Articles

Triorganoazidometalates−Compounds with Unusual Structural Motifs

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The reaction of $Ga(CH_2Ph)_3$ with CsN_3 in THF gives, after recrystallization from toluene, the metalate $[Cs(toluene)_{0.5}\{(PhCH_2)_3GaN_3\}]$ (**1**), whereas the corresponding reaction of $In(CH_2Ph)_3$ with CsN_3 in THF yields, after recrystallization from toluene, the solvent-free salt $Cs[(PhCH_2)_3InN_3]$ (**2**). **1** and **2** have been characterized by NMR, IR, and MS techniques as well as by X-ray analyses. According to the X-ray structure determination, **1** and **2** can be described as coordination polymers $[\mathbf{1}]_n$ and $[\mathbf{2}]_n$ in the solid state. $[\mathbf{1}]_n$ consists of layers, packed along the crystallographic *a*-axis. The monomers **1** are connected by $Cs\cdots N_3$ and Cs···aryl contacts to form polymeric sheets. $[\mathbf{2}]_n$ mainly consists of chains aligned along the directions [011] and $[01\bar{1}]$. Here, the monomers **2** are connected by Cs···phenyl contacts. In addition, weak $In\cdots N_3$ interactions of 2.901(5) Å are observed, leading to a strongly distorted trigonal bipyramidal coordination sphere of the indium center (angular sum, equatorial plane, 355°) and to a cross-linking of the chains in the direction [100].

Organometallic azides of group 13 elements, such as $[R_2GaN_3]_n$ (R = alkyl, NMe_2),[1−7] and Lewis acid−base adducts, such as $[GaCl_3(Me_3SiN_3)]$[8] or $[(py)_3M(N_3)_3]$ (M = Al, Ga),[9] have attracted significant interest due to their potential use in MOCVD processes for metal nitrides. However, very little is known about alkali triorganometalates of Ga and In. $K[Me_3GaN_3]$[10] and similar compounds, such as $[Me_4N][Et_3GaN_3]$ and $[Me_4N][Me_2Ga(N_3)_2]$,[11,12] were characterized mainly by their vibrational spectra and melting points. Recently, new attempts to synthesize and characterize organoazido metalates have been successful. The azide $Ga(N_3)_3$ reacts with MeLi to give $Li[MeGa(N_3)_3]$.[9a] However, no structural information about these complex salts has been reported. For the $[Me_4N]^+$ salts, distorted tetrahedral coordination for the anions can be expected. In contrast, a complex such as $M'[R_{4-n}M(N_3)_n]$ (M′ = alkali metal; M = Ga, In; $n = 1-3$) may show a complex architecture. An indication of this is given by the structures of alkali organohalogenometalates such as $Cs[R_3MF]$,[13−15] $[Cs\{(PhCH_2)_3InCl\}]_2\cdot 0.5$toluene,[16] $Cs[(PhCH_2)_2GaF_2]$,[17] $Cs[MesGaF_3]$, and $K[MesInBr_3]$.[18] In these compounds, the formation of chains and layers of the metalates is dominated by alkali-metal−halide interactions. This feature is even more evident for pseudohalides due to their possible multidentate functionality.[9] In addition, π-electron−alkali metal contacts should influence the build-up of the structural motifs as well.[15,17]

Experimental Section

General Procedures. All experiments were carried out under an atmosphere of argon using Schlenk techniques. Purification and drying of the solvents were performed using standard methods.[19] $Ga(CH_2Ph)_3$[17,20] and $In(CH_2Ph)_3$[21,22] were prepared following literature procedures.

The ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-300 spectrometer (^1H, 300.134 MHz; ^{13}C, 75.469 MHz). The standard is TMS (external) with $\delta = 0.0$ ppm. The IR spectra

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Table 1. Crystallographic Data for the Compounds [1]$_n$ and [2]$_n$

	[**1**]$_n$	[**2**]$_n$
formula	$C_{24.5}H_{29}CsGaN_3$	$C_{21}H_{21}CsInN_3$
fw	568.15	563.14
cryst size (mm)	0.6 × 0.35 × 0.35	0.19 × 0.24 × 0.13
a (Å)	13.024(1)	12.359(1)
b (Å)	10.131(1)	17.474(1)
c (Å)	17.887(1)	9.841(1)
β (deg)	95.80(1)	
V (Å^3)	2348.0(3)	2125.3(3)
space group	$P2_1/c$	$Pna2_1$
no.[33]	14	33
Z	4	4
ρ_{calcd} (g/cm^3)	1.607	1.760
temp (K)	190	190
abs corr	numerical	numerical
μ (cm^{-1})	27.1	28.1
$2\theta_{max}$ (deg)	51.77	51.66
h, *k*, *l* values	$-15 \le h \le 15$, $-12 \le k \le 12$, $-19 \le l \le 19$	$-14 \le h \le 14$, $-21 \le k \le 21$, $-12 \le l \le 12$
no. of reflns	18351	16650
no. of unique reflns	4248	3997
no. of reflns with $F_o > 4\sigma(F_o)$ for R_1	3101	3305
no. of params	364	318
R_1^{a}	0.0261	0.0218
wR_2^{b}	0.0584	0.0388
weight factor^a	0.0351	0.0169
max/min resid electron density (e/Å^3)	0.68/−0.42	0.36/−0.37

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_c|$. ^{b} $wR_2 = \{[\sum w(F_o^2 - F_c^2)^2]/w(F_o^2)^2]\}^{1/2}$. ^{c} $w = 1/[\sigma^2(F_o^2) + (aP)^2]$.

were obtained using a Bruker IFS-88 instrument (Nujol mulls, CsI disks for the range 4000−500 cm^{-1}; polyethylene disks for the range 500−100 cm^{-1}). For the EI mass spectra, a Varian CH7a mass spectrometer (70 eV) was used. The melting points were measured with a Dr. Tottoli (Büchi) melting point apparatus in sealed capillaries under argon (values not corrected).

Synthesis of [Cs(toluene)$_{0.5}${(PhCH$_2$)$_3$GaN$_3$}], 1. A mixture of 2.49 g (7.26 mmol) of $Ga(CH_2Ph)_3$ and 1.37 g (7.26 mmol) of CsN_3 was stirred in 50 mL of THF for 24 h at 20 °C. The solvent was removed under vacuum. The residue was treated with 25 mL of toluene, whereupon a colorless oil was separated, which crystallized completely during 2 h (3.94 g, 96% yield, mp 99 °C (dec)). ^{1}H NMR (DMSO-d_6, ppm): 1.57 (s, 6 H, GaCH_2Ph), 2.37 (s, 1.5 H, CH_3-C_6H_5), 6.77−7.03 (m, 17.5 H, *H*−Ph, $CH_3C_6$$H_5$). ^{13}C NMR (DMSO-$d_6$, ppm): 21.6 (Ga*C*H$_2$Ph), 20.9 (*C*H$_3C_6H_5$), 120.1 ($C^4$, CH$_2$Ph), 125.2 ($C^4$, toluene), 126.5 ($C^{3/5}$, CH$_2$Ph), 128.1 ($C^{3/5}$, toluene), 127.2 ($C^{2/6}$, CH$_2$Ph), 128.8 ($C^{2/6}$, toluene), 148.1 ($C^1$, CH$_2$Ph), 138.2 ($C^1$, toluene). IR (cm^{-1}): 3382 (w), 3341 (w), 2725 (m), 2692 (m), 2633 (m), 2412 (m), 2361 (m), 2266 (m), 2077 (vs), 2014 (m), 1954 (m), 1890 (m), 1810 (m), 1747 (m), 1664 (m), 1592 (s), 1344 (s), 1313 (s), 1298 (2), 1261 (m), 1204 (2), 1178 (s), 1153 (s), 1097 (s), 1049 (s), 993 (s), 903 (m), 849 (w), 822 (w), 802 (2), 795 (s), 756 (vs), 698 (vs), 660 (s), 619 (m), 608 (m), 579 (m), 564 (m), 551 (m), 538 (s), 453 (s), 397 (m), 354 (m), 332 (m), 245 (m), 225 (m), 172 (m), 148 (w). EI-MS (*m*/*z* relative intensity fragment): 342 (6, $[Ga(CH_2Ph)_3]^+$), 251 (94, $[Ga(CH_2Ph)_2]^+$), 160 (36, $(GaCH_2Ph)^+$), 133 (3, Cs$^+$), 91 (50, $(CH_2Ph)^+$), 69 (100, Ga$^+$). Anal. Calcd: C, 52.16; H, 4.47; N, 7.45. Found: C, 52.13; H, 4.33; N, 7.74.

