[5] a) Y. Matsushita, T. Matsui, *Tetrahedron Lett.* **1993**, *34*, 7433–7437; b) W. Iwanek, J. Mattay, *Liebigs Anal.* **1995**, 1463–1469; c) M. T. El Gihani, H. Heaney, A. M. Z. Slawin, *Tetrahedron Lett.* **1995**, 4905–4908; d) R. Arnecke, V. Böhmer, E. F. Paulus, W. Vogt, *J. Am. Chem. Soc.* **1995**, *117*, 3286–3287.

[6] K. Airola, V. Böhmer, E. F. Paulus, K. Rissanen, C. Schmidt, I. Thondorf, W. Vogt, *Tetrahedron* **1997**, 10709–10724.

[7] Crystallographic data measurements were carried out at 173.0(2) K on a Kappa-CCD diffractometer using $Mo_{K\alpha}$ radiation (graphite monochromator, $\lambda = 0.7107$ Å). Direct methods (G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467) and full-matrix-block refinement versus F^2 (G. M. Sheldrick, SHELXL-97, Programm for the Refinement of Crystal Structures, Universität Göttingen, Germany, **1997**) were used to solve the structure. The disordered parts of the butyl chains and one water molecule with partial occupancy were treated isotropically. No absorption correction was applied. $C_{52}H_{80}N_4O_8Cl_4 \times 2\,MeCN \times 1.75\,H_2O$; crystal dimensions $0.4 \times 0.2 \times 0.2$ mm^3, monoclinic, $P2_1/a$, $a = 22.4419(3)$, $b = 22.9653(5)$, $c = 24.8565(4)$ Å, $\beta = 113.457(9)^\circ$, $Z = 4$, $V = 12263.7(4)$ Å^3, $\rho_{calcd} = 1.217$ g cm^{-3}, $2\theta_{max} = 50.02^\circ$, $\mu = 0.25$ mm^{-1}, 1485 parameters, $R = 0.1172$ (for 14640 reflections $I > 2\sigma(I)$), $wR(F^2) = 0.3185$ for all 21494 reflections ($R_{int} = 0.044$), $S = 1.057$, min/max residual electron density $= -0.52/0.79$ e Å^{-3}. 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-142155. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[8] For the extension of the resorcarene cavity by hydrogen-bonded pyridine bases, see a) L. R. MacGillivray, J. L. Atwood, *J. Am. Chem. Soc.* **1997**, *119*, 6931–6932; b) L. R. MacGillivray, J. L. Atwood, *Chem. Commun.* **1999**, 181–182; c) L. R. MacGillivray, H. A. Spinney, J. L. Reid, J. A. Ripmeester, *Chem. Commun.* **2000**, 517–518.

[9] For anion recognition, see F. Schmidtchen, M. Berger, *Chem. Rev.* **1997**, *97*, 1609–1646.

[10] Compare with, for example, W. Xu, J. J. Vittal, R. J. Puddephat, *J. Am. Chem. Soc.* **1995**, *117*, 8362–8371.

[11] The inverse ratio of 4:1 was observed for these signals with $[Et_3NH^+Br^-]:[\mathbf{1c}^{4+} \cdot 4\,Cl^-] = 1:1$.

[12] This result is also in accordance with the fact that no interaction occurs between the acetonitrile molecule and $\mathbf{1c}^{4+} \cdot 4\,Cl^-$ in $CDCl_3$.

[13] D. J. Cram, S. Karbach, H.-E. Kim, C. B. Knobler, E. F. Maverick, J. L. Ericson, R. C. Helgeson, *J. Am. Chem. Soc.* **1988**, *110*, 2229–2237.

Synthesis of the Square-Planar Gallium Species $K_2[Ga_4(C_6H_3\text{-}2,6\text{-}Trip_2)_2]$ (Trip = C_6H_2-2,4,6-*i*Pr_3): The Role of Aryl–Alkali Metal Ion Interactions in the Structure of Gallium Clusters[**]

Brendan Twamley and Philip P. Power*

Electron-precise one- or two-dimensional, molecular gallium clusters can in principle be reduced to afford species which may contain Ga–Ga multiple bonds. For example, reduction of tetraorganodigallanes yields the radical anions $[R_2GaGaR_2]^{-\bullet}$ **1**[1] and **2**.[2]

