Table 1. Selected geometric parameters (Å, °)

| | U | • | |
|----------|-------------|----------|------------|
| U1O1 | 1.744 (5) | U1—08 | 2.486 (4) |
| U1—O2 | 1.755 (6) | U1-06 | 2.488 (4) |
| U1_07 | 2.441 (4) | U1-04 | 2.490 (3) |
| U1-05 | 2.464 (3) | O11—C13 | 1.201 (8) |
| U1—O3 | 2.469 (3) | O12—C13 | 1.300 (10) |
| 01—U1—02 | 179.6 (3) | 08—U1—06 | 120.90 (14 |
| 07—U1—05 | 121.62(12) | 08—U1—O4 | 119.37 (12 |
| 05 | 118.99 (12) | 06—U1—04 | 119.51 (12 |

Table 2. Hydrogen-bonding geometry (Å, °)

| D — $H \cdot \cdot \cdot A$ | <i>D</i> H | $\mathbf{H} \cdot \cdot \cdot \mathbf{A}$ | $D \cdot \cdot \cdot A$ | $D = H \cdot \cdot \cdot A$ |
|---------------------------------------|------------|---|-------------------------|-----------------------------|
| N2—H2···O13 | 0.86 | 1.98 | 2.840(7) | 175 |
| N1—H82A···O10 ⁱ | 0.89 | 1.98 | 2.820 (6) | 157 |
| N1—H82 <i>B</i> ···O11" | 0.89 | 2.27 | 2.882 (7) | 126 |
| N1—H82 <i>B</i> ···O8 ⁱⁿ | 0.89 | 2.41 | 2.968 (5) | 121 |
| N1—H82 <i>C</i> ···O3 [™] | 0.89 | 2.03 | 2.899 (8) | 165 |
| N3—H85A···O10 [™] | 0.86 | 2.11 | 2.946 (5) | 164 |
| N3—H85 <i>B</i> ····O4 [™] | 0.86 | 2.09 | 2.917 (6) | 160 |
| N4—H4D···O5 ^{iv} | 0.86 | 2.09 | 2.937 (6) | 167 |
| N4—H4 <i>E</i> ···O6` | 0.86 | 2.45 | 3.143 (7) | 138 |
| 012—H14· · · 09 ^{v1} | 0.82 | 1.75 | 2.565 (6) | 170 |
| 013-H13A···O2 ^{vi} | 0.85 | 2.32 | 2.965 (9) | 133 |
| $O13 - H13B \cdot \cdot \cdot O7^{v}$ | 0.85 | 1.93 | 2.762 (6) | 164 |
| Symmetry codes: (i) | x 1 1 | π (ii) $r = 1$ | | × 1 |

Symmetry codes: (i) $-x, \frac{1}{2}+y, 1-z$; (ii) x-1, y, z; (iii) $1-x, \frac{1}{2}+y, 1-z$; (iv) $-x, y - \frac{1}{2}, 1-z$; (v) x-1, y, z-1; (v) $1-x, y - \frac{1}{2}, 1-z$.

All H atoms were placed at calculated positions and refined as riding using the *SHELXL*97 (Sheldrick, 1997) defaults, except those of the water molecule, which could not be located directly and were positioned at calculated positions given by an energy profile calculation (see *Comment*). One of the methyl groups (C2) is disordered over two alternate positions with occupancies close to 50%. The two disordered C atoms were refined isotropically with a common atomic displacement parameter. Examination of the crystal structure with *PLATON* (Spek, 1995) showed that there are no further solvent-accessible voids in the crystal lattice.

Data collection: CAD-4 Software (Enraf-Nonius, 1989). Cell refinement: CAD-4 Software. Data reduction: HEL-ENA (Spek, 1997). Program(s) used to solve structure: SHELXS97 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL97. Molecular graphics: ORTEPII (Johnson, 1976). Software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1332). Services for accessing these data are described at the back of the journal.

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Absolute configuration of *exo-syn-syn*dicarbonyl(η^5 -cyclopentadienyl)-[(1,2,3- η)-(1*R*,2*S*,3*S*)-1-phenylbut-2en-1-yl]molybdenum(II)

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Abstract

The absolute configuration of the title complex, $[Mo(C_5H_5)(C_{10}H_{11})(CO)_2]$, has been determined. The allyl moiety adopts an *exo* conformation with respect to the cyclopentadienyl group.

