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Lewis Base Induced Reductions in Organolanthanide Chemistry**

*Daniel Bojer, Ajay Venugopal, Beate Neumann, Hans-Georg Stammler, and Norbert W. Mitzel**

Dedicated to Professor Dr. Gerd Becker on the occasion of his 70th birthday

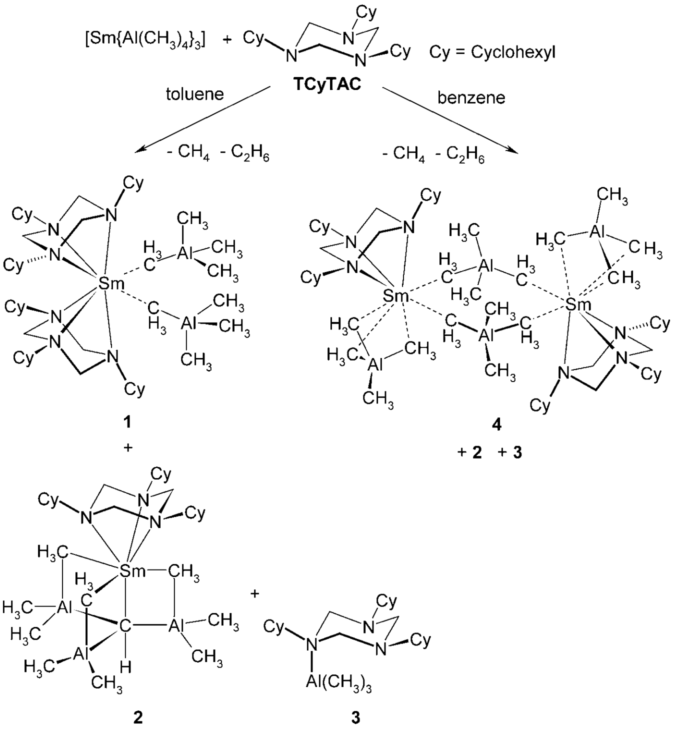
Recent years have seen a remarkable progress in the molecular chemistry of divalent lanthanides,[1] which was previously restricted to just the three ions Eu^{2+}, Yb^{2+}, and Sm^{2+}.[2] Today even compounds of Tm^{II},[3] Dy^{II},[4,5] Nd^{II},[6,7] and La^{II}[8] are known. Samarium(II) (usually as SmI_2) is in widespread use as a powerful reducing agent in synthetic chemistry.[9] It has a relatively strong negative redox potential (Sm^{3+}/Sm^{2+} $E_{1/2} = -1.55$ V)[10] compared to europium and ytterbium and is not accesible under mild conditions. It should be noted that the potentials for the reduction M^{III}/M^{II} are generally more negative for organometallic systems than for reductions in aqueous solution and that both solvent and ligand contributions are important in lanthanide redox chemistry.[11]

A striking variant of redox reactivity of samarium compounds was found by Evans and Davis when they investigated pentamethylcyclopentadienyl lanthanide compounds.[12] The tris(pentamethylcyclopentadienyl) complex $[(C_5Me_5)_3Sm]$ was previously thought to be non-existent for steric reasons,[13] but it turned out to behave as a strong one-electron reducing agent analogous to the divalent compound $[(C_5Me_5)_2Sm]$. The steric demand of the $(C_5Me_5)^-$ ligand facilitates reduction to $[(C_5Me_5)_2Sm]$, whereby the third $(C_5Me_5)^-$ unit is oxidized and then dimerizes to give $(C_5Me_5)_2$. The term “sterically induced reduction” (SIR)[14] was coined to describe such observations. A recent intriguing example found by Harder et al. is the ability of the extremely bulky perarylated cyclopentadiene (4-*n*Bu-C_6H_4)$_5$$C_5H$ ($Cp^{BIG}H$) to reduce [(2-Me_2N-benzyl)$_3$$Sm^{III}$] to the divalent samarocene analogue $[Sm(Cp^{BIG})_2]$.[15]

We have recently demonstrated that the steric effect exerted by the cyclic triaminal 1,3,5-trimethyl-1,3,5-triazacyclohexane (TMTAC) onto the ligands in $[M(AlMe_4)_3]$ (M = La, Sm, Y), initiates multiple C–H activation.[16] The products are species comprising methylene (CH_2^{2-}) and even hexacoordinate carbide (C^{4-}) fragments. These results are related to the work of Anwander et al. on base-induced cleavage and multiple C–H activation of $[M(AlMe_4)_3]$.[17] Herein, we demonstrate that the action of more bulky polybases of the cyclic triamine type[18] on treatment with $[Sm(AlMe_4)_3]$ not only causes C–H activation, but also leads to base-induced reductions. It should be emphasized that these reductions occur in the complete absence of any cyclopentadiene-based ligand or reagent, which are involved in the above-mentioned SIR processes.

