GOLD CLUSTER CHEMISTRY WITH THE TIN NUCLEOPHILE STANNA-*closo*-DODECABORATE

Hartmut SCHUBERT[1], Fritz-Robert KÜCHLE[2] and Lars WESEMANN[3,*]

Institut für Anorganische Chemie, Universität Tübingen,
Auf der Morgenstelle 18, 72076 Tübingen, Germany; e-mail: [1] nobbe@gmx.de,
[2] fr.kuechle@gmx.de; [3] lars.wesemann@uni-tuebingen.de

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Dedicated to Professor Bohumil Štíbr on the occasion of his 70th birthday.

The tin nucleophile $[SnB_{11}H_{11}]^{2-}$ reacts with the gold cluster $[Au_9(PPh_3)_8][NO_3]_3$ under formation of the tin–gold complex $[Au_8(PPh_3)_7(SnB_{11}H_{11})]$ (**1**). In reaction with four equivalents of the heteroborate a mixed valence tetrahedral gold cluster $[Au_4(PPh_3)_4(SnB_{11}H_{11})_2]^{2-}$ with two edge bridging tin ligands was isolated. The reaction products were characterized by elemental analysis, NMR spectroscopy and single crystal X-ray crystallography.

Keywords: Tin; Gold; Heteroboranes; Stannaboranes; Metallaboranes; Boron clusters; Gold clusters.

Gold cluster chemistry is a fascinating and attractive field of research[1]. Selective aggregation and degradation reactions of clusters with various nuclearities have been established over the years. Cluster formation can either be carried out by reduction of a suitable Au(I) complex fragment or direct reaction of gold vapour with ligands. By reduction of the nitrate $[Au(PPh_3)][NO_3]$ with sodium borohydride, the nonanuclear cluster $[Au_9(PPh_3)_8][NO_3]_3$ is easily accessible[2]. The reactions of this cluster with a variety of nucleophiles was investigated leading to smaller clusters like tetra-, hexa- or octanuclear gold complexes[3–5] or for example with $[Au(C_6F_5)_2]^-$ to give a decanuclear cluster[6]. Tin substituted gold clusters have been reported with the $SnCl_3$-ligand: an octanuclear $[Au_8(PPh_3)_7(SnCl_3)]^+$ and a tetranuclear gold cluster $[Au_4(PPh_3)_4(SnCl_3)_2]$ were structurally characterized[7,8]. We are studying the coordination chemistry of heteroborate ligands like $[SnB_{11}H_{11}]^{2-}$ [9–17], $[GeB_{11}H_{11}]^{2-}$ [18], $[Sn_2B_{10}H_{10}]^{2-}$ [19], $[Ge_2B_{10}H_{10}]^{2-}$ [20], and $[SnCB_{10}H_{11}]^-$ [21]. With the versatile tin ligand stanna-

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closo-dodecaborate $[SnB_{11}H_{11}]^{2-}$ we have characterized a variety of coordination complexes also with the coinage metals silver[16] and gold. In the case of gold a dinuclear **A** [13], trinuclear **B** [14] and a tetranuclear cluster **C** [14] were synthesized (Chart 1). In this publication we present the reaction of the tin nucleophile with the gold cluster $[Au_9(PPh_3)_8][NO_3]_3$.

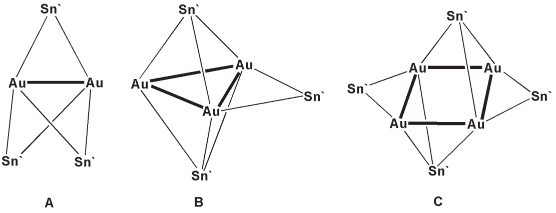


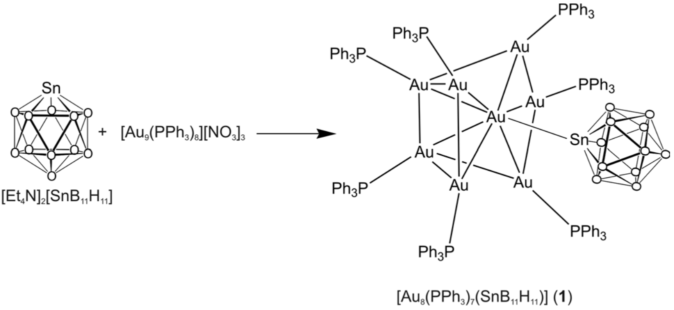
CHART 1
Schematic drawings of gold–tin clusters with the stanna-*closo*-dodecaborate ligand (Sn′ = $SnB_{11}H_{11}$). One phosphorus atom is coordinated at each gold atom (**A** = PPh_3, **B** = PEt_3, **C** = dppm (= bisdiphenylphosphinomethane))[13,14].

