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# Synthesis and Magnetic and Structural Characterization of the Binuclear Complex Di-$\mu$-hydroxobis{[tris(2-pyridylmethyl)amine]chromium(III)} Perchlorate Tetrahydrate, $[(tpa)CrOH]_2(ClO_4)_4 \cdot 4H_2O$

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## Abstract

The binuclear complex di-$\mu$-hydroxobis{[tris(2-pyridylmethyl)amine]chromium(III)} perchlorate tetrahydrate, $[Cr(C_{18}H_{18}N_4)OH]_2(ClO_4)_4 \cdot 4H_2O$ or $[Cr(tpa)OH]_2(ClO_4)_4 \cdot 4H_2O$, has been synthesized and characterized. The complex crystallizes in space group $P2_1/n$ of the monoclinic system with two binuclear units in a cell of dimensions $a = 11.381(5)$, $b = 17.856(4)$, $c = 13.050(7)$ Å, $\beta = 111.83(4)°$. The structure has been refined to a final value of the conventional $R$ factor of 0.056 on the basis of 3546 independent intensities. The geometry at the chromium is roughly octahedral, and the bridging unit has a Cr–O–Cr angle ($\phi$) of 100.53(8)°. The Cr–Cr separation is 3.003(1) Å, and the hydrogen atom on the bridging OH group sits 0.30 Å from the $Cr_2O_2$ plane, leading to a dihedral angle $\theta$ of 26.6°. The magnetic susceptibility of the complex indicates antiferromagnetic coupling, with the ground state singlet lying 30.58(6) $cm^{-1}$ below the lowest lying triplet state.

## Introduction

In recent years both we and others [1–9] have examined the structural and magnetic properties of numerous binuclear complexes with the aim of discovering relationships between these properties. For the case of the di-$\mu$-hydroxochromium(III) species, $[L_2CrOH]_2^{n+}$, we have suggested a quantitative correlation between the isotropic magnetic exchange coupling constant ($J$) and the structural parameters $R$, $\phi$ and $\theta$, where $R$ is the bridging Cr–O bond length, $\phi$ is the bridging Cr–O–Cr angle, and $\theta$ is the dihedral angle between the O–H vector and the $Cr_2O_2$ bridging plane [10].

Recently, we have focussed our attention on complexes with tetradentate ligands, $[LCrOH]_2^{n+}$, in the expectation that such complexes might show significant distortions from octahedral geometry at the metal center; the study of such complexes would allow us to examine our earlier conclusion that the local geometry at the metal plays little or no role in determining the magnetic properties since the only structural parameters in our relationship concern the bridging geometry [10]. This conclusion is consistent with our own work on some classes of hydroxo-bridged [11, 12] and halogen-bridged [13, 14] complexes of copper(II), and with the results of Merz and Haase [15] and of Kahn *et al.* [16] on related systems. Butcher and Sinn [17] and Willett *et al.* [18], however, have demonstrated experimentally that significant distortions at the metal center can have an impact on the value of $J$, and Bencini and Gatteschi [19] have reached the same conclusion on the basis of calculations.

We have described elsewhere the synthesis of iron(II) complexes of the ligand tris(2-pyridylmethyl)amine (tpa) (I) and its derivatives [20]. We here describe the synthesis, magnetic properties, and structural characterization of a binuclear chromium complex of tpa, $[(tpa)CrOH]_2(ClO_4)_4 \cdot 4H_2O$.

## Experimental

### Synthesis

#### Tris(2-pyridylmethyl)amine (tpa)

The ligand was prepared by the method described by Højland *et al.* [20].

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### *Di-μ-hydroxobis{[tris(2-pyridylmethyl)amine]-chromium(III)} perchlorate tetrahydrate $[(tpa)CrOH]_2(ClO_4)_4 \cdot 4H_2O$*

Tris-(2-pyridylmethyl)amine triperchlorate (2 g, 3.4 mmol) and chromium(III) nitrate enneahydrate (0.7 g, 1.7 mmol) were dissolved in water (20 ml) and refluxed for 5 h while lithium hydroxide (3.5 ml, 2 M) was gradually added at such a rate that the pH never exceeded 4. The red solution was allowed to cool slowly and the red crystals were separated and washed with water. Yield 0.3 g (30%). The crude product was recrystallized from water. *Anal.* Found: C, 36.12; H, 3.81; N, 9.38; Cl, 11.94. Calc. for $[(C_{18}H_{18}N_4)Cr(OH)]_2(ClO_4)_4 \cdot 4H_2O$: C, 36.37; H, 3.90; N, 9.43; Cl, 11.93%.

