}^{-1}$ . It is therefore reasonable to assume that the magnetic coupling through the carbonate bridge involves the  $\pi$ -orbitals perpendicular to the carbonate plane.

**EPR spectra.** The X-band EPR spectra were measured in the temperature range 3.8–200 K on frozen glasses of the perchlorate salt of the dimeric cation dissolved in *N*-methylformamide. The spectrum shown in Fig. 5 was measured at 3.8 K. The intensity was interpreted as a function of temperature in terms of eqn. (2), which gave  $E_q = 16(2)$

$$I \propto \frac{1}{T} \frac{\exp(-E_q/kT)}{\sum_i \exp(-E_i/kT)} \quad (2)$$

$\text{cm}^{-1}$ . This energy corresponds to the quintet energy and gives  $J = 5.3(7) \text{ cm}^{-1}$ , which is in good agreement with the value obtained from the susceptibility data. At higher temperatures some broad extra features are seen in the spectrum. These were not assigned, but are probably part of the septet spectrum (*vide infra*).

The EPR spectrum has been simulated by using eqn. (3), the spin Hamiltonian for two equivalent metal centres.

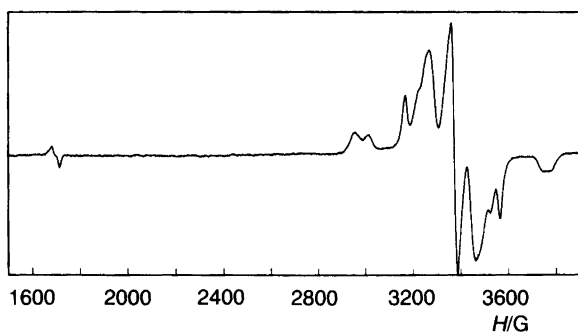


Fig. 5. The EPR spectrum of a frozen glass of  $\{trans-[Cr(cyclam)(NH_3)O]_2CO\}(ClO_4)_4$  dissolved in *N*-methylformamide measured at 3.8 K and a frequency of 9.36 GHz.

$$\hat{H} = g\mu_B\hat{S}_a \cdot \hat{H} + D[\hat{S}_{az}^2 - 1/3S_a(S_a + 1)] + E(\hat{S}_{ax}^2 - \hat{S}_{ay}^2) + g\mu_B\hat{S}_b \cdot \hat{H} + D[\hat{S}_{bz}^2 - 1/3S_b(S_b + 1)] + E(\hat{S}_{bx}^2 - \hat{S}_{by}^2) + J\hat{S}_a \cdot \hat{S}_b + D_e(2\hat{S}_{az}\hat{S}_{bz} - \hat{S}_{ax}\hat{S}_{bx} - \hat{S}_{ay}\hat{S}_{by}) + E_e(\hat{S}_{ax}\hat{S}_{bx} - \hat{S}_{ay}\hat{S}_{by}) \quad (3)$$

To simplify the calculation it has been assumed that the two chromium atoms are equivalent in the frozen glass even though they are not crystallographically equivalent. This condition implies the existence of one of the following symmetry operations:  $C_2$ ,  $\sigma_h$  or  $i$ , which interchanges the position of the two metal atoms in the complex. This means that the  $g$  values and the zero-field splitting parameters  $D$  and  $E$  are the same for the two metal atoms. With this symmetry condition fulfilled it is easily verified that the spin states with even spin numbers do not mix with the spin states with uneven spin numbers. The matrix of dimension

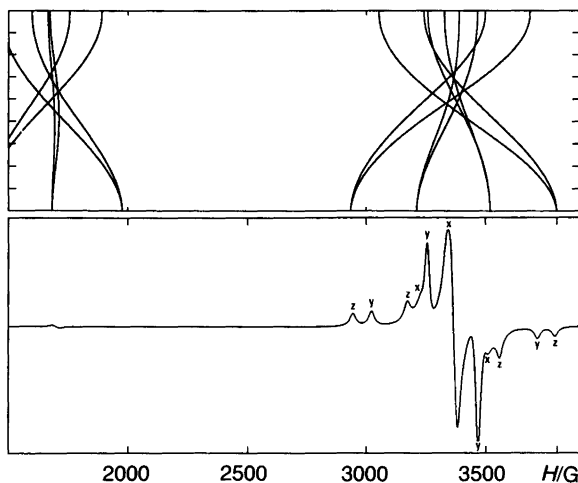


Fig. 6. The simulated EPR spectrum of  $\{trans-[Cr(cyclam)(NH_3)O]_2CO\}(ClO_4)_4$ . The upper graph shows the angular dependence of the resonance condition, where the ordinate is the angle between the magnetic field and the molecular  $z$ -axis. The lines representing the other Euler angle are only depicted when the magnetic field is in the  $xz$ - or the  $yz$ -plane, respectively. The lower graph shows the simulated spectrum, where the symbols  $x$ ,  $y$  and  $z$  give the orientation of the magnetic field relative to the molecular coordinate system.

