# The First Azaindatrane and Unprecedented Structural Features

Pavel L. Shutov,[a] Sergey S. Karlov,*[b] Klaus Harms,[a] Oleg Kh. Poleshchuk,[c]
Jörg Lorberth,*[a] and Galina S. Zaitseva[b]

**Keywords:** Azametallatranes / Indium / Tripodal ligands

The reaction between $[In(NEt_2)_3]_2$ and $N(CH_2CH_2NMeH)_3$ yields the *N*,*N'*,*N''*-trimethylazaindatrane dimer $[N(CH_2CH_2NMe)_3In]_2$ (**1**). The composition and structure of **1** were established by $^1H$ and $^{13}C$ NMR spectroscopy as well as by an X-ray diffraction study. The X-ray structure shows that both indium atoms are pentacoordinate, with widely differing In–N distances. The structural parameters of **1** were compared with those obtained from a computational study.
(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2003)

## Introduction

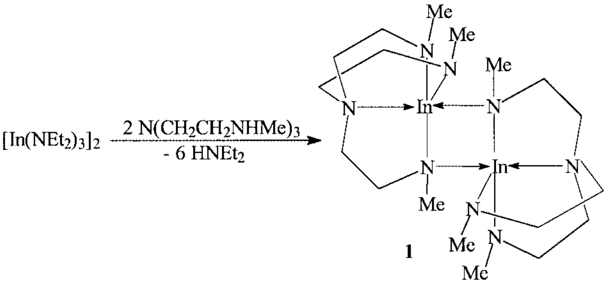
Compounds containing intramolecular interactions have found widespread application for the stabilisation of low-valent species or for achieving unusual molecular geometries. Of particular interest are metallatranes of the type $[N(CH_2CH_2Y)_3M-X$, where X = substituent, electron lone pair or nothing and Y = O, NR, $CH_2$, S] containing tetradentate, $c_3$-symmetric ligands such as tris(alkoxyamine) groups $[N(CH_2CH_2O)_3]^{3-}$ and tris(amidoamine) groups $[N(CH_2CH_2NR)_3]^{3-}$.[1–3] These ligands bind to various main-group elements or transition metals in a tridentate or tetradentate manner to form complexes. The latter are usually characterised by a transannular N→M interaction. The strength of this N→M interaction depends on the nature of the central atom M and the equatorial substituents Y.

Verkade et al. have recently prepared azametallatranes of boron, aluminium, and gallium,[4–7] but, to the best of our knowledge, no azaindatranes have been reported yet. However, it should be noted that the chemistry of indium-nitrogen compounds, especially indium amides, has been the focus of much interest during the last two decades for their importance in the preparation of nitride ceramic materials and semiconductors.[8]

In this paper we report on the synthesis of the *N*,*N'*,*N''*-trimethylazaindatrane dimer $[N(CH_2CH_2NMe)_3In]_2$ (**1**). Details of the X-ray crystal and molecular structures of **1** are also described. Our aim was to prepare the first azaindatrane **1** and to compare its structure with the structures of closely related derivatives of Al and Ga (**2** and **3**, respectively).

## Results and Discussion

Treatment of $[In(NEt_2)_3]_2$ with equimolar amounts of $N(CH_2CH_2NMeH)_3$ ($Me_3$-tren) in toluene afforded azaindatrane **1** in high yield [Equation (1)]. The crystals of compound **1** contain variable amounts of toluene, which could not completely be removed.



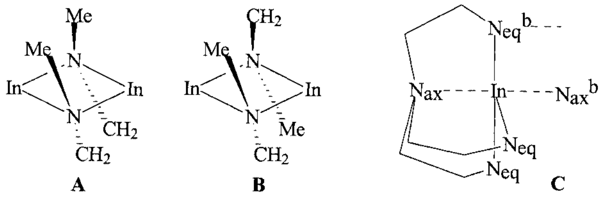
(1)

The NMR spectroscopic data ($^1H$, $^1H$ COSY and $^{13}C$) of **1** are consistent with its formulation as a dimer $[N(CH_2CH_2NMe)_3In]_2$: compound **1** exists in solution as one of two geometrical isomers of the $In_2N_2$ core [**A** (cis) and **B** (trans); Scheme 1] analogous to the previously described complexes $[N(CH_2CH_2NMe)_3M]_2$ [M = Al (**2**), Ga (**3**)].[7] This is supported by the appearance of three singlets for the Me groups and 12 partially overlapping multiplets for each of the non-equivalent hydrogens of six methylene groups for both atrane moieties in the $^1H$ NMR spectrum

