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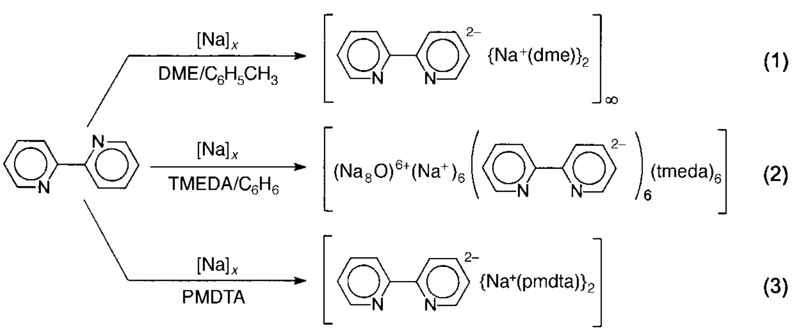
Sodium Salts of the Bipyridine Dianion: Polymer $[(bpy)^{2-}\{Na^+(dme)\}_2]_\infty$, Cluster $[(Na_8O)^{6+}Na_6^+(bpy)_6^{2-}(tmeda)_6]$, and Monomer $[(bpy)^{2-}\{Na^+(pmdta)\}_2]$**

Hans Bock,* Jean-Marie Lehn,* Jochen Pauls,
Sven Holl, and Volker Krenzel

Dedicated to Professor Gottfried Huttner

Polypyridines $H_4NC_5\text{-}(C_5NH_3)_n\text{-}C_5NH_4$ are excellent chelate ligands for metal cations, and the resulting complexes are suitable model compounds for studying supramolecular self-recognition and ion-pair aggregation to chains, ladders, or networks.[1,2] Despite the numerous known metal cation bipyridyl complexes, a search in the Cambridge Structural Database (version 5.10) produced no hit with regard to structures of alkali metal salts with bipyridine ligands. The preparation and crystallization of contact-ion pairs containing the most advantageous Na^+ ion[3] can be accomplished by the reduction in aprotic solution at a sodium metal mirror; a method employed on numerous occasions for organic compounds.[3,4] In the reactions (1)–(3) contact-ion multiples are formed whose structures are decisively dependent on the cation solvation by the solvent.[5] From dimethoxyethane (DME) and toluene a polymer crystallizes [reaction (1)], from *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) and benzene a novel $Na_{14}^+O^{2-}$ cluster [reaction (2)], and from pentamethyldiethylenetriamine (PMDTA) a monomeric sodium salt of the bipyidine dianion [reaction (3)].



The polymeric contact-ion triple crystallizes as deep red platelets, which according to their structure determination[6] contain two additional toluene molecules in the unit cell. The sodium cations in the chains stretching in *y* direction (Figure 1 A and B) are alternatingly bridged by a bipyridine dianion and two dme ligands; the $Na^+\cdots Na^+\cdots Na^+$ angles are 165°.

The structure determination confirms that the bipyridine dianions are planar (torsion angle $\omega(NC-CN) = 0°$) and that their nitrogen centers adopt a cisoid arrangement. The sodium metal reduction of bipyridine[7,8] shortens the C–C connection between the pyridine rings by 11 pm and stretches the C–N bonds to the bridge carbon centers by 9 pm and the C–C ring bonds by 5 pm. The internal angles of the ring at the carbon bridge centers are compressed by 6°. The sodium cations coordinate to both nitrogen centers and to the bridge carbon centers of the bypridine dianion with $Na^+\cdots N$ distances of 237 and an 240 pm and a $Na^+\cdots C$ distance of 287 pm. Additional $Na^+\cdots O$ contacts exist to both oxygen centers of one dme ligand and two further ones to an inversion symmetric second solvent ligand (Figure 1 C). The mirror-symmetric sodium cations $Na^+\cdots Na^+$ coordinated to the same bipyridine dianion are 332 pm apart, and the $Na^+\cdots O$ contact distances to the second ligand are 374 pm.

