Synthesis and Characterization of L-Tartrato Chromate(III) Complexes with Acetylacetonate Ions

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Two acetylacetonato L-tartrato complexes, mononuclear $[Cr(acac)_2(Htart)]^{2-}$ and dinuclear $[Cr_2(acac)_2\{(tart)_2H\}]^{3-}$ where tart = $C_4H_2O_6^{4-}$, were synthesised and characterized by CD or ^2H NMR and/or FAB mass spectroscopy. The former complex was found to be the first example to contain bidentate tartrato-O^2,O^3 bound through the alkoxo and hydroxyl oxygen atoms. The latter complex has a dinuclear structure bridged by two tetradentate tartrato-O^1,O^2 ligands with a Δ–Δ absolute configuration. The stereospecificity or -selectivity and magnetic behaviour were examined in comparison with analogous complexes.

The L-tartrate ligand (tart) is well known to form various kinds of metal complexes.[1] The most historically famous L-tartrato complex is believed to be tris(L-tartrato)chromate(III) for which the Cotton effect was first observed in 1896,[2,3] and which seems to be formed stereospecifically with the Λ absolute configuration about chromium(III).[4,5] Until recently, however, in solution it had not been definitely determined whether the ligand adopts either one of two possible co-ordination modes in this complex: *i.e.* one (O^1,O^2) involving oxygen atoms of a carboxylato group and of an adjacent ionized (alkoxo) or unionized hydroxyl group, and the other (O^2,O^3) involving both alkoxo/hydroxyl oxygens.[5] Such co-ordination modes govern the stereospecificity or -selectivity of this type of complex. The O^1,O^2 mode gives perfect stereospecificity for two tetradentate L-tartrate-bridged dinuclear complexes with a Δ–Δ configuration,[6,7] whereas bidentate mono(L-tartrato-O^1,O^2) complexes exhibit low stereoselectivity.[8,9] Nevertheless, no complex has been isolated with the O^2,O^3 co-ordination mode. This mode may be important in asymmetric oxidation of allylic alcohol catalysed by titanium diethyl L-tartrate.[10]

In this paper, the syntheses and characterization of mono- and di-nuclear L-tartratochromium(III) complexes with acetylacetonate (acac) ligand(s) are reported; the former exhibit a novel O^2,O^3 co-ordination mode through each alkoxo and hydroxyl oxygen of the L-tartrate ligand and the latter have a dinuclear structure bridged by two L-tartrate ligands with a Δ–Δ absolute configuration which is imposed stereospecifically.

Experimental

Preparation of Complexes.—$Na_2[Cr(acac)_2(Htart)]\cdot4.5H_2O$ **1**. A mixture of *trans*-$[Cr(acac)_2(H_2O)_2]Cl$[11] (0.66 g, 2.1 mmol), L-tartaric acid (0.15 g, 1 mmol) and lithium hydroxide (0.17 g, 4 mmol) in water (40 cm^3) was heated at 80 °C on a water-bath for 2 h. The colour changed from red to dark green. Red crystals of $[Cr(acac)_3]$ were gradually formed after 1 h. They were filtered off after further heating for 1 h. The filtrate was diluted and then poured onto a column (4 × 20 cm) of QAE-Sephadex A-25 anion exchanger. The column was washed with water and eluted with a NaCl solution (0.1 mol dm^{-3} in the early stages and then 0.2 mol dm^{-3}). Two main bands (red, **1**; blue-green, **2**) were obtained in order of elution together with several minor bands near the top of the column. The eluate containing complex **1** was concentrated to dryness in a vacuum rotary evaporator at 30 °C. The residue was dissolved in methanol and the sodium chloride filtered off. After this procedure had been repeated a few times, complete removal of sodium chloride was carried out by Sephadex G-10 column chromatography. A red precipitate was obtained by adding acetone to the eluate. This was filtered off, washed with acetone and diethyl ether, and dried *in vacuo*. Yield: 30% (Found: C, 31.45; H, 4.90; Cr, 9.70. $C_{14}H_{26}CrNa_2O_{14.5}$ requires C, 32.05; H, 5.00; Cr, 9.90%). The corresponding deuteriated DL-tart complex was obtained by the same method and identified by its absorption spectrum.

