New Hetero- and Homo-metallic Dihydroxo-bridged Dinuclear Complexes of Cobalt(III) and Chromium(III): Synthesis, Spectroscopy and Crystal Structures†

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Sixteen new unsymmetrical hetero- and homo-metallic dinuclear complexes $[(nta)Cr(\mu\text{-}OH)_2ML_4]Cl\cdot nH_2O$ [M = Co^{III} or Cr^{III}; L_4 = $(NH_3)_4$, $(en)_2$, $(tn)_2$, $\{(R,R)chxn\}_2$, (trien), $(amp)_2$, $(bipy)_2$ or $(phen)_2$; nta = nitrilotriacetate, en = ethane-1,2-diamine, chxn = *trans*-cyclohexane-1,2-diamine, tn = propane-1,3-diamine, amp = 2-aminomethylpyridine, trien = triethylenetetramine, bipy = 2,2′-bipyridine and phen = 1,10-phenanthroline] were synthesized and characterized by elemental analysis, UV/VIS absorption, circular dichroism and ^2H NMR spectra, acid strengths of bridging hydroxide, magnetic properties and crystal structures. The crystals of $[(nta)Cr(\mu\text{-}OH)_2M(tn)_2]Cl\cdot 1.5H_2O$ (M = Co or Cr) are isomorphous and belong to the monoclinic system, space group $C2/c$, $Z = 8$, with $a = 16.384(2)$, $b = 14.660(2)$, $c = 18.874(2)$ Å, $\beta = 110.77(1)°$ and $a = 16.465(3)$, $b = 14.727(2)$, $c = 19.057(2)$ Å, $\beta = 110.28(1)$ for M = Co and Cr respectively. The crystal structure of $[(nta)Cr(\mu\text{-}OH)_2Cr(phen)_2]Cl\cdot 7H_2O$ was found to be triclinic with space group $P\bar{1}$, $a = 15.79(1)$, $b = 18.04(1)$, $c = 12.77(1)$ Å, $\alpha = 96.39(8)°$, $\beta = 102.23(7)$, $\gamma = 102.83(7)°$ and $Z = 4$. The structural parameters of the bridging moiety around each metal ion were almost the same as in the corresponding symmetrical dinuclear species. The ^2H NMR spectra of $[([^2H_6]nta)Cr(\mu\text{-}OH)_2ML_4]^+$ reflected the stereochemistry of the nta chelate rings and the M–N(of L_4) bond properties.

Hydroxide-bridged chromium(III) or cobalt(III) dinuclear complexes have been widely investigated from magnetic, spectroscopic and structural points of view.[1–4] The heterometallic dinuclear complexes which contain two different metal cations bridged by hydroxide ions are also of interest. Some heterometallic di- or tetra-nuclear complexes containing chromium(III) and metal(II) cations bridged by hydroxide and/or acetate were studied in detail.[5] The dinuclear complex $[(en)_2Cr(OH)_2Co(en)_2]^{4+}$ (en = ethane-1,2-diamine) was synthesized by solid-state dehydration of a 1 : 1 mixture of Λ-*cis*-$[Cr(en)_2(OH)(H_2O)][S_2O_6]$ and Δ-*cis*-$[Co(OH)(H_2O)(en)_2][S_2O_6]$.[6]

In this paper, we describe the detailed synthesis and characterization of new hetero- and homo-metallic dihydroxide-bridged dinuclear complexes with general formula $[(nta)Cr(\mu\text{-}OH)_2ML_4]Cl\cdot nH_2O$ [M = Co^{III} or Cr^{III}; nta = nitrilotriacetate; L_4 = $(NH_3)_4$, $(en)_2$, $(tn)_2$ (tn = propane-1,3-diamine), $\{(R,R)chxn\}_2$ (chxn = *trans*-cyclohexane-1,2-diamine), trien (triethylenetetramine), $(amp)_2$ (amp = 2-aminomethylpyridine), $(bipy)_2$ (bipy = 2,2′-bipyridine) or $(phen)_2$ (phen = 1,10-phenanthroline)]. The crystal structures of heterometallic $[(nta)Cr(OH)_2Co(tn)_2]Cl\cdot 1.5H_2O$ and of $[(nta)Cr(OH)_2Cr(tn)_2]Cl\cdot 1.5H_2O$ and $[(nta)Cr(OH)_2Cr(phen)_2]Cl\cdot 7H_2O$ have been determined and are compared with those of symmetrical homometallic dihydroxide-bridged dinuclear complexes. The ^{14}N NMR spectra of the $M(en)_2$ moiety of $[(nta)Cr(OH)_2M(en)_2]^+$ (M = Cr^{III} or Co^{III}) complexes have been reported.[7]

Experimental

Materials.—The precursor complexes $K_2[Cr_2(nta)_2(OH)_2]\cdot 4H_2O$,[8] *cis*-$[Co(NH_3)_4(H_2O)_2]_2[SO_4]_3\cdot 3H_2O$,[9] $[Co(CO_3)(en)_2]Cl$,[10] $[Co(CO_3)(tn)_2]Cl$,[11] *cis*-$[CoCl_2\{(R,R)\text{-}chxn\}_2]Cl$,[12] *cis*-$\alpha$-$[Co(trien)(H_2O)_2][ClO_4]_3$,[13] *cis*-$\alpha$-*trans*-(py)-$[CoCl_2(mpa)_2]Cl\cdot H_2O$,[14] $[Co(CO_3)(bipy)_2]Cl\cdot 2H_2O$,[15] $[Co(CO_3)(phen)_2]Cl\cdot 4.5H_2O$,[15] *cis*-$[CrCl(H_2O)(NH_3)_4]SO_4$,[16] *cis*-$[CrCl_2(en)_2]Cl\cdot H_2O$,[17] *cis*-$[CrCl(dmso)\{(R,R)\text{-}chxn\}_2]Cl_2$ (dmso = dimethyl sulfoxide),[17] *cis*-$[Cr(tn)_2(H_2O)_2][NO_3]_3$,[18] *cis*-$\alpha$-$[CrCl_2(trien)]Cl\cdot H_2O$,[19] *cis*-$\alpha$-*trans*-(py)-$[CrCl_2(amp)_2]Cl$,[20] *cis*-$[Cr(OH)(H_2O)(bipy)_2][ClO_4]_2$[21] and *cis*-$[Cr(phen)_2(H_2O)_2][NO_3]_3\cdot 2H_2O$[21] were synthesized by the reported methods and identified by elemental analysis and UV/VIS absorption spectra. All other materials were commercially available.

Preparation of Aqueous Solutions of $[ML_4(H_2O)_2]^{3+}$.—The aqueous solutions of diaqua complexes $[ML_4(H_2O)_2]^{3+}$ were obtained from the corresponding precursor complexes by the following procedures except for the diaqua and aquahydroxo ones. The dichloro ones except *cis*-α-*trans*(py)-$[MCl_2(amp)_2]Cl$ (2.5 mmol) were aquated by dissolving in water (25 cm^3) and stirring for 20 min at 60 °C. The *cis*-α-*trans*(py)-$[MCl_2(amp)_2]Cl$ were aquated with moist Ag_2O as described.[20] The carbonato ones were aquated by dissolving in 1 mol dm^{-3} $HClO_4$ (25 cm^3).

Preparation of the $[(nta)Cr(OH)_2ML_4]Cl\cdot nH_2O$ *Complexes* **1a**–**8a** *and* **1b**–**8b**.—To an aqueous solution (25 cm^3) containing $[ML_4(H_2O)_2]^{3+}$ (2.5 mmol) was added solid $K_2[Cr_2(nta)_2(OH)_2]\cdot 4H_2O$ (0.84 g, 1.25 mmol) with stirring. The mixture was adjusted to pH 7 by adding 2 mol dm^{-3} NaOH solution. This was stirred for 30 min at 60 °C (at 40 °C for **1a** and **1b**). The reaction solution was cooled to room temperature and loaded on a column (SP-Sephadex C-25 cation exchanger, 40 × 3 cm diameter). The column was washed with water and eluted by 0.2 mol dm^{-3} NaCl solution. After washing with water the column gave only one band. The collected eluate was evaporated and desalted by adding methanol and ethanol. Finally, the crude complex was precipitated by adding ethanol and acetone. Recrystallization was carried out from water by adding ethanol and acetone. The crystals were washed with acetone and diethyl

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Analytical data, colours and yields of the $[(nta)Cr(OH)_2ML_4]Cl{\cdot}nH_2O$ complexes