$[R_2GaGaR_2]^{-\bullet}$

1: R = Trip **2**: R = CH(SiMe$_3$)$_2$

The Ga–Ga distances in **1** and **2** are 0.14–0.17 Å shorter than those in the neutral R_2GaGaR_2 precursors, and EPR data show that the unpaired electron resides in a π orbital to give a formal Ga–Ga bond order of 1.5. However, the attempted addition of a second electron to **1** results in rearrangement to the tetrametallic trigallylgallane salt **3**, which has shorter Ga–Ga bonds (av 2.39 Å) than the unreduced species **4** (Ga–Ga, av 2.47 Å) consistent with a formal Ga–Ga bond order of 1.33.[3]

$Na_2[Ga(GaTrip_2)_3]$ **3** $Ga(GaTrip_2)_3$ **4**

An important aspect of the structure of **3** is that the shortest of the three Ga–Ga bonds corresponds to the complexation of the two Na^+ ions between the Trip substituents spanning the bond. Parallel work involving direct reduction of terphenylgallium dihalides has afforded the unprecedented cyclic trigallyl compounds **5**[4a] and **6**[4b] (Mes = C_6H_2-2,4,6-Me_3), or the dimeric **7**[5] which also involve similar interactions between the alkali metal the aryl group across the Ga–Ga bond(s). However, the description of **7** as a "gallyne" on the basis of its short Ga–Ga bond (2.319(3) Å) has generated controversy,[6] since the Na^+–aryl interactions could also have caused the shortened Ga–Ga distance.[7] Density functional theory (DFT) calculations[8] on the model compounds for **7**–**9**, $Na_2[(GaC_6H_3\text{-}2,6\text{-}Ph_2)_2]$ (**8**), and $Na_2[(GaPh)_2]$ (**9**), suggest that such effects are structurally important since the Ga–Ga distance in **8** (2.362 Å), which has Na^+–aryl interactions, is about 0.1 Å shorter than that in **9** (2.461 Å) which has no Na^+–aryl contacts.

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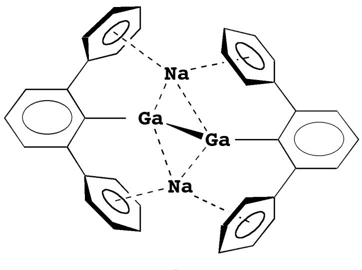
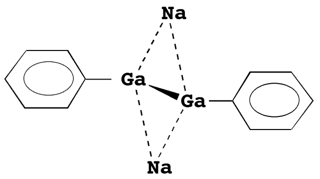
$M_2[(GaC_6H_3\text{-}2,6\text{-}Mes_2)_3]$ $Na_2[(GaC_6H_3\text{-}2,6\text{-}Trip_2)_2]$

5: M = Na **6**: M = K **7**



8



9

In an earlier publication[9] it was suggested that the structural effects of the Na^+ ions in **7** could be investigated by synthesizing a solvent-separated species of the type $[NaL_n]_2[(GaC_6H_3\text{-}2,6\text{-}Trip_2)_2]$ (L = complexing ligand; e.g., crown ether or cryptand) with no Na^+–aryl interactions. Unfortunately, no species of this type are known. An alternative investigative approach involves varying the alkali metal cations themselves. In essence, if the Ga–Ga moiety observed in **7** is a stable one, changing or removing the alkali metal countercations should afford a similar structure. The observation of essentially identical structures for **5** and **6** which have Na^+–aryl or K^+–aryl interactions similar to those in **7** lends further support to this hypothesis. Accordingly, the reduction of $Ga(C_6H_3\text{-}2,6\text{-}Trip_2)Cl_2$[10] with several alkali metals has been undertaken and our initial results are given herein.

Reduction of $Ga(C_6H_3\text{-}2,6\text{-}Trip_2)Cl_2$ in diethyl ether by Li, Na, K, or Cs initially afforded a green solution. For Li, the green color was persistent but with the other metals the color changed to dark red. These solutions possessed considerable stability in the case of those from Na and K but that from the Cs reduction rapidly (2 h) changed to brown. To date, X-ray quality crystals have only been obtained from the reactions with Na or K. The crystals from the Na reduction afforded X-ray data to high 2θ angles which resulted in a refinement to a relatively low residual value.[11] The structural parameters derived from this data set (Ga–Ga 2.324(1), Ga–C(av) 2.041(5) Å) were similar to those already reported for **7** (Ga–Ga 2.319(3), Ga–C(av) 2.04(2) Å)[5] although it was found that the two Ga-Ga-C angles differ by over 8° which suggests considerable flexibility in the C-Ga-Ga-C array.[12]

