

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).

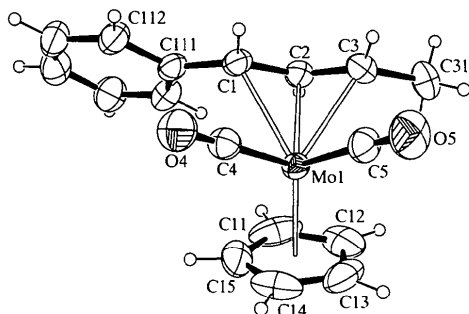


Fig. 1. The molecular structure of (I) with the atom-numbering scheme and 50% probability displacement ellipsoids. H atoms are drawn as spheres of arbitrary radii.

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—C31 = 179.8 (4)° and C3—C2—C1—C111 = -179.9 (3)°], 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)°. 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 π - σ - π 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⁺·(C₅H₅)⁻. 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(C₅H₅)(C₁₀H₁₁)(CO)₂]
M_r = 348.24
 Orthorhombic
*P*2₁2₁
a = 8.5420 (5) Å
b = 11.8734 (7) Å
c = 15.0938 (5) Å
V = 1530.85 (14) Å³
Z = 4
D_x = 1.511 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 25 reflections
 θ = 3.68–20.95°
 μ = 0.855 mm⁻¹
T = 291 (2) K
 Hexagonal prism
 0.50 × 0.50 × 0.45 mm
 Yellow

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 $I > 2\sigma(I)$

*R*_{int} = 0.029
 θ_{\max} = 26.96°
h = -10 → 1
k = -15 → 2
l = -19 → 2
 4 standard reflections
 frequency: 120 min
 intensity decay: 1%

Refinement

Refinement on *F*²
R(*F*) = 0.026
wR(*F*²) = 0.070
S = 1.056
 2408 reflections
 184 parameters
 H atoms: see below
 $w = 1/[\sigma^2(F_o^2) + (0.0503P)^2 + 0.2169P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 0.469 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.518 \text{ e } \text{Å}^{-3}$

Extinction correction: *SHELXL97* (Sheldrick, 1997)
 Extinction coefficient: 0.087 (3)
 Scattering factors from *International Tables for Crystallography* (Vol. C)
 Absolute structure: Flack (1983)
 Flack parameter = -0.06 (6)

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)
C2—C3	1.412 (6)	C3—Mo1	2.354 (4)
C3—C31	1.506 (6)	C4—Mo1	1.941 (4)
C4—O4	1.155 (4)	C5—Mo1	1.931 (4)
C5—O5	1.150 (5)		
C111—C1—Mo1	120.8 (2)	C1—C2—C3	118.9 (4)
C1—C2—Mo1	77.85 (19)	C2—C3—C31	120.7 (4)
C2—C1—Mo1	66.39 (17)	C5—Mo1—C4	82.04 (17)
C2—C3—Mo1	67.13 (19)	Mo1—C4—O4	177.9 (4)
C3—C2—Mo1	77.1 (2)	Mo1—C5—O5	177.0 (4)
C31—C3—Mo1	119.5 (3)		
C111—C1—C2—C3	-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: *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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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

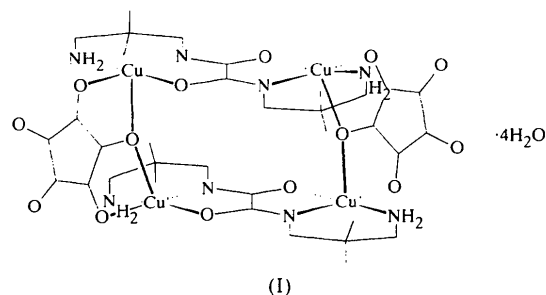
The title compound, di- μ -croconato-bis{ μ -[*N,N'*-bis(3-amino-2,2-dimethylpropyl)oxamidato(2-)-*N,O'*:*N',O*]-

dicopper(II)} tetrahydrate, [Cu₄(C₁₂H₂₄N₄O₂)₂(C₅O₅)₂·4H₂O], comprises two μ -oxamidato-dicopper(II) units bridged by croconate ligands to give a tetracopper(II) ring system with crystallographic $\bar{1}$ symmetry; all the copper centres are five-coordinate.

Comment

In the course of our work on copper(II) compounds with the general formula Cu₂(L)X₂, where *L* is *N,N'*-bis(3-amino-2,2-dimethylpropyl)oxamidate (Cornia *et al.*, 1993), we have found that the complex Cu₂(L)(croc) (croc is croconate) has an unusual structure compared with the chain-like structures of Cu₂(L)(OAc)₂, Cu₂(L)Cl₂ and Cu₂(L)Br₂.

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···Cu2¹ = 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 square-pyramidal coordination.

The basal plane at Cu1 is coplanar with the central oxamidate moiety [4.0(1)°]. 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