to the π–π* transition ($\lambda_{max} = 635$ nm, lg$\varepsilon = 4.3$, vibrational progression towards lower wavelengths: 1310 cm^{-1}) and the n–π* transition ($\lambda_{max} = 444$ nm, lg$\varepsilon = 4.7$) involving the N substituents.

[10] Crystal data for **5a**: "$[Me_3SiN]_4$–perylene": $C_{32}H_{46}N_4Si_4$, $M_r = 599.09$, monoclinic, space group $P2_1/c$, $a = 13.727(17)$, $b = 10.587(10)$, $c = 12.885(10)$ Å, $\beta = 111.32(7)°$, $V = 1744(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.141$ g cm^{-3}, $F(000) = 644$, $\mu(Mo_{K\alpha}) = 0.197$ mm^{-1}, $T = 293(2)$ K. All samples inspected diffracted extremely poorly. A dark green block ($0.72 \times 0.44 \times 0.32$ mm^3) was mounted in a Lindemann tube for data collection with a Siemens P4 diffractometer. The structure was determined by direct methods and refined on F^2 for 1198 independent reflections of 2189 collected ($1.59 \leq \theta \leq 18.00°$), $R(int) = 0.1955$. Anisotropic thermal parameters were assigned for all non-hydrogen atoms, and chemically equivalent bonds in the structure were constrained to common values. Hydrogen atoms were included in idealized positions and assigned $U_{iso} = 1.5\,U_{eq}$ or $U_{iso} = 1.2\,U_{eq}$ of the parent carbon atom for methyl groups and aromatic carbon atoms, respectively. The amino hydrogen was disordered over two sites of equal occupancy and assigned a fixed isotropic thermal parameter of 0.10 Å^2. At final convergence $R_1 = 0.1063$, $wR_2 = 0.2020$ ($I > 2\sigma(I)$), $R_1 = 0.2421$, $wR_2 = 0.3195$ (all data), GOF (F^2) = 1.053 for 181 parameters. For programs, see reference [19]. Crystal data for **5b**: "$[tBuMe_2SiN]_4$-perylene": $C_{44}H_{70}N_4Si_4$, $M_r = 767.40$, triclinic, space group $P\bar{1}$, $a = 11.034(2)$, $b = 13.852(2)$, $c = 15.485(2)$ Å, $\alpha = 84.411(8)$, $\beta = 79.200(10)$, $\gamma = 80.047(9)°$, $V = 2284.5(6)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.116$ g cm^{-3}, $F(000) = 836$, $\mu(Mo_{K\alpha}) = 0.164$ mm^{-1}, $T = 198(2)$ K. A dark green block ($0.60 \times 0.50 \times 0.34$ mm^3) was mounted in a Lindemann tube for data collection on a Siemens P4 diffractometer. The structure was determined by direct methods and refined on F^2 for 8055 independent reflections corrected for absorption (T_{max} 0.954, T_{min} 0.532) of 16109 collected ($1.34 \leq \theta \leq 25.00°$), $R(int) = 0.0591$. Anisotropic thermal parameters were assigned for all non-hydrogen atoms. The asymmetric unit consists of the halves of two independent molecules each of which is exactly centrosymmetric. The two amino hydrogen atoms in the asymmetric unit were disordered over the four independent nitrogen atoms and were assigned half occupancy and a common isotropic thermal parameter which refined to 0.04 Å^2. The remaining hydrogen atoms were included in idealized positions and assigned $U_{iso} = 1.2\,U_{eq}$ of the parent carbon atom for methylene groups and aromatic hydrogen atoms, and $U_{iso} = 1.5\,U_{eq}$ for methyl hydrogen atoms. At final convergence $R_1 = 0.0674$, $wR_2 = 0.1525$ ($I > 2\sigma(I)$), $R_1 = 0.1228$, $wR_2 = 0.1858$ (all data), GOF(F^2) = 0.981 for 490 parameters. For programs, see reference [19]. b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101183. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+49)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[18] All attempts to observe diradical intermediates by performing the thermolysis in an ESR tube and subsequent quenching the reaction in liquid N_2 were unsuccessful. The use of spin-trapping reagents was precluded by the extremely high reactivity of **4**, which thermally and unspecifically reacted with the trapping agents prior to its thermolysis. Attempts to detect radical intermediates by NMR spectroscopy at different field strengths and temperatures through observation of a CIDNP effect were equally unsuccessful. These results either indicate the absence of a free radical species in the coupling reaction or, alternatively, their short-lived nature.