RESULTS AND DISCUSSION

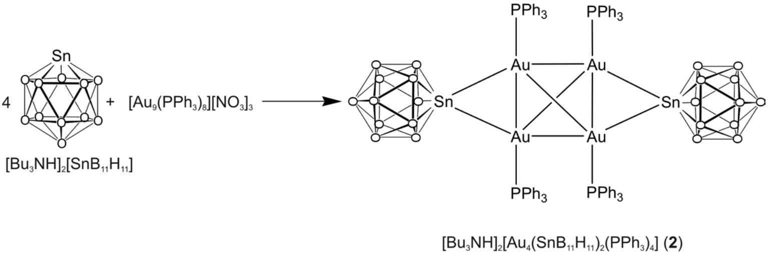
The gold cluster electrophile $[Au_9(PPh_3)_8][NO_3]_3$ was reacted with one equivalent of the stannylene $[SnB_{11}H_{11}]^{2-}$ to give in dependency on the stoichiometry an octanuclear **1** or a tetranuclear **2** gold cluster. During the studies of the synthesis of the zwitterion $[Au_8(PPh_3)_7(SnB_{11}H_{11})]$ (**1**) we found a degradation reaction of this octanuclear stannaborate–gold complex to give the tetranuclear product **2**. Therefore shorter reaction times and keeping the exact stoichiometry are absolutely necessary for the synthesis of **1**. Furthermore the water soluble $[Et_4N]$ salt of the nucleophilic stannaborate was used in order to separate by water washing before crystallization the remaining tin ligand. In order to dissolve the $[Et_4N]$–tincluster salt we had to use acetonitrile in this synthesis.

Following the described procedure we were able to synthesize and isolate the octanuclear cluster **1** in yields around 30% (Scheme 1). From the reaction of the starting material $[Au_9(PPh_3)_8][NO_3]_3$ with four equivalents of the stanna-*closo*-dodecaborate we isolated the tetranuclear complex **2** in yields of 32% (Scheme 2). After crystallization the two gold–tin complexes **1** and **2** were characterized by elemental analysis, X-ray crystal structure analysis and NMR spectroscopy.

In Figs 1 and 2 the structures of the neutral zwitterionic cluster molecule **1** and the dianion of compound **2** are presented and in Table I details of the



SCHEME 1



SCHEME 2

structure solution are listed. In complex **1** the found Au–Sn interatomic distance of 2.6086(9) Å is slightly shorter than the respective Au–Sn bond length of 2.625(3) Å [7] in the trichlorostannate complex $[Au_8(PPh_3)_7(SnCl_3)]$-$[SnCl_6]$. So far the characterized stannaborate gold complexes exhibit a bridging coordination mode for the tin ligand and therefore longer Au–Sn bond lengths[13,14,16]. The gold cluster geometry of the neutral molecule **1** can be compared with the structure of the cation $[Au_8(PPh_3)_7(SnCl_3)]^{+}$ [7]. In both cases the tin is bonded at the central gold atom of the cluster. This gold atom (central) in complex **1** shows relatively short Au–Au interatomic distances to the other gold atoms (peripheral) of the cluster skeleton. The complete Au–Au interatomic distances lie in a range of 2.6017(6)–3.0064(7) Å for **1** and in the case of the $SnCl_3$ derivative between 2.625(3) and 2.965(3) Å. In both clusters the central Au–Au separations are shorter than the distances between the peripheral gold atoms.