In contrast to these findings, the reduction of $Ga(C_6H_3\text{-}2,6\text{-}Trip_2)Cl_2$ with K did not yield $K_2[(GaC_6H_3\text{-}2,6\text{-}Trip_2)_2]$[13] but the new tetragallium species **10** (Figure 1). The structure of **10** is centrosymmetric with a planar, almost square, Ga_4 core. The Ga–Ga distances are 2.4624(4) and 2.4685(3) Å and the internal angles are 87.228(11)° at Ga(1) and 92.772(11)° at Ga(2). The Ga(1) and Ga(1A) atoms are each substituted by a $C_6H_3\text{-}2,6\text{-}Trip_2$ group which has a Ga–C bond length of 2.006(2) Å. Although Ga(1) and Ga(1A) are planar coordinated, the external C(1)-Ga(1)-Ga(2) and C(1)-Ga(1)-Ga(2A) angles differ by almost 6°. The structure is completed by two K^+ ions on either side of the Ga_4 plane. They do not lie directly above the center of the Ga_4 array, however, but are displaced such that the K(1)–Ga(1) and K(1)–Ga(2) distances (ca. 3.82 Å) are somewhat longer than the K(1)–Ga(1A) and K(1)–Ga(2A) distances (ca. 3.53 Å). The K^+ ions interact almost equally strongly with the two Trip rings to which they are coordinated and the closest distances involve C(10), C(11) (ca. 3.29 Å) and C(16A), C(17A) (ca. 3.30 Å).

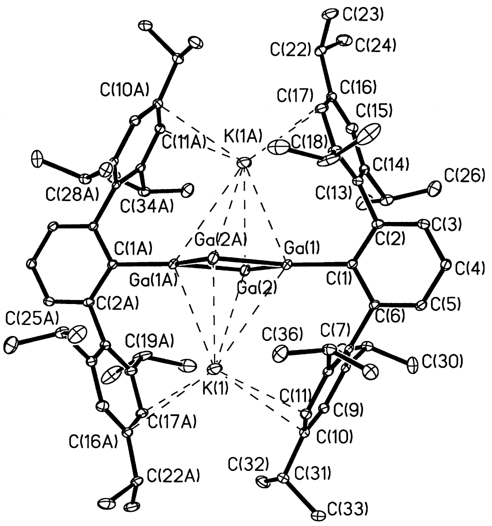


Figure 1. Structure of **10** (H atoms are not shown). Selected interatomic distances [Å] and angles [°]: Ga(1)-Ga(2) 2.4623(4), Ga(1)-Ga(2A) 2.4685(3), Ga(1)-C(1) 2.0058(19), Ga(1)-K(1) 3.8017(6), Ga(2)-K(1) 3.8330(6), Ga(1)-K(1A) 3.5883(6), Ga(2)-K(1A) 3.4710(6), K(1)-C(10) 3.2636(19), K(1)-C(11) 3.323(2), K(1)-C(16A) 3.327(2), K(1)-C(17A) 3.268(2), C(1)-Ga(1)-Ga(2) 139.33(6), C(1)-Ga(1)-Ga(2A) 133.44(6), Ga(2)-Ga(1)-Ga(2A) 87.222(11), Ga(1)-Ga(2)-Ga(1A) 92.778(11), C(6)-C(1)-C(2) 117.82(17).

$K_2[Ga_4(C_6H_3\text{-}2,6\text{-}Trip_2)_2]$

10

Compound **10** differs from the known Ga_4 clusters which feature either a tetrahedral Ga_4 array in electron-deficient $(GaR)_4$ species,[14] a trigonal-planar $Ga(Ga)_3$ framework as in **4**,[3] or a pyramidal arrangement as in the ion $[RGa(GaR)_3I_3]^-$ ($R = Si(SiMe_3)_3$).[15] The Ga–Ga distances in **10** are consistent with single bonding and are very close to the Ga–Ga bond length of about 2.47 Å in **4**.[3] Apparently, Ga(1) and Ga(1A) use their three valence electrons to bond a carbon and two other gallium atoms. Similarly, Ga(2) and Ga(2A) each employ an electron to bond to Ga(1) and Ga(1A) and their remaining coordination site is occupied by a lone pair—the extra electrons being provided by the 2− charge.