As a continuation of our studies into ion aggregation,[8] from a TMEDA/benzene solution under optimized conditions a novel sodium cluster $[((Na_8^+)O^{2-})(Na^+)_6]^{12+}$ has been crystallized as deep red blocks[9] (Figure 2). The cluster is lipophilically wrapped by six bipyridine dianions and six tmeda ligands. The inversion-symmetric Na_{14} cluster, wrapped by six bipyridine dianions and six tmeda ligands, contains a hexagonal bipyramid of Na^+ ions with a disordered O^{2-} dianion in its center (Figure 2 B), which balances the charge of 14 sodium cations and only six bipyridine dianions.

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[*] Prof. Dr. H. Bock, Dipl.-Chem. J. Pauls, Dipl.-Chem. S. Holl, Dipl.-Chem. V. Krenzel
Institut für Anorganische Chemie der Universität
Marie-Curie-Strasse 11, D-60439 Frankfurt am Main (Germany)
Fax: (+49) 69-7982-9188

Prof. Dr. J.-M. Lehn
Laboratoire de Chimie Supramoléculaire
Institut le Bel, Université Louis Pasteur
4, rue Blaise Pascal, F-67000 Strasbourg (France)
Fax: (+33) 3-8841-1020

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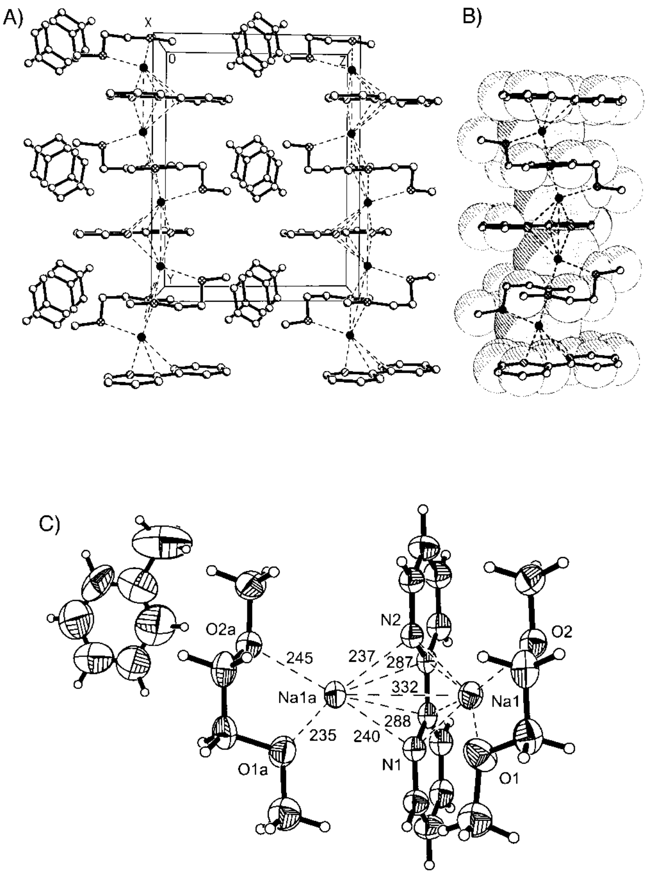


Figure 1. Crystal structure of $[(bpy)^{2-}\{Na^+(dme)\}_2]_\infty \cdot C_6H_5CH_3$ at 200 K: A) Unit cell (monoclinic $P2_1/m$, $Z = 2$) with packing in x direction, B) space-filling representation of the polymer strand, and C) one chain link (50% thermal ellipsoids) with numbering of the N, O, and Na centers as well as with Na^+ contact distances.