The reaction proceeding of the octanuclear gold cluster **1** with the nucleophilic stanna-*closo*-dodecaborate dianion resulted in the formation of a tetrahedral gold cluster **2**. Tetrahedral gold complexes with a $[Au_4]^{2+}$ cluster core are known with ligands coordinating each at one gold atom:

L = P*t*Bu$_3$ [22], P(mesityl)$_3$ [23] for $[Au_4L_4][BF_4]_2$ and $[Au_4\{(PPh_2)_2C_2B_9H_{10}\}_2(AsPh_3)_2]$[24,25]. Derivatives with ligands bridging an Au–Au cluster edge have been reported with bridging iodide $[Au_4I_2(PPh_3)_4]$ [5], bridging trichlorostannate $[Au_4(SnCl_3)_2(PPh_3)_4]$ [8] and bridging tin heteroborate ligand $[Au_4(SnCHB_{10}H_{10})_2(PPh_3)_4]$ [21]. The structures with the bridging ligands are closely related to the structure of complex **2**. In these coordination compounds the Au–Au distances of the tetrahedron are extremely different: the bridged edges are shorter than the unbridged ones (Table II). Interestingly the new complex shows the shortest Au–Au edge. In the stanna-*closo*-dodecaborate chemistry it is a known phenomenon to find extremely short coinage metal bonds upon bridging with a stannylene $[SnB_{11}H_{11}]^{2-}$. In the complexes shown in Chart 1 the Au–Au interatomic distances in the Au_2Sn triangles are also short (**A**: 2.590(1), **B**: 2.605(1), **C**: 2.6217(4) Å), however

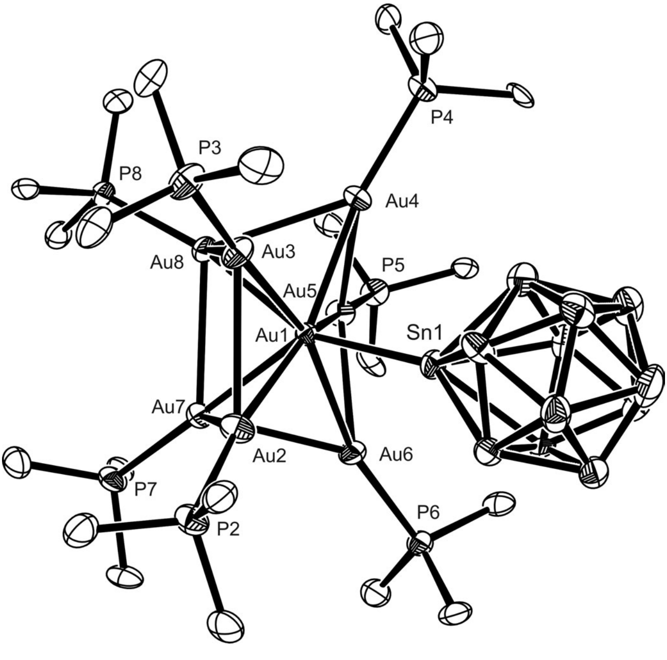


FIG. 1
Molecular structure of **1** in the crystal. Hydrogen and carbon atoms, except the *ipso*-carbon atoms, are omitted for the sake of clarity, ellipsoids with 50%. Selected interatomic distances (in Å): Au1–Sn1 2.6086(9), central gold Au1: Au1–Au2 2.6329(6), Au1–Au3 2.6364(6), Au1–Au4 2.6441(6), Au1–Au5 2.6681(6), Au1–Au6 2.6285(6), Au1–Au7 2.6597(6), Au1–Au8 2.6017(6), peripheral gold atoms: Au8–Au3 3.0073(7), Au8–Au4 2.9478(7), Au8–Au7 3.0064(7), Au2–Au7 2.8925(7), Au2–Au3 2.9946(7), Au7–Au6 2.8610(7), Au4–Au5 2.9301(7), Au5–Au6 2.8773(7), Au8–P8 2.268(3)

TABLE I
Crystallographic data for compounds **1** and **2**

Parameter	**1**·5 THF	**2**·acetone
Empirical formula	$C_{146}H_{156}Au_8B_{11}O_5P_7Sn$	$C_{99}H_{144}Au_4B_{22}N_2OP_4Sn_2$
Formula weight, g/mol	4020.89	2765.17
Crystal system	monoclinic	monoclinic
Space group	*Cc*	$P2_1/c$
Unit cell dimensions		
a, Å	30.0321(6)	20.1841(3)
b, Å	17.1840(3)	21.8552(2)
c, Å	30.1064(4)	26.9690(4)
β, °	116.5570(10)	110.1140(10)
V, Å^3	13897.7(4)	11171.2(3)
Z; Density, g cm^{-3}	4; 1.922	4; 1.644
Absorption coeficient, mm^{-1}	8.721	5.776
Absolute structure parameter	0.007(6)	
T, K	173	173
Reflections collected/unique	87350/28479	149741/23682
$R_{(int)}$	0.0869	0.1668
Data/restraints/parameters	28479/38/1478	23682/3/1077
Final R indices $[I > \sigma(I)]$	$R_1 = 0.0470$, $wR_2 = 0.0971$	$R_1 = 0.0576$, $wR_2 = 0.1292$
R indices (all data)	$R_1 = 0.0593$, $wR_2 = 0.1066$	$R_1 = 0.0740$, $wR_2 = 0.1368$

