Table 1. Selected geometric parameters $\left(\AA,^{\circ}\right)$

| U1-O1 | 1.744 (5) | UI-O8 | 2.486 (4) |
| :---: | :---: | :---: | :---: |
| U1-O2 | 1.755 (6) | U1-06 | 2.488 (4) |
| U1-07 | 2.441 (4) | U1-O4 | 2.490 (3) |
| U1-O5 | 2.464 (3) | $\mathrm{Ol1}-\mathrm{Cl} 3$ | 1.201 (8) |
| U1-O3 | 2.469 (3) | O12-C13 | 1.300 (10) |
| O1-U1-O2 | 179.6 (3) | O8-U1-06 | 120.90 (14) |
| O7-U1-O5 | 121.62 (12) | O8-U1-O4 | 119.37 (12) |
| O5-UI-O3 | 118.99 (12) | O6-U1-O4 | 119.51 (12) |

Table 2. Hydrogen-bonding geometry ( $\left(\AA^{\circ}\right)$

| D-H. ${ }^{\text {A }}$ | $D-\mathrm{H}$ | H $\cdots$ A | D.. $A$ | $D-\mathrm{H} \cdots \cdot \mathrm{A}$ |
| :---: | :---: | :---: | :---: | :---: |
| N2-H2 . O13 | 0.86 | 1.98 | 2.840 (7) | 175 |
| $\mathrm{N} 1-\mathrm{H} 82 \mathrm{~A} \cdots \mathrm{Ol} 0^{1}$ | 0.89 | 1.98 | 2.820 (6) | 157 |
| N1-H82B...O11" | 0.89 | 2.27 | 2.882 (7) | 126 |
| $\mathrm{N} 1-\mathrm{H} 82 \mathrm{~B} \cdots \mathrm{O}^{\text {i'1 }}$ | 0.89 | 2.41 | 2.968 (5) | 121 |
| $\mathrm{N} 1-\mathrm{H} 82 \mathrm{C} \cdots \mathrm{O}^{\prime \prime \prime}$ | 0.89 | 2.03 | 2.899 (8) | 165 |
| N3-H85A $\cdots$ O10 ${ }^{16}$ | 0.86 | 2.11 | 2.946 (5) | 164 |
| $\mathrm{N} 3-\mathrm{H} 85 \mathrm{~B} \cdots \mathrm{O}^{1{ }^{12}}$ | 0.86 | 2.09 | 2.917 (6) | 160 |
| N4-H4D . .O5 ${ }^{\text {- }}$ | 0.86 | 2.09 | 2.937 (6) | 167 |
| N4-H4E. . $\mathrm{Ob}^{\text {b }}$ | 0.86 | 2.45 | 3.143 (7) | 138 |
| $\mathrm{O} 12-\mathrm{H} 14 \cdots \mathrm{O}^{\text {¹ }}$ | 0.82 | 1.75 | 2.565 (6) | 170 |
| O13-H13A . $\mathrm{O}^{\text {2 }}$ | 0.85 | 2.32 | 2.965 (9) | 133 |
| $\mathrm{O} 13-\mathrm{H} 13 \mathrm{~B} \cdots \mathrm{O}^{*}$ | 0.85 | 1.93 | 2.762 (6) | 164 |

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) $-x, y-\frac{1}{2}, 1-z ;(\mathrm{v}) x-1, y, z-1 ;$ (vi) $1-x, y-\frac{1}{2}, 1-z$.

All H atoms were placed at calculated positions and refined as riding using the SHELXL97 (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: HELENA (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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## Absolute configuration of exo-syn-syndicarbonyl ( $\eta^{5}$-cyclopentadienyl)-[(1,2,3- $\eta)-(1 R, 2 S, 3 S)-1-p h e n y l b u t-2-$ en-1-yl]molybdenum(II)

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## Abstract

The absolute configuration of the title complex, $\left[\mathrm{Mo}\left(\mathrm{C}_{5} \mathrm{H}_{5}\right)\left(\mathrm{C}_{10} \mathrm{H}_{11}\right)(\mathrm{CO})_{2}\right]$, 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( $\eta^{5}$-cyclopentadienyl) [(1,2,3-$\eta)$-( $1 R, 2 S, 3 S$ )-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 $\eta^{3}$-allyl moiety adopts an exo conformation with respect to the cyclopentadienyl ligand and is nearly fully eclipsed with respect to the $\mathrm{Mo}(\mathrm{CO})_{2}$ fragment. The three C atoms of the $\eta^{3}$-allyl unit in (I) are more symmetrically bonded to the Mo atom than in a related tris-pyrazolylborate complex (Ward et al.,

(I)