In contrast to the reactivity of $[M(AlMe_4)_3]$ reagents observed by Anwander et al. and us, the reaction of $[Sm(AlMe_4)_3]$ with the bulky 1,3,5-tricyclohexyl-1,3,5-triazacyclohexane (TCyTAC) leads to spontaneous reduction of the trivalent samarium atom into its highly reactive +2 oxidation state, along with C–H activation of the tetramethylaluminate ligands as only a secondary reaction. Depending on the solvent employed in the reactions, we observed two different products (Scheme 1).

The addition of two equivalents of TCyTAC to a solution of $[Sm(AlMe_4)_3]$ in toluene results in a color change from yellow to red, and after prolonged stirring for three days to dark green. Fractional crystallization allowed the isolation of three products: dark green crystals of the samarium(II) complex $[(TCyTAC)_2Sm(AlMe_4)_2]$ (**1**) being the least soluble, yellow crystals of the C–H activation product



Scheme 1. Reaction pathways of $[Sm(AlMe_4)_3]$ with TCyTAC in toluene or benzene.

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[*] D. Bojer, Dr. A. Venugopal, B. Neumann, Dr. H.-G. Stammler, Prof. Dr. N. W. Mitzel
Fakultät für Chemie, Universität Bielefeld
Universitätsstrasse 25, 33615 Bielefeld (Germany)
Fax: (+49) 521-106-6026
E-mail: mitzel@uni-bielefeld.de

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[(TCyTAC)Sm{CH(AlMe$_3$)$_3$}] (**2**), and a mono-AlMe$_3$ adduct of TCyTAC (**3**), which is the most soluble of the three. The reaction proceeds by evolution of a mixture of methane and ethane, as identified by GC-MS. Methane stems from the redox-neutral condensation of (AlMe$_4$)$^-$ units to the methine function in **2**. Ethane is likely to be the product of oxidative coupling of two methyl anions, which is therefore the source of reductive power in the system. Considering the strongly negative redox potential Sm^{3+}/Sm^{2+}, and the fact that [(C$_5$Me$_5$)$_2$Sm] is even able to reduce the "inert" gas nitrogen,[19] the easy accessibility and stability of complex **1** is remarkable, as is the fact that the components Sm^{3+} and CH$_3^-$ were already present and mutually unreactive in the precursor compound [Sm(AlMe$_4$)$_3$]. The redox process is therefore initiated by the base TCyTAC, which itself is not redox active, but obviously changes the redox potential in a way that CH$_3^-$ can act as a reducing agent, thus paralleling the [(C$_5$Me$_5$)$_3$Sm] system of Evans, in which the (C$_5$Me$_5$)$^-$ anion has been identified as the reducing agent.

Considering this parallel, one could be tempted to postulate that the bulk of the ligand TCyTAC leads to a type of sterically induced reduction by pushing one of the (AlMe$_4$)$^-$ ligands aside and reducing the hapticity of two others from η^2 to η^1. This interpretation could be supported by the molecular structure of compound **1** as determined by X-ray diffraction (Figure 1). The samarium atom is bonded to two TCyTAC ligands that form an angle of 30.9° between their N$_3$ planes. This allows only for the end-on coordination of two (AlMe$_4$)$^-$ anions, resulting in a total coordination number of eight at the samarium atom, with Sm–C bond lengths of 2.944(4) Å and 2.951(4) Å and angles Sm-C-Al of 174.0(2)° and 170.2(2)°. This type of [(μ-Me)AlMe$_3$] end-on coordination has only been reported once in the case of a lanthanum tetramethylaluminate–imino–amido–pyridine complex;[20] however, despite the larger lanthanum atom, the La–C bond in this compound is shorter at 2.825(7) Å, which indicates the steric pressure in **1** exerted by the two TCyTAC ligands on the (AlMe$_4$)$^-$ anions.

