



# Transition metal complexes of dibenzoyl-L-tartaric acid (db-L-tarH<sub>2</sub>) and L-tartaric acid (L-tarH<sub>2</sub>); X-ray crystal structure of {[Cu(L-tar)(phen)]·6H<sub>2</sub>O}<sub>n</sub> (phen = 1,10-phenanthroline)

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**Abstract**—Dibenzoyl-L-tartaric acid (db-L-tarH<sub>2</sub>) reacts with [Cu<sub>2</sub>(μ-O<sub>2</sub>CCH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>] to form the tartrate complex [Cu(L-tar)] (1) (L-tarH<sub>2</sub> = L-tartaric acid). 1 reacts with 2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen) yielding [Cu(L-tar)(bipy)]·6H<sub>2</sub>O (2) and [Cu(L-tar)(phen)]·4H<sub>2</sub>O (3), respectively. A crystal of composition {[Cu(L-tar)(phen)]·6H<sub>2</sub>O}<sub>n</sub> (4) was taken directly from the original mother liquor of 3. The X-ray crystal structure of the polymeric complex 4 shows each copper(II) ion to be six-coordinate, being chelated by a phenanthroline ligand and also chelated by a carboxylate oxygen atom and a hydroxyl oxygen atom from one end of a tartrate group. A carboxylate oxygen atom and a hydroxyl oxygen atom from one end of a symmetry-related tartrate ligand also chelates to the metal. Dibenzoyl-L-tartaric acid also reacts with [Mo<sub>2</sub>(μ-O<sub>2</sub>CCH<sub>3</sub>)<sub>4</sub>], [Mo<sub>2</sub>(CH<sub>3</sub>CN)<sub>8</sub>][BF<sub>4</sub>]<sub>4</sub>, {[Ru<sub>2</sub>(μ-O<sub>2</sub>CCH<sub>3</sub>)<sub>4</sub>Cl]<sub>n</sub> and Na<sub>4</sub>[Rh<sub>2</sub>(μ-CO<sub>3</sub>)<sub>4</sub>]·2.5H<sub>2</sub>O to give {[Mo<sub>2</sub>(db-L-tar)<sub>2</sub>]·5H<sub>2</sub>O}<sub>n</sub> (5), [Mo<sub>2</sub>(db-L-tar)(CH<sub>3</sub>CN)<sub>4</sub>][BF<sub>4</sub>]<sub>2</sub>·7H<sub>2</sub>O (6), {[Ru<sub>2</sub>(db-L-tar)<sub>2</sub>]<sub>n</sub>·2H<sub>2</sub>O}<sub>n</sub> (7) and {[Rh<sub>2</sub>(db-L-tar)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O}<sub>n</sub> (8), respectively. © 1997 Elsevier Science Ltd

**Keywords:** dibenzoyl-L-tartaric acid; L-tartaric acid; copper; molybdenum; ruthenium; rhodium; X-ray.

The current demand for new chiral metal complexes for possible use in the area of organic asymmetric synthesis prompted us to investigate the coordination chemistry of dibenzoyl-L-tartaric acid (db-L-tarH<sub>2</sub>) with respect to copper, molybdenum, ruthenium and rhodium. This paper outlines the synthesis and the physical properties of copper(II), dimolybdenum(II,II), diruthenium(II,III) and dirhodium(II,II) complexes containing the dibenzoyl-L-tartrate ligand. In addition, the X-ray crystal structure of the copper(II) complex {[Cu(L-tar)(phen)]·6H<sub>2</sub>O}<sub>n</sub> (L-tarH<sub>2</sub> = L-tartaric acid, phen = 1,10-phenanthroline) is described.

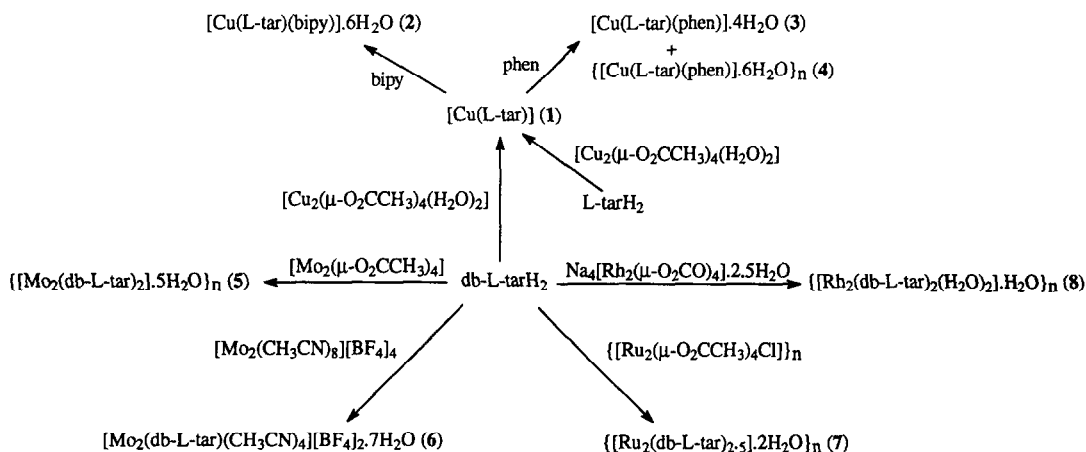
## RESULTS AND DISCUSSION

Synthetic routes to the dibenzoyl-L-tartrate and L-tartrate complexes are summarised in Scheme 1.

