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Preparation of transition metal complexes of bicyclo[2.2.1]hept-5-ene-2-carboxylic acid ($C_7H_9CO_2H$) and X-ray crystal structure of $[Cu_2\{(\pm)\text{-}endo\text{-}\mu\text{-}O_2CC_7H_9\}_4(CH_3OH)_2]\cdot 2CH_3OH$

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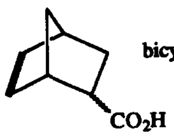
Abstract—Metathesis reactions were used to prepare a range of dicopper(II), monocopper(I), diruthenium(II, III), dimolybdenum(II,II) and dirhodium(II,II) complexes of either racemic or resolved forms of *endo*- and *exo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid ($C_7H_9CO_2H$). The X-ray crystal structure of $[Cu_2\{(\pm)\text{-}endo\text{-}\mu\text{-}O_2CC_7H_9\}_4(CH_3OH)_2]\cdot 2CH_3OH$ shows the two copper(II) ions bridged by two (+)-*endo*-bicyclo[2.2.1]hept-5-ene-2-carboxylate anions and two (−)-*endo*-bicyclo[2.2.1]hept-5-ene-2-carboxylate anions. Methanol molecules occupy the two *trans* axial sites, and there are also two methanol molecules hydrogen bonded to opposite carboxyl oxygens. © 1997 Elsevier Science Ltd

Keywords: bicyclo[2.2.1]hept-5-ene-2-carboxylic acid; complex; copper; ruthenium; molybdenum; rhodium.

Metal carboxylates are a useful class of reagents, particularly for organic synthesis [1]. For example, rhodium carboxylates are very versatile hydrogenation catalysts, and inter- and intramolecular hydrogen transfers from alcohols to olefins have been achieved using a variety of ruthenium carboxylates. In addition, there has been much interest in the role played by copper(I) carboxylates in the decarboxylation of organic acids, and copper(II) carboxylates have found use in organic oxidations. Diruthenium(II,III) and dimolybdenum(II,II) tetracarboxylates have also been successfully employed as catalysts for the polymerization of cyclic alkenes [2].

The present paper concerns the coordination chemistry of bicyclo[2.2.1]hept-5-ene-2-carboxylic acid ($C_7H_9CO_2H$). The attractive features of this particular acid are that it is easy to synthesise, it can be resolved into enantiomeric forms and, as it has a somewhat large and spherical organic framework, its metal complexes are likely to be soluble in a wide range of organic solvents. Herein we detail the preparation and properties of a range of dicopper(II), monocopper(I), diruthenium(II,III), dimolybdenum(II,II) and dirhodium(II,II) complexes comprising either racemic or resolved forms of bicyclo[2.2.1]hept-5-ene-2-carboxylic acid. In addition, the X-ray crystal structure of $[Cu_2\{(\pm)\text{-}endo\text{-}\mu\text{-}O_2CC_7H_9\}_4(CH_3OH)_2]\cdot 2CH_3OH$ (**4**) is presented.



bicyclo[2.2.1]hept-5-ene-2-carboxylic acid
$C_7H_9CO_2H$

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RESULTS AND DISCUSSION

In the past we have used a mixture of racemic (±)-*endo*- and racemic (±)-*exo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acids (*ca.* 4 : 1 (±)-*endo* : (±)-*exo*) to prepare the neutral bimetallic complexes [Mo_2{(±)-*endo*-/(±)-*exo*-μ-$O_2CC_7H_9$)$_4$}], [Ru_2{(+)-*endo*-/(±)-*exo*-μ-$O_2CC_7H_9$)$_4$}Cl}] and [Cu_2{(+)-*endo*-/(+)-*exo*-μ-$O_2CC_7H_9$)$_4$}(H_2O)$_2$] [3], and also the dicationic complex salt [Mo_2{(±)-*endo*-/(±)-*exo*-μ-$O_2CC_7H_9$)$_2$}(CH_3CN)$_4$][BF_4]$_2$·2H_2O [4].* The present dicopper(II) complexes [Cu_2{(±)-*exo*-μ-$O_2CC_7H_9$}$_4$(H_2O)$_2$] (**1**), [Cu_2{(±)-*endo*-μ-$O_2CC_7H_9$}$_4$(H_2O)$_2$] (**2**). [Cu_2{(±)-*endo*-μ-$O_2CC_7H_9$}$_4$] (**3**), [Cu_2{(±)-*endo*-μ-$O_2CC_7H_9$}$_4$(CH_3OH)$_2$·2CH_3OH (**4**), [Cu_2{(−)-*endo*-μ-$O_2CC_7H_9$}$_4$(H_2O)$_2$] (**5**) and [Cu_2{(−)-*endo*-μ-$O_2CC_7H_9$}$_4$] (**6**) were readily prepared by reacting either [Cu_2(μ-O_2CCH_3)$_4$(H_2O)$_2$] or $Cu(OH)_2$ with the appropriate form of bicyclo[2.2.1]hept-5-ene-2-carboxylic acid. The reduced mononuclear copper(I) complexes [Cu{(±)-*endo*-μ-$O_2CC_7H_9$}(PPh_3)$_2$] (**7**) and [Cu{(−)-*endo*-μ-$O_2CC_7H_9$}(PPh_3)$_2$] (**8**) were isolated in good yield upon reacting the corresponding dicopper(II) parent tetracarboxylates **2** and **5**, respectively, with an excess of triphenylphosphine. The copper(II) complexes **1–6** were soluble in methanol, ethanol, acetronitrile, ethyl acetate and *n*-hexane, and the copper(I) complexes **7** and **8** were soluble in methanol and ethanol.

