

Synthesis, Characterization and Structure of a New μ -Acetato-di- μ -hydroxo Bridged Chromium(III) Complex with a Sexidentate Binucleating Pyridylamine Ligand

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The new binuclear chromium(III) complex $[\text{Cr}_2(\text{OH})_2(\text{ac})\text{tpen}](\text{ClO}_4)_3$ (tpen \equiv *N,N,N',N'*-tetrakis(2-pyridylmethyl)-1,2-ethanediamine) and monomeric chromium(III) complex $[\text{Cr}(\text{tpen})\text{ac}](\text{ClO}_4)_2$ were obtained by reacting chromium(II) acetate with the ligand tpen in the presence of air.

The binuclear complex crystallizes in space group $P2_1/n$ of the monoclinic system with four binuclear units in a cell of dimensions $a = 15.175(3)$, $b = 16.503(3)$, $c = 15.020(3)$ Å, $\beta = 97.39(1)^\circ$.

The structure of the cation is based on two octahedral chromium(III) centres bridged by two hydroxo groups, one symmetric acetato group and the tpen ligand. The Cr–Cr separation is 2.818(2) Å. The magnetic susceptibility of the complex indicates an unusually strong antiferromagnetic coupling, with the ground-state singlet lying 67 cm^{-1} below the lowest lying triplet state.

A superexchange coupling path through both the hydroxy and the acetato groups is suggested.

Several examples of binuclear complexes bridged by oxo or hydroxo and carboxylato groups have been reported in recent years. Some of these systems serve as models for a series of metalloproteins such as hemerythein,^{2,3} methane monooxygenase⁴ and the oxygen-evolving centre in Photosystem II.

As a continuation of our work on polynuclear iron(III) complexes of the sexidentate tetrakis(2-pyridylmethyl)diamine ligands³ (Fig. 1) we have in the present work investigated the corresponding chromium(III) complexes.

The strategy was to create a rigid binuclear complex by strapping the two tridentate bis(2-pyridylmethyl)amine units together by $(\text{CH}_2)_n$ chains. In the case of iron (III) the resulting complexes turned out to be tetranuclear, whereas the present chromium(III) complex has the anticipated binuclear structure where the pyridylamine ligands span over

the μ -acetato-di- μ -hydroxodichromium(III) units. A similar structure has been found for a binuclear Mo(III) EDTA complex⁵ and a binuclear oxovanadium(IV) tpen complex.⁶ This work presents the first well-characterized example with this coordination geometry for a Cr(III) complex.

Previously we have shown that one of the hydroxo bridges in di- μ -hydroxodichromium(III) complexes can be replaced by a symmetrically bridged carboxylato bridge.⁷

Results and discussion

Preparation. Chromium(II) acetate hydrate reacts quickly with the ligand *N,N,N',N'*-tetrakis(2-pyridylmethyl)-1,2-ethanediamine (tpen) in a methanol–water mixture to give a mixture of the orange complex μ -acetato-di- μ -hydroxy- μ -{tetrakis(2-pyridylmethyl)-1,2-ethanediamine}dichromium(III) complex $[\text{Cr}_2(\text{OH})_2(\text{CH}_3\text{COO})\text{tpen}]^{3+}$ and a purple complex with the composition $[\text{Cr}(\text{tpen})(\text{CH}_3\text{COOH})](\text{ClO}_4)_2$. In this last complex the tpen ligand probably is quinquidentate. The crude product of the perchlorate salts was precipitated by addition of sodium perchlorate. Pure samples of the perchlorates of the two complexes were obtained by fractional crystallization. Both complexes are stable for days in neutral aqueous solution. The red form, however, is changed into an other orange complex with the composition $[\text{Cr}(\text{tpen})(\text{H}_2\text{O})_2](\text{ClO}_4)_3$ on heating in 0.01 M perchloric acid. We suggest that in this complex the tpen ligand functions as a quadridentate ligand, and two water molecules complete the coordination sphere.

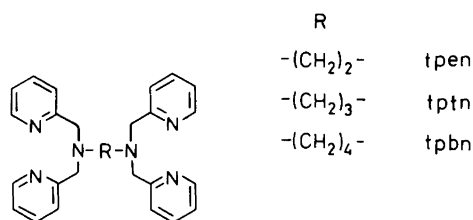


Fig. 1. *N,N,N',N'*-Tetrakis(2-pyridylmethyl)diamines.

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Table 1. Spectral data for a series of binuclear chromium(III) complexes in water.