Hydrolysis of dibenzoyl-L-tartaric acid to L-tartaric acid occurred upon reaction with [Cu<sub>2</sub>(μ-O<sub>2</sub>CCH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>], and the light-blue, insoluble tartrate complex [Cu(L-tar)] (1) was isolated. Complex 1 was also obtained by the direct reaction of L-tartaric acid with [Cu<sub>2</sub>(μ-O<sub>2</sub>CCH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]. Complex 1 is undoubtedly related to the structurally characterised, blue, polymeric complex {[Cu<sub>2</sub>(L-tar)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]·4H<sub>2</sub>O}<sub>n</sub>, which was previously prepared by reacting an aqueous solution of CuCl<sub>2</sub> with L-tartaric acid [1]. In the latter complex the two crystallographically independent copper atoms in the asymmetric unit are linked together by two similarly independent tartrate dianions to form dimeric complexes. Each tartrate chelates both copper atoms at opposite ends by using one carboxylate oxygen and one hydroxyl oxygen in each case. The coordination around each copper atom is completed by a water molecule and a non-chelating carboxylate oxygen atom of another dimer, giving an overall polymeric structure.

Reaction of an aqueous suspension of 1 with the

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Scheme 1. L-tarH<sub>2</sub> = L-tartaric acid; db-L-tarH<sub>2</sub> = dibenzoyl-L-tartaric acid; bipy = 2,2'-bipyridine; phen = 1,10-phenanthroline

Scheme 1.

chelating ligands 2,2'-bipyridine (bipy) and 1,10-phenanthroline yielded the light-blue complex [Cu(L-tar)(bipy)]·6H<sub>2</sub>O (**2**) and the dark-green complex [Cu(L-tar)(phen)]·4H<sub>2</sub>O (**3**), respectively. A crystal of composition {[Cu(L-tar)(phen)]·6H<sub>2</sub>O}<sub>n</sub> (**4**) was taken directly from the original mother liquor of **3** and used (without drying) for X-ray diffraction studies. The X-ray crystal structure of **4** is shown in Figs 1–3 and selected bond distances and bond angles are

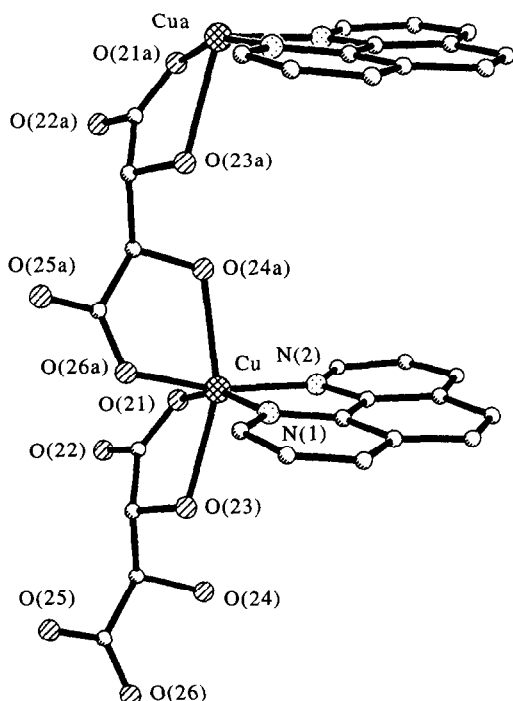


Fig. 1. X-ray crystal structure of {[Cu(L-tar)(phen)]·6H<sub>2</sub>O}<sub>n</sub> (**4**) showing the repeat unit in the polymer chain (water molecules of hydration not shown).

listed in Table 1. The asymmetric unit (Fig. 1) contains one copper ion, one phenanthroline, one doubly deprotonated tartrate ion and six water molecules. The copper ions are six-coordinate, being bound to the nitrogen atoms of a phenanthroline ligand, to O(21) and O(23) of one tartrate group and to O(24) and O(26) of a symmetry-related tartrate. The geometry at copper is quite irregular and approximating to tetragonal, with the long bonds to the alcohol groups at O(23) and O(24) [2.328(3) and 2.308(4) Å, respectively]. The tartrate dianions behave as 1,4-bidentate ligands to two copper ions; each set of donors consists of one oxygen from a carboxylate group and one alcohol oxygen donor. The resulting polymeric chain lies along the *x*-axis of the cell (Fig. 2). All of the lattice water molecules are involved in hydrogen-bonding, either to the tartrate ligands or to other water molecules. These interactions are summarised in Table 2.

