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Synthesis and Characterization of the Chromium(III) complexes of Ethylene Cross-Bridged Cyclam and Cyclen Ligands

Danny L. Maples^a, Randall D. Maples^a, Wesley A. Hoffert^b, Trenton H. Parsell^b, Alan van asselt^b, Jon D. Silversides^c, Stephen J. Archibald^c, and Timothy J. Hubin^a

^a Department of Chemistry and Physics, Southwestern Oklahoma State University, Weatherford, OK 73096, USA

^b Department of Natural Sciences, McPherson College, McPherson, KS 67460

^c Department of Chemistry, University of Hull, Hull, HU6 7RX, UK

Abstract

Dichloro(4,10-dimethyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane)chromium(III) chloride, Dichloro(4,10-dibenzyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane) chromium(III) chloride, and Dichloro(4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2] hexadecane)chromium(III) chloride have been prepared by the reaction of anhydrous chromium(III) chloride with the appropriate cross-bridged tetraazamacrocyclic. Aquation of these complexes proved difficult, but Chlorohydroxo(4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane)chromium(III) chloride was synthesized directly from chromium(II) chloride complexation followed by exposure or the reaction to air in the presence of water. The four complexes were characterized by X-ray crystal structure determination. All contain the chromium(III) ion in a distorted octahedral geometry and the macrocycle in the *cis*-V configuration, as dictated by the ethylene cross-bridge. Further characterization of the hydroxo complex reveals a magnetic moment of $\mu_{\text{eff}} = 3.95$ B.M. and electronic absorptions in acetonitrile at $\lambda_{\text{max}} = 583\text{nm}$ ($\epsilon = 65.8$ L/cm³·mol), 431nm ($\epsilon = 34.8$ L/cm³·mol) and 369nm ($\epsilon = 17$ L/cm³·mol).

Keywords

chromium(III); bridged tetraazamacrocyclic; cyclam; cyclen

Introduction

Chromium(III) complexes have played an important historical role in the development of transition metal photochemistry, primarily due to their relative kinetic inertness.¹ Enhancing that stability in order to study aquation rates of the ion has been achieved by using macrocyclic ligands.² The photochemical behavior of Cr³⁺cyclam complexes have been thoroughly studied due to their low photoreactivity and long excited-state lifetimes.^{3–6} More recently, stable chromium(III) cyclam complexes have been used to generate NO by photolysis of bound NO₂[–] in oxygenated aqueous solutions.^{7–10} Even more complex stability can be gained by bridging the macrocycle between donor atoms.¹¹ Recently, cyclams bridged between adjacent

*Corresponding author. Tel. 580-774-3026; Fax: 580-774-3115; tim.hubin@swosu.edu.

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nitrogen atoms have been complexed to Cr^{3+} in order to study the effect of ligand constraint on the photochemistry.^{12–14}

Our own research program has centered on transition metal complexes of the ethylene cross-bridged tetraazamacrocycles first synthesized by Weisman.^{15,16} We have previously demonstrated a large advantage in kinetic stability versus unbridged macrocycles for these cross-bridged ligands.^{17–19} In addition, the cis-V configuration of the bridged macrocycle dictated by the short ethylene cross-bridge, results in a distorted octahedral geometry around most first-row transition metal ions.^{17–22} The extent of the distortion depends on the size of the parent macrocycle ring and the radius of the metal ion.^{18–22} These facts have led us to conclude that the chromium(III) complexes of the cross-bridged tetraazamacrocycles might have interesting photochemical properties. In addition, chromium is a catalytically active metal ion. Cross-bridged tetraazamacrocycles have demonstrated an ability to stabilize first-row transition metal ions to make them catalytically useful.^{18,23–27} For these various reasons, we have begun to synthesize and characterize chromium complexes of the cross-bridged tetraazamacrocycles. This report focuses on the synthesis and structural characterization of several of these chromium(III) complexes.