The second band (**2**) is considered to contain a dinuclear complex as described below. This was prepared in better yield as follows.

$Na_3[Cr_2(acac)_2\{(tart)_2H\}]\cdot7H_2O$ **2**. An analogous method to that for complex **1** was employed but under milder conditions. A mixture of *trans*-$[Cr(acac)_2(H_2O)_2]Cl$ (2.00 g, 6.2 mmol) and potassium L-tartrate semihydrate (2.82 g, 12 mmol) in water (20 cm^3) was heated at 80 °C on a water-bath for 30 min. The colour changed from red to green. After filtering and diluting the reaction solution, the filtrate was poured onto a column (4 × 20 cm^3) of QAE-Sephadex A-25 anion exchanger. The column was washed with water, then eluted with 0.2 mol dm^{-3} NaCl solution. Four bands were obtained but only the fourth was collected since this was found to give a large CD intensity ($\Delta\varepsilon = -4.0$ dm^3 mol^{-1} cm^{-1}) in the first ligand-field band region by chromium(III) ion analysis. This was concentrated using a rotary vacuum evaporator. Sodium chloride was removed and the blue-green precipitate obtained was purified as above. Yield: 5% (Found: C, 27.45; H, 4.30; Cr, 13.25. $C_{18}H_{33}Cr_2Na_3O_{23}$ requires C, 27.35; H, 4.20; Cr, 13.15%).

$H[Cr_2\{(tart)_2H\}(bipy)_2]\cdot3.5H_2O$ **3**, $H[Cr_2\{(meso\text{-}tart)_2H\}(bipy)_2]\cdot6H_2O$ **4** (*bipy* = 2,2′-*bipyridine*) *and* $Na[Cr_2\{([^2H_2]\text{-}tart)_2H\}(phen)_2]\cdot6.5H_2O$ **5** (*phen* = 1,10-*phenanthroline*). These tartrato complexes were prepared by the method of Robbins and Tapscot[7] (Found: C, 43.30; H, 3.85; N, 7.15. $C_{28}H_{29}Cr_2N_4O_{15.5}$ **3** requires C, 43.50; H, 3.80; N, 7.25. Found: C, 41.70; H, 4.20; N, 6.95. $C_{28}H_{34}Cr_2N_4O_{18}$ **4** requires C, 41.10; H, 4.20; N, 6.95%).

Deuteriation of Tartaric Acid.—Hexadeuteriated DL-tartaric acid was obtained by refluxing a mixture of sodium tartrate (7.4 g) and NaOH (10 g) in D_2O (22 cm^3) for 4 h according to the modified literature method.[12] Optical resolution of it was carried out by the literature method.[13]

Measurements.—Absorption spectra were obtained on a Shimadzu UV-2100 spectrophotometer, CD spectra on a JASCO J-500C spectropolarimeter and ^2H NMR spectra on a JEOL JNM GSX-270 and/or JNM GSX-400 spectrometer in

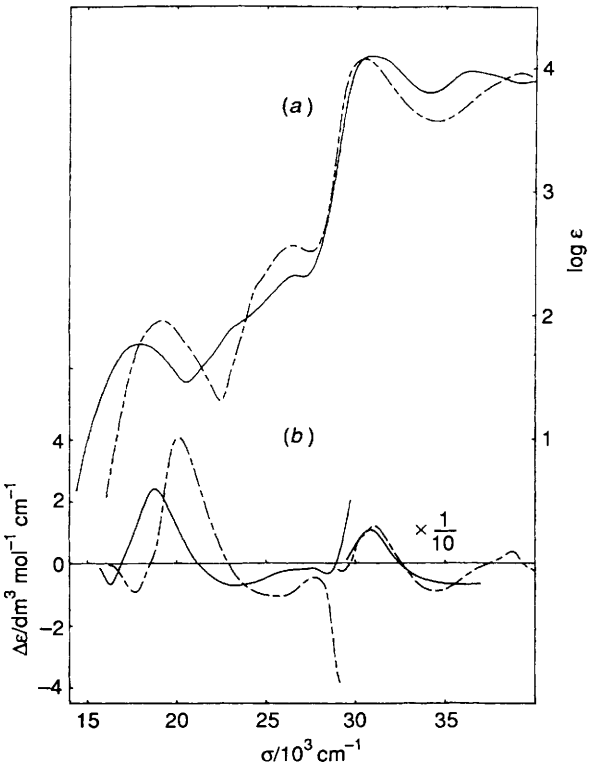
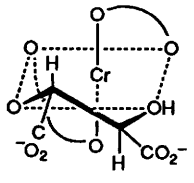