---

[a] Fachbereich Chemie, Philipps-Universität Marburg,
Hans-Meerwein-Strasse, 35032 Marburg-Lahn, Germany
Fax: (internat.) +49-6421/282-5642
E-mail: lorberth@chemie.uni-marburg.de
[b] Chemistry Department, Moscow State University,
234 Leninskie Gory, 119899 Moscow, Russia
Fax: (internat.) +7-095/932-8846
E-mail: sergej@org.chem.msu.su
[c] Tomsk Pedagogical University,
Komsomolskii 75, 634041 Tomsk, Russia
E-mail: root@polsh.tomsk.su

of **1**. Nine signals of the atrane skeleton were found in the $^{13}$C NMR spectrum of **1**; however, according to Verkade et al. NMR spectroscopy alone is not suitable for the unambiguous attribution of a cis or a trans structure to the $(\mathrm{In{-}N})_2$ core.[5]



Scheme 1

The dimeric structure of **1** in the solid state was established by an X-ray diffraction study. The molecular structure of **1**·0.5toluene (one of two independent molecules) is shown in Figure 1. Important atomic distances and bond angles are summarised in Table 1. Similarly to both **2** and **3** (M = Al, Ga) molecules of **1** possess a conformation of type **A**, which is unusual for solid-state structures of Group 13 elements.[9] The central $(\mathrm{In{-}N})_2$ units are non-planar for both independent molecules and form a puckered rectangle (153.0° and 151.1°) with a pseudo-twofold axis through its centre, analogously to both **2** and **3**. The coordination polyhedron of the indium atoms in **1** is a distorted trigonal bipyramid (**C**, Scheme 1).

The transannular bonded nitrogen atoms ($\mathrm{N_{ax}}$ and $\mathrm{N^{b}_{ax}}$) are in axial positions and the covalently bonded nitrogen atoms (two of $\mathrm{N_{eq}}$, and $\mathrm{N^{b}_{eq}}$) in the equatorial sites. The indium atoms are displaced by 0.36−0.46 Å from a plane defined by the three equatorial nitrogen atoms towards the bridging nitrogen atom of another atrane part of the dimeric structure ($\mathrm{N^{b}_{ax}}$). The $\mathrm{N_{ax}{-}In{-}N^{b}_{ax}}$ angles [150.3(1)−157.77(9)°] are smaller than those for other closely related $[\mathrm{N(CH_2CH_2NMe)_3M}]_2$ complexes [average: 160.3°, M = Al (**2**) and 162.3°, M = Ga (**3**)].[7] It should be noted that in contrast to both **2** and **3**, there is an unusual set of In−N distances in **1** (Table 1). It is very surprising that the transannular bond lengths In(1)−N(4) and In(1)−N(14) are similar to the values of In−N covalent bonds found in monomeric indium amides [2.02(1)−2.166(4) Å][10,11] and, to the best of our knowledge, these are the shortest transannular In−N distances found to date. Other values of transannular In−N distances in **1** are within the typical range [2.20−2.62 Å],[12,13] although the In(4)-N(43) distance is rather long. Interestingly, values for In←$\mathrm{N_{ax}}$ distances of three known indium atranes investigated are 2.39(1) Å for $\mathrm{N(CH_2CH_2S)_3In}$,[14] 2.386(6) Å for $\mathrm{N(CH_2}$-*o*-$\mathrm{C_6H_4\text{-}S)_3In}$·1-Me-imidazole, 2.345(9) Å for $\mathrm{N(CH_2}$-*o*-$\mathrm{C_6H_4\text{-}S)_3In}$·DMF, and 2.29(1) Å for $\mathrm{N[2\text{-}CH_2\text{-}(4,6\text{-}Me_2C_6H_2)\text{-}O]_3In}$·$(1\text{-Me-imidazole})_2$.[15]