				Analysis (%)[b]		
	Complex	Colour	Yield (%)[a]	C	H	N
1a	$[(nta)Cr(OH)_2Co(NH_3)_4]Cl{\cdot}3H_2O$	Violet	65	14.70 (14.65)	5.35 (5.10)	14.25 (14.00)
2a	$[(nta)Cr(OH)_2Co(en)_2]Cl{\cdot}2.5H_2O$	Violet	75	22.50 (23.00)	5.50 (5.40)	13.10 (13.05)
3a	$[(nta)Cr(OH)_2Co(tn)_2]Cl{\cdot}1.5H_2O$	Violet	71	26.50 (27.30)	5.75 (5.60)	12.90 (13.15)
4a	$[(nta)Cr(OH)_2Co\{(R,R)chxn\}_2]Cl{\cdot}3H_2O$	Violet	70	33.40 (33.50)	5.90 (5.85)	10.85 (10.90)
5a	$[(nta)Cr(OH)_2Co(trien)]Cl{\cdot}2.5H_2O$	Violet	77	25.75 (25.70)	5.60 (5.50)	12.50 (12.40)
6a	$[(nta)Cr(OH)_2Co(amp)_2]Cl{\cdot}2H_2O$	Violet	73	34.80 (34.70)	4.55 (4.45)	11.30 (11.20)
7a	$[(nta)Cr(OH)_2Co(bipy)_2]Cl{\cdot}3H_2O$	Brown	81	42.50 (42.30)	4.10 (4.10)	9.55 (9.40)
8a	$[(nta)Cr(OH)_2Co(phen)_2]Cl{\cdot}2H_2O$	Brown	80	47.10 (47.10)	3.70 (3.65)	9.15 (9.15)
1b	$[(nta)Cr(OH)_2Cr(NH_3)_4]Cl{\cdot}2.5H_2O$	Violet	68	15.20 (15.40)	5.30 (5.20)	14.35 (14.75)
2b	$[(nta)Cr(OH)_2Cr(en)_2]Cl{\cdot}3.5H_2O$	Violet	75	22.05 (22.00)	5.75 (5.85)	12.85 (12.65)
3b	$[(nta)Cr(OH)_2Cr(tn)_2]Cl{\cdot}1.5H_2O$	Violet	79	26.85 (26.90)	5.80 (5.85)	13.05 (13.05)
4b	$[(nta)Cr(OH)_2Cr\{(R,R)chxn\}_2]Cl{\cdot}3.5H_2O$	Violet	72	33.10 (33.05)	6.65 (6.65)	10.70 (10.60)
5b	$[(nta)Cr(OH)_2Cr(trien)]Cl{\cdot}2H_2O$	Violet	70	26.50 (26.50)	5.55 (5.50)	12.90 (12.90)
6b	$[(nta)Cr(OH)_2Cr(amp)_2]Cl{\cdot}2.5H_2O$	Violet	75	34.70 (33.80)	4.70 (4.60)	11.25 (10.95)
7b	$[(nta)Cr(OH)_2Cr(bipy)_2]Cl{\cdot}5.5H_2O$	Green	79	39.80 (40.40)	4.55 (4.40)	9.05 (8.95)
8b	$[(nta)Cr(OH)_2Cr(phen)_2]Cl{\cdot}7H_2O$	Green	85	42.50 (42.30)	4.50 (4.45)	8.25 (8.10)

[a] Based on chromium. [b] Calculated values in parentheses.

ether and air dried. Analytical data, colours and yields of the dinuclear complexes are in Table 1.

Deuteriated Nitrilotriacetic Acid $[^2H_6]H_3nta$.—The deuteriation was carried out by the method of Koine *et al.*[8]

Crystal Structure Determinations.—Crystals suitable for X-ray analysis of $[(nta)Cr(OH)_2M(tn)_2]Cl{\cdot}1.5H_2O$ (M = Co **3a** or Cr **3b**) and $[(nta)Cr(OH)_2Cr(phen)_2]Cl{\cdot}7H_2O$ **8b** were obtained by slow evaporation of corresponding concentrated aqueous solutions. All measurements were made on a Rigaku AFC5R diffractometer with graphite-monochromated Mo-Kα radiation (λ 0.710 69 Å) and the calculations were performed using TEXSAN[22] in the Crystal Structural Center of the Faculty of Science, Osaka University. The unit-cell parameters were determined from 25 reflections in the range $20 < 2\theta < 30°$. Three standard reflections were monitored every 100 and showed good stability. The data collection was carried out at 23 ± 1 °C using the ω–2θ scan method. Direct methods followed by normal heavy-atom procedures were used for structure analysis. The positional and thermal parameters were refined by block-diagonal-matrix least squares. Absorption and decay corrections were applied. All hydrogen atoms except for those of complex **8b** were found in the Fourier-difference-maps and refined isotropically. Non-hydrogen atoms were refined with anisotropic thermal parameters except for the seven oxygen atoms of crystalline water [O(101)–O(107)] and Cl(2) in complex **8b** which were refined isotropically. The crystallographic data for the three complexes are listed in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Measurements.—Absorption and CD spectra were recorded on a Hitachi 330 spectrophotometer and a JASCO J-500 spectropolarimeter, respectively at room temperature in aqueous solutions. Magnetic susceptibilities were measured on powdered samples of Cr^{III}_2 complexes by using the Faraday method in the temperature range 5–300 K. Corrections for diamagnetism were applied by use of Pascal's constants as described before.[23] The pH measurements were carried out by using a Horiba F-7SS pH meter with a no. 6028 coupling electrode at 25 °C and the ionic strength was 0.1 mol dm^{-3} (KCl aqueous solution). Acid dissociation constants were estimated by the method of Mønsted and Mønsted[24] using pH measurements and absorption spectra. The uncertainty was estimated at ± 0.1 pK_a unit. Deuterium NMR spectra were measured using a JEOL GSX-270 FT spectrometer with C^2HCl_3 (δ 7.24) as external standard and downfield shifts defined as positive.

Results and Discussion

Preparation of the Complexes.—The analytical data shown in Table 1 do not exclude the possibility of hydroxoaqua-bridged aggregates with $[Cr(nta)(OH)(H_2O)]^-$ and $[ML(OH)(H_2O)]^{2+}$ as found in $[\{Cr(bipy)_2(OH)(H_2O)\}_2]^{4+}$.[25] Since they did not separate on SP-Sephadex column chromatography they are not aggregates but dihydroxo-bridged complexes. This is confirmed by their magnetic properties and crystal structure analysis as described later.

Column chromatography of the reaction solution and elution with 0.2 mol dm^{-3} NaCl aqueous solution gave only one band, $[(nta)Cr(OH)_2ML_4]^+$. No symmetrical dinuclear complexes like $[Cr_2(\mu\text{-}OH)_2L_4]^{4+}$ and $[Cr_2(nta)_2(\mu\text{-}OH)_2]^{2-}$ were detected. Specific formation of the unsymmetrical $[(nta)Cr(OH)_2ML_4]^+$ dinuclear complexes occurs in these reactions. These complexes except for **1a** are so stable that there is no change in UV/VIS spectra for several days in aqueous solutions. Complex **1a** decomposes relatively rapidly to the monomeric species.

The important factor in the formation of such stable unsymmetrical dinuclear complexes is supposed to be the intramolecular hydrogen bonds between non-bridging ligands.[4] However, even the amp, bipy and phen complexes having no hydrogen atoms for intramolecular hydrogen bonding form stable $[(nta)Cr(OH)_2ML_4]^+$. In addition, they are preferentially formed even in the present aqueous solutions in contrast with the solid-state formation of the heterometallic $[(en)_2Cr(\mu\text{-}OH)_2Co(en)_2]^{4+}$.[6] This is due to the facile formation of hydroxoaqua-bridged aggregates as intermediates by intermolecular hydrogen bonding and electrostatic attractions in aqueous solution at pH 7. The results suggest that the latter forces also play an important role in the formation of these types of dinuclear complexes.

The geometrical and absolute configurations of the ML_4 moieties in the precursor complexes are retained in the corresponding dinuclear complexes in view of the mild reaction conditions and simple reaction process: the bis(amp) complexes **6a** and **6b** are of the *trans*-(py) type, the trien ones (**5a** and **5b**) are of the *cis*-α type, and the bis[(R,R)chxn] ones **4a** and **4b** have the Δ absolute configuration.