Fig. 1 Absorption (*a*) and CD spectra (*b*) of $[Cr(acac)_2(Htart)]^{2-}$ **1** (——) and $(+)_{546}[Cr(acac)_2(en)]^+$ (— — — —) in water



Scheme 1

water at room temperature. High-performance liquid chromatography (HPLC) was performed on a JASCO 807-IT integrator with a BIP-I HPLC pump and a 875-UV/VIS detector. Methanol–propan-2-ol (1:2) was used as eluent with a Chiralpack OT(+) column. Positive-ion mass spectra were obtained in methanol solution on a JEOL JMS-SX102 mass spectrometer.

The concentration of the chromium(III) complexes was determined by the spectroscopic method after oxidation with alkaline hydrogen peroxide on using the molar absorption coefficient of chromate(VI) ion as $\varepsilon = 4830$ dm^3 mol^{-1} cm^{-1} at 372 nm.

Magnetic susceptibility data were obtained on powdered samples with an automated Faraday balance in the range 80–295 K. The observed susceptibilities were fitted by a theoretical equation using a non-linear least-squares SIMPLEX parameter optimization routine, minimizing the residual function $R = [\Sigma(\chi_{obs} - \chi_{calc})^2/\Sigma(\chi_{obs})^2]^{\frac{1}{2}}$.

Results and Discussion

Mononuclear Complex.—The elemental analysis indicates that complex **1** has two acetylacetonates and one L-tartrate ion. The CD spectrum exhibits a positive major band in the first ligand-field transition region and two positive and negative intense peaks at longer wavelengths in the intraligand transition region (30 000–35 000 cm^{-1}). This behaviour is very similar to that for $(+)_{546}[Cr(acac)_2(en)]^+$ (en = ethane-1,2-diamine) as shown in Fig. 1.[14] In view of the column chromatographic

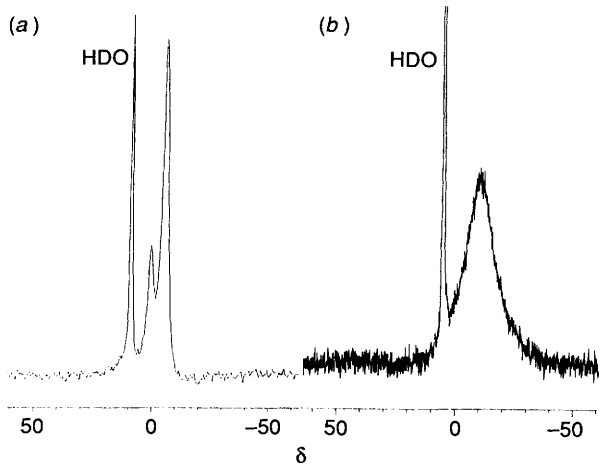


Fig. 2 The ^{2}H NMR spectra of $[Cr(acac)_2\{(DL\text{-}[^2H_2]tart)H\}]^{2-}$ (*a*) and $[Cr_2\{(L\text{-}[^2H_2]tart)_2H\}(phen)_2]^-$ (*b*) in water

