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Binary Polyazides Of Cerium And Gadolinium

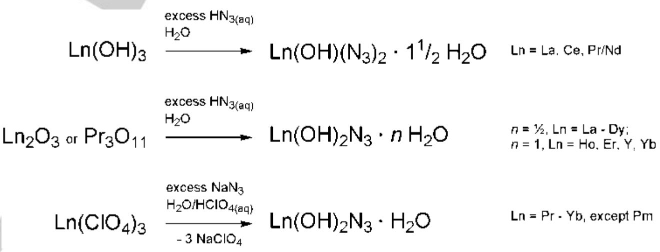
Kati Rosenstengel,[a] Axel Schulz,[a,b] Oliver Niehaus,[c] Oliver Janka,[c] Rainer Pöttgen,[c] and Alexander Villinger*[a]

Abstract: Herein, we report on the preparation and full characterization (m.p., ATR-IR/Raman, elemental analysis, ^{14}N NMR) of binary gadolinium(III) azide as DMSO solvate $Gd(N_3)_3 \cdot {}^8/_3$ DMSO (DMSO = dimethylsulfoxide), along with the partially hydroxide substituted species $Gd_4(OH)_2(N_3)_{10} \cdot n$ DMSO (n = 8, 10). Moreover, the isolation and comprehensive characterization of hexaazido lanthanate(III) anions $[Ln(N_3)_6]^{3-}$ (Ln = Ce, Gd) in a series of $[Ph_4P]^+$ and $[EtPh_3P]^+$ salts is presented. Single crystal structures of all compounds were determined, and the magnetic susceptibility in solution (NMR, Evans Method), as well as in the solid state (VSM), was investigated.

Introduction

Binary polyazides of transition-metal and main-group elements form a class of highly endothermic compounds, which often tend to decompose explosively.[1] Nevertheless, the synthesis and isolation of these nitrogen-rich species has attracted much attention in the last decades.[2,3] However, the chemistry of binary azides of the rare earth elements in specific has scarcely been investigated, and only few reports on structural and spectroscopic properties are available, to date.

The first attempted preparation of rare earth azides in aqueous medium was carried out by Curtius and Darapsky as early as 1900.[4] However, according to elemental analyses, the reactions of lanthanum, cerium and didymium hydroxides (didymium = Pr/Nd)[5] with concentrated hydrazoic acid in water yielded only basic lanthanide azides instead of the expected binary azides (Scheme 1). In agreement with these findings, Ant-Wuorinen could demonstrate that basic lanthanide azides can selectively be precipitated from an aqueous mixture of lanthanide nitrates by addition of sodium azide.[6] While the constitution of these rare earth hydroxide azides was formulated as $Ln(OH)(N_3)_2 \cdot 1^1/_2\,H_2O$ (Ln = La, Ce, Dy) by Curtius and Darapsky,[4] Rosenwasser *et al.* reported on the reaction of rare earth sesquioxides Ln_2O_3 (Ln = La, Nd, Sm - Er, Yb, Y) or Pr_6O_{11} in aqueous hydrazoic acid, which in contrary yielded basic lanthanide azides of the empiric formula $Ln(OH)_2N_3 \cdot n\,H_2O$ (n = ½, Ln = La – Dy; n = 1, Ln = Ho, Er, Y, Yb) while no reaction was observed for CeO_2, Tb_4O_7, Lu_2O_3 and Sc_2O_3 (Scheme 1).[7] Moreover, Abdel-Aziz and coworker succeeded in isolating rare earth hydroxide azides in yet another composition, $Ln(OH)_2N_3 \cdot H_2O$ (Ln = Pr – Yb, except Pm). The latter were obtained by addition of sodium azide to the corresponding lanthanide perchlorates $Ln(ClO_4)_3$ in aqueous perchloric acid (Scheme 1).[8] While numerous elemental analyses,[4,7a,8b-d] DTA measurements (DTA = differential thermal analysis),[7b] IR spectra,[7a,8d] susceptibility measurements,[8b,d] electron-beam sensitivities,[9] as well as spectrophotometric and radiometric measurements (^{143}Pr) of complex stability constants[8a-c] were reported in the last decades, the exact constitution of basic lanthanide azides remains still unclear, since no structural data is available to date.



Scheme 1. Reported syntheses of rare earth hydroxide azides.

Already in 1966, the formation of binary praseodymium and neodymium polyazides in anhydrous DMSO or TMP (TMP = trimethylphosphate, $(MeO)_3PO$) was observed by Gutmann *et al.*[10] The reactions of the corresponding lanthanide(III) perchlorate solvates $Ln(ClO_4)_3 \cdot n$ solvent (Ln = Pr, Nd; solvent = DMSO (n = 10), TMP (n = 8)) with azide ions were studied by spectrophotometric, conductometric and potentiometric methods, which indicated the formation of species such as $Ln(N_3)_3 \cdot n$ solvent or $[Ln(N_3)_4(\text{solvent})_n]^-$, however, without any further characterization. Only recently, Schnick, Kraus and coworkers successfully synthesized binary europium(II) azide, obtained from the reaction of silver azide and elemental europium in liquid ammonia at −40 °C (Scheme 2).[11] Thereby, thermal treatment of the initially formed ammonia solvate $Eu(N_3)_2 \cdot n\,NH_3$ (n = unknown) resulted in the formation of binary europium(II) azide, $Eu(N_3)_2$, as deduced from elemental analyses and vibrational spectra (IR, Raman). While structural data could not be recorded due to the amorphous nature of $Eu(N_3)_2$, it was possible to isolate the corresponding holmium(III) amide azide as ammonia solvate,

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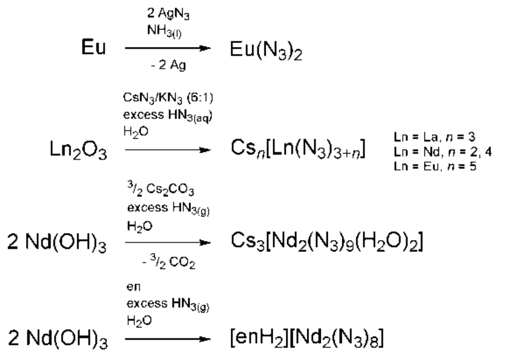
$[Ho_2(NH_2)_3(NH_3)_{10}][N_3]_3 \cdot 1^1/_4\ NH_3$. Furthermore, the latter could be characterized by single crystal structure determination and IR spectroscopy, which however implied, that this species is better described as dinuclear holmium amide ammonia solvate displaying no metal-azide bonds.



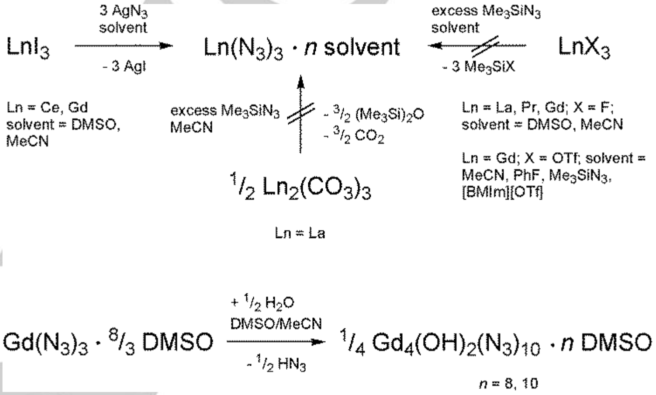
Scheme 2. Preparation of $Eu(N_3)_2$, $Cs_3[La(N_3)_6]$, $Cs_2[Nd(N_3)_5]$, $Cs_4[Nd(N_3)_7]$, $Cs_5[Eu(N_3)_8]$, $Cs_3[Nd_2(N_3)_9(H_2O)_2]$ and $[enH_2][Nd_2(N_3)_8]$ (en = ethylendiamine).

Pioneering work in the field of polyazido lanthanates was carried out by Mautner, Fritzer and coworkers.[12a-d] In the year 1982 they reported on the reaction of lanthanide sesquioxides Ln_2O_3 (Ln = La, Nd) with a mixture of CsN_3 and KN_3 (6:1) in concentrated aqueous hydrazoic acid, resulting in the formation of crystalline $Cs_3[La(N_3)_6]$, $Cs_2[Nd(N_3)_5]$ and $Cs_4[Nd(N_3)_7]$, respectively (Scheme 2).[12a] Similarly, the synthesis of $Cs_5[Eu(N_3)_8]$ was achieved starting from Eu_2O_3, CsN_3 and hydrazoic acid in water (Scheme 2).[12c] Besides elemental analyses,[12] all compounds were characterized by IR spectroscopy (IR/Raman),[12a] susceptibility measurements,[12a, 13 b] diffuse reflectance spectroscopy,[12a] and optical spectra (electronic absorption, luminescence and laser excitation).[13c] Later, Starynowicz *et al.* isolated polyazido neodymate salts $Cs_3[Nd_2(N_3)_9(H_2O)_2]$ and $[enH_2][Nd_2(N_3)_8]$ (en = ethylendiamine, $C_2H_4(NH_2)_2$) by vapor diffusion of gaseous hydrazoic acid into an aqueous solution of $Nd(OH)_3$ and Cs_2CO_3 or ethylendiamine, respectively (Scheme 2).[14] Single-crystal structures were determined, with exception of $Cs_4[Nd(N_3)_7]$, which decomposed when exposed to X-ray radiation.[12,14] For the latter, a model for the micro symmetry was refined to fit the optical spectra, indicating a six-fold coordination environment for the Nd(III) atoms[13a] while the coordination numbers in the other polyazido lanthanate anions range from eight in $Cs_5[Eu(N_3)_8]$, $Cs_3[Nd_2(N_3)_9(H_2O)_2]$ and $Cs_2[Nd(N_3)_5]$, to nine in $Cs_3[La(N_3)_6]$ and $[enH_2][Nd_2(N_3)_8]$.[12,13,14] In 2005, Crawford et al. succeeded in the isolation and structural characterization of the heavy analog actinide salt $[Bu_4N]_3[U(N_3)_7]$, which displays the heptaazido uranate(III) anions in a distorted pentagonal-bipyramidal ligand sphere.[15]

Results and Discussion

Synthesis of $Gd(N_3)_3 \cdot {}^8/_3$ DMSO and $Gd_4(OH)_2(N_3)_{10} \cdot n$ DMSO (*n* = 8, 10)

Following our interest in element nitrogen compounds with a high nitrogen content, we envisaged the preparation of binary lanthanide(III) azides by means of a halide/azide exchange reaction, starting from the trihalides according to Scheme 3. Two routes seemed feasible: i) Reaction of lanthanide trifluorides LnF_3 with excess trimethylsilyl azide Me_3SiN_3 and ii) treatment of lanthanide triiodides LnI_3 with silver azide in a suitable, anhydrous solvent.



Scheme 3. Preparation of $Ln(N_3)_3 \cdot n$ solvent and $Gd_4(OH)_2(N_3)_{10} \cdot n$ DMSO (*n* = 8, 10).

Indeed, the reactions of cerium(III)- and gadolinium(III) iodide with stoichiometric amounts of silver azide in DMSO proceeded well within a few minutes at ambient temperature. Separation of silver iodide by filtration resulted in a deep red solution in case of cerium, and a yellow solution for gadolinium, respectively (Scheme 3).[16] An iodide/azide exchange in acetonitrile was also observed, but co-precipitation of all products rendered these conditions unsuitable in a preparative sense. However, careful layering of the DMSO solution of gadolinium(III) azide with MeCN, followed by further vapor diffusion of MeCN, allowed to selectively crystallize silver iodide as large hexagonal crystals. Subsequently, $Gd(N_3)_3 \cdot {}^8/_3$ DMSO (= $[Gd(N_3)_3]_3 \cdot 8$ DMSO) was obtained as yellow needle-like crystals (Figure 1).[16] Interestingly, after the separation of silver azide the partially hydroxide substituted gadolinium(III) azide $Gd_4(OH)_2(N_3)_{10} \cdot 10$ DMSO was reproducibly obtained, when both solvents were solely dried by distillation from CaH_2. The formation of this formal basic gadolinium(III) azide could be completely prevented when the solvents were stored over molecular sieves (4 Å) prior to use (Scheme 3, Figure 2).[16] On the other hand, large colorless crystals of $Gd_4(OH)_2(N_3)_{10} \cdot 10$ DMSO could be prepared in bulk, when a DMSO solution of $Gd(N_3)_3$ was directly layered by moist MeCN (Figure 2). Thereby, $Gd_4(OH)_2(N_3)_{10} \cdot 10$ DMSO crystallizes as mixture of a monoclinic phase ($P2_1/c$, denoted as *β*-$Gd_4(OH)_2(N_3)_{10} \cdot 10$ DMSO) as major component, besides small amounts of a triclinic modification ($P\bar{1}$, α-$Gd_4(OH)_2(N_3)_{10} \cdot 10$ DMSO), which could not be separated for analytical purposes. Nevertheless, some crystals could be manually separated, which allowed for the determination of both single crystal X-ray structures (Figure 2).[16] Moreover, slow conversion into colorless, crystalline $Gd_4(OH)_2(N_3)_{10} \cdot 8$ DMSO was observed upon storage of $Gd_4(OH)_2(N_3)_{10} \cdot 10$ DMSO in a mixture of DMSO/MeCN for several weeks at ambient temperature, according to X-ray structure determination (Figure 2). In case of cerium, the same procedure (ii) resulted in bright red, oily residues, which could thus far not be separated or isolated. Nevertheless, the presence of cerium(III) azides $Ce(N_3)_3 \cdot n$ DMSO in solution can be assumed, since further treatment with excess $[M]N_3$ ($[M]^+ = [Ph_4P]^+$, $[EtPh_3P]^+$) led to the formation of hexaazido cerate salts $[M]_3[Ce(N_3)_6] \cdot n$ MeCN ($[M]^+ = [Ph_4P]^+$ ($n = 2$), $[EtPh_3P]^+$ ($n = 0$); *vide infra*).