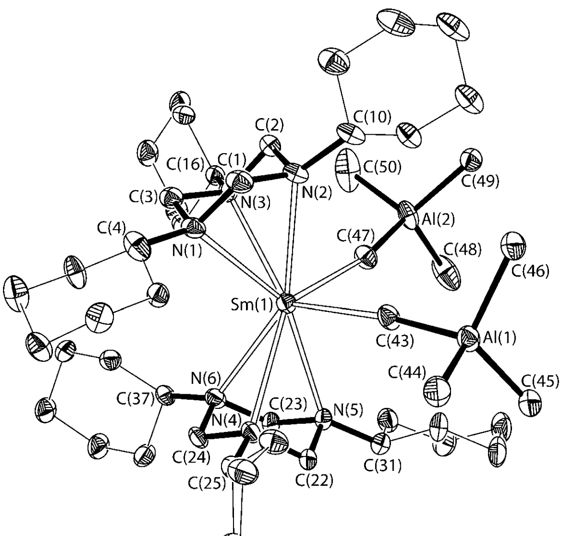

Figure 1. Molecular structure of **1** in the solid state (ellipsoids set at the 50% level). Hydrogen atoms and solvent molecules are omitted for clarity. Bonds to samarium are drawn open, and C–C bonds are shown as thin lines. Selected bond lengths [Å] and angles [°]: Sm1–N1 2.745(4), Sm1–N2 2.854(4), Sm1–N3 2.834(3) Sm1–N4 2.894(3), Sm1–N5 2.788(4), Sm1–N6 2.875(4), Sm1–C43 2.944(4), Sm1–C47 2.951(4); Al1-C43-Sm1 174.0(2), Al2-C47-Sm1 170.2(2), C43-Sm1-C47 97.9(1), centroid(N1–N3)-Sm-centroid(N4–N6) 149.1, N1-Sm1-N2 50.5(1), N2-Sm1-N3 49.0(1), N1-Sm1-N3 49.9(1), N2-Sm1-C43 78.1(1), N2-Sm1-C47 83.8(1), C44-Al1-C43 112.3(2), C45-Al1-C43 106.5(2), C46-Al1-C43 107.4(2).

With compound **2**, [(TCyTAC)Sm{CH(AlMe$_3$)$_3$}], we have crystallographically identified a further compound (Figure 2) that is a key step in the proposed mechanism in reactions of [M(AlMe$_4$)$_3$] (M = La, Sm, Y) with TMTAC.[16] Therefore, the replacement of methyl by cyclohexyl groups at the C$_3$N$_3$ rings not only changes the preference for reduction instead of C–H activation, but also the product type of the latter reactivity. Whilst with TMTAC two CH-activation products, [(TMTAC)Sm(Me$_3$AlCH$_2$AlMe$_2$CH$_2$AlMe$_3$)] and [{(TMTAC)Sm}{Sm$_2$(μ$_2$-Me)}{(μ$_6$-C)[Al(μ$_2$-Me)$_2$(Me)]$_3$}{(μ$_3$-CH$_2$)(μ$_2$-Me)AlMe$_2$}$_2$],[16] both containing formal CH$_2^{2-}$and the latter C^{4-} anions, complex **2** contains a tris(aluminate)-trianion [CH(AlMe$_3$)$_3$]$^{3-}$ with a methine function (CH^{3-}) as the most striking feature. This methine unit is bonded to one samarium and three aluminum atoms. The carbon atom therefore adopts a trigonal bipyramidal coordination geometry with H and Sm being the axial ligands. The three aluminum atoms form the equatorial plane with Al-C-Al bond angles ranging from 118.4(1)° to 121.6(1)°, whilst the Sm1-C22-Al angles are between 87.8 and 87.9°. With 2.340(2) Å the Sm–C22 distance is quite short and compara-