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The Behavior of $[RAlX_2 \cdot THF]$ Compounds under Reductive Conditions: Tetrakis[tris(trimethylsilyl)methylaluminum(I)]—A Neutral Aluminum(I) Compound with σ-Bound Alkyl Groups and a Tetrahedral Structure[**]

Christoph Schnitter, Herbert W. Roesky,[*] Cord Röpken, Regine Herbst-Irmer, Hans-Georg Schmidt, and Mathias Noltemeyer

Dedicated to Professor Bernt Krebs
on the occasion of his 60th birthday

The great interest in low-valent compounds of the higher homologues of Group 13 is reflected in several recent reviews on this class of compounds.[1] The first univalent aluminum compound that is stable at room temperature—$[\{AlCp^*\}_4]$, $Cp^* = \eta^5\text{-}C_5Me_5$, which contains π-bound C_5Me_5 groups—was synthesized and structurally characterized in 1991 by Schnöckel et al. It was prepared by the treatment of $(AlCl)_x$ with $[MgCp^*_2]$.[2] Somewhat later we reported a more facile synthesis of this compound: the reductive dehalogenation of $[\{Cp^*AlCl(\mu\text{-}Cl)\}_2]$ with potassium.[3] Despite many attempts, only two further neutral organoaluminum(I) compounds of type $[\{AlR\}_n]$ ($[\{AlCH_2CMe_3\}_4]$[4a] and $[\{AlSitBu_3\}_4]$)[4b,c,e] have been reported; this is due to the tendency of this type of compound to disproportionate into elemental aluminum and AlR_3. The disproportionation reaction can be largely inhibited by the use of very bulky substituents. However, it has not as yet been possible to characterize these two compounds by diffraction methods.[4c,e]

The tris(trimethylsilyl)methyl group (trisyl group) is regarded as a particularly bulky group with electronically stabilizing properties.[5] The use of this substituent permitted the synthesis of the tetrameric compounds $[\{MC(SiMe_3)_3\}_4]$ of gallium,[6] indium,[7] and thallium.[8] We recently reported the synthesis of the trisylaluminum dihalides $[\{(Me_3Si)_3CAlF_2\}_3]$ and $[(Me_3Si)_3CAlX_2 \cdot THF]$ (X = F, Cl, Br, I),[9] which should be suitable precursors for the synthesis of low-valent trisylaluminum compounds.

We began our reduction experiments with the THF-free difluoride $[\{(Me_3Si)_3CAlF_2\}_3]$; however, it could not be dehalogenated, even with Na/K alloy in refluxing toluene. In contrast, the reaction of the THF-containing dichloride compound $[(Me_3Si)_3CAlCl_2 \cdot THF]$ with the appropriate reducing agent in toluene did not lead to the expected $[\{AlC(SiMe_3)_3\}_n]$, but to the tricyclic chiral compound **1** in high yields [Eq. (1)]. During the reductive dehalogenation the ring of the coordinated THF molecule had opened, which resulted in dimerization. Compound **1** is a colorless solid (m.p. 246 °C) that was completely characterized by ^{1}H NMR, ^{29}Si NMR, and IR spectroscopy as well as by mass spectrom-

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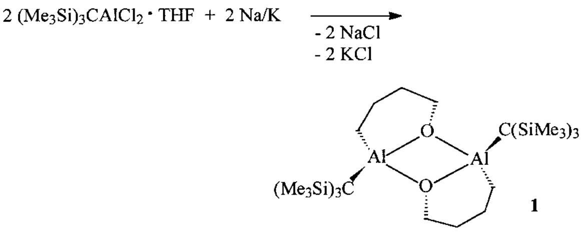


(1)