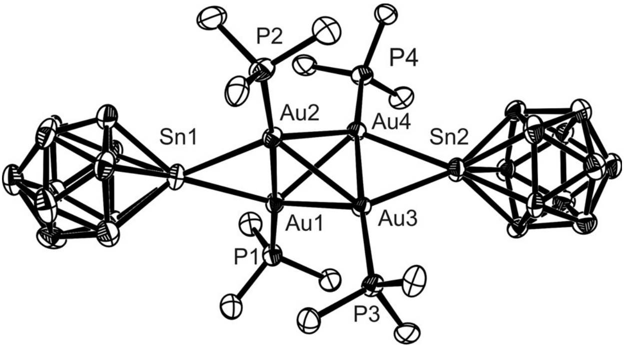


FIG. 2
Molecular structure of the anion of **2** in the crystal. Hydrogen and carbon atoms, except the *ipso*-carbon atoms, are omitted for the sake of clarity, ellipsoids with 50%. Selected interatomic distances (in Å) and angles (in °): Au1–Au2 2.5864(4), Au1–Au3 2.8344(4), Au1–Au4 2.8849(4), Au2–Au4 2.8407(4), Au2–Au3 2.8409(4), Au3–Au4 2.5828(4), Au1–Sn1 2.8839(7), Au2–Sn1 2.7731(7), Au3–Sn2 2.7620(6), Au4–Sn2 2.8714(6), Au1–P1 2.291(2), Au2–P2 2.299(2), Au3–P3 2.293(2), Au4–P4 2.285(2) and Au2–Sn1–Au1 54.371(14), Au3–Sn2–Au4 54.537(13), P1–Au1–Au2 173.58(6), P2–Au2–Au1 176.77(6), P3–Au3–Au4 172.14(6), P4–Au4–Au3 171.29(6)

the found distances of 2.5864(4) Å of Au1–Au2 and 2.5828(4) Å of Au3–Au4 in complex **2** are the shortest bonds in this type of chemistry. The gold–tin interatomic distances in complex **2** of 2.8839(7), 2.7731(7), 2.7620(6) and 2.8714(6) Å should be compared with the distances in the Au_2Sn triangle in complex $[Au_4(SnB_{11}H_{11})_4(dppm)_2]^{4-}$ 2.728(1) and 2.710(1) Å (Chart 1 **C**) and $[Au_2(SnB_{11}H_{11})_3(PPh_3)_2]^{4-}$ 2.727(1), 2.711(1) and 2.718(1) Å (Chart 1 **A**).

TABLE II
Comparison of the Au–Au interatomic distances (in Å)

	Iodide	$SnCl_3$	$SnCHB_{10}H_{10}$	$SnB_{11}H_{11}$
Bridged	2.649(1)	2.634(5)	2.6058(8) 2.5993(8)	2.5828(4) 2.5864(4)
Unbridged	2.744(1)–2.828(1)	2.766(6)–2.813(5)	2.7799(9)–2.8611(9)	2.8344(4)–2.8849(4)

CONCLUSION

The reaction of the tin nucleophile $[SnB_{11}H_{11}]^{2-}$ with the gold cluster $[Au_9(PPh_3)_8][NO_3]_3$ is presented. The first product of this reaction is an octanuclear gold cluster with the tin ligand coordinated at the central gold atom. In a following reaction the Au_9Sn cluster is degraded to give a tetranuclear gold cluster in which two cluster edges are bridged by the stanna-*closo*-dodecaborate resulting to give very short gold–gold interatomic distances.

