Data collection

Siemens SMART diffractometer
ω scans
Absorption correction: multi-scan (*SHELXTL*; Sheldrick, 1994)
$T_{\min} = 0.287$, $T_{\max} = 0.560$
9492 measured reflections
5842 independent reflections
5407 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.028$
$\theta_{\max} = 27.51°$
$h = -11 \rightarrow 11$
$k = -8 \rightarrow 12$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.064$
$S = 1.120$
5660 reflections
427 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.011P)^2 + 2.5925P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.13$ e Å^{-3}
$\Delta\rho_{\min} = -0.67$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0000 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Au—N	2.019 (3)	C3—C4	1.403 (6)
Au—P	2.2420 (8)	C4—C12	1.375 (5)
N—C1	1.336 (4)	C9—C11	1.453 (5)
N—H1	0.89 (5)	C9—C14	1.496 (5)
O1—C9	1.247 (4)	C10—C13	1.485 (6)
O2—C10	1.229 (5)	C10—C12	1.489 (5)
C1—C2	1.433 (5)	C11—C12	1.426 (5)
C1—C11	1.442 (5)	C13—C14	1.404 (5)
C2—C3	1.365 (6)		
N—Au—P	178.21 (9)	C11—C9—C14	119.0 (3)
C1—N—Au	128.0 (3)	O2—C10—C13	120.8 (4)
C1—N—H1	111 (3)	O2—C10—C12	121.3 (4)
Au—N—H1	122 (3)	C13—C10—C12	117.9 (3)
N—C1—C2	119.7 (3)	C12—C11—C1	119.2 (3)
N—C1—C11	123.6 (3)	C12—C11—C9	120.0 (3)
C2—C1—C11	116.7 (3)	C1—C11—C9	120.8 (3)
C3—C2—C1	122.1 (4)	C4—C12—C11	121.6 (3)
C2—C3—C4	121.0 (4)	C4—C12—C10	117.0 (3)
C12—C4—C3	119.4 (4)	C11—C12—C10	121.4 (3)
O1—C9—C11	123.1 (3)	C14—C13—C10	120.3 (3)
O1—C9—C14	117.9 (3)	C13—C14—C9	121.3 (3)

Crystal decay was checked during the data reduction and no decay was observed. The structure was solved by direct methods. H atoms were found from the difference Fourier synthesis and refined in the isotropic approximation. The largest peak in the difference electron-density map was found at a distance of 0.94 Å from the Au atom.

Data collection: *SMART* (Siemens, 1995*a*). Cell refinement: *SAINT* (Siemens, 1995*b*). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL* (Sheldrick, 1994). Software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1166). Services for accessing these data are described at the back of the journal.

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3-(η^3-Allyl)-3,3-dicarbonyl-4-(dimethyl sulfido)-3,1,2-molybdadicarba-*closo*-dodecaborane(12)

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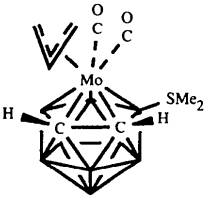
Abstract

The title charge-compensated allyl carbamolybdaborane 3-(η^3-C_3H_5)-3,3-$(CO)_2$-4-SMe_2-3,1,2-*closo*-$MoC_2B_9H_{10}$, or $[Mo(C_3H_5)(C_4H_{16}B_9S)(CO)_2]$, has been synthesized and its solid-state structure determined. In the solid state, the conformation of the $\{Mo(\eta^3\text{-}C_3H_5)(CO)_2\}$ fragment is such that the carbonyl ligands are approximately *trans* to the cage C atoms and the conformation of the allyl group is *exo*.

Comment

We are currently interested in the syntheses and stereochemistries of charge-compensated carbametallaboranes derived from 9-SMe_2-7,8-*nido*-$C_2B_9H_{11}$ (carb′H) (Plesek *et al.*, 1978; Cowie *et al.*, 1988) and its analogues (Rosair *et al.*, 1997). These investigations have included the preparation of compounds in which the carb′ ligand (*i.e.* deprotonated carb′H) is bound to $\{ML\}$, $\{ML_2\}$ and $\{ML_3\}$ fragments (Douek & Welch, 1993). We report here an example of such a metal complex, (I), of carb′ with an $\{ML_4\}$ fragment, $\{Mo(\eta^3\text{-}C_3H_5)(CO)_2\}$.