The different structures of **10** and **7** are in sharp contrast to previous results for Na^+ and K^+ salts of related dianions with bulky terphenyl substituents. That work has shown that there are no stoichiometric and relatively minor structural differences between salts of these two alkali metals. Examples include the dianionic trigallium Na^+ and K^+ species, **5** and **6**[4] (see above), the compounds $M_2[(M'C_6H_3\text{-}2,6\text{-}Trip_2)_2]$ (M = Na or K; M′ = Ge or Sn),[16] which are stoichiometrically and structurally very similar to **7**, and the salts $M_2(SC_6H_3\text{-}2,6\text{-}Trip_2)_2$ (M = Na or K).[17] Part of the explanation for the differences between **10** and **7** may lie in the geometric constraints caused by the unequal sizes of the Na^+ and K^+ ions and the probable weakness of the Ga–Ga bond in **7**.

Theoretical opinion[8, 18] on the nature of this bond is sharply divided but it is noteworthy that, apart from the DFT work on **8** and **9**,[8] no other calculations address the role of interactions between the alkali metal and aryl group in **7** or related species, and there are no calculations on the strength of the Ga–Ga interactions in such compounds. It is likely, however, that the Ga–Ga bonding in **7** is weakened owing to Coulombic and steric repulsions. This is consistent with the above-mentioned attempts[3] to synthesize $[R_2GaGaR_2]^{2-}$ (also involving significant Coulombic interactions) which afforded a rearrangement to the tetrametallic **3** where, presumably, Coulombic effects are dispersed over four metals as they are in **10**. Steric effects are also significant since a reduction in the size of the terphenyl group from C_6H_3-2,6-$Trip_2$ to C_6H_3-2,6-Mes_2 results in the trimeric structures in **5** and **6**[4] instead of the dimeric **7**.[5] The use of the ligand C_6H_3-2,6-Ph_2 in calculations on model compounds such as **8**[8, 18a] does not provide a sufficiently accurate estimate of the steric effects of the *i*Pr substituents. However, its use is clearly superior to the ligands H or Me which neglect the aryl–alkali metal interactions entirely.

In summary it is probable that the alkali metal–aryl interactions in **7** and **10** play a unique and crucial role in their stabilization. Theoretical data[19] have shown that interactions between alkali metals and aryl rings involve considerable binding energies (e.g., M–benzene: M = Li, 37.9 $kcal\,mol^{-1}$; M = Na, 28 $kcal\,mol^{-1}$; M = K, 18.3 $kcal\,mol^{-1}$) which supports their potential stabilizing effect.[20] The seemingly integral role of the Na^+ ions in the stabilization of **7** raises the question of the stability of the solvent-separated dianion $[(GaC_6H_3\text{-}2,6\text{-}Trip_2)_2]^{2-}$ in the absence of the sodium cations. Interestingly, perhaps, there do not appear to be any stable species known that involve multiple bonding between two negatively charged atoms without contact-solvated counter cations. Clearly, further experimental data on a range of main group dianionic species will be required to resolve such questions.