Experimental

The ethylene cross-bridged ligands 4,10-dimethyl-1,4,7,10-tetraazabicyclo[5.5.2] tetradecane (**1**); 4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane (**2**); and 4,10-dibenzyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane (**3**) were prepared according to literature procedures (Figure 1).^{15,16} Electronic spectra were recorded using a Shimadzu UV-240 UV-Vis Spectrometer. Magnetic moments were obtained on finely ground solid samples at ambient temperatures using a Johnson Matthey MSB Auto magnetic susceptibility balance. Metal complexation was carried out as follows:

Dichloro(4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane)chromium(III) chloride, $[\text{Cr}(2)\text{Cl}_2]\text{Cl}$

Anhydrous CrCl_3 (0.316 g, 2.00 mmol) and ligand **2** (0.508 g, 2.00 mmol) were added to 20 ml of anhydrous DMF in an inert atmosphere glovebox. The reaction was stirred at 50–60 °C for 18 hours during which it became a dark green solution. After cooling, the solution was removed from the glovebox and excess diethyl ether was added, causing a green precipitate to form. The precipitate was filtered off, washed with ether and dried under vacuum, giving 0.317 g (77%) of the green solid product. Anal. Calcd. (found) for $\text{CrC}_{14}\text{H}_{30}\text{N}_4\text{Cl}_3 \cdot 1\text{DMF} \cdot 5\text{H}_2\text{O}$: C 35.45 (35.56); 8.23 (8.38); N 12.16 (11.82). X-ray quality, dark purple crystals were grown from ether diffusion into a DMF solution.

Dichloro(4,10-dimethyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane)chromium(III) chloride, $[\text{Cr}(1)\text{Cl}_2]\text{Cl}$

Anhydrous CrCl_3 (0.316 g, 2.00 mmol) and ligand **1** (0.453 g, 2.00 mmol) were added to 20 ml of anhydrous DMF in an inert atmosphere glovebox. The reaction was stirred at 50–60 °C for 18 hours during which it became a dark purple solution. After cooling, the solution was removed from the glovebox and excess diethyl ether was added, causing a purple precipitate to form. The precipitate was filtered off, washed with ether and dried under vacuum, giving 0.731 g (95%) of the purple solid product. Anal. Calcd. (found) for $\text{CrC}_{12}\text{H}_{26}\text{N}_4\text{Cl}_3 \cdot 2\text{H}_2\text{O}$: C 34.26 (34.03); 7.16 (6.87); N 13.32 (13.04). X-ray quality, dark purple crystals were grown from ether diffusion into a DMF solution.

Dichloro(4,10-dibenzyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane)chromium(III) chloride, [Cr(3)Cl₂]Cl

Anhydrous CrCl₃ (0.316 g, 2.00 mol) and ligand **3** (0.757 g, 2.00 mmol) were added to 20 ml of anhydrous DMF in an inert atmosphere glovebox. The reaction was stirred at 50–60 °C for 18 hours during which it became a dark purple solution with dark purple precipitate. After cooling, the solution was removed from the glovebox. The dark purple precipitate product was filtered off, washed with ether and dried under vacuum, giving 0.731 g (93%) of the purple solid product. Anal. Calcd. (found) for CrC₂₄H₃₄N₄Cl₃·H₂O : C 51.94 (51.66); 6.53 (6.34); N 10.10 (10.09). X-ray quality, dark purple crystals were grown from ether diffusion into a DMF solution.

Chlorohydroxo(4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane) chromium(III) chloride, [Cr(2)Cl(OH)]Cl

Ligand **2** (0.254 g, 1.00 mol) was dissolved in 20 ml of DMF. Anhydrous CrCl₂ (0.123 g, 1.00 mol) was added and the solution was stirred at 50–60 °C for 48 hours in the air. The reaction originally had a green color, but became dark blue over the reaction time. The solution was cooled and filtered. Ether diffusion into the filtrate resulted in the formation of blue, X-ray quality crystals of the product (0.0958 g yield, 23%). Anal. Calcd. (found) for [CrC₁₄H₃₀N₄Cl(OH)]Cl·1.67 H₂O : C 39.63 (39.76); H 8.15 (8.39); N 13.20 (12.87).