behaviour, elemental analysis and CD spectrum, the chemical formula of **1** seems to be $Na_2[Cr(acac)_2(Htart)]$. The large CD intensity comparable to that for $(+)_{546}[Cr(acac)_2(en)]^+$ (ref. 14) suggests stereo-selective or -specific formation of Λ-$[Cr(acac)_2(Htart)]^{2-}$. If the tart co-ordination mode is O^1,O^2 through carboxylate and alkoxide oxygens such stereoselectivity is not expected as observed for diastereomers of $[Cr(H_2tart)(bipy)_2]^+$.[9c] A strong infrared absorption band at 1610 cm^{-1} indicates the existence of only unco-ordinated carboxylate groups. Therefore, the most probable co-ordination mode is O^2,O^3 through each oxygen of the alkoxo and hydroxyl groups as shown in Scheme 1. This is confirmed by the ^{2}H NMR spectrum.

The ^{2}H NMR spectrum of the deuteriated DL-tartrato complex **1** gives two contact shifts with different intensities upfield as expected for a mixture of diastereomers with O^2,O^3 co-ordination as found for $[Cr_2\{([^2H_2]tart)_2H\}(bipy)_2]^-$ (Fig. 2). This shows that two methine deuterons of the Htart ligand cannot be discriminated by ^{2}H NMR spectroscopy and that they are equivalent in appearance despite the unsymmetrical alkoxo and hydroxyl co-ordination in both the mono- and di-nuclear complexes. Thus, the carboxylato and alkoxo (O^1,O^2) co-ordination is disregarded where two ^{2}H NMR contact shifts due to two inequivalent methine deuterons in each diastereomer could be observed up(negative)- and down(positive)-field, resulting in four signals. The O^2,O^3 co-ordination mode leads to a δ *gauche* conformation of the chelate ring with two equatorially oriented carboxylate and hydroxyl groups. This is in line with the high stereoselectivity as mentioned below, in contrast with the low one for carboxylato and alkoxo or hydroxyl (O^1,O^2) chelation[8,9] which brings about a more flattened chelate conformation.

In order to obtain the quantitative ratio of the diastereomers in complex **1**, HPLC was carried out on a Chiralpack OT(+) column using methanol–propan-2-ol (1:2) as eluent. The UV/VIS and CD chromatograms obtained are shown in Fig. 3. From these the ratio of Λ_L and Δ_L diastereomers is estimated to be 9:1. This high stereoselectivity may be ascribed to the fact that the tart chelate in this Λ tris(chelate) complex takes a more stable lel(δ) conformation from a geometrical viewpoint. The pure Λ_L diastereomer is assumed to be contained in the eluate after 6 min of retention time in HPLC. Therefore, the CD spectrum of the Λ_L complex can be obtained from this portion, but the CD curve of the Δ_L isomer may be calculated on the basis of the estimated ratio of the diastereomers as shown in Fig. 4. It is to be noted that the difference in CD intensity between the Λ_L and Δ_L isomers is small in the ligand-field transition region but significantly large in the intraligand transition region. This indicates that there is a dominant

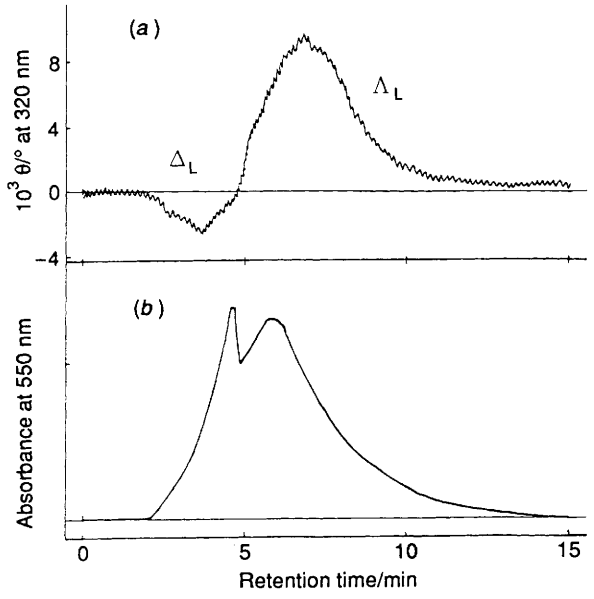


Fig. 3 The CD (*a*) and UV/VIS (*b*) HPLC chromatograms for two diastereoisomers of $[Cr(acac)_2(Htart)]^{2-}$