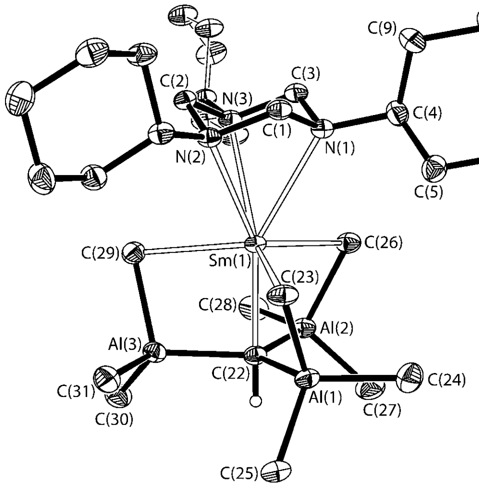

Figure 2. Molecular structure of **2** in the solid state (ellipsoids set at the 50% level). Hydrogen atoms (except H22 at C22) and solvent molecules are omitted, and bonds to Sm1 are drawn open for clarity. Selected bond lengths [Å] and angles [°]: Sm1–C22 2.340(2), Sm1–C23 2.637(3), Sm1–C26 2.634(3), Sm1–C29 2.636(3), Sm1–N1 2.724(2), Sm1–N2 2.712(2), Sm1–N3 2.718(2), C22–H22 0.98(3); Al1-C22-Al2 119.6(1), Al2-C22-Al3 121.6(1), Al1-C22-Al3 118.4(1), Al2-C22-Sm1 87.9(1), Al1-C22-Sm1 87.9(1), Al3-C22-Sm1 87.8(1), Sm1-C22-H22 179.3(13).

ble to the Sm−C distances in the homoleptic three-coordinate compound [Sm{CH(SiMe$_3$)$_2$}$_3$].[21]

As a third product of the reaction, colorless crystals of the adduct TCyTAC•AlMe$_3$ (**3**) were obtained, thus meeting our expectations based on the results of the earlier investigated reactions of TMTAC with [Sm(AlMe$_4$)$_3$].[16] Compound **3** was further identified by multinuclear NMR spectroscopy (including comparison with data of a sample independently prepared from TCyTAC and one equivalent of AlMe$_3$ and by determination of its crystal structure; see the Supporting Information).

Surprisingly, a different reduction product was obtained upon carrying out the reaction between TCyTAC and [Sm(AlMe$_4$)$_3$] (Scheme 1) in a solvent that is chemically only slightly different, namely benzene, and a different stoichiometry. As in the reaction in toluene, the formation of only a minor quantity of the trivalent C−H activation product **2** and the adduct **3** was observed, but we isolated a different divalent samarium species (**4**). Compound **4**, which was identified by means of elemental analysis and single-crystal X-ray diffraction (Figure 3), contains a samarium atom coordinated only by one TCyTAC ligand and two (AlMe$_4$)$^-$ anions. The compound is an inversion-symmetric dimer, because each of two bridging (AlMe$_4$)$^-$ anions is η^1-bonded to both samarium atoms, which leads to an eight-membered ring. Compared to **1**, the steric crowding at the samarium atoms in **4** is remarkably small, which is also reflected by the fact that the one terminal aluminate ligand per samarium atom adopts an asymmetric η^3 binding mode, with Sm−C distances of 2.890(2) Å for Sm1−C22, 3.098(1) Å for Sm1−C24, and 3.225(1) Å for Sm1−C23. In this way the coordination number of samarium is again eight, as in **1**; that is, the binding isomerism of the (AlMe$_4$)$^-$ ligand enables replenishing the coordination sphere defined by the other ligands.

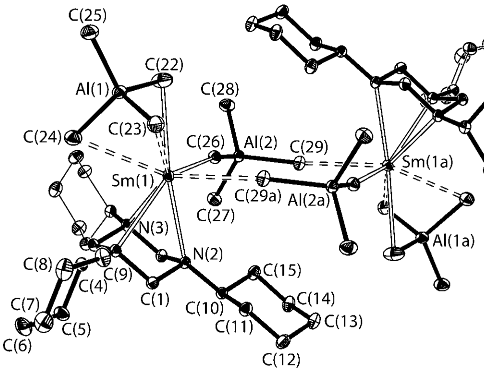

Figure 3. Molecular structure of **4** in the solid state (ellipsoids set at the 50% level). Hydrogen atoms and solvent molecules are omitted for clarity. Bonds to samarium are drawn open, and those longer than 3 Å are shown dashed. Selected bond lengths [Å] and angles [°]: Sm1–N1 2.754(1), Sm1–N2 2.811(1), Sm1–N3 2.727(1), Sm1–C22 2.890(1), Sm1–C23 3.225(1), Sm1–C24 3.098(1), Sm1–C26 2.976(1), Sm1–C29a 3.008(1); C22-Sm1-C24 66.1(3), C26-Sm1-C29a 82.2(2), Sm1-C26-Al2 169.0(1), Sm1-C29a-Al2a 167.1(1).