Experimental Section

All work was carried out under anaerobic and anhydrous conditions. Et_2O (60 mL) was added to a mixture of freshly cut potassium (1.75 g, 44.8 mmol) and $Ga(C_6H_3\text{-}2,6\text{-}Trip_2)Cl_2$ (3.83 g, 6.15 mmol) with rapid stirring. After 10–12 h the suspension underwent a color change from gray to green, and after a further 1–2 h the green color became red-brown. Stirring was continued for 36 h at which point the stirrer was switched off and all precipitates were allowed to settle overnight. The supernatant liquid was decanted, and the red-brown solution was concentrated to about 25 mL and cooled at about 4 °C overnight to afford red-brown crystals of **10**. Yield 0.65 g, 32 % (based on Ga). M.p. 226 °C (decomp). ^1H NMR (400 MHz, C_6D_6): $\delta = 0.96$ (d, $^3J_{H,H} = 6.8$ Hz, 12 H; o-$CH(CH_3)_2$), 1.19 (d, $^3J_{H,H} = 6.8$ Hz, 12 H; *o*-$CH(CH_3)_2$), 1.52 (d, $^3J_{H,H} = 6.8$ Hz, 12 H; *p*-$CH(CH_3)_2$), 2.41 (sept, $^3J_{H,H} = 6.8$ Hz, 4 H; *o*-$CH(CH_3)_2$), 3.87 (sept, $^3J_{H,H} = 6.8$ Hz, 2 H; *p*-$CH(CH_3)_2$), 6.71 (s, 4 H; *m*-Trip), 7.22 (d, $^3J_{H,H} = 6.8$ Hz, 2 H; *m*-C_6H_3), 7.33 (t, $^3J_{H,H} = 6.8$ Hz, 1 H; *p*-C_6H_3); $^{13}C\{^1H\}$ NMR (100 MHz): $\delta = 24.65$ (*p*-$CH(CH_3)_2$), 25.43 (*o*-$CH(CH_3)_2$), 25.98 (*o*-$CH(CH_3)_2$), 30.75 (o-$CH(CH_3)_2$), 34.12 (*p*-$CH(CH_3)_2$), 119.46 (*m*-Trip), 127.885 (*m*-C_6H_3), 128.15 (*p*-C_6H_3), 142.91 (o-C_6H_3), 144.12 (*ipso*-Trip), 146.28 (*p*-Trip), 150.24 (*o*-Trip), 172.54 (*ipso*-C_6H_3); UV/Vis: λ (ε) = 435 (5200), 705 (270). The compound **7**·Et_2O was synthesized in about 35 % yield under very similar conditions.

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[1] X. He, R. A. Bartlett, M. M. Olmstead, P. P. Power, *Angew. Chem.* **1993**, *105*, 761; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 717.

[2] W. Uhl, U. Schutz, W. Kaim, E. Waldhör, *J. Organomet. Chem.* **1995**, *501*, 79.

[3] R. J. Wehmschulte, P. P. Power, *Angew. Chem.* **1998**, *110*, 3344; *Angew. Chem. Int. Ed.* **1998**, *37*, 3154. Monomeric $[GaR_2]^-$ ions have been stabilized as the species $[(tBuN_2C_2)Ga]^-$: S. Schmid, A. Jockisch, H. Schmidbaur, *J. Am. Chem. Soc.* **1999**, *121*, 9758.

[4] a) X.-W. Li, W. T. Pennington, G. H. Robinson, *J. Am. Chem. Soc.* **1995**, *117*, 7578; b) X.-W. Li, Y. Xie, P. R. Schreiner, K. D. Gripper, R. C. Crittendon, C. F. Campana, H. F. Schaefer, G. H. Robinson, *Organometallics* **1996**, *15*, 3798.

[5] J. Su, X.-W. Li, R. C. Crittendon, G. H. Robinson, *J. Am. Chem. Soc.* **1997**, *119*, 5471.

[6] For a recent critical review of this controversy see: A. J. Downs, *Coord. Chem. Rev.* **1999**, *189*, 59.

[7] In addition, the C-Ga-Ga-C skeleton in **7** has a *trans*-bent rather than linear geometry (C-Ga-Ga = ca. 130°) which suggests lone-pair character at the gallium centers and reduced electron density in the Ga–Ga bond

[8] F. A. Cotton, A. H. Cowley, X. Feng, *J. Am. Chem. Soc.* **1998**, *120*, 1795.

[9] P. P. Power, *Dalton Trans.* **1998**, 2939.

[10] B. Twamley, P. P. Power, *Chem. Commun.* **1999**, 1805.

[11] Crystal structure analysis data for **7**·Et_2O (90 K) with $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å) radiation: $a = 14.6020(8)$, $b = 18.2193(10)$, $c = 26.8103(15)$ Å, $\beta = 97.662(1)°$, $Z = 4$, space group $P2_1/c$, $R_1 = 0.0586$ for 11757 ($I > 2\sigma(I)$) data. Important interatomic distances [Å] and angles [°]: Ga(1)-Ga(2) 2.324(1), Ga(1)-C(1) 2.045(6), Ga(2)-C(37) 2.036(6), Ga(1)-Na(1) 3.103(3), Ga(1)-Na(2) 3.065(3), Ga(1)-Na(2) 3.065(3), Ga(2)-Na(2) 3.102(3), Na-C 2.847(6)–3.105(6); C(1)-Ga(1)-Ga(2) 125.93(17), C(37)-Ga(2)-Ga(1) 136.20(7). Crystal structure analysis data for **10** (90 K) with $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å) radiation: $a = 12.7152(7)$, $b = 17.1567(9)$, $c = 16.9160(9)$ Å, Z = 2, space group $P2_1/c$, $R_1 = 0.0359$ for 11255 ($I > 2\sigma(I)$) data. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-143883 (**7**) and CCDC-144502 (**10**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk)..