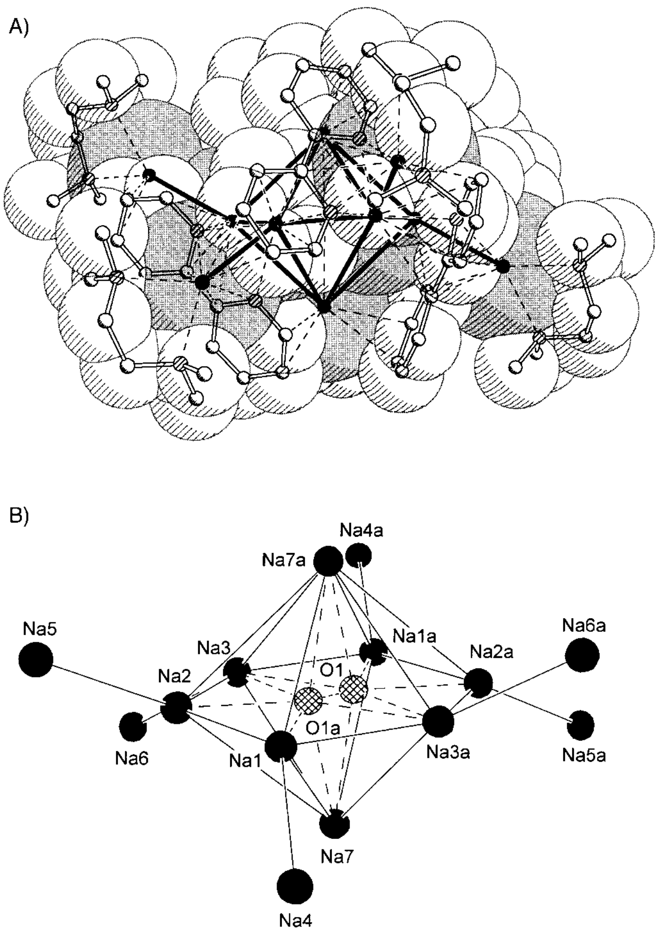


Figure 2. Crystal structure of the lipophilically wrapped sodium cluster $[(Na_8O)^{6+}Na_6^+(bpy)_6^{2-}(tmeda)_6] \cdot 4\,C_6H_6$ at 150 K: A) A side of view of a space-filling representation with partly sketched complex skeleton and B) arrangement of the Na^+ centers as well as of the disordered dianion O^{2-} in the cluster nucleus.

According to the triclinic lattice symmetry of the crystal, the clusters are stacked in all three directions of the unit cell, and eight clusters form a parallelepiped with four benzene molecules enclosed in a diamond-shaped fashion.

In the cluster, the six equatorial cations (Figure 2B, Na1–Na3) surround the disordered oxygen dianion in a slightly pronounced chair conformation with torsion angles of only about 8°. The $Na^+ \cdots O^{2-}$ distances to the three different equatorial cations are between 257 and 277 pm, and the ones to the axial cations of 290 and 296 pm are, despite the reduced precision of the measurements due to the disorder of the O^{2-} anion, significantly longer. The contact distances $Na^+ \cdots Na^+$ vary over a wide range: they are between 296 and 306 pm within the equatorial ring and between 392 and 422 pm to the axial sodium cations, which are shifted by 13 pm out of the central position above the ring. Another sodium cation is coordinated to each of the equatorial Na^+ centers, the positions of which alternate above and below the idealized plane of the Na_6^+ six-membered ring. The angles between this plane and the outwardly oriented cation contacts are between 118° and 120°. Each two centers $Na^+ \cdots Na^+$ are bridged by a bipyridine dianion; the contact distances are: $Na^+ \cdots Na^+$ 312–316 pm, $Na^+ \cdots N$ 236–254, and $Na^+ \cdots C$ 276–290 and 313 pm. In the bipyridine dianion, the approximately planar pyridine rings are twisted by between 5 and 8° around the central C–C axis. The outer Na^+ ions are each additionally solvated by a tmeda ligand with contact distances $Na^+ \cdots N$ of between 247 and 269 pm.

The monomeric contact-ion triple $[(bpy)^{2-}\{Na^+(pmdta)\}_2]$ was crystallized from a solution in the more strongly Na^+-solvating PMDTA.[10] The structure determination of the deep red blocks[10] confirms a monoclinic unit cell containing four complexes, which are separated by their solvent shells and packed in layers within the crystal (Figure 3A).