Compound **4** can be interpreted as a dimer of **1** under loss of one TCyTAC ligand per metal atom. This and the more relaxed structural situation in the samarium coordination sphere raises the question as to whether the SIR concept can serve to rationalize the reactivity in these cases. However, and although unlikely, it cannot be excluded that in the first step, **1** is formed, which is then transferred into **4** by loss of two TCyTAC units. The existence of an equilibrium between **1** and **4** is unlikely, as we have only been able to isolate one of each of the compounds from the reactions described above.

The preference for the formation of divalent samarium can also be rationalized in terms of its greater ionic radius, which better accommodates poly-N-ligands. This effect has parallels to the known case in which [Yb{N(SiMe$_3$)$_2$}$_3$] reacts with the NMe$_2$-donor-functionalized indene 1-(Me$_2$NCH$_2$CH$_2$)C$_9$H$_7$ in a spontaneous redox reaction to give [Yb^{II}{1-(Me$_2$NCH$_2$CH$_2$)C$_9$H$_7$}$_2$] and N$_2$(SiMe$_3$)$_4$.[22] In the case of **1** and **4**, however, the much higher Sm^{3+}/Sm^{2+} redox potential has to be overcome.

Contrary to expectations, the present investigations have shown that not only C−H activation but also reduction processes occur in reactions of [Sm(AlMe$_4$)$_3$] with the neutral tripodal nitrogen base 1,3,5-tricyclohexyl-1,3,5-triazacyclohexane. This reactivity of a base-induced reduction is unprecedented in organosamarium chemistry and is a promising alternative approach for organolanthanide redox chemistry. The fact that the less bulky 1,3,5-trimethyl-1,3,5-triazacyclohexane (TMTAC) leads to C−H activation products only, and not to the redox processes as observed herein, is a convincing argument for steric influence. This effect has now to be investigated in more detail. The goal is to transfer this reaction type to other f-element compounds and to achieve conditions for selectivity to either base-induced reduction, including fine-tuning the redox potentials of lanthanide ions, or C−H activation.

Experimental Section

All manipulations were performed under rigorously dry inert atmosphere of argon using advanced Schlenk and glove box techniques and using freshly dried solvents. [Sm(AlMe$_4$)$_3$] and TCyTAC were prepared according to literature procedures.[23,24]

[(TCyTAC)$_2$Sm(AlMe$_4$)$_2$] (**1**), [(TCyTAC)Sm{CH(AlMe$_3$)$_3$}] (**2**), and TCyTAC•AlMe$_3$ (**3**): In a glovebox, TCyTAC (333 mg, 1.00 mmol) was slowly added as a solid to a solution of [Sm(AlMe$_4$)$_3$] (206 mg, 0.5 mmol) in 10 mL of toluene. An instant color change from yellow to red and then to dark brown accompanied by gas evolution was observed. After 3 days of stirring, the color of the reaction mixture had turned dark green and was filtered. The clear green solution was concentrated to 3 mL and kept for crystallization at room temperature. Well-formed crystals of [(TCyTAC)$_2$Sm(AlMe$_4$)$_2$] (**1**) could be obtained after 3 days. The remaining solution was concentrated to 1 mL leading to crystallization of yellow crystals of **2**. By cooling this supernatant solution to −30 °C, colorless crystals of **3** were obtained. Yields: **1**, 238 mg (48%); **2**, 83 mg (21%); **3**, 28 mg (7%). Elemental analysis (%) calcd for **1** (C$_{50}$H$_{102}$Al$_2$N$_6$Sm): C 60.56, H 10.37, N 8.47; found C 60.22, H 9.79, N 8.14. NMR for **3**: ^{1}H NMR (500 MHz, 20 °C, C$_6$D$_6$): $\delta = -0.22$ (s, 9H, Al(CH_3)$_3$), 0.95–1.72 (m, 10H, (CH_2)$_5$CHN), 2.65 (b, 3H, CHN), 3.40 and 3.95 ppm (b, 6H, NCH_2N); ^{13}C NMR (125 MHz, 20 °C, C$_6$D$_6$): $\delta = -5.1$ (s, Al(CH$_3$)$_3$, 26.1 (s, CH$_2$CH$_2$CH$_2$CHN), 26.2 (CH$_2$CH$_2$CHN), 29.2 (CH$_2$CHN), 59.7 (CHN), 67.8 ppm (NCH$_2$N); ^{27}Al NMR (130 MHz, 20 °C, C$_6$D$_6$): $\delta = 178$ ppm.