Complex	λ_{\max}/nm	$(\epsilon_{\max})/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$	λ_{\max}/nm	$(\epsilon_{\max})/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$	Ref.
$[(\text{tpa})\text{Cr}(\text{OH})_2\text{Cr}(\text{tpa})]^{4+}$	538	(269)	383	(282)	9
$[(\text{tcn})\text{Cr}(\text{OH})_2(\text{CO}_3)\text{Cr}(\text{tcn})]^{3+}$	510	(101)	373	(84)	26
$[(\text{dpa})\text{Cr}(\text{OH})_2(\text{SO}_4)\text{Cr}(\text{dpa})]^{3+}$	536	(87)	392	(90)	10
$[(\text{en})_2\text{Cr}(\text{OH})(\text{ac})\text{Cr}(\text{en})_2]^{4+}$	505	(210)	378	(99)	7
$[\text{Cr}_2(\text{OH})_2(\text{ac})\text{tpen}]^{3+}$	500	(74)	378	(88)	This work
	678	(3.6)	353	(81)	This work
$[\text{Cr}(\text{tpen})(\text{ac})]^{2+}$	528	(109)	397	(80)	This work
$[\text{Cr}(\text{tpen})(\text{H}_2\text{O})_2]^{3+}$	480	(139)	380	(sh)	This work
$[\text{Cr}(\text{tpen})(\text{OH})_2]^+$	569	(112)	402	(75)	This work

Infrared spectra. The binding mode of carboxylates can be judged from the infrared spectra in the C=O stretching frequency ν_{CO} region.⁸ We have shown that symmetrically bridged carboxylate groups in binuclear chromium(III) complexes typically are characterized by a difference $\Delta\nu$ between the antisymmetric and symmetric stretching frequencies in the range 134–193 cm^{-1} .⁷

The orange binuclear complex investigated in the present study shows two intense CO frequencies at 1518 and 1425 cm^{-1} . The difference $\Delta\nu$ of 93 cm^{-1} is the lowest yet observed for a symmetrical acetato bridged chromium(III) complex. The purple complex, on the other hand, has an unusually large separation, $\Delta\nu = 335 \text{ cm}^{-1}$, between the two CO lines at 1645 and 1308 cm^{-1} . This clearly suggests an unsymmetrical binding mode for this acetato group, either a unidentate or a bridged structure with only one carboxylate oxygen coordinated to two chromium(III) centres. This finding supports the structure where the tpen ligand only is quinquidentate (Case II in Fig. 2).

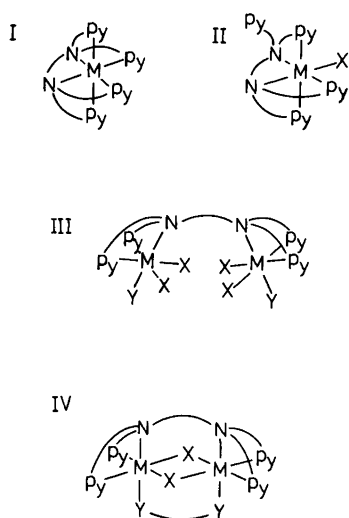


Fig. 2. Two examples of monomeric (I, II) and two examples of binuclear (III, IV) coordination modes of tetrakis(2-pyridylmethyl)diamines.

Electronic spectra. The visible absorption spectral data are listed in Table 1 along with data from similar complexes.

The spectrum of $[\text{Cr}_2(\text{OH})_2(\text{ac})\text{tpen}]^{3+}$ in water undergoes less than 1 % changes in extinction coefficients within 1 h, so the bridges seem to resist any hydrolytic reaction. In strong alkaline solution (0.01 M $[\text{OH}^-]$), however, the complex changes colour to deep brown. The spectrum is similar to the spectrum observed for μ -oxo- μ -hydroxotris(2-pyridylmethyl)aminodichromium(III)⁹ [tris(2-pyridylmethyl)amine \equiv tpa].

The average Δ value calculated for the μ -acetato-di- μ -hydroxo complex is 20 000 cm^{-1} , which is surprisingly high compared with the value of 18 660 cm^{-1} calculated for the $[\text{Cr}_2(\text{OH})_2\text{SO}_4(\text{dpa})_2]^{3+}$ complex [dpa \equiv bis(2-pyridylmethyl)amine].¹⁰ These two complexes ought to be comparable, as they have very similar donor groups. Changing acetate for sulfate should only weaken the ligand field by about 1 %, so the 7 % observed in this case must reflect some major changes in geometry due to the ethylene strapping of the two dpa groups in $[\text{Cr}_2(\text{OH})_2(\text{ac})\text{tpen}]^{3+}$. Additional narrow lines were observed around 680 and 350 nm. These are often observed in dihydroxo and trihydroxo bridged chromium(III) dimers having appreciable antiferromagnetic coupling. These lines are due to spin-forbidden transitions which gain intensity as the coupling increases.¹¹

The electronic spectrum of $[\text{Cr}(\text{tpen})(\text{H}_2\text{O})_2]^{3+}$ should reflect the ligand field strength of the tpen ligand when it is four coordinated. The average Δ value of 20 830 cm^{-1} is higher than the expected (around 20 360 cm^{-1} for a chromophore consisting of $[\text{Cr}(\text{en})(\text{py})_2(\text{H}_2\text{O})_2]^{3+}$).¹² The high ligand field might be due to the chelate effect.

The spectrum of the purple complex, $[\text{Cr}(\text{tpen})(\text{CH}_3\text{COO})]^{2+}$, is unusual too. The position of the first ligand field band could better match a substitution of two of the pyridines for acetate than the single substitution suggested by the analysis.