Table 2 Crystallographic data for [(nta)Cr(OH)$_2$M(tn)$_2$]Cl·1.5H$_2$O (M = Co **3a** or Cr **3b**) and [(nta)Cr(OH)$_2$Cr(phen)$_2$]Cl·7H$_2$O **8b**

	3a	**3b**	**8b**
Formula	$C_{12}H_{31}ClCoCrN_5O_{9.5}$	$C_{12}H_{31}ClCr_2N_5O_{9.5}$	$C_{30}H_{38}ClCr_2N_5O_{15}$
M	543.79	536.85	848.10
Crystal colour	Violet	Violet	Dark green
Crystal size/mm	0.17 × 0.17 × 0.20	0.15 × 0.20 × 0.20	0.20 × 0.20 × 0.10
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	*C*2/*c*(no. 15)	*C*2/*c*(no. 15)	$P\bar{1}$(no. 2)
a/Å	16.384(2)	16.465(3)	15.79(1)
b/Å	14.660(2)	14.727(2)	18.04(1)
c/Å	18.874(2)	19.057(2)	12.77(1)
α/°			96.39(8)
β/°	110.77(1)	110.28(1)	102.23(7)
γ/°			102.83(7)
U/Å^3	4239(1)	4334.5(9)	3418(5)
Z	8	8	4
D_c/g cm^{-3}	1.676	1.645	1.648
μ(Mo-Kα)/cm^{-1}	14.60	11.56	7.76
2θ range/°	3–60	3–60	3–48
h, *k*, *l*	+23, +21, ±27	+23, +21, ±27	+18, ±20, ±14
No. of unique reflections	6438	6604	10 803
Transmission factors	0.90–1.00	0.92–1.00	0.91–1.00
No. of observed reflections [$F > 3\sigma(F)$]	4311	3946	5619
No. of variables	426	416	965
F(000)	2216	2232	1752
R^a	0.038	0.042	0.077
R'^b	0.048	0.049	0.100

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$; $w = 1/\sigma^2(F)$.

Crystal Structures of [(nta)Cr(OH)$_2$M(tn)$_2$]Cl·1.5H$_2$O (M = Co **3a** or Cr **3b**).—The atomic parameters and selected bond lengths and angles are listed in Tables 3 and 4, respectively.

A perspective view of the dinuclear complex cation of **3a** is shown in Fig. 1. The chromium(III) and cobalt(III) ions are in an approximately octahedral environment. The bridging unit Cr(OH)$_2$Co is almost flat. The Co–N(tn) bond lengths fall in the range 1.956(3)–1.994(3) Å (average 1.969 Å). These are almost the same as values for reported Co–tn complexes.[26] The Cr–N (nta) and Cr–O (nta) bond lengths are 2.060(3) and 1.975 Å (average), respectively. The bond lengths and angles in the Cr(nta) moiety are almost the same those of K$_2$[Cr$_2$(nta)$_2$(μ-OH)(μ-O$_2$CMe)]·4H$_2$O[27] and Cs$_2$[Cr$_2$(nta)$_2$(μ-OH)$_2$]·4H$_2$O.[28] The Cr ··· Co distance is 2.9493(7) Å.

The (nta)Cr–O(8)H distance [1.913(2) Å] *trans* to the nta amine nitrogen atom is significantly shorter (by 0.054 Å) than the (nta)Cr–O(7)H distance [1.967(2) Å] *cis* to one as shown in Table 4. This difference is not obviously found in the symmetrical di-μ-OH complex Cs$_2$[Cr$_2$(nta)$_2$(OH)$_2$]·4H$_2$O.[28] Similar differences in Cr–O bonds between *cis* and *trans* positions of the tertiary amine nitrogen atoms are found in analogous nta monomeric complexes [CrL(Him)$_2$] [HL = (*S*)-*N*,*N*-bis(carboxymethyl)-L-leucine or -L-phenylalanine, Him = imidazole] by Bocarsly *et al.*[29] Contrary to the (nta)Cr–OH bonds, the (tn)$_2$Co–OH bond lengths showed little differences [Co–O(7)H 1.935(2) and Co–O(8)H 1.921(2) Å], which are comparable with Co–OH (1.93 Å) in [Co$_2$(OH)$_2$(en)$_4$][NO$_3$]$_4$.[30]

Chelate ring 1 in the propane-1,3-diamine ligand has a chair conformation and the disordered rings 2A and 2B with equal occupancies have skewboat conformations. The overall conformation of the Cr(tn)$_2$ moiety is Δ*a-chair*λ(δ), where *a-chair* is defined by Jurnak and Raymond.[31]

Intramolecular hydrogen bonds are expected between the amine protons of the propane-1,3-diamine ligands and co-ordinated oxygen atoms of nta as observed in [(edda)Co(μ-OH)$_2$Co(en)(glyO)]$^{+}$[4c] and [(H$_2$O)(tacn)Cr(μ-OH)$_2$Cr(tacn)(H$_2$O)]$^{4+}$[32] (H$_2$edda = ethane-1,2-diamine-*N*,*N'*-diacetic acid, glyO = glycinate, tacn = 1,4,7-triazacyclononane). The distances N(2) ··· O(3) and N(5) ··· O(5) are 3.192(4) and 2.967(4) Å, respectively. Since the N ··· O distances are in the range 2.57–3.24 Å,[33] there are two intramolecular hydrogen bonds between the tn and nta ligands. The amine proton of chelate ring 1 forms a hydrogen bond with the co-ordinated nta oxygen atom in a neighbouring molecule [N(3) ··· O(2') 2.860(4) Å]. Since two hydrogen bonds (intra- and inter-molecular) exist in chelate ring 1, the chair conformation of this ring could be fixed. However, since such an intramolecular hydrogen bond does not exist in ring 2, the relevant conformation is not fixed and is disordered. The hydrogen atoms of the bridging OH groups are bonded to the oxygen atom of water of crystallization [O(8) ··· O(9) 2.723(3) Å] and to the Cl$^-$ counter anion [O(8) ··· Cl 3.171(2) Å].

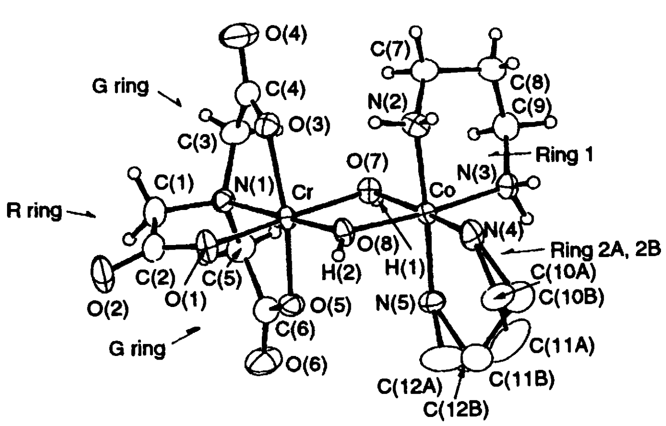

Fig. 1 An ORTEP drawing of [(nta)Cr(OH)$_2$Co(tn)$_2$]$^+$ **3a** with thermal ellipsoids drawn at the 50% probability level

Complex **3b** is isostructural to **3a** as shown in Fig. 2. The characteristics of the bond lengths and angles of the Cr(tn)$_2$ moiety are the same as those for previously reported Cr–tn complexes.[34] The three carbon atoms C(10), C(11) and C(12) look fairly anisotropic and ring 2 may be disordered in view of the relation to **3a**, although this has not been modelled. The Cr ··· Cr distance is 2.9816(9) Å.

Table 3 Positional parameters for $[(nta)Cr(OH)_2M(tn)_2]Cl\cdot1.5H_2O$ (M = Co **3a** or Cr **3b**)