### *$[(tpa)CrOH]_2Br_4$*

This salt was prepared by a method which is a modification of a procedure described by Michelsen [21]. $[Cr(H_2O)_4Br_2] \cdot 2H_2O$ (4 g, 10 mmol) was dissolved in methoxyethanol (15 ml). Anhydrous chromium(II) chloride (0.5 g, 4 mmol) and tris(2-pyridylmethyl)amine (3 g, 10.4 mmol) was added with stirring. The mixture was refluxed for 20 min. The color changed from green to violet and the product was precipitated. Yield of crude product 2.4 g (44%).

### *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 [22]. The molar susceptibilities were corrected for ligand diamagnetism by Pascal's constants. C, H, N and Cl analyses were made by the microanalytical laboratory at the H. C. Ørsted Institute, Copenhagen.

### *X-ray Data Collection*

The data were collected and reduced as described elsewhere [23], using a 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: $Cr_2C_{36}H_{46}Cl_4O_{22}N_8$ | $D_o = 1.59(3)$ g cm$^{-3}$ |
| $a = 11.381(5)$ Å | $Z = 2$ |
| $b = 17.856(4)$ Å | $D_c = 1.603$ g cm$^{-3}$ |
| $c = 13.050(7)$ Å | Space group: $P2_1/n$ |
| $\beta = 111.83(4)°$ | $\mu = 7.69$ cm$^{-1}$ |
| $V = 2462(4)$ Å$^3$ | Data range: $1 \leqslant \theta < 27.5°$ |
| $NO = 3456$ ($>3\sigma$) | Radiation: Mo K$\alpha$ |
| $T = 21$ ℃ | Data collected: $+h, +k, \pm l$ |

### *Structure Solution and Refinement*

The location of the one independent 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 34 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 0.135 and 0.147, respectively. Anisotropic refinement reduced these values to 0.096 and 0.113, respectively. Examination of a difference Fourier summation at this stage convinced us that one of the perchlorate anions is disordered around a pseudo-threefold axis [the Cl(2)-O(21) bond]. Thus, the two sets of positions O(22), O(23), O(24) and O(22′), O(23′), O(24′) are rotated from each other by approximately 60° and are equally occupied. The position of the hydrogen atom on the bridging hydroxo group was located in a difference Fourier map and was refined isotropically in subsequent calculations. Ligand hydrogen atom positions were calculated on the basis of tetrahedral or trigonal geometry at carbon as appropriate, and these parameters were not varied. Attempts to locate the hydrogen atoms on the solvent molecules were unsuccessful. The final values of $R_1$ and $R_2$ were 0.056 and 0.062, respectively, with no parameter experiencing a shift of more than $0.56\sigma$. A final difference Fourier was featureless, the highest peak being 0.34 e Å$^{-3}$. All computer programs used were those provided by Enraf-Nonius in the CAD4/SDP package; atomic scattering factors were from ref. 24. The refined atomic positional parameters, along with their estimated standard deviations, are collected in Table II. See also 'Supplementary Material'.

## Results and Discussion

### *Isomerism*

Tris(2-pyridylmethyl)amine is a symmetrical tripod quadridentate ligand of the same general type as tris(2-aminoethyl)amine (tren). This type of ligand will only coordinate in a symmetrical fashion if the central nitrogen is situated at a molecular threefold axis. However, if it is coordinated as a tetradentate ligand in a pseudo octahedral complex, the three terminal nitrogen atoms will be non-equivalent; two 'axial' and one 'equatorial', where the designations axial and equatorial refer to the plane through the central atom containing the remaining two coordination sites. Since the terminal groups must coordinate *cis* to the bridgehead nitrogen atom, the whole complex is necessarily of *cis* configuration. The equatorial plane will also be a mirror plane of the molecule, so this type of complex will not exhibit any optical isomerism either. Two geometrical isomers are possible