The two sodium ions coordinate as in the polymer (see Figure 1C) mirror-symmetrically to the two nitrogen and two bridge carbon centers of the bipyridine dianion (Figure 3C). The $Na^+ \cdots N$ distances are 237 and 244 pm as well as 239 and 243 pm on both sides, the $Na^+ \cdots C$ distances are 278 and 279 pm as well as 274 and 278 pm, and the $Na^+ \cdots Na^+$ distance is 366 pm. The bipyridine dianion exhibits slightly distorted pyridyl rings that are twisted relative to each other around the C–C axis by a torsion angle ω(NC-CN) of 3°, and the ring centers C2 and C5 are shifted out of the idealized double ring plane by 2 and 6°. The remaining bond lengths and angles correspond to those in the polymer (Figure 1), the C–C bond between the two pyridyl rings is similarly shortened by 11 pm and the C–N bond lengths extended by 9 pm. The sodium

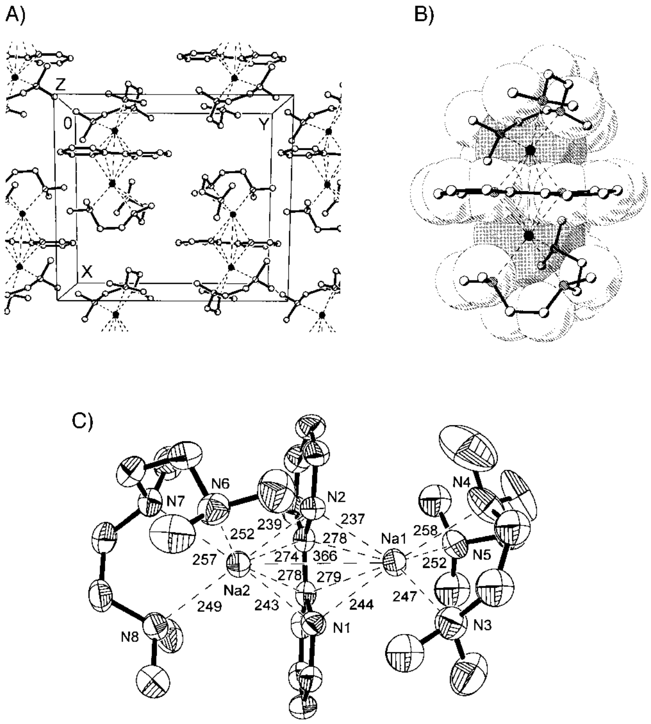
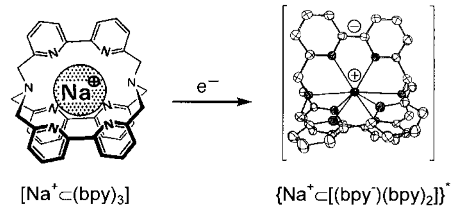


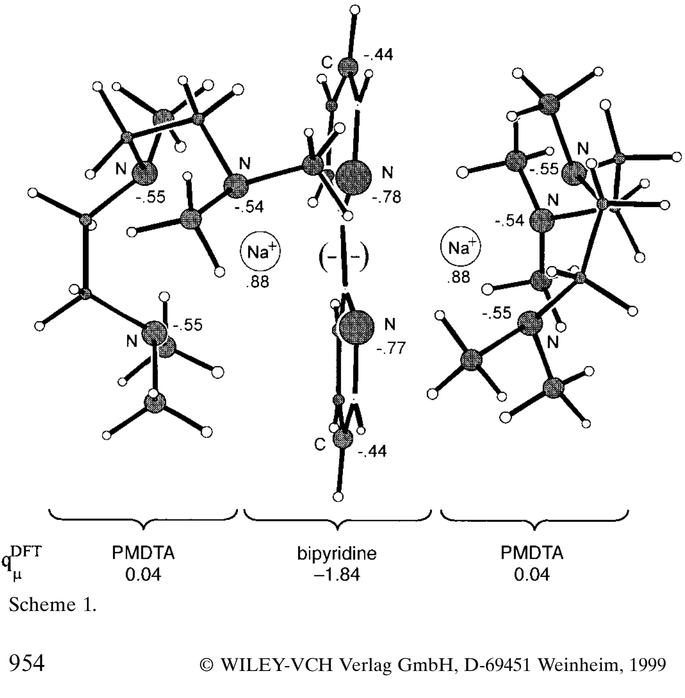
Figure 3. Crystal structure of $[(bpy)^{2-}\{Na^+(pmdta)\}_2]$ at 200 K: A) Unit cell (monoclinic $P2_1/c$, $Z = 2$) packed in y direction, B) space-filling representation of the complex, and C) side view (50 % thermal ellipsoids) with numbering of the Na and N centers as well as with Na^+ contact distances.

cation coordination spheres are completed by three $Na^+ \cdots N$ contacts to the solvating pmdta ligand; the $Na^+ \cdots N$ distances are between 247 and 258 pm (Figure 3C).