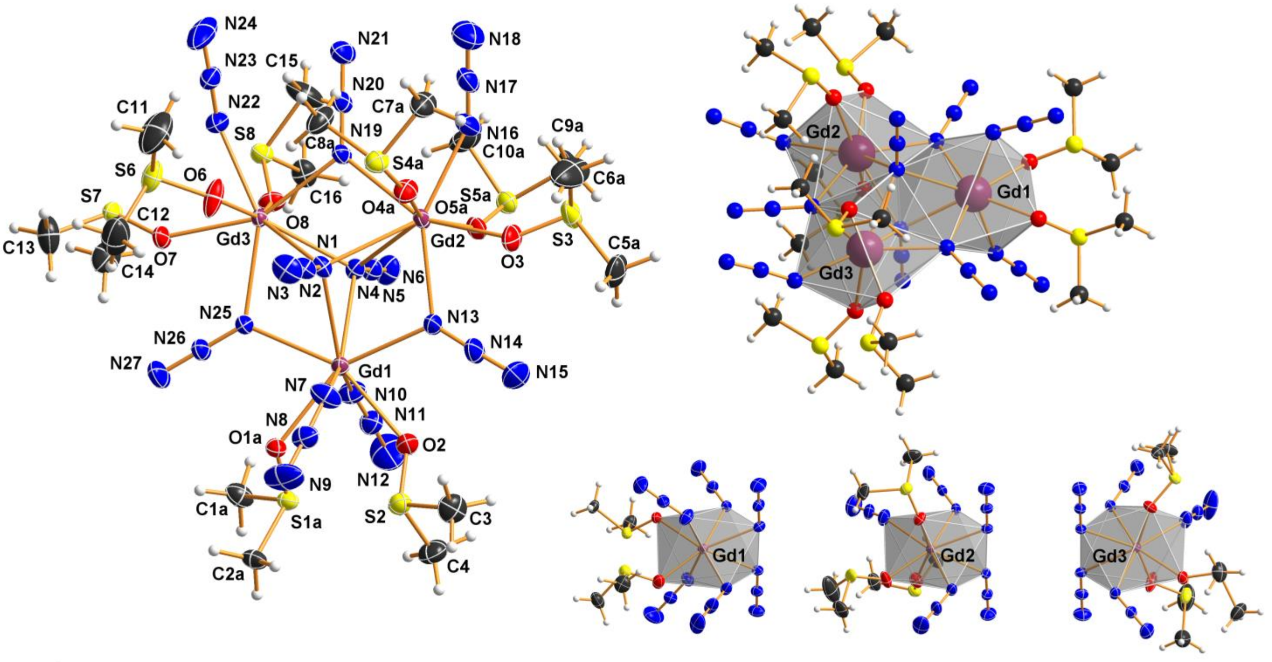
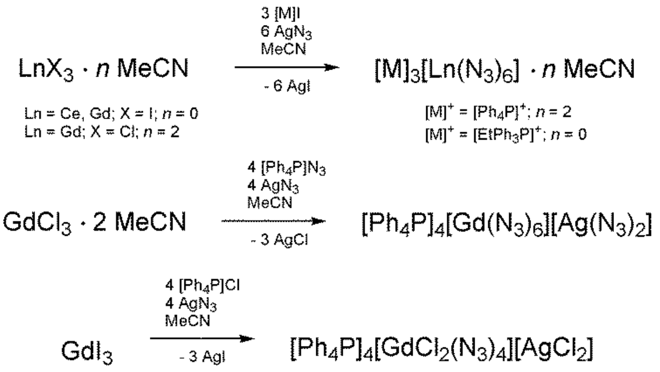


Figure 1. Left: ORTEP drawing of $Gd(N_3)_3 \cdot {}^8/_3$ DMSO in the solid state. Displacement ellipsoids with 50 % probability at 173 K. Disorder not displayed. Right (top): Perspective view of $Gd(N_3)_3 \cdot {}^8/_3$ DMSO (ball-and-stick representation); Right (bottom): ORTEP drawings of the square anti-prismatic coordination spheres of $Gd(N_3)_3 \cdot {}^8/_3$ DMSO in the crystal. Selected bond lengths (Å): Gd1–O2 2.381(3), Gd1–N10 2.386(4), Gd1–O1A 2.404(3), Gd1–N7 2.408(4), Gd1–N13 2.453(4), Gd1–N25 2.472(4), Gd1–N4 2.603(4), Gd1–N1 2.649(4), Gd2–O4A 2.330(5), Gd2–O3 2.339(3), Gd2–O5A 2.355(4), Gd2–N16 2.423(4), Gd2–N13 2.455(4), Gd2–N19 2.473(4), Gd2–N1 2.641(4), Gd2–N4 2.666(4), Gd3 O8 2.330(3), Gd3–O6 2.332(3), Gd3–O7 2.365(3), Gd3–N22 2.443(4), Gd3–N19 2.455(4), Gd3–N25 2.491(4), Gd3–N4 2.586(4), Gd3–N1 2.622(4).

Astonishingly, the fluoride/azide exchange reaction by treatment of lanthanide(III) fluorides with excess Me_3SiN_3 in MeCN or DMSO was not successful.[16] Even after thermal treatment at 120 °C for several days, no conversion of LnF_3 (Ln = La, Pr, Gd) was observed, as indicated by the almost quantitative recovery of starting materials in all attempted reactions (Scheme 3). Similarly, the formation of lanthanide azides by means of a OTf^-/N_3^- (OTf^- = triflate, trifluoromethyl sulfonyl) exchange failed in the solvothermal reaction of $Gd(OTf)_3$ and Me_3SiN_3 in various solvents (MeCN, fluorobenzene, Me_3SiN_3, [BMIm][OTf] ($[BMIm]^+$ = *N*,*N*-butyl-methyl imidazolium)).[16] Likewise, no reaction could be observed upon treatment of elemental cerium with hydrazoic acid HN_3 in fluorobenzene.[16]

Synthesis of $[M]_3[Ln(N_3)_6] \cdot n$ MeCN ($[M]^+ = [Ph_4P]^+$ ($n = 2$), $[EtPh_3P]^+$ ($n = 0$)) and $[Ph_4P]_4[Gd(N_3)_6][Ag(N_3)_2]$

For the synthesis of polyazido lanthanate(III) salts $[M]_3[Ln(N_3)_6]$ with the bulky $[Ph_4P]^+$ and $[EtPh_3P]^+$ counterions, we intended a one-pot procedure in acetonitrile starting from lanthanide triiodides LnI_3 (Ln = Ce, Gd) or $GdCl_3 \cdot 2$ MeCN, respectively, and the corresponding phosphonium iodides [M]I, followed by addition of AgN_3 in the required stoichiometry (Scheme 4).[16] The reaction of cerium(III) iodide as well as gadolinium(III) halides with six equivalents of AgN_3 and three equivalents of the required [M]I was complete within half an hour at ambient temperature, and after filtration and concentration of the reaction solution, all hexaazido lanthanates $[M]_3[Ln(N_3)_6] \cdot n$ MeCN were obtained as colorless crystals (Figure 3). Salts containing the $[EtPh_3P]^+$ cation crystallized free of solvent (n = 0), whereas both tetraphenylphosphonium derivatives were isolated as acetonitrile di-solvates $[Ph_4P]_3[Ln(N_3)_6] \cdot 2$ MeCN (*cf.* V_{ion}: $[Ph_4P]^+$ 464 *vs.* $[EtPh_3P]^+$ 409 Å^3).[16,17]



Scheme 4. Preparation of $[M]_3[Ln(N_3)_6]$ n MeCN and $[Ph_4P]_4[Gd(N_3)_6][Ag(N_3)_2]$.

$[Ph_4P]_3[Ce(N_3)_6] \cdot 2$ MeCN was isolated as a crystalline mixture of two different triclinic modifications (denoted as *α*- and *β*-$[Ph_4P]_3[Ce(N_3)_6] \cdot 2$ MeCN), evident from single crystal X-ray structure analyses. Interestingly, the same iodide/azide exchange procedure was not successful when $CeI_3 \cdot 4$ THF was used as a starting material instead of neat CeI_3. Besides colorless crystals of $[Ph_4P]N_3$, which could be separated and identified by means of a single crystal X-ray determination, only intense colored decomposition products were obtained in the course of the reaction.[16] The formation of polyiodo cerates in the reaction of $CeI_3 \cdot 4$ THF with $[Ph_4P]I$ in MeCN was also not observed. After workup, a crystalline mixture of $[Ph_4P]I$ and $[Ph_4P]I_3$ was isolated, which clearly indicated that cerium(III) iodides tend to decompose in the presence of THF.[16]

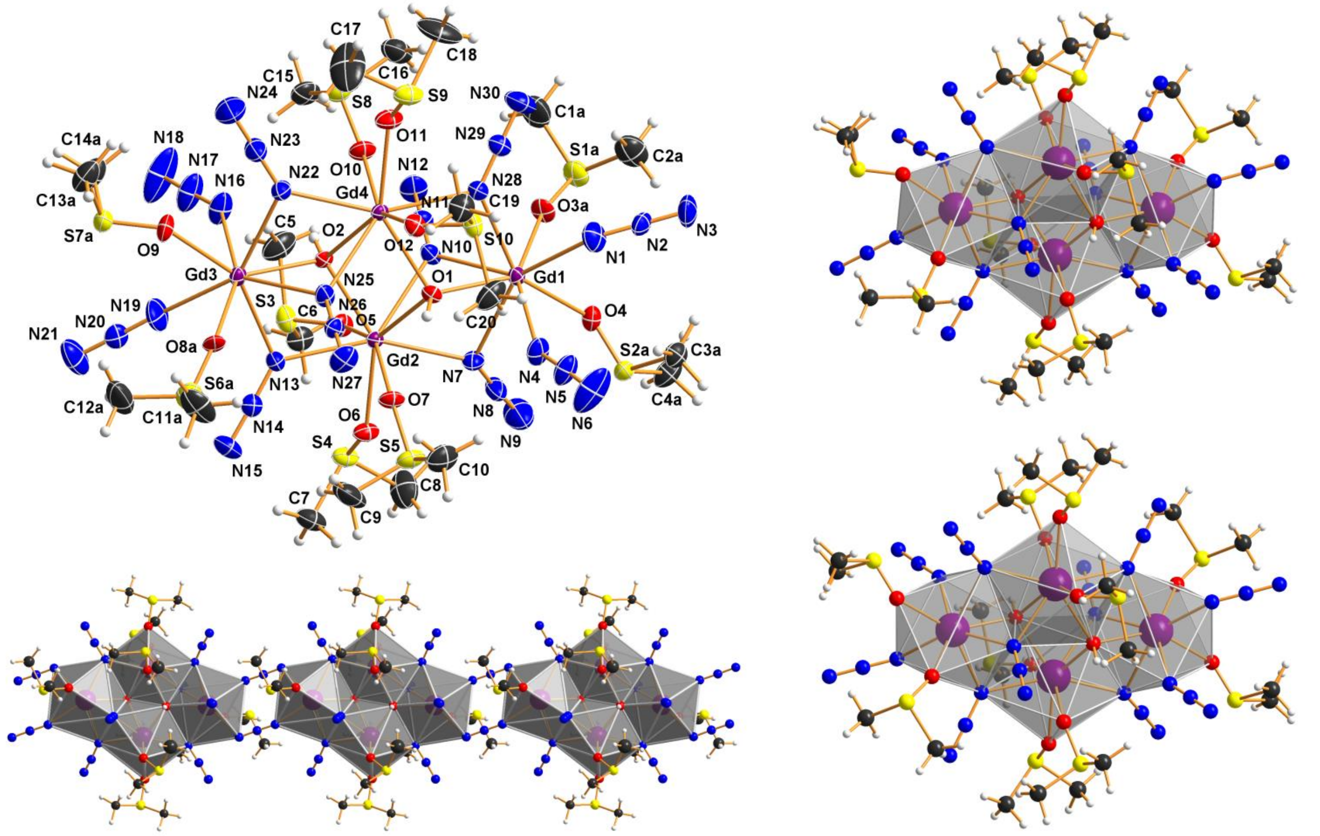


Figure 2. Left (top): ORTEP drawing of *β*-$Gd_4(OH)_2(N_3)_{10} \cdot 10$ DMSO (1) in the solid state. Displacement ellipsoids with 50 % probability at 173 K. Disorder not displayed. Selected bond lengths (Å): Gd1–O3A 2.261(9), Gd1–O1 2.364(4), Gd1–O4 2.377(4), Gd1–N1 2.435(6), Gd1–N4 2.450(5), Gd1–N28 2.510(5), Gd1–N10 2.522(5), Gd1–N7 2.545(5), Gd2–O5 2.346(4), Gd2–O2 2.351(4), Gd2–O7 2.362(4), Gd2–O6 2.384(4), Gd2–O1 2.389(4), Gd2–N7 2.500(5), Gd2–N13 2.508(5), Gd2–N10 2.597(5), Gd3–O9 2.374(4), Gd3–O8A 2.379(6), Gd3–O2 2.388(4), Gd3–N19 2.421(6), Gd3–N16 2.444(6), Gd3–N13 2.489(5), Gd3–N22 2.545(5), Gd3–N25 2.549(5), Gd4–O12 2.349(4), Gd4–O10 2.360(4), Gd4–O2 2.380(4), Gd4–O11 2.387(4), Gd4–O1 2.388(4), Gd4–N28 2.484(5), Gd4–N22 2.495(5), Gd4–N25 2.569(5). Right: Perspective view (ball-and-stick representation) of *β*-$Gd_4(OH)_2(N_3)_{10} \cdot 10$ DMSO (top), and *α*-$Gd_4(OH)_2(N_3)_{10} \cdot 10$ DMSO (bottom). *Remark*: The *α*- and *β*-phase differ in the orientation of two DMSO ligands. Left (bottom): Perspective view of the chains of $Gd_4(OH)_2(N_3)_{10} \cdot 8$ DMSO in the crystal (ball-and-stick representation, view along [001]).