	3a			**3b**		
Atom	*X/a*	*Y/b*	*Z/c*	*X/a*	*Y/b*	*Z/c*
M	0.298 53(2)	0.667 86(3)	0.362 13(2)	0.299 50(3)	0.667 25(4)	0.363 65(3)
Cr	0.259 72(3)	0.549 68(3)	0.472 65(3)	0.261 65(3)	0.548 00(3)	0.474 98(3)
O(1)	0.313 4(1)	0.530 4(2)	0.582 3(1)	0.313 6(2)	0.529 5(2)	0.582 7(1)
O(2)	0.317 5(2)	0.434 4(2)	0.674 1(1)	0.315 7(2)	0.435 6(2)	0.674 1(2)
O(3)	0.166 3(1)	0.627 2(1)	0.486 3(1)	0.168 3(2)	0.624 5(2)	0.488 2(1)
O(4)	0.023 9(2)	0.628 8(2)	0.463 4(2)	0.026 1(2)	0.625 4(2)	0.464 7(2)
O(5)	0.326 9(1)	0.445 5(1)	0.456 2(1)	0.329 6(2)	0.445 3(2)	0.458 6(1)
O(6)	0.319 8(2)	0.297 1(2)	0.432 9(2)	0.324 8(2)	0.297 5(2)	0.436 2(2)
O(7)	0.212 2(1)	0.578 6(1)	0.363 8(1)	0.214 4(1)	0.575 0(2)	0.366 8(1)
O(8)	0.336 9(1)	0.646 1(1)	0.469 3(1)	0.338 3(1)	0.644 7(2)	0.471 1(1)
O(9)	−0.003 8(2)	0.817 4(2)	0.438 6(2)	−0.001 3(2)	0.812 8(2)	0.439 0(2)
O(10)	1.0	0.492 3(8)	0.75	1.0	0.484 2(7)	0.75
N(1)	0.174 2(2)	0.448 7(2)	0.477 2(1)	0.177 5(2)	0.447 3(2)	0.479 5(2)
N(2)	0.222 6(2)	0.762 5(2)	0.379 3(1)	0.218 0(2)	0.766 4(2)	0.379 5(2)
N(3)	0.248 8(2)	0.692 8(2)	0.253 3(1)	0.247 2(2)	0.695 6(2)	0.250 0(2)
N(4)	0.389 3(2)	0.760 7(2)	0.377 5(2)	0.395 6(2)	0.764 0(2)	0.377 8(2)
N(5)	0.368 9(2)	0.564 1(2)	0.346 3(2)	0.375 3(2)	0.561 6(2)	0.344 8(2)
C(1)	0.195 4(2)	0.426 7(2)	0.559 5(2)	0.196 8(2)	0.425 9(2)	0.560 4(2)
C(2)	0.282 7(2)	0.465 2(2)	0.610 2(2)	0.282 4(2)	0.465 5(2)	0.610 6(2)
C(3)	0.086 8(2)	0.489 9(2)	0.442 7(2)	0.090 2(2)	0.486 9(2)	0.445 6(2)
C(4)	0.090 9(2)	0.590 0(2)	0.466 1(2)	0.093 5(2)	0.586 7(2)	0.467 8(2)
C(5)	0.191 3(2)	0.370 2(2)	0.435 1(2)	0.195 6(2)	0.368 7(2)	0.438 3(2)
C(6)	0.286 1(2)	0.368 4(2)	0.441 9(2)	0.290 5(2)	0.368 1(2)	0.445 1(2)
C(7)	0.129 2(2)	0.768 4(2)	0.331 8(2)	0.125 6(2)	0.767 9(2)	0.330 2(2)
C(8)	0.116 2(2)	0.775 2(3)	0.249 0(2)	0.116 4(2)	0.778 7(2)	0.249 1(2)
C(9)	0.152 8(2)	0.696 9(2)	0.217 8(2)	0.151 1(2)	0.700 2(3)	0.217 3(2)
C(10A)*	0.476 4(4)	0.748 6(5)	0.376 3(4)	0.477 0(4)	0.744 9(4)	0.363 9(5)
C(10B)*	0.460 5(5)	0.734 0(6)	0.340 4(5)			
C(11A)*	0.486 0(6)	0.665 9(7)	0.336 2(6)	0.503 0(5)	0.657 7(5)	0.359 8(6)
C(11B)*	0.510 7(4)	0.648 5(5)	0.379 1(4)			
C(12A)*	0.467 2(5)	0.573 9(6)	0.374 9(6)	0.467 0(3)	0.572 8(4)	0.351 3(5)
C(12B)*	0.456 7(5)	0.571 6(5)	0.338 1(5)			
Cl	0.819 60(8)	0.577 12(7)	0.759 65(7)	0.822 18(9)	0.578 19(9)	0.755 64(7)

* The population parameter is 0.5 for complex **3a**.

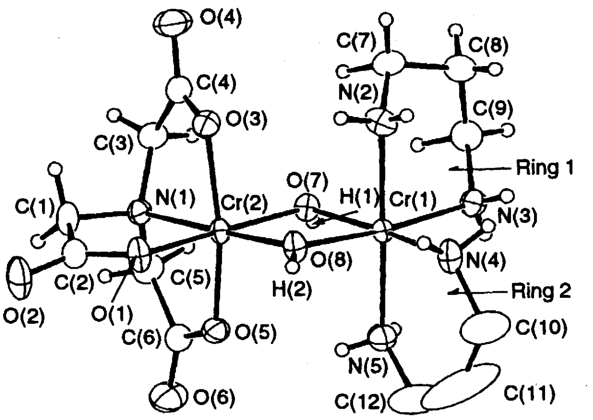

Fig. 2 An ORTEP drawing of $[(nta)Cr(OH)_2Cr(tn)_2]^+$ **3b** with thermal ellipsoids drawn at the 50% probability level

Crystal Structure of $[(nta)Cr(OH)_2Cr(phen)_2]Cl\cdot7H_2O$ **8b**.—Selected atomic parameters, bond lengths and angles are listed in Tables 5 and 6, respectively. Two crystallographically independent but similar complex cations (molecules 1 and 2 in Tables 5 and 6) are contained in an asymmetric unit. Each of the chromium(III) ions is in an approximately octahedral environment. The bridging units are almost flat. Fig. 3 shows a perspective view of molecule 1.

The average Cr–N (phen) bond length is 2.06 Å. This is almost the same as in $[Cr_2(\mu\text{-}OH)_2(phen)_4]X_4$ (X = Cl^{35} or I^{36}). The average Cr–N (nta) and Cr–O (nta) bond lengths are 2.05 and 1.96 Å, respectively. The average Cr ··· Cr distance is 2.981 Å.

The difference in the (nta)Cr–OH bonds between those *trans* and *cis* to the nta nitrogen atom is 0.02 Å (average) in complex **8b** similarly to those in **3a** and **3b**. The bond *trans* to the nta nitrogen atom is significantly longer (about 0.03 Å) than the corresponding bonds in the aliphatic diamine complexes **3a** and **3b**. The differences in the Cr–O bonds for **3a** or **3b** and **8b** may be influenced by the extent of the π-bond interaction in the L_4M–OH bond as examined below in the context of the acid strength of the bridging hydroxide. It is noticeable that the (nta)Cr–OH bonds *trans* to the nta nitrogen atom vary with the extent of this π-bond interaction but that those *cis* are almost unaltered.

The CrL_4–OH bond lengths of complex **8b** are significantly shorter (0.04 Å) than those of **3b**. A similar situation is encountered for $[Cr_2(OH)_2(phen)_4]^{4+}$ [35,36] (1.92 Å) and $[Cr_2(OH)_2(en)_4]^{4+}$ [37] (1.95 Å). This difference is due to the π-bond interaction. From these structural characteristics of the unsymmetrical dinuclear complexes, it is seen that the structural parameters of the bridging moiety around the Cr(nta) and CrL_4 are almost retained in the corresponding symmetrical dinuclear complexes.

Magnetic Properties.—For homometallic Cr^{III}_2 complexes the temperature-dependent magnetic susceptibility data were fitted by the van Vleck equation (1) defined by the exchange

$$\chi = \frac{Ng^2\beta^2}{kT}\cdot\frac{2\exp(2J/kT) + 10\exp(6J/kT) + 8\exp(12J/kT)}{1 + 3\exp(2J/kT) + 5\exp(6J/kT) + 7\exp(12J/kT)} \quad (1)$$

Table 4 Selected bond lengths (Å), angles (°) and torsion angles (°) for $[(nta)Cr(OH)_2M(tn)_2]Cl{\cdot}1.5H_2O$(M = Co **3a** or Cr **3b**)