The charge distribution in the complex $[(bpy)^{2-}\{Na^+(pmdta)\}_2]$ has been approximated by a density functional theory (DFT) calculation (B3LYP with basis set 6-31G*)[11] including a "natural bond orbital" analysis (Scheme 1). The negative charges are predicted to be delocalized over the bipyridine dianion, and the positive ones to be localized at the Na^+ ions.[12] In contrast to complexes of π-hydrocarbon anions,[3,4] the cations coordinate here almost exclusively to the nitrogen centers of the dianion and the pmdta ligands. A similiar arrangement has been reported previously for the "sodium cryptatium",[13] the bypridine radical anion salt that crystallizes during the electrochemical reduction of sodium tris(bypridyl)cryptate at a platinum cathode [reaction (4)]. The contact distances $Na^+ \cdots N$ to the different bipyridine ligand units are only 259 pm for the radical anion bridge, whereas the connections to the neutral bipyridine links are stretched by almost 20 pm to 278 pm.[13]



(4)



Scheme 1.

The different sodium salts of the bipyridine dianion, which crystallize depending on the sodium solvation from polyethers or polyamines as chain polymer (Figure 1), as Na_4^+ cluster (Figure 2), or as monomeric contact-ion triple (Figure 3), together with the tris(bipyridine)cryptate radical anion confirm that bipyridine is well-suited to serve as a model ligand in solvent-dependent self-aggregation studies. Of special advantage in crystal growth experiments is the observation that twofold reduction of bipyridine at an alkali metal mirror in usual solvents is accompanied by a brownish violet color. Further investigation will be predominantly directed to polypyridines of greater length, for which these bipyridine experiments served as a preliminary study.

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[6] Preparation and single crystal growth of $[(C_{10}H_8N_2^{2-})\{Na^+(dme)\}_2]_\infty \cdot C_7H_8$: Freshly cut sodium (200 mg, 8.7 mmol) was weighed into a

Schlenk trap, dried by heating at 10^{-2} mbar, and evaporated to a metal mirror at 10^{-6} mbar. Under argon pure 2,2′-bipyridine (78 mg, 0.5 mmol) was added and this was covered with toluene (10 mL) and dimethoxyethane (5 mL). The trap was fixed in a diagonal position such that the bipyridyl solution was always in contact with the metal mirror. Deep red air-sensitive platelets grew from the violet-brown solution within 3 d. Crystal structure determination: Deep red platelets, $C_{10}H_8N_2Na_2 \cdot 2\,C_4H_{10}O_2 \cdot C_7H_8$ ($M_r = 474.54$), $a = 865.0(1)$, $b = 1386.2(1)$, $c = 1077.2(2)$ pm, $\beta = 95.22(3)^\circ$, $V = 1286.3(3) \times 10^6$ pm^3 ($T = 200$ K), $\rho_{calcd.} = 1.225$ g cm^{-3}, monoclinic, $P2_1/m$ (No. 11), $Z = 2$, Siemens P4 four-circle diffractometer, $Mo_{K\alpha}$ radiation, $\mu = 0.11$ mm^{-1}, 3090 measured reflections within $3^\circ \leq 2\theta \leq 50^\circ$, of which 2355 are independent ($R_{int} = 0.0237$). Structure solution by direct methods and difference Fourier technique (SHELXS-86), structure refinement against F^2 (SHELXL-93), 198 parameters, $w = 1/[\sigma^2(F_o^2) + (0.0690\,P)^2 + 0.4713\,P]$, R for 1647 $F_o > 4\sigma(F_o) = 0.0492$, wR_2 for all 2355 data = 0.1383, GOOF = 1.034, residual electron density $0.39/-0.22$ e Å^{-3}. Centers C, N, and O were refined by using anisotropic displacement parameters, disordered C center with isotropic displacement parameters, and hydrogen centers (in geometrically ideal positions) with fixed isotropic displacement parameters [$U_{iso(H)} = 1.2 \times U_{eq(C)}$ (CH/CH$_2$)]; [$U_{iso(H)} = 1.5 \times U_{eq(C)}$ (CH$_3$)] using the riding model. The free refinement of the carbon centers in the toluene molecule, disordered around a twofold axis did not provide a chemically reasonable arrangement of the centers and, therefore, as starting point a planar structure was chosen with equal C–C distances in the phenyl ring and a methyl bond length of 149 pm. One methyl group of the dme ligand is disordered in two positions, which are occupied by 71 % and 29 %.[10b]