Additionally, the iodide/azide exchange in GdI_3 was carried out with four eqivalents of AgN_3/[M]I (Scheme 4), which, however, resulted in the unintended isolation of the double salt $[Ph_4P]_4[Gd(N_3)_6][Ag(N_3)_2]$ (Figure 4), instead of possible polyazido gadolinate(III) salts $[Ph_4P]_n[Gd(N_3)_{3+n}]$ with an higher degree of azide substitution ($n > 3$; vide supra). Like in the previous case, the formation and co-crystallization of an argentate(I) anion was also observed in the partially azide substituted species $[Ph_4P]_4[GdCl_2(N_3)_4][AgCl_2]$ (Scheme 4), which was obtained in the reaction of GdI_3 with four equivalents of AgN_3 and [M]Cl (Figure 4).[16] The same species, $[Ph_4P]_4[GdCl_2(N_3)_4][AgCl_2]$, was also formed as preferred product in the reaction of $GdCl_3 \cdot 2\,MeCN$ and three equivalents of AgN_3 and [M]I. It is interesting to note, that in both reactions involving less than six equivalents of AgN_3, the co-crystallization of small amounts of the mixed chlorido/iodo diargentate(I) salt $[Ph_4P][Ag_2Cl_2I]$ as tiny, needle-like crystals was observed.[16]

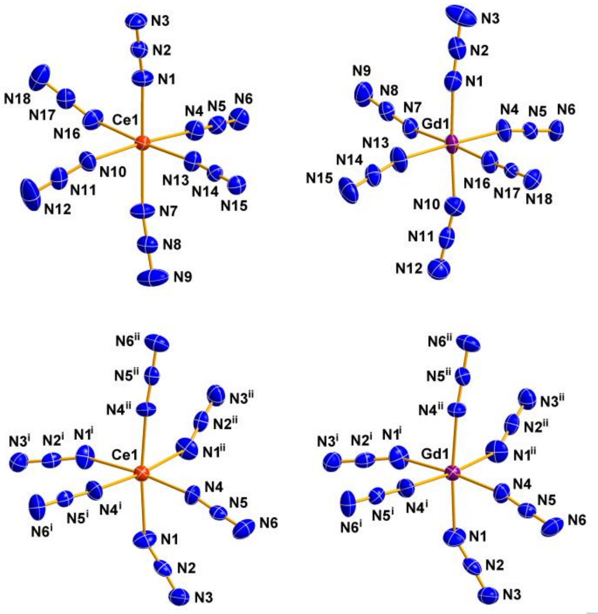


Figure 3. ORTEP drawings of the molecular structure of the $[Ln(N_3)_6]^{3-}$ anions in the solid state (top: $[Ph_4P]^+$, bottom: $[EtPh_3P]^+$ salts). For $[Ph_4P]_3[Ln(N_3)_6] \cdot 2\,MeCN$ salts, only one of four independent anions in the asymmetric unit are displayed. $[Ph_4P]_3[Ce(N_3)_6] \cdot 2\,MeCN$ exists in two modifications, only the α-modification is displayed. For α-$[Ph_4P]_3[Ce(N_3)_6] \cdot 2\,MeCN$, only one of two independent anions in the asymmetric unit is shown. Displacement ellipsoids with 50 % probability at 173 K. Selected bond lengths (Å): $[Ph_4P]_3[Ce(N_3)_6] \cdot 2\,MeCN$: Ce1–N10 2.435(4), Ce1–N4 2.436(4), Ce1–N7 2.445(3), Ce1–N13 2.446(3), Ce1–N1 2.452(3), Ce1–N16 2.457(3); $[Ph_4P]_3[Gd(N_3)_6] \cdot 2\,MeCN$: Gd1–N4 2.331(3), Gd1–N13 2.338(3), Gd1–N1 2.342(4), Gd1–N10 2.345(4), Gd1–N7 2.354(3), Gd1–N16 2.371(3); $[EtPh_3P]_3[Ce(N_3)_6]$ (symmetry codes:(i) −x+y+1, −x+1, z; (ii) −y+1, x−y, z): Ce1–N1 2.458(8), Ce1–$N1^i$ 2.458(8), Ce1–$N1^{ii}$ 2.458(8), Ce1–N4 2.411(8), Ce1–$N4^i$ 2.411(8) Ce1–$N4^{ii}$ 2.411(8); $[EtPh_3P]_3[Gd(N_3)_6]$ (symmetry codes:(i) −x+y+1, −x+1, z; (ii) −y+1, x−y, z): Gd1–N1 2.357(5), Gd1–$N1^i$ 2.357(5), Gd1–$N1^{ii}$ 2.357(5), Gd1–N4 2.344(5), Gd1–$N4^i$ 2.344(5), Gd1–$N4^{ii}$ 2.344(5).

The preferred formation of double salts was further indicated by the unintended isolation of crystalline $[Ph_4P]_4[Gd(N_3)_6][N_3(daa)] \cdot$ acetone (daa = diacetone alcohol), which could be obtained in small amounts in the attempted re-crystallization of $[Ph_4P]_3[Gd(N_3)_6] \cdot 2\,MeCN$ from acetone (Figure 4). According to X-ray structure determination, the co-crystallized azide anion is coordinated by the hydroxyl group of the diacetone alcohol. Presumably, the latter was formed as product of the aldol reaction of acetone upon longer standing (vide infra).[16,18]

It is interesting to note, that a complete halide/azide exchange in GdX_3 (X = Cl, I) was observed for all reactions, irrespective of the applied trihalide. The double-salt $[Ph_4P]_4[Gd(N_3)_6][Ag(N_3)_2]$ is an exception which was found to be slightly contaminated by chloride. According to X-ray structure determination, the latter contained about 8 % of the dichlorido argentate(I) anion $[AgCl_2]^-$ as impurity (= $[Ph_4P]_4[Gd(N_3)_6][AgCl_{0.16}(N_3)_{1.84}]$) when $GdCl_3 \cdot 2\,MeCN$ was used instead of GdI_3 (Table S4).[16]

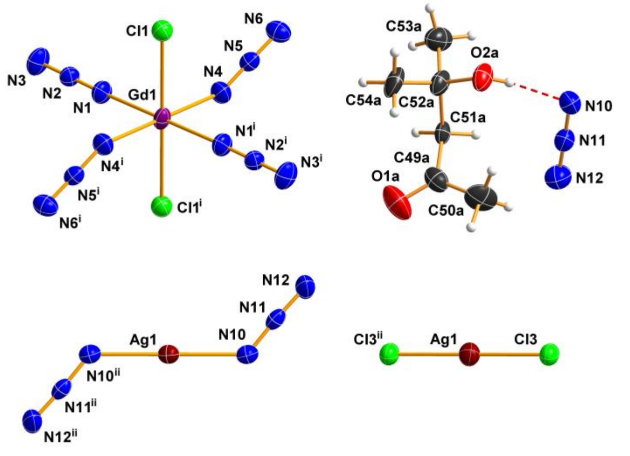


Figure 4. ORTEP drawings of the molecular structure of the $[GdCl_2(N_3)_4]^{3-}$ anion (top, left), the $[Ag(N_3)_2]^-$ anion (bottom, left), the $[N_3(daa)]^-$ anion (top, right) and the $[AgCl_2]^-$ anion (bottom, right) in the solid state. Disorder of the $[GdCl_2(N_3)_4]^{3-}$ and $[N_3(daa)]^-$ anions not displayed. Displacement ellipsoids with 50 % probability at 173 K. Selected bond lengths (Å): $[Ph_4P]_4[GdCl_2(N_3)_4][AgCl_2]$ (**1**) (symmetry codes: (i) −x, −y, 1−z; (ii) 1−x, 1−y, −z): Gd1–N4 2.326(7), Gd1–$N4^i$ 2.326(7), Gd1–N1 2.345(2), Gd1–$N1^i$ 2.3449(19), Gd1–N7 2.35(3), Gd1–$N7^i$ 2.35(3), Gd1–Cl1 2.7107(9), Gd1–$Cl1^i$ 2.7107(9), Ag1–Cl3 2.3440(6), Ag1–$Cl3^{ii}$ 2.3440(6); $[Ph_4P]_4[Gd(N_3)_6][Ag(N_3)_2]$ (symmetry code: (ii) 1−x, 1−y, −z): Ag1–N10 2.0882(19), Ag1–N10 2.0882(19), N10–N11 1.194(3), N11–N12 1.156(3); $[Ph_4P]_4[Gd(N_3)_6][N_3(daa)] \cdot$ acetone: N10–N11 1.195(5), N11–N12 1.174(5), C49a–C51a 1.495(8), C49a–C50a 1.502(11), C51a–C52a 1.551(7), C52a–C53a 1.523(9), C52a–C54a 1.524(8), O1a–C49a 1.212(8), O2a–C52a 1.431(7).

Physical and spectroscopic data

All considered azide compounds could be fully characterized by ^{14}N NMR, ATR-IR and Raman spectroscopy, elemental analysis, DSC and single-crystal structure elucidation.[16] The magnetic properties in solution as well as in solid state were examined by ^{1}H NMR (Evans Method),[19] and magnetic susceptibility measurements carried out in a PPMS (PPMS = physical property measurement system), respectively.[16] The characterization data of all isolated compounds is summarized in Table 1.

Neither gadolinium(III) azide $Gd(N_3)_3 \cdot {}^8/_3$ DMSO and its hydroxide analogs $Gd_4(OH)_2(N_3)_{10} \cdot n$ DMSO (n = 8, 10), nor the hexaazido lanthanate salts $[M]_3[Ln(N_3)_6] \cdot n$ MeCN (Ln = Ce, Gd; $[M]^+ = [Ph_4P]^+$ (n = 2), $[EtPh_3P]^+$ (n = 0)) were sensitive to friction or shock, and notably did not explode upon burning in a flame. All compounds were found to be highly hygroscopic and slowly decomposed in air, but were stable for several months under argon atmosphere in crystalline state. Moreover, all compounds were found to be slightly sensitive to light and should therefore be stored in the dark.

$Gd(N_3)_3 \cdot {}^8/_3$ DMSO and $Gd_4(OH)_2(N_3)_{10} \cdot 10$ DMSO decomposed on gentle heating (heating-rate 5–20 °C/min) at 157 and 173 °C, respectively, which was accompanied by a color change to black (cf. $Cd(N_3)_2 \cdot {}^3/_2$ DMSO 120 °C (m.p.), $Bi(N_3)_3 \cdot$ DMSO 200 °C (detonation)).[20a,b] In contrast, all hexaazido lanthanate salts $[M]_3[Ln(N_3)_6] \cdot n$ MeCN showed sharp melting points and were stable in the molten state. Thereby, the $[EtPh_3P]^+$ salts of both different lanthanides showed similar melting points (Ce: 213, Gd: 229 °C), while the $[Ph_4P]^+$ derivatives, which additionally contained acetonitrile as solvate, melted at slightly lower temperatures (Ce: 187 °, Gd 216 °C). Likewise, the double salts $[Ph_4P]_4[Gd(N_3)_6][Ag(N_3)_2]$ as well as $[Ph_4P]_4[GdCl_2(N_3)_4][AgCl_2]$ displayed melting points in a similar range with 222 and 229 °C, respectively (*cf.* 235 °C for $[Ph_4P]N_3$).[20a]

Table 1. Selected analytical data (melting points, ^{14}N NMR data, magnetic susceptibility data, IR and Raman data of $\nu_{as}(N_3)$).[a]

Gd	M.p.[°C]	^{14}N NMR [ppm][a]	μ_{eff}(soln.)[b] NMR [μ_B]	μ_{eff}(solid) PPMS [μ_B]	IR $\nu_{as}(N_3)$ [cm^{-1}][c]	Raman $\nu_{as}(N_3)$ [cm^{-1}][d]
$Gd(N_3)_3 \cdot {}^8/_3$ DMSO	157[e]	−284(824)	7.71(1)	8.03(1)	2126(s), 2084(s),2046(s)	2123(0.9), 2088(0.9), 2080(0.8), 2075(0.7)
$Gd_4(OH)_2(N_3)_{10} \cdot 10$ DMSO[f]	173[e]	−283(991)	7.30(1)	8.33(1)	2092(m), 2066(s), 2047(s)	2109(0.7), 2073(0.4)
$Gd_4(OH)_2(N_3)_{10} \cdot 8$ DMSO	-[g]	-[g]	-[g]	-[g]	-[g]	2104(1.0), 2062(1.0)
Ce	M.p.	^{14}N NMR[a]			IR $\nu_{as}(N_3)$[c]	Raman $\nu_{as}(N_3)$[d]
$[EtPh_3P]_3[Ce(N_3)_6]$	213	−126(100), −232(394)	2.14(1)	–	2105(w), 2044(s)	2149(0.6), 2140(0.5), 2095(0.6), 2037(0.5)
$[Ph_4P]_3[Ce(N_3)_6] \cdot 2$ MeCN[f]	187	−126(101), −228(434)	2.21(1)	–	2101(w), 2040(s)	2153(4.4), 2098(4.7), 2043(4.2),
Gd	M.p.	^{14}N NMR[a]			IR $\nu_{as}(N_3)$[c]	Raman $\nu_{as}(N_3)$[d]
$[EtPh_3P]_3[Gd(N_3)_6]$	229	−243(634)	7.70(1)	8.04(1)	2110(w), 2052(s)	2111(0.1), 2057(0.1), 2050(0.1)
$[Ph_4P]_3[Gd(N_3)_6] \cdot 2$ MeCN	216	−240(750)[h]	7.74(1)	7.87(1)	2111(w), 2052(s)	2110(1.8), 2054(1.6)
$[Ph_4P]_4[Gd(N_3)_6][Ag(N_3)_2]$	222	−214(557)	7.77(1)	8.20(1)	2111(w), 2058(s)[i]	2112(1.6), 2052(1.6)
$[Ph_4P]_4[GdCl_2(N_3)_4][AgCl_2]$	229	−252(830)	-[g]	-[g]	2102(w), 2067 (m), 2053 (s)	2113(0.1), 2105(0.1), 2097(0.1), 2056(0.1)
$[Ph_4P]_4[Gd(N_3)_6][N_3(daa)] \cdot$ acetone	-[g]	-[g]	-[g]	-[g]	2110(w), 2092(sh, w), 2060(m)[j]	-[g]

[a] Values from $[D_6]$DMSO, in parenthesis $\Delta\nu_{1/2}$ values in Hz. [b] Measured values were corrected for the diamagnetic contribution of DMSO ($\chi_{\mathrm{mol},DMSO} = -0.5549 \cdot 10^{-9}\ m^3 \cdot mol^{-1}$). [c] Relative IR intensities denoted as weak (w), medium (m), strong (s), shoulder (sh). [d] Relative Raman intensities scaled to 10. [e] Decomposition. [f] Mixture of α- and β-phase. [g] Measurement not performed. [h] acetonitrile: ^{14}N δ = –136(190). [i] $[Ag(N_3)_2]^-$: $\nu_{as}(N_3)$ 2035(s) (IR). [j] $[N_3(daa)]^-$: $\nu_{as}(N_3)$ 2007(m) (IR).