Stereochemistry. Sexidentate ligands of the tetrakis(2-pyridylmethyl)diamine type, Fig. 1, can function either as multidentate ligands towards one metal centre I and II, Fig. 2, or as a bridging unit between two metal centres III and IV, Fig. 2. In case I a pair of enantiomeric pseudo-octahedral

complexes are formed. This coordination mode is found for Fe(II), Co(III) and Ni(II).¹⁴ The pseudo-octahedral structure of [Fetpen](ClO₄)₂ has been confirmed by X-ray diffraction.¹⁵

Five-coordination has been found for the Cu(II) complex,^{16,17} and the purple compound described in this work probably has the structure II [M=Cr(III), X=unidentate acetate].

Binuclear systems, where the aliphatic chain between the two tertiary nitrogen atoms is the only bridge, type III, Fig. 2, have been found for the copper(II) complex [Cu₂Cl₂tpbn](ClO₄)₂¹⁷ [tpbn = *N,N,N',N'*-tetrakis(2-pyridylmethyl)-1,4-diaminobutane] and [Cu₂tpen(CO)₂](BF₄)₂.¹⁸ The same coordination mode has been found for the vanadyl¹⁹ and chromium(III)²⁰ complexes of the ligand triethylenetetraminehexaacetate.

In two cases it has been demonstrated that the tpen type of ligands can function as a bridge between binuclear centres of the type μ -oxo-di- μ -acetodimetal(III).

In the tetranuclear complex [Fe₄O₂(ac)₄(tpbn)₂](NO₃)₄³ the two units are strapped by two butane chains, whereas the centres in the analogous [Mn₄O₂(ac)₄(tptn)₂](ClO₄)₄²¹ [tptn = *N,N,N',N'*-tetrakis(2-pyridylmethyl)-1,3-diaminopropane] are strapped by two propane chains.

There are several examples of binuclear complexes where a binucleating ligand and some exogenic bridge ligands keep two transition-metal ions together. See Ref. 22 for a recent review. Here we shall only discuss systems directly related to the title compound.

Very recently and independent of the present work Wieghardt has reported the system [(VO)₂(OH)₂tpen]I₂⁶ with two bridging hydroxo ions. Similar structures have been found for some EDTA-bridged Mo(III) complexes.²³⁻²⁵

Finally, the unique tetrabridged structure IV in Fig. 2 adopted by the orange chromium(III) complex is described in the present work (X = OH, Y–Y = O, O-bridged acetate). A similar coordination mode has been found for the complex K[Mo₂(OH)₂(ac) EDTA].⁵

Description of the crystal structure. The asymmetric unit is formed by a binuclear cation and three perchlorate ions, two of which are hydrogen-bonded to the cation. The binuclear cation is shown in Fig. 3. The bond lengths and bond angles are listed in Table 3.

The overall symmetry of the cation is close to C₂; however, there are no crystallographic symmetry elements imposed on the ion. The geometry around each chromium centre is roughly octahedral. The interplanar angle between the Cr1, O1, O2 and Cr2, O1, O2 is 11.45°, which is less than half the values reported for [Cr₂(OH)₂SO₄(dpa)₂]²⁺,¹⁰ and [Cr₂(OH)₂CO₃(tcn)₂]²⁺,²⁶ (tcn \equiv 1,4,7-triazacyclononane), 23 and 28°, respectively. The reason seems to be that the ethylene strap tends to bring the (O3–Cr1–N1/O4–Cr2–N2) axes closer to a parallel position than in the unstrapped structures.

The short O–O distance in the acetate bridge increases the strain from the ethylene strap, so another consequence of the strapped arrangement is a shortening of the Cr1–Cr2 interatomic distance to 2.818(2) Å. In di- μ -hydroxy bridged chromium complexes with planar Cr1, Cr2, O1 and O2 groups the Cr–Cr distances reported are in the range 2.950–3.059 Å, so the one reported here is abnormally short. It is interesting that the Mo...Mo distance in [Mo₂(OH)₂(ac) EDTA][–] is as short as 2.430 Å.⁶

The Cr–O bonds involving the OH groups are symmetric within the standard deviations. The values, from 1.937(4) to 1.946(4) Å, fall in the range observed in other studies.²⁷ Because of the short Cr1–Cr2 distance the Cr–O–Cr angles become close to 90° (93.1(2)°), whereas the O–Cr–O angles, 84.5(2)° and 84.7(2)°, are a little above the usual values.²⁷

The six independent Cr–N distances are of similar magnitude, 2.014(5)–2.088(5) Å. these results are consistent with the Cr–N distances found in related complexes (Table 4).