The unit cell plot viewed along the *x*-axis (Fig. 3) shows the intricate packing in the structure. The phenanthroline groups of each polymeric chain are interwoven with those of a second chain to form a  $\pi$ - $\pi$  stack along *x* (mean interplanar distances 3.2 and 3.4 Å for the phenanthroline rings). Sets of four of these columns then surround a central cavity containing the hydrogen-bonded molecules.

The formulation of the bipyridine adduct [Cu(L-tar)(bipy)]·6H<sub>2</sub>O (**2**) suggests that it may have a similar structure to the phenanthroline complex **4**. The structural similarity of the two complexes is substantiated by the fact that the IR spectrum of each contains  $\nu_{\text{asymm.}}(\text{OCO})$  and  $\nu_{\text{symm.}}(\text{OCO})$  bands at *ca* 1620 and 1360 cm<sup>-1</sup>, respectively. The magnetic moments of complexes **1**–**3** were within the expected range ( $\mu_{\text{eff}} = 1.7$ – $2.2$  B.M.) for mononuclear copper(II) complexes, i.e. those lacking a Cu–Cu interaction [2].

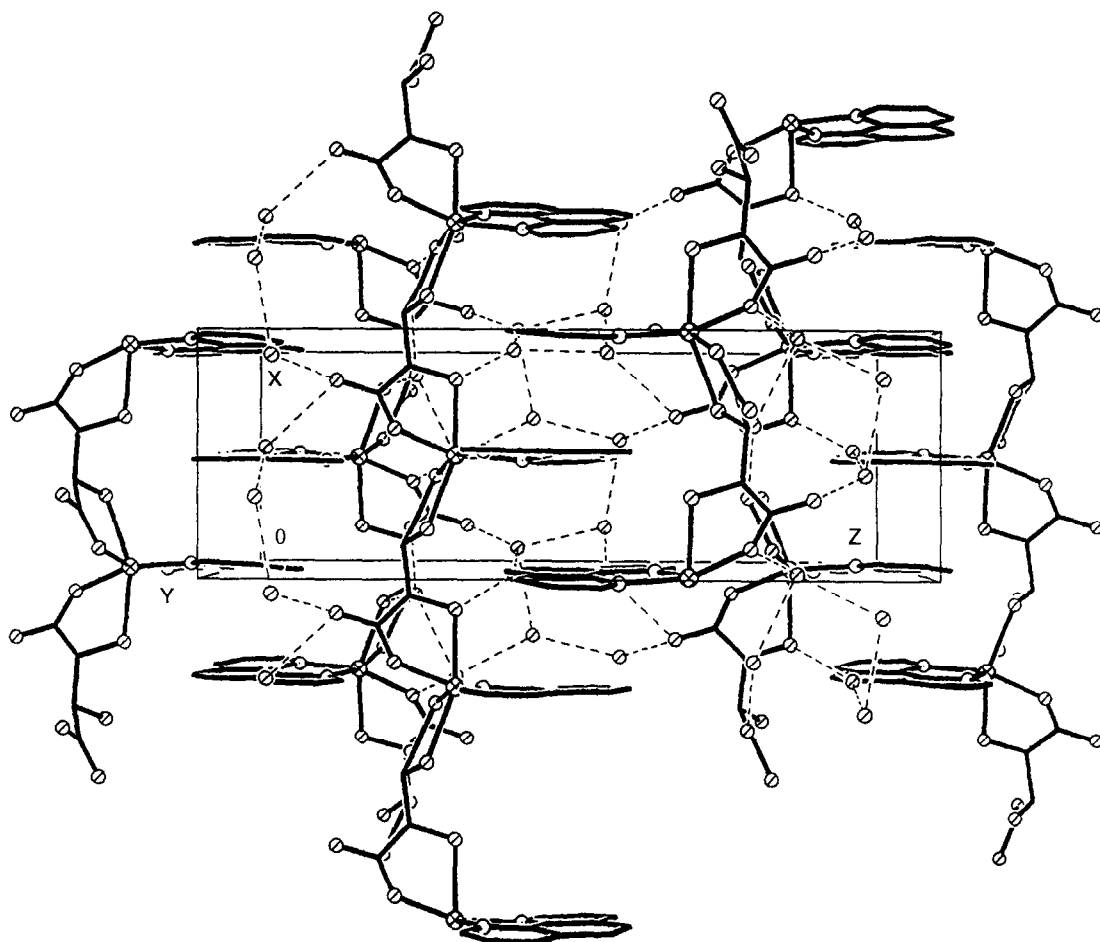


Fig. 2. Polymeric chain of **4** viewed along the *x*-axis.