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[9] Preparation and single crystal growth of $[(Na_8O)^{6+}Na_6^+(bpy)_6^{2-}$-$(tmeda)_6] \cdot 4\,C_6H_6$: Freshly cut sodium (224 mg, 9.74 mmol) was weighed into a Schlenk trap, dried by heating at 10^{-3} mbar, and evaporated to a metal mirror at 10^{-6} mbar. Under argon pure 2,2′-bipyridine (78 mg, 0.5 mmol) was added and this was covered with TMEDA (3 mL) and benzene (10 mL). The trap was fixed in a diagonal position such that the bipyridyl solution was always in contact with the metal mirror. Black air-sensitive blocks grew from the violet-brown solution within 3 d. Crystal structure determination: Black blocks $[(C_{10}H_8N_2Na_2 \cdot C_6H_{16}N_2)_6 \cdot O \cdot 2\,Na] \cdot 4\,C_6H_6$ ($M_r = 2284.64$), $a = 1427.8(2)$, $b = 1442.3(3)$, $c = 1667.1(2)$ pm, $\alpha = 90.74(2)$, $\beta = 111.97(1)$, $\gamma = 92.03(2)^\circ$, $V = 3180.5(9) \times 10^6$ pm^3 ($T = 150$ K), $\rho_{calcd} = 1.193$ g cm^{-3}, triclinic, $P\bar{1}$ (No. 2), $Z = 1$, Siemens P4 four-circle diffractometer, $Mo_{K\alpha}$ radiation, $\mu = 0.114$ mm^{-1}, 12552 measured reflections within $3^\circ \leq 2\theta \leq 50^\circ$, of which 11096 are independent ($R_{int} = 0.0274$). Structure solution by direct methods and difference Fourier technique (SHELXS-86); atomic form factors for O^{2-}: P. Azavant, A. Lichanot, *Acta Crystallogr. A*, **1993,** *49*, 91, basic set B; all others from *International Tables*, **1992**, *Vol. C*, Table 6.1.1.4. Structure refinement against F^2 (SHELXL-93), 721 parameters, $w = 1/[\sigma^2(F_o^2) + (0.0525\,P)^2 + 2.8532\,P]$, R for 6930 $F_o > 4\sigma(F_o) = 0.0568$, wR_2 for all 11096 data = 0.1509, GOOF = 1.014, residual electron density $0.42/-0.28$ e Å^{-3}. N and Na centers, as well as non-disordered C centers refined by using anisotropic displacement parameters, disordered C and O centers with isotropic displacement parameters, and hydrogen centers (in geometrically ideal positions) with fixed isotropic displacement parameters [$U_{iso(H)} = 1.2 \times U_{eq(C)}$ (CH/CH$_2$)]; [$U_{iso(H)} = 1.5 \times U_{eq(C)}$ (CH$_3$)] using the riding mocel. The anisotropic displacement parameters of the benzene molecules indicate a rotational disordering in the bonding plane, which however could not be refined. The carbon centers C60 and C61 of one dimethylamino group are disordered at two positions with occupancies of 45 % and 55 %, and the central oxygen center at two positions with occupancies of 28 % and 71 %. The oxygen center was refined as a dianion and to achieve charge neutrality Na7 as a cation. The significantly different isotropic displacement parameters of the O split positions together with the residual electron densities within the cluster point to a diffuse disordering, which cannot be dealt with satisfactorily using a simple split model.[10b]