Synthesis of Cs[(PhCH$_2$)$_3$InN$_3$], 2. A mixture of 7.38 g (19 mmol) of $In(CH_2Ph)_3$ and 3.33 g (19 mmol) of CsN_3 was stirred in 50 mL of THF for 24 h at 20 °C. The reaction mixture was filtered, and the solvent was removed under vacuum. Treatment of the residue with 50 mL of toluene gave a viscous, clear oil, which crystallized within 2 days. The crystals were washed with a small amount of toluene and filtered. Crystals suitable for X-ray analysis were obtained by cooling the filtrate to −25 °C (9.8 g, 92% yield, mp 102 °C (dec)). ^{1}H NMR (DMSO-d_6, ppm): 1.73 (s, 2 H, InCH_2Ph), 6.71−7.03 (m, 5 H, Ph−*H*). ^{13}C NMR (DMSO-d_6, ppm): 22.5 (*C*H$_2$Ph), 119.6 (C^4), 125.8 ($C^{2/6}$), 127.4 ($C^{3/5}$), 148.9 (C^1). IR (cm^{-1}): 3325 (vw), 3277 (vw), 2723 (m), 2415 (w), 2026 (vs), 1588 (vs), 1330 (m), 1306 (m), 1207 (s), 1178 (m), 1155 (m), 1030 (vs), 993 (vs), 896 (s), 849 (m), 815 (w), 759 (vs), 701 (vs), 679 (s), 618 (m), 539 (m), 536 (m), 437 (m), 423 (m), 400 (m), 354 (vw), 325 (vw), 301 (vw), 280 (w), 242 (w), 223 (m), 211 (m), 204 (m), 173 (w), 151 (w), 137 (vw), 120 (vw). EI-MS (*m*/*z* relative intensity fragment): 182 (11, $(PhCH_2CH_2Ph)^+$), 108 (64, $(PhCH_2NH_3)^+$), 91 (100 $(CH_2Ph)^+$). Anal. Calcd: C, 44.79; H, 3.76; N, 7.46. Found: C, 44.50; H, 3.68; N, 7.23.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of [1]$_n$ and [2]$_n$

	Compound [**1**]$_n$		
Cs1−N1	3.198(3)	Ga1−C2	2.028(4)
Cs1−N3b	3.159(3)	Ga1−C3	2.013(4)
Ga1−N1	2.031(3)	N1−N2	1.194(4)
Ga1−C1	2.003(4)	N2−N3	1.153(4)
N1−Cs1−N3b	91.24(8)	C2−Ga1−C3	115.2(2)
N1−Ga1−C1	107.0(2)	Cs1−N1−Ga1	119.0(1)
N1−Ga1−C2	105.0(2)	Cs1−N1−N2	122.4(2)
N1−Ga1−C3	101.8(2)	Ga1−N1−N2	115.8(2)
C1−Ga1−C2	112.3(2)	N1−N2−N3	177.8(4)
C1−Ga1−C3	114.2(2)	N2−N3−Cs1a	144.9(3)
	Compound [**2**]$_n$		
Cs1−N1	3.155(3)	In1−C2	2.218(5)
In1−N1	2.312(5)	In1−C3	2.209(5)
In1−N3b	2.901(5)	N1−N2	1.144(5)
In1−C1	2.205(5)	N2−N3	1.191(6)
N1−In1−C1	99.0(2)	C2−In1−N3b	83.4(2)
N1−In1−C2	97.6(2)	Cs1−N1−In1	110.3(2)
N1−In1−C3	96.3(2)	Cs1−N1−N2	104.5(3)
C1−In1−C2	112.8(2)	In1−N1−N2	114.7(3)
C1−In1−C3	118.8(2)	N1−N2−N3	176.3(5)
C2−In1−C3	123.2(2)	N1−In1−N3b	178.8(2)
C1−In1−N3b	81.3(2)	In1−N3b−N2b	105.1(4)