X-ray crystallography

The diffraction data sets were collected on a Stöe IPDS-II imaging plate diffractometer using Moα radiation ($\lambda = 0.71073 \text{ \AA}$). The crystals were kept at 150K during data collection using the Oxford Cryosystems Cryostream Cooler. The structures were solved using direct methods (SHELXS-97) and refined against F₂ (SHELXL-97). H atoms were placed in idealised positions or located on the difference map, and refined using a riding model with C-H = 0.97 Å, N-H = 0.91 Å, O-H = 0.85 Å and Uiso(H) = 1.2 or 1.5 times Ueq of the carrier atom. All non-H atoms were refined anisotropically. The WinGX package was used for refinement and production of data tables, and ORTEP-3 was used for structure visualization.²⁸ All ORTEP representations show ellipsoids at the 50% probability level. CCDC 699882 – 699885 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

The syntheses of the dichloride complexes were fairly straightforward, involving the complexation of CrCl₃ with the respective ligand in DMF. The reactions were generally done in an inert atmosphere glovebox with anhydrous solvents in order to protect the proton sponge ligands^{16,19,21} from protonation, which can defeat complexation. The product obtained in all cases from this reaction was [Cr(L)Cl₂]Cl. Interestingly, the complexes with cyclen-based ligands **1** and **3** were purple powders, while the complex of cyclam-based ligand **2** was isolated as a green powder. However, upon crystallization, this complex yielded purple crystals. Perhaps the color change was due to interaction with DMF, which was present according to the elemental analysis of the green powder, but was not present in the purple crystals.

Aquation of [Cr(2)Cl₂]Cl was attempted in water, but no satisfactory product was obtained. For this reason, we attempted to synthesize the aqua complex from CrCl₂ and the ligand by reacting them in DMF open to the air. The blue mono-hydroxo complex was isolated in low yield from this reaction. The protonation state of the bound oxygen is assumed from the total number of ions and the apparent 3+ oxidation state of the chromium in the complex. The magnetic moment of this complex was determined on the solid as $\mu_{\text{eff}} = 3.95 \text{ B.M.}$, which corresponds to $n = 3$, the chromium(III) ion.²⁹ UV-Vis Spectroscopy was performed on this

complex in acetonitrile. The complex was a blue color in an acetonitrile solution. Three absorption bands were present with the greatest band occurring at $\lambda_{\text{max}} = 583 \text{ nm}$ ($\epsilon = 66 \text{ L/cm}\cdot\text{mol}$), a secondary peak at 431 nm ($\epsilon = 35 \text{ L/cm}\cdot\text{mol}$) and a very small peak at approximately 369 nm ($\epsilon = 17 \text{ L/cm}\cdot\text{mol}$). These bands are consistent with the distorted octahedral geometry of other Cr^{3+} cyclam derivatives.^{14,30,31}

Crystals suitable for X-ray structure determination were obtained for all four complexes (Figures 2 and 3). The *cis-V* conformation expected to be dictated by the ligand cross-bridge is evident for all of the complexes structurally characterized here. Apparently, neither the identity of the metal ion, nor that of the alkyl substituents effects this conformation. To our knowledge, this same ligand conformation has been seen in all published metal complexes with ethylene cross-bridged cyclams and cyclens.

There are two independent $\text{Cr}(\mathbf{1})\text{Cl}_2^+$ cations in the unit cell of this structure, although the bond lengths and angles are similar in both. The thermal ellipsoids are quite a bit smaller for the cation labeled Cr(1), so the following discussion will refer to that cation. Comparison between the two cyclen-based structures (Figure 2) reveals little difference in the metal coordination geometry due to the differing alkyl groups. The bulkier benzyl substituents are directed away from the chloride binding site of Cr^{3+} . In Mn^{2+} and Fe^{2+} complexes with ligand **3**, π - π stacking between benzyl groups of adjacent molecules is apparent.³² In the Cr^{3+} structure, the chloride counter ions (not present in the other cases) appear to disrupt this interaction. The $\text{N}_{\text{ax}}\text{-Cr-N}_{\text{ax}}$ and $\text{N}_{\text{eq}}\text{-Cr-N}_{\text{eq}}$ bond angles for both cyclen complexes differ little: $160.83(19)^\circ$ and $83.50(18)^\circ$ for $\text{Cr}(\mathbf{1})\text{Cl}_2^+$ versus $160.35(19)^\circ$ and $83.6(2)^\circ$ for $\text{Cr}(\mathbf{3})\text{Cl}_2^+$, respectively. Likewise, the Cr-N_{ax} and Cr-N_{eq} bond lengths are very similar: averaging $2.103 \text{ \AA}$ and $2.050 \text{ \AA}$ for $\text{Cr}(\mathbf{1})\text{Cl}_2^+$ versus $2.117 \text{ \AA}$ and $2.064 \text{ \AA}$ for $\text{Cr}(\mathbf{3})\text{Cl}_2^+$, respectively. These parameters indicate that the larger benzyl groups do little to disrupt the binding of Cr^{3+} to the bridged cyclen macrocycle. Aromatic pendants can function as antennae to absorb more light for photochemical processes,⁸ motivating the use of this ligand.