EXPERIMENTAL

All manipulations were carried out under argon in Schlenk glassware. Solvents were dried and purified by standard methods and stored under argon. NMR spectra were recorded with a Bruker DRX-250 NMR spectrometer equipped with a 5-mm ATM probe head and operating at 250.13 (^{1}H), 80.25 (^{11}B), 62.90 (^{13}C), 101.25 (^{31}P) and 93.25 MHz (^{119}Sn), a Bruker DRX-400 NMR spectrometer equipped with a 5-mm QNP (quad nucleus probe) head and operating at 400.13 (^{1}H) and 100.13 MHz (^{13}C), and a Bruker AV-500 NMR spectrometer equipped with a 5-mm ATM probe head. Chemical shifts (δ in ppm) are reported relative to external TMS (^{1}H, ^{13}C), $BF_3 \cdot Et_2O$ (^{11}B), 85% aqueous H_3PO_4 (^{31}P) or $SnMe_4$ (^{119}Sn) using the chemical shift of the solvent ^{2}H resonance frequency. Coupling constants J and half-widths $w_{1/2}$ are given in Hz. Elemental analyses were performed at the Institut für Anorganische Chemie Universität of Tübingen using a Vario EL analyzer.

Complex $[Au_9(PPh_3)_8][NO_3]_3$ was prepared following the procedure in ref.[2]. $[Bu_3NH]_2$-$[SnB_{11}H_{11}]$ was prepared following a modified procedure of Todd's original protocol[26].

$[Au_8(PPh_3)_7(SnB_{11}H_{11})]$ (**1**)

An acetonitrile solution (5 ml) of $[Au_9(PPh_3)_8][NO_3]_3$ (40.5 mg, 0.01 mmol) reacted with $[Et_4N]_2[SnB_{11}H_{11}]$ (5.0 mg, 0.01 mmol). After stirring for 5 min at room temperature the solvent was evaporated under reduced pressure. The remaining solid was washed with small amounts of water, ether and was dried under vacuum. Crystallization from THF/ether gave dark red crystals. Yield 11 mg (30%). For $C_{126}H_{116}Au_8B_{11}P_7Sn$ (3660.49) calculated: 41.34% C, 3.19% H; found: 40.78% C, 3.03% H. $^{11}B\{^1H\}$ NMR (CD_2Cl_2): –14.2 (10 B, B2-B12), the signal for B12 was not detected. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 53.1 (s, $^3J(^{31}P\text{-}^{119}Sn) = 247$, $^3J(^{31}P\text{-}^{117}Sn) = 237$). $^{119}Sn\{^1H\}$ NMR (CD_2Cl_2): –286 (s, $w_{1/2} = 850$).

$[Bu_3NH]_2[Au_4(SnB_{11}H_{11})_2(PPh_3)_4]$ (**2**)

A THF suspension (5 ml) of $[Au_9(PPh_3)_8][NO_3]_3$ (81 mg, 0.02 mmol) reacted with $[Bu_3NH]_2[SnB_{11}H_{11}]$ (48 mg, 0.08 mmol). After stirring for 30 min the solvent was evaporated under reduced pressure. Crystallization from acetone/hexane gave orange crystals. Yield 39 mg (32%). For $C_{96}H_{138}Au_4B_{22}N_2P_4Sn_2$ (2707.17) 42.59% C, 5.14% H, 1.03% N; found 41.93% C, 4.88% H, 1.24% N. $^{11}B\{^1H\}$ NMR (CD_2Cl_2): –14.2 (10 B, B2-B12), the signal for B12 was not detected. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 62.0 (s, $J(^{31}P\text{-}^{119/117}Sn) = 184$). $^{119}Sn\{^1H\}$ NMR (CD_2Cl_2): –312 (s, $w_{1/2} = 890$).

X-ray Crystallography

X-ray data for compounds **1** and **2** were collected with a Stoe IPDS 2T diffractometer and corrected for Lorentz and polarization effects and absorption by air. The programs used in this work were Stoe's X-Area and WinGX suite of programs including SHELXS and SHELXL for structure solution and refinement. Numerical absorption correction based on crystal-shape optimization was applied for **1** and **2** with Stoe's X-Red and X-Shape[27–32]. CCDC 774621 (**1**) and 774622 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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REFERENCES

1. Dyson P., Mingos D. M. P.: *Gold, Progress in Chemistry, Biochemistry and Technology* (H. Schmidbaur, Ed.), Chap. 15, p. 511. John Wiley & Sons, Chichester 1999.
2. Cariati F., Naldini L. L.: *Dalton Trans.* **1972**, 2286.
3. Vollenbroe F. A., Bosman W. P., Bour J. J., Noordik J. H., Beurskens P. T.: *Chem. Commun.* **1979**, 387.
4. van der Velden J. W. A., Bour J. J., Steggerda J. J., Beurskens P. T., Roseboom M., Noordik J. H.: *Inorg. Chem.* **1982**, *21*, 4321.
5. Demartin F., Manassero M., Naldini L., Ruggeri R., Sansoni S.: *Chem. Commun.* **1981**, 222.
6. Laguna A., Laguna M., Gimeno M. C., Jones P. G.: *Organometallics* **1992**, *11*, 2759.