There is no significant difference between the two Cr–O distances associated with the bridging acetate group; the average Cr–O distance, 1.958 Å, is significantly shorter than the values observed for the bridging carbonato group

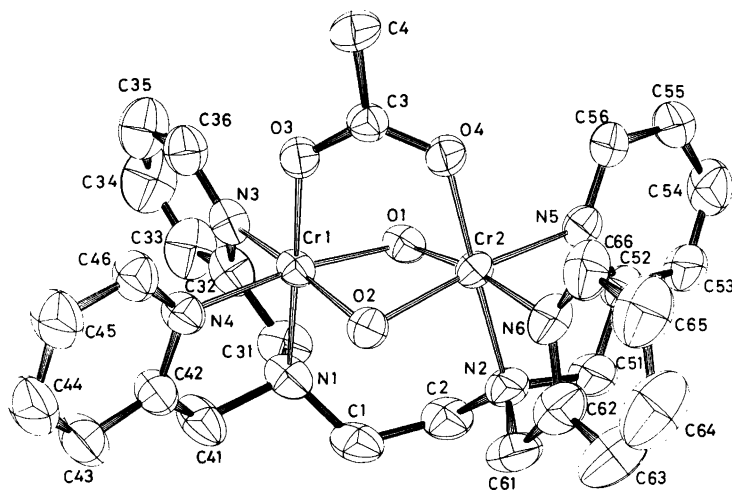


Fig. 3. A perspective drawing (ORTEP) of the μ -acetato-di- μ -hydroxo-*N,N,N',N'*-tetrakis-(2-pyridylmethyl)dichromium(III) cation showing the atom numbering scheme. The atoms are represented by ellipsoids enclosing 50% of the thermal displacements. Hydrogen atoms are omitted.

in $[\text{Cr}_2(\text{OH})_2(\text{CO}_3)(\text{tcn})_2]^{2+}$,²⁶ and the bridging acetato groups in $[\text{Cr}_3\text{O}(\text{ac})_6(\text{H}_2\text{O})_3]\text{Cl}(\text{aq})$.²⁸ The strain in the bridging ethylene bridge is reflected in two unusually large N–C–C angles: N1–C1–C2 = 120.1(6)° and N2–C2–C1 =

Table 2. Fractional coordinates and equivalent isotropic thermal parameters of non-H atoms. The perchlorate oxygen atoms have numbers in the range 11–34. $B_{\text{eq}} = 4/3 \sum_i \sum_j \beta_{ij}(a_i a_j)$.

Atom	x	y	z	B_{eq}
Cr1	0.93388(6)	0.21771(6)	0.27150(6)	2.74(5)
Cr2	1.06495(6)	0.23551(6)	0.15598(6)	2.88(6)
Cl1	0.5988(1)	0.0764(1)	0.1489(1)	4.6(1)
Cl2	0.4380(1)	0.4431(1)	0.2816(1)	4.9(2)
Cl3	0.2959(1)	0.1735(1)	0.4812(1)	5.1(2)
O1	1.0521(3)	0.1748(3)	0.2639(3)	3.3(3)
O2	0.9659(3)	0.2990(3)	0.1880(3)	3.2(3)
O3	0.8810(3)	0.1486(3)	0.1733(3)	3.3(3)
O4	0.9865(3)	0.1605(3)	0.0817(3)	3.4(3)
O11	0.5579(4)	0.1545(4)	0.1478(4)	7.4(6)
O12	0.5498(5)	0.0201(4)	0.1929(6)	9.0(8)
O13	0.6046(8)	0.0472(6)	0.0624(5)	13(1)
O14	0.6832(4)	0.0816(5)	0.1992(5)	9.1(8)
O21	0.4544(4)	0.3674(4)	0.2430(4)	6.9(6)
O22	0.4753(7)	0.5012(5)	0.2298(5)	11(1)
O23	0.4847(5)	0.4519(6)	0.3693(4)	10.0(9)
O24	0.3476(4)	0.4525(5)	0.2866(6)	10.1(9)
O31	0.2356(6)	0.1255(5)	0.4275(7)	13(1)
O32	0.3514(5)	0.1331(4)	0.5507(5)	8.6(7)
O33	0.3485(7)	0.206(1)	0.4235(9)	20(2)
O34	0.2563(7)	0.2425(6)	0.5116(7)	13(1)
N1	0.9888(3)	0.2869(4)	0.3805(3)	4.0(4)
N2	1.1486(3)	0.3192(3)	0.2290(4)	3.9(4)
N3	0.9124(3)	0.1398(3)	0.3710(3)	3.7(4)
N4	0.8210(3)	0.2782(3)	0.2845(3)	3.5(4)
N5	1.1803(3)	0.1761(3)	0.1411(4)	3.6(4)
N6	1.0818(4)	0.3141(4)	0.0552(4)	4.3(5)
C1	1.0587(5)	0.3494(5)	0.3640(5)	4.6(6)
C2	1.1427(5)	0.3231(5)	0.3293(5)	4.7(6)
C3	0.9132(4)	0.1331(4)	0.1020(4)	3.1(4)
C4	0.8602(5)	0.0777(5)	0.0358(5)	4.4(6)
C31	1.0232(5)	0.2261(5)	0.4516(5)	4.8(6)
C32	0.9592(5)	0.1574(5)	0.4514(5)	4.7(6)
C33	0.9487(6)	0.1102(6)	0.5263(5)	6.3(8)
C34	0.8925(7)	0.0464(7)	0.5175(6)	7(1)
C35	0.8448(6)	0.0277(6)	0.4360(6)	6.4(8)
C36	0.8561(5)	0.0768(5)	0.3622(5)	4.6(6)
C41	0.9119(5)	0.3329(5)	0.4165(5)	5.2(7)
C42	0.8296(4)	0.3354(4)	0.3517(5)	4.1(5)
C43	0.7620(5)	0.2889(5)	0.3616(6)	5.7(7)
C44	0.6834(5)	0.3834(6)	0.3048(7)	6.9(9)
C45	0.6727(5)	0.3222(6)	0.2404(6)	6.1(8)
C46	0.7430(4)	0.2725(5)	0.2303(5)	4.3(6)
C51	1.2433(4)	0.2959(5)	0.2194(6)	5.5(7)
C52	1.2544(4)	0.2132(4)	0.1817(5)	4.2(5)
C53	1.3367(4)	0.1781(5)	0.1845(5)	4.7(6)
C54	1.3423(5)	0.1030(6)	0.1460(6)	5.8(8)
C55	1.2678(5)	0.0654(5)	0.1027(6)	5.0(6)
C56	1.1870(4)	0.1037(4)	0.1018(5)	4.1(5)
C61	1.1265(5)	0.3998(4)	0.1848(6)	5.0(6)
C62	1.1118(5)	0.3872(5)	0.0854(6)	5.1(7)
C63	1.1258(7)	0.4480(6)	0.0232(7)	7(1)
C64	1.1078(7)	0.4327(7)	−0.0657(7)	8(1)
C65	1.0749(6)	0.3569(7)	−0.0988(6)	7.2(9)
C66	1.0619(5)	0.2990(5)	−0.0338(5)	5.1(7)