X-ray Structure Determination of [1]$_n$ and [2]$_n$. The crystals were covered with a high-boiling paraffin oil and mounted on the top of a glass capillary under a flow of cold gaseous nitrogen. The reflections were collected with a IPDS system (Stoe; graphite-monochromated Mo Kα radiation; λ = 0.710 73 Å). The final cell parameters were determined with 5000 reflections. The intensities have been corrected for Lorentz and polarization effects (for cell parameters and collecting of the intensities, see Table 1). The structures of [**1**]$_n$ and [**2**]$_n$ have been solved by the Patterson method using the program SHELXTL-Plus[23] and refined against F^2 by full-matrix least-squares with the program SHELXTL.[24] [**2**]$_n$ crystallizes in the noncentrosymmetric space group $Pna2_1$. The Flack parameter was determined as 0.04(2). A transformation into the centrosymmetric space group *Pnma* is not possible because of the missing mirror symmetry perpendicular to the *c*-axis (see also Figure 6). The hydrogen atoms were freely refined except the H atoms of the disordered toluene molecule in [**1**]$_n$. The toluene is disordered around a center of symmetry, and the H atoms were calculated for ideal positions and refined with a common displacement parameter. The calculation of the bond lengths, bond angles, and U_{eq} values was performed using the program PLATON.[25]

Selected bond lengths and angles of [**1**]$_n$ and [**2**]$_n$ are listed in Table 2. Table 3 shows additional Cs$^+$···carbon contacts.

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Table 3. Additional Metal−Carbon Contacts in [1]$_n$ and [2]$_n$ (Å)

		Compound [**1**]$_n$			
Cs1···C11	3.629(3)	Cs1···C21a	3.968(3)	Cs1···C40	3.808(7)
Cs1···C12	3.501(3)	Cs1···C22a	3.818(3)	Cs1···C40a	3.784(7)
Cs1···C13	3.482(3)	Cs1···C23a	3.618(3)	Cs1···C41	3.726(8)
Cs1···C14	3.558(4)	Cs1···C24a	3.540(4)	Cs1···C41a	3.846(8)
Cs1···C15	3.634(4)	Cs1···C25a	3.644(4)	Cs1···C42	3.753(7)
Cs1···C16	3.656(4)	Cs1···C26a	3.839(3)	Cs1···C42a	3.864(8)
Cs1···(C11−C16)[a]	3.300	Cs1···C32	3.666(3)		
Cs1···(C21a−C26a)[a]	3.476	Cs1···C33	3.753(3)		
Cs1···(C40−C42a)[a]	3.549				
		Compound [**2**]$_n$			
Cs1···C11	3.600(4)	Cs1···C21a	3.623(4)	Cs1···C31	3.758(4)
Cs1···C12	3.567(5)	Cs1···C22a	3.520(5)	Cs1···C32	3.514(6)
Cs1···C13	3.517(5)	Cs1···C23a	3.466(5)	Cs1···C33	3.396(6)
Cs1···C14	3.493(6)	Cs1···C24a	3.482(5)	Cs1···C34	3.472(7)
Cs1···C15	3.495(6)	Cs1···C25a	3.542(6)	Cs1···C35	3.659(7)
Cs1···C16	3.546(6)	Cs1···C26a	3.600(6)	Cs1···C36	3.781(6)
Cs1···(C11−C16)[a]	3.255				
Cs1···(C21a−C26a)[a]	3.257				
Cs1···(C31−C36)[a]	3.332				

[a] Ring centroid.