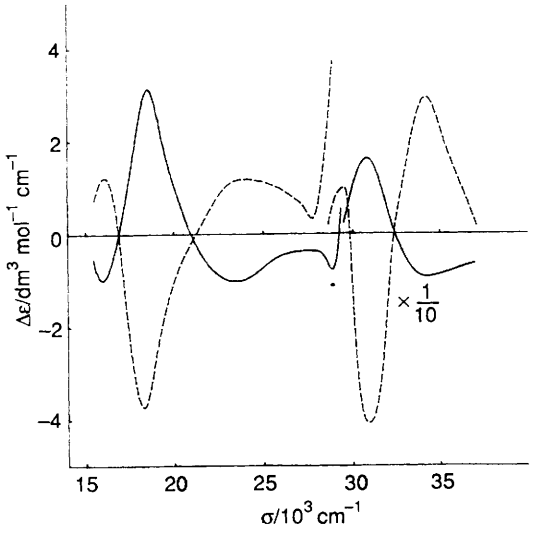


Fig. 4 The CD curves of Λ_L- (——) and Δ_L-$[Cr(acac)_2(Htart)]^{2-}$ (— — —)

contribution to the ligand-field CD from the configurational effect but to the intraligand CD from the vicinal effect. This CD behaviour is opposite to that observed for the $[Co(H_2tart)(bipy)_2]^+$ diastereomers.[9a,b]

Johansson and Norden[5] reported that the composition $[Cr(Htart)_3]^{6-}$ in solution was characterized by CD and potentiometric data as a *fac*-Λ form with three bidentate tartrato-O^1,O^2 ligands. This might be stabilized by attractive hydrogen bonds between free axially oriented hydroxyl groups and co-ordinated alkoxo oxygens.[5] In view of the possible existence of the present O^2,O^3 co-ordination mode, however, it is more plausible to adopt stereospecifically a Λ form having two equatorially oriented carboxylate groups in a bidentate tartrate chelate with O^2,O^3 co-ordination. Moreover, this mode is expected to result in more pronounced, almost perfect, stereospecificity for the $\Lambda(lel_3)\delta\delta\delta$ tris(tart) complex

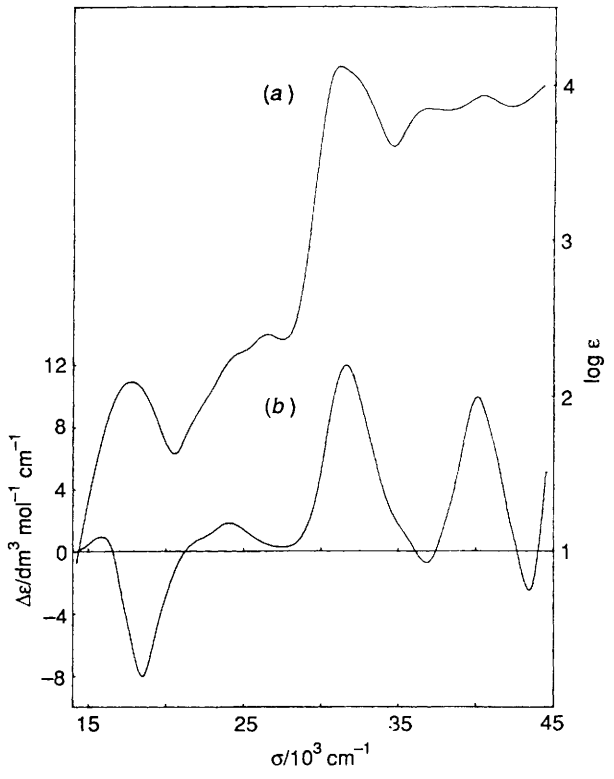


Fig. 5 Absorption (*a*) and CD (*b*) spectra of $[Cr_2(acac)_2\{(tart)_2H\}]^{3-}$ **2**

as found for the most stable predominantly formed Λ-$(lel_3)\delta\delta\delta$-$[M(S,S\text{-chxn})_3]^{3+}$ [*S,S*-chxn = (1*S*,2*S*)-*trans*-cyclohexane-1,2-diamine].[15]