The two cyclam based structures (Figure 3) differ not in macrocycle substitution, but in monodentate ligands at the *cis* sites not occupied by the cross-bridged macrocycle. The $\text{N}_{\text{ax}}\text{-Cr-N}_{\text{ax}}$ and $\text{N}_{\text{eq}}\text{-Cr-N}_{\text{eq}}$ bond angles for both cyclam complexes differ little: $172.46(11)^\circ$ and $84.63(11)^\circ$ for $\text{Cr}(\mathbf{2})\text{Cl}_2^+$ versus $172.23(14)^\circ$ and $84.07(14)^\circ$ for $\text{Cr}(\mathbf{2})\text{Cl}(\text{OH})^+$, respectively. Likewise, the Cr-N_{ax} and Cr-N_{eq} bond lengths are very similar: averaging $2.156 \text{ \AA}$ and $2.102 \text{ \AA}$ for $\text{Cr}(\mathbf{2})\text{Cl}_2^+$ versus $2.149 \text{ \AA}$ and $2.112 \text{ \AA}$ for $\text{Cr}(\mathbf{2})\text{Cl}(\text{OH})^+$, respectively. The Cr-Cl bond in $\text{Cr}(\mathbf{2})\text{Cl}(\text{OH})^+$ is $2.3341 \text{ \AA}$, which is similar to the Cr-Cl bond distances in $\text{Cr}(\mathbf{2})\text{Cl}_2^+$, which average $2.331 \text{ \AA}$. The Cr-Cl bond distances in the cyclen complexes average $2.318 \text{ \AA}$ for $\text{Cr}(\mathbf{1})\text{Cl}_2^+$ and $2.319 \text{ \AA}$ for $\text{Cr}(\mathbf{3})\text{Cl}_2^+$. These distances are similar to what has been reported in the literature for $\text{Cr}^{3+}\text{-Cl}$, with an average for several other complexes being $2.335 \text{ \AA}$.³³ The Cr-OH bond in $\text{Cr}(\mathbf{2})\text{Cl}(\text{OH})^+$ is much shorter, at $1.964 \text{ \AA}$. The same literature source³³ lists an average for this bond at $1.929 \text{ \AA}$, although it does not specify the oxidation state of the chromium. Our value is significantly longer than this, but it is definitely shorter than the Cr-OH_2 value specified for six-coordinate Cr^{3+} , given as $1.997 \text{ \AA}$.³³ The magnetic moment, UV-Vis spectrum, and number of other anions present in the crystal structure (vide supra) all point to a $\text{Cr}^{3+}\text{-OH}$ species as being most likely for this complex.

In a final comparison, the ring size of the parent macrocycle makes a difference on how fully the metal ion is engulfed by the bridged macrocycle. The easiest to use parameter to discuss this trend is the $\text{N}_{\text{ax}}\text{-Cr-N}_{\text{ax}}$ bond angle, where N_{ax} is an axially coordinated nitrogen. This bond angle averages 160.59° in the smaller cyclen cases, while it averages 172.35° for the cyclam complexes. The larger the bond angle, the closer to linearity and thus the better fit, or complementarity, between the ligand and the preferred octahedral geometry of the chromium (III) ion. A more subtle difference in the $\text{N}_{\text{eq}}\text{-Cr-N}_{\text{eq}}$ angles shows the same trend: this angle

averages 83.55° for the cyclen complexes and 84.35° for the cyclam complexes. Finally, the Cr—N bond distances are somewhat affected by the ligand size as well. The four Cr—N bond distances average 2.083 Å in the cyclen complexes, while this average is 2.130 Å in the cyclam complexes. The average value for a number of Cr—NR₃ bonds in the literature is 2.093 Å.³³