Comment

We report herein the structure and absolute configuration of *exo-syn-syn*-dicarbonyl(η^5 -cyclopentadienyl)[(1,2,3- η)-(1*R*,2*S*,3*S*)-1-phenylbut-2-en-1-yl]molybdenum(II), (I), a key intermediate in the on-going synthesis of cryptophycin antibiotics (Golakoti *et al.*, 1995). As Fig. 1 reveals, the η^3 -allyl moiety adopts an *exo* conformation with respect to the cyclopentadienyl ligand and is nearly fully eclipsed with respect to the Mo(CO)₂ fragment. The three C atoms of the η^3 -allyl unit in (I) are more symmetrically bonded to the Mo atom than in a related tris-pyrazolylborate complex (Ward *et al.*,



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1995) and the Mo—C distances are consistently shorter. This more symmetrical arrangement is reflected in the bow angle β (Murrall & Welch, 1986) of 90.5 (7)°, and the small bond-length difference of 0.02 Å between the Mo atom and the two terminal C atoms of the η^3 -allyl ligand. The tilt angle τ (Murrall & Welch, 1986) is 103.1 (6)°, which is in the expected range for similar η^3 -allyl complexes (Kaduk *et al.*, 1977; Murrall & Welch, 1986).



Fig. 1. The molecular structure of (I) with the atom-numbering scheme and 50% probability displacement ellipsoids. H atoms are drawn as spheres of arbitrary radii.

Fig. 1 shows that the substituents on the η^3 -allyl group adopt a syn configuration. While the substituent C atoms are virtually coplanar with the central C atoms of the allyl unit $[C1-C2-C3-C3] = 179.8 (4)^{\circ}$ and $C3-C2-C1-C111 = -179.9(3)^{\circ}$, the C2-C1-C111-C116 torsion angle of 13.0(5)° indicates that the phenyl group is rotated out of the η^3 -allyl plane and is projected away from the metal. This is assumed to be due to unfavourable steric interactions between the ortho-phenyl-H atoms and the neighbouring allyl-H atoms (H116···H2 = 2.19 and H112···H1 = 2.39 Å). This steric strain is further relieved by the opening of the C2—C1—C111 bond angle to $124.1(3)^{\circ}$. The undistorted nature of the central η^3 -allyl moiety and the relatively short distance of 2.07 Å between the Mo atom and the centroid of the allylic C atoms may be taken as an indication of stronger bonding and hence greater configurational stability of (I) compared with related tris-pyrazolylborate complexes, which are prone to undergo $\pi - \sigma - \pi$ rearrangements (Ward *et al.*, 1995). Furthermore, the confirmation that complex (I) possesses a syn configuration, reflecting the stereochemistry of the starting alkene (II), is of prime importance for its utility as a synthon.

Experimental

The title complex, (I), was synthesized by the oxidative addition of the homochiral allylic benzoate, (II), to $Mo(CO)_6$ and subsequent ligand exchange with $Li^+ \cdot (C_5H_5)^-$. Single crystals suitable for X-ray analysis were obtained from petroleum ether (fraction 313–353 K) under an argon atmosphere (m.p. 343.5 K).

Crystal data

 $[Mo(C_5H_5)(C_{10}H_{11})(CO)_2]$ $M_r = 348.24$ Orthorhombic $P2_12_12_1$ a = 8.5420 (5) Å b = 11.8734 (7) Å c = 15.0938 (5) Å $V = 1530.85 (14) Å^3$ Z = 4 $D_x = 1.511 \text{ Mg m}^{-3}$ D_{m} not measured

Data collection

Enraf-Nonius Turbo CAD-4 diffractometer Non-profiled $\omega/2\theta$ scans Absorption correction: none 2605 measured reflections 1915 independent reflections (plus 493 Friedel-related reflections) 2291 reflections with

 $I > 2\sigma(I)$

Refinement

| Refinement on F^2 | Extinction correction: |
|---|------------------------------|
| R(F) = 0.026 | SHELXL97 (Sheldrick, |
| $wR(F^2) = 0.070$ | 1997) |
| S = 1.056 | Extinction coefficient: |
| 2408 reflections | 0.087 (3) |
| 184 parameters | Scattering factors from |
| H atoms: see below | International Tables for |
| $w = 1/[\sigma^2(F_o^2) + (0.0503P)^2]$ | Crystallography (Vol. C) |
| + 0.2169 <i>P</i>] | Absolute structure: |
| where $P = (F_o^2 + 2F_c^2)/3$ | Flack (1983) |
| $(\Delta/\sigma)_{\rm max} = 0.002$ | Flack parameter = $-0.06(6)$ |
| $\Delta \rho_{\rm max} = 0.469 \ {\rm e} \ {\rm \AA}^{-3}$ | - |
| $\Delta \rho_{\rm min} = -0.518 \ {\rm e} \ {\rm \AA}^{-3}$ | |

