metal-organic compounds

Cubic di-μ-amido-bis[bis(η^5-cyclopenta-dienyl)ytterbium(III)]

Martin Zeuner and Wolfgang Schnick*

Department Chemie und Biochemie, Ludwig-Maximilians-Universität München, Lehrstuhl für Anorganische Festkörperchemie, Butenandtstrasse 5-13 (D), D-81377 München, Germany

Correspondence e-mail: Wolfgang.Schnick@uni-muenchen.de

The title compound, [Yb$_2$(C$_5$H$_5$)$_4$(NH$_2$)$_2$], was synthesized in a Parr high-pressure vessel starting from monoclinic [Cp$_2$YbNH$_2$]$_2$ (where Cp = cyclopentadienyl). The complex is located on a special position of site symmetry *mmm* with just an eighth of the complex in the asymmetric unit. The Yb atom is in a distorted tetrahedral coordination environment, coordinated by two cyclopentadienyl rings and two amino groups forming a dimeric complex bridged through the amino groups. This compound represents the high-pressure cubic modification of monoclinic [Cp$_2$YbNH$_2$]$_2$ obtained at 250 bar (1 bar = 10^5 Pa) under an atmosphere of argon.

Related literature

The monoclinic [Cp$_2$YbNH$_2$]$_2$ complex was first described by Fischer & Fischer (1966). The first single X-ray diffraction data of this compound were presented by Baisch, Pagano, Zeuner, Barros *et al.* (2006). For related literature, see Schumann *et al.* (1995); Hayes & Thomas (1989); Hammel & Weidlein (1990); Baisch, Pagano, Zeuner & Schnick (2006).
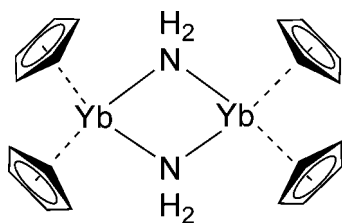
Experimental

Crystal data

[Yb$_2$(C$_5$H$_5$)$_4$(NH$_2$)$_2$]	Z = 6
M_r = 638.5	Mo $K\alpha$ radiation
Cubic, $Im\bar{3}$	μ = 9.32 mm^{-1}
a = 14.4104 (17) Å	T = 293 (2) K
V = 2992.5 (6) Å^3	0.22 × 0.17 × 0.12 mm

Data collection

Stoe IPDS diffractometer	16043 measured reflections
Absorption correction: multi-scan (*XPREP* in *SHELXTL-Plus*; Sheldrick, 1996)	843 independent reflections
	578 reflections with $I > 2\sigma(I)$
T_{min} = 0.160, T_{max} = 0.390 (expected range = 0.134–0.327)	R_{int} = 0.080

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.025	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.051	
S = 0.87	
843 reflections	$\Delta\rho_{max}$ = 0.58 e Å^{-3}
36 parameters	$\Delta\rho_{min}$ = −0.50 e Å^{-3}
1 restraint	

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL97*.

References

Baisch, U., Pagano, S., Zeuner, M., Barros, N., Maron, L. & Schnick, W. (2006). *Chem. Eur. J.* **12**, 4785–4798.

Baisch, U., Pagano, S., Zeuner, M. & Schnick, W. (2006). *Eur. J. Inorg. Chem.* pp. 3517–3524.

Brandenburg, K. (1999). *DIAMOND*. Release 2.1c. Crystal Impact GbR, Bonn, Germany.

Fischer, E. O. & Fischer, H. (1966). *J. Organomet. Chem.* **6**, 141–148.

Hammel, A. & Weidlein, J. (1990). *J. Organomet. Chem.* **388**, 75–87.

Hayes, G. & Thomas, J. L. (1989). *Inorg. Chem.* **8**, 2521–2522.