1

etry, elemental analysis, and X-ray crystal structure analysis (Figure 1).[10] It consists of a central four-membered Al_2O_2 ring, in which two oppositely positioned Al–O units are bridged by a C_4 chain. The distorted Al_2O_2 ring (Al-O-Al 99.9°, O-Al-O 77.9°) is not planar (average deviation from the best plane: 13.0 pm). The two Al-O-C_4 rings take up a *cis* conformation with an angle of 118.8° to the Al_2O_2 plane, which gives the molecule the appearance of a thumb screw. This is in contrast to the comparable other tricyclic compound known ($[\{\text{Trip-}\overline{\text{Al}(\mu\text{-O}(\text{CH}_2)_3\text{C}}\text{H}_2)\}_2]$ (Trip = 2,4,6-$i\text{Pr}_3\text{C}_6\text{H}_2$),[11] in which the Al_2O_2 ring is planar and the two Al-O-C_4 rings are *trans* to one another. The average Al–O distance in **1** (187.4 pm) is similar to the Al–O distances in the dimeric aluminum alkoxides $[\{\text{Me}_2\text{Al}(\mu\text{-O}t\text{Bu})\}_2]$ (186.4 pm),[12a] $[\{t\text{Bu}_2\text{Al}(\mu\text{-O-2,6-Me}_2\text{C}_6\text{H}_3)\}_2]$ (187.2 pm),[12b] and $[\{\text{Me}_2\text{Al}(\mu\text{-OCH}_2\text{-2,4,6-}t\text{Bu}_3\text{C}_6\text{H}_2)\}_2]$ (184.9 pm).[12c] This result shows clearly the influence of the THF molecule in the reduction of the aluminum center.

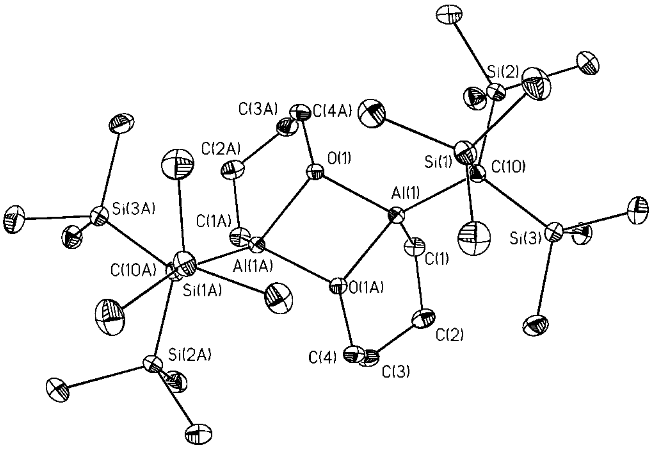
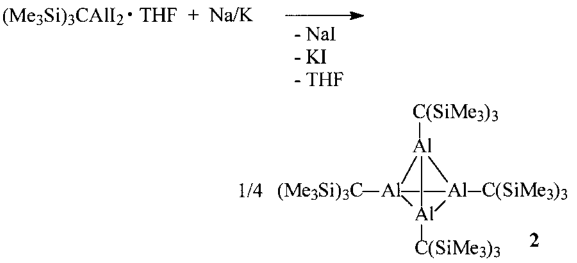


Figure 1. Crystal structure of **1** (thermal ellipsoids at the 50% probability level). The H atoms are omitted for clarity. Selected bond lengths [pm] and angles [°]: Al(1)–C(1) 198.5(2), Al(1)–C(10) 202.4(2), Al(1)–O(1) 186.3(2), Al(1)–O(1A) 188.4(2), O(1A)–C(4) 145.6(2), C(1)–C(2) 154.1(3), C(2)–C(3) 152.4(3), C(3)–C(4) 151.0(3); C(1)-Al(1)-C(10) 116.2 (1), C(1)-Al(1)-O(1) 115.4(1), C(1)-Al(1)-O(1A) 96.6(1), C(10)-Al(1)-O(1) 115.4(1), C(10)-Al(1)-O(1A) 129.6(1), O(1)-Al(1)-O(1A) 77.9(1), Al(1)-O(1)-Al(1A) 99.9(1), Al(1)-O(1)-C(4A) 124.2(1), Al(1A)-O(1)-C(4A) 121.4(1).