(II)
1995) and the Mo-C distances are consistently shorter. This more symmetrical arrangement is reflected in the bow angle $\beta$ (Murrall \& Welch, 1986) of 90.5 (7) ${ }^{\circ}$, and the small bond-length difference of $0.02 \AA$ between the Mo atom and the two terminal C atoms of the $\eta^{3}$-allyl ligand. The tilt angle $\tau$ (Murrall \& Welch, 1986) is 103.1 (6) ${ }^{\circ}$, which is in the expected range for similar $\eta^{3}$ 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 $\eta^{3}$-allyl group adopt a syn configuration. While the substituent C atoms are virtually coplanar with the central C atoms of the allyl unit $\left[\mathrm{C} 1-\mathrm{C} 2-\mathrm{C} 3-\mathrm{C} 31=179.8(4)^{\circ}\right.$ and $\mathrm{C} 3-\mathrm{C} 2-\mathrm{C} 1-\mathrm{C} 111=-179.9(3)^{\circ}$ ], the $\mathrm{C} 2-\mathrm{C} 1-$ C111-C116 torsion angle of $13.0(5)^{\circ}$ indicates that the phenyl group is rotated out of the $\eta^{3}$-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 ( $\mathrm{H} 116 \cdots \mathrm{H} 2=2.19$ and $\mathrm{H} 112 \cdots \mathrm{H} 1=2.39 \AA$ ). This steric strain is further relieved by the opening of the $\mathrm{C} 2-\mathrm{C} 1-\mathrm{C} 111$ bond angle to $124.1(3)^{\circ}$. The undistorted nature of the central $\eta^{3}$-allyl moiety and the relatively short distance of $2.07 \AA$ 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 $\mathrm{Mo}(\mathrm{CO})_{6}$ and subsequent ligand exchange with $\mathrm{Li}^{+} \cdot\left(\mathrm{C}_{5} \mathrm{H}_{5}\right)^{-}$. 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
[ $\left.\mathrm{Mo}\left(\mathrm{C}_{5} \mathrm{H}_{5}\right)\left(\mathrm{C}_{10} \mathrm{H}_{11}\right)(\mathrm{CO})_{2}\right] \quad$ Mo $K \alpha$ radiation
$M_{r}=348.24$
Orthorhombic
$P 2_{1} 2_{1} 2_{1}$
$a=8.5420(5) \AA$
$b=11.8734(7) \AA$
$c=15.0938(5) \AA$
$V=1530.85(14) \AA^{3}$
$Z=4$
$D_{x}=1.511 \mathrm{Mg} \mathrm{m}^{-3}$
$D_{m}$ 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 $F^{2}$
$R(F)=0.026$
$w R\left(F^{2}\right)=0.070$
$S=1.056$
2408 reflections
184 parameters
H atoms: see below
$w=1 /\left[\sigma^{2}\left(F_{o}^{2}\right)+(0.0503 P)^{2}\right.$
$+0.2169 P]$
where $P=\left(F_{o}^{2}+2 F_{c}^{2}\right) / 3$
$(\Delta / \sigma)_{\max }=0.002$
$\Delta \rho_{\text {max }}=0.469 \mathrm{e}^{-3}$
$\Delta \rho_{\text {max }}=0.469 \mathrm{e}^{\AA} \AA^{-3}$
$\Delta \rho_{\text {min }}=-0.518 \mathrm{e}^{-3}$
Table 1. Selected geometric parameters $\left(\AA^{\circ},{ }^{\circ}\right)$

| $\mathrm{Cl}-\mathrm{C} 2$ | $1.419(5)$ | $\mathrm{Cl}-\mathrm{Mol}$ | $2.374(3)$ |
| :--- | :---: | :--- | :---: |
| $\mathrm{C} 1-\mathrm{C} 111$ | $1.473(5)$ | $\mathrm{C} 2-\mathrm{Mol}$ | $2.225(3)$ |
| $\mathrm{C} 2-\mathrm{C} 3$ | $1.412(6)$ | $\mathrm{C} 3-\mathrm{Mol}$ | $2.354(4)$ |
| $\mathrm{C} 3-\mathrm{C} 31$ | $1.506(6)$ | $\mathrm{C} 4-\mathrm{Mol}$ | $1.941(4)$ |
| $\mathrm{C} 4-\mathrm{O} 4$ | $1.155(4)$ | $\mathrm{C} 5-\mathrm{Mol}$ | $1.931(4)$ |
| $\mathrm{C} 5-\mathrm{O} 5$ | $1.150(5)$ |  |  |
| $\mathrm{Cl11-Cl-Mol}$ | $120.8(2)$ | $\mathrm{Cl}-\mathrm{C} 2-\mathrm{C} 3$ | $118.9(4)$ |
| $\mathrm{Cl}-\mathrm{C} 2-\mathrm{Mol}$ | $77.85(19)$ | $\mathrm{C} 2-\mathrm{C} 3-\mathrm{C} 31$ | $120.7(4)$ |
| $\mathrm{C} 2-\mathrm{C} 1-\mathrm{Mol}$ | $66.39(17)$ | $\mathrm{C}-\mathrm{Mol}-\mathrm{C} 4$ | $82.04(17)$ |
| $\mathrm{C} 2-\mathrm{C} 3-\mathrm{Mol}$ | $67.13(19)$ | $\mathrm{Mol}-\mathrm{C} 4-\mathrm{O} 4$ | $177.9(4)$ |
| $\mathrm{C} 3-\mathrm{C} 2-\mathrm{Mol}$ | $77.1(2)$ | $\mathrm{Mol}-\mathrm{C} 5-\mathrm{O}$ | $177.0(4)$ |
| $\mathrm{C} 31-\mathrm{C} 3-\mathrm{Mol}$ | $119.5(3)$ |  |  |
| $\mathrm{C} 111-\mathrm{Cl}-\mathrm{C} 2-\mathrm{C} 3$ | $-179.9(3)$ | $\mathrm{C} 2-\mathrm{Cl}-\mathrm{Cl11-C116}$ | $13.0(5)$ |
| $\mathrm{Cl}-\mathrm{C} 2-\mathrm{C} 3-\mathrm{C} 31$ | $179.8(4)$ |  |  |