TABLE II. Atomic Positional Parameters for $[Cr(tpa)OH]_2(ClO_4)_4 \cdot 4H_2O$

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Cr | 0.11380(5) | 0.01865(4) | 0.10099(5) |
| Cl1 | 0.2397(1) | 0.36875(7) | 0.03255(9) |
| Cl2 | 0.7269(1) | 0.25122(8) | 0.06099(11) |
| O | −0.0389(2) | 0.0659(1) | −0.0064(2) |
| O11 | 0.2512(3) | 0.4477(2) | 0.0435(3) |
| O12 | 0.1121(3) | 0.3459(2) | 0.0091(3) |
| O13 | 0.3182(4) | 0.3345(2) | 0.1320(4) |
| O14 | 0.2758(3) | 0.3455(2) | −0.0553(3) |
| O21 | 0.7478(5) | 0.1753(3) | 0.0705(5) |
| O22 | 0.7666(9) | 0.2966(6) | −0.0034(7) |
| O23 | 0.8027(10) | 0.2681(7) | 0.1773(9) |
| O24 | 0.6072(7) | 0.2699(6) | 0.0477(12) |
| O22′ | 0.8329(7) | 0.2786(6) | 0.0480(8) |
| O23′ | 0.6932(8) | 0.2880(5) | 0.1302(7) |
| O24′ | 0.6290(10) | 0.2428(6) | −0.0473(8) |
| OW1 | 0.9415(3) | 0.2057(2) | −0.0894(3) |
| OW2 | 0.5630(4) | 0.2343(3) | 0.2824(3) |
| N1 | 0.0272(3) | 0.0097(2) | 0.2143(2) |
| N2 | 0.2778(3) | −0.0297(2) | 0.2071(2) |
| N3 | 0.1854(3) | 0.1127(2) | 0.1958(3) |
| N4 | 0.2309(3) | 0.0558(2) | 0.0223(2) |
| C12 | 0.0202(4) | 0.0760(2) | 0.2624(3) |
| C13 | −0.0404(4) | 0.0808(3) | 0.3370(4) |
| C14 | −0.0900(4) | 0.0170(3) | 0.3633(4) |
| C15 | −0.0801(4) | −0.0502(3) | 0.3170(3) |
| C16 | −0.0194(4) | −0.0518(3) | 0.2428(3) |
| C22 | 0.3542(4) | 0.0175(3) | 0.2815(3) |
| C23 | 0.4776(4) | −0.0007(3) | 0.3464(4) |
| C24 | 0.5219(4) | −0.0704(3) | 0.3342(4) |
| C25 | 0.4434(4) | −0.1198(3) | 0.2600(4) |
| C26 | 0.3209(4) | −0.0981(2) | 0.1959(3) |
| C31 | 0.0793(4) | 0.1414(2) | 0.2279(3) |
| C32 | 0.2957(4) | 0.0911(3) | 0.2961(3) |
| C34 | 0.2228(4) | 0.1667(2) | 0.1268(4) |
| C42 | 0.2762(3) | 0.1257(2) | 0.0520(3) |
| C43 | 0.3643(4) | 0.1570(3) | 0.0138(4) |
| C44 | 0.4048(4) | 0.1158(3) | −0.0546(4) |
| C45 | 0.3610(4) | 0.0439(3) | −0.0831(4) |
| C46 | 0.2735(3) | 0.0151(3) | −0.0433(3) |
| H | −0.043(3) | 0.101(2) | −0.024(2) |

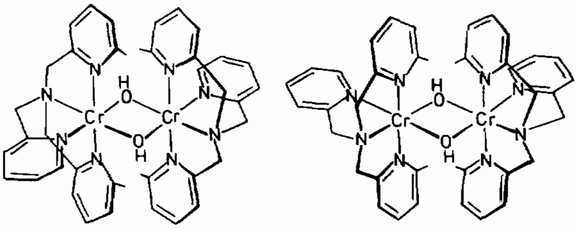


Fig. 1. The possible geometrical isomers of $[Cr(tpa)OH]_2^{4+}$.

for the doubly-bridged binuclear complexes derived from monomers containing tpa ligands, however; the two isomers are shown in Fig. 1. They are distinguished by having either the two aliphatic N atoms *cis* (meso form) or *trans* with respect to the $CrO_2$ core unit. As the 6-hydrogen atoms of the axial pyridine groups on adjacent metal ions will interact in the *cis* form, this form is expected to be destabilized with respect to the *trans* form.