Table 3. Bond lengths (Å) and bond angles (°).

Cr1–O1	1.946(4)	N4–C42	1.375(9)
Cr1–O2	1.940(4)	N4–C46	1.350(8)
Cr1–O3	1.954(4)	N5–C52	1.354(8)
Cr1–N1	2.080(5)	N5–C56	1.344(9)
Cr1–N3	2.029(6)	N6–C62	1.35(1)
Cr1–N4	2.014(5)	N6–C66	1.355(9)
Cr2–O1	1.937(4)	C1–C2	1.50(1)
Cr2–O2	1.943(4)	C3–C4	1.505(9)
Cr2–O4	1.962(4)	C31–C32	1.49(1)
Cr2–N2	2.088(5)	C32–C33	1.39(1)
Cr2–N5	2.043(5)	C33–C34	1.35(1)
Cr2–N6	2.034(6)	C34–C35	1.37(1)
O3–C3	1.259(7)	C35–C36	1.40(1)
O4–C3	1.274(7)	C41–C42	1.482(9)
N1–C1	1.523(9)	C42–C43	1.38(1)
N1–C31	1.510(9)	C43–C44	1.38(1)
N1–C41	1.55(1)	C44–C45	1.39(1)
N2–C2	1.523(9)	C45–C46	1.37(1)
N2–C51	1.512(9)	C51–C52	1.50(1)
N2–C61	1.506(9)	C52–C53	1.371(9)
N3–C32	1.351(8)	C53–C54	1.38(1)
N3–C36	1.342(9)	C54–C55	1.38(1)
C55–C56	1.38(1)		
C61–C62	1.50(1)	Cr1–O1–Cr2	93.1(2)
C62–C63	1.41(1)	Cr1–O2–Cr2	93.1(2)
C63–C64	1.35(1)	O1–Cr1–O2	84.5(2)
C64–C65	1.41(2)	O1–Cr1–O3	92.0(2)
C65–C66	1.40(1)	O1–Cr1–N1	88.1(2)
Cl1–O11	1.429(7)	O1–Cr1–N3	92.8(2)
Cl1–O12	1.407(8)	O1–Cr1–N4	171.3(2)
Cl1–O13	1.399(9)	O2–Cr1–O3	91.6(2)
Cl1–O14	1.403(6)	O2–Cr1–N1	91.2(2)
Cl2–O21	1.413(7)	O2–Cr1–N3	172.4(2)
Cl2–O22	1.399(9)	O2–Cr1–N4	90.4(2)
Cl2–O23	1.421(7)	O3–Cr1–N1	177.2(2)
Cl2–O24	1.392(7)	O3–Cr1–N3	95.6(2)
Cl3–O31	1.319(9)	O3–Cr1–N4	95.2(2)
Cl3–O32	1.420(7)	N1–Cr1–N3	81.6(2)
Cl3–O33	1.36(1)	N1–Cr1–N4	84.9(2)
Cl3–O34	1.39(1)	N3–Cr1–N4	91.3(2)
		O1–Cr2–O2	84.7(2)
		O1–Cr2–O4	91.8(2)
		O1–Cr2–N2	91.3(2)
		O1–Cr2–N5	91.3(2)
		O1–Cr2–N6	171.3(2)
		O2–Cr2–O4	92.8(2)
O2–Cr2–N2	87.2(2)	O31–C13–O34	110.7(6)
O2–Cr2–N5	170.7(2)	O32–C13–O33	108.2(6)
O32–C13–O34	112.6(4)	O33–C13–O34	101.4(8)
O2–Cr2–N6	90.9(2)	Cr1–O3–C3	126.5(4)
O4–Cr2–N2	176.9(2)	Cr2–O4–C3	124.9(4)
O4–Cr2–N5	95.8(2)	Cr1–N1–C1	117.4(4)
O4–Cr2–N6	96.0(2)	Cr1–N1–C31	105.1(4)
N2–Cr2–N5	84.4(2)	Cr1–N1–C41	107.5(4)
N2–Cr2–N6	81.0(2)	C1–N1–C31	112.3(5)
N5–Cr2–N6	91.9(2)	C1–N1–C41	107.3(5)
O11–Cl1–O12	110.3(4)	C31–N1–C41	106.6(5)
O11–Cl1–O13	112.2(5)	Cr2–N2–C2	116.0(4)
O11–Cl1–O14	108.0(5)	Cr2–N2–C51	107.7(4)
O12–Cl1–O13	108.4(4)	Cr2–N2–C61	105.5(4)
O12–Cl1–O14	106.8(5)	C2–N2–C51	106.4(5)
O13–Cl1–O14	111.1(6)	C2–N2–C61	111.1(6)
O21–Cl2–O22	105.9(5)	C51–N2–C61	110.1(6)
O21–Cl2–O23	112.1(5)	Cr1–N3–C32	114.0(5)
O21–Cl2–O24	110.3(4)	Cr1–N3–C36	125.4(4)
O22–Cl2–O23	104.9(5)		contd