16 can then be split into one matrix of dimension 6 ( $S = 0$  and 2) and one of dimension 10 ( $S = 1$  and 3). The usual formulas based upon an effective spin quantum number  $S$  for a dimeric complex, which represents an unnecessary approximation, have therefore not been used. The use of such formulas, which ignore non-diagonal matrix elements between the singlet and the quintet and between the triplet and the septet states, respectively, can only be justified for large  $J$ -values.

Based upon the abovementioned spin Hamiltonian, the quintet spectrum in Fig. 6 was simulated with the parameters  $g = 1.98(1)$ ,  $D = 0.120(5) \text{ cm}^{-1}$ ,  $E = -0.060(5) \text{ cm}^{-1}$ ,  $D_e = -0.0090(1) \text{ cm}^{-1}$  and  $E_e = -0.0038(1) \text{ cm}^{-1}$ , and taking the half-width of the Lorentzian curve as 30 G.

All the lines observed are seen in the simulated spectrum, and in spite of the crude model for linewidths the overall fit is good. The sign for the parameter  $D_e$  has deliberately been chosen as negative, because  $D_e$  can be written as a sum of a dipolar term and a pseudodipolar term where the dipolar term is negative.<sup>8</sup> The dipolar term is calculated to be  $-0.0082 \text{ cm}^{-1}$ , based upon the distance of 5.964 Å found between the two chromium atoms, which is in agreement with the value determined from the simulation. For monomeric complexes the relation  $3|E| \leq |D|$  can be used to constrain the parameters; however, this is not the case for a dimeric complex. The single-atom parameter  $D$  is within the expected range found in other *trans* complexes.<sup>9,10</sup>

The triplet and septet spectra have also been simulated with the same set of parameters. The calculated relative intensities (triplet : quintet : septet) are 1 : 130 : 26, without considering the Boltzmann distribution. Assuming the different spectra to have the same bandwidth, the quintet spectrum should be dominant in the measured temperature range. At 3.8 K no sign of the triplet spectrum has been observed, while the abovementioned spectrum observed, especially at temperatures  $> 50 \text{ K}$ , must be the septet spectrum; however, the lines are much broader than the observed quintet lines. There has been no attempt to adjust the parameters further to fit the septet spectrum, because this spectrum consists of only a few diffuse and ill-defined lines. This is unfortunate, because fitting both spectra with the same parameters would give more reliable parameters. However, simulation of EPR spectra measured on glasses as performed here is presently the only way to obtain a detailed picture of the splittings in the different spin states when no diamagnetic host is available. For large  $J$ -values<sup>11</sup> the crystal itself behaves as a diamagnetic host. For  $\mu$ -cyanobis[pentaamminechromium(III)] perchlorate the analogous cobalt complex has been used as a host<sup>12</sup> whereby the septet state has been identified.

## Experimental

$\{trans-[Cr(cyclam)(NH_3)O]_2CO\}X_n$ , ( $X^- = Cl^-, Br^-, I^-$  and  $ClO_4^-$ ). 2.5 g crude *trans*- $[Cr(cyclam)(NH_3)_2]Cl_3$ , prepared from  $[Cr(cyclam)Cl_2]Cl$  and liquid ammonia without

special precautions to prevent entry of carbon dioxide, were dissolved in 15 ml 0.1 M HCl(aq) at 80°C. The solution was filtered and 4 ml aqueous saturated LiCl were added dropwise to the warm filtrate. The mixture was allowed to cool to room temperature and then cooled in ice-water. The precipitate was filtered off and washed twice with acetone. Yield: 2.2 g of partly purified *trans*-[Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub>]Cl<sub>3</sub>.