### *Solution Chemistry*

The di-$\mu$-hydroxobis{[tris(2-pyridylmethyl)amine]-chromium(III)} cation was prepared in solution by a self assembly reaction either directly from the chromium(III) hexaquaion or a mixture of $[Cr(H_2O)_4Br_2]^+$ and chromium(II) chloride. The red perchlorate salt is only slightly soluble in water.

The crude bromide product gave only one fraction on a SP-Sephadex-C25 cation exchange column indicating that the synthesis is stereospecific and no byproducts are precipitated.

Spectral data are listed in Table III along with data from similar complexes. The unusual high intensity of the ligand field bands, compared to the analogous systems, probably reflects the large deviation from perfect octahedral coordination imposed by the tpa ligand. A similar effect was observed for the cyclen analogue [5]. The spectrum undergoes less than 1% change in the extinction coefficients within one hour so the presumed equilibrium between the di-$\mu$-hydroxo and $\mu$-hydroxo forms must lie much more to the di-$\mu$-hydroxo side than in the ethylenediamine case [26].

The complex changes color to greenish yellow in basic solution. The spectrum corresponds very well with the spectrum reported for the $\mu$-oxo-$\mu$-hydroxo-tetrakis(2-pyridylmethyl)dichromium(III) complex [27]. The basic solution is not stable. Thus, within 30 min the intensity at 363 nm was decreased by 23%. The decrease in intensity, no doubt, is due to the formation of the di-hydroxo $\mu$-hydroxo complex by analogy with the reactions of several other di-$\mu$-hydroxochromium(III) complexes [26].

TABLE III. Spectral Data for Binuclear Pyridyl Chromium(III) Complexes in Water

| Complex | $\lambda_{max}$ (nm) | $\epsilon_{max}$ (l/mol cm) | $\lambda_{max}$ (nm) | $\epsilon_{max}$ (l/mol cm) | Reference |
|---|---|---|---|---|---|
| $[Cr(bipy)_2OH]_2^{4+}$ | 537 | 106 | 447 | 158 | 25 |
| $[Cr(pic)_2OH]_2^{4+}$ | 540 | 197 | 380 | 120 | 21 |
| $[Cr(tpa)OH]_2^{4+}$ | 538 | 269 | 383 | 282 | this work |

### *Description of the Structure*

The structure consists of binuclear $[(tpa)CrOH]_2^{4+}$ cations, perchlorate anions, and water molecules which are hydrogen bonded to each other. The coordination geometry at the metal centers is depicted in Fig. 2, while a view of the whole cation is shown in Fig. 3. The principal bond lengths and bond angles are listed in Tables IV and V, respectively.

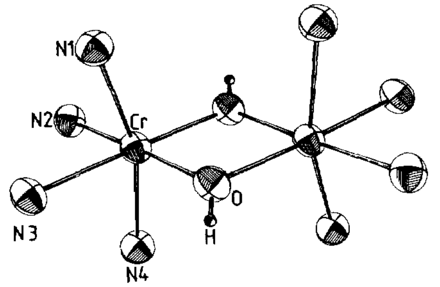


Fig. 2. View of the inner coordination geometry in the $[Cr(tpa)OH]_2^{4+}$ cation. The hydrogen atom is shown as a sphere of arbitrary size.