Metathesis of the diruthenium(II,III) complex [Ru_2(μ-O_2CCH_3)$_4$Cl] with the selected form of bicyclo[2.2.1]hept-5-ene-2-carboxylic acid afforded [Ru_2{(±)-*exo*-μ-$O_2CC_7H_9$)}$_4$Cl] (**9**), [Ru_2{(±)-*endo*-μ-$O_2CC_7H_9$)}$_4$Cl]·H_2O (**10**) and [Ru_2{(−)-*endo*-μ-$O_2CC_7H_9$}$_4$Cl]·H_2O (**11**). The mixed-acid pentacarboxylates [Ru_2{(±)-*endo*-/(±)-*exo*-μ-$O_2CC_7H_9$)}$_5$]·2H_2O (**12**) and [Ru_2{(±)-*endo*-/(±)-*exo*-μ-$O_2CC_7H_9$)}$_4$(CF_3CO_2)] (**13**) were made by reacting [Ru_2{(±)-*endo*-/(±)-*exo*-μ-$O_2CC_7H_9$}$_4$Cl}]^3 with the silver salts Ag{(±)-*endo*-/(±)-*exo*-$O_2CC_7H_9$} and Ag(O_2CCF_3), respectively. [Ru_2{(±)-*exo*-μ-$O_2CC_7H_9$)}$_5$] (**14**), [Ru_2{(±)-*endo*-μ-$O_2CC_7H_9$)}$_5$] (**15**) and [Ru_2{(−)-*endo*-μ-$O_2CC_7H_9$)}$_5$] (**16**) formed in high yield upon metathesis of [Ru_2(μ-O_2CCH_3)$_4$(O_2CCH_3)$_2$]·0.7H_2O with the chosen bicyclo[2.2.1]hept-5-ene-2-carboxylic acid. The diruthenium(II,III) complexes **9–16** were soluble in methanol, ethanol, THF and acetone.

The air-sensitive, yellow dimolybdenum(II,II) complexes [Mo_2{(±)-*exo*-μ-$O_2CC_7H_9$)}$_4$] (**17**), [Mo_2(±)-*endo*-μ-$O_2CC_7H_9$)}$_4$] (**18**) and [Mo_2{(−)-*endo*-μ-$O_2CC_7H_9$)}$_4$] (**19**) were prepared in almost quantitative yield by treating the parent tetraacetate [Mo_2(μ-O_2CCH_3)$_4$] with an excess of the respective (±)-*exo*, (±)-*endo*- and (−)-*endo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid. Complexes **17–19** were air-sensitive, and were slightly soluble only in hot methanol.

The dirhodium(II,II) complex [Rh_2{(−)-*endo*-μ-$O_2CC_7H_9$)}$_4$]·2H_2O (**20**) was obtained directly upon reacting the tetracarbonate salt Na_4[Rh_2(μ-CO_3)$_4$]·2.5H_2O with resolved (−)-*endo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid. Complex **20** was slightly soluble in methanol and in ethanol.

The binuclear complexes are all thought to contain four bridging bidentate carboxylate ligands and this has indeed been demonstrated in the case for [Cu_2{(±)-*endo*-μ-$O_2CC_7H_9$}$_4$(CH_3OH)$_2$]·2CH_3OH (**4**). The X-ray crystal structure of **4** is shown in Fig. 1 and selected bond lengths and angles are listed in Table 1. One crystallographic asymmetric unit consists of half of the depicted molecule, the other half being generated by the inversion centre. The complex comprises two copper(II) ions bridged by two (+)-*endo*- and two (−)-*endo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid anions. Methanol molecules occupy the two *trans* axial sites, and there are also two methanol molecules hydrogen bonded to opposite carboxyl oxygens {O(5)}. The Cu—Cu separation (2.580 Å) is similar to that reported for other complexes of the general formula [Cu_2(μ-O_2CR)$_4$(L)$_2$] [1].

The mononuclear bis(triphenylphosphine) copper(I) complexes [Cu{(±)-*endo*-μ-$O_2CC_7H_9$}(PPh_3)$_2$] (**7**) and [Cu{(−)-*endo*-μ-$O_2CC_7H_9$}(PPh_3)$_2$] (**8**) are thought to be four-coordinate with the carboxylate ligand in the O,O chelating (η^2) coordination mode. Although the complexes appeared to be quite air-stable in the solid state they slowly oxidized when dissolved in alcohol.

EXPERIMENTAL

Literature methods were used to prepare [Ru_2(μ-O_2CCH_3)$_4$Cl] [5], [Ru_2(μ-O_2CCH_3)$_4$(O_2CCH_3)$_2$]·0.7H_2O [6], [Ru_2{(±)-*endo*-/(±)-*exo*-μ-$O_2CC_7H_9$)}$_4$Cl}] [3], [Mo_2(μ-O_2CCH_3)$_4$ [7] and Na_4[Rh_2(μ-CO_3)$_4$]·2.5H_2O [8]. (±)-*endo*]-/(±)-*exo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (which is a mixture of racemic (±)-*endo*- and racemic (±)-*exo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acids was prepared as outlined below, and the racemic (±)-*exo*- and racemic (±)-*endo*- acids were separated from one another by the previously reported [9] iodolactone method. Resolved (−)-*endo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid was synthesised using the $TiCl_4$-catalysed Diels–Alder addition of the propenoate of D-pantolactone to cyclopentadiene [10]. (**CAUTION**—all bicyclo[2.2.1]hept-5-ene-2-carboxylic acids give off a stench.) IR spectra (KBr discs) were recorded in the region 4000–200 cm^{-1} on a Perkin-Elmer 783 grating spectrometer, and solution electronic absorption spectra were obtained using a Milton Roy Spectronic 3000 Array. Conductivity readings (25°C, 10^{-3} M solutions

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*These complexes were originally formulated simply as [Mo_2(μ-$O_2CC_7H_9$)$_4$], [Ru_2(μ-$O_2CC_7H_9$)$_4$Cl}], [Cu_2(μ-$O_2CC_7H_9$)$_4$(H_2O)$_2$] and [Mo_2(μ-$O_2CC_7H_9$)$_2$(CH_3CN)$_4$][BF_4]$_2$·2H_2O in [3] and [4].