(I)

The molecule 3-(η^3-C_3H_5)-3,3-$(CO)_2$-4-SMe_2-3,1,2-*closo*-$MoC_2B_9H_{10}$ crystallized with no imposed symmetry. A perspective view of the compound showing the numbering scheme adopted is presented in Fig. 1.

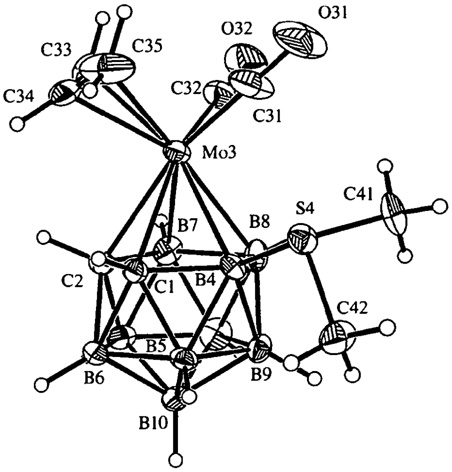


Fig. 1. Perspective view of compound (I) with 40% probability displacement ellipsoids, except for H atoms, which have artificial radii of 0.1 Å for clarity. B11 is antipodal to B4 and B12 is antipodal to C1.

Compound (I) displays the expected *closo* molecular architecture, as predicted by empirical electron-counting rules (Wade, 1976). The cage C—C connectivity is 1.595 (9) Å in length, which is essentially the same as that found in 3,3,3-$(CO)_3$-4-SMe_2-3,1,2-*closo*-$MnC_2B_9H_{10}$ [1.585 (3) Å; Cowie *et al.*, 1990]. The C1—B4 connectivity is 1.666 (9) Å in length, showing no lengthening compared with the other C—B connectivities, which range from 1.653 (12) to 1.738 (9) Å. The B—B connectivities lie in the range 1.746 (13)–1.808 (11) Å. The Mo—C_{cage} distances of 2.414 (6) and 2.407 (6) Å for Mo3—C1 and Mo3—C2, respectively, are marginally shorter than those in the analogous charge-compensated dimethyl-substituted carbamolybdaborane 3-(η^3-C_3H_5)-3,3-$(CO)_2$-8-OEt_2-1,2-Me_2-3,1,2-*closo*-$MoC_2B_9H_{10}$, (II) [2.436 (3) and 2.484 (3) Å; Mullica *et al.*, 1994]. The Mo—B lengths are 2.417 (8), 2.379 (8) and 2.445 (9) Å for bonds involving atoms B4, B7 and B8, respectively. The allyl fragment is bound symmetrically to the Mo atom [C33—C34 1.40 (2) and C34—C35 1.39 (2) Å] and adopts an *exo* conformation, as found in compound (II) and also in the cyclopentadienyl analogue (η^5-C_5H_5)$Mo(CO)_2$(η^3-C_3H_5), (III) (Faller *et al.*, 1980). The $\{Mo(\eta^3\text{-}C_3H_5)(CO)_2\}$ fragment adopts a conformation in which the carbonyl ligands are approximately *trans* to the cage C atoms and *cis* to B4, B7 and B8. Such a conformation is expected and has been rationalized in terms of the frontier molecular orbitals of the carb′ fragment (Douek & Welch, 1993). The Mo—C_{allyl} lengths of 2.337 (8), 2.221 (9) and 2.334 (10) Å for bonds involving C33, C34 and C35, respectively, are similar to the corresponding distances found in (II) [2.342 (4), 2.234 (4) and 2.365 (4) Å] and (III) [2.359 (3), 2.236 (4) and 2.359 (3) Å]. Likewise, the Mo—$C_{carbonyl}$ lengths of 1.904 (9) and 1.929 (9) Å for Mo3—C31 and Mo3—C32, respectively, are similar to those found in (II) [1.905 (3) and 1.941 (3) Å] and that in (III) [1.951 (3) Å].