Schumann, H., Messe-Marktscheffel, J. A. & Esser, L. (1995). *Chem. Rev.* **95**, 865–986.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1996). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

Stoe & Cie (2002). *X-AREA*. Stoe & Cie, Darmstadt, Germany.

supplementary materials

Cubic di-μ-amido-bis[bis(η^5-cyclopentadienyl)ytterbium(III)]

M. Zeuner and W. Schnick

Comment

The stucture of the title compound, $[Cp_2YbNH_2]_2$, shows the high-pressure cubic modification of the monoclinic compound $[Cp_2YbNH_2]_2$. The assymetric unit consists of three C atoms, one N atom and one Yb atom (figure 1). Gometric parameters of the title compound are in the usual ranges. It crystalizes isotyp with cubic $[Cp_2ErNH_2]_2$, which was the only cubic compound of the system $[Cp_2LnNH_2]_2$ so far.

Experimental

Anhydrous ammonia was condensed at 195 K (dry ice, *i*PrOH) onto YpCp$_3$ (4–10 mmol). The resulting colourless mixture was stirred rapidly for 5 h and then further stirred for additional 6 − 24 h without further cooling. After complete evaporation of residual ammonia the pale-coloured solid was dried under vakuum and sublimed under reduced pressure yielding green Cp_3YbNH_3. Heating of Cp_3YbNH_3 to 523 K yielded yellow monoclinic $[Cp_2YbNH_2]_2$. Subsequent treatment of this compound to 250 bar yielded yellow cubic $[Cp_2YbNH_2]_2$.

Refinement

The H atoms bonded to C were positioned geometrically and refined using a riding model, C—H = 0.93 A and $U_{iso}(H) = 1.2\ U_{iso}(C)$. The amino H atom was freely refined.
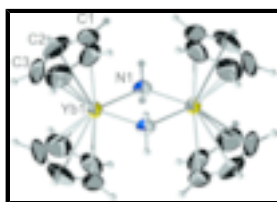
Figures

Fig. 1. A view of the title compound showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.
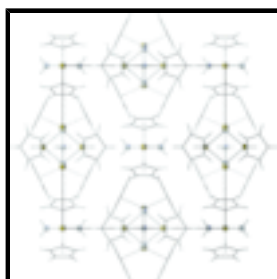

Fig. 2. shows the crystal packing diagram of the title compound viewed along the *c* axis.

supplementary materials

di-µ-amido-bis[bis(η^5-cyclopentadienyl)ytterbium(III)]

Crystal data

[Yb$_2$(C$_5$H$_5$)$_4$(NH$_2$)$_2$]	$Z = 6$
$M_r = 638.5$	$F_{000} = 1788$
Cubic, $Im\overline{3}$	$D_x = 2.126$ Mg m^{-3}
Hall symbol: -I223	Melting point: not measured K
$a = 14.4104$ (17) Å	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$b = 14.4104$ (17) Å	Cell parameters from 6512 reflections
$c = 14.4104$ (17) Å	$\theta = 4.6$–60.9º
$\alpha = 90$º	$\mu = 9.32$ mm^{-1}
$\beta = 90$º	$T = 293$ (2) K
$\gamma = 90$º	Platelet, yellow
$V = 2992.5$ (6) Å^3	0.22 × 0.17 × 0.12 mm

Data collection

Stoe IPDS diffractometer	843 independent reflections
Radiation source: fine-focus sealed tube	578 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.080$
$T = 293(2)$ K	$\theta_{max} = 30.4$º
oscillation scans	$\theta_{min} = 2.8$º
Absorption correction: multi-scan correction based on equivalents (XPREP in SHELXTL-PLUS; Sheldrick, 1996)	$h = -20\rightarrow20$
$T_{min} = 0.160$, $T_{max} = 0.390$	$k = -20\rightarrow20$
16043 measured reflections	$l = -20\rightarrow20$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.025$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.051$	$w = 1/[\sigma^2(F_o^2) + (0.0285P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.87$	$(\Delta/\sigma)_{max} < 0.001$
843 reflections	$\Delta\rho_{max} = 0.58$ e Å^{-3}
36 parameters	$\Delta\rho_{min} = -0.50$ e Å^{-3}
1 restraint	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	y	z	$U_{iso}*/U_{eq}$
Yb1	0.5000	0.12174 (2)	0.5000	0.03854 (11)
N1	0.5000	0.0000	0.6022 (4)	0.0400 (14)
C1	0.3244 (3)	0.1320 (4)	0.4523 (4)	0.0776 (17)
H1	0.3009	0.0854	0.4143	0.093*
C2	0.3644 (4)	0.2112 (5)	0.4235 (5)	0.090 (2)
H2	0.3739	0.2286	0.3621	0.108*
C3	0.3888 (6)	0.2621 (5)	0.5000	0.105 (4)
H3	0.4167	0.3202	0.5000	0.126*
H11	0.551 (3)	0.0000	0.638 (4)	0.07 (2)*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Yb1	0.03668 (19)	0.03207 (18)	0.0469 (2)	0.000	0.000	0.000
N1	0.044 (4)	0.049 (4)	0.026 (3)	0.000	0.000	0.000
C1	0.040 (2)	0.071 (3)	0.122 (4)	0.015 (2)	−0.018 (2)	−0.026 (3)
C2	0.068 (4)	0.103 (5)	0.100 (5)	0.034 (4)	−0.004 (3)	0.036 (4)
C3	0.057 (5)	0.036 (4)	0.224 (14)	0.018 (3)	0.000	0.000