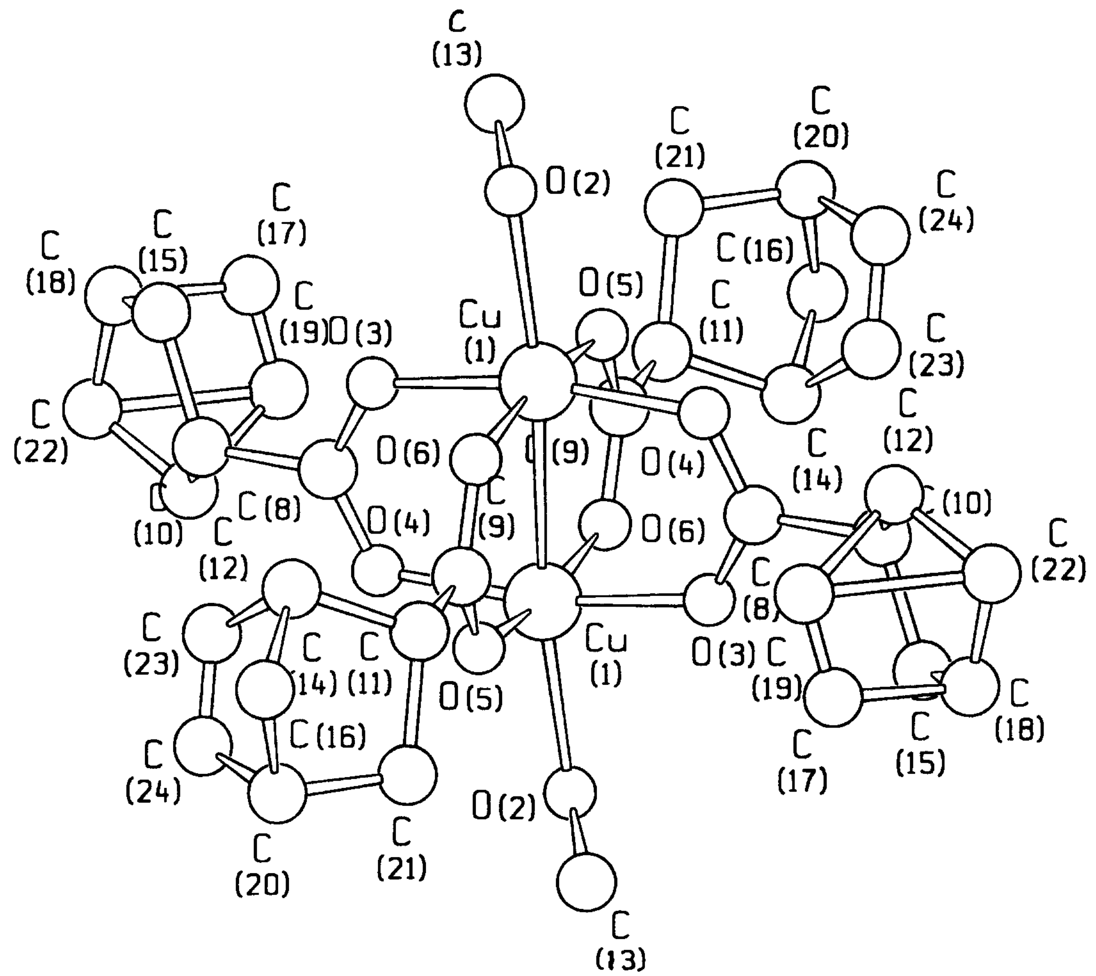

Fig. 1. X-ray crystal structure of $[Cu_2\{(\pm)\text{-}endo\text{-}\mu\text{-}O_2CC_7H_9\}_4(CH_3OH)_2]\cdot 2CH_3OH$ (**4**) (methanol molecules of solvation not shown).

in MeOH) were taken with an AGB model 10 conductivity meter and optical rotations were measured with an Optical Activity Ltd AA-100 polarimeter ($\lambda = 589$ nm). Solid-state, room temperature magnetic susceptibilities were made on a Johnson Matthey Magnetic Susceptibility Balance. FAB mass spectra were run on a Kratos Analytical Profile HV-4 double focusing high resolution spectrometer using a CsI gun. Complex (**16**) was mixed in a glycerol : nitrobenzyl alcohol (50 : 50) matrix and the accelerating potential was 8 kV. Complex (**20**) was mixed in nitrobenzyl alcohol and the accelerating potential was 10 kV. Elemental analyses were carried out by the Microanalytical Laboratory, University College Cork, Ireland.