Previously, the twist of the appended SMe_2 group has been described by the parameter τ (Hamilton & Welch, 1991). For the free carb′H ligand and its uncrowded metalla derivatives, τ adopts low values (−3 to −21°; Douek & Welch, 1993), with the S-atom lone pair orientated towards the cage carbon H atom. In compound (I), τ has a value of −34.4°, which

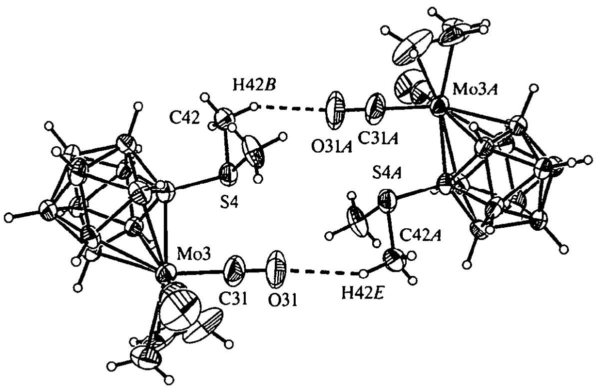


Fig. 2. View of the intermolecular hydrogen bonding in compound (I), between two molecules related by a centre of inversion. Mo3*A* is obtained from Mo3 by application of the operation (1 − *x*, −*y*, 2 − *z*).

is significantly different to those in other systems. In the absence of severe steric congestion in the molecule, we ascribe the larger twist of the SMe$_2$ group to an intermolecular interaction of 2.422 (10) Å between H42*B* and O31; C42—H42*B*···O31*A* 153.2 and C31*A*—O31*A*···H42*B* 171.2° (atoms with labels appended by *A* are at $1-x$, $-y$, $2-z$) (Fig. 2).

Taken as a whole, this result further underlines the analogous relationship between the ligands [carb′]$^-$ and [η^5-C_5H_5]$^-$. It also provides a suitable reference point for the discussion of the structures of analogues of compound (I) that are substantially more crowded (Dunn *et al.*, 1998).

Experimental

9-SMe$_2$-7,8-*nido*-$C_2B_9H_{11}$ (100 mg, 0.51 mmol) was deprotonated with NaH (60 mg, excess) in THF (20 ml) for 1 h and left to settle. The resulting solution was decanted *via* syringe into a cooled (273 K) solution of MoBr(NCMe)$_2$(η^3-C_3H_5)(CO)$_2$ (180 mg, 0.51 mmol) in THF (10 ml) and stirred for 2 h. The solvent was removed and the residue redissolved in CH_2Cl_2 (10 ml). Filtration through Celite afforded an orange–brown solution which was then passed through a short silica plug (5 cm) to afford a bright yellow solution of 3-(η^3-C_3H_5)-3,3-(CO)$_2$-4-SMe$_2$-3,1,2-*closo*-MoC$_2$B$_9$H$_{10}$, (I). Recrystallization from light petroleum (333–353 K)/CH_2Cl_2 gave pale yellow microcrystals (105 mg, 54%). $C_9H_{21}B_9MoO_2S$ requires 27.9 C, 5.44% H; analysis found 27.8 C, 5.49% H. ^{1}H FT–NMR (200 MHz, TMS): δ = 1.43 [*dd*, 1H, H$_{anti}$, *J*(HH) = 10, 3 Hz], 1.48 [*dd*, 1H, H$_{anti}$, *J*(HH) = 11, 2 Hz], 1.94 (*br*, 1H, CH), 2.50 (*s*, 3H, SMe), 2.93 (*s*, 3H, SMe), 3.07 [*ddd*, 1H, H$_{syn}$, *J*(HH) = 7, 3, 2 Hz], 3.17 (*br*, 1H, CH), 3.60 [*ddd*, 1H, H$_{syn}$, *J*(HH) = 7, 2, 2 Hz], 3.90 p.p.m. [*dddd*, 1H, H$_{central}$, *J*(HH) = 11, 10, 7, 7 Hz]. ^{11}B-{^{1}H} FT–NMR (128.4 MHz, BF$_3$.Et$_2$O): δ = −1.16 (1B), −3.17 (1B), −4.29 (1B), −7.63 (1B), −8.88 (2B), −15.41 (1B), −16.81 (1B), −18.38 p.p.m. (1B). IR (CH_2Cl_2): 1953, 1938 cm^{-1}. NMR spectra were recorded on Brüker DPX400 and AC200 spectrometers, from CDCl$_3$ solutions at 293 K.