Results and Discussion

The cesium triorganoazidometalates Cs[$(PhCH_2)_3GaN_3$] and Cs[$(PhCH_2)_3InN_3$] have been synthesized by the reaction of the corresponding tribenzylgallium and -indium compounds with CsN_3 in THF at room temperature according to eq 1. Treatment with toluene gave

$$M(CH_2Ph)_3 + CsN_3 \rightarrow Cs[(PhCH_2)_3MN_3] \qquad (1)$$

$$M = Ga, In$$

viscous oils which crystallized to yield the colorless compounds [Cs(toluene)$_{0.5}$\{$(PhCH_2)_3GaN_3$\}]$_n$ ([**1**]$_n$) and [Cs\{$(PhCH_2)_3InN_3$\}]$_n$ ([**2**]$_n$). Both salts are very sensitive to oxygen and moisture and soluble in donor solvents such as DMSO and THF, forming solvated ion pairs of the type [Cs(L)$_n$][R_3MN_3] (L, donor solvent). The chemical shifts of the ^1H and ^{13}C NMR signals of **1** and **2** in DMSO-d_6 are typical for benzyl groups attached to Ga and In centers.[17,21,22,26]

More important are the vibrational investigations. The IR spectra of [**1**]$_n$ and [**2**]$_n$ show the characteristic combination bands ν(as + s) at 3382 and 3341 cm^{-1} for [**1**]$_n$ and at 3325 and 3277 cm^{-1} for [**2**]$_n$ of the N_3 groups.[10,27,28] The most significant absorptions are the ν_{as} and ν_s bands. The more covalent the element−N_3 bond, the higher than usual is the asymmetric valence bond, the more prone to explosion is the compound. A possible reason for this behavior is the dominance of the N−N≡N resonance form. The values of 2077 ([**1**]$_n$) and 2026 cm^{-1} ([**2**]$_n$) can be attributed to a highly ionic character in the M−N_3 bonds (N_3^- in KN_3, ν_{as} = 2036 cm^{-1}).[28] Therefore, no tendency for explosive decomposition could be detected. The spectra show the ν_s and δ bands at 1298 and 660 cm^{-1} for [**1**]$_n$ and at 1306 and 679 cm^{-1} for [**2**]$_n$, respectively. The Ga−N and In−N stretching vibration has been attributed to the absorptions at 332 ([**1**]$_n$) and 211 cm^{-1} ([**2**]$_n$). The low value for [**2**]$_n$ is due to the long In−N bond and the multidentate function of the N_3^- group. The bands at 538 and 437 cm^{-1} are characteristic of the Ga−C and the In−C valence vibrations, respectively.

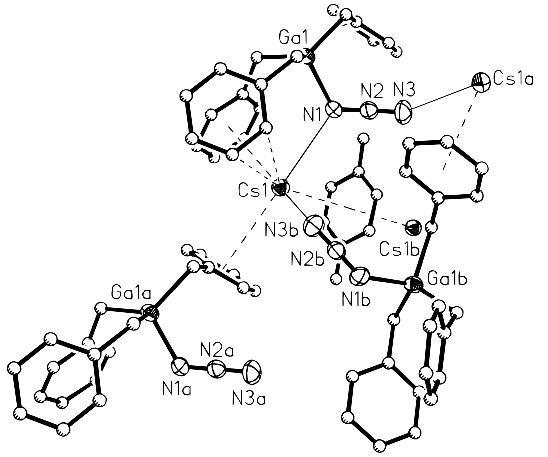

Figure 1. Coordination sphere of the Cs^+ and the N_3^- ion in [**1**]$_n$. The carbon atoms are drawn as spheres for clarity (Cs, Ga, and N with 50% probability level; without H atoms).

The EI mass spectra of [**1**]$_n$ and [**2**]$_n$ are not very informative. The highest observed fragments are [$Ga(CH_2Ph)_3$]$^+$ and $(PhCH_2CH_2Ph)^+$.

The structures of [**1**]$_n$ and [**2**]$_n$ differ from each other in several important features. The azido groups in [**1**]$_n$ act as μ^2,μ^0,μ^1-ligands (N1,N2,N3; connections counted only for the metal centers; Figure 1), while the pseudohalide ligand in [**2**]$_n$ prefers a μ^2,μ^1,μ^1-coordination (N1,N2,N3). In [**1**]$_n$, the Ga1−N1 bond length of 2.031(3) Å is somewhat longer than in complexes with two or more electronegative ligands. Gallium−nitrogen distances of 1.914(4) and 1.928(4) Å (μ^1,μ^0,μ^0) were observed in [2,6-$(Me_2NCH_2)_2C_6H_3$]$Ga(N_3)_2$,[29] 1.919(4) and 3.431 Å in [$(Me_2N)_2GaN_3$]$_2$ (μ^1,μ^0,μ^1),[6] and 1.994(6) Å in [$GaCl_3(Me_3SiN_3)$].[8] A better agreement results when comparing [**1**]$_n$ with compounds such as [$(py)_3Ga(N_3)_3$][9] (2.008−2.017 Å; μ^1,μ^0,μ^0) and [Me_2GaN_3]$_n$[5] [2.039(6), 2.051(6) Å; μ^2,μ^0,μ^0]. The other coordination partners of the N_3^-