The H atoms on the three C atoms of the $\eta^{3}$-allyl ligand were found from difference Fourier maps. All other H atoms were placed in calculated positions ( $\mathrm{C}-\mathrm{H}=0.96 \AA$ ) 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: SHELXL97 (Sheldrick, 1997). Molecular graphics: ORTEP-3 for Windows (Farrugia, 1997). Software used to prepare material for publication: WinGX (Farrugia, 1999).

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## A tetracopper(II) complex containing two $\mu$-oxamidato-dicopper(II) units linked by croconate anions

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#### Abstract

The title compound, di- $\mu$-croconato-bis $\left\{\mu\right.$ - $\left[N, N^{\prime}\right.$-bis(3-amino-2,2-dimethylpropyl)oxamidato(2-)-N, $\left.O^{\prime}: N^{\prime}, O\right]$ -


dicopper(II) $\}$ tetrahydrate, $\left[\mathrm{Cu}_{4}\left(\mathrm{C}_{12} \mathrm{H}_{24} \mathrm{~N}_{4} \mathrm{O}_{2}\right)_{2}\left(\mathrm{C}_{5} \mathrm{O}_{5}\right)_{2}\right]$-$4 \mathrm{H}_{2} \mathrm{O}$, comprises two $\mu$-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 $\mathrm{Cu}_{2}(L) X_{2}$, where $L$ is $N, N^{\prime}$ -bis(3-amino-2,2-dimethylpropyl)oxamidate (Cornia et al., 1993), we have found that the complex $\mathrm{Cu}_{2}(L)$ (croc) (croc is croconate) has an unusual structure compared with the chain-like structures of $\mathrm{Cu}_{2}(L)(\mathrm{OAc})_{2}$, $\mathrm{Cu}_{2}(L) \mathrm{Cl}_{2}$ and $\mathrm{Cu}_{2}(L) \mathrm{Br}_{2}$.

The title compound, di- $\mu$-croconato-bis $\left\{\mu\right.$ - $\left[N, N^{\prime}\right.$-bis-(3-amino-2,2-dimethylpropyl) oxamidato(2-)- $N, O^{\prime}:-$ $N^{\prime}, O$ ]dicopper(II) \} tetrahydrate, (I), has the molecular formula $\left[\mathrm{Cu}_{2}(L)\left(\mathrm{C}_{5} \mathrm{O}_{5}\right)\right]_{2}$ and can be described as two $\mathrm{Cu}_{2}(L)$ 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 $\cdots \mathrm{Cu} 2=$ 5.1919 (9) $\AA$ ], the croconate dianion exhibits an unprecedented coordination mode involving three adjacent donor O atoms [Cu1 $\cdots \mathrm{Cu} 2^{i}=4.9925$ (7) $\AA$; symmetry code: (i) $1-x, 1-y, 1-z$ ], which leads to a marked inequivalence of the two independent copper(II) ions.

(I)

An almost perfectly square-planar geometry is formed around the Cul atom by the $\mathrm{N} 1 / \mathrm{N} 3 / \mathrm{O} 4$ donor set of the bridging oxamidate and the Ol donor of the croconate dianion [maximum deviation from the best plane is $0.057 \AA$ and Cul deviates from this plane by 0.0749 (9) $\AA$ A . However, the O 6 atom provides a longer axial contact [ $2.619(2) \AA$ ], completing a squarepyramidal coordination.

The basal plane at Cu 1 is coplanar with the central oxamidate moiety [ $4.0(1)^{\circ}$ ]. In contrast, the coordination geometry around Cu 2 is approximately square pyramidal, with notable distortions.

The croconate dianion provides two O -atom donors, O 2 and O6, in basal and apical coordination sites, respectively. The Cu 2 atom is displaced from the average basal plane towards the apical 06 atom by 0.1496 (9) $\AA$. The basal plane is affected by a twist-like distortion, with a dihedral angle of $22.07(6)^{\circ}$ between