The vibrational spectra (ATR-IR/Raman) of $Gd(N_3)_3 \cdot {}^8/_3$ DMSO as well as the mixed azide/hydroxide derivate $Gd_4(OH)_2(N_3)_{10} \cdot n$ DMSO (n = 8, 10) confirmed the presence of azido ligands as shown by the antisymmetric stretching mode ($\nu_{as}(N_3)$) in the range 2126–2046 cm^{-1}, the symmetric stretching mode ($\nu_s(N_3)$) at 1367–1227 cm^{-1}, and the deformation mode ($\gamma/\delta(N_3)$) at 659–613 cm^{-1} (Table 1, Scheme S5 – S20).[16] In addition, the combination mode of antisymmetric and symmetric vibration ($\nu_{as}+\nu_s(N_3)$) in the range 3390–3326 cm^{-1} was found in the IR spectra (*cf.* $\nu_{as}(N_3)$: 2103–2036, $\nu_s(N_3)$: 1401–1220 and $\gamma/\delta(N_3)$; 632–545 cm^{-1} for binary $Eu(N_3)_2$).[11] In good accordance with theoretical data, the existence of more than one azido ligand resulted in in-phase (i.p.) and out-of-phase (o.p.) coupling of vibrational modes (Table 1).[16] Moreover, the characteristic O–H stretching mode (ν(O-H)) at 3583 (Raman) and 3581 cm^{-1} (IR) was found in the spectra of $Gd_4(OH)_2(N_3)_{10} \cdot 10$ DMSO, while the X-Ln-X stretching modes ($\nu_{i.p./o.p.}$(X-Ln-X), X = N, O) could not be identified due to overlap with vibrations caused by the DMSO molecules. While the vibrational modes of the azide units in $Gd(N_3)_3 \cdot {}^8/_3$ DMSO and $Gd_4(OH)_2(N_3)_{10} \cdot n$ DMSO (n = 8, 10) lay in a similar range, the vibrational spectra of hexaazido gadolinate salts $[M]_3[Gd(N_3)_6] \cdot n$ MeCN, double salts $[Ph_4P]_4[Gd(N_3)_6][Ag(N_3)_2]$, $[Ph_4P]_4[GdCl_2(N_3)_4][AgCl_2]$, and $[Ph_4P]_4[Gd(N_3)_6][N_3(daa)] \cdot$ acetone differed considerably, which may be attributed to the more ionic bonding situation in the latter. Thereby, the antisymmetric stretching modes ($\nu_{as}(N_3)$) in the range 2113–2050 cm^{-1} were shifted to slightly lower wavenumbers (*cf.* $[N_3(daa)]^-$ ($\nu_{as}(N_3$) 2007 cm^{-1}), while the symmetric stretching modes ($\nu_s(N_3)$) at 1378–1350 cm^{-1} as well as combination modes of antisymmetric and symmetric vibration ($\nu_{as}+\nu_s(N_3)$) were observed at higher wavenumbers in the range 3475–3386 cm^{-1}. Furthermore, the deformation modes ($\gamma/\delta(N_3)$) at 628–623 cm^{-1}, which lie in a similar range, were visible in the ATR-IR and Raman spectra, respectively.

Moreover, the diazido argentate(I) anion in $[Ph_4P]_4[Gd(N_3)_6][Ag(N_3)_2]$ ($\nu_{as}(N_3)$: 2035, $\nu_s(N_3)$: 1330–1329 and $\gamma/\delta(N_3)$; 640 cm^{-1}) were identified in the ATR-IR and Raman spectra, in good agreement with the values found by Klapötke *et al.* (*cf.* $\nu_{as}(N_3)$: 2036–1993 (IR), $\nu_s(N_3)$: 1328 cm^{-1} (Raman) in $[Ph_4P][Ag(N_3)_2]$).[21]On the other hand, the vibrational spectra of hexaazido cerate salts $[M]_3[Ce(N_3)_6] \cdot n$ MeCN displayed the azide units in a slightly more ionic bonding situation (*cf.* $r_{ion}(Ce^{3+})$ 1.23 *vs.* $r_{ion}(Gd^{3+})$ 1.19 Å, ε(Ce) = 1.12 vs. ε(Gd) = 1.2).[22] Compared to the analogous gadolinium compounds, the antisymmetric stretching modes ($\nu_{as}(N_3)$) in the range 2105–2037 cm^{-1} were shifted to slightly lower wavenumbers, while the symmetric stretching modes ($\nu_s(N_3)$) at 1378–1345 cm^{-1}, were observed in a similar range. Consequently, the combination modes of antisymmetric and symmetric vibration ($\nu_{as}+\nu_s(N_3)$) at 3453–3375 cm^{-1} were also slightly shifted to lower frequency, in accord with the expectations.

As displayed in Table 1, the ^{14}N NMR resonances of all considered cerium and gadolinium azides measured in [D$_6$]DMSO at 300 K were strongly influenced by the paramagnetic moments of the corresponding lanthanide(III) nuclei (Ce^{3+}: [Xe]4f^1, $^2F_{5/2}$; Gd^{3+}: [Xe]4f^7, $^8S_{7/2}$). In the spectra of the hexaazido cerates $[M]_3[Ce(N_3)_6] \cdot n$ MeCN two well-resolved resonances, a medium-sharp signal for the N$_\beta$ atoms ([M]$^+$ = [EtPh$_3$P]$^+$ –126 ($\Delta\nu_{1/2}$ = 100 Hz); [Ph$_4$P]$^+$ –126 ($\Delta\nu_{1/2}$ = 101 Hz)) and a remarkably broadened N$_{\alpha/\gamma}$-resonance ([M]$^+$ = [EtPh$_3$P]$^+$ –232 ($\Delta\nu_{1/2}$ = 394 Hz); [Ph$_4$P]$^+$ –228 ($\Delta\nu_{1/2}$ = 434 Hz)) were observed (Table 1).[16] In comparison to previously reported diamagnetic hexaazido bismuthates $[M]_3[Bi(N_3)_6]$ ([M]$^+$ = [EtPh$_3$P]$^+$, [Ph$_4$P]$^+$), these values were reasonably shifted to lower field ([M]$^+$ = [EtPh$_3$P]$^+$ –134 (N$_\beta$; $\Delta\nu_{1/2}$ = 72 Hz); –260 (N$_{\alpha/\gamma}$; $\Delta\nu_{1/2}$ = 547 Hz); [Ph$_4$P]$^+$: –132 (N$_\beta$, $\Delta\nu_{1/2}$ = 42 Hz), –258 (N$_{\alpha/\gamma}$, $\Delta\nu_{1/2}$ = 390 Hz).[23] Analogous to known binary azides, the observation of only one set of azide signals, along with the absence of a separate N$_\alpha$ resonance indicate a rapid ligand exchange relative to the NMR timescale.[24]

In contrast, the ^{14}N NMR spectra of the corresponding hexaazido gadolinate salts $[M]_3[Gd(N_3)_6] \cdot n$ MeCN displayed only the resonance for the N$_{\alpha/\gamma}$ atoms ([M]$^+$ = [EtPh$_3$P]$^+$: –243 ($\Delta\nu_{1/2}$ = 634 Hz); [Ph$_4$P]$^+$: –240 ($\Delta\nu_{1/2}$ = 700 Hz), while the N$_\beta$-resonance was completely absent due to the strong magnetic field of Gd^{3+} cations.[16] As a result, the ^{14}N NMR resonance for the N atom of acetonitrile in $[Ph_4P]_3[Gd(N_3)_6] \cdot 2$ MeCN became visible at –136 ($\Delta\nu_{1/2}$ = 190 Hz), while no ^{14}N NMR resonance for MeCN could be detected in the spectrum of $[Ph_4P]_3[Ce(N_3)_6] \cdot 2$ MeCN, due to strong overlap with the N$_\beta$ resonance of the azide groups (Table 1). Interestingly, also only one signal for the N$_{\alpha/\gamma}$ atoms of the azide units in $[Ph_4P]_4[Gd(N_3)_6][Ag(N_3)_2]$ at very low frequency (δ = –214 ($\Delta\nu_{1/2}$ = 557 Hz)) could be detected, indicating a fast ligand exchange between gadolinium(III) and silver(I) ions. In contrast, the N$_{\alpha/\gamma}$-resonance of the azide units in the chloride substituted species $[Ph_4P]_4[GdCl_2(N_3)_4][AgCl_2]$ was considerably shifted to higher frequency (δ = –252 ($\Delta\nu_{1/2}$ = 830 Hz)). Again, no resonances for the N$_\beta$ atoms were visible in the double-salts.[16] Between spectra of the hexaazido lanthanates for both different counter ions [EtPh$_3$P]$^+$ and [Ph$_4$P]$^+$, respectively (Table 1), only negligible differences were found indicating only weak cation–anion interactions in solution.

The ^{14}N NMR spectra of $Gd(N_3)_3 \cdot {}^8/_3$ DMSO, as well as the mixed azide/hydroxide derivate $Gd_4(OH)_2(N_3)_{10} \cdot 10$ DMSO showed almost identical resonances at δ = –284 ($\Delta\nu_{1/2}$ = 824 Hz) and δ = –283 ($\Delta\nu_{1/2}$ = 991 Hz), both considerably shifted to lower frequency compared to the hexaazido gadolinate salts $[M]_3[Gd(N_3)_6] \cdot n$ MeCN (*cf.* Bi(N$_3$)$_3$ *δ* = –137 (N$_\beta$, $\Delta\nu_{1/2}$ = 71 Hz), –260 (N$_{\alpha/\gamma}$, $\Delta\nu_{1/2}$ = 632 Hz)).[16,23]

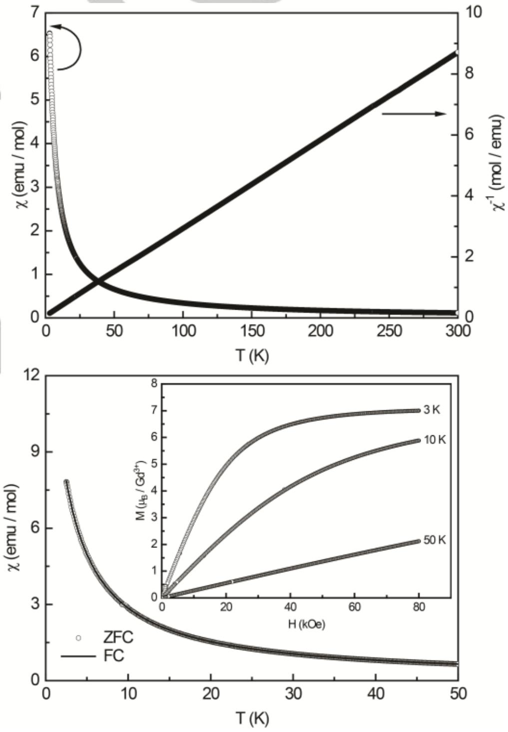


Figure 5. Magnetic properties of $Gd_4(OH)_2(N_3)_{10} \cdot 10$ DMSO: (*top*) temperature dependence of the magnetic susceptibility (χ and χ^{-1} data) measured at 10 kOe; (*bottom*) zero-field-cooled / field cooled (ZFC/FC) measurements at 100 Oe; (*bottom inset*) magnetization isotherms at 3, 10 and 50 K.

The paramagnetic susceptibilities of all presented compounds in solution were determined by the Evans method (Table 1).[16] In a slight variation of the original procedure, a NMR sample tube containing a dilute solution of the corresponding paramagnetic compound in [D$_8$]DMSO/DMSO and HMDS (HMDS = hexamethyldisiloxane, (Me$_3$Si)$_2$O) as inert probe molecule, as well as a sealed capillary containing solely a solution of the probe (HMDS in [D$_8$]DMSO/DMSO) was used.

Given a known concentration of lanthanide(III) ions cLn^{3+}, the molar magnetic susceptibility $\chi_{mol}$of the sample solution is proportional to the shift difference $\Delta\delta$ between the ^{1}H NMR resonance of the HMDS methyl protons of the metal-free solution and the solution containing the paramagnetic sample (Eq. 1).[16]

$$\chi_{\mathrm{mol}} = \frac{3\Delta\delta}{c\mathrm{Ln}^{3+}} \qquad (1)$$

The molar susceptibility χ_{mol} is connected to the effective magnetic moment μ_{eff} by equation 2, which gives a measure for the sample magnetism in terms of the Bohr magneton number μ_{B}.

$$\mu_{\mathrm{eff}}^2 = \frac{3kT\chi_{\mathrm{mol}}}{\mu_0 N_A \mu_B^2} \qquad (2)$$

For metal ions with a small spin-orbit coupling constant, the pure spin magnetism can be described by the spin-only formula, which neglects all spin-orbit contributions to μ_{eff} (Eq. 3):

$$\mu_{\mathrm{eff}}^2 = 4S(S+1) \qquad (3)$$

For Gd^{3+} ions with seven un-paired spins in high-spin f^7 configuration (S = $^7/_2$, L = 0), the effective magnetic moment μ_{eff}(spin-only) amounts to 7.94 μ_{B}, which is in good agreement with the experimental values (*cf.* 7.30–7.77 μ_{B}, Table 1). In contrast, considerably large spin-orbit coupling constants may be expected for cerium(III) ions (S = $^1/_2$, L = 3). In this case, orbital contributions have to be included in the calculation of μ_{eff} using equation 4:

$$\mu_{\mathrm{eff}} = g_J\sqrt{J(J+1)} \qquad (4)$$

where $$g_J = 1 + \frac{S(S+1) - L(L+1) + J(J+1)}{2J(J+1)}$$

The calculated value of 2.54 μ_{B} for a Ce^{3+} ion compares well with the measured effective magnetic moments of 2.14 and 2.21 μ_{B} for $[\mathrm{EtPh_3P}]_3[\mathrm{Ce(N_3)_6}]$ and $[\mathrm{Ph_4P}]_3[\mathrm{Ce(N_3)_6}] \cdot n$ MeCN, respectively (*cf.* μ_{eff}(spin-only) 1.73 μ_{B}).