[12] Also, H atoms bound to Ga in either a terminal or bridging manner (a possibility which was not completely excluded by previous data)[5, 8] could not be located on a difference map. In view of the increased accuracy of the present data set, and the lack of Ga–H stretching bands in the IR spectrum, Ga–H bonds can be deemed absent.

[13] It could be argued that $K_2[(GaC_6H_3\text{-}2,6\text{-}Trip_2)_2]$ is present in solution but it does not crystallize. This possibility cannot be ruled out completely, but it is unlikely in view of the ease with which both Na^+ and K^+ salts of related terphenyl anions crystallize. Also the fact that **10** is present in significant quantities suggests that, at the minimum, it has comparable stability to the putative $K_2[(GaC_6H_3\text{-}2,6\text{-}Trip_2)_2]$ species which indicates weak multiple Ga–Ga bonding in the latter.

[14] a) W. Uhl, W. Hiller, M. Layh, W. Schwarz, *Angew. Chem.* **1992**, *104*, 1378; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1364; b) G. Linti, *J. Organomet. Chem.* **1996**, *520*, 107; W. Uhl, A. Jantschak, *J. Organomet. Chem.* **1998**, *555*, 263; c) G. Linti, A. Rodig, *Chem. Commun.* **2000**, 127.

[15] W. Köstler, G. Linti, *Angew. Chem.* **1997**, *109*, 2758; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2644.

[16] a) L. Pu, M. O. Senge, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **1998**, *120*, 12682; b) L. Pu, M. M. Olmstead, S. T. Haubrich, P. P. Power, unpublished results.

[17] M. Niemeyer, P. P. Power, *Inorg. Chem.* **1996**, *35*, 7264.

[18] a) Y. Xie, R. S. Grev, J. Gu, H. F. Schaefer III, P. von R. Schleyer, J. Su, X.-W. Li, G. H. Robinson, *J. Am. Chem. Soc.* **1998**, *120*, 3773; b) K. W. Klinkhammer, *Angew. Chem.* **1997**, *109*, 2414; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2320; c) I. Bytheway, Z. Lin, *J. Am. Chem. Soc.* **1998**, *120*, 12133; d) Y. Xie, H. F. Schaefer III, G. H. Robinson, *Chem. Phys. Lett.* **2000**, *317*, 174; e) T. L. Allen, W. H. Fink, P. P. Power, *J. Chem. Soc. Dalton Trans.* **2000**, 407; f) R. Köppe, H. Schnöckel, *Z. Anorg. Allg. Chem.* **2000**, *626*, 1095; g) H. Grützmacher, T. F. Fässler, *Chem. Eur. J.* **2000**, *6*, 2317.

[19] a) R. L. Woodin, J. L. Beauchamp, *J. Am. Chem. Soc.* **1978**, *100*, 501; b) B. C. Guo, J. W. Purnell, A. W. Castelman, *Chem. Phys. Lett.* **1990**, *168*, 155; c) J. Sunder, K. Nishizawa, P. Kebarle, *J. Phys. Chem.* **1981**, *85*, 1814; d) M. Tacke, *Eur. J. Inorg. Chem.* **1998**, 537.

[20] Recent calculations on related species such as $[R_2MMR_2]^{2-}$ (M = Al, Ga, In, Tl) indicate strong solvation of the countercation is the key to their stabilization. A. J. Bridgeman, N. A. Nielsen, *Inorg. Chim. Acta* **2000**, *303*, 107.

Light-Driven Microfabrication: Assembly of Multicomponent, Three-Dimensional Structures by Using Optical Tweezers**

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George M. Whitesides*

Methods to generate well-defined structures composed of cells have the potential to be useful in areas where aggregates of cells are relevant: a) analytical systems that use cells as sensors; b) systems for fundamental studies of metabolism, signaling, toxicology, cellular ecology, and the biophysics of cell–cell interactions; and c) systems that investigate relationships between cell attachment, development, and growth. Here, we have used optical tweezers to fabricate ordered, two-dimensional (2D) and three-dimensional (3D), composite microstructures in which the components are biological cells (erythrocytes and lymphocytes) and polystyrene microspheres. This method of fabrication, light-driven microfabrication, provides a method of generating a range of structurally well-defined arrays of cells in the form of composites incorporating cells and microspheres.