Table 1. Selected bond lengths (Å) and angles (°) for **1**

| | **1** | **1′** |
|---|---|---|
| In←$\mathrm{N_{ax}}$ | In(1)−N(4) 2.099(2) | In(3)−N(30) 2.366(3) |
| | In(2)−N(17) 2.327(3) | In(4)−N(43) 2.610(3) |
| In←$\mathrm{N^{b}_{ax}}$ | In(1)−N(14) 2.063(3) | In(3)−N(46) 2.294(3) |
| | In(2)−N(1) 2.224(3) | In(4)−N(36) 2.376(3) |
| In−$\mathrm{N^{b}_{eq}}$ | In(1)−N(1) 2.393(3) | In(3)−N(36) 2.174(3) |
| | In(2)−N(14) 2.456(3) | In(4)−N(46) 2.073(2) |
| In−$\mathrm{N_{eq}}$ | In(1)−N(10) 2.083(3) | In(3)−N(27) 2.241(3) |
| | In(1)−N(7) 2.350(3) | In(3)−N(33) 2.178(3) |
| | In(2)−N(20) 1.960(3) | In(4)−N(40) 2.103(3) |
| | In(2)−N(23) 2.208(3) | In(4)−N(49) 2.023(3) |
| $\mathrm{N_{ax}{-}In{-}N^{b}_{ax}}$ | N(4)−In(1)−N(14) 150.3(1) | N(30)−In(3)−N(46) 157.77(9) |
| | N(1)−In(2)−N(17) 153.3(1) | N(36)−In(4)−N(43) 156.34(9) |

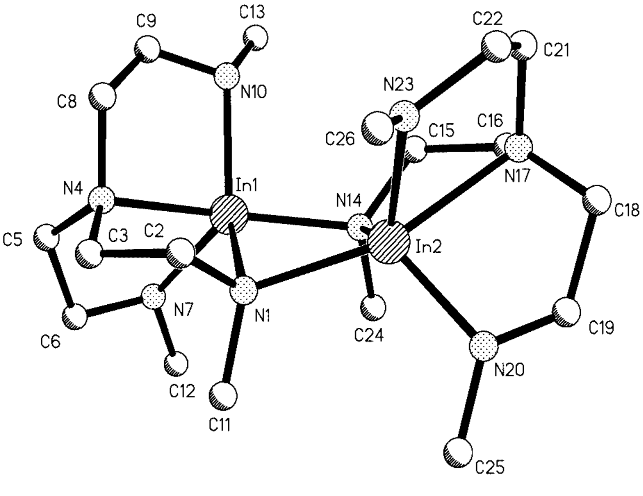
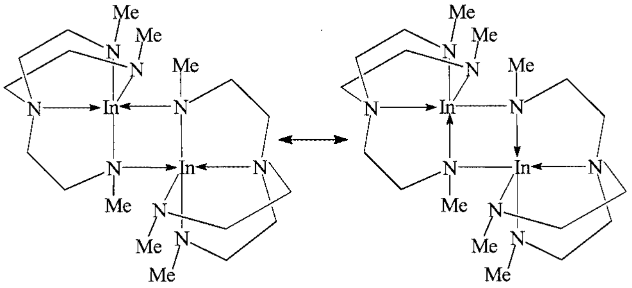


Figure 1. Molecular structure of dimeric azaindatrane **1** (one independent molecule); hydrogen atoms have been omitted for clarity

The nonbridging covalent distances In−$\mathrm{N_{eq}}$ in compound **1** are within the range 1.960(3)−2.350(3) Å and are therefore markedly different from those found in indium tris(amides) [2.049(1)−2.130(4) Å].[16,17] In a similar manner, the bridging covalent bonds In−$\mathrm{N^{b}_{eq}}$ in compound **1** also vary from 2.073(2) Å to 2.456(3) Å, the previously reported values lie in the range 2.199(7)−2.305(3) Å.[12,18]

The geometry of the $\mathrm{N_{ax}}$ atoms is a distorted tetrahedron with $\mathrm{C{-}N_{ax}{-}C}$ and $\mathrm{C{-}N_{ax}{-}In}$ angles ranging from 97.0(2)° to 121.0(3)° for **1**. The same situation was observed for $\mathrm{N^{b}_{eq}}$ [$\mathrm{C{-}N_{ax}{-}C}$ and $\mathrm{C{-}N_{ax}{-}In}$: 89.1(1)−121.6(2)°]. The environment of the nonbridged $\mathrm{N_{eq}}$ is a pyramid with a sum of bond angles from 334.9° to 352.6°. All five-membered rings of the atrane skeleton in **1** adopt an "envelope"-like conformation. For both **1** and **3**, all carbon atoms in the β-positions to the $\mathrm{N_{ax}}$ atom occupy "flap" sites, while the C-α atoms form the base of these envelope planes.