Crystallography

The diffraction data was measured on a MAR image plate scanner, with a 3 kW sealed tube Mo-K_α X-ray source. 95 frames were measured with an exposure time of 120 s per frame and oscillation of 2°. Data reduction/processing was carried out using MARXDS. 469 strong points were extracted from the first 15 frames, 379 of which had intensity greater than 100 and were used to index the diffraction pattern. The structure was solved by direct methods using SHELXS 86 [11], and least squares refinement carried out using SHELXL 93 [12]. The large anisotropic thermal parameters for the carboxylate ligands indicate disorder. Thermal analysis was not possible because the *R*-index of the observed and calculated U_{ij}'s was too high. Since it also proved impossible to resolve the positions which the atoms would occupy should there be more than one conformation present in the crystal lattice, the nature of the disorder could not be confirmed. Crystal data and structure refinement are shown in Table 2.

(±)-*endo*-/(±)-*exo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid

The mixture of (±)-*endo* and (±)-*exo* acids was prepared using a modification of the method of Alder

Table 1. Molecular dimensions for **4**, bond lengths (Å) and angles (°)

Cu(1)—O(4)	1.930(4)
Cu(1)—O(3)	1.934(3)
Cu(1)—O(5)	1.937(4)
Cu(1)—O(2)	1.944(4)
Cu(1)—O(1)	2.189(4)
Cu(1)—Cu(1)#1	2.5804(12)
O(4)—Cu(1)—O(3)	90.8(2)
O(4)—Cu(1)—O(5)	169.6(2)
O(3)—Cu(1)—O(5)	88.1(2)
O(4)—Cu(1)—O(2)	89.3(2)
O(3)—Cu(1)—O(2)	169.3(2)
O(5)—Cu(1)—O(2)	89.9(2)
O(4)—Cu(1)—O(1)	95.1(2)
O(3)—Cu(1)—O(1)	100.6(2)
O(5)—Cu(1)—O(1)	95.3(2)
O(2)—Cu(1)—O(1)	90.0(2)
O(4)—Cu(1)—Cu(1)#1	82.20(12)
O(3)—Cu(1)—Cu(1)#1	87.48(12)
O(5)—Cu(1)—Cu(1)#1	87.42(12)
O(2)—Cu(1)—Cu(1)#1	81.97(12)
O(1)—Cu(1)—Cu(1)#1	171.56(11)
C(6)—O(1)—Cu(1)	115.6(4)

Hydrogen bonding exists between donor oxygen atom O(6) on the solvent methanol group and carboxyl group O(5) with the following bond lengths and angle; Donor—H···Acceptor D—A (Å) D—H (Å) H···A (Å) D—H···A (°) O(6)—H(7)···O(5) 2.7721 0.8199 1.9770 163.22.

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

and Stein [13]. Redistilled propenoic acid (36 g, 0.5 mol) was dissolved in diethyl ether (50 cm^3) and the solution was then cooled on ice. Freshly cracked cyclopentadiene (40 g, 0.6 mol) was added dropwise and with stirring, maintaining the temperature at 0°C. The resulting mixture was stirred for 18 h with the solution temperature being allowed to warm to room temperature after 12 h. The ether was evaporated off and the crude acid mixture was then dissolved in water (200 cm^3) containing potassium carbonate (64 g, 0.5 mol) producing a vigorous effervescence. This aqueous solution containing a mixture of potassium bicyclo[2.2.1]hept-5-ene-2-carboxylate salts was washed with 50 : 50 ether : *n*-hexane (3 x 50 cm^3) to remove any dicyclopentadiene, and then acidified to pH 1–2 with HCl (effervescence). The acid mixture separated as oily drops which were then extracted into ether (3 x 50 cm^3). The combined extracts were dried over magnesium sulphate containing decolourizing charcoal. After evaporating off the ether the acid mixture was redistilled under high vacuum, the fraction boiling at 95–96°C (0.6 mm Hg) being collected (unreacted propenoic acid distilled over at *ca* 35°C (0.6 mm Hg)). This product was found to be a mixture of *ca* 4 : 1 (±)-*endo* : (±)-*exo* acids. Mixtures of racemic (±)-*exo*-and racemic (±)-*endo*- acids containing enhanced amounts of the (±)-*exo*- acid were prepared in refluxing cyclohexane using the method outlined by Rooney *et al.* [14].

Ag{(±)-*endo*-/(±)-*exo*-$O_2CC_7H_9$}

Aqueous ammonium hydroxide (1.0 mol dm^{-3}, 12 cm^3, 12 mmol) was added to a suspension of the acid mixture (±)-*endo*-/(±)-*exo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (1.5 g, 11 mmol) in water (20 cm^3). After dissolution of the acid mixture was complete a solution of silver nitrate (1.7 g, 10 mmol) in water (20 cm^3) was added dropwise with stirring. The creamy white precipitate was filtered off, washed with water (4 x 2 cm^3) and dried *in vacuo* at 40°C.