Conductivity measurements carried out on aqueous solutions of  $[\text{Cu}(\text{L-tar})(\text{bipy})] \cdot 6\text{H}_2\text{O}$  **2** ( $\Lambda_{\text{M}} = 95 \text{ S cm}^2 \text{ mol}^{-1}$ ) and  $[\text{Cu}(\text{L-tar})(\text{phen})] \cdot 4\text{H}_2\text{O}$ , **3** ( $\Lambda_{\text{M}} = 94 \text{ S cm}^2 \text{ mol}^{-1}$ ) indicated that there was some dissociation of the complexes in that solvent to form the ions  $[\text{Cu}(\text{NN})(\text{H}_2\text{O})_n]^{2+}$  and  $(\text{L-tar})^{2-}$  (NN = bipy or phen). In the potential range +0.7 to -0.6 V (versus Ag/AgCl) the cyclic voltammograms of aqueous solu-

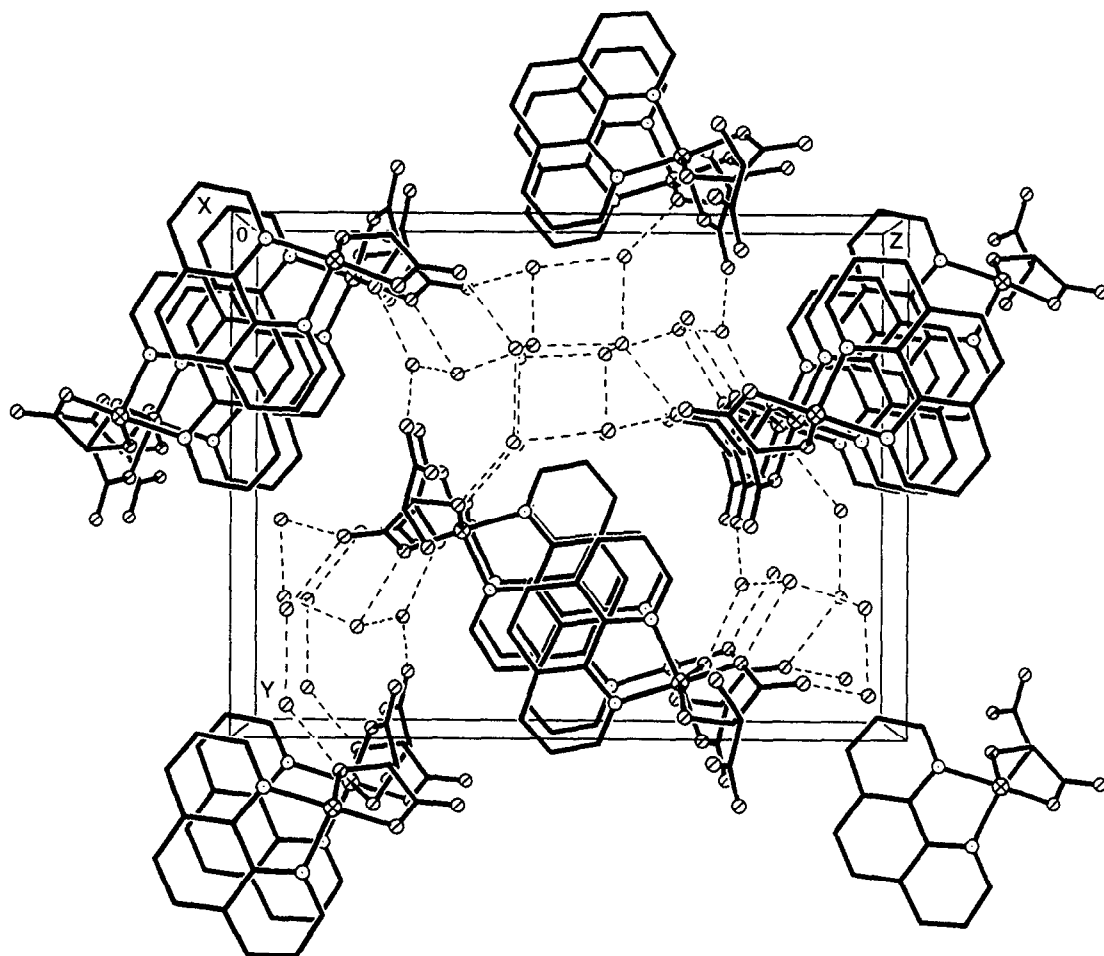
tions of **2** and **3** each showed a single, quasi-reversible wave ( $E_{\text{pc}} - E_{\text{pa}} = 184 \text{ mV}$ ;  $E_{1,2} = 153 \text{ mV}$  and  $E_{\text{pc}} - E_{\text{pa}} = 113 \text{ mV}$ ;  $E_{1,2} = 119 \text{ mV}$ , respectively) for the  $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$  couple.