In Figure 5, the magnetic properties of solid $\mathrm{Gd_4(OH)_2(N_3)_{10}} \cdot 10$ DMSO are depicted. The sample shows paramagnetism over the whole temperature range (Fig. 5, top) and no magnetic coupling down to 2.5 K (Fig. 5, bottom).[16] The effective magnetic moment was calculated to 8.33(1) μ_{B}, which is slightly higher compared to the calculated moment of 7.94 μ_{B}. The magnetization isotherm (Fig. 5, bottom inset) at 3 K shows saturation at 7.00(1) μ_{B} above 40 kOe, in line with the calculated saturation magnetization of 7 μ_{B} according to $g_{\mathrm{J}} \times J$. The other gadolinium compounds all exhibit magnetic moments close to the theoretical one, in line with the solution data. Additional information on the magnetic properties of the other investigated compounds are summarized in Table 1 and in the Supporting Information (Table S2, Figures S1 – S4).[16]

X-ray crystallography

Single crystal X-ray structures of all synthesized lanthanide(III) azides, as well as the structures of the starting materials $\mathrm{CeI_3} \cdot 4$ THF, $\mathrm{GdCl_3} \cdot 2$ MeCN and $\mathrm{Gd(OTf)_3} \cdot 3$ MeCN were determined from single crystal X-ray data. The crystallographic data is summarized in the supporting materials (Tables S3 – S25).[16] CCDC 1575812 – 1575830 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

As depicted in Figures 3 and 4, all examined azido lanthanate(III) salts display the $[\mathrm{LnX_6}]^{3-}$ anions (X = $\mathrm{N_3}$, Cl) in a slightly distorted octahedral ligand sphere, with X–Ln–X angles averaging to the ideal values of 90 and 180 °, respectively (Gd: 83.8–96.2 °, 174.3–180.0 °; Ce: 83.2–97.6 °, 173.5–178.3 °; Table 2). Within these structures, well separated lanthanate anions $[\mathrm{LnX_6}]^{3-}$ with metal-metal distances in the range 11.077–13.404 Å (Gd) and 11.128–11.709 Å (Ce) were found, which lie in a similar range for both, the homologous cerate, as well as gadolinate salts (*cf.* $[\mathrm{EtPh_3P}]_3[\mathrm{Ln(N_3)_6}]$: 11.135 (Gd) *vs.* 11.128 Å (Ce); $[\mathrm{Ph_4P}]_3[\mathrm{Ln(N_3)_6}] \cdot 2$ MeCN: 11.560 (Gd), vs. 11.675–11.709 Å (Ce)). The Gd···Ag, as well as Ag···Ag distances in both mixed gadolinate/argentate double salts $[\mathrm{Ph_4P}]_4[\mathrm{Gd(N_3)_6}][\mathrm{Ag(N_3)_2}]$ and $[\mathrm{Ph_4P}]_4[\mathrm{GdCl_2(N_3)_4}][\mathrm{AgCl_2}]$, covered a comparable range ($[\mathrm{Ph_4P}]_4[\mathrm{Gd(N_3)_6}][\mathrm{Ag(N_3)_2}]$: Gd···Ag 9.352, Ag···Ag 11.077 Å; $[\mathrm{Ph_4P}]_4[\mathrm{GdCl_2(N_3)_4}][\mathrm{AgCl_2}]$: 9.156, 12.804 Å).[16]

In all investigated lanthanate salts, only weak N···H interactions between the anions and cations ($[\mathrm{M}]^+$ = $[\mathrm{EtPh_3P}]^+$ 2.424 (Ce), 2.439 Å (Gd); $[\mathrm{Ph_4P}]^+$ 2.335 Å), within the sum of the van der Waals radii of Σr_{vdW}(N–H) 3.00 Å were observed in the solid state.[22] The closest intramolecular N···H contacts were found between the hydroxyl group of the diacetone alcohol molecule and the adjacent azide anion in $[\mathrm{Ph_4P}]_4[\mathrm{Gd(N_3)_6}][\mathrm{N_3(daa)}] \cdot$ acetone, with a donor–acceptor distance (D–H···A) of 2.776 Å (*cf.* Σr_{vdW} (N–O) 3.10 Å,[22] Figure 4).

In contrast, the structures of gadolinium(III) azide DMSO solvate $\mathrm{Gd(N_3)_3} \cdot {}^8/_3$ DMSO as well as the mixed azide/hydroxide derivates $\mathrm{Gd_4(OH)_2(N_3)_{10}} \cdot n$ DMSO (n = 8, 10) were composed of eight-coordinated gadolinium atoms, resembling slightly distorted square anti-prismatic coordination polyhedra (Figures 1 and 2). Thereby, all angles A-M-B, A-M-C and A-M-D as defined in Scheme 5, lay within the expected range, and averaged to the ideal values of 82.06, 70.53 and 109.47 ° ($\mathrm{Gd(N_3)_3} \cdot {}^8/_3$ DMSO 59.4–96.2, 68.1–85.8, 92.9–136.0 °; *α*-$\mathrm{Gd_4(OH)_2(N_3)_{10}} \cdot 10$ DMSO 64.4–85.4, 65.7–82.0, 97.6–131.3 °; *β*-$\mathrm{Gd_4(OH)_2(N_3)_{10}} \cdot 10$ DMSO 64.3–85.7, 65.3–82.5, 96.5–132.0 °; $\mathrm{Gd_4(OH)_2(N_3)_{10}} \cdot 8$ DMSO 66.5–87.7, 66.0–83.3, 99.0–131.0 °).[16] The structural units within these compounds were associated in the solid state, forming aggregates or chains, respectively (Figures 1 and 2). Accordingly, short Gd···Gd distances were observed ($\mathrm{Gd(N_3)_3} \cdot {}^8/_3$ DMSO 3.934–3.950 Å, *α*- and *β*-$\mathrm{Gd_4(OH)_2(N_3)_{10}} \cdot 10$ DMSO 3.748–6.794 Å, $\mathrm{Gd_4(OH)_2(N_3)_{10}} \cdot 8$ DMSO 3.729–6.676 Å), which lie only slightly above the sum of the van der Waals radii (Σr_{vdW}(Gd–Gd) = 3.57 Å).[22] The square anti-prismatic $\mathrm{GdX_8}$ coordination polyhedra within these structures are either connected by $\mu_{2(1,1)}$-, $\mu_{2(1,3)}$ or $\mu_{3(1,1,1)}$-bridging azide ligands, as well as $\mu_{3(1,1,1)}$-bridging hydroxide groups (Figures 1 and 2), leading either to common corner-sharing, edge-sharing or face-sharing between two or three polyhedra, respectively.

Table 2. Selected structural data from single crystal X-ray determinations. Distances in Å, angles in °.

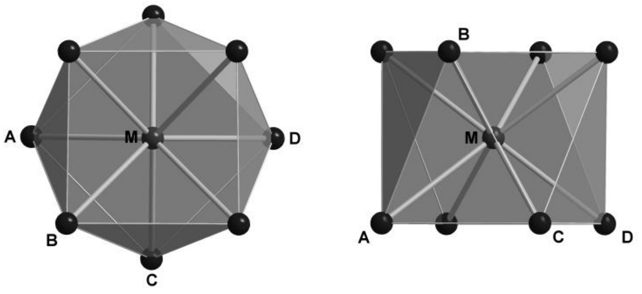
Gd	Gd···Gd[a]	X–Gd–X (X = N, O)[b]	Gd–X[c] (X = O, Cl)	Gd–N	N_α–N_β	N_β–N_γ	N_α–N_β–N_γ
$Gd(N_3)_3 \cdot {}^8/_3$ DMSO	3.934–3.950	59.4–96.2, 68.1–85.8, 92.9–136.0	2.355	2.415 2.467 $\mu_{2(1,1)}$[d] 2.628 $\mu_{3(1,1,1)}$	1.167 1.197 1.211	1.153 1.152 1.149	177.9 178.6 179.5
α-$Gd_4(OH)_2(N_3)_{10} \cdot 10$ DMSO	3.748–6.789	64.4–85.4, 65.7–82.0, 97.6–131.3	2.376 (OH) 2.361 (O_{DMSO})	2.435 2.522 $\mu_{2(1,1)}$	1.158 1.191	1.147 1.145	177.4 178.6
β-$Gd_4(OH)_2(N_3)_{10} \cdot 10$ DMSO	3.748–6.794	64.3–85.7, 65.3–82.5, 96.5–132.0	2.377 (OH) 2.358 (O_{DMSO})	2.438 2.526 $\mu_{2(1,1)}$	1.167 1.190	1.156 1.151	178.0 178.4
$Gd_4(OH)_2(N_3)_{10} \cdot 8$ DMSO	3.729–6.676	66.5–87.7, 66.0–83.3, 99.0–131.0	2.372 (OH) 2.367 (O_{DMSO})	2.382 2.502 $\mu_{2(1,1)}$ 2.487 $\mu_{2(1,3)}$	1.180 1.205 1.164	1.160 1.140 1.167	178.4 178.3 178.6
$[EtPh_3P]_3[Gd(N_3)_6]$	11.135	84.5–92.6, 174.3	-	2.351	1.179	1.158	177.8
$[Ph_4P]_3[Gd(N_3)_6] \cdot 2$ MeCN	11.560	87.9–93.8, 178.7	-	2.346	1.170	1.158	178.5
$[Ph_4P]_4[Gd(N_3)_6][Ag(N_3)_2]$	11.077[e]	88.5–91.6, 180.0	-	2.343	1.179	1.156	179.2
$[Ph_4P]_4[GdCl_2(N_3)_4][AgCl_2]$	12.804[f]	83.8–96.2, 180.0	2.711	2.337	1.181	1.156	179.1
$[Ph_4P]_4[Gd(N_3)_6][N_3(daa)] \cdot$ acetone	13.404	87.9–92.1, 180.0	-	2.243	1.163	1.145	178.9

Ce	Ce···Ce[a]	N–Ce–N[b]	Ce–N	N_α–N_β	N_β–N_γ	N_α–N_β–N_γ
$[EtPh_3P]_3[Ce(N_3)_6]$	11.128	83.2–93.6, 173.5	2.435	1.189	1.158	178.0
α-$[Ph_4P]_3[Ce(N_3)_6] \cdot 2$ MeCN	11.709	86.1–97.6, 174.2	2.443	1.177	1.158	178.9
β-$[Ph_4P]_3[Ce(N_3)_6] \cdot 2$ MeCN	11.675	86.9–92.2, 178.3	2.435	1.177	1.156	178.8

[a] Closest Ln···Ln distances. [b] For a square anti-prismatic coordination sphere, the angles are listed in the order: range A–M–B, range A–M–C and range A–M–D according to Scheme 5; for an octahedral coordination sphere, the angles are listed in the order: range of X_{cis}–Ln–X_{cis} and average of X_{trans}–Ln–X_{trans}. [c] If there are more than one azide, tetrazolate or DMSO ligand, the average value is given. In case of disorder, only geometrical parameters of the major part were used. [d] $\mu_{n(k,l,m)}$ denotes the bridging mode of the N_3 unit. [e] Closest Gd···Ag/Ag···Ag distances: 9.352/11.077 Å. [f] Closest Gd···Ag/Ag···Ag distances: 9.156/12.804 Å.

In the structure of $Gd(N_3)_3 \cdot {}^8/_3$ DMSO, only face-sharing interactions were observed, leading to the formation of a molecular, cyclic assembly of three GdX_8 polyhedra (Figure 1). Thereby, each gadolinium cation is connected to both adjacent Gd atoms by two $\mu_{2(1,1)}$- as well as two $\mu_{3(1,1,1)}$-bridging azide units, while all DMSO ligands are bound in terminal positions. Between the molecular units, only weak N···H_{DMSO} distances in the range 2.485–2.794 Å are found, all within the sum of the van der Waals radii (Σr_{vdW}(N–H) 3.00 Å).[22]

Likewise, face-sharing square anti-prismatic Gd units were found in α- and β-$Gd_4(OH)_2(N_3)_{10} \cdot 10$ DMSO, each connected to one adjacent GdX_8 polyhedron by two $\mu_{2(1,1)}$-bridging azide ligands as well as one $\mu_{3(1,1,1)}$-bridging hydroxide group (Figure 2). Further edge-sharing interactions via one $\mu_{2(1,1)}$-bridging azide ligand and one $\mu_{3(1,1,1)}$-bridging hydroxide ligand results in the aggregation of four GdX_8 polyhedra, forming a bicyclic, tetranuclear structure. As shown in Figure 2, the molecular units in α- and β-$Gd_4(OH)_2(N_3)_{10} \cdot 10$ DMSO differ only with respect to the orientation of two adjacent DMSO ligands. While the structural units in α-$Gd_4(OH)_2(N_3)_{10} \cdot 10$ DMSO resemble local C_i symmetry ($P\bar{1}$, d = 2.01 g/cm^3), the rotation of both DMSO molecules led to a distortion to C_1-symmetry in β-$Gd_4(OH)_2(N_3)_{10} \cdot 10$ DMSO ($P2_1/c$, d = 2.00 g/cm^3), along with a slightly lower density in the crystal (*cf.* d(N···H) α-$Gd_4(OH)_2(N_3)_{10} \cdot 10$ DMSO: 2.493 Å; β-$Gd_4(OH)_2(N_3)_{10} \cdot 10$ DMSO: 2.588 Å). In the structure of $Gd_4(OH)_2(N_3)_{10} \cdot 8$ DMSO the GdX_8 polyhedra adopt the same bicyclic arrangement as discussed for $Gd_4(OH)_2(N_3)_{10} \cdot 10$ DMSO, except that two terminal DMSO ligands are replaced by azide groups of the adjacent $Gd_4(OH)_2(N_3)_{10} \cdot 8$ DMSO units (Figure 2). These $\mu_{2(1,3)}$-bridging interactions resulted in the condensation of molecular units and the formation of a chain-like structure along [1 −1 0]. Between these polymeric units, only weak N···H_{DMSO} interactions can be found, with N···H distances in the range 2.2566–3.1612 Å, all within the sum of the van der Waals radii (Σr_{vdW}(N–H) 3.00 Å).[22]



Scheme 5. Ideal square-antiprismatic ligand sphere (left: top-view, right: side-view).