Summary

The synthesis, X-ray crystal structures, and some other characterization of four different Cr³⁺ complexes of ethylene cross-bridged tetraazamacrocycles have been presented. Because of the utility of these ligands in the coordination of other metal ions, and the catalytic and photochemical utility of Cr³⁺ coordination compounds, these complexes will likely provide much interesting chemistry for future study.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

The ethylene cross-bridged tetraazamacrocycles used in this study: a) 4,10-dimethyl-1,4,7,10-tetraazabicyclo[5.5.2] tetradecane (**1**) b) 4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2] hexadecane (**2**) and c) 4,10-dibenzyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane (**3**).

Figure 2. Thermal ellipsoid plots at the 50% probability level for the cations of a) $[\text{Cr}(\mathbf{1})\text{Cl}_2]\text{Cl}$ b) $[\text{Cr}(\mathbf{3})\text{Cl}_2]\text{Cl}$.

Figure 3. Thermal ellipsoid plots at the 50% probability level for the cations of a) $[\text{Cr}(\mathbf{2})\text{Cl}_2]\text{Cl}$ and b) $[\text{Cr}(\mathbf{2})\text{Cl}(\text{OH})]\text{Cl}$

Table 1

Selected Bond Lengths and Angles.

(a) [Cr(1)Cl ₂]Cl			
N(1)-Cr(1)	2.052(4)	N(4)-Cr(1)-Cl(1)	94.90(15)
N(2)-Cr(1)	2.098(5)	N(3)-Cr(1)-Cl(2)	93.61(13)
N(3)-Cr(1)	2.047(4)	N(1)-Cr(1)-Cl(2)	177.11(14)
N(4)-Cr(1)	2.107(5)	N(2)-Cr(1)-Cl(2)	93.66(14)
N(5)-Cr(2)	2.036(5)	N(4)-Cr(1)-Cl(2)	99.52(14)
N(6)-Cr(2)	2.088(5)	Cl(1)-Cr(1)-Cl(2)	91.48(7)
N(7)-Cr(2)	2.050(5)	N(5)-Cr(2)-N(7)	82.8(2)
N(8)-Cr(2)	2.089(6)	N(5)-Cr(2)-N(8)	82.2(3)
Cr(1)-Cl(1)	2.3132(18)	N(7)-Cr(2)-N(8)	82.8(2)
Cr(1)-Cl(2)	2.3225(16)	N(5)-Cr(2)-N(6)	83.4(2)
Cr(2)-Cl(4)	2.301(2)	N(7)-Cr(2)-N(6)	81.3(2)
Cr(2)-Cl(3)	2.3179(17)	N(8)-Cr(2)-N(6)	159.7(2)
N(3)-Cr(1)-N(1)	83.50(18)	N(5)-Cr(2)-Cl(4)	176.41(17)
N(3)-Cr(1)-N(2)	80.72(19)	N(7)-Cr(2)-Cl(4)	93.76(16)
N(1)-Cr(1)-N(2)	85.73(19)	N(8)-Cr(2)-Cl(4)	98.3(2)
N(3)-Cr(1)-N(4)	84.58(19)	N(6)-Cr(2)-Cl(4)	95.21(18)
N(1)-Cr(1)-N(4)	80.41(19)	N(5)-Cr(2)-Cl(3)	93.29(15)
N(2)-Cr(1)-N(4)	160.83(19)	N(7)-Cr(2)-Cl(3)	176.04(15)
N(3)-Cr(1)-Cl(1)	174.91(13)	N(8)-Cr(2)-Cl(3)	96.48(18)
N(1)-Cr(1)-Cl(1)	91.41(14)	N(6)-Cr(2)-Cl(3)	98.53(15)
N(2)-Cr(1)-Cl(1)	98.65(15)	Cl(4)-Cr(2)-Cl(3)	90.19(9)
(b) [Cr(3)Cl ₂]Cl			
Cr(1)-N(3)	2.056(5)	N(4)-Cr(1)-N(2)	160.35(19)
Cr(1)-N(1)	2.072(6)	N(3)-Cr(1)-Cl(1)	175.98(18)
Cr(1)-N(4)	2.112(5)	N(1)-Cr(1)-Cl(1)	92.65(14)
Cr(1)-N(2)	2.122(5)	N(4)-Cr(1)-Cl(1)	100.30(13)
Cr(1)-Cl(1)	2.3172(16)	N(2)-Cr(1)-Cl(1)	93.71(13)
Cr(1)-Cl(2)	2.320(2)	N(3)-Cr(1)-Cl(2)	93.00(17)
N(3)-Cr(1)-N(1)	83.6(2)	N(1)-Cr(1)-Cl(2)	176.19(15)
N(3)-Cr(1)-N(4)	80.75(18)	N(4)-Cr(1)-Cl(2)	92.92(16)
N(1)-Cr(1)-N(4)	84.9(2)	N(2)-Cr(1)-Cl(2)	100.64(17)
N(3)-Cr(1)-N(2)	84.38(19)	Cl(1)-Cr(1)-Cl(2)	90.82(8)
N(1)-Cr(1)-N(2)	80.7(2)		
(c) [Cr(2)Cl ₂]Cl			
N(1)-Cr(1)	2.104(3)	N(4)-Cr(1)-N(2)	172.46(11)
N(2)-Cr(1)	2.160(3)	N(3)-Cr(1)-Cl(1)	172.96(9)
N(3)-Cr(1)	2.100(3)	N(1)-Cr(1)-Cl(1)	91.01(8)
N(4)-Cr(1)	2.151(3)	N(4)-Cr(1)-Cl(1)	89.70(8)
Cr(1)-Cl(1)	2.3279(10)	N(2)-Cr(1)-Cl(1)	95.37(8)