In order to get a better understanding of the structural trends for compound **1** we have carried out a computational study on **1** using the Gaussian 98W program.[19,20] A geometry optimisation of *cis*-**1** leads to the expected parameters of the coordination environment at the indium atoms. Both calculated $\mathrm{N_{ax}{-}In{-}N^{b}_{ax}}$ angles (154.9 °) are in good agreement with our X-ray data. The calculated In←$\mathrm{N_{ax}}$ distances (2.342 Å) are appreciably longer than those in In←$\mathrm{N^{b}_{ax}}$ (2.179 Å) and especially than those of covalent bonds: In−N$_{eq}^{b}$ (2.293 Å) and In−N$_{eq}$ (2.043 and 2.030 Å). Thus, the unusual geometry of the indium atoms in the solid state is probably due to a strong influence of crystal field forces, as is normal in atrane structural chemistry.[21] However, it should be noted that compound **1** may exist as two mesomeric forms (Scheme 2), which could also be a possible reason for the unusual geometry of **1**.



Scheme 2

## Conclusion

We have presented the synthesis of *N*,*N′*,*N′′*-trimethylazaindatrane (**1**). Its dimeric structure was confirmed by X-ray diffractometry and by $^{1}$H and $^{13}$C NMR spectroscopy. The In−N distances in the solid state for this compound show an unusual variety. Further studies on the synthesis of azaindatranes and an investigation of their structure are in progress.

## Experimental Section

**General Remarks:** All manipulations were performed under a dry, oxygen-free argon atmosphere using standard Schlenk techniques. Solvents were dried by standard methods and distilled prior to use. The starting materials Me$_3$-tren[22] and [In(NEt$_2$)$_3$]$_2$ [23] were prepared according to the literature procedures. C$_6$D$_6$ was obtained from Deutero GmbH and dried over sodium. $^{1}$H and $^{13}$C NMR spectra were recorded on a Bruker AC 300 spectrometer. $^{1}$H and $^{13}$C chemical shifts are reported in ppm relative to Me$_4$Si as external standard.

***N*,*N′*,*N′′*-Trimethylazaindatrane Dimer (1):** A solution of Me$_3$-tren (1.92 g, 10.20 mmol) in 15 mL of toluene was added dropwise via cannula within 10 min to a solution of [In(NEt$_2$)$_3$]$_2$ (3.38 g, 10.20 mmol) in 15 mL of toluene at room temperature. The reaction mixture was stirred for 48 h and then all volatiles were removed under reduced pressure. The crude product was washed with *n*-pentane (3 × 10 mL). After recrystallisation (toluene/*n*-pentane) **1** (2.23 g, 73%) was obtained as colourless crystals. $^{1}$H NMR (C$_6$D$_6$, 300.130 MHz): $\delta = 1.73-3.54$ (m, 24 H, 12CH$_2$), 2.75 (s, 6 H, 2CH$_3$), 3.26 (s, 6 H, 2CH$_3$), 2.32 (s, 6 H, 2CH$_3$) ppm. $^{13}$C NMR (C$_6$D$_6$, 75.47 MHz): $\delta = 42.03$, 44.61, 45.56 (CH$_3$); 48.72, 53.03, 53.34, 54.13, 54.20, 55.90 (CH$_2$) ppm.

### X-ray Crystallographic Study

**Crystal Data for 1:** C$_{43}$H$_{93}$In$_4$N$_{16}$, $M = 1293.61$, triclinic, $a = 12.4845(7)$, $b = 15.3700(8)$, $c = 15.1624(10)$ Å, $\alpha = 78.938(5)$, $\beta = 85.708(5)$, $\gamma = 76.988(4)°$, $V = 2780.6(3)$ Å$^3$, space group $P\bar{1}$, $Z = 2$, $d_{calc} = 1.545$ g·cm$^{-3}$, $F(000) = 1318$, $\mu$(Mo-$K_{\alpha}$) = 1.682 mm$^{-1}$, colourless block with dimensions ca. 0.45 × 0.45 × 0.30. Total of 36385 reflections (11919 unique, $R_{int} = 0.0449$) were measured on a Stoe IPDS diffractometer (graphite-monochromated Mo-$K_{\alpha}$ radiation, $\lambda = 0.71073$ Å) at 193(2) K. Data were collected in the range $1.68 < \theta < 30.50$ ($-15 \le h \le 15$, $-19 \le k \le 19$, $-19 \le l \le 19$). The structure was solved by direct methods[24] and refined by full-matrix least-squares on $F^2$ [25] with anisotropic thermal parameters for all non-hydrogen atoms. All H atoms were placed in calculated positions and refined using a riding model. The final residuals were: $R_1 = 0.0271$, $wR_2 = 0.0808$ for 10623 reflections with $I > 2\sigma(I)$ and 0.0323, 0.0940 for all data and 607 parameters. Goof = 1.101, maximum shift/e.s.d. = 0.002, maximum $\Delta\rho = 0.685$ e·Å$^{-3}$. CCDC-194359 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

## Acknowledgments

We thank Dr. Evgueni Avtomonov and Dr. Andrei Churakov for helpful discussion. We also acknowledge the excellent service offered by the Hochschulrechenzentrum of the Philipps-Universität Marburg. This work was supported by INTAS under Grant No YSF 2001/2-135 for S. S. K. as well as by the Philipps-University Marburg, Chemistry Department, with a grant for P. L. S.