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(27) The notation of ν_{as} and ν_s is only correct for a free N_3-ion, but it is applied generally today (see ref 28).

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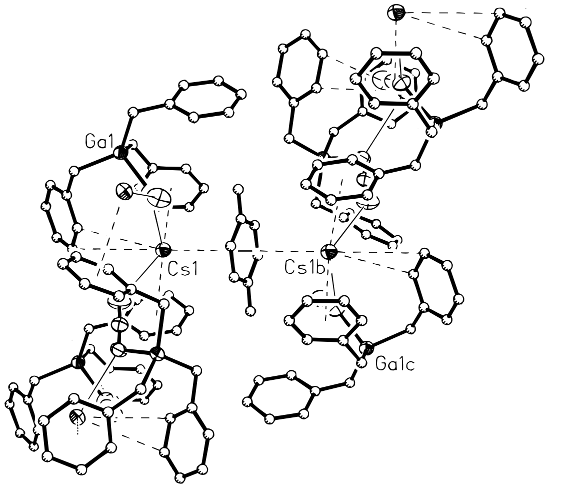

Figure 2. Centrosymmetric arrangement of six metalate units around the disordered toluene molecule in [**1**]$_n$.

ions in [**1**]$_n$ are Cs centers. The corresponding Cs−N contacts are 3.159(4) (Cs1a−N3) and 3.198(3) Å (Cs1−N1). These values are in good agreement with the Cs-N distances in CsN_3[30] (3.28(2) Å), if one takes the higher coordination number (CN) of Cs^+ and N_3^- in CsN_3 into consideration. A value of 3.20 Å is also typical for weak, mainly electrostatic Cs−N distances, as observed for Cs^+-acetonitrile complex fragments.[15,31] Therefore, a wide variation of the angle Cs−N−C is not unusual, which was also found for the complex fragments Cs−N_3 (Table 2).

Every Cs^+ ion in [**1**]$_n$ is coordinated by two azido functions and four aryl groups. Two benzyl ligands make their phenyl rings available for an η^6-interaction (C11−C16 average 3.577 Å; C21a−C26a average 3.738 Å; see Table 3), whereas one ring (C31−C36) participates only with two atoms (Cs1⋯C32 3.666(3) Å; Cs1⋯C33 3.753(3) Å. The fourth aryl ligand is the toluene molecule, disordered around a center of symmetry (C40−C42a average 3.797 Å; Figure 2). This molecule links as an η^{12}-bridge between two Cs centers (Cs1, C1b), as observed for $[Cs\{(PhCH_2)_3InCl\}]_2{\cdot}0.5$toluene.[16,32] N_3^- and the phenyl ligands form a distorted octahedral coordination sphere for every Cs^+ ion. The Cs−ligand interactions lead to layers parallel to (100), separated by the benzyl groups (Figure 3).

In contrast to [**1**]$_n$, the azido groups in [**2**]$_n$ possess an μ^2,μ^1,μ^1 function (N1, N2, N3). The very long In1−N1 distance of 2.312(5) Å can be unterstood if one considers the coordination sphere of the In center (Figure 4). The bonding to the N_3^- group leads to an angular sum of 355° (concerning the atoms In1, C1, C2, and C3). The reason for this is the additional coordination of In1 by a neighboring N_3^- group (In1−N3b 2.901(5) Å), resulting in a distorted trigonal-bipyramidal environment for In1. N1 and N2 of the N_3^- ligand donate to Cs1 in an asymmetric side-on fashion (Cs1−N1 3.155(4); Cs1⋯N2 3.615(4) Å) with a short and a long Cs1⋯N contact. Three phenyl rings belong to the coordination sphere of Cs1, two from the same asymmetric unit (C11−C16, average 3.536 Å; C31−C36, average 3.597 Å) and one from the neighboring metalate unit (C21a−C26a, average 3.539 Å). This leads to the