[10] a) Preparation and single crystal growth of $[(C_{10}H_8N_2^{2-})$-$\{Na^+(pmdta)\}_2]$: Freshly cut sodium (189 mg, 8.2 mmol) was weighed into a Schlenk trap, dried by heating at 10^{-3} mbar, and evaporated to a metal mirror at 10^{-6} mbar. Under argon pure 2,2′-bipyridine (52 mg, 0.33 mmol) was added and this was covered with PMDTA (5 mL). The trap was fixed in a diagonal position such that the bipyridyl solution was always in contact with the metal mirror. Deep red air-sensitive blocks grew from the violet-brown solution within 3 d. Crystal structure determination: Deep red blocks $C_{10}H_8N_2Na_2 \cdot 2\,C_9H_{23}N_3$ ($M_r = 548.77$), $a = 1322.7(2)$, $b = 1427.6(2)$, $c = 1803.2(2)$ pm, $\beta = 105.380(8)^\circ$, $V = 3283.0(8) \times 10^6$ pm^3 ($T = 200$ K), $\rho_{calcd} = 1.110$ g cm^{-3}, monoclinic, $P2_1/c$ (No. 14), $Z = 4$, Siemens P4 four-circle diffractometer, $Mo_{K\alpha}$ radiation, $\mu = 0.091$ mm^{-1}, 6376 measured reflections within $3^\circ \leq 2\theta \leq 48^\circ$, of which 5103 are independent ($R_{int} = 0.0289$). Structure solution by direct methods and difference Fourier technique (SHELXS-86). Structure refinement against F^2 (SHELXL-93), 342 parameters, $w = 1/[\sigma^2(F_o^2) + (0.0634\,P)^2 + 2.8032\,P]$, R for 3120 $F_o > 4\sigma(F_o) = 0.0592$, wR_2 for all 5103 data = 0.1625, GOOF = 1.008, residual electron density $0.33/-0.25$ e Å^{-3}. N and Na centers, as well as non-disordered C centers with isotropic displacement parameters, hydrogen centers (in geometrically ideal positions) refined with fixed isotropic displacement parameters [$U_{iso(H)} = 1.2 \times U_{eq(C)}$ (CH/CH$_2$)]; [$U_{iso(H)} = 1.5 \times U_{eq(C)}$ (CH$_3$)] using the riding model. In one of the two PMDTA molecules several carbon centers are displaced over two positions exhibiting occupancies of at least 30 % and 70 %. b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-101832 ($[(C_{10}H_8N_2^{2-})\{Na^+(dme)\}_2]_\infty \cdot C_7H_8$), CCDC-101842 ($[(C_{10}H_8N_2Na_2 \cdot C_6H_{16}N_2)_6 \cdot O \cdot 2\,Na] \cdot 4\,C_6H_6$), and CCDC-101833 ($[(C_{10}H_8N_2^{2-})\{Na^+(pmdta)\}_2]$). 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).

[11] The density functional theory calculations were performed starting from the experimental structural data[10] using the program Gaussian 94 (Revision E.2, authors: M. J. Frisch, g. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Pertersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzales, J. A. Pople, Gaussian Inc., Pittsburgh PA, USA, **1995**). For the *method Density Functional Theory B3LYP* cf. a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; b) C. Lee, W. Yang, R. G. Paar, *Phys. Rev.* B **1988**, *37*, 785; c) B. Miehlich, A. Sariu, H. Stoll, H. Preuss, *Chem. Phys. Lett.* **1989**, *157*, 200. The calculation were carried out with 6–31G* basis sets (W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **1972**, *56*, 2257; M. S. Gordon, *Chem. Phys. Lett.* **1980**, *76*, 163) starting from the structural coordinates of the compound[10] using the computer "Biturbo" (Dual Intel-Pentium II PC) in the research group.

[12] The assumption of partly solvent-separated ion triples $[M_{solv}^+(bpy)^{2-}]^-[M_{solv}^+]$ (S. Herzog, R. Taube, *Z. Chem.* **1962**, *2*, 208) therefore, does not apply to crystalline salts.

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