Table 3. (contd)

O22–C12–O24	115.2(5)	C41–C42–C43	121.6(7)
O23–C12–O24	108.4(5)	C42–C43–C44	119.3(8)
O31–C13–O32	113.0(5)	C43–C44–C45	119.5(8)
O31–C13–O33	110.3(7)	C32–N3–C36	120.6(6)
Cr2–N5–C52	114.1(4)	Cr1–N4–C42	114.2(4)
Cr2–N5–C56	126.1(4)	Cr1–N4–C46	126.7(5)
C52–N5–C56	119.6(5)	C42–N4–C46	118.9(6)
Cr2–N6–C62	113.0(5)	C44–C45–C46	119.3(7)
Cr2–N6–C66	125.8(5)	N4–C46–C45	121.7(7)
C62–N6–C66	121.2(7)	N2–C51–C52	115.0(6)
N1–C1–C2	120.1(6)	N5–C52–C51	117.1(6)
C1–C2–N2	121.1(6)	N5–C52–C53	121.7(7)
O3–C3–O4	125.3(5)	C51–C52–C53	121.2(6)
O3–C3–C4	116.9(5)	C52–C53–C54	118.1(6)
O4–C3–C4	117.8(5)	C53–C54–C55	121.0(7)
N1–C31–C32	109.7(5)	C54–C55–C56	118.2(7)
N3–C32–C31	115.6(6)	N5–C56–C55	121.4(6)
N3–C32–C33	120.0(7)	N2–C61–C62	108.2(6)
C31–C32–C33	124.3(6)	N6–C62–C61	117.4(7)
C32–C33–C34	119.5(7)	N6–C62–C63	119.3(8)
C33–C34–C35	121.1(9)	C61–C62–C63	123.3(7)
N3–C36–C35	120.8(7)	C62–C63–C64	119.7(9)
N1–C41–C42	113.2(6)	C63–C64–C65	122.0(1)
N4–C42–C41	117.1(6)	N6–C66–C65	122.1(8)
N4–C42–C43	121.2(6)		

121.1(6)°. The torsion angle N1–C1–C2–N2 of 90.3(8)° is also significantly larger than the ideal, 60°.

The hydrogen atoms in the bridging hydroxo groups in the dimeric cations are involved in hydrogen bonds to two perchlorate ions. The O...O distances are O1...O22 = 2.898(9) Å and O2...O32 = 2.758(8) Å.

The hydrogen atoms on the bridging hydroxo groups lie 0.57 Å out of the O–O line in a plane, perpendicular to the Cr–Cr axis, leading to an O–O–H angle Θ of 36.6°.

Magnetic properties. The magnetic susceptibilities for the two complexes were measured in the temperature range 4–300 K using the Faraday method. For the orange form the data were fitted to the usual expression given by

$$\chi'_A = -\frac{N}{H} \frac{\sum_i \left(\frac{\partial E_i}{\partial H} \right) \exp(-E_i/kT)}{\sum_i \exp(-E_i/kT)} \quad (1)$$

Table 4. Comparison of selected bond lengths (Å) and bond angles (°).