2, **3**, and $[(\mathrm{TCyTAC})\mathrm{Sm}(\mathrm{AlMe}_4)_2]_2$ (**4**): The above procedure was carried out in benzene as solvent with only one equivalent (167 mg, 0.5 mmol) of TCyTAC. Similar observations of color changes and gas evolution were made. The reaction mixture was filtered and concentrated to 3 mL. Dark green blocks of **4** could be obtained overnight at room temperature. After concentrating and stepwise cooling of the solution, single crystals of **2** and **3** again precipitated. Yields: **4**, 363 mg (55 %); **2**, 87 mg (22 %); **3**, 14 mg (11 %). Elemental analysis (%) calcd for **4** ($C_{58}H_{126}Al_4N_6Sm_2$): C 52.92, H 9.65, N 6.38; found C 52.89, H 9.63, N 6.20.

Crystal structure determinations: Diffraction data were recorded on a Nonius KappaCCD with crystals selected and mounted under inert oil; $\lambda = 0.71073$ Å. **1**: $C_{50}H_{102}Al_2N_6Sm{\cdot}2(C_7H_8)$, $M_r = 1175.95$, $T = 100(2)$ K; monoclinic, Pn, $a = 19.2521(2)$, $b = 14.4899(1)$, $c = 23.3100(2)$ Å, $\beta = 90.8663(5)°$; $Z = 4$, θ_{max} 30.0°; 154 290 reflections collected, 36 742 unique ($R_{int} = 0.068$); $R1 = 0.0438$, $wR2 = 0.0975$ [$I > 2\sigma(I)$]; $R1 = 0.0520$, $wR2 = 0.1024$ (all data); $\rho_{max/min}$ 3.65/−1.49 e Å^{-3}. Disorder of C5 to C9 on two positions (64:36); the crystal was racemically and pseudohedrally twinned; BASF factors are (0.0562/0.4194/0.0572). **2**: $C_{37}H_{73}Al_3N_3Sm$, $M_r = 791.27$, $T = 100(2)$ K; monoclinic, $P2_1/c$, $a = 11.1380(2)$, $b = 19.2583(3)$, $c = 19.9265(3)$ Å, $\beta = 103.3559(9)°$; $Z = 4$, θ_{max} 30.0°; 81 202 reflections collected, 12 106 unique ($R_{int} = 0.064$); $R1 = 0.0329$, $wR2 = 0.0701$ [$I > 2\sigma(I)$]; $R1 = 0.0531$, $wR2 = 0.0761$ (all data); $\rho_{max/min}$ 2.10/−0.71 e Å^{-3}. **3**: $C_{24}H_{48}AlN_3$, $M_r = 405.63$, $T = 100(2)$ K; monoclinic, $P2_1/n$; $a = 10.6018(2)$, $b = 10.9947(3)$, $c = 21.6911(5)$ Å, $\beta = 102.2031(14)°$; $Z = 4$, θ_{max} 30.0°; 48 795 reflections collected, 7174 unique ($R_{int} = 0.045$); $R1 = 0.0399$, $wR2 = 0.0986$ [$I > 2\sigma(I)$]; $R1 = 0.0548$, $wR2 = 0.1061$ (all data); $\rho_{max/min}$ 0.36/−0.31 e Å^{-3}. **4**: $C_{58}H_{126}Al_4N_6Sm_2{\cdot}4(C_6H_6)$, $M_r = 1628.70$, $T = 100(2)$ K; triclinic, $P\bar{1}$; $a = 11.5112(9)$, $b = 11.9251(12)$, $c = 15.9519(17)$ Å, $\alpha = 94.901(9)$, $\beta = 94.817(9)$, $\gamma = 91.558(8)°$; $Z = 1$, θ_{max} 30.0°; 85 054 reflections collected, 12 645 unique ($R_{int} = 0.029$); $R1 = 0.0172$, $wR2 = 0.0374$ [$I > 2\sigma(I)$]; $R1 = 0.0231$, $wR2 = 0.0398$ (all data); $\rho_{max/min}$ 0.87/−0.56 e Å^{-3}. Programs: G. M. Sheldrick, SHELXL-97, *Program for Crystal Structure Refinement*, Universität Göttingen, Göttingen, Germany, **1997**. CCDC 752100 (**1**), 752101 (**2**), 752102 (**3**), and 752103 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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