This product was extracted with 5 ml portions of 6 M HCl(aq) at 90°C. The extraction was discontinued when the colour of the filtrate changed from orange to yellow. The resultant solution, about 20 ml, was allowed to cool to room temperature and then further cooled in ice-water. Yellow *trans*-[Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub>]Cl<sub>3</sub>, about 0.4 g, was filtered off and the mother liquor was then evaporated to dryness in a vacuum at 50°C. This gave an orange product which was recrystallized from 1 ml of boiling 1 M HCl(aq), and then cooling this solution in ice-water. Yield: about 0.15 g of an orange chloride salt of the *trans*-[Cr(cyclam)-(NH<sub>3</sub>)<sub>2</sub>O]<sub>2</sub>CO<sup>4+</sup> cation.

This compound was not characterized in detail. It was found, however, to contain only one coloured component, which by elution on a SP Sephadex C25 column moved as a band with the characteristics of a 4+ charged species. The spectral characteristics showed no variations through the band and are shown in Fig. 1. Salts of various other anions were prepared from the chloride salt. The solubilities were found to decrease along the series, Cl<sup>-</sup> > Br<sup>-</sup> > I<sup>-</sup> ≈ ClO<sub>4</sub><sup>-</sup>, which is normal for this type of complex. The iodide salt was found to be suitable for a single-crystal structure determination. A crude product was prepared by precipitating a concentrated aqueous solution of the chloride salt with a saturated aqueous solution of NaI at room temperature. Suitable single crystals were obtained by slowly cool-

Table 3. Crystal data and data collection and reduction characteristics.

Formula	I <sub>4</sub> Cr <sub>2</sub> O <sub>5</sub> N <sub>10</sub> C <sub>21</sub> H <sub>58</sub>
Space group	P2 <sub>1</sub> /n
M <sub>w</sub> /g mol <sup>-1</sup>	1142.4
Cell parameters:	
<i>a</i> /Å	9.368(5)
<i>b</i> /Å	21.977(5)
<i>c</i> /Å	19.341(4)
β/°	96.45(2)
<i>Z</i>	4
<i>V</i> /Å <sup>3</sup>	2527(2)
μ(Mo Kα)/cm <sup>-1</sup>	34.4
Crystal size/mm <sup>3</sup>	0.2×0.1×0.1
No. of reflections:	
Independent	6939
Observed [F <sup>2</sup> > 2σ(F <sup>2</sup> )]	5099
Used in calculations [sin θ/λ < 0.5]	3941
No. of parameters	199
R = Σ(F <sub>obs</sub> - F <sub>calc</sub> ) <sup>2</sup>	0.042
w <sup>-1</sup>	σ <sup>2</sup> (F) + 0.037 F  + 0.000 034F <sup>2</sup>
R <sub>w</sub> = Σw(F <sub>obs</sub> - F <sub>calc</sub> ) <sup>2</sup>	0.053

Table 4. Fractional coordinates and isotropic thermal parameters.