	3a	**3b**		**3a**	
M–N(2)	1.965(3)	2.075(3)	Cr–N(1)	2.060(3)	2.052(3)
M–N(3)	1.956(3)	2.077(3)	Cr–O(1)	1.960(2)	1.951(2)
M–N(4)	1.961(3)	2.076(3)	Cr–O(3)	1.995(3)	1.991(3)
M–N(5)	1.994(3)	2.102(3)	Cr–O(5)	1.971(2)	1.970(3)
M–O(7)	1.935(2)	1.967(3)	Cr–O(7)	1.967(2)	1.976(2)
M–O(8)	1.921(2)	1.951(2)	Cr–O(8)	1.913(2)	1.921(3)
O(7)–M–O(8)	80.69(9)	80.63(9)	O(1)–Cr–O(7)	174.97(9)	175.7(1)
O(7)–M–N(2)	88.1(1)	88.8(1)	O(1)–Cr–O(8)	94.97(9)	95.1(1)
O(7)–M–N(3)	96.3(1)	97.3(1)	O(1)–Cr–N(1)	84.8(1)	84.9(1)
O(7)–M–N(4)	170.9(1)	171.4(1)	O(1)–Cr–O(3)	91.4(1)	91.3(1)
O(7)–M–N(5)	87.2(1)	88.0(1)	O(1)–Cr–O(5)	89.3(1)	89.6(1)
O(8)–M–N(2)	86.2(1)	87.7(1)	O(3)–Cr–O(5)	163.52(9)	163.8(1)
O(8)–M–N(3)	174.7(1)	174.5(1)	O(3)–Cr–O(7)	88.52(9)	88.7(1)
O(8)–M–N(4)	90.6(1)	91.4(1)	O(3)–Cr–O(8)	97.46(9)	97.6(1)
O(8)–M–N(5)	92.3(1)	93.2(1)	O(3)–Cr–N(1)	80.8(1)	80.9(1)
N(2)–M–N(3)	89.4(1)	87.4(1)	O(5)–Cr–O(7)	92.23(9)	91.6(1)
N(2)–M–N(4)	88.6(1)	90.0(1)	O(5)–Cr–O(8)	98.9(1)	98.4(1)
N(2)–M–N(5)	175.2(1)	176.4(1)	O(5)–Cr–N(1)	82.9(1)	83.2(1)
N(3)–M–N(4)	92.2(1)	91.1(1)	O(7)–Cr–N(1)	100.11(9)	99.3(1)
N(3)–M–N(5)	91.9(1)	91.6(1)	O(8)–Cr–N(1)	178.2(1)	178.4(1)
N(4)–M–N(5)	95.9(1)	93.4(1)	M–O(7)–Cr	98.20(8)	98.27(9)
O(7)–Cr–O(8)	80.07(8)	80.1(1)	M–O(8)–Cr	100.61(8)	100.72(9)
Cr–N(1)–C(1)–C(2)	−14.1(3)	−13.9(4) (R ring)*	Cr–N(1)–C(5)–C(6)	30.7(3)	30.4(3) (G_2 ring)*
Cr–N(1)–C(3)–C(4)	−37.6(3)	−36.8(4) (G_1 ring)*			

* R and G rings are defined in the text.

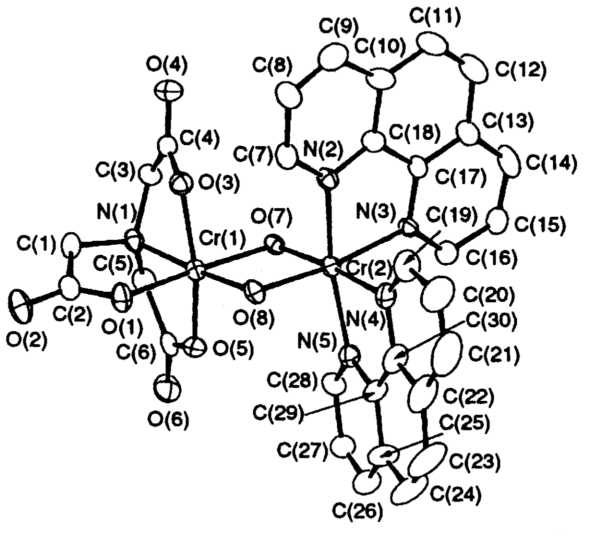

Fig. 3 An ORTEP drawing of $[(nta)Cr(OH)_2Cr(phen)_2]^+$ **8b** (molecule 1) with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity

Hamiltonian $H = -2J(S_1{\cdot}S_2)$ where $2J$ is the spin-exchange coupling constant in cm^{-1}. The coupling constants were derived from non-linear least-squares fits of χ *vs.* T. The best fit of the susceptibility data reveals that the homodinuclear complexes give antiferromagnetic couplings. The data are listed in Table 7. These $2J$ values [−17.2(2) to −31.4(3) cm^{-1}] are in the range of those found for other dinuclear di-μ-hydroxochromium(III) complexes.[38]

The structure analysis for complex **3b** described above reveals that the angle θ, between the Cr_2O_2 plane and the hydrogen atom of the bridging hydroxide ligand, is 22.7° (average). From the Glerup–Hodgson–Pedersen (GHP) model,[38] the coupling constant ($2J$) for **3b** is estimated to be −23.1 cm^{-1} by using the structural parameters (average) $r = 1.954$ Å, $\theta = 22.7°$ and $\varphi = 99.5°$ where r is the Cr–OH bond length and φ is the Cr–O–Cr bond angle. This differs from the observed value of −17.2(2) cm^{-1}. The disagreement arises from the different Cr–O lengths [1.976(2)–1.921(3) Å] in Table 4, since the calculated $2J$ value is sensitive to small changes in r as Hodgson *et al.*[39] reported in the case of $[Cr_2(\mu\text{-}OH)_2(tpma)_2][ClO_4]_4{\cdot}4H_2O$ [tpma = tris(2-pyridylmethyl)amine].

Acid Strength of Bridging Hydroxide.—The colours of aqueous solutions of complexes **1a**–**5a** and **1b**–**5b** instantaneously change from red to blue by adding sodium hydroxide solution. The reactions are reversible and presumably due to deprotonation of the hydroxo bridges giving μ-hydroxo-μ-oxo complexes as observed for $[Cr_2(\mu\text{-}OH)_2(NH_3)_8]^{4+}$,[40] $[Cr_2(\mu\text{-}OH)_2(en)_4]^{4+}$,[41] $[Cr_2(\mu\text{-}OH)(\mu\text{-}SO_4)(en)_2]^{3+}$,[42] and $[Cr_2(\mu\text{-}OH)(\mu\text{-}O_2CMe)(en)_4]^{4+}$.[43] The pK_{a1} values were found to be about 12 for the aliphatic diamine [NH_3, en, tn, (*R*, *R*)chxn and trien] complexes, 11.0 (**6a**) and 9.8 (**6b**) for the amp ones and about 9 (9.3 for **7a**, 9.0 for **7b**, 9.4 for **8a** and 9.2 for **8b**) for the bipy and phen ones. Similar values were found for the symmetrical $[Cr_2(\mu\text{-}OH)_2L_8]^{4+}$ dinuclear complexes.[1] This trend in the acid strength depends on the $M{-}L_4$ bond character. As the M–N bond is strengthened by the π-acceptor interaction, the M–O bond is enhanced by the π-donor interaction simultaneously as a push-pull action.

Absorption and CD Spectra.—The UV/VIS absorption spectra of four complexes (**2a**, **8a**, **2b** and **8b**) are shown in Fig. 4. The dinuclear complexes give broad absorption bands because of the two different chromophores $CrNO_5$ and MN_4O_2 (M = Cr^{III} or Co^{III}) in the first spin-allowed d–d region. Split components in this region were observed for some complexes. Each maximum is assigned to the $(nta)Cr(OH)_2$ or $(HO)_2ML_4$ chromophores (Table 7). A broad band occurred at *ca.* 300 nm for the $Cr^{III}Co^{III}$ aliphatic diamine complexes [Fig. 4(*b*)] as for the di-μ-hydroxo-dicobalt(III) complexes. It is assigned to the charge-transfer (c.t.) transition of the Co–OH moiety for $Co(\mu\text{-}OH)_2Co$ type complexes.[44] The absorption intensities of c.t. transitions for the $Cr^{III}Co^{III}$ complexes are about one-fourth less than those of $Co^{III}{}_2$ ones.[4] An inflection at 285 nm appears for the $Cr^{III}{}_2$ aliphatic diamine complexes. Complex **4b** exhibits