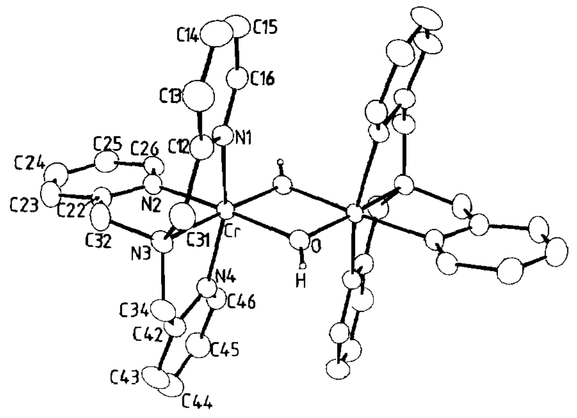


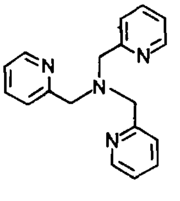
Fig. 3. View of the binuclear $[Cr(tpa)OH]_2^{4+}$ cation in the crystals of $[Cr(tpa)OH]_2(ClO_4)_4 \cdot 4H_2O$. Unlabelled atoms are related to labelled atoms by inversion through the center of the dimer.

The geometry about each chromium center is roughly octahedral. The *trans* angles at chromium fall in the range of 161.12(9)° to 176.88(8)°, the greatest distortion from linearity occurring at the intraligand angle N(1)–Cr–N(4) defined by the two axial nitrogen atoms; a similar observation was made in the cyclen analogue [cyclen is 1,4,7,10-tetraazacyclododecane], where this distortion is even greater [5]. The three chelate bond angles fall in the range 79.67(8) to 83.18(8)°, with an average value of 81.5(18)°.

We are aware of only two published structures of tpa complexes, the trigonal bipyrimidal monomeric $[Cu(tpa)Cl]PF_6$ complex described by Karlin *et al.* [28] and our own recent description of the binuclear mixed-valence manganese species $[(tpa)MnO]_2^{3+}$ [29]. In $[Cu(tpa)Cl]^+$ the amine is, as expected (*vide supra*), in the axial site and the pyridyl groups are equatorial. Very recently, we learned that Beck and Strähle [30] have examined the structure of $[Mo(tpa)(CO)_3]$, a molybdenum(0) complex of tpa; in $[Mo(tpa)(CO)_3]$ the tpa ligand is only terdentate, one of the pyridine nitrogen atoms remaining uncoordinated. As is the case for the $d^3$ Mn(IV) center in the manganese dimer [29], in the present chromium complex the four Cr–N distances are all similar, falling in the range of 2.056(2) to 2.071(2) Å, while in $[Mo(tpa)(CO)_3]$ the Mo–N (amine) bond is 0.05 Å longer than the average of the two Mo–N(pyridine) bonds. In the molybdenum complex, however, the observation of shorter Mo–N(pyridyl) bonds probably reflects the ability of Mo(0) to be involved in π-back donation to the pyridine ligands. It is also noteworthy that Karlin *et al.* have examined the structures of several copper complexes of the related ligand tepa (**II**) [31].

TABLE IV. Bond Lengths (Å) in $[(tpa)CrOH]_2(ClO_4)_4 \cdot 4H_2O$

| Atoms | Distance | Atoms | Distance |
|---|---|---|---|
| Cr–Cr′ | 3.003(1) | | |
| Cr–N(1) | 2.065(2) | C(25)–C(26) | 1.388(4) |
| Cr–N(2) | 2.056(2) | N(2)–C(26) | 1.344(3) |
| Cr–N(3) | 2.064(2) | C(22)–C(32) | 1.518(4) |
| Cr–N(4) | 2.071(2) | N(4)–C(42) | 1.351(3) |
| Cr–O | 1.971(2) | C(42)–C(43) | 1.392(4) |
| Cr–O′ | 1.934(2) | C(43)–C(44) | 1.363(5) |
| N(3)–C(31) | 1.507(3) | C(44)–C(45) | 1.377(5) |
| N(3)–C(32) | 1.489(3) | C(45)–C(46) | 1.382(4) |
| N(3)–C(34) | 1.486(3) | N(4)–C(46) | 1.344(3) |
| N(1)–C(12) | 1.358(3) | C(42)–C(34) | 1.517(4) |
| C(12)–C(13) | 1.389(4) | Cl(1)–O(11) | 1.417(2) |
| C(13)–C(14) | 1.369(4) | Cl(1)–O(12) | 1.428(2) |
| C(14)–C(15) | 1.368(4) | Cl(1)–O(13) | 1.413(3) |
| C(15)–C(16) | 1.383(4) | Cl(1)–O(14) | 1.416(2) |
| N(1)–C(16) | 1.330(3) | Cl(2)–O(21) | 1.374(3) |
| C(12)–C(31) | 1.498(4) | Cl(2)–O(22) | 1.360(9) |
| N(2)–C(22) | 1.334(3) | Cl(2)–O(23) | 1.471(8) |
| C(22)–C(23) | 1.383(4) | Cl(2)–O(24) | 1.350(6) |
| C(23)–C(24) | 1.373(4) | Cl(2)–O(22′) | 1.370(9) |
| C(24)–C(25) | 1.368(4) | Cl(2)–O(23′) | 1.287(6) |
| | | Cl(2)–O(24′) | 1.445(6) |