Routes to the dimolybdenum(II,II) dibenzoyl-L-tartrate complexes are shown in Scheme 1. The air-sensitive, yellow, insoluble complex  $\{[\text{Mo}_2(\text{db-L-tar})] \cdot 5\text{H}_2\text{O}\}_n$  (**5**) formed in almost quantitative yield

Table 1. Selected bond distances (Å) and angles (°) for  $\{[\text{Cu}(\text{L-tar})(\text{phen})] \cdot 6\text{H}_2\text{O}\}_n$  (**4**)

Cu—O(26)#1	1.965(3)	Cu—O(21)	1.997(3)
Cu—N(2)	2.011(4)	Cu—N(1)	2.021(3)
Cu—O(24)#1	2.308(4)	Cu—O(23)	2.328(3)
O(26)#1—Cu—O(21)	95.68(14)	O(26)#1—Cu—N(2)	164.6(2)
O(21)—Cu—N(2)	94.4(2)	O(26)#1—Cu—N(1)	91.97(14)
O(21)—Cu—N(1)	161.6(2)	N(2)—Cu—N(1)	81.95(14)
O(26)#1—Cu—O(24)#1	76.07(13)	O(21)—Cu—O(24)#1	89.22(13)
N(2)—Cu—O(24)#1	92.5(2)	N(1)—Cu—O(24)#1	108.9(2)
O(26)#1—Cu—O(23)	88.23(13)	O(21)—Cu—O(23)	74.93(13)
N(2)—Cu—O(23)	105.6(2)	N(1)—Cu—O(23)	88.6(2)
O(23)#1—Cu—O(23)	156.57(11)		

Symmetry transformations used to generate equivalent atoms: #1  $x+1, y, z$ .

Fig. 3. The unit cell plot of **4** viewed along the *x*-axis.Table 2. Hydrogen bonding distances OH...O (Å) in (**4**)

O21—O1W	2.858(4)	O1W—O5W	2.753(5)
O22—O2W#1	2.784(5)	O1W—O6W#3	2.777(6)
O22—O4W	2.857(5)	O2W—O3W	2.786(5)
O23—O3W	2.663(5)	O2W—O5W#4	2.751(5)
O24—O6W	2.643(4)	O2W—O5W#5	2.743(6)
O25—O1W#2	2.995(6)	O3W—O4W#6	2.806(4)
O25—O6W#2	2.749(5)	O4W—O5W	2.815(5)

Symmetry transformations used to generate equivalent atoms: #1  $1-x, y-0.5, 1.5-z$ ; #2  $1-x, 0.5+y, 1.5-z$ ; #3  $1+x, y, z$ ; #4  $1.5-x, 1-y, 0.5+z$ ; #5  $2-x, 0.5+y, 1.5-z$ ; #6  $1.5-x, 1-y, 0.5+z$ .

by treating the parent tetraacetate  $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_4]$  with an excess of dibenzoyl-*L*-tartaric acid. The red, dimolybdenum(II,II) dicationic complex salt of empirical formula  $[\text{Mo}_2(\text{db-L-tar})(\text{CH}_3\text{CN})_4][\text{BF}_4]_2 \cdot 7\text{H}_2\text{O}$  (**6**) was prepared by reacting the blue salt  $[\text{Mo}_2(\text{CH}_3\text{CN})_8][\text{BF}_4]_4$  with dibenzoyl-*L*-tartaric acid. The red solution formed upon dissolution of **6** in

acetonitrile under nitrogen rapidly decomposed (went dark brown).

Metathesis of the diruthenium(II,III) complex  $\{[\text{Ru}_2(\mu\text{-O}_2\text{CCH}_3)_4\text{Cl}]\}_n$  with dibenzoyl-*L*-tartaric acid gave a high yield of a brown, insoluble complex of formulation  $\{[\text{Ru}_2(\text{db-L-tar})_{2.5}]\}_n \cdot 2\text{H}_2\text{O}$  (**7**) (Scheme 1). The room temperature magnetic moment of **7** (4.1 B.M. per  $\text{Ru}_2$  unit) was in the region reported for other diruthenium(II,III) carboxylates [3].

The green, diamagnetic dirhodium(II,II) complex  $\{[\text{Rh}_2(\text{db-L-tar})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}\}_n$  (**8**) was obtained directly upon reacting the tetracarboxylate salt  $\text{Na}_4[\text{Rh}_2(\mu\text{-O}_2\text{CO})_4] \cdot 2.5\text{H}_2\text{O}$  with dibenzoyl-*L*-tartaric acid (Scheme 1).