As illustrated in Table 2, the Ln–N and N–N distances varied strongly dependent on the coordination mode of the azide units. Accordingly, the shortest Ln–N distances are found for the single bonded, terminal azide groups in the octahedrally coordinated hexaazido gadolinate anions $[Gd(N_3)_6]^{3-}$, with averaged Gd–N bond lengths in the range 2.243–2.351 Å, within the sum of the ion radii (Σr_{ion}(Gd–N) = 2.40 Å) for an octahedral coordination sphere (*cf.* Ce-N 2.435–2.443 Å in $[M]_3[Ce(N_3)_6] \cdot n$ MeCN, Σr_{ion}(Ce–N) = 2.47 Å).[22,25] Slightly longer Ln–N distances with average Gd–N bond lengths in the range 2.382–2.377 Å were observed in the square anti-prismatic GdX_8 coordination polyhedra in $Gd(N_3)_3 \cdot {}^8/_3$ DMSO as well as $Gd_4(OH)_2(N_3)_{10} \cdot n$ DMSO (*n* = 8, 10), which lay also well within the sum of the ion radii for an eight-coordinated Gd^{3+} ion (Σr_{ion}(Gd–N) = 2.51 Å). The azide units adopt a typical trans-bent structure with short averaged N_α–N_β (1.158–1.181 Å) and N_β–N_γ distances (1.145–1.160 Å), as well as N_α–N_β–N_γ angles in the range 177.4–179.2 °, which deviated considerably from linearity (*cf.* $[M]_3[Ce(N_3)_6] \cdot n$ MeCN N_α–N_β 1.177–1.189 Å, N_β–N_γ 1.156–1.158 Å, N_α–N_β–N_γ 178.0–178.9 °).

On the other hand, the Gd–N distances to the $\mu_{2(1,1)}$-, $\mu_{2(1,3)}$- or $\mu_{3(1,1,1)}$-bridging azide ligands in the square anti-prismatic coordination sphere of the Gd atoms in $Gd(N_3)_3 \cdot {}^8/_3$ DMSO and $Gd_4(OH)_2(N_3)_{10} \cdot n$ DMSO (*n* = 8, 10) were considerably elongated ($\mu_{2(1,1)}$ 2.467–2.526 Å, $\mu_{2(1,3)}$ 2.487 Å, $\mu_{3(1,1,1)}$ 2.628 Å), in good agreement with the sum of the ionic radii (Σr_{ion}(Gd–N) = 2.51 Å) This, together with the slightly longer N_α–N_β distances (N_α–N_β 1.190–1.211 Å, N_β–N_γ 1.140–1.167), and flat angles in the range 178.3–179.5° indicated a higher degree of ionic bonding (Table 2).

The Gd–O_{DMSO} bond lengths in the range 2.355–2.367 Å were slightly longer than the sum of the covalent radii Σr_{cov}(Gd–O) = 2.32 Å,[25] but within with the sum of ionic radii Σr_{ion}(Gd–O) of 2.40 Å for a square anti-prismatic coordination environment.[22] In accord with a higher coordination number of the oxygen atom in the $\mu_{3(1,1,1)}$-bridging hydroxide group, the Gd–O_{OH} bonds were slightly elongated in the range 2.372–2.377 Å.

As depicted in Figure 4, well separated argentate(I) $[AgX_2]^-$ anions (X = N_3, Cl) were found in the double salts $[Ph_4P]_4[Gd(N_3)_6][Ag(N_3)_2]$ and $[Ph_4P]_4[GdCl_2(N_3)_4][AgCl_2]$ with closest intramolecular N···H contacts of 2.489 and 2.591 Å (*cf.* Σr_{vdW}(N–H) 3.00 Å).[22] In both structures, the $[AgX_2]^-$ anions were linearly coordinated (X–Ag–X 180 °) and obey ideal $D_{\infty h}$- ($[AgCl_2]^-$) and C_{2h}-symmetry ($[Ag(N_3)_2]^-$), respectively. Accordingly, both Ag–N bond lengths in the diazido argentate(I) anion were equal and amount to 2.088 Å, which lies only slightly above the sum of the covalent radii for a silver nitrogen single bond (Σr_{cov}(Ag–N) = 1.99 Å), but within the sum of the ion radii for a linearly coordinated Ag^+ ion (Σr_{ion}(Ag–N) = 2.13 Å).[25,22] Only recently, the structures of two diazido argentate(I) salts $[M][Ag(N_3)_2]$ ($[M]^+$ =$[Ph_3S]$, $[Ph_4P]$) could be determined by Klapötke *et al.*, which, however, displayed the silver cations in a distorted tetrahedral or distorted trigonal-planar coordination sphere, resulting in considerably elongated Ag–N bond lengths ($[M]^+$ = $[Ph_3S]^+$ Ag–N 2.291–2.331 Å; $[Ph_4P]^+$Ag–N 2.139–2.485 Å).[21] To the best of our knowledge, the present structure represents the only example for an isolated, linearly coordinated diazido argentate(I) anion in the literature.

Conclusions

A series of $[Ph_4P]^+$ and $[EtPh_3P]^+$ salts of hexaazido lanthanate(III) anions $[M]_3[Ln(N_3)_6] \cdot n$ MeCN (Ln = Ce, Gd; $[M]^+$ = $[Ph_4P]^+$ (*n* = 2), $[EtPh_3P]^+$ (*n* = 0)), along with the double-salts $[Ph_4P]_4[Gd(N_3)_6][Ag(N_3)_2]$ and $[Ph_4P]_4[GdCl_2(N_3)_4][AgCl_2]$ was synthesized and comprehensively characterized. All salts were easily accessible by means of an iodide/azide exchange starting from the corresponding lanthanide(III) iodide LnI_3, AgN_3, and the desired [M]I in acetonitrile or DMSO. Likewise, gadolinium(III) azide as DMSO solvate $Gd(N_3)_3 \cdot {}^8/_3$ DMSO, as well as the mixed azide/hydroxide derivates $Gd_4(OH)_2(N_3)_{10} \cdot n$ DMSO (*n* = 8, 10) were synthesized by the reaction of GdI_3 and AgN_3 in DMSO. In the solid state, only slightly distorted, octahedral coordinated lanthanide(III) atoms are observed in the $[Ln(N_3)_6]^{3-}$ anions, while the structures of $Gd(N_3)_3 \cdot {}^8/_3$ DMSO and $Gd_4(OH)_2(N_3)_{10} \cdot n$ DMSO (*n* = 8, 10) display the Gd^{3+} cations in a distorted square anti-prismatic coordination environment.

Experimental Section

Caution! *Covalent azides are potentially hazardous and can decompose explosively under various conditions! Especially dry, crystalline AgN_3 is extremely sensitive to shock and friction and can explode violently upon the slightest provocation. Appropriate safety precautions (safety shields, face shields, leather gloves, protective clothing) should be taken.*

$Gd(N_3)_3 \cdot {}^8/_3$ DMSO: To a solution of gadolinium(III) iodide GdI_3 (0.261 g, 0.49 mmol) in DMSO (5 mL) silver azide AgN_3 (0.222 g, 1.46 mmol) was added. After stirring for 40 minutes, the resulting yellow precipitate was filtered off and the resulting clear, orange filtrate was concentrated to 2 mL by evaporation of the solvent. Dried acetonitrile was added by gas diffusion over a period of several days. The formed AgI crystals were removed by filtration, and the filtrate was concentrated to 1 mL and layered with 2 mL of dried acetonitrile. Over the course of a few days yellow, needle-like crystals were deposited. The supernatant was removed by decantation and the crystals of $Gd(N_3)_3 \cdot {}^8/_3$ DMSO were dried in vacuum (yield: 60–70 %). M.p. 157 °C (decomp.), ^{14}N NMR (300 K, $[D_6]$DMSO, 36.1 MHz): δ = -284 ppm ($N_{\alpha/\gamma}$, $\Delta\nu_{1/2}$ = 824 Hz). IR (ATR, 32 scans): $\tilde{\nu}$ = 3390 (w), 3326 (w), 3001 (w), 2917 (w), 2664 (w), 2586 (w), 2126 (s), 2084 (s), 2046 (s), 1411 (m), 1402 (m), 1351 (m), 1325 (m), 1314 (m), 1297 (m), 1288 (sh, m), 1257 (m), 1231 (w), 999 (s), 958 (s), 911 (m), 714 (m), 681 (w), 656 (m), 643 (m), 616 cm^{-1} (m); Raman (633 nm, 6 mW, 25 °C, 40 s, 8 acc.): $\tilde{\nu}$ = 3002 (2.0), 2916 (5.1), 2123 (0.9), 2088 (0.9), 2080 (0.8), 2075 (0.7), 1413 (1.5), 1352 (4.0), 1332 (1.3), 1295 (0.8), 1259 (0.7), 1008 (1.1), 958 (1.0), 942 (sh, 0.8), 712 (3.2), 680 (5.4), 654 (1.2), 638 (1.1), 405 (1.5), 380 (1.5), 341 (2.3), 312 (2.9), 254 (3.6), 172 (4.1), 97 cm^{-1} (10); elemental analysis calcd (%) for $C_{16}H_{48}N_{27}Gd_3O_8S_8$: C 13.03, H 3.28, N 25.64, S 17.39; found C 13.40, H 3. 29, N 25.21, S 17.02.

$Gd_4(N_3)_{10}(OH)_2 \cdot 10$ DMSO and $Gd_4(N_3)_{10}(OH)_2 \cdot 8$ DMSO: To a solution of gadolinium(III) iodide GdI_3 (0.133 g, 0.25 mmol) in DMSO (3 mL) silver azide AgN_3 (0.112 g, 0.75 mmol) was added. After stirring for 30 minutes, the resulting yellow precipitate was removed by filtration and the clear, orange filtrate was concentrated by evaporation of the solvent. Moist, degassed acetonitrile was added by slow gas diffusion into the DMSO solution. The formation of crystalline silver iodide AgI was observed which was separated by decantation from the supernatant. The solution was concentrated and layered with moist, degassed acetonitrile. Storage at ambient temperature for several days resulted in the deposition of colorless, block-like crystals of $Gd_4(N_3)_{10}(OH)_2 \cdot 10$ DMSO. According to X-ray structure determinations,

$Gd_4(N_3)_{10}(OH)_2 \cdot 10$ DMSO was found to be a mixture of a triclinic (α) and a monoclinic (β) modification (space groups $P\bar{1}$ and $P2_1/c$) in varying compositions (yield: 20–30 %). Storage of crystalline $Gd_4(N_3)_{10}(OH)_2 \cdot 10$ DMSO in DMSO/acetonitrile (excess MeCN) solution for several months resulted in the slow transformation into crystals of $Gd_4(N_3)_{10}(OH)_2 \cdot 8$ DMSO as confirmed by single crystal X-ray diffraction.

$Gd_4(N_3)_{10}(OH)_2 \cdot 10$ DMSO (Mixture of α- and β-phase): M.p. 173 °C (decomp.); ^{14}N NMR (300 K, [D$_6$]DMSO, 36.1 MHz): δ = -283 ppm ($N_{\alpha/\gamma}$, $\Delta\nu_{1/2}$ = 991 Hz). IR (ATR, 32 scans): $\tilde{\nu}$ = 3581 (w), 3390 (w), 3343 (w), 2997 (w), 2916 (w), 2653 (w), 2092 (m), 2066 (s), 2047 (s), 1413 (m), 1404 (sh, m), 1350 (m), 1315 (m), 1298 (m), 1290 (m), 1233 (w), 1227 (w), 1007 (s), 964 (s), 942 (m), 911 (m), 712 (m), 679 (m), 657 (m), 650 (m), 613 cm^{-1} (m); Raman (633 nm, 5 mW, 25 °C, 20 s, 10 acc.): $\tilde{\nu}$ = 3583 (0.5), 3002 (1.6), 2918 (4.0), 2109 (0.7), 2073 (0.4), 1416 (0.9), 1357 (3.8), 1320 (0.2), 1299 (0.3), 1291 (0.4), 1030 (0.5), 1013 (0.4), 968 (0.4), 946 (0.1), 717 (2.0), 684 (5.2), 659 (0.3), 615 (0.2), 404 (0.4), 342 (1.0), 318 (1.5), 293 (1.3), 223 (2.3), 174 (2.3), 87 cm^{-1} (10); elemental analysis calcd (%) for $C_{20}H_{62}N_{30}Gd_4O_{12}S_{10}$: C 12.88, H 3.35, N 22.54, S 17.20; found C 13.21, H 2.80, N 19.28, S 15.45.

$Gd_4(N_3)_{10}(OH)_2 \cdot 8$ DMSO: Raman (633 nm, 5 mW, 25 °C, 20 s, 10 acc.): $\tilde{\nu}$ = 2998 (3.3), 2912 (8.6), 2104 (1.0), 2062 (1.0), 1409 (1.1), 1367 (3.4), 1354 (2.3), 1304 (0.8), 1294 (0.9), 1233 (0.4), 1027 (0.5), 1006 (0.6), 970 (0.2), 954 (0.3), 799 (2.6), 739 (1.7), 710 (1.7), 675 (4.6), 635 (0.4), 527 (0.5), 402 (0.5), 328 (2.2), 296 (3.0), 217 (3.1), 203 (3.0), 175 (4.2), 71 cm^{-1} (10).