[Cu_2{(±)-*exo*-$O_2CC_7H_9$}$_4$(H_2O)$_2$] (**1**)

Freshly prepared $Cu(OH)_2$ (0.2 g, 2.1 mmol) was added to a solution of (±)-*exo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (1.1 g, 8.0 mmol) in methanol (20 cm^3) and the resulting solution was stirred at room temperature for 96 h. The solution was filtered and then concentrated by rotary evaporation to a blue oil. Ethyl acetate (10 cm^3) was added and then the solution was again reduced to a low volume. Diethyl ether (3 cm^3) and *n*-hexane (3 cm^3) were sequentially added and a pale blue solid (**a**) precipitated. This solid was filtered off and the filtrate was stored at *ca* 4°C for 12 h. Solid (**a**) was washed with diethyl ether and dried *in vacuo*; yield: 0.09 g. The light blue product (**1**) precipitated from the filtrate, and this was filtered off, washed with diethyl ether and then allowed to air dry; yield: 0.19 g (25%). (**1**) Found: C, 54.3; H, 5.6. Calc.: C, 54.0; H, 5.7%; μ_{eff} = 2.0 B.M. per Cu_2, 1.4 B.M. per Cu; IR: 3400, 3060, 2967, 2873, 1732, 1707, 1581, 1413, 1282, 905, 862, 718, 694, 428 cm^{-1}; λ_{max}(MeCN) = 669 mm (ε = 571 dm^3 mol^{-1} cm^{-1}). Product (**a**): no empirical formula could be fitted to this complex. Found: C, 43.3; H, 4.4%; IR: 3060, 2980, 2880, 1580, 1415, 1335, 1310, 1285, 1250, 1225, 1130, 1035, 1020, 905, 860, 780, 760, 725, 690, 540, 500, 425, 295 cm^{-1}.

[Cu_2{(±)-*endo*-μ-$O_2CC_7H_9$}$_4$(H_2O)$_2$] (**2**) *and* [Cu_2{(±)-*endo*-μ-$O_2CC_7H_9$}$_4$] (**3**)

Method (*i*). Freshly prepared $Cu(OH)_2$ (0.2 g, 2.1 mmol) was added to a solution of (±)-*endo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (1.1 g, 8.0 mmol) in methanol (20 cm^3) and the resulting solution was stirred at room temperature for 96 h. Precipitated **2** was removed by filtration, washed with diethyl ether and dried *in vacuo*; yield: 0.095 g (13%). The filtrate was concentrated by rotary evaporation to a blue oil. Ethyl acetate (10 cm^3) was added and the solution was again reduced to a low volume. Diethyl ether (3 cm^3) and *n*-hexane (3 cm^3) were sequentially added and a

Table 2. Crystal data and structure refinement for **4**

Empirical formula	$C_{36}H_{52}Cu_2O_{12}$
Formula weight	802.21
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	9.420(6)
b (Å)	9.756(6)
c (Å)	10.937(6)
α (°)	90.47(6)
β (°)	100.39(6)
γ (°)	105.55(6)
V (Å^3)	950.7
Z	1
Density (calculated) (Mg/m^3)	1.400
Absorption coefficient (mm^{-1})	1.178
F(000)	420
Crystal size (mm)	0.1 × 0.3 × 0.3
2θ range (°)	3.46–25.03
Index ranges	$0 <= h <= 11, -11 <= k <= 11, -12 <= l <= 12$
Reflections collected	5769
Independent reflections	2927 [R(int) = 0.0290]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2927/0/231
Goodness-of-fit on F^2	1.111
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0613$, $wR_2 = 0.1609$
R indices (all data)	$R_1 = 0.0810$, $wR_2 = 0.1748$
Extinction coefficient	0.024(6)
Largest diff. peak and hole (e Å^{-3})	0.443 and −0.584

pale blue solid (**b**) precipitated. This solid was filtered off and the filtrate was stored at *ca* 4°C for 12 h. Solid (**b**) was washed with diethyl ether and then dried *in vacuo*; yield: 0.015 g. The light blue anhydrous product (**3**) precipitated from the filtrate, and this was filtered off, washed with diethyl ether and allowed to air dry; yield of **3**: 0.12 g (17%).

Method (*ii*). $[Cu_2(\mu\text{-}O_2CCH_3)_4(H_2O)_2]$ (0.4 g, 1.0 mmol) and (±)-*endo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (1.16 g, 8.4 mmol) were refluxed in a water : methanol (1 : 1) mixture (30 cm^3) for 12 h. The light blue solid (**2**) was filtered off, washed with diethyl ether and air dried; yield: 0.36 g (51%). (**2**) Found: C, 54.0; H, 5.5. Calc.: C, 54.0; H, 5.7% $\mu_{eff} = 2.0$ B.M. per Cu_2, 1.4 B.M. per Cu; IR: 3400, 3050, 2970, 2860, 1585, 1420, 1335, 1305, 1290, 1255, 1220, 1150, 1125, 1105, 1020, 910, 835, 810, 770, 705, 680, 465, 290 cm^{-1}; λ_{max}(MeCN) = 668 nm (ε = 568 dm^3 mol^{-1} cm^{-1}). Product (**b**): no empirical formula could be fitted to this complex. Found: C, 43.1; H, 4.2%; IR: 3050, 2970, 2860, 1585, 1420, 1335, 1305, 1290, 1105, 990, 910, 770, 705, 635, 600, 465, 290 cm^{-1}. (**3**) Found: C, 56.9; H, 6.0. Calc.: C, 56.9; H, 5.4%; $\mu_{eff} = 2.0$ B.M. per Cu_2, 1.4 B.M. per Cu; IR: 3050, 2970, 2860, 1585, 1420, 1335, 1305, 1290, 1255, 1220, 1150, 1125, 1105, 1020, 910, 835, 810, 770, 705, 680, 465, 290 cm^{-1}.

$[Cu_2\{(\pm)\text{-}endo\text{-}\mu\text{-}O_2CC_7H_9\}_4(CH_3OH)_2]\cdot 2CH_3OH$ (**4**)

Crystals of **4** suitable for X-ray structural analysis were obtained by slow evaporation of a methanolic solution of **2**.