The IR spectra of all of the dibenzoyl-*L*-tartrate complexes contained a prominent band at *ca* 1730  $\text{cm}^{-1}$  for the acetyl C=O vibration, and bands attributable to the carboxylate  $\nu_{\text{asym}}(\text{OCO})$  and  $\nu_{\text{sym}}(\text{OCO})$  vibrations were discernible at *ca* 1550 and 1420  $\text{cm}^{-1}$ , respectively. The  $\Delta\nu(\text{OCO})$  values ( $\Delta\nu(\text{OCO}) = \nu_{\text{asym}}(\text{OCO}) - \nu_{\text{sym}}(\text{OCO}) \text{ cm}^{-1}$ ) suggests that the tartrate carboxylate groups in these complexes are in a bridging bidentate coordination mode,

and that there is retention of the metal-to-metal bonded cores of the parent second row precursor complexes.  $\{[\text{Mo}_2(\text{db-L-tar})_2] \cdot 5\text{H}_2\text{O}\}_n$ , **5** and  $\{[\text{Rh}_2(\text{db-L-tar})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}\}_n$ , **8** are likely to have polymeric structures in which opposite ends of the dicarboxylate ligands are bridging different bimetallic cores. This is similar to the general structure postulated to form upon reaction of the tetra(monocarboxylate)  $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_4]$  with dicarboxylic acids [4]. The structure of  $\{[\text{Ru}_2(\text{db-L-tar})_{2.5}] \cdot 2\text{H}_2\text{O}\}_n$ , **7** is believed to be similar to that of polymers **5** and **8**, and with an additional db-L-tar<sup>2-</sup> ligand spanning the axial sites of two adjacent diruthenium cores.  $[\text{Mo}_2(\text{db-L-tar})(\text{CH}_3\text{CN})_4][\text{BF}_4]_2 \cdot 7\text{H}_2\text{O}$  (**6**) may be essentially isostructural with the structurally characterised butanedioic acid salt  $[\text{Mo}_4(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2)_2(\text{CH}_3\text{CN})_{12}][\text{BF}_4]_4 \cdot 3\text{CH}_3\text{CN}^5$  where each dicarboxylate ligand links the two halves of the tetranuclear complex together. Dibenzoyl-L-tartric acid and butanedioic acid each have a four-carbon C–C–C backbone.

## EXPERIMENTAL

Chemicals were purchased from commercial sources and used without further purification. Literature methods were used to prepare  $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_4]$  [6],  $[\text{Mo}_2(\text{CH}_3\text{CN})_8][\text{BF}_4]_4$  [7],  $\{[\text{Ru}_2(\mu\text{-O}_2\text{CCH}_3)_4\text{Cl}]\}_n$  [8] and  $\text{Na}_4[\text{Rh}_2(\mu\text{-O}_2\text{CO})_4] \cdot 2.5\text{H}_2\text{O}$  [9]. Synthesis and reactions of the air- and moisture-sensitive dimolybdenum(II,II) complexes were carried out under N<sub>2</sub> using standard Schlenk techniques. Infrared spectra were recorded as KBr discs in the region 4000–400 cm<sup>-1</sup> on a Nicolet Impact 400D FT-IR Spectrometer. Electronic spectra were run on a Milton Roy Spectronic 3000 Array, and magnetic susceptibility measurements were made at room temperature using a Johnson Matthey Magnetic Susceptibility Balance ( $\mu_{\text{eff}} \pm 0.2$  B.M.). Conductivity measurements were made at 25°C using an AGB Scientific Ltd. model 10 conductivity meter. Cyclic voltammograms (ca 20°C and under N<sub>2</sub>) were recorded using an EG&G Model 264A Polarographic Analyser and the data analysed using the EG&G Condecon software package. A platinum bead and a platinum wire were used as the working and counter electrodes, respectively. Potentials were recorded with respect to a silver–silver chloride reference electrode (3.5 M aqueous KCl). Tetraethylammonium perchlorate (0.1 M) dissolved in water was used as the supporting electrolyte/solvent system. Sample concentration was 4.0 mM. Elemental analysis were carried out by the Microanalytical Laboratory, University College Cork, Ireland.

### Crystal data for **4**

C<sub>16</sub>H<sub>24</sub>CuN<sub>2</sub>O<sub>12</sub>,  $M = 499.91$ , green needle, crystal dimensions 0.75 × 0.12 × 0.10 mm, orthorhombic,  $a = 6.664(1)$ ,  $b = 15.303(1)$ ,  $c = 19.885(2)$  Å,

$U = 2027.9(4)$  Å<sup>3</sup>,  $\mu = 1.146$  mm<sup>-1</sup>, space group  $P2_12_12_1$ ,  $Z = 4$ ,  $F(000) = 1036$ .