As a result of the strongly decreasing aluminum–halogen bond energies in the series Al–F > Al–Cl > Al–Br > Al–I,[13] the reductive dehalogenation of $[(\text{Me}_3\text{Si})_3\text{CAlI}_2 \cdot \text{THF}]$[9] should be more facile. The reaction of the diiodide in toluene with Na/K alloy (2 equiv) gave after workup $[\{\text{AlC(SiMe}_3)_3\}_4]$ (**2**) as orange platelets in yields of up to 24% [Eq. (2)]. So far, we have only been able to unambiguously identify the side product $HC(SiMe_3)_3$, which is formed in low yields.



(2)

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Compound **2** is thermally very stable and only starts to decompose at 282 °C with a brown discoloration (for comparison: $[\{\text{AlCp}^*\}_4]$ decomposes at 205 °C,[3] and $[\{\text{GaC(SiMe}_3)_3\}_4]$ decomposes at 255 °C).[6] In the EI mass spectrum, signals from $[\{\text{AlR}\}_n^+]$ ($n = 1-3$, R = $\text{C(SiMe}_3)_3$) are present along with the signal from the ion fragment $M-\text{R}$. This is in contrast to $[\{\text{GaC(SiMe}_3)_3\}_4]$, for which only the monomeric unit $[\text{GaC(SiMe}_3)_3]$ is observed.[6] This indicates a successive decomposition of **2** in the gas phase. In the UV/Vis spectrum of **2**, the absorption band with the longest wavelength (418 nm with a shoulder at 444 nm) only has a slight hypsochromic shift with respect to that for the analogous gallium compound (435 nm). The ^{1}H and ^{29}Si NMR spectra of **2** each exhibit, in addition to the expected singulet, further singlets of lower intensity which could not be unequivocally assigned. It could not be ascertained whether these are due to impurities (oxidation products), in spite of repeated measurements (with variation of the concentration and the temperature) on different samples.[14]

The crystal structure analysis[15] of **2** showed the presence of an almost perfect tetrahedral Al_4 skeleton, with an average Al-Al-Al angle of 60.00° (Figure 2). The Al–Al bonds in the Al_4 cluster ($\bar{d} = 273.9$ pm) are shorter than those in both elemental aluminum (286 pm)[16] and $[\{\text{AlCp}^*\}_4]$ ($\bar{d} =$ 276.9 pm).[2] However, they are somewhat longer than the

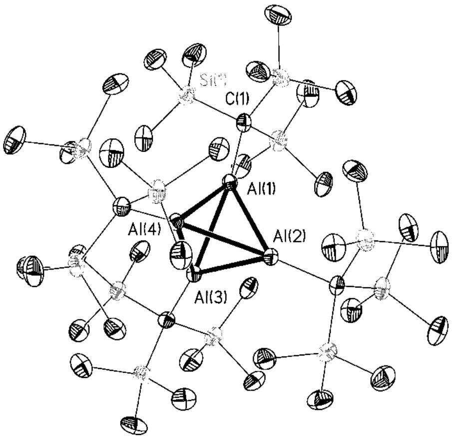

Figure 2. Crystal structure of **2** (thermal ellipsoids at the 50% probability level). The H atoms are omitted for clarity. Selected bond lengths [pm] and angles [°]: Al(1)–Al(2) 274.7(2), Al(1)–Al(3) 274.5(2), Al(1)–Al(4) 273.3(2), Al(2)–Al(3) 273.5(2), Al(2)–Al(4) 274.7(2), Al(3)–Al(4) 273.0(2), Al(1)–C(1) 202.7(5), Al(2)–C(2) 202.8(5), Al(3)–C(3) 202.7(5), Al(4)–C(4) 203.1(5); Al-Al-Al 59.67(5)–60.36(5), Al-Al-C 144.2(2)–145.3(2).

Table 1. Properties of the tetrahedranes $[\{MC(SiMe_3)_3\}_4]$ (M = Al, Ga, In, Tl).