$[Ph_4P]_3[Ce(N_3)_6] \cdot 2$ MeCN: To a solution of cerium(III) iodide CeI_3 (0.130 g, 0.25 mmol) and tetraphenylphosphonium azide $[Ph_4P]N_3$ (0.286 g, 0.75 mmol) in acetonitrile (7 mL) silver azide AgN_3 (0.113 g, 0.75 mmol) was added and stirred for 45 minutes. After filtration the clear, black-brown solution was slowly concentrated by evaporation, resulting in the deposition of colorless crystals. The supernatant was removed by decantation and the colorless crystals of $[Ph_4P]_3[Ce(N_3)_6] \cdot 2$ MeCN were washed with acetonitrile. According to X-ray structure determinations, $[Ph_4P]_3[Ce(N_3)_6] \cdot 2$ MeCN was found to be a mixture of two triclinic modifications (denoted as (α) and (β), space group $P\bar{1}$) in varying compositions. Drying in vacuum led to the non-stoichiometric loss of solvent (yield: 10–20 %). M.p. 187 °C (heating rate 20 °C/min); ^1H NMR (300 K, [D$_6$]DMSO, 500.13 MHz): δ = 7.95 (m, 4 H, para), 7.81 (m, 8 H, meta), 7.75 (m, 8 H, ortho), 2.04 ppm (s, CH_3CN); ^{13}C NMR (300 K, [D$_6$]DMSO, 125.8 MHz): δ = 135.39 (d, $^4J(^{13}C - {}^{31}P)$ = 2.75 Hz, para), 134.58 (d, $^2J(^{13}C - {}^{31}P)$ = 10.08 Hz, ortho), 130.50 (d, $^3J(^{13}C - {}^{31}P)$ = 12.83 Hz, meta), 117.73 ppm (d, $^1J(^{13}C - {}^{31}P)$ = 88.89 Hz, P*C*); ^{31}P NMR (300 K, [D$_6$]DMSO, 202.5 MHz): δ = 22.29 ppm (s, $^1J(^{13}C - {}^{31}P)$ = 88.89 Hz); ^{14}N NMR (300 K, [D$_6$]DMSO, 36.1 MHz): δ = -126 (N_β; $\Delta\nu_{1/2}$ = 101 Hz), -228 ppm ($N_{\alpha/\gamma}$, $\Delta\nu_{1/2}$ = 434 Hz); IR (ATR, 32 scans): $\tilde{\nu}$ = 3453 (w), 3375 (w), 3163 (w), 3079 (w), 3058 (w), 3022 (w), 2993 (w), 2931 (w), 2692 (w), 2584 (w), 2247 (w), 2101 (w), 2040 (s), 1834 (w), 1788 (w), 1585 (m), 1483 (m), 1435 (s), 1350 (m), 1316 (m), 1277 (w), 1226 (w), 1187 (m), 1162 (w), 1105 (s), 1076 (sh, w), 1026 (m), 995 (m), 939 (w), 848 (w), 755 (m), 719 (s), 686 (s), 665 (m), 616 cm^{-1} (m); Raman (473 nm, 2 mW, 25 °C, 15 s, 10 acc.): $\tilde{\nu}$ = 3171 (6.0), 3146 (6.0), 3062 (10), 3012 (5.4), 2963 (5.3), 2938 (5.5), 2251 (4.0), 2153 (4.4), 2098 (4.7), 2043 (4.2), 1587 (5.5), 1485 (2.6), 1442 (2.6), 1362 (4.1), 1355 (sh, 3.2), 1347 (sh, 2.7), 1187 (2.2), 1168 (2.2), 1110 (2.6), 1099 (3.8), 1028 (4.1), 1001 (6.8), 932 (1.6), 725 (1.4), 679 (2.2), 615 (2.0), 548 (1.4), 383 (0.9), 288 (1.1), 260 (1.5), 249 (1.6), 198 (1.4), 156 cm^{-1}(1.7); elemental analysis calcd (%) for $C_{76}H_{66}N_{20}CeP_3$: C 61.16, H 4.46, N 18.77; found C 58.91, H 5.08, N 17.62.

$[Ph_4P]_3[Gd(N_3)_6] \cdot 2$ MeCN: Gadolinium(III) chloride $GdCl_3 \cdot 2$ MeCN (0.086 g, 0.25 mmol) and tetraphenylphosphonium iodide $[Ph_4P]I$ (0.351 g, 0,75 mmol) were dissolved in acetonitrile (10 mL) and silver azide AgN_3 (0.229 g, 1.53 mmol) was added. After stirring for one hour, the yellow precipitate was removed by filtration. Evaporation of the solvent resulted in the deposition of colorless crystals. For purification the product was recrystallized from acetonitrile. After decantation of supernatant, the crystals of $[Ph_4P]_3[Gd(N_3)_6] \cdot 2$ MeCN were washed with acetonitrile. Drying in vacuum led to non-stoichiometric loss of solvent (yield: 20–30 %). M.p. 216 °C; ^1H NMR (300 K, [D$_6$]DMSO, 500.13 MHz): δ = 2.17 (s, CH_3CN, $\Delta\nu_{1/2}$ = 240 Hz), 7.88 ppm (s, 20 H; *Aryl*, $\Delta\nu_{1/2}$ = 340 Hz); ^{13}C NMR (300 K, [D$_6$]DMSO, 125.8 MHz): δ = 135.79 (s, para), 134.97 (s, ortho), 130.89 (s, meta), 118.10 ppm (d, $^1J(^{13}C - {}^{31}P)$ = 87 Hz, P*C*); ^{31}P NMR (300 K, [D$_6$]DMSO, 202.5 MHz): δ = 22.34 ppm (s); ^{14}N NMR (300 K, [D$_6$]DMSO, 36.1 MHz): δ = -136 (MeCN, $\Delta\nu_{1/2}$ = 190 Hz), -240 ppm ($N_{\alpha/\gamma}$, $\Delta\nu_{1/2}$ = 750 Hz); IR (ATR, 32 scans): $\tilde{\nu}$ = 3468 (w), 3392 (w), 3168 (w), 3079 (w), 3058 (w), 3022 (w), 2993 (w), 2963 (w), 2690 (w), 2581 (w), 2111 (w), 2052 (s), 1828 (w), 1790 (w), 1585 (m), 1483 (m), 1434 (m), 1357 (m), 1316 (m), 1222 (w), 1186 (w), 1163 (w), 1105 (s), 1079 (sh, m), 1027 (w), 995 (m), 937 (w), 850 (w), 754 (m), 719 (s), 686 (s), 665 (sh, m), 615 cm^{-1} (m); Raman (473 nm, 0.36 mW, 25 °C, 40 s, 12 acc.): $\tilde{\nu}$ = 3168 (3.4), 3144 (3.4), 3061 (10), 3025 (3.0), 3010 (3.0), 2993 (3.0), 2959 (2.9), 2931 (3.3), 2248 (2.2), 2110 (1.8), 2054 (1.6), 1585 (6.3), 1482 (1.0), 1438 (1.2), 1364 (4.8), 1340 (sh, 1.1), 1274 (0.8), 1223 (0.7), 1188 (1.1), 1163 (1.0), 1106 (sh, 1.9), 1096 (3.2), 1076 (0.7), 1026 (4.1), 999 (7.5), 935 (0.6), 854 (0.4), 749 (0.4), 724 (0.5), 677 (1.5), 614 (1.1), 533 (0.2), 454 (0.2), 394 (0.1), 376 (0.1), 283 (0.6), 254 (1.3), 196 (0.9), 154 cm^{-1} (1.6); elemental analysis calcd (%) for $C_{76}H_{66}N_{20}GdP_3$: C 60.47, H 4.41, N 18.56; found C 58.81, H 4.65, N 17.54.

$[EtPh_3P]_3[Ce(N_3)_6]$: To a solution of cerium(III) iodide CeI_3 (0.130 g, 0.25 mmol) and silver azide AgN_3 (0.114 g, 0.76mmol) in acetonitrile (4 mL), a suspension of ethyltriphenylphosphonium iodide $[EtPh_3P]I$ (0.313 g, 0.75 mmol) and AgN_3 (0.114 g, 0.76 mmol) in acetonitrile (4 mL) was added. After stirring for 30 minutes, the resulting black-brownish solution was separated from the yellow precipitate by filtration (F4) and concentrated to about 3 mL in vacuum. Storage at ambient temperature for several hours resulted in the deposition of colorless crystals of $[EtPh_3P]_3[Ce(N_3)_6]$ besides small amounts of a brownish, amorphous precipitate, which was removed by washing with acetonitrile (yield: 10–20 %). M.p. 213 °C; ^1H NMR (300 K, [D$_6$]DMSO, 500.13 MHz): δ = 7.73 - 7.90 (m, 15 H, *Aryl*), 3.61 ($d_{quartett}$, 2 H, $J(^1H - {}^1H)$ = 7.4 Hz, $J(^1H - {}^{31}P)$ = 13.6 Hz, CH_2CH$_3$), 1.22 ($d_{triplett}$, 3 H, $J(^1H - {}^1H)$ = 7.4 Hz, 53 $J(^1H - {}^{31}P)$ = 20.2 Hz, CH$_2$CH_3); ^{13}C NMR (300 K, [D$_6$]DMSO, 125.8 MHz): δ = 134.91 (d, $^4J(^{13}C - {}^{31}P)$ = 2.8 Hz, *para*), 133.52 (d, $^2J(^{13}C - {}^{31}P)$ = 10.1 Hz, *ortho*), 130.28 (d, $^3J(^{13}C - {}^{31}P)$ = 12.8 Hz, *meta*), 118.33 (d, $^1J(^{13}C - {}^{31}P)$ = 85.2 Hz, P*C*), 14.41 (d, $^1J(^{13}C - {}^{31}P)$ = 51.5 Hz, *C*H$_2$), 6.27 (d, $^2J(^{13}C - {}^{31}P)$ = 5.5 Hz, *C*H$_3$); ^{31}P NMR (300 K, [D$_6$]DMSO, 202.5 MHz): δ = 26.01 (s, $^1J(^{13}C - {}^{31}P)$ = 85.2 Hz); ^{14}N NMR (300 K, [D$_6$]DMSO, 36.1 MHz): δ = -126 (N_β, $\Delta\nu_{1/2}$ = 100 Hz), -232 ($N_{\alpha/\gamma}$, $\Delta\nu_{1/2}$ = 394 Hz); IR (ATR, 32 scans): $\tilde{\nu}$ = 3446 (w), 3376 (w), 3082 (w), 3064 (w), 3053 (w), 2993 (w), 2983 (w), 2936 (w), 2902 (w), 2877 (w), 2648 (w), 2105 (w), 2044 (s), 1824 (w), 1781 (w), 1585 (m), 1573 (w), 1483 (m), 1450 (w), 1434 (m), 1402 (m), 1383 (w), 1347 (m), 1315 (m), 1293 (w), 1279 (w), 1238 (w), 1225 (w), 1186 (w), 1160 (m), 1111 (s), 1073 (m), 1037 (m), 1028 (m), 1013 (w), 996 (m), 978 (w), 929 (w), 848 (w), 770 (sh, w), 746 (m), 737 (s), 721 (s), 690 (s), 665 (m), 617 (m), 530 cm^{-1} (s). Raman (633 nm, 6 mW, 25 °C, 30 s, 12 acc.): $\tilde{\nu}$ = 3166 (0.7), 3139 (0.7), 3062 (2.5), 3051 (2.1), 3004 (0.7), 2980 (0.7), 2933 (1.3), 2900 (1.0), 2874 (0.8), 2245 (0.6), 2149 (0.6), 2140 (0.5), 2095 (0.6), 2037 (0.5), 1581 (3.3), 1569 (0.9), 1480 (0.4), 1447 (0.4), 1434 (0.4), 1399 (0.4), 1379 (0.4), 1351 (2.1), 1345 (sh, 1.0), 1312 (0.3), 1185 (0.6), 1159 (0.7), 1099 (2.1), 1069 (0.3) 1022 (2.8), 994 (5.5), 922 (0.2), 849 (0.1), 765 (0.1), 733 (0.1), 717 (0.1), 704 (0.1), 686 (0.1), 660 (2.0), 617 (sh, 0.3), 610 (0.8), 524 (0.1), 482 (0.1), 462 (0.1), 449 (0.1), 430 (0.1), 391 (0.1), 374 (0.3), 304 (0.4), 293 (0.2), 275 (0.6), 248 (1.9), 210 (0.9), 196 (0.9), 82 cm^{-1} (10); elemental analysis calcd (%) for $C_{60}H_{60}N_{18}CeP_3$: C 56.91, H 4.71, N 19.91; found C 54.72, H 5.00, N 19.46.