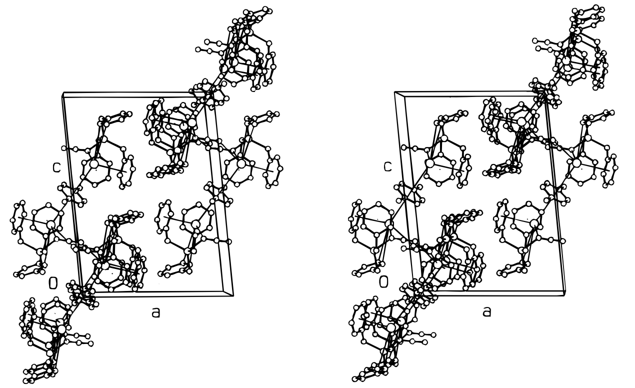

Figure 3. Stereoscopic view of the unit cell of [**1**]$_n$. The layers are stacked along [100] (ORTEP).[34]

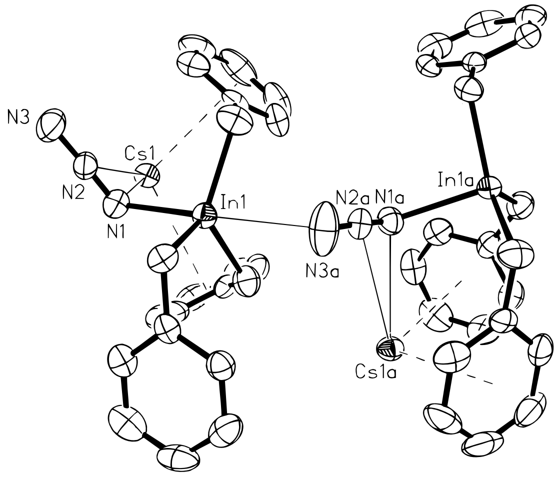

Figure 4. Coordination sphere of the N_3^- ion and the In center in [**2**]$_n$ (50% probability level, without H atoms).

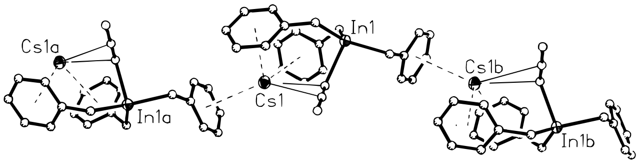

Figure 5. Formation of one string of **2** along [011] or [$01\bar{1}$] by $Cs^+{\cdots}\pi$-electron interactions (the C and N atoms are drawn as spheres for clarity).

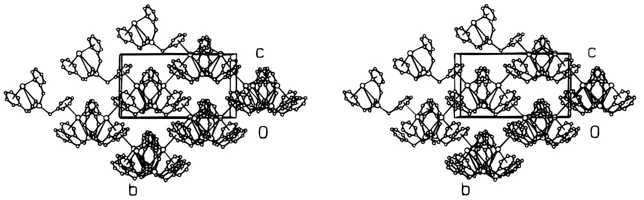

Figure 6. Stereoscopic view of the unit cell of [**2**]$_n$. The infinite metalate chains are cross-linked by In1⋯N3b contacts along [100].

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formation of polymeric chains parallel to [011] and [01$\bar{1}$] (Figure 5), connected by the In1···N3b interaction and a short Cs···H11b contact of 3.07(3) Å from the next anion (Figure 6). The In1···N3b contact is responsible for the cross-linking of the chains along the direction [100], causing a three-dimensional network of strings which are perpendicular to each other.

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Supporting Information Available: Tables of crystal data, atomic coordinates, bond lengths and angles, and isotropic or anisotropic displacement parameters for all atoms in [**1**]$_n$ and [**2**]$_2$ (10 pages). Ordering information is given on any current masthead page.

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