Compound	Color	$\bar{d}_{\text{M-M}}$ [pm]	$\bar{d}_{\text{M-C}}$ [pm]	$\sphericalangle_{\text{M-M-M}}$	M.p. [°C]	$\lambda_{\text{max.}}$[a] [nm]
2	orange	273.9	202.8	60.0	282 (decomp)	418 (444)
$[\{GaC(SiMe_3)_3\}_4]$[6]	dark red	268.8	208	60.1	255 (decomp)	435
$[\{InC(SiMe_3)_3\}_4]$[7]	black-violet	300.2	225	60.0	180 (decomp)	487 (570)
$[\{TlC(SiMe_3)_3\}_4]$[8]	black	332.2 – 363.8	233 – 238	54.9 – 64.7	65 (decomp)	515

[a] UV/Vis band with the longest wavelength; shoulders at even greater wavelengths are given in brackets.

metal – metal distances in $[\{GaC(SiMe_3)_3\}_4]$ ($\bar{d} = 268.8$ pm)[6] and in the compounds $[K_2\{Al_{12}i\text{Bu}_{12}\}]$ ($\bar{d} = 268.5$ pm)[17a] and $[R_2AlAlR_2]$ ($R = CH(SiMe_3)_2$) (266.0 pm) synthesized by Uhl et al.[17b] The Al – Al distances in $[\{AlSi t\text{Bu}_3\}_4]$[4b,c] were calculated by Ahlrichs et al. to be 263.8 pm.[4d] That these Al – Al distances are markedly shorter than in **2** could be due to the Al – Si bonds in $[\{AlSi t\text{Bu}_3\}_4]$ (260 pm), which are longer than the Al – C bonds in **2** ($\bar{d} = 202.8$ pm), and the associated smaller ligand repulsion. This effect has already been observed for the only other two reported tetrahedral Ga_4 clusters, $[\{GaC(SiMe_3)_3\}_4]$ (Ga – Ga 268.8, Ga – C 208 pm)[6] and $[\{GaSi(SiMe_3)_3\}_4]$ (Ga – Ga 258.4, Ga-Si 240.6 pm).[18] However, the exchange of one carbon atom for a silicon atom should also have an electronic effect on the substituents. The average Al – C distance in **2** (202.8 pm) is somewhat larger than that in the starting material $[(Me_3Si)_3CAlI_2 \cdot THF]$ (198.1 pm),[9] but almost identical to that in $[(Me_3Si)_3CAlMe_2 \cdot THF]$ (203.0 pm).[19] Table 1 gives some physical and crystallographic data for **2** and the tetrahedranes $[\{MC(SiMe_3)_3\}_4]$ (M = Ga, In, Tl).

Compound **2** is the first neutral, crystallographically characterized aluminum cluster that contains σ-bound alkyl groups. The new compounds illustrate impressively that the THF ring can be opened and fixed to an aluminum center, and that it is moreover expedient to use THF – aluminum adducts for the reduction. The systematic investigation of $RAlI_2$ compounds under reductive conditions should lead to the isolation of further aluminum clusters.

Experimental Section

All the reactions were carried out under N_2 in anhydrous solvents.