Table 5 Positional parameters for $[(nta)Cr(OH)_2Cr(phen)_2]Cl\cdot7H_2O$ **8b**

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Cr(1)	0.6867(1)	0.1863(1)	0.7084(1)	O(14)	0.9163(6)	−0.2622(5)	0.6605(8)
Cr(2)	0.7351(1)	0.0724(1)	0.8454(2)	O(15)	0.6780(6)	−0.2812(5)	0.2551(7)
O(1)	0.7032(6)	0.2112(5)	0.5687(7)	O(16)	0.7142(8)	−0.1919(7)	0.150(1)
O(2)	0.6773(7)	0.2900(6)	0.4531(8)	O(17)	0.8005(5)	−0.3691(5)	0.3334(7)
O(3)	0.5648(6)	0.1210(5)	0.6388(7)	O(18)	0.6457(5)	−0.4202(5)	0.3434(7)
O(4)	0.4252(6)	0.1099(6)	0.6505(8)	N(11)	0.7973(7)	−0.2045(6)	0.429(1)
O(5)	0.7878(6)	0.2748(5)	0.7815(7)	N(12)	0.7661(6)	−0.5055(5)	0.4378(8)
O(6)	0.8236(7)	0.3963(5)	0.8640(8)	N(13)	0.8218(6)	−0.5261(5)	0.2591(8)
O(7)	0.6756(5)	0.1544(4)	0.8485(6)	N(14)	0.6263(7)	−0.5278(6)	0.2318(8)
O(8)	0.7467(6)	0.1026(5)	0.7084(6)	N(15)	0.6868(7)	−0.4599(6)	0.1304(8)
N(1)	0.6148(7)	0.2682(5)	0.7054(8)	C(51)	0.745(1)	−0.1603(8)	0.483(1)
N(2)	0.6173(7)	−0.0093(6)	0.7777(8)	C(52)	0.666(1)	−0.2099(9)	0.511(1)
N(3)	0.7051(7)	0.0385(6)	0.9859(8)	C(53)	0.8806(8)	−0.2068(7)	0.503(1)
N(4)	0.8062(7)	−0.0110(6)	0.8316(9)	C(54)	0.8606(8)	−0.2676(7)	0.574(1)
N(5)	0.8632(7)	0.1377(6)	0.9221(9)	C(55)	0.808(1)	−0.1794(8)	0.326(1)
C(1)	0.602(1)	0.2890(8)	0.594(1)	C(56)	0.726(1)	−0.218(1)	0.235(1)
C(2)	0.667(1)	0.2640(8)	0.533(1)	C(57)	0.7370(9)	−0.4938(8)	0.527(1)
C(3)	0.5283(9)	0.2295(8)	0.724(1)	C(58)	0.775(1)	−0.5151(8)	0.623(1)
C(4)	0.5018(8)	0.1469(8)	0.666(1)	C(59)	0.843(1)	−0.5494(8)	0.628(1)
C(5)	0.667(1)	0.3325(8)	0.790(1)	C(60)	0.8748(9)	−0.5647(8)	0.537(1)
C(6)	0.768(1)	0.3371(7)	0.814(1)	C(61)	0.947(1)	−0.6001(8)	0.533(1)
C(7)	0.575(1)	−0.0316(7)	0.673(1)	C(62)	0.975(1)	−0.6109(9)	0.442(1)
C(8)	0.493(1)	−0.0865(8)	0.638(1)	C(63)	0.9348(9)	−0.5874(7)	0.345(1)
C(9)	0.453(1)	−0.1170(8)	0.714(1)	C(64)	0.960(1)	−0.5992(8)	0.247(1)
C(10)	0.4968(9)	−0.0974(7)	0.828(1)	C(65)	0.917(1)	−0.5279(9)	0.158(1)
C(11)	0.464(1)	−0.1278(8)	0.916(1)	C(66)	0.8460(8)	−0.5381(8)	0.167(1)
C(12)	0.509(1)	−0.1050(8)	1.019(1)	C(67)	0.8638(8)	−0.5518(7)	0.346(1)
C(13)	0.596(1)	−0.0476(7)	1.048(1)	C(68)	0.8340(8)	−0.5400(7)	0.443(1)
C(14)	0.645(1)	−0.020(1)	1.156(1)	C(69)	0.5941(9)	−0.6255(8)	0.287(1)
C(15)	0.721(1)	0.0367(9)	1.174(1)	C(70)	0.525(1)	−0.6907(9)	0.238(2)
C(16)	0.7495(9)	0.0660(8)	1.089(1)	C(71)	0.490(1)	−0.6987(8)	0.126(2)
C(17)	0.6269(8)	−0.0168(7)	0.965(1)	C(72)	0.5186(9)	−0.6454(8)	0.068(1)
C(18)	0.5794(8)	−0.0411(7)	0.853(1)	C(73)	0.485(1)	−0.648(1)	−0.047(1)
C(19)	0.779(1)	−0.0844(7)	0.794(1)	C(74)	0.517(1)	−0.591(1)	−0.100(1)
C(20)	0.836(1)	−0.1305(9)	0.780(1)	C(75)	0.586(1)	−0.527(1)	−0.043(1)
C(21)	0.922(1)	−0.101(1)	0.805(1)	C(76)	0.623(1)	−0.465(1)	−0.090(1)
C(22)	0.962(1)	−0.019(1)	0.843(1)	C(77)	0.689(1)	−0.405(1)	−0.029(1)
C(23)	1.056(1)	0.023(1)	0.872(2)	C(78)	0.721(1)	−0.402(1)	0.083(1)
C(24)	1.084(1)	0.098(1)	0.919(1)	C(79)	0.6220(9)	−0.5213(8)	0.070(1)
C(25)	1.021(1)	0.139(1)	0.938(1)	C(80)	0.5893(8)	−0.5812(8)	0.126(1)
C(26)	1.045(1)	0.2141(9)	0.989(1)	Cl(1)	0.7070(3)	0.2768(2)	0.0481(3)
C(27)	0.979(1)	0.2503(8)	1.009(1)	Cl(2)	0.4677(5)	0.5121(4)	0.3794(6)
C(28)	0.8897(9)	0.2114(7)	0.972(1)	O(101)	0.0488(5)	0.2900(4)	0.7423(6)
C(29)	0.9271(8)	0.1006(8)	0.907(1)	O(102)	0.1233(7)	0.4433(6)	0.0805(9)
C(30)	0.897(1)	0.0219(8)	0.860(1)	O(103)	0.1858(7)	0.3394(6)	0.2052(9)
Cr(3)	0.7253(1)	−0.4724(1)	0.2911(2)	O(104)	1.0009(8)	0.4002(7)	0.882(1)
Cr(4)	0.7201(1)	−0.3151(1)	0.3892(2)	O(105)	0.7647(8)	0.2459(7)	0.288(1)
O(11)	0.6371(6)	−0.2776(5)	0.4588(8)	O(106)	0.9072(9)	0.1790(7)	0.293(1)
O(12)	0.6321(8)	−0.1834(7)	0.580(1)	O(107)	0.705(1)	0.023(1)	0.474(1)
O(13)	0.7873(5)	−0.3189(5)	0.5388(7)				

a CD maximum at 285 nm. These absorption bands are considered to be characteristic of the Cr^{III}_2 complexes.

^2H *NMR Spectra and Stereochemistry*.—The ^2H NMR signals of $[([^2H_6]nta)Cr(OH)_2ML_4]^+$ (M = Cr or Co) exhibited large contact shifts as is seen in Fig. 5 and Table 8. The dinuclear complexes with the aliphatic diamines (**1a**–**5a** and **1b**–**5b**) show similar spectral patterns to each other and to those of reported Cr–nta complexes.[8,27] The tetradentate nta^{3-} ligand has two equivalent acetate chelate rings (G rings) each with inequivalent methylene deuterons and one acetate chelate ring (R ring) with equivalent methylene ones.[8,27] According to the signal assignment made for Cr–nta[8,27] and $[Cr(edta)]^-$ (H_4edta = ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid) complexes,[45] the lower (δ −4.4 to −10.6) and higher (δ −27.2 to −34.6) field signals are assigned to the inequivalent methylene deuterons in the G rings, and the middle (δ −9.1 to −23.6) ones to the equivalent methylene protons in the R ring (Table 8). The aromatic diamine complexes give different NMR patterns from those of the aliphatic diamine complexes. There is similarity in ^2H NMR behaviour among the aromatic amine complexes. Since the homometallic Cr^{III}_2 complexes with both aliphatic and aromatic diamine ligands give similar spectral patterns to those of corresponding heterometallic $Cr^{III}Co^{III}$ ones, the ^2H NMR spectra are most influenced by the L_4 ligands and insignificantly by the metal ion M in the ML_4 moieties.

The isotropic contact shifts for the deuteriated acetate methylenes in the edta-like chromium(III) complexes was related to a glycinate-like chelate-ring conformation according to relationship between the chemical shifts and the torsion angles in the Cr–N–C–C(O) fragment of the acetato(glycinato) rings (Karplus-like or $\cos^2\theta$ relation).[45] The $\cos^2\theta$ relation gives equations (2) and (3) for the A(axial) and B(equatorial) vicinal

$$\delta_A = C\cos^2\theta \qquad (2)$$

$$\delta_B = C\cos^2(\theta + 120°) \qquad (3)$$

Table 6 Selected bond lengths (Å), angles(°) and torsion angles(°) for [(nta)Cr(OH)$_2$Cr(phen)$_2$]$^+$ **8b**