Cr(1)-Cl(2)	2.3341(12)	N(3)-Cr(1)-Cl(2)	91.60(9)
N(3)-Cr(1)-N(1)	84.63(11)	N(1)-Cr(1)-Cl(2)	172.71(9)
N(3)-Cr(1)-N(4)	84.77(12)	N(4)-Cr(1)-Cl(2)	96.23(9)
N(1)-Cr(1)-N(4)	89.64(12)	N(2)-Cr(1)-Cl(2)	89.05(10)
N(3)-Cr(1)-N(2)	89.73(12)	Cl(1)-Cr(1)-Cl(2)	93.33(4)
N(1)-Cr(1)-N(2)	84.71(13)		
(d) [Cr(2)Cl(OH)]Cl			
Cr(1)-O(1)	1.964(3)	N(2)-Cr(1)-N(3)	89.75(14)
Cr(1)-N(4)	2.110(3)	O(1)-Cr(1)-N(1)	89.24(14)
Cr(1)-N(2)	2.114(4)	N(4)-Cr(1)-N(1)	89.55(14)
Cr(1)-N(3)	2.144(4)	N(2)-Cr(1)-N(1)	84.70(14)
Cr(1)-N(1)	2.153(4)	N(3)-Cr(1)-N(1)	172.23(14)
Cr(1)-Cl(1)	2.3339(14)	O(1)-Cr(1)-Cl(1)	92.84(9)
O(1)-Cr(1)-N(4)	90.58(13)	N(4)-Cr(1)-Cl(1)	173.72(10)
O(1)-Cr(1)-N(2)	171.93(14)	N(2)-Cr(1)-Cl(1)	93.06(10)
N(4)-Cr(1)-N(2)	84.07(14)	N(3)-Cr(1)-Cl(1)	89.95(11)
O(1)-Cr(1)-N(3)	95.76(13)	N(1)-Cr(1)-Cl(1)	95.75(11)
N(4)-Cr(1)-N(3)	84.46(14)		