7. Demidowicz Z., Johnston R. L., Machell J. C., Mingos D. M. P., Williams I. D.: *Dalton Trans.* **1988**, 1751.
8. Mingos D. M. P., Powell H. R., Stolberg T. L.: *Transition Met. Chem.* **1992**, *17*, 334.
9. Marx T., Wesemann L., Dehnen S.: *Z. Anorg. Allg. Chem.* **2001**, *627*, 1146.
10. Marx T., Wesemann L., Pantenburg I.: *Organometallics* **2001**, *20*, 5241.
11. Hagen S., Marx T., Pantenburg I., Wesemann L., Nobis M., Driessen-Hölscher B.: *Eur. J. Inorg. Chem.* **2002**, 2261.
12. Marx T., Mosel B., Pantenburg I., Hagen S., Schulze H., Wesemann L.: *Chem. Eur. J.* **2003**, *9*, 4472.
13. Hagen S., Pantenburg I., Weigend F., Wickleder C., Wesemann L.: *Angew. Chem., Int. Ed.* **2003**, *42*, 1501.
14. Hagen S., Wesemann L., Pantenburg I.: *J. Chem. Soc., Chem. Commun.* **2005**, 1013.
15. Gädt T., Wesemann L.: *Organometallics* **2007**, *26*, 2474.
16. Hagen S., Schubert H., Maichle-Mössmer C., Pantenburg I., Weigend F., Wesemann L.: *Inorg. Chem.* **2007**, *46*, 6775.
17. Kirchmann M., Eichele K., Schappacher F. M., Pöttgen R., Wesemann L.: *Angew. Chem., Int. Ed.* **2008**, *47*, 963.
18. Dimmer J.-A., Schubert H., Wesemann L.: *Chem. Eur. J.* **2009**, *15*, 10613.
19. Joosten D., Pantenburg I., Wesemann L.: *Angew. Chem., Int. Ed.* **2006**, *45*, 1085.
20. Nickl C., Joosten D., Eichele K., Maichle-Mössmer C., Törnroos K. W., Wesemann L.: *Angew. Chem., Int. Ed.* **2009**, *48*, 7920.
21. Joosten D., Weissinger I., Kirchmann M., Maichle-Mössmer C., Schappacher F., Pöttgen R., Wesemann L.: *Organometallics* **2007**, *26*, 5696.
22. Zeller E., Beruda H., Schmidbaur H.: *Inorg. Chem.* **1993**, *32*, 3203.
23. Yang Y., Sharp P. R.: *J. Am. Chem. Soc.* **1994**, *116*, 6983.
24. Crespo O., Gimeno M. C., Jones P. G., Laguna A., Villacampa M. D.: *Angew. Chem., Int. Ed.* **1997**, *36*, 993.
25. Calhorda M. J., Crespo O., Gimeno C., Jones P. G., Laguna A., López-de-Luzuriaga J. M., Perez J. L., Ramon M. A., Veiros L. F.: *Inorg. Chem.* **2000**, *39*, 4280.
26. Chapman R. W., Kester J. G., Folting K., Streib W. E., Todd L. J.: *Inorg. Chem.* **1992**, *31*, 979.
27. *X-AREA 1.26*. Stoe & Cie GmbH, Darmstadt 2004.
28. Farrugia L. F.: *J. Appl. Crystallogr.* **1999**, *32*, 837.
29. Sheldrick G. M.: *SHELXS97, Program for the Solution of Crystal Structures*. University of Göttingen, Göttingen 1997.
30. Sheldrick G. M.: *SHELXS97, Program of the Crystal Structure Refinement*. University of Göttingen, Göttingen 1997.
31. *X-RED 1.26, Data Reduction for STAD4 and IPDS*. Stoe & Cie, Darmstadt 1996.
32. *X-SHAPE 2.05, Crystal Optimization for Absorption Correction*. Stoe & Cie, Darmstadt 1996.