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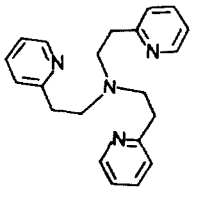

**II**

TABLE V. Selected Bond Angles (°) in $[(tpa)CrOH]_2(ClO_4)_4 \cdot 4H_2O$

| Atoms | Angle | Atoms | Angle |
|---|---|---|---|
| Metal coordination | | | |
| N(1)–Cr–N(2) | 92.34(8) | N(2)–Cr–O′ | 100.15(8) |
| N(1)–Cr–N(3) | 79.67(8) | N(3)–Cr–N(4) | 81.60(8) |
| N(1)–Cr–N(4) | 161.12(9) | N(3)–Cr–O | 97.19(8) |
| N(1)–Cr–O | 90.77(8) | N(3)–Cr–O′ | 176.65(8) |
| N(1)–Cr–O′ | 100.47(8) | N(4)–Cr–O | 94.01(8) |
| N(2)–Cr–N(3) | 83.18(8) | N(4)–Cr–O′ | 98.36(8) |
| N(2)–Cr–N(4) | 82.98(8) | O–Cr–O′ | 79.47(8) |
| N(2)–Cr–O | 176.88(8) | Cr–O–Cr′ | 100.53(8) |
| Ligand | | | |
| Cr–N(1)–C(12) | 113.0(2) | C(32)–N(3)–C(34) | 111.3(2) |
| Cr–N(1)–C(16) | 127.6(2) | N(1)–C(12)–C(13) | 120.6(3) |
| C(12)–N(1)–C(16) | 119.5(2) | N(1)–C(12)–C(31) | 115.5(2) |
| Cr–N(2)–C(22) | 114.1(2) | C(13)–C(12)–C(31) | 124.0(3) |
| Cr–N(2)–C(26) | 125.8(2) | N(2)–C(22)–C(23) | 122.4(3) |
| C(22)–N(2)–C(26) | 119.1(2) | N(2)–C(22)–C(32) | 116.1(2) |
| Cr–N(4)–C(42) | 113.6(2) | C(23)–C(22)–C(32) | 121.3(3) |
| Cr–N(4)–C(46) | 126.4(2) | N(4)–C(42)–C(43) | 121.1(3) |
| C(42)–N(4)–C(46) | 119.6(2) | N(4)–C(42)–C(34) | 115.4(2) |
| Cr–N(3)–C(31) | 105.4(1) | C(43)–C(42)–C(34) | 123.5(3) |
| Cr–N(3)–C(32) | 109.4(2) | N(3)–C(31)–C(12) | 108.3(2) |
| Cr–N(3)–C(34) | 107.7(1) | N(3)–C(32)–C(22) | 112.3(2) |
| C(31)–N(3)–C(32) | 110.2(2) | N(3)–C(34)–C(42) | 110.5(2) |
| C(31)–N(3)–C(34) | 112.7(2) | | |
| Anions | | | |
| O(11)–Cl(1)–O(12) | 110.7(1) | O(12)–Cl(1)–O(13) | 108.6(2) |
| O(11)–Cl(1)–O(13) | 109.5(1) | O(12)–Cl(1)–O(14) | 108.7(2) |
| O(11)–Cl(1)–O(14) | 109.3(1) | O(13)–Cl(1)–O(14) | 110.0(2) |

As was noted above, when tpa coordinates as a tetradentate ligand in a pseudo-octahedral complex an unfavorable meridional fusion of two of the pyridylmethylamine chelate rings is inevitable. The strain introduced by this geometrical requirement leads to increased C–N(3)–C angles and a decreased axial N(1)–Cr–N(4) angle. Thus, the average C–N(3)–C angle of 111.4° is approximately 2° larger than the idealized tetrahedral angle while the N(1)–Cr–N(4) angle of 161.12(8)° is approximately 19° smaller than the idealized octahedral value.