### Data collection and processing

Data were collected at 153(2) K on a Siemens P4 four-circle diffractometer using graphite monochromated Mo–K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Unit cell parameters were determined by non-linear least-squares refinement of 41 accurately-centered reflections ( $8 < 2\theta < 25^\circ$ ). Using 1.2°  $\omega$ -scans at 5 min<sup>-1</sup>, 2635 reflections were collected in the range  $4 < 2\theta < 50^\circ$ , 2446 independent reflections ( $R_{\text{int}} = 0.0182$ ) were used in the refinement. Crystal stability was monitored by recording three check reflections every 97 reflections and no decay was observed. Data were collected for Lorentz and polarisation effects and an empirical absorption correction (based on  $\psi$ -scans) was applied ( $T_{\text{min}} = 0.767$ ,  $T_{\text{max}} = 0.831$ ).

### Structure solution and refinement

The positions of the copper atom and some of the diacid were determined by direct methods [10], and a tangent expansion was used to overcome pseudo-symmetry problems. The solvate water molecules were located from difference Fourier maps. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Hydrogen atoms bonded to carbon were inserted at calculated positions with isotropic atomic displacement parameters riding on those of their carrier atoms. The hydrogen atoms associated with oxygen atoms were located from difference maps, assigned a common isotropic atomic displacement parameter and not further refined. All the data were used for refinement on  $F^2$  which converged with  $wR2 = 0.0765$ ,  $GOF = 1.051$  and the conventional  $R = 0.0351$  ( $I > 2\sigma(I)$ ) for 281 parameters. The final difference map showed no residual electron density greater than  $\pm 0.36$  eÅ<sup>-3</sup>. All programs used in the structure refinement are contained in the SHELXL-93 package [11].

### [Cu(L-tar)] (**1**)

*Method (a).* To a stirred solution of dibenzoyl-L-tartaric acid (0.45 g, 1.26 mmol) in distilled water (100 cm<sup>3</sup>) was added  $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2]$  (0.25 g, 0.63 mmol). The resulting green–blue suspension was refluxed for 3.5 h and during this time the condenser was periodically removed to allow some of the liberated acetic acid to escape from the reaction flask. The suspension was filtered whilst hot, and the blue solid product was washed with distilled water, ethanol and ether and then dried *in vacuo*. Yield: 0.12 g (45%).

*Method (b).* The complex was prepared in a similar manner to that outlined in method (a) using the same molar ratios of reactants and employing L-tartaric

acid instead of dibenzoyl-L-tartaric acid. Yield: 0.15 g (56%). %Calc.: C, 22.5; H, 2.8. Found: C, 22.3; H, 2.5%. IR: 3410, 3350, 3100, 2970, 2780, 2640, 1705, 1645, 1580, 1440, 1400, 1370, 1330, 1270, 1245, 1225, 1105, 1080, 1060, 1015, 920, 890, 830, 750, 725, 650, 540, 500, 435  $\text{cm}^{-1}$ .  $\mu_{\text{eff}}$ : 2.2 B.M. per Cu.

[Cu(L-tar)(bipy)] · 6H<sub>2</sub>O (2)

[Cu(L-tar)] (1) (0.1 g, 0.47 mmol) and 2,2'-bipyridine (0.15 g, 0.96 mmol) were refluxed in water (30  $\text{cm}^3$ ) for 1 h. The resulting blue-green solution was filtered whilst hot and on standing the light-blue microcrystalline product deposited. The solid was filtered off, washed with ethanol and diethyl ether, and then dried *in vacuo*. Yield: 0.18 g (80%). Calc.: C, 35.2; H, 5.5; N, 5.9. Found: C, 34.7; H, 3.1; N, 6.1%. IR: 3400, 1620, 1590, 1470, 1450, 1360, 1305, 1285, 1270, 1180, 1160, 1140, 1070, 1060, 1040, 1030, 830, 780, 730, 715, 530  $\text{cm}^{-1}$ .  $\mu_{\text{eff}}$ : 2.2 B.M. per Cu. UV-vis (H<sub>2</sub>O):  $\lambda_{\text{max}} = 707 \text{ nm}$  ( $\epsilon = 168 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ).  $\Lambda_{\text{M}}(\text{H}_2\text{O})$ : 94 S  $\text{cm}^2 \text{ mol}^{-1}$ .

[Cu(L-tar)(phen)] · 4H<sub>2</sub>O (3)

[Cu(L-tar)] (1) (0.1 g, 0.47 mmol) and 1,10-phenanthroline (0.17 g, 0.94 mmol) were refluxed in water (30  $\text{cm}^3$ ) for 1 h. The resulting dark-green solution was filtered whilst hot and on standing the product precipitated as dark-green crystals. The solid was filtered off, washed with ethanol and diethyl ether and then dried *in vacuo*. Yield: 0.17 g (72%). Calc.: C, 41.3; H, 4.8; N, 6.0. Found: C, 41.8; H, 3.6; N, 6.6%. IR: 3380, 1610, 1520, 1430, 1365, 1220, 1140, 1110, 1070, 1000, 920, 880, 855, 830, 720, 520  $\text{cm}^{-1}$ .  $\mu_{\text{eff}}$ : 1.8 B.M. per Cu. UV-vis (H<sub>2</sub>O):  $\lambda_{\text{max}} = 686 \text{ nm}$  ( $\epsilon = 129 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ).  $\Lambda_{\text{M}}(\text{H}_2\text{O})$ : 94 S  $\text{cm}^2 \text{ mol}^{-1}$ .