$[Cu_2\{(-)\text{-}endo\text{-}\mu\text{-}O_2CC_7H_9\}_4(H_2O)_2]$ (**5**) *and* $[Cu_2(-)\text{-}endo\text{-}\mu\text{-}O_2CC_7H_9\}_4]$ (**6**)

Method (*i*). Freshly prepared $Cu(OH)_2$ (0.1 g, 1.0 mmol) was added to a solution of resolved (−)-*endo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (0.55 g, 4.0 mmol) in methanol (20 cm^3) and the resulting solution was stirred at room temperature for 96 h. Precipitated complex **5** was removed by filtration, washed with diethyl ether and dried *in vacuo*; yield: 0.04 g (11%). The filtrate was concentrated by rotary evaporation to a blue oil. Ethyl acetate (10 cm^3) was added and the solution was again reduced to a low volume. Diethyl ether (3 cm^3) and *n*-hexane (3 cm^3) were sequentially added and a pale blue solid (**c**) precipitated. Solid (**c**) was filtered off and the filtrate was stored at *ca.* 4°C for 12 h. Solid (**c**) was washed with diethyl ether and dried *in vacuo*; yield: 0.01 g. The light blue product (**6**) precipitated from the filtrate, and this was filtered off, washed with diethyl ether and allowed to air dry; yield: 0.055 g (16%).

Method (*ii*). $[Cu_2(\mu\text{-}O_2CCH_3)_4(H_2O)_2]$ (0.2 g, 0.5 mmol) and resolved (−)-*endo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (0.58 g, 4.2 mmol) were refluxed in a water : methanol (1 : 1) mixture (20 cm^3) for 12 h. The light blue solid (**5**) was filtered off, washed with diethyl ether and air dried; yield: 0.16 g (45%). (**5**) Found: C, 54.4; H, 5.7. Calc.: C, 54.0; H, 5.7%. $\mu_{eff} = 2.0$ B.M. per Cu_2, 1.4 B.M. per Cu; IR: 3400, 3060, 2930, 2860, 1580, 1425, 1380, 1340, 1310, 1290, 1255, 1225, 1155, 1135, 1110, 1030, 915, 840, 810, 710, 685, 600, 555, 470, 370, 285 cm^{-1}; λ_{max}(MeCN) = 668 nm ($\varepsilon = 552$ dm^3 mol^{-1} cm^{-1}); $[\alpha]^{20}_{589} = -154°$ (*c*, 0.033, CH_3OH). (**6**) Found: C, 56.7; H, 5.8. Calc.: C, 56.9; H, 5.4%; $\mu_{eff} = 2.0$ B.M. per Cu_2, 1.4 B.M. per Cu; IR: 3060, 2930, 2860, 1580, 1425, 1380, 1340, 1310, 1290, 1255, 1225, 1155, 1135, 1110, 1030, 915, 840, 810, 710, 685, 600, 555, 470, 370, 285 cm^{-1}. (**c**) No empirical formula could be fitted to this complex. Found: C, 43.3; H, 4.5%; IR: 3060, 2970, 2870, 1580, 1420, 1335, 1315, 1290, 1260, 1230, 1135, 1110, 1025, 990, 840, 810, 775, 710, 640, 615, 570, 380, 295 cm^{-1}.

[Cu{(±)-*endo*-μ-$O_2CC_7H_9$}$(PPh_3)_2$] (7)

Complex (**2**) (0.1 g, 0.14 mmol) and triphenylphosphine (0.2 g, 0.76 mmol) were refluxed together in methanol (15 cm^3) until the blue colour of the solution was discharged (*ca* 1.5 h). The solution was reduced to near dryness and then diethyl ether (5 cm^3) was added. Stirring of the resulting mixture resulted in the precipitation of the white product. The solid was filtered off, washed with diethyl ether and then dried *in vacuo*; yield: 0.12 g (59%). Found: C, 72.4; H, 5.8. Calc.: C, 72.9; H, 5.4%; IR: 3060, 2970, 2870, 1640, 1585, 1570, 1560, 1480, 1435, 1400, 1340, 1265, 1255, 1225, 1185, 1160, 1130, 1100, 1070, 1030, 1000, 905, 860, 840, 780, 745, 695, 515, 505, 440, 425 cm^{-1}.

[Cu{(−)-*endo*-μ-$O_2CC_7H_9$}$(PPh_3)_2$] (8)

Complex **8** was prepared by the same method as **7** and using complex **5** instead of complex **2** as the starting material. Yield: 0.1 g (49%). Found: C, 72.4; H, 5.9. Calc.: C, 72.9; H, 5.4%; IR: same as complex **7**.

[Ru_2{(±)-*exo*-μ-$O_2CC_7H_9$)}$_4$Cl] (9)

$[Ru_2(\mu\text{-}O_2CCH_3)_4Cl]$ (0.1 g, 0.21 mmol) and racemic (±)-*exo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (0.18 g, 1.3 mmol) were refluxed for 4 h in a water : methanol (1 : 1) mixture (30 cm^3). The brown solution was filtered and concentrated to low volume *in vacuo*, and upon standing the light-brown product began to precipitate. Ethyl acetate (*ca* 15 cm^3) was then added and the mixture stirred well. The resulting suspension was again concentrated to low volume and a small quantity of *n*-hexane added. The solid was filtered off, washed with an *n*-hexane : diethyl ether (1 : 1) mixture (10 cm^3) and then air dried; yield: 0.14 g (85%). Found: C, 49.0; H, 4.7; Cl, 3.3. Calc.: C, 48.9; H, 4.6; Cl, 4.5%; $\mu_{eff} = 3.39$ B.M. per Ru_2; IR: 3030, 2980, 2870, 1520, 1475, 1455, 1420, 1335, 1310, 1285, 1270, 1225, 1035, 1020, 910, 865, 800, 720, 690, 580, 520, 455, 345 cm^{-1}; λ_{max}(MeOH) = 432 nm ($\varepsilon = 632$ dm^3 mol^{-1} cm^{-1}); Λ_M(MeOH) = 68 S cm^2 mol^{-1}.