Crystal data

[Mo(C_3H_5)($C_4H_{16}B_9S$)-
(CO)$_2$]
M_r = 386.55
Monoclinic
$P2_1/n$
a = 6.9732 (11) Å
b = 25.252 (3) Å
c = 9.6780 (11) Å
β = 93.386 (10)°
V = 1701.2 (4) Å^3
Z = 4
D_x = 1.509 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 27
reflections
θ = 4.76–12.33°
μ = 0.887 mm^{-1}
T = 293 (2) K
Block
0.55 × 0.40 × 0.25 mm
Pale yellow

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction:
semi-empirical *via* ψ
scans (Siemens, 1994)
T_{min} = 0.680, T_{max} = 0.801
4059 measured reflections
2975 independent reflections
1817 reflections with
$I > 2\sigma(I)$

R_{int} = 0.085
θ_{max} = 25°
$h = -1 \rightarrow 8$
$k = -1 \rightarrow 30$
$l = -11 \rightarrow 11$
3 standard reflections
every 97 reflections
intensity decay: 2.10%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.141
S = 1.030
2973 reflections
199 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.039P)^2$
$+ 0.5738P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.224 e Å^{-3}
$\Delta\rho_{min}$ = −1.149 e Å^{-3}
Extinction correction: none
Scattering factors from
International Tables for
Crystallography (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Mo3—C1	2.414 (6)	B4—B8	1.756 (11)
Mo3—C2	2.407 (6)	B4—B9	1.771 (11)
Mo3—C31	1.904 (9)	B5—B6	1.771 (11)
Mo3—C32	1.929 (9)	B5—B9	1.778 (11)
Mo3—C33	2.337 (8)	B5—B10	1.774 (11)
Mo3—C34	2.221 (9)	B6—B10	1.764 (11)
Mo3—C35	2.334 (10)	B6—B11	1.772 (13)
Mo3—B4	2.417 (8)	B7—B8	1.808 (11)
Mo3—B7	2.379 (8)	B7—B11	1.807 (11)
Mo3—B8	2.445 (9)	B7—B12	1.787 (12)
S4—C41	1.795 (8)	B8—B9	1.798 (12)
S4—C42	1.831 (7)	B8—B12	1.799 (12)
S4—B4	1.927 (8)	B9—B10	1.768 (10)
C1—C2	1.595 (9)	B9—B12	1.755 (11)
C1—B4	1.666 (9)	B10—B11	1.773 (10)
C1—B5	1.706 (9)	B10—B12	1.775 (13)
C1—B6	1.738 (9)	B11—B12	1.746 (13)
C2—B6	1.737 (10)	C31—O31	1.179 (11)
C2—B7	1.653 (12)	C32—O32	1.161 (11)
C2—B11	1.702 (10)	C33—C34	1.40 (2)
B4—B5	1.774 (10)	C34—C35	1.39 (2)
C31—Mo3—C32	75.7 (5)	C41—S4—C42	98.8 (4)
C34—Mo3—C35	35.5 (5)	C41—S4—B4	101.7 (4)
C34—Mo3—C33	35.5 (4)	C42—S4—B4	108.0 (3)