Atom	x	y	z	100 U <sub>iso</sub> /Å <sup>2</sup>
Cr a	0.20629(14)	0.17976(6)	0.55435(7)	2.24(8)
N0 a	0.2877(7)	0.2277(3)	0.4715(4)	3.10(19)
N1 a	0.3638(8)	0.2154(4)	0.6258(4)	4.0(2)
N4 a	0.0912(8)	0.2557(4)	0.5764(4)	4.1(2)
N8 a	0.0480(8)	0.1431(3)	0.4829(4)	3.32(19)
N11 a	0.3238(8)	0.1050(3)	0.5352(4)	3.8(2)
C2 a	0.3192(12)	0.2788(5)	0.6406(6)	6.0(3)
C3 a	0.1663(12)	0.2816(5)	0.6414(6)	6.1(3)
C5 a	-0.0653(12)	0.2448(5)	0.5785(6)	5.9(3)
C6 a	-0.1360(13)	0.2161(6)	0.5131(6)	7.0(4)
C7 a	-0.0999(12)	0.1505(5)	0.5010(6)	5.7(3)
C9 a	0.0959(11)	0.0778(5)	0.4748(5)	5.1(3)
C10 a	0.2500(12)	0.0761(5)	0.4713(6)	5.4(3)
C12 a	0.4834(12)	0.1122(5)	0.5352(6)	6.2(3)
C13 a	0.5488(13)	0.1431(5)	0.6015(6)	6.6(3)
C14 a	0.5129(13)	0.2081(5)	0.6129(6)	6.4(3)
O a	0.1168(6)	0.1336(2)	0.6237(3)	2.54(14)
C0	0.1599(9)	0.1164(4)	0.6867(4)	2.5(2)
O c	0.2801(7)	0.1292(3)	0.7163(3)	4.15(17)
O b	0.0680(6)	0.0845(3)	0.7176(3)	2.71(14)
Cr b	0.07057(14)	0.05420(6)	0.81247(6)	2.12(8)
N0 b	0.0532(8)	0.0201(3)	0.9142(4)	3.22(19)
N1 b	0.2107(8)	0.1208(3)	0.8535(4)	3.8(2)
N4 b	-0.0877(8)	0.1158(3)	0.8276(4)	3.7(2)
N8 b	-0.0669(8)	-0.0137(3)	0.7716(4)	3.6(2)
N11 b	0.2286(8)	-0.0064(3)	0.7966(4)	3.36(19)
C2 b	0.1201(12)	0.1668(5)	0.8821(6)	5.5(3)
C3 b	-0.0154(12)	0.1748(5)	0.8366(6)	5.7(3)
C5 b	-0.2168(12)	0.1146(5)	0.7719(6)	5.5(3)
C6 b	-0.2791(12)	0.0535(5)	0.7610(6)	5.7(3)
C7 b	-0.1949(12)	0.0073(5)	0.7253(6)	5.8(3)
C9 b	0.0231(11)	-0.0577(5)	0.7390(5)	5.0(3)
C10 b	0.1588(11)	-0.0664(15)	0.7834(5)	4.9(3)
C12 b	0.3617(12)	-0.0081(5)	0.8486(6)	6.0(3)
C13 b	0.4238(12)	0.0550(5)	0.8632(6)	5.5(3)
C14 b	0.3385(12)	0.1001(5)	0.8994(6)	5.6(3)
I1	0.75679(7)	0.10881(3)	0.98755(3)	3.89(4)
I2	0.63699(8)	0.03147(3)	0.36915(3)	5.06(5)
I3	0.21963(9)	0.10096(3)	0.09872(4)	6.10(6)
I4	0.00252(9)	0.23955(3)	0.32687(3)	5.47(5)
O1 w	0.3146(10)	0.2038(4)	0.2402(5)	9.6(3)
O2 w	0.4722(10)	0.1762(4)	0.3695(5)	9.3(3)

ing a saturated aqueous solution of this crude product from 100°C to room temperature. This gave the dihydrate: {*trans*-[Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub>O]<sub>2</sub>CO}I<sub>4</sub>·2H<sub>2</sub>O, analyses: I, Cr, N, C and H.

**Structure determination.** {*trans*-[Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub>O]<sub>2</sub>CO}I<sub>4</sub>·2H<sub>2</sub>O crystals are strongly pleochroic, orange–yellow, and form prisms or flat needles with the *a*-axis as the needle axis. The space group could be assigned to P2<sub>1</sub>/n through Weissenberg and precession photographs. Data were collected on an Enraf–Nonius CAD4 diffractometer with Mo Kα radiation at room temperature. The data were corrected for absorption with transmission coefficients between 0.506 and 0.570. The heavy atoms were located from the Patterson function, and the program DIRDIF<sup>13</sup> gave

the remaining non-hydrogen atom positions. Most hydrogen atoms could be seen in successive difference Fourier maps, and those remaining were introduced in idealized calculated positions. The X-RAY program system<sup>14</sup> was used for the refinements, with atomic scattering factors and corrections for anomalous dispersion taken from Refs. 15 and 16. Iodine and chromium atom parameters were refined anisotropically, and oxygen, nitrogen and carbon atom parameters isotropically. Hydrogen atom parameters were not refined. Instead the positional parameters were taken as those calculated for the idealized geometries, and a common isotropic thermal parameter of  $0.080 \text{ \AA}^2$  was employed. The maximum peak in the final difference map was  $1.1 \text{ e \AA}^{-3}$  and the maximum parameter shift in the final refinement cycle was  $0.8\sigma$ . Crystal data and data collection and reduction characteristics are given in Table 3 and fractional coordinates are given in Table 4. Lists of anisotropic temperature parameters and  $F_{\text{obs}}$  and  $F_{\text{calc}}$  are available from the authors upon request.

**Magnetic measurements.** The Faraday balance for the susceptibility measurement has been described elsewhere.<sup>17</sup> The measurements were performed at a field strength of 13 kG.

The EPR spectra have been recorded on a Bruker ESP 300 spectrometer equipped with an Oxford ESR-900 continuous-flow cryostat. The spectra were recorded at 9.36 GHz, 20 mW microwave power and with a modulation frequency of 100 kHz and a modulation width of 5 G.