The Cr–O bonds in the bridging unit are asymmetric, the values of 1.971(2) and 1.934(2) Å falling within the range observed in other studies [1]. The bridging unit is rigorously planar by symmetry, the Cr–O–Cr′ angle $\phi$ being 100.53(8)° and the Cr–Cr′ separation being 3.003(1) Å; these parameters are also well within the established ranges. The hydrogen atoms on the bridging hydroxo groups lie 0.30 Å out of the $Cr_2O_2$ plane, leading to a dihedral angle $\theta$ of 26.6°.

A complete analysis of the hydrogen bonding in the crystals is precluded by our inability to locate the hydrogen atoms associated with the water molecules. The binuclear cation, however, has only one potential hydrogen bonding site; the bridging hydroxo group forms a strong hydrogen bond to water molecule OW(1), with O...OW(1) and H...OW(1) separations of 2.698(4) and 2.03(2) Å, respectively, and an associated O–H...OW(1) angle of 175(3)°.

The geometry of the ordered perchlorate ion is close to that of an idealized tetrahedron, with no O–Cl–O angle deviating from the tetrahedral value by more than 1.2°. The Cl–O distances fall in the range 1.413(1) to 1.428(2) Å [average 1.419(7) Å], which is consistent with earlier observations [2, 3].

### *Magnetic Properties*

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

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

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

$$\mathcal{H} = J\vec{S}_1\vec{S}_2 + g\mu_\beta M_{S'}$$

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 30.69(7) $\text{cm}^{-1}$. Inclusion of a second-order term in the Hamiltonian

$$\mathcal{H} = J\vec{S}_1\vec{S}_2 - j(\vec{S}_1\vec{S}_2)^2 + g\mu_\beta M_{S'}$$

slightly improved the fit, giving values of $J = 25.3(2)$ and $j = 0.75(3)$ $\text{cm}^{-1}$ and a triplet energy of 30.2(2) $\text{cm}^{-1}$. Finally, in a third model we allowed the energies of the three excited states to vary independently by writing the generalized Hamiltonian

$$\mathcal{H} = E(S') + g\mu_\beta M_{S'}$$

where $S'$ is the total spin of the state and $E(S')$ is its energy. This model gave a value of 30.58(8) $\text{cm}^{-1}$ for $E(1)$, the triplet state energy. This result can be compared with those that we have obtained for other dimeric species of this type. Using the values of $R$ = 1.953 Å, $\phi = 100.53°$, and $\theta = 26.6°$ we calculate by means of the GHP model which we have described elsewhere [10] a value for $J$ of 20.4 $\text{cm}^{-1}$. This calculated value of $J$ is, of course, in poor agreement with the observed value of 30.58 $\text{cm}^{-1}$. The problem here is that in this parameter range the calculated value of $J$ is very sensitive to small changes in $R$ and insensitive to relatively large changes in $\theta$ and $\phi$. In the present crystallographic experiment we obtain two independent measures of $R$, namely Cr–O [1.971(2) Å] and Cr–O′ [1.934(2) Å], which differ widely. Substitution of the shorter of these distances for the average value used above leads to a calculated value of $J$ of 29.7 $\text{cm}^{-1}$, which is in excellent agreement with the observed energy. Thus, while it is certainly possible that the GHP model is in need of some refinement, it appears that the structural data obtained in this experiment are inadequate to provide an appropriate test of the model.

## Supplementary Material

Tables of hydrogen atom coordinates, anisotropic thermal parameters, and observed and calculated structure amplitude (29 pages) are available from the authors on request.

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