Molecule 1		Molecule 2		Molecule 1		Molecule 2	
Cr(1)–O(1)	1.94(1)	Cr(4)–O(11)	1.93(1)	Cr(2)–N(3)	2.07(1)	Cr(3)–N(13)	2.06(1)
Cr(1)–O(3)	1.979(8)	Cr(4)–O(13)	1.996(9)	Cr(2)–N(4)	2.08(1)	Cr(3)–N(14)	2.058(9)
Cr(1)–O(5)	1.969(8)	Cr(4)–O(15)	1.918(9)	Cr(2)–N(5)	2.07(1)	Cr(3)–N(15)	2.07(1)
Cr(1)–O(8)	1.95(1)	Cr(4)–O(18)	1.947(8)	N(1)–C(1)	1.49(2)	N(11)–C(51)	1.48(2)
Cr(1)–O(7)	1.970(9)	Cr(4)–O(17)	1.96(1)	N(1)–C(3)	1.47(2)	N(11)–C(53)	1.46(2)
Cr(1)–N(1)	2.05(1)	Cr(4)–N(11)	2.04(1)	N(1)–C(5)	1.45(1)	N(11)–C(55)	1.46(2)
Cr(2)–O(7)	1.92(1)	Cr(3)–O(17)	1.923(8)	C(1)–C(2)	1.52(2)	C(51)–C(52)	1.50(2)
Cr(2)–O(8)	1.92(1)	Cr(3)–O(18)	1.91(1)	C(3)–C(4)	1.51(2)	C(53)–C(54)	1.52(2)
Cr(2)–N(2)	2.05(1)	Cr(3)–N(12)	2.05(1)	C(5)–C(6)	1.54(2)	C(55)–C(56)	1.51(2)
O(1)–Cr(1)–O(7)	175.2(4)	O(11)–Cr(4)–O(17)	169.3(4)	O(7)–Cr(2)–N(4)	174.3(4)	O(17)–Cr(3)–N(14)	168.8(4)
O(1)–Cr(1)–O(5)	89.4(4)	O(11)–Cr(4)–N(15)	93.8(4)	O(8)–Cr(2)–N(2)	93.5(4)	O(18)–Cr(3)–N(12)	92.5(4)
O(1)–Cr(1)–O(8)	95.7(4)	O(11)–Cr(4)–O(18)	95.3(4)	O(8)–Cr(2)–N(4)	93.4(4)	O(18)–Cr(3)–N(14)	92.8(4)
O(3)–Cr(1)–O(7)	89.(4)	O(13)–Cr(4)–O(17)	87.8(4)	N(2)–Cr(2)–N(3)	80.8(4)	N(12)–Cr(3)–N(13)	79.6(4)
O(3)–Cr(1)–N(1)	79.7(4)	O(13)–Cr(4)–N(11)	80.8(4)	N(2)–Cr(2)–N(5)	169.3(4)	N(12)–Cr(3)–N(15)	168.6(4)
O(5)–Cr(1)–O(8)	100.9(4)	O(15)–Cr(4)–O(18)	95.0(4)	N(3)–Cr(2)–N(5)	94.8(4)	N(13)–Cr(3)–N(15)	91.5(4)
O(7)–Cr(1)–O(8)	79.5(4)	O(17)–Cr(4)–O(18)	77.6(4)	O(7)–Cr(2)–O(8)	81.4(4)	O(17)–Cr(3)–O(18)	79.4(4)
O(8)–Cr(1)–N(1)	175.8(3)	O(18)–Cr(4)–N(11)	177.1(4)	O(7)–Cr(2)–N(3)	94.2(4)	O(17)–Cr(3)–N(13)	97.5(4)
O(1)–Cr(1)–O(3)	90.8(4)	O(11)–Cr(4)–O(13)	85.9(4)	O(7)–Cr(2)–N(5)	97.6(4)	O(17)–Cr(3)–N(15)	93.2(4)
O(1)–Cr(1)–N(1)	85.3(4)	O(11)–Cr(4)–N(11)	86.0(4)	O(8)–Cr(2)–N(3)	172.6(4)	O(18)–Cr(3)–N(13)	171.3(4)
O(3)–Cr(1)–O(5)	162.8(4)	O(13)–Cr(4)–O(15)	163.1(4)	O(8)–Cr(2)–N(5)	91.6(4)	O(18)–Cr(3)–N(15)	96.8(4)
O(3)–Cr(1)–O(8)	96.2(4)	O(13)–Cr(4)–O(18)	95.3(4)	N(2)–Cr(2)–N(3)	80.8(4)	N(12)–Cr(3)–N(14)	93.3(4)
O(5)–Cr(1)–O(7)	91.3(4)	O(15)–Cr(4)–O(17)	94.7(4)	N(2)–Cr(2)–N(5)	169.3(4)	N(13)–Cr(4)–N(14)	91.3(4)
O(5)–Cr(1)–N(1)	83.1(4)	O(15)–Cr(4)–N(11)	82.3(4)	N(3)–Cr(2)–N(5)	94.8(4)	N(14)–Cr(3)–N(15)	79.7(4)
O(7)–Cr(1)–N(1)	99.6(4)	O(17)–Cr(4)–N(11)	101.5(4)	Cr(1)–O(7)–Cr(2)	99.3(4)	Cr(3)–O(17)–Cr(4)	101.0(4)
O(7)–Cr(2)–N(2)	92.5(4)	O(17)–Cr(3)–N(12)	95.0(4)	Cr(1)–O(8)–Cr(2)	99.9(4)	Cr(3)–O(18)–Cr(4)	101.9(4)

Cr(1)–N(1)–C(1)–C(2)	−17(1)	Cr(4)–N(11)–C(11)–C(12)	11(1) (R ring)*	Cr(1)–N(1)–C(5)–C(6)	27(1)
Cr(1)–N(1)–C(3)–C(4)	−37(1)	Cr(4)–N(11)–C(13)–C(14)	−35(2) (G$_1$ ring)*	Cr(4)–N(11)–C(15)–C(16)	31(2) (G$_2$ ring)*

* R and G rings are defined in the text.

Table 7 Absorption and CD spectral data for the visible region and magnetic parameters for dinuclear complexes

	λ/nm (ε/dm^3 mol^{-1} cm^{-1})[a]				Magnetic parameters[b]	
	σ_I					
Complex	(nta)Cr(OH)$_2$	LM(OH)$_2$	σ_{II}		g	$2J$/cm^{-1}
1a		545 (146)	380 (223)			
2a	600 (sh) (100)	510 (161)	380 (sh) (210)			
3a		531 (125)	390 (sh) (170)			
4a[c]		516 (313)	380 (sh) (380)			
5a		508 (318)	380 (sh) (360)			
6a		510 (180)	370 (sh) (360)			
7a	580 (sh) (90)	485 (129)				
8a		512 (133)				
1b		555 (91)	401 (118)	285 (70)[d]	2.01(1)	−19.5(1)
2b	585 (sh) (90)	520 (111)	398 (131)	285 (70)[d]	2.01(2)	−19.8(3)
3b	580 (87)	522 (93)	402 (123)	285 (75)[d]	2.01(1)	−17.2(2)
4b[e]	590 (sh) (90)	520 (119)	398 (133)	285 (75)[d]	1.98(2)	−25.5(3)
5b		555 (148)	400 (140)	285 (75)[d]	1.96(1)	−21.5(4)
6b		540 (128)	402 (141)		1.99(2)	−20.5(2)
7b		565 (96)			2.02(1)	−31.4(3)
8b		565 (97)			1.98(1)	−22.6(2)

[a] In water. [b] Chloride salts; $2J$ refers to the coupling constant determined from the observed susceptibility data. Values in parentheses are standard deviations in the least significant figure. [c] CD maxima [λ/nm (Δε/dm^3 mol^{-1} cm^{-1})]: 538 (0.900), 496 (−1.024) and 370 (0.696). [d] Inflection. [e] CD maxima [λ/nm (Δε/dm^3 mol^{-1} cm^{-1})]: 698 (0.058), 590 (0.595), 489 (−2.950), 370 (0.320) and 285 (0.046)

deuterons as shown in Fig. 3 in ref. 45. The difference between the NMR shifts is expressed in equation (4), where α is the

$$\Delta\delta_{A,B} = \delta_A - \delta_B = (\sqrt{-3}/2)C\sin(2\alpha) \qquad (4)$$

torsion angle for Cr–N–C–C(O) and C is a constant including the spin density. The appreciable difference in the inequivalent dihedral angles for the nta chelate rings in dinuclear complexes **3a**, **3b** and **8b** (Tables 4 and 6) may lead to splitting of two G-ring signals into three or four. However, only one set of G-ring signal is observed for complexes **3a** and **3b** (Table 8). It is likely that the nta chelate conformations of the G rings are not frozen, but are averaged in solution. The hydrogen bonds between the tn and nta ligands do not seem to lead to retention of the nta chelate-ring conformations in solution.