Dinuclear Complex.—From the elemental analysis of complex **2** the ratio of Cr:tart:acac is assumed to be 1:1:1. This leads to the tentative chemical formula, $Na_3[Cr_2(acac)_2\{(tart)_2H\}]$, excluding a mononuclear composition. This dinuclear formulation is supported by the positive-ion FAB mass spectrum. Three types of quasi-molecular ion peaks are observed together with a peak corresponding to loss of an acetylacetone molecule or acetylacetonate ion: m/z = 687, $[M + Na]^+$; 665, $[M + H]^+$; 643, $[M + 2H - Na]^+$; 587, $[M - Na - Hacac]^+$; 565, $[M - acac]^+$; where *M* refers to the molecular weight of $Na_3[Cr_2(acac)_2\{(tart)_2H\}]$. The CD spectrum in the ligand-field and intraligand transition region shows a negative and two positive intense components, respectively as shown in Fig. 5. This pattern is similar to that of $[Cr_2\{(tart)_2H\}(bipy)_2]^-$ (ref. 6) as well as of Δ-$(-)_{546}[Cr(acac)(en)_2]^{2+}$.[14] In view of the CD intensity in the first band region ($\Delta\varepsilon$ = −4.0 $dm^3\,mol^{-1}\,cm^{-1}$ per Cr^{3+} ion), this complex is formed stereospecifically to take a Δ–Δ absolute configuration as a result of two tetradentate tartrato-O^1,O^2 bridging ligands as in the case of the corresponding bipy or phen complexes.[6] The magnetic susceptibility measurement mentioned below also supports the dinuclear structure as shown in Fig. 6. The acac complex seems to have a proton attached to the bridging moiety, through hydrogen bonding of two co-ordinated alkoxo oxygens, as revealed by X-ray structural analysis of the corresponding bipy complex.[16,17]

Magnetic Properties.—As shown in Fig. 7, the temperature-dependent magnetic susceptibility data for complex **2** along with other tartrate-bridged dinuclear complexes were fitted by

$$\chi = \frac{Ng^2\beta^2}{kT}\cdot\frac{2\exp[(2J - 6.5j)/kT] + 10\exp[6J - 13.5j)/kT] + 8\exp[(12J - 9j)/kT]}{1 + 3\exp[(2J - 6.5j)/kT] + 5\exp[(6J - 13.5j)/kT] + 7\exp[(12J - 9j)/kT]} \quad (1)$$

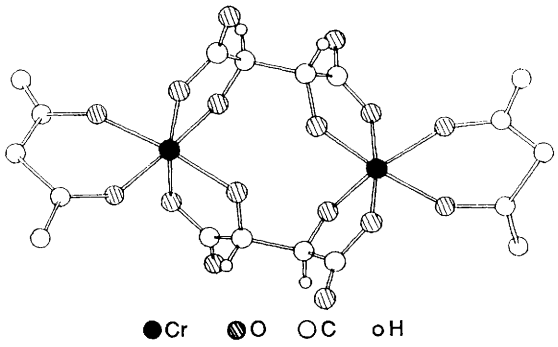


Fig. 6 Proposed structure of $[Cr_2(acac)_2\{(tart)_2H\}]^{3-}$. Hydrogen atoms of the acetylacetonate and the hydroxy group of tart are not shown for clarity