[Ru_2{(±)-*endo*-μ-$O_2CC_7H_9$)}$_4$Cl]·H_2O (10)

This complex was prepared in a similar manner to (**9**) using racemic (±)-*endo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid; yield: (80%). Found: C, 47.6; H, 4.8; Cl, 4.1. Calc.: C, 47.8; H, 4.8; Cl, 4.4%; $\mu_{eff} = 4.0$ B.M. per Ru_2; IR: 3420, 3050, 2960, 2860, 1730, 1630, 1420, 1364, 1333, 1287, 1258, 1020, 905, 836, 773, 712, 682, 595, 485, 335 cm^{-1}; λ_{max}(MeOH) = 429 nm ($\varepsilon = 640$ dm^3 mol^{-1} cm^{-1}); Λ_M(MeOH) = 79 S cm^2 mol^{-1}.

[Ru_2{(−)-*endo*-μ-$O_2CC_7H_9$}$_4$Cl]·H_2O (11)

This complex was prepared in a similar manner to (**9**) using resolved (−)-*endo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid; yield: 0.13 g (79%). Found: C, 48.2; H, 5.1; Cl, 4.1. Calc.: C, 47.8; H, 4.8; Cl, 4.4%; $\mu_{eff} = 4.0$ B.M. per Ru_2; IR: 3700, 3050, 2960, 2860, 1605, 1540, 1465, 1420, 1330, 1300, 1285, 1260, 1220, 1125, 1105, 1020, 910, 830, 810, 770, 710, 680, 600, 490, 330 cm^{-1}; λ_{max}(MeOH) = 429 nm ($\varepsilon = 643$ dm^3 mol^{-1} cm^{-1}); Λ_M(MeOH) = 65 S cm^2 mol^{-1}.

[Ru_2{(±)-*endo*-/(±)-*exo*-μ-$O_2CC_7H_9$)}$_5$]·$2H_2O$ (12)

[Ru_2{(±)-*endo*-/(±)-*exo*-μ-$O_2CC_7H_9$}$_4$Cl}] (0.39 g, 0.5 mmol), Ag{(±)-*endo*-/(±)-*exo*-$O_2CC_7H_9$} (0.12 g, 0.5 mmol) and the mixture (±)-*endo*-/(±)-*exo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (0.1 g, 0.7 mmol) were stirred in methanol (30 cm^3) with gentle heating for 0.5 h. The precipitated AgCl was filtered off and the filtrate was evaporated *in vacuo* at *ca* 30°C to a dark brown tar. The tar was dissolved in ethyl acetate (30 cm^3) and again evaporated to low volume. On addition of diethyl ether (20 cm^3) and *n*-hexane (30 cm^3) the product precipitated as a dull brown powder. The solid was filtered off, washed with diethyl ether : *n*-hexane (10 cm^3) and dried *in vacuo*; yield: 0.34 g (74%). Found: C, 51.8; H, 5.1. Calc.: C, 52.0; H, 5.4%; IR: 3060, 2970, 2870, 1730, 1635, 1525, 1440, 712 cm^{-1}.

[Ru_2{(±)-*endo*-/(±)-*exo*-μ-$O_2C_7H_9$)}$_4$$(CF_3CO_2)$] (13)

[Ru_2{(±)-*endo*-/(±)-*exo*-μ-$O_2CC_7H_9$}$_4$Cl}] (0.39 g, 0.5 mmol) and silver trifluoroacetate (0.11 g, 0.5

mmol) were reacted in the manner described for the synthesis of **12** (none of the mixture (±)-*endo*-/(±)-*exo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid was used in this preparation). The product was recovered as bright orange-brown microcrystals; yield: 0.35 g (81%). Found: C, 46.0; H, 4.2; F, 6.6. Calc.: C, 47.3; H, 4.2; F, 6.6%; $\mu_{eff} = 4.0$ B.M. per Ru_2; IR: 3060, 2970, 2870, 1730, 1635, 1450, 1420, 1290, 710 cm^{-1}; $\lambda_{max}(CH_3OH) = 432$ nm ($\varepsilon = 700$ dm^3 mol^{-1} cm^{-1}).

$[Ru_2\{(\pm)\text{-}exo\text{-}\mu\text{-}O_2CC_7H_9)\}_5]$ (**14**)

$[Ru_2(\mu\text{-}O_2CCH_3)_4(O_2CCH_3)_2]\cdot 0.7H_2O$ (0.1 g, 0.18 mmol) and (±)-*exo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (0.22 g, 1.6 mmol) were refluxed together in a water : methanol (1 : 1) mixture (30 cm^3) for 5 h, and the resulting red-brown solution was then concentrated to low volume *in vacuo*. Upon standing at room temperature the product precipitated out as a brown solid. Ethyl acetate was added with stirring, and the mixture was again concentrated to low volume and *n*-hexane (*ca* 2 cm^3) then added. The product was filtered off, washed with an *n*-hexane : diethyl ether (1 : 1) mixture (10 cm^3) and then dried *in vacuo*; yield: 0.12 g (76%). Found: C, 54.4; H, 5.1. Calc.: C, 54.1; H, 5.1%; $\mu_{eff} = 4.3$ B.M. per Ru_2; IR: 3060, 2970, 2875, 1520, 1475, 1455, 1420, 1335, 1310, 1285, 1270, 1225, 1035, 1020, 910, 865, 800, 720, 690, 580, 520, 455, 350 cm^{-1}; $\lambda_{max}(MeOH) = 430$ nm ($\varepsilon = 659$ dm^3 mol^{-1} cm^{-1}); $\Lambda_M(MeOH) = 47$ S cm^2 mol^{-1}.