1: To Na/K alloy in toluene (20 mL), prepared from sodium (0.06 g, 2.61 mmol) and potassium (0.19 g, 4.86 mmol), was added dropwise at room temperature a solution of $[(Me_3Si)_3CAlCl_2 \cdot THF]$ (1.45 g, 3.61 mmol) in toluene (40 mL). The colorless solution was stirred for 2 d at room temperature and then heated at reflux for 2 h. The yellow solution was filtered through Celite and concentrated (10 mL), and pure **1** was obtained as colorless rods upon crystallization at –26 °C; yield: 0.86 g (72 %). M.p. 246 °C; IR (Nujol, KBr): $\tilde{\nu}$ [cm^{-1}] = 1437 (s), 1287 (m), 1262 (vs), 1250 (vs), 1121 (s), 1082 (m), 1021 (s), 998 (s), 924 (s), 888 (vs), 850 (vs), 807 (vs), 785 (s), 752 (s), 721 (s), 670 (vs), 654 (vs), 635 (s), 617 (m), 593 (s), 575 (s), 555 (vs); ^{1}H NMR (200.13 MHz, C_6D_6, 25 °C, TMS): $\delta = 4.20 - 3.85$ (m, 4 H, $OCH_2CH_2CH_2CH_2Al$), 2.20 – 1.75 and 1.35 – 1.20 (m, 8 H, $OCH_2CH_2CH_2CH_2Al$), 0.80 – 0.40 (m, 4 H, $OCH_2CH_2CH_2CH_2Al$), 0.39 (s, 54 H, $Si(CH_3)_3$); ^{29}Si NMR (49.69 MHz, C_6D_6): $\delta = -4.4$; MS (EI): m/z (%): 660 ([M^+], 5), 645 ([$M^+ - Me$], 25), 429 ([$M^+ - C(SiMe_3)_3$], 86), 315 ([$(M/2)^+ - Me$], 100); elemental analysis calcd for $C_{28}H_{70}Al_2O_2Si_6$ (661.34): C 50.85, H 10.67; found: C 50.3, H 10.4.

2: To Na/K alloy in toluene (20 mL), prepared from sodium (0.04 g, 1.74 mmol) and potassium (0.13 g, 3.32 mmol), was added dropwise at room temperature a solution of $[(Me_3Si)_3CAlI_2 \cdot THF]$ (1.46 g, 2.50 mmol) in toluene (30 mL). The colorless solution was stirred for 2 d at room temperature and then heated at reflux for 4 h. The solvent was removed from the red-brown solution in vacuo, and the red-brown viscous residue taken up in *n*-hexane (15 mL). The mixture was filtered through Celite, the solvent removed in vacuo, and the dark orange residue recrystallized twice from toluene (10 mL) at 2 °C to give pure **2** as orange platelets; yield: 0.16 g (24 %). Single crystals suitable for X-ray diffraction analysis were obtained by recrystallization from diisopropyl ether at 2 °C. Decomposition (under nitrogen) at 282 °C. ^{1}H NMR (200.13 MHz, [D$_8$]toluene, 25 °C, TMS): $\delta =$ 0.51 (s, 4 H), 0.49 (s, 12 H), 0.42 (s, 1 H), 0.41 (s, 1 H), 0.40 (s, 1 H); ^{13}C NMR (100.60 MHz, C_6D_6, 25 °C, TMS): $\delta = 17.13$, 8.06, 7.50, 6.98, 6.45, 6.34; ^{29}Si NMR (49.69 MHz, C_6D_6, 25 °C, TMS): $\delta = -4.09$ (s), –4.16 (s), –4.55 (s), –6.37 (s); MS(EI): m/z: 801 ([$M^+ - C(SiMe_3)_3$], 5), 774 ([$(3/4\,M)^+$], 8), 516 ([$(M/2)^+$], 35), 258 ([$(M/4)^+$], 55), 201 ([$C(SiMe_3)_3^+ - 2Me$], 100); IR (Nujol, CsI): $\tilde{\nu}$ [cm^{-1}] = 1261 (vs), 1098 (s), 1018 (s), 863 (vs), 844 (vs), 800 (vs), 679 (m), 659 (m), 393 (m); UV/Vis (*n*-hexane): λ_{max} [nm] (ε) = 243 (shoulder, 31000), 249 (shoulder, 39000), 255 (49000), 261 (54000), 269 (52000), 418 (3000), 444 (shoulder, 1600); elemental analysis calcd for $C_{40}H_{108}Al_4Si_{12}$ (1034.25): C 46.45, H 10.53; found: C 46.2, H 10.2.