$[EtPh_3P]_3[Gd(N_3)_6]$: To a solution of gadolinium(III) chloride $GdCl_3 \cdot 2$ MeCN (0.086 g, 0.25 mmol) in acetonitrile (10 mL), ethyltriphenylphosphonium iodide (0.318 g, 0.76 mmol) followed by silver azide AgN_3 (0.225 g, 1.50 mmol) were added. After stirring for 90 minutes, the resulting yellow precipitate was removed by filtration (F4). Evaporation of the solvent in vacuum led to the deposition of $[EtPh_3P]_3[Gd(N_3)_6]$ as colorless, needle-like crystals (yield: 20–30 %). M.p. 229 °C; ^{1}H NMR (300 K, [D$_6$]DMSO, 500.13 MHz): δ = 7.86 (s, 15 H, *Aryl*, $\Delta\nu_{1/2}$ = 341 Hz), 3.67 (s, 2 H, CH_2CH_3, $\Delta\nu_{1/2}$ = 302 Hz), 1.26 ppm (s, 3 H, CH_2CH_3, $\Delta\nu_{1/2}$ = 322 Hz); ^{13}C NMR (300 K, [D$_6$]DMSO, 125.8 MHz): δ = 135.36 (s, *para*), 134.03 (s, *ortho*), 130.70 (s, *meta*), 118.75 (d; $^1J(^{13}C - ^{31}P)$ = 84 Hz, P*C*), 14.80 (s, *C*H$_2$), 6.68 ppm (s, *C*H$_3$); ^{31}P NMR (300 K, [D$_6$]DMSO, 202.5 MHz): δ = 26.3 ppm (s); ^{14}N NMR (300 K, [D$_6$]DMSO, 36.1 MHz): δ = -243 ppm ($N_{\alpha/\gamma}$, $\Delta\nu_{1/2}$ = 634 Hz); IR (ATR, 32 scans): $\tilde{\nu}$ = 3463 (w), 3387 (w), 3081 (w), 3063 (w), 3052 (w), 3024 (w), 3010 (w), 2994 (w), 2983 (w), 2935 (w), 2901 (w), 2879 (sh, w), 2110 (w), 2052 (s), 1826 (w), 1779 (w), 1585 (m), 1573 (w), 1483 (m), 1451 (w), 1434 (m), 1402 (m), 1383 (w), 1352 (m), 1315 (m), 1279 (w), 1239 (w), 1187 (w), 1159 (m), 1111 (s), 1073 (m), 1037 (m), 1027 (w), 1013 (m), 996 (m), 980 (m), 935 (w), 928 (w), 847 (w), 770 (w), 760 (w), 746 (s), 737 (s), 721 (s), 690 (s), 665 (m), 617 cm^{-1} (m); Raman (785 nm, 10 mW, 25 °C, 20 s, 12 acc.): 3065 (0.1), 3055 (0.1), 2983 (0.1), 2939 (0.1), 2904 (0.1), 2111 (0.1), 2057 (0.1), 2050 (0.1), 1586 (0.6), 1574 (0.2), 1485 (0.1), 1454 (0.2), 1436 (0.2), 1404 (0.2), 1384 (0.2), 1363 (0.7), 1355 (0.4), 1318 (0.2), 1275 (0.2), 1242 (0.2), 1193 (0.3), 1162 (0.4), 1113 (sh, 0.4), 1105 (0.7), 1074 (0.2), 1028 (1.1), 1000 (2.2), 929 (0.3), 855 (0.3), 848 (0.3), 771 (0.3), 752 (0.3), 739 (0.4), 722 (0.4), 710 (0.4), 690 (0.4), 665 (1.2), 623 (sh, 0.4), 615 (0.8), 531 (0.4), 526 (sh, 0.4), 505 (0.4), 489 (0.5), 452 (0.4), 436 (0.4), 380 (0.7), 310 (0.9), 301 (0.7), 280 (0.9), 260 (sh, 1.4), 253 (1.7), 220 (1.2), 202 (1.1), 141 (3.5), 94 (10), 72 cm^{-1} (8.4); elemental analysis calcd (%) for $C_{60}H_{60}N_{18}GdP_3$: C 56.15, H 4.71, N 19.64; found C 55.80, H 4.43, N 19.3.

$[Ph_4P]_4[Gd(N_3)_6][Ag(N_3)_2]$: Gadolinium(III) iodide GdI_3 (0.081 g, 0.15 mmol) and tetraphenylphosphonium azide (0.227 g, 0.59 mmol) were mixed and suspended in acetonitrile (7 mL). Silver azide AgN_3 (0.090 g, 0.60 mmol) was added, and after stirring for one hour at ambient temperature, the resulting yellow precipitate was removed by filtration. The filtrate was slowly evaporated in vacuum, resulting in the deposition of colorless crystals. Washing with acetonitrile and drying in vacuum yielded $[Ph_4P]_4[Gd(N_3)_6][Ag(N_3)_2]$ as colorless, crystalline solid (yield: 20–30 %). M.p. 222 °C; ^{1}H NMR (300 K, [D$_6$]DMSO, 500.13 MHz): δ = 7.80 ppm (s, 20 H; *Aryl*, $\Delta\nu_{1/2}$ = 294 Hz); ^{13}C NMR (300 K, [D$_6$]DMSO, 125.8 MHz): δ = 135.74 (s, para), 134.92 (s, ortho), 130.84 (s, meta), 118.05 ppm (d, $^1J(^{13}C - ^{31}P)$ = 86 Hz, P*C*); ^{31}P NMR (300 K, [D$_6$]DMSO, 202.5 MHz): δ = 22.36 ppm (s); ^{14}N NMR (300 K, [D$_6$]DMSO, 36.1 MHz): δ = -214 ppm ($N_{\alpha/\gamma}$, $\Delta\nu_{1/2}$ = 557 Hz); IR (ATR, 32 scans): $\tilde{\nu}$ = 3469 (w), 3411 (w), 3393 (w), 3168 (w), 3146 (w), 3085 (w), 3061 (w), 3022 (w), 2994 (w), 2692 (w), 2579 (w), 2111 (w), 2058 (s), 2035 (s), 1828 (w), 1789 (w), 1586 (m), 1575 (w), 1483 (m), 1435 (m), 1368 (m), 1358 (m), 1340 (m), 1316 (m), 1223 (m), 1185 (m), 1164 (m), 1107 (s), 1074 (m), 1027 (w), 997 (m), 984 (sh, m), 935 (w), 853 (w), 754 (m), 722 (s), 689 (s), 666 (m), 640 (m), 616 cm^{-1} (m); Raman (633 nm, 6 mW, 25 °C, 15 s, 20 acc.): $\tilde{\nu}$ = 3170 (2.3), 3145 (2.4), 3088 (2.7), 3063 (4.1), 2112 (1.6), 2052 (1.6), 1587 (2.9), 1576 (1.3), 1483 (0.7), 1439 (0.7), 1372 (1.6), 1363 (1.5), 1330 (1.0), 1314 (sh, 0.6), 1279 (0.1), 1188 (0.7), 1169 (0.8), 1111 (0.7), 1100 (1.6), 1078 (0.1), 1028 (2.0), 1002 (4.3), 990 (0.3), 939 (0.2), 853 (0.1), 756 (0.1), 728 (0.2), 682 (1.2), 617 (0.7), 537 (0.1), 530 (0.1), 460 (0.1), 453 (0.1), 312 (0.1), 286 (0.5), 274 (0.4), 256 (1.6), 200 (1), 159 (1.8), 91 cm^{-1} (10.0); elemental analysis calcd (%) for $C_{96}H_{80}N_{24}AgGdP_4$: C 58.86, H 4.12, N 17.16; found C 58.86, H 3.87, N 17.12.

$[Ph_4P]_4[Gd(N_3)_4Cl_2][AgCl_2]$: Gadolinium(III) iodide GdI_3 (0.134 g, 0.25 mmol) and tetraphenylphosphonium chloride $[Ph_4P]Cl$ (0.375 g, 1.00 mmol) were combined and dissolved in acetonitrile (10 mL). To the colorless solution, silver azide AgN_3 (0.150 g, 1.00 mmol) was added in one portion. After stirring for 30 minutes, the off-white precipitate was filtered off. The clear, colorless solution was slowly evaporated to half volume in vacuum. Storage at ambient temperature for 18 hours resulted in the deposition of tiny amounts of colorless, needle-like crystals, which could be identified as $[Ph_4P][Ag_2Cl_2I]$ by single crystal X-ray diffraction. The crystals were removed by decantation/filtration, and the resulting solution was concentrated to a volume of about 1 mL. Storage at ambient temperature for 12 hours resulted in the deposition of large, block-like crystals. Removal of supernatant, washing with acetonitrile (0.2 mL) and drying in vacuum yielded $[Ph_4P]_4[Gd(N_3)_4Cl_2][AgCl_2]$ as colorless, crystalline solid. The mother liquor was further concentrated, which yielded a second crop of crystals (combined yield: 50–60%). M.p: 227 - 229 °C; ^{1}H NMR (300 K, [D$_6$]DMSO, 500.13 MHz): δ = 7.83 ppm (s, 20 H; *Aryl*, $\Delta\nu_{1/2}$ = 270 Hz); ^{13}C NMR (300 K, [D$_6$]DMSO, 125.8 MHz): δ = 135.66 (s, para), 134.83 (s, ortho), 130.80 (s, meta), 117.96 ppm (d, $^1J(^{13}C - ^{31}P)$ = 88 Hz, P*C*); ^{14}N NMR (300 K, [D$_6$]DMSO, 36.1 MHz): δ = -252 ppm ($N_{\alpha/\gamma}$, $\Delta\nu_{1/2}$ = 830 Hz); IR (ATR, 32 scans): $\tilde{\nu}$ = 3459 (sh, w), 3413 (w), 3386 (w), 3167 (w), 3090 (w), 3057 (w), 3021 (w), 2993 (w), 2683 (w), 2579 (w), 2102 (w), 2067 (m), 2053 (s), 1830 (w), 1784 (w), 1682 (w), 1614 (w), 1584 (w), 1575 (sh, m), 1481 (m), 1432 (m), 1412 (sh, m), 1369 (m), 1350 (m), 1340 (sh, m), 1316 (m), 1232 (w), 1223 (m), 1186 (w), 1163 (m), 1158 (w), 1104 (s), 1073 (m), 1025 (w), 995 (m), 936 (w), 851 (w), 759 (m), 752 (m), 719 (s), 687 (s), 625 (w), 615 cm^{-1} (m); Raman (633 nm, 3.0 mW, 25 °C, 20 s, 10 acc.): $\tilde{\nu}$ = 3168 (0.2), 3141 (0.2), 3092 (0.3),3064 (1.8), 3025 (0.1), 3008 (0.1), 2991 (0.1), 2959 (0.1), 2113 (0.1), 2105 (0.1), 2097 (0.1), 2056 (0.1), 1585 (2.6), 1573 (0.5), 1484 (0.2), 1439 (0.2), 1433 (0.2), 1372 (3.8), 1354 (0.2), 1340 (0.1), 1315 (0.2), 1223 (0.2), 1187 (0.7), 1166 (0.6), 1159 (0.7), 1105 (0.4), 1096 (1.7), 1073 (1.9),1026 (2.1), 1000 (6.6), 986 (0.4), 978 (0.2), 964 (0.1), 940 (0.1), 933 (0.1), 856 (0.1), 848 (0.1), 806 (broad, 0.1), 761 (sh, 0.1), 750 (0.1), 728 (0.2), 725 (0.2), 696 (0.1), 678 (1.4), 615 (0.7), 533 (0.1), 525 (0.1), 470 (sh, 0.1), 464 (0.1), 456 (0.1), 440 (0.1), 432 (0.1), 406 (sh, 0.1), 395 (0.1), 284 (0.3), 274 (0.5), 256 (sh, 1.6), 250 (1.8), 205 (1.5), 197 (sh, 1.0), 158 (sh, 1.4), 112 (7.8), 85 cm^{-1} (10); elemental analysis calcd (%) for $C_{96}H_{80}N_{12}AgCl_4GdP_4$: C 59.66, H 4.17, N 8.70; found C 59.40, H 3.70, N 8.73.

$[Ph_4P]_4[Gd(N_3)_6][N_3(daa)] \cdot$ acetone (daa = diacetonealcohol): Gadolinium(III) chloride $GdCl_3 \cdot 2\,MeCN$ (0.086 g, 0.25 mmol) and tetraphenylphosphonium iodide $[Ph_4P]I$ (0.351 g, 0,75 mmol) were dissolved in acetonitrile (10 mL). Silver azide AgN_3 (0.229 g, 1.53 mmol) was added, and after stirring for one hour, the yellow precipitate was removed by filtration. The clear, colorless solution was evaporated in vacuum and the resulting solid was re-crystallized from acetone, yielding small amounts of $[Ph_4P]_4[Gd(N_3)_6][N_3(daa)] \cdot$ acetone (daa = diacetonealcohol) as colorless, crystals. IR (ATR, 32 scans): $\tilde{\nu}$ = 3475 (w), 3400 (w), 3305 (w), 3273 (w), 3064 (w), 3023 (w), 2991 (w), 2971 (w), 2917 (w), 2686 (w), 2580 (w), 2110 (w), 2092 (sh, w), 2060 (m), 2007 (m), 1830 (w), 1788 (w), 1755 (w), 1710 (m), 1691 (m), 1615 (w), 1587 (m), 1577 (sh, w), 1485 (m), 1436 (m), 1417 (m), 1360 (m), 1314 (m), 1238 (m), 1223 (m), 1187 (m), 1164 (m), 1129 (w), 1107 (s), 1076 (w), 1061 (m), 1027 (m), 1014 (w), 999 (m), 985 (m), 949 (m), 905 (w), 856 (w), 811 (w), 756 (m), 721 (s), 689 (s), 654 (sh, m), 644 (m), 630 (m), 617 cm^{-1} (m).

Magnetic Properties: Samples of $[EtPh_3P]_3[Gd(N_3)_6]$, $[Ph_4P]_3[Gd(N_3)_6] \cdot 2\,MeCN$, $[Ph_4P]_4[Gd(N_3)_6][Ag(N_3)_2]$, $Gd(N_3)_3 \cdot 8/3\,DMSO$ and $Gd_4(OH)_2(N_3)_{10} \cdot 10\,DMSO$ were packed into polyethylene (PE) capsules in an argon filled drybox and attached to the sample holder rod of a Vibrating Sample Magnetometer unit (VSM) for measuring the magnetization *M*(*T*,*H*) in a Quantum Design Physical Property Measurement System (PPMS). The samples were investigated in the temperature range of 2.5-300 K with magnetic flux densities up to 80 kOe.[16]

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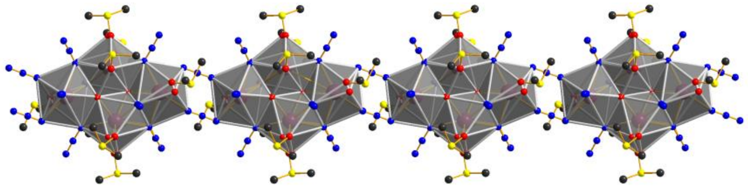

Gadolinium(III) azide $\mathrm{Gd(N_3)_3} \cdot {}^{8}/_{3}$ DMSO, the mixed azide/hydroxide derivates $\mathrm{Gd_4(OH)_2(N_3)_{10}} \cdot n$ DMSO (n = 8, 10), and a series of hexaazido lanthanate(III) salts $\mathrm{[M]_3[Ln(N_3)_6]} \cdot n$ MeCN (Ln = Ce, Gd; $\mathrm{[M]^+ = [Ph_4P]^+}$ (n = 2), $\mathrm{[EtPh_3P]^+}$ (n = 0)) were synthesized and comprehensively characterized. The magnetic susceptibilities in solution as well as in the solid state were investigated.

*Kati Rosenstengel, Axel Schulz, Oliver Niehaus, Oliver Janka, Rainer Pöttgen, and Alexander Villinger**

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