The cage H atoms were constrained to idealized positions (B—H 1.10 and C—H 1.15 Å), as were the allyl H atoms (C34—H34*A* 0.98 Å; methylide, *e.g.* C33—H33*A*, 0.97 Å) and the methyl H atoms (C—H 0.96 Å). All H-atom positions were calculated. The isotropic displacement parameter of each cage H atom was defined as 1.2U_{iso} of the bound cage atom. For allyl H atoms, U_{iso} = 1.2U_{iso}(bound C), and for methyl H atoms, U_{iso} = 1.5U_{iso}(bound C). The largest feature in the difference map is 1.70 Å from Mo3 and 1.39 Å from C32.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

We thank the EPSRC for provision of postdoctoral fellowships (ASW and GMR), the ERASMUS scholarship and university exchange programme (KJ) and the Callery Chemical Company for a generous gift of $B_{10}H_{14}$.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1502). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 217–219

Bis[di-2-pyridylmethanediolato(1−)-*N*,*O*,*N*′]cobalt(III) Perchlorate Trihydrate

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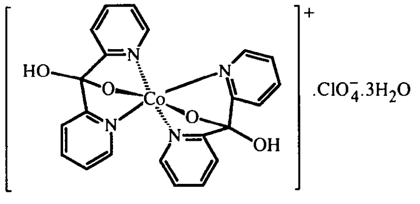
Abstract

In the title compound, $[Co(C_{11}H_9N_2O_2)_2]ClO_4.3H_2O$, the metal atom is *N*,*O*,*N*′-chelated by the two di-2-pyridylmethanediolato anions with distorted octahedral CoN_4O_2 geometry. The Co—O bonds [1.876 (1) and 1.879 (1) Å] are *cis* to each other.

Comment

Di-2-pyridyl ketone undergoes hydrolysis when reacted with transition metal ions to form polynuclear di-2-pyridyl ketal complexes (Byers *et al.*, 1985; Wang *et al.*, 1986). The diol can be deprotonated and in complexes, the anion binds through the N, O and N′ atoms (Baggio *et al.*, 1993; Deveson *et al.*, 1996; Tangoulis *et al.*, 1996). The title complex, (I), which has the Co atom in the +3 oxidation state, was obtained in an attempt to prepare a cobalt(II) complex containing di-2-pyridyl ketone and betaine ligands.



(I)

The complex consists of discrete monomeric cations, perchlorate anions and lattice water molecules. The Co^{III} atom is surrounded by four N atoms and two O atoms of the two tridentate ligands in a distorted octahedral CoN_4O_2 arrangement, with the greatest distortion from octahedral geometry being displayed by the angles N1—Co1—N4 and O3—Co1—N4. The Co—N bond lengths [1.929 (1)–1.944 (1) Å] are similar to those (1.994–2.098 Å) found in the di-2-pyridyl ketal complexes of nickel(II) and copper(II) reported by Wang *et al.* (1986). In these complexes, the pair of metal–oxygen bonds are in a *trans* alignment. On the other hand, the Co—O bonds in the title complex are mutually *cis*; thus, the title complex presents an unusual mode of binding of this tridentate ligand to a metal centre.

The structure is consolidated by an extensive three-dimensional hydrogen-bonding network which involves the lattice water molecules, the hydroxy groups of the

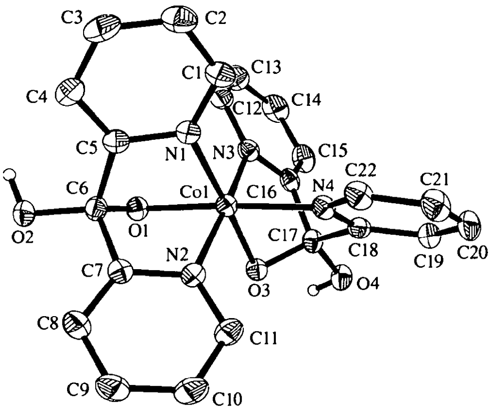


Fig. 1. *ORTEP*II (Johnson, 1976) plot of the title cation with 35% probability displacement ellipsoids. H atoms bonded to C atoms are not included.

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