**Methods of calculation.** The temperature dependence of the magnetic susceptibility,  $\chi'_{\text{mol,exp}}$  was approximated by eqn. (4).  $E_i$  are the energies of the 16 components of the

$$\chi'_{\text{mol,exp}}(T) \approx \chi'_{\text{mol,calc}}(T) = -\frac{N}{H} \frac{\sum_i \frac{\partial E_i}{\partial H} \exp(-E_i/kT)}{\sum_i \exp(-E_i/kT)} + K + \frac{C}{T} \quad (4)$$

groundstate manifold, the term  $C/T$  accounts for paramagnetic impurities, and  $K$  accounts for temperature-independent paramagnetism (TIP) and minor deviations in the correction for diamagnetism. The fitting was accomplished by minimization of expression (5) within the frame-

$$\sum_T \frac{[\chi'_{\text{mol,exp}}(T) - \chi'_{\text{mol,calc}}(T)]^2}{\sigma^2(\chi') + \left(\frac{\partial \chi}{\partial T}\right)^2 \sigma^2(T)} \quad (5)$$

work of nonlinear regression analysis.  $\sigma(\chi')$  and  $\sigma(T)$  are the estimated standard deviations on the measured magnetic susceptibility and temperature, respectively. The two constants  $K$  and  $C$  were found to be  $2.6(1) \times 10^{-4}$  and  $7(1) \times 10^{-3}$ , respectively.

**Computer simulations.** The simulation of the EPR spectrum was performed by generating the energy matrix for each orientation of the molecule relative to the magnetic field. The resonance condition for each transition was then found by successive diagonalizations and iterations, and the relative intensity was calculated from the eigenvectors. Summation of all the transitions over the whole space, where each transition is represented by a differentiated Lorentzian curve, gives the simulated spectrum. A more detailed description of the numerical method will be given elsewhere.

**Acknowledgements.** Thanks are due to F. Hansen, Chemistry Department IV, H. C. Ørsted Institute, for supervising the collection of the diffractometer data. The diffractometer, the EPR spectrometer and the computer were made available by grants from *Statens naturvidenskabelige Forskningsråd* (J. nr. 11-1837, 11-5680 and 11-7623).

## References

- Bang, E. and Mønsted, O. *Acta Chem. Scand., Ser. A36* (1982) 353.
- Kane-Maguire, N. A. P., Wallace, K. C. and Miller, D. G. *Inorg. Chem.* 24 (1985) 597.
- Palmer, D. A. and van Eldik, R. *Chem. Rev.* 83 (1983) 651 and references therein.
- Mønsted, L. and Mønsted, O. *Coord. Chem. Rev.* 94 (1989) 109.
- Cline, S. J., Glerup, J., Hodgson, D. J., Jensen, G. S. and Pedersen, E. *Inorg. Chem.* 20 (1981) 2229.
- Hodgson, D. J. and Pedersen, E. *Inorg. Chem.* 19 (1980) 3116.
- Veal, J. T., Jeter, D. Y., Hempel, J. C., Eckberg, R. P., Hatfield, W. E. and Hodgson, D. J. *Inorg. Chem.* 12 (1973) 2928.
- Owen, J. and Harris, E. H. In: Geschwind, S., Ed., *Electron Paramagnetic Resonance*, Plenum Press, New York 1972, p. 427.
- Pedersen, E. and Toftlund, H. *Inorg. Chem.* 13 (1974) 1603.
- Pedersen, E. and Kallesøe, S. *Inorg. Chem.* 14 (1975) 85.
- Kremer, S. *Inorg. Chem.* 24 (1985) 887.
- Glerup, J. and Weihe, H. *Acta Chem. Scand. Submitted.*
- Beurskens, P. T., Bosman, W. P., Doesburg, H. M., Gould, R. O., van den Hark, T. E. M., Prick, P. A., Noordik, J. H., Beurskens, G. and Pathasarthi, W. *DIRDIF: Direct methods for Difference Structures*, Technical Report 1981/2, Crystallographic Laboratory, Toernooiveld, Nijmegen, The Netherlands 1981.
- Stewart, J. M., Machin, P. H., Dickinson, C., Ammon, H. L. and Flack, H. L. *The X-Ray System Version 1976*, Technical Report TR 446, Computer Science Center, University of Maryland, College Park, MD 1976.
- Cromer, D. T. and Mann, J. B. *Acta Crystallogr., Sect. A24* (1968) 321.
- Cromer, D. T. and Lieberman, D. *J. Chem. Phys.* 53 (1970) 1891.
- Josephsen, J. and Pedersen, E. *Inorg. Chem.* 16 (1977) 2534.

Received September 6, 1990.