Figure 1 illustrates the important elements of light-driven microfabrication. We used erythrocytes, disk-shaped cells approximately 12 μm in width, and lymphocytes, roughly spherical cells approximately 5 μm in diameter, as model components with which to explore microassembly. The surfaces of these cells present multiple oligosaccharides that terminate in *N*-acetyl glucosamine (GlcNAc) and *N*-acetyl neuraminic acid (NeuAc);[1] these sugars provide well-defined ligands when biospecific adhesion is required. There are three potential mechanisms for the attachment of cells to surfaces: nonbiospecific interactions (e.g. hydrogen bonds,[2] hydrophobic interactions,[2] or electrostatic interactions);[3] biospecific interactions that are exclusively adhesive (for example, lectins binding to sugars);[4] and biospecific interactions that are both adhesive and functional (for example, integrins binding to RGD (peptide sequence Arg–Gly–Asp) or fibronectin;[5] selectins binding to cadherins).[6] To connect cells biospecifically, we used polystyrene microspheres linked covalently to wheat germ agglutinin (WGA), a well-characterized dimeric lectin that recognizes NeuAc and GlcNAc;[7, 8] to connect cells nonbiospecifically, we used unmodified polystyrene microspheres. It should also be possible to use

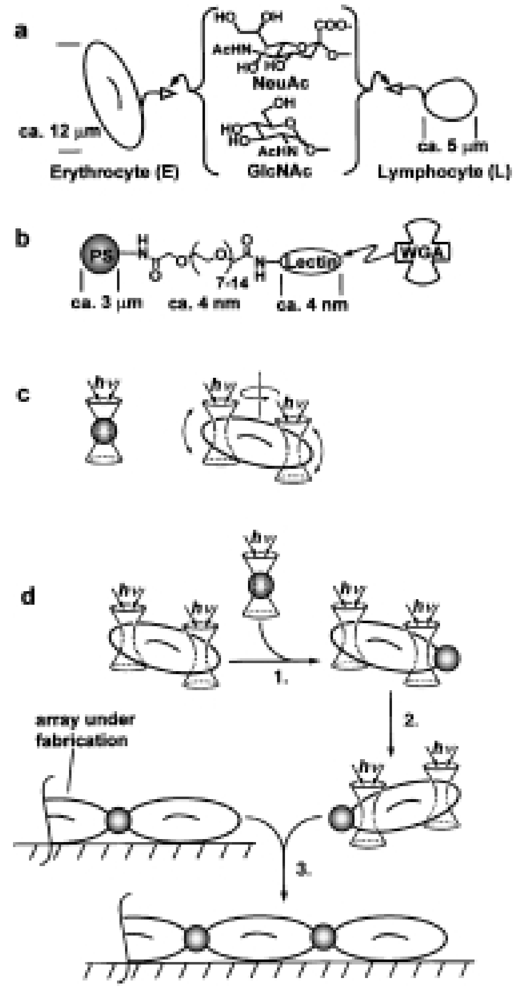

Figure 1. Fabrication of composite structures of cells and polymer microspheres by using optical tweezers. a) The oligosaccharides on surfaces of a chicken erythrocyte and chicken lymphocyte terminate in *N*-acetyl neuraminic acid (NeuAc) and *N*-acetyl glucosamine (GlcNAc). b) A polystyrene microsphere (3 μm in diameter) is linked with WGA, a lectin that binds to NeuAc and GlcNAc. c) One optical trap is used to support a WGA-linked microsphere, and two optical trapping beams orient and transport an erythrocyte. d) Light-driven microfabrication has three steps: The sequence begins with a cell supported in two traps. 1.) We use a third trap to bring a microsphere into contact with the surface of the cell. The sphere adheres to the cell by polyvalent, biospecific interactions between WGA and the NeuAc and GlcNAc groups. 2.) The two traps focused on the erythrocyte (with the attached microsphere) move the aggregate of microsphere and cell into the orientation desired for further steps in fabrication. 3.) The multiple traps are translated to bring the microsphere that is attached to the cell into contact with an assembly that is resting on the glass floor of the sample container. Repetition of this procedure generates the desired structure.

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