Mo $K\alpha$ radiation

Cell parameters from 25 reflections

 $0.50 \times 0.50 \times 0.45$ mm

 $\lambda = 0.71073 \text{ Å}$

 $\theta = 3.68 - 20.95^{\circ}$

 $\mu = 0.855 \text{ mm}^{-1}$

Hexagonal prism

T = 291 (2) K

Yellow

 $R_{\rm int} = 0.029$ $\theta_{\rm max} = 26.96^{\circ}$

 $h = -10 \rightarrow 1$

 $k = -15 \rightarrow 2$

 $l = -19 \rightarrow 2$

4 standard reflections

frequency: 120 min

intensity decay: 1%

Table 1. Selected geometric parameters (Å, °)

| C1-C2 | 1.419 (5) | C1-Mo1 | 2.374 (3) |
|--------------|------------|-----------------|------------|
| C1-C111 | 1.473 (5) | C2—Mo1 | 2.225 (3) |
| C2C3 | 1.412 (6) | C3—Mo1 | 2.354 (4) |
| C3-C31 | 1.506 (6) | C4—Mol | 1.941 (4) |
| C4—O4 | 1.155 (4) | C5Mo1 | 1.931 (4) |
| C505 | 1.150 (5) | | |
| CIII-CI-Mol | 120.8 (2) | C1C2C3 | 118.9 (4) |
| C1-C2-Mo1 | 77.85 (19) | C2-C3-C31 | 120.7 (4) |
| C2C1Mo1 | 66.39 (17) | C5-Mo1-C4 | 82.04 (17) |
| C2-C3-Mol | 67.13 (19) | Mo1C4O4 | 177.9 (4) |
| C3-C2-Mol | 77.1 (2) | Mo1-C5-05 | 177.0 (4) |
| C31-C3-Mo1 | 119.5 (3) | | |
| C111C1C2C3 | -179.9 (3) | C2-C1-C111-C116 | 13.0 (5) |
| C1-C2-C3-C31 | 179.8 (4) | | |

The H atoms on the three C atoms of the η^3 -allyl ligand were found from difference Fourier maps. All other H atoms were placed in calculated positions (C—H = 0.96 Å) and all H atoms were refined with a riding model.

Data collection: CAD-4 EXPRESS (Enraf-Nonius, 1994). Cell refinement: CAD-4 EXPRESS. Data reduction: XCAD4 (Harms & Wocadlo, 1995). Program(s) used to solve structure: SIR92 (Altomare *et al.*, 1993). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997). Software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1047). Services for accessing these data are described at the back of the journal.

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A tetracopper(II) complex containing two μ -oxamidato-dicopper(II) units linked by croconate anions

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Abstract

The title compound, di- μ -croconato-bis{ μ -[N,N'-bis(3-amino-2,2-dimethylpropyl)oxamidato(2-)-N,O':N',O]-

dicopper(II)} tetrahydrate, $[Cu_4(C_{12}H_{24}N_4O_2)_2(C_5O_5)_2]$ -4H₂O, comprises two μ -oxamidato-dicopper(II) units bridged by croconate ligands to give a tetracopper(II) ring system with crystallographic $\overline{1}$ symmetry; all the copper centres are five-coordinate.

Comment

In the course of our work on copper(II) compounds with the general formula $Cu_2(L)X_2$, where L is N, N'bis(3-amino-2, 2-dimethylpropyl)oxamidate (Cornia *et al.*, 1993), we have found that the complex $Cu_2(L)(croc)$ (croc is croconate) has an unusual structure compared with the chain-like structures of $Cu_2(L)(OAc)_2$, $Cu_2(L)Cl_2$ and $Cu_2(L)Br_2$.

The title compound, di- μ -croconato-bis{ μ -[N, N'-bis-(3-amino-2,2-dimethylpropyl)oxamidato(2-)-N, O':-N', O]dicopper(II)} tetrahydrate, (I), has the molecular formula [Cu₂(L)(C₅O₅)]₂ and can be described as two Cu₂(L) units bridged by croconate ligands to give a tetracopper(II) ring system with crystallographic inversion symmetry. Whereas the oxamidate ligand adopts the common *trans*-bridging mode [Cu₁...Cu₂ = 5.1919(9)Å], the croconate dianion exhibits an unprecedented coordination mode involving three adjacent donor O atoms [Cu₁...Cu₂ⁱ = 4.9925(7)Å; symmetry code: (i) 1 - x, 1 - y, 1 - z], which leads to a marked inequivalence of the two independent copper(II) ions.



An almost perfectly square-planar geometry is formed around the Cu1 atom by the N1/N3/O4 donor set of the bridging oxamidate and the O1 donor of the croconate dianion [maximum deviation from the best plane is 0.057 Å and Cu1 deviates from this plane by 0.0749 (9) Å]. However, the O6 atom provides a longer axial contact [2.619 (2) Å], completing a squarepyramidal coordination.

The basal plane at Cu1 is coplanar with the central oxamidate moiety $[4.0(1)^{\circ}]$. In contrast, the coordination geometry around Cu2 is approximately square pyramidal, with notable distortions.

The croconate dianion provides two O-atom donors, O2 and O6, in basal and apical coordination sites, respectively. The Cu2 atom is displaced from the average basal plane towards the apical O6 atom by 0.1496 (9) Å. The basal plane is affected by a twist-like distortion, with a dihedral angle of 22.07 (6)° between