---

[1] J. G. Verkade, *Coord. Chem. Rev.* **1994**, *137*, 233−295.

[2] S. S. Karlov, G. S. Zaitseva, *Chem. Heterocycl. Comp.* **2001**, *37*, 1325−1357.

[3] R. R. Schrock, *Acc. Chem. Res.* **1997**, *30*, 9−16.

[4] J. Pinkas, B. Gaul, J. G. Verkade, *J. Am. Chem. Soc.* **1993**, *115*, 3925−3931.

[5] J. Pinkas, T. Wang, R. A. Jacobson, J. G. Verkade, *Inorg. Chem.* **1994**, *33*, 4202−4210.

[6] J. Pinkas, J. G. Verkade, *Phosphorus, Sulfur, and Silicon* **1994**, *93−94*, 333−337.

[7] J. Pinkas, T. Wang, R. A. Jacobson, J. G. Verkade, *Inorg. Chem.* **1994**, *33*, 5244−5253.

[8] A. P. Purdy, *Inorg. Chem.* **1994**, *33*, 282−286.

[9] C. J. Carmalt, J. D. Mileham, A. J. P. White, D. J. Williams, J. W. Steed, *Inorg. Chem.* **2001**, *40*, 6035−6038.

[10] H. Sussek, O. Stark, A. Devi, H. Pritzkow, R. A. Fischer, *J. Organomet. Chem.* **2000**, *602*, 29−36.

[11] M. Porchia, F. Benetollo, N. Brianese, G. Rossetto, P. Zanella, G. Bombieri, *J. Organomet. Chem.* **1992**, *424*, 1−13.

[12] J. Kim, S. G. Bott, D. M. Hoffman, *J. Chem. Soc., Dalton Trans.* **1999**, 141−146.

[13] D. C. Bradley, H. Haves, D. M. Frigo, M. B. Hursthouse, M. B. Hussain, *J. Organomet. Chem.* **1987**, *325*, 55−67.

[14] D. J. Rose, J. Zubieta, A. J. Fischman, S. Hillier, J. W. Babich, *Inorg. Chem. Commun.* **1998**, *1*, 164−166.

[15] R. J. Motekaitis, A. E. Martell, S. A. Koch, J. Hwang, D. A. Quarless, M. J. Welch, *Inorg. Chem.* **1998**, *37*, 5902−5911.

[16] M. A. Petrie, K. Ruhlandt-Senge, H. Hope, P. P. Power, *Bull. Soc. Chim. Fr.* **1993**, *130*, 851−855.

[17] J. Kim, S. G. Bott, D. M. Hoffman, *Inorg. Chem.* **1998**, *37*, 3835−3841.

[18] K. A. Aitchison, J. D. J. Backer-Dirks, D. C. Bradley, M. M. Faktor, D. M. Frigo, M. B. Hursthouse, B. Hussain, R. L. Short, *J. Organomet. Chem.* **1989**, *366*, 11−23.

[19] GAUSSIAN 98W. User's Reference, Pittsburgh, Gaussian Inc., 1998, 280.

[20] Ab initio molecular orbital calculations were carried out using the Gaussian 98 program. Geometry optimisations were performed at the HF level of theory. The basis set used in this work was LANL2DZ. This basis set consists of an ecp basis set for the indium atoms and the D95V [T. H. Dunning, P. J. Hay, Modern Theoretical Chemistry, Plenum: New York, 1976.] basis set for another atoms. The LANL2DZ is of double-ζ quality in the valence region.

[21] S. Belyakov, L. Ignatovich, E. Lukevics, *J. Organomet. Chem.* **1999**, *577*, 205−210.

[22] H. Schmidt, C. Lensink, S. K. Xi, J. G. Verkade, *Z. Anorg. Allg. Chem.* **1989**, *578*, 75−80.

[23] G. Rossetto, N. Brianese, A. Camporese, M. Porchia, P. Zanella, R. Bertoncello, *Main Group Met. Chem.* **1991**, *14*, 113−122.

[24] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467−473.

[25] G. M. Sheldrick, *SHELXL-97, Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.

Received November 26, 2002
[I02645]