Complex	Cr–OH	Cr–N	Cr–N(py)	Cr–O ^a	Cr–Cr	CrOcr	OCrO	OHO	CrO1O2	Ref.
[(dpa)Cr(OH) ₂ SO ₄ Cr(dpa)] ²⁺	1.946	2.064	2.054	1.973	2.916	97.0	80.3	2.71	23	10
[(tcn)Cr(OH) ₂ CO ₃ Cr(tcn)] ²⁺	1.962	2.081	–	1.976	2.898	95.2	80.9	–	28	26
[Cr ₂ (OH) ₂ (ac)tpen] ³⁺	1.942	2.084	2.030	1.958	2.818	93.1	84.6	2.75	11	This work
[(tpa)Cr(OH) ₂ Cr(tpa)] ⁴⁺	1.954	2.064	2.056	–	3.003	100.5	79.5	2.70	0	9

^aAcetate, carbonate or sulfate.

eqn. (1), 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,

$$H = J\hat{S}_1 \cdot \hat{S}_2 + \beta gH \cdot \hat{S}' \quad (2)$$

eqn. (2) where $\hat{S}' = \hat{S}_1 + \hat{S}_2$, and the only exchange variable is J , and the triplet, quintet and septet energies are J , $3J$ and $6J$, respectively. The fitting was performed as previously described³⁰ and leads to a value for J of 67 cm⁻¹.

This value is the highest seen for a dimeric species of this type. This result is even more remarkable in view of the very low value of $J = 7$ cm⁻¹ found for the related complex, [Cr₂(OH)₂(SO₄)(dpa)₂]S₂O₆.¹⁰

The strong antiferromagnetic coupling between the two Cr(III) centres in the title compound cannot be explained as a pure superexchange coupling through the Cr(OH)₂Cr framework as in genuine di- μ -hydroxo complexes.²⁹ Using the values of $r = 1.940$ Å, $\Phi = 93.1^\circ$ and $\Theta = 0^\circ$ we calculate according to the GHP model²⁹ a value of $J = 29.6$ cm⁻¹, which is the theoretically largest possible value of J , limited by the parameters r and Φ .

As the GHP model describes almost all other chromium diols remarkably well, we have to assume an alternative coupling path in the present case. Saturated alkane bridges have never been shown to give rise to J values exceeding a few cm⁻¹. So we are left with the acetato bridge as an additional coupling path.

This assumption is supported by the observation of significantly shorter Cr–O (acetate) distances for the present compound compared to other μ -carboxylatochromium(III) complexes.^{26,28} Consequently, it is suggested that the μ -acetato bridge in the title compound provides a coupling path which is comparable with that obtained from the two hydroxo bridges.

Experimental

μ -Acetato-di- μ -hydroxy- μ -{N,N,N',N'-tetrakis(2-pyridylmethyl)1,2-ethanediamine}dichromium(III) perchlorate [Cr₂(OH)₂(CH₃COO)tpen](ClO₄)₃. The ligand tpen (0.73 g, 1.72 mmol) was dissolved in a 4:1 water-methanol mixture (20 ml). Chromium(II) acetate hydrate (0.64 g, 3.4 mmol) was added with stirring. The stirring was continued for 3 h. A saturated solution of sodium perchlorate in

water (3.4 ml) was added. The red precipitate was filtered off after 18 h and washed with water. Drying in air yielded 1.18 g of crude product (91 %).

The crude product was recrystallized from a 1:2 mixture of water and acetonitrile. Slow evaporation resulted in the formation of large orange and purple crystals, which could be separated manually. The purple complex was the main product. The title compound is the orange form. Anal. Found: C, 36.57; H, 3.57; N, 9.13; Cl, 11.45. Calc. for $[\text{Cr}_2\text{C}_{26}\text{H}_{26}\text{N}_6(\text{CH}_3\text{COO})(\text{OH})_2](\text{ClO}_4)_3$; C, 36.52; H, 3.62; N, 9.16; Cl, 11.56%.

O-Acetato-(N,N,N',N'-tetrakis(2-pyridylmethyl)-1,2-ethanediamine)chromium(III) perchlorate $[\text{Cr}(\text{tpen})\text{CH}_3\text{COO}](\text{ClO}_4)_2$. A pure sample of the purple complex was obtained by recrystallization of the crude product from an acetonitrile water mixture. Anal. Found: C, 44.54; H, 4.62; N, 11.13; Cr, 6.92. Calc. for $[\text{CrC}_{28}\text{H}_{33}\text{N}_6\text{O}_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$; C, 44.69; H, 4.42; N, 11.17; Cr, 6.91.

Diaqua-N,N,N',N'-tetrakis(2-pyridylmethyl)-1,2-ethanediaminechromium(III) perchlorate $[\text{Cr}(\text{tpen})(\text{H}_2\text{O})_2](\text{ClO}_4)_3$. $[\text{Cr}(\text{tpen})\text{CH}_3\text{COO}](\text{ClO}_4)_2$ (0.1 g) was dissolved in a mixture of 0.02 M perchloric acid (5 ml) and acetonitrile (5 ml). The solution was heated to 70°C for 15 min and left for crystallization for 18 h. The large orange crystals were filtered off and washed with water. Anal. Found: C, 37.86; H, 3.63; N, 10.18. Calc. for $[\text{CrC}_{26}\text{H}_{24}\text{N}_6](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$; C, 38.51; H, 3.97; N, 10.36.