Geometric parameters ($Å$, °)

Yb1—N1^i	2.291 (4)	Yb1—C1^{iv}	2.626 (5)
Yb1—N1	2.291 (4)	Yb1—H11	2.75 (3)
Yb1—C3^{ii}	2.580 (6)	N1—Yb1^i	2.291 (4)
Yb1—C3	2.580 (6)	N1—H11	0.894 (10)
Yb1—C2^{iii}	2.588 (5)	C1—C2	1.344 (8)
Yb1—C2^{ii}	2.588 (5)	C1—C1^{iii}	1.376 (12)
Yb1—C2	2.588 (5)	C1—H1	0.9300
Yb1—C2^{iv}	2.588 (5)	C2—C3	1.369 (8)
Yb1—C1^{iii}	2.626 (5)	C2—H2	0.9300
Yb1—C1	2.626 (5)	C3—C2^{iii}	1.369 (8)

Yb1—C1^{ii}	2.626 (5)	C3—H3	0.9300
N1^{i}—Yb1—N1	80.1 (2)	C2^{ii}—Yb1—C1^{ii}	29.87 (19)
N1^{i}—Yb1—C3^{ii}	126.87 (15)	C2—Yb1—C1^{ii}	144.2 (2)
N1—Yb1—C3^{ii}	126.87 (15)	C2^{iv}—Yb1—C1^{ii}	49.90 (19)
N1^{i}—Yb1—C3	126.87 (15)	C1^{iii}—Yb1—C1^{ii}	148.9 (3)
N1—Yb1—C3	126.87 (15)	C1—Yb1—C1^{ii}	173.6 (2)
C3^{ii}—Yb1—C3	76.8 (4)	N1^{i}—Yb1—C1^{iv}	82.80 (12)
N1^{i}—Yb1—C2^{iii}	130.95 (16)	N1—Yb1—C1^{iv}	102.21 (14)
N1—Yb1—C2^{iii}	96.19 (19)	C3^{ii}—Yb1—C1^{iv}	50.0 (2)
C3^{ii}—Yb1—C2^{iii}	94.5 (3)	C3—Yb1—C1^{iv}	123.7 (3)
C3—Yb1—C2^{iii}	30.72 (18)	C2^{iii}—Yb1—C1^{iv}	144.2 (2)
N1^{i}—Yb1—C2^{ii}	130.95 (16)	C2^{ii}—Yb1—C1^{iv}	49.90 (19)
N1—Yb1—C2^{ii}	96.19 (19)	C2—Yb1—C1^{iv}	126.0 (2)
C3^{ii}—Yb1—C2^{ii}	30.72 (18)	C2^{iv}—Yb1—C1^{iv}	29.87 (19)
C3—Yb1—C2^{ii}	94.5 (3)	C1^{iii}—Yb1—C1^{iv}	173.6 (2)
C2^{iii}—Yb1—C2^{ii}	98.1 (3)	C1—Yb1—C1^{iv}	148.9 (3)
N1^{i}—Yb1—C2	96.19 (19)	C1^{ii}—Yb1—C1^{iv}	30.4 (3)
N1—Yb1—C2	130.95 (16)	N1^{i}—Yb1—H11	88.7 (8)
C3^{ii}—Yb1—C2	94.5 (3)	N1—Yb1—H11	17.5 (5)
C3—Yb1—C2	30.72 (18)	C3^{ii}—Yb1—H11	109.6 (4)
C2^{iii}—Yb1—C2	50.4 (3)	C3—Yb1—H11	131.6 (12)