$[Ru_2\{(\pm)\text{-}endo\text{-}\mu\text{-}O_2CC_7H_9)\}_5]$ (**15**)

This complex was prepared in a similar manner to **14** and using (±)-*endo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid; yield: 0.133 g (83%). Found: C, 54.4; H, 5.1. Calc.: C, 54.1; H, 5.1%; $\mu_{eff} = 4.3$ B.M. per Ru_2; IR: 3050, 2970, 2870, 1625, 1520, 1425, 1340, 1300, 1290, 840, 810, 775, 710, 680, 590, 490, 335 cm^{-1}.

$[Ru_2\{(-)\text{-}endo\text{-}\mu\text{-}O_2CC_7H_9)\}_5]$ (**16**)

This complex was prepared in a similar manner to **14** and using resolved (−)-*endo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid; yield: 0.12 g (76%). Found: C, 54.2; H, 5.1. Calc.: C, 54.1; H, 5.1% $\mu_{eff} = 4.2$ B.M. per Ru_2; IR: 3050, 2970, 2870, 1625, 1520, 1420, 1340, 1300, 1290, 840, 810, 775, 710, 680, 590, 490, 335 cm^{-1}; $\lambda_{max}(MeOH) = 427$ nm ($\varepsilon = 660$ dm^3 mol^{-1} cm^{-1}); $\Lambda_M = 45$ S cm^2 mol^{-1}; FAB/MS (*m*/*z*): $[Ru_2(\mu\text{-}O_2CC_7H_9)_4 + H]^+$ (751).

$[Mo_2\{(\pm)\text{-}exo\text{-}\mu\text{-}O_2CC_7H_9)\}_4]\cdot 2H_2O$ (**17**)

A mixture of $[Mo_2(\mu\text{-}O_2CCH_3)_4]$ (0.25 g, 0.58 mmol) and (±)-*exo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (1.1 g, 7.9 mmol) in dry methanol (15 cm^3) was stirred under nitrogen at room temperature for 12 h. The volume of the suspension was then reduced to *ca* 5 cm^3 *in vacuo* (without heating). The yellow product was filtered off, washed with ice-cold, deoxygenated methanol and then with diethyl ether, and then dried *in vacuo*; yield: 0.38 g (84%). Found: C, 49.8; H, 4.9. Calc.: C, 49.5; H, 5.2%; IR: 3060, 2970, 2870, 1635, 1615, 1500, 1415, 1330, 1305, 1280, 1265, 1220, 1020, 970, 905, 860, 790, 720, 685, 555, 505, 425 cm^{-1}.

$[Mo_2\{(\pm)\text{-}endo\text{-}\mu\text{-}O_2CC_7H_9)\}_4]\cdot 2H_2O$ (**18**)

This was prepared in a similar manner to **17** and using (±)-*endo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid; yield: 0.4 g (89%). Found: C, 49.5; H, 4.9. Calc.: C, 49.5; H, 5.2%; IR: 3060, 2970, 2870, 1635, 1615, 1500, 1420, 1335, 1305, 1290, 1260, 1225, 1150, 1130, 1020, 910, 840, 810, 770, 710, 680, 570, 460, 385, 320 cm^{-1}.

$[Mo_2\{(-)\text{-}\mu\text{-}O_2CC_7H_9)\}_4]\cdot 2H_2O$ (**19**)

This was prepared in a similar manner to **17** and using resolved (−)-*endo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid; yield: 0.39 g (87%). Found: C, 49.5; H, 4.8. Calc.: C, 49.5; H, 5.2%; IR: 3050, 2960, 2860, 1615, 1490, 1420, 1330, 1300, 1285, 1260, 1220, 1150, 1125, 1105, 1020, 980, 910, 835, 805, 765, 710, 680, 570, 460, 385, 325 cm^{-1}.

$[Rh_2\{(-)\text{-}endo\text{-}\mu\text{-}O_2CC_7H_9)\}_4]\cdot 2H_2O$ (**20**)

$Na_4[Rh_2(\mu\text{-}CO_3)_4]\cdot 2.5H_2O$ (0.1 g, 0.17 mmol) and resolved (−)-*endo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (0.24 g, 1.7 mmol) were refluxed for 10 h in a water : methanol (1 : 1) mixture (15 cm^3). The precipitated dark green product was filtered off, washed with hot water, methanol and finally with diethyl ether; yield: 0.07 g (50%). Found: C, 49.0; H, 5.4. Calc.: C, 48.6; H, 5.1%; IR: 3400, 2960, 2870, 1585, 1420, 1335, 1295, 1255, 1220, 1105, 1020, 915, 835, 810, 775, 750, 715, 685, 600, 595 cm^{-1}; FAB/MS (*m*/*z*): $[Rh_2(\mu\text{-}O_2CC_7H_9)_4 + H]^+$ (755), $[Rh_2(\mu\text{-}O_2CC_7H_9)_5 + 3H]^+$ (894).

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