A crystal of composition {[Cu(L-tar)(phen)] · 6H<sub>2</sub>O}<sub>n</sub> (4) was taken directly from the original mother liquor and used (without drying) for X-ray diffraction studies.

{[Mo(dbLta)<sub>2</sub>] · 5H<sub>2</sub>O}<sub>n</sub> (5)

A suspension of [Mo<sub>2</sub>( $\mu$ -O<sub>2</sub>CCH<sub>3</sub>)<sub>4</sub>] (0.1 g, 0.232 mmol) and dibenzoyl-L-tartaric acid (0.73 g, 0.93 mmol) in deaerated water (20  $\text{cm}^3$ ) was stirred under N<sub>2</sub> at room temperature for 24 h. The yellow product was filtered off, washed with deaerated water, methanol and diethyl ether and then dried *in vacuo*. Yield: 0.19 g (83%). Calc.: C, 43.6; H, 3.2. Found: C, 43.8; H, 3.1%. IR: 3500, 1740, 1720, 1600, 1550, 1455, 1425, 1265, 1180, 1110, 1070, 1025, 715  $\text{cm}^{-1}$ .

[Mo<sub>2</sub>(dbLta)(MeCN)<sub>4</sub>][BF<sub>4</sub>]<sub>2</sub> · 7H<sub>2</sub>O (6)

A blue solution of [Mo<sub>2</sub>(CH<sub>3</sub>CN)<sub>8</sub>][BF<sub>4</sub>]<sub>4</sub> (0.1 g, 0.118 mmol) and dibenzoyl-L-tartaric acid (0.042 g,

0.118 mmol) in acetonitrile (15  $\text{cm}^3$ ) was stirred for 36 h at room temperature. The resulting red solution was reduced to low volume and CH<sub>2</sub>Cl<sub>2</sub> was added slowly with stirring to precipitate the red product. The solid was filtered off, washed with CH<sub>2</sub>Cl<sub>2</sub> and diethyl ether and then dried *in vacuo*. Yield: 0.09 g (80%). Calc.: C, 30.9; H, 3.8; N, 5.5. Found: C, 30.9; H, 3.3; N, 5.5%. IR: 3410, 2340, 2280, 1720, 1600, 1550, 1450, 1420, 1265, 1070, 715, 685, 535, 525  $\text{cm}^{-1}$ . UV-vis (MeCN):  $\lambda_{\text{max}} = 520 \text{ nm}$  ( $\epsilon = 838 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ).

{[Ru<sub>2</sub>(dbLta)<sub>2.5</sub>] · 2H<sub>2</sub>O}<sub>n</sub> (7)

{[Ru<sub>2</sub>( $\mu$ -O<sub>2</sub>CCH<sub>3</sub>)<sub>4</sub>Cl]}<sub>n</sub> (0.1 g, 0.21 mmol) and dibenzoyl-L-tartaric acid (0.3 g, 0.84 mmol) were refluxed for 4 h in a water:methanol (1:1) mixture (30  $\text{cm}^3$ ). The precipitated brown product was filtered off, washed with water, methanol and diethyl ether and then dried *in vacuo*. Yield: 0.17 g (70%). Calc.: C, 47.9; H, 3.0. Found: C, 48.2; H, 3.4%. IR: 3420, 1730, 1625, 1605, 1500, 1455, 1415, 1320, 1265, 1180, 1110, 1075, 1030, 710  $\text{cm}^{-1}$ .  $\mu_{\text{eff}}$ : 4.1 B.M. per Ru<sub>2</sub>.

{[Rh<sub>2</sub>(dbLta)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] · H<sub>2</sub>O}<sub>n</sub> (8)

To a stirred suspension of Na<sub>4</sub>[Rh<sub>2</sub>(O<sub>2</sub>CO)<sub>4</sub>] · 2.5H<sub>2</sub>O (0.025 g, 0.043 mmol) in H<sub>2</sub>O (5  $\text{cm}^3$ ) was added dibenzoyl-L-tartaric acid (0.06 g, 0.17 mmol). The resulting blue solution was heated at 90°C for 1 h, and the product precipitated as a green powder. The solid was filtered off, washed with hot water, a small amount of methanol, diethyl ether and then dried *in vacuo*. Yield: 0.036 g (86%). Calc.: C, 44.6; H, 2.9. Found: C, 44.9; H, 2.9. IR: 3500, 1730, 1620, 1455, 1410, 1320, 1270, 1180, 1110, 1070, 715, 520  $\text{cm}^{-1}$ .

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