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[10] Crystal structure analysis of **1**: $C_{28}H_{70}Al_2O_2Si_6$, $M_r = 661.34$, monoclinic, space group $C2$, $a = 1531.2(3)$, $b = 967.5(2)$, $c = 1457.7(3)$ pm, $\beta = 116.07(2)°$, $V = 1.9398(7)$ nm^3; $Z = 2$, $\rho_{calcd} = 1.132$ g cm^{-3}, $F(000) = 728$, $\lambda = 71.073$ pm, $\mu(Mo_{K\alpha}) = 0.283$ mm^{-1}. The data were

recorded on a Stoe-Siemens-Huber four-circle diffractometer equipped with a Siemens SMART CCD area detector. The reflections were collected at −140 °C on a shock-cooled crystal of dimensions $0.4 \times 0.3 \times 0.2$ mm^3 in a drop of oil[20] with a $2\theta/\omega$-scan in the range $5.0 \leq 2\theta \leq 49.6°$. Of the 21552 observed reflections, 3333 were independant ($R_{int} = 0.033$). The structure was solved by direct methods (SHELXS-97)[21] and refined against F^2.[22] The hydrogen atoms were placed in ideal positions and refined with a riding model that allows the rotation of the methyl groups about their local axes; max./min. residual electron density after the final difference Fourier synthesis 207/−174 e nm^{-3}, $R1 = 0.027$ ($I > 2\sigma(I)$) and $wR2 = 0.060$ (all data). The values of $R1$ and $wR2$ are defined as $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$. The absolute structure was determined by refinement of the Flack parameter[23] to 0.0(1). A total of 181 parameters were refined.[15b]

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$TeS_2^{\bullet-}$ Radical Anions in $CuBrCu_{1.2}TeS_2$**

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Dedicated to Professor W. H. E. Schwarz
on the occasion of his 60th birthday

Copper(I) halides have recently proven to be "solid solvents" for molecules of the elements of Groups 15 and 16. Thus, neutral and low-charged phosphorus polymers were detected and structurally characterized in, for example, $(CuI)_3P_{12}$[1] and $(CuBr)_{10}Cu_2P_{20}$.[2] Compounds of copper(I) halides with selenium or tellurium contain neutral homoatomic chains, such as $^1_\infty$[Te] in $CuClTe_2$,[3] or six-membered rings, as in $CuISe_3$.[4] Heteroatomic chalcogen chains in which selenium and tellurium ($^1_\infty$[SeTe][5]) or sulfur and tellurium atoms alternate ($^1_\infty$[STe][6]) can also be obtained in a copper(I) halide matrix. In $CuISe_{1.93}Te_{1.07}$ tellurium-rich six-membered rings $Se_{6-x}Te_x$ ($x \leq 3$) were detected for the first time in the solid state.[7] Degradation of the neutral chalcogen chains $^1_\infty$[STe] led to $(CuI)_3Cu_2TeS_3$, which is the first copper chalcogenide halide to contain a complex thiotellurate(IV) ion.[8] Like $(CuI)_2Cu_3SbS_3$,[9] this compound can be described as a composite compound of copper(I) iodide and a copper thiometalate.

Here we report the preparation, crystal structure determination, and ESR spectroscopic investigations of $CuBrCu_{1.2}TeS_2$ (**1**). In this compound the novel $TeS_2^{\bullet-}$ radical anion and the unknown polychalcogenide ion TeS_2^{2-} were identified and structurally characterized. Compound **1** crystallizes as very thin, square or rectangular black platelets. Top illumination of the crystals indicates their tendency for twinning by a characteristic reflection pattern. Scanning electron micrographs of the edge of a broken platelet (Figure 1) show the pronounced two-dimensional character of the solid compound. The thickness of the single sheets is significantly smaller than 1 µm. Nevertheless, the crystal structure could be determined.[10] Figure 2a shows the three-dimensional structure of **1**. The copper atoms Cu4, which are located between the layers on a position with an occupancy of 20 %, are omitted in order to emphasize the two-dimensional character of the structure. The layers are stacked along [001] and are made up of tetrahedrally coordinated copper atoms. The coordination polyhedra are $[CuBr_2S_2]$ for Cu1 and Cu2, and $[CuS_4]$ for Cu3. The Cu–S distances are 2.288 Å, and the Cu–Br distances 2.512 Å. The $[CuS_4]$ polyhedra are located in the center, and the $[CuBr_2S_2]$ polyhedra at the upper and lower borders of the layers. Further building blocks are bent TeS_2

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