Table 2

Crystal data and structure refinement

Identification code	sja19_06	sja77_06	sja18_06	sja1_03
Compound	[Cr(1)Cl ₂ Cl ₂ H ₂ O]	[Cr(3)Cl ₂ Cl ₂ ·H ₂ O]	[Cr(2)(OH)(Cl)]Cl·3H ₂ O	
Empirical formula	C12 H26 Cl3 Cr N4 O	C24 H36 Cl3 Cr N4 O	C14 H30 Cl3 Cr N4	C28 H62 Cl4 Cr2 N8 O7
Formula weight	400.72	554.92	412.77	868.66
Temperature	150(2) K	150(2) K	150(2) K	150(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	triclinic	orthorhombic	monoclinic	monoclinic
Space group	P-1	F dd2	P21/n	C2/c
Unit cell dimensions	a = 9.209(2) Å	a = 26.673(5) Å	a = 9.1410(13) Å	a = 28.741(5) Å
	b = 13.635(3) Å	b = 44.485(5) Å	b = 16.831(2) Å	b = 15.605(3) Å
	c = 13.962(3) Å	c = 8.3004(9) Å	c = 11.9603(17) Å	c = 9.0259(15) Å
	α = 82.349(15)°	α = 90°	α = 90°	α = 90°
	β = 87.766(16)°	β = 90°	β = 102.254(11)°	β = 99.010(14)°
	γ = 84.149(16)°	γ = 90°	γ = 90°	γ = 90°
Volume	1727.9(6) Å ³	9849(2) Å ³	1798.2(4) Å ³	3998.2(13) Å ³
Z	4	16	4	4
Density (calculated)	1.540 Mg/m ³	1.497 Mg/m ³	1.525 Mg/m ³	1.443 Mg/m ³
Absorption coefficient	1.129 mm ⁻¹	0.816 mm ⁻¹	1.084 mm ⁻¹	0.862 mm ⁻¹
F(000)	836	4656	868	1832
Crystal size (mm ³)	0.1 × 0.1 × 0.05 mm ³	0.37 × 0.19 × 0.08 mm ³	0.20 × 0.15 × 0.10 mm ³	0.1 × 0.1 × 0.07
Theta range	2.57 to 34.91°	2.61 to 34.86°	2.83 to 34.63°	2.61 to 34.75°
Index ranges	-14 < h < 14, -21 < k < 21	-42 < h < 41 -70 < k < 69	-14 < h < 14 -26 < k < 26	-45 < h < 45 -24 < k < 25
Reflections collected	44250	28303	41458	42296
Independent reflections	14774 [R(int) = 0.1602]	9843 [R(int) = 0.2654]	7669 [R(int) = 0.2302]	8549 [R(int) = 0.2315]
Completeness to theta	97.7 %	98.7 %	99.4 %	98.9 %
Refinement method	Full-matrix F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix on F ²

Identification code	sja19_06	sja77_06	sja18_06	sja1_03
Data/restraints/parameters	14774/0/380	9843/1/298	7669/0/200	8549/0/227
Goodness-of-fit on F ²	0.789	0.652	0.814	0.687
Final R indices [I>2sigma(I)]	R1 = 0.0785, wR2 = 0.1811	R1 = 0.0637, wR2 = 0.1243	R1 = 0.0606, wR2 = 0.1131	R1 = 0.0595, wR2 = 0.1095
R indices (all data)	R1 = 0.2626, wR2 = 0.2520	R1 = 0.2531, wR2 = 0.1619	R1 = 0.1817, wR2 = 0.1399	R1 = 0.2618, wR2 = 0.1563
Largest diff. peak and hole	1.180 and -1.424 e.Å ⁻³	0.895 and -1.186 e.Å ⁻³	0.685 and -1.227 e.Å ⁻³	0.556 and -1.175 e.Å ⁻³

$$^a [I > 2\sigma(I)]$$

$$^b wR1 = \Sigma ||F_o| - |F_c|| / |F_o|$$

$$^c wR2 = \{ \Sigma w(F_o^2 - F_c^2)^2 / \Sigma [w(F_o^2)^2]^{1/2} \} w = 1 / [s^2(F_o^2) + (aP)^2 + bP] \text{ where } P = (F_o^2 + 2F_c^2) / 3$$