C2^{ii}—Yb1—C2	120.2 (3)	C2^{iii}—Yb1—H11	102.1 (13)
N1^{i}—Yb1—C2^{iv}	96.19 (19)	C2^{ii}—Yb1—H11	79.0 (4)
N1—Yb1—C2^{iv}	130.95 (16)	C2—Yb1—H11	145.7 (12)
C3^{ii}—Yb1—C2^{iv}	30.72 (18)	C2^{iv}—Yb1—H11	115.2 (10)
C3—Yb1—C2^{iv}	94.5 (3)	C1^{iii}—Yb1—H11	95.8 (12)
C2^{iii}—Yb1—C2^{iv}	120.2 (3)	C1—Yb1—H11	118.7 (9)
C2^{ii}—Yb1—C2^{iv}	50.4 (3)	C1^{ii}—Yb1—H11	65.9 (8)
C2—Yb1—C2^{iv}	98.1 (3)	C1^{iv}—Yb1—H11	88.3 (12)
N1^{i}—Yb1—C1^{iii}	102.21 (14)	Yb1^{i}—N1—Yb1	99.9 (2)
N1—Yb1—C1^{iii}	82.80 (12)	Yb1^{i}—N1—H11	112 (3)
C3^{ii}—Yb1—C1^{iii}	123.7 (3)	Yb1—N1—H11	112 (3)
C3—Yb1—C1^{iii}	50.0 (2)	C2—C1—C1^{iii}	107.9 (4)
C2^{iii}—Yb1—C1^{iii}	29.87 (19)	C2—C1—Yb1	73.5 (3)
C2^{ii}—Yb1—C1^{iii}	126.0 (2)	C1^{iii}—C1—Yb1	74.82 (13)
C2—Yb1—C1^{iii}	49.90 (19)	C2—C1—H1	126.0
C2^{iv}—Yb1—C1^{iii}	144.2 (2)	C1^{iii}—C1—H1	126.0
N1^{i}—Yb1—C1	82.80 (12)	Yb1—C1—H1	117.7
N1—Yb1—C1	102.21 (14)	C1—C2—C3	108.5 (7)
C3^{ii}—Yb1—C1	123.7 (3)	C1—C2—Yb1	76.6 (3)
C3—Yb1—C1	50.0 (2)	C3—C2—Yb1	74.3 (4)

C2^{iii}—Yb1—C1	49.90 (19)	C1—C2—H2	125.8
C2^{ii}—Yb1—C1	144.2 (2)	C3—C2—H2	125.8
C2—Yb1—C1	29.87 (19)	Yb1—C2—H2	115.4
C2^{iv}—Yb1—C1	126.0 (2)	C2^{iii}—C3—C2	107.2 (9)
C1^{iii}—Yb1—C1	30.4 (3)	C2^{iii}—C3—Yb1	74.9 (3)
N1^{i}—Yb1—C1^{ii}	102.21 (14)	C2—C3—Yb1	74.9 (3)
N1—Yb1—C1^{ii}	82.80 (12)	C2^{iii}—C3—H3	126.4
C3^{ii}—Yb1—C1^{ii}	50.0 (2)	C2—C3—H3	126.4
C3—Yb1—C1^{ii}	123.7 (3)	Yb1—C3—H3	116.0
C2^{iii}—Yb1—C1^{ii}	126.0 (2)		

Symmetry codes: (i) $-x+1$, $-y$, $-z+1$; (ii) $-x+1$, y, $-z+1$; (iii) x, y, $-z+1$; (iv) $-x+1$, y, z.

Fig. 1

Fig. 2