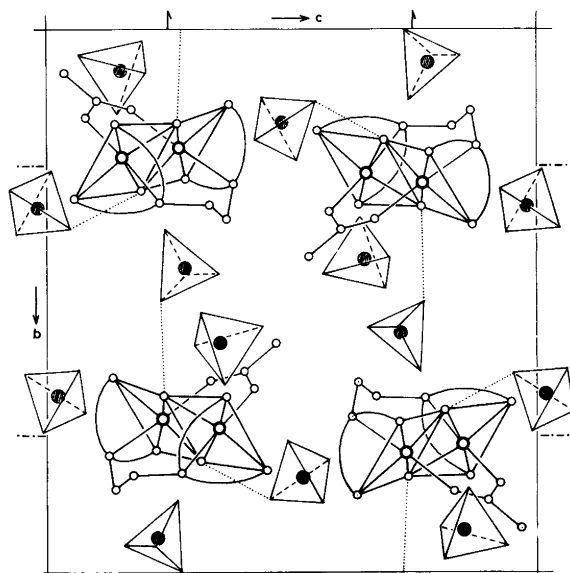


Fig. 4. Projection of the crystal structure down the a axis. The curved lines represent the pyridylmethylamine chelates. Some of the lines from O1, O2, N3, N4, N5 and N6 are not bonds, but are drawn to clarify the structure. The perchlorate ions are symbolized by tetrahedra. The dotted lines are the hydrogen bonds.

Crystal data for μ -acetato-di- μ -hydroxo- μ -(N,N,N',N'-tetrakis(2-pyridylmethyl)-1,2-ethanediamine)dichromium(III) perchlorate. $\text{Cr}_2\text{C}_{28}\text{H}_{33}\text{N}_6\text{O}_{16}\text{Cl}_3$, $M=919.96$, monoclinic, $P2_1/n$, $a=15.175(3)$, $b=16.503(3)$, $c=15.020(3)\text{\AA}$, $\beta=97.39(1)^\circ$, $D_m=1.64(1)$, $D_x=1.638\text{ g cm}^{-3}$, $Z=4$.

X-Ray crystallography, general. A crystal with the dimensions $0.15 \times 0.29 \times 0.39\text{ mm}$ was selected to collect intensities on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda(\text{MoK}\alpha_1)=0.71073\text{ \AA}$), $T=295\text{ K}$. Lattice parameters were determined from 20 diffractometer setting angles ($2.39 < \Theta < 14.24^\circ$). The data collection range was ($2 < \Theta < 30^\circ$), ($h\ 0 \rightarrow 21$, $k\ 0 \rightarrow 23$, $l\ -21 \rightarrow 20$). Three reflections were used for orientation control every 100 reflections, with an intensity check every third hour of exposure time, with one reflection. A total of 11010 reflections were measured in the $\omega-2\Theta$ mode with scan angle = $(1.00+0.35\tan \Theta)^\circ$. A total of 5566 reflections were considered as observed [$I > 2.5\sigma(I)$]. Lorentz and polarization corrections were applied; no absorption correction was made; $\mu=8.61\text{ cm}^{-1}$.

Structure solution and refinement. The structure was solved by direct methods and difference electron density calculations. The positions of the two chromium atoms, all the coordinating nitrogen and oxygen atoms, the chlorine atoms and five further atoms were deduced from a direct methods calculation. Two subsequent difference density calculations revealed the remaining non-H atoms. The 5566 observed reflections were used in anisotropic full matrix least-squares refinements of the Cr, Cl, O, N and C atoms.

All the H-atom positions were calculated, except for the hydroxo and one methyl H, which were located from a $\Delta\rho$ map when the R -index was below 8%. Refinements of $\text{H}(x,y,z)$ were made with $\sin \Theta/\lambda < 0.40\text{ \AA}^{-1}$; a fixed isotropic H-temperature factor was used. Calculated positions were used for 11 H atoms which refined to "unrealistic" C-H distances. $\sum w(|F_o| - |F_c|)^2$ was minimized; final values of $R = 0.068$ and $wR = 0.082$ were obtained; $w = 1$ when $F_o < 80$, otherwise $w = (80/F_o)^2$. The quality of fit, defined as $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{param}})]^{1/2}$ was 2.73. $(\Delta/\sigma)_{\text{max}} = 0.15$. The minimum and maximum in the final $\Delta\rho$ map were -0.74 and 1.1 e \AA^{-3} , respectively. The scattering factors were taken from Ref. 31, while the computer programs were from XRAY76.³²

The positional and isotropic thermal parameters are given in Table 2.

Physical measurements. All visible absorption spectra were measured on a Cary 219 spectrophotometer at room temperature. Magnetic susceptibilities were measured according to the Faraday method. Preliminary descriptions of the instruments are found in Ref. 30 and references therein.

Supplementary material. Tables of anisotropic thermal parameters as well as observed and calculated structure amplitudes are available from one of the authors (H.T.).

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