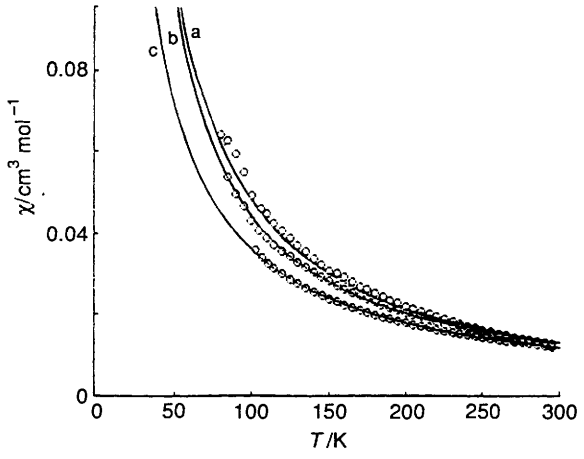


Fig. 7 Temperature-dependent magnetic susceptibilities of $H[Cr_2\{(L\text{-tart})_2H\}(bipy)_2]\cdot 3.5H_2O$ (*a*), $H[Cr_2\{(meso\text{-tart})_2H\}(bipy)_2]\cdot 6H_2O$ (*b*), and $Na_3[Cr_2(acac)_2\{(L\text{-tart})_2H\}]\cdot 7H_2O$ (*c*). Experimental points are shown as open circles. The full lines represent the best fit using the Van Vleck equation ($S = \frac{3}{2},\frac{3}{2}$)

the Van Vleck equation (1) where J and j are defined by the exchange Hamiltonian expressed as $H = -2JS_1 \cdot S_2 - j(S_1 \cdot S_2)^2$. The results of the data fitting revealed a ferromagnetic superexchange interaction between two chromium(III) ions in these complexes as summarized in Table 1. The bipy L-tart complex and the *meso*-tart analogue give a comparatively large ferromagnetic coupling in spite of the relatively long Cr···Cr distance (*ca.* 5 Å).[16,17] This ferromagnetic behaviour is analogous to that of the corresponding tart-bridged vanadyl dinuclear complexes[18] with V···V distance 4.08–4.35 Å,[19] but different from that of the antiferromagnetic copper(II) analogue[20] as shown in Table 1. To our knowledge, the former L-tart bipy chromium(III) complex exhibits the strongest ferromagnetism among the complexes with long Cr···Cr distances around *ca.* 5 Å.[21] The long-distance magnetic interaction of the acac complex is found to be much weaker than that of the corresponding bipy complex. In absolute magnitude this magnetic coupling is comparable to those[22] found in hydroxoaqua-bridged dinuclear complexes with similar hydrogen-bonding bridges to that of the acac L-tart complex. Such a significant difference in magnetic behaviour between the bipy and the acac L-tart complexes may arise from the structural difference in the bridging moieties, which is probably brought about by the change in hydrogen-bonding properties as a result of the different co-ordination bond character of the 'end cap' non-bridging ligands, *i.e.* the π acceptor and donor for the α-diimine and the acetylacetonate, respectively.

Table 1 Metal–metal distances and magnetic properties of tartrate-bridged dinuclear complexes

Complex	M···M/Å	$2J^a$/cm^{-1}
$Na_3[Cr_2(acac)_2\{(L\text{-tart})_2H\}]\cdot 7H_2O$		$+0.45^b$
$H[Cr_2\{(L\text{-tart})_2H\}(bipy)_2]\cdot 3.5H_2O$	4.968(av.)[c]	$+38.3^b$
$H[Cr_2\{(meso\text{-tart})_2H\}(bipy)_2]\cdot 6H_2O$	4.799(2)[d]	$+13.0^b$
$[NH_4]_4[(VO)_2(L\text{-}H_2tart)_2]\cdot 2H_2O$	4.352(7)[e]	$+14.0^f$
$Na_4[(VO)_2(L\text{-}H_2tart)(D\text{-}H_2tart)]\cdot 12H_2O$	4.082(2)[g]	$+4.5^h$
$Na_2[Cu_2(L\text{-}H_2tart)(D\text{-}H_2tart)]\cdot 5H_2O$	2.9865(9)[j]	-18^i

[a] The coupling constant determined from the observed susceptibility data. [b] This work. [c] Ref. 16. [d] Ref. 17. [e] Ref. 19(*b*). [f] Ref. 18(*b*). [g] Ref. 19(*a*). [h] Ref. 18(*a*). [i] Ref. 20.

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