On the other hand, the complexes with pyridine rings (**6a**–**8a** and **6b**–**8b**) show different spectral patterns. At lowest field, two signals for the G-ring deuterons appeared with equivalent intensities from δ −4.0 to −14.0 [Fig. 5(*b*), Table 8]. This may arise from differences in the distances and angles between the

Table 8 Hydrogen-2 NMR chemical shifts for $[([^2H_6]nta)Cr(OH)_2ML_4]^+$ complexes in aqueous solutions

	δ (degeneracy)						
Complex	R ring		G ring			$\Delta\delta_{A,B}$ (G ring)[a]	
1a	−10.6(2)[b]		−10.6(2)[b]		−34.6(2)	24.0	
2a	−9.1(2)[b]		−9.1(2)[b]		−33.7(2)	24.6	
3a	−12.5(2)		−9.0(2)		−33.5(2)	24.5	
4a	−12.5(2)		−5.6(2)		−33.4(2)	27.8	
5a	−10.4(2)		−4.4(2)		−33.4(2)	29.0	
6a	−15.6(2)		−4.0(1)	−10.0(1)	−31.7(2)	27.7	21.7
7a	−23.6(2)		−6.0(1)	−10.0(1)	−32.1(2)	26.1	22.1
8a	−23.6(2)		−7.8(1)	−14.0(1)	−32.5(2)	24.7	18.5
c	−23.0(2)	−9.0(1)	−15.0(1)	−32.0(1)	−36.0(1)	27.0	17.0
1b	−10.1(2)[b]		−10.1(2)[b]		−28.8(4)	18.7	
2b	−9.4(2)		−6.0(2)		−27.2(2)	21.2	
3b	−10.3(2)		−7.0(2)		−28.7(2)	17.3	
4b	−12.7(2)		−7.7(2)		−28.1(2)	20.4	
5b	−10.2(2)[b]		−10.2(2)[b]		−27.5(2)	21.7	
6b	−14.0(2)		−4.0(1)	−9.5(1)	−26.8(2)	22.8	17.3
7b	−17.9(2)		−5.2(1)	−8.9(1)	−26.4(2)	21.2	17.5
8b	−18.1(2)		−7.5(1)	−10.6(1)	−27.1(2)	19.6	16.5
d[1]	−18.0(1)	−8.1(1)	−14.2(1)	−28.0(1)	−34.0(1)	25.9	13.8

[a] $\Delta\delta_{A,B} = \delta_A - \delta_B$; see text. [b] Degenerate signal. [c] $[([^2H_6]nta)CrO(OH)Co(phen)_2]$ in $NH_4Cl–NH_3$ buffered solution. [d] $[([^2H_6]nta)CrO(OH)-Cr(phen)_2]$ in $NH_4Cl–NH_3$ buffered solution.

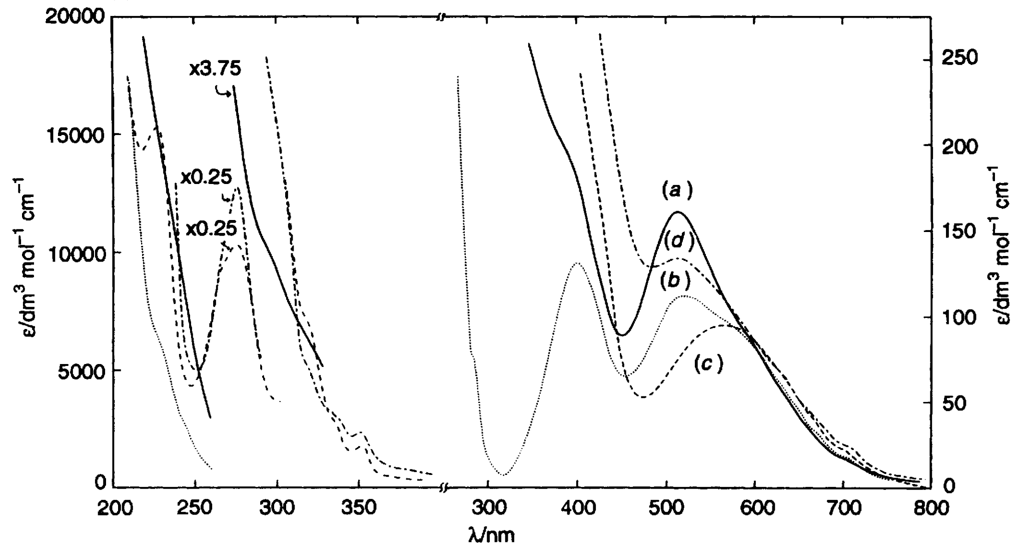

Fig. 4 The UV/VIS absorption spectra of $[(nta)Cr(OH)_2ML_4]^+$ complexes in aqueous solution (*a*) **2a**, (*b*) **2b**, (*c*) **8a** and (*d*) **8b**

oxygen atoms of the two G rings and the hydrogen atoms of the phen ligands in the two inequivalent G rings as seen in the crystal structure of **8b**. The H···O distances are 2.68 [C(7)–H···O(3)] and 2.82 Å [C(28)–H···O(5)], respectively (Fig. 3). The first is closer to the sum of the van der Waals radii for hydrogen and oxygen atoms (2.6 Å). By such van der Waals contact interactions, the inequivalent G-ring chelate conformations are frozen in solution. In the μ-oxo complex $[(nta)Cr(\mu\text{-}O)(\mu\text{-}OH)M(phen)_2]$, moreover, the highest-field signal is separated into two components probably as a result of the pronounced non-bonding interaction.

The average torsion angles α of the two G rings, 34.2 and 33.6°, for complexes **3a** and **3b**, give small differences between sin (2α), 0.929 and 0.922, respectively. Therefore, the shift difference of the ^2H NMR signals in the G ring between **3a** and **3b** results from the different *C* values. Since the parameter *C* includes the spin density, these differences are caused by the decrease in the effective paramagnetic unpaired electrons owing to the antiferromagnetic interaction in the homometallic Cr^{III}_2 complexes.

Influence of the Non-bridging Ligands on ^2H *NMR Spectra.*— The ^2H NMR chemical shifts of the R-ring methylene deuterons in the aliphatic amine complexes vary from δ −9.1 to −12.7 (**1a–5a** and **1b–5b**), −14.0 and −15.6 (**6a** and **6b**) for the amp ones and −17.9 to −23.6 (**7a**, **8a**, **7b** and **8b**) for the bipy and phen ones with all-aromatic nitrogen ligators. This is in accord with the variation in the ligands in the ML_4 moieties as shown in Table 8.

Though the structure analyses suggest that the signals of the R rings also split for complexes **3a**, **3b** and **8b** judging from the reported torsion angles α,[45] only one signal was observed for all the complexes. This implies that the R ring becomes planar in solution. From equation (4), the shift differences between each complex are caused by the variation of *C* or the spin density in the deuteron atom. The Cr(nta)–OH bond lengths *trans* to the nta nitrogen atom vary with the L_4 ligands. Those of the aliphatic diamine complexes **3a** and **3b** are significantly shorter (about 0.03 Å) than those of the aromatic diamine complex **8b**. This difference could affect the Cr–N(nta) bond owing to the *trans* influence, though no significant change in the Cr–N(nta) bond lengths was detected in the structural analysis. Therefore, the isotropic contact shift or the unpaired electron density of the deuteron nuclei in the R ring on the Cr_2O_2 plane increases with lengthening of the ML_4–OH bond *trans* to the nta nitrogen atom. In other words, the ^2H NMR chemical shifts of the R ring

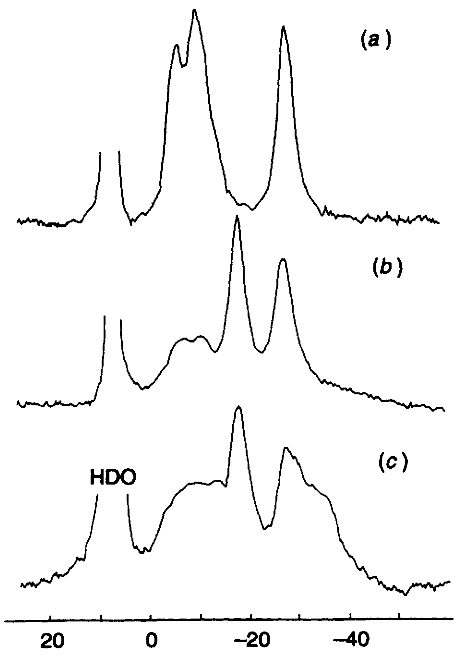

Fig. 5 The ^2H NMR spectra of $[([^2H_6]nta)Cr(OH)_2CrL_4]^+$ [L_4 = $(en)_2$ (*a*) or $(phen)_2$ (*b*)] and $[([^2H_6]nta)CrO(OH)Cr(phen)_2]$ (*c*)

in the $[^2H_6]nta^{3-}$ ligand are sensitive to the M–L_4 π-bond interaction *via* the L_4M–OH bond in these dinuclear complexes through the six bonds (*D*–C–N–Cr–O–M–N[(am(m)ine)].

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