

# Synthesis and characterisation of macrocyclic palladium(II)–sodium(I) complexes: generation of an unusual metal-mediated electron delocalisation †

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Reaction of sodium perchlorate–crown ether derivative (LH<sub>2</sub>) complex [Na<sub>2</sub>LH<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (**1**) with palladium acetate afforded two related compounds of macrocyclic palladium(II)–sodium(I) dimeric tetranuclear complexes, [Pd<sub>2</sub>Na<sub>2</sub>L<sub>2</sub>(μ-OH<sub>2</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>(CH<sub>2</sub>Cl<sub>2</sub>)<sub>3</sub> (**2**) and [Pd<sub>2</sub>Na<sub>2</sub>(L<sup>-</sup>)<sub>2</sub>](CH<sub>3</sub>CN)<sub>2</sub>(C<sub>3</sub>H<sub>6</sub>O)<sub>2</sub> (**3**) and their structures were characterised by IR, NMR, mass and X-ray analysis; the latter was revealed as an unusual metal-mediated electron delocalised complex.

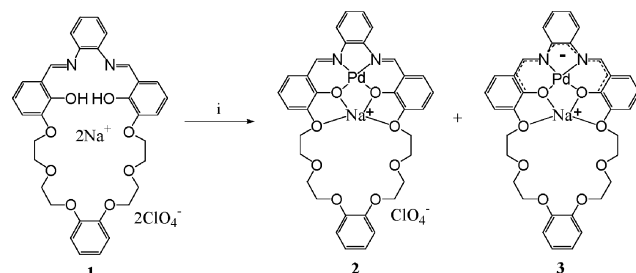
Transition metal complexes of the ligands based on the salophen [*N,N'*-*o*-phenylenebis(salicylidene-iminato) dianion] or salen [*N,N'*-ethylenebis(salicylideneiminato) dianion] moiety are of particular interest in recent years, and whose versatile properties are promising in relation to molecular recognition,<sup>1</sup> metallocatalyst,<sup>2</sup> non-linear optical responses,<sup>3</sup> and electron transfer.<sup>4</sup> The salophen as a tetradentate ligand reacts with transition metals to form square-planar complexes.<sup>5</sup> In some cases, further reactions of the transition metal complexes of the chelates incorporating the salophen moiety with alkali metals affords the bifunctional transition metal–alkali metal complexes.<sup>4b,c,6</sup> In particular, the bifunctional transition metal–alkali metal complexes may lead to the generation of electron-rich species, either by forcing electrons into the ligand (*e.g.*, formation of new C–C bond<sup>7</sup>) or by reducing the oxidation state of the metal.<sup>8</sup>

Recently, we have successfully synthesised bis-compartmental heterobinuclear macrocyclic palladium(II)–sodium(I) complexes (**2** and **3**) by the reaction of sodium perchlorate–crown ether complex incorporating a salophen moiety [Na<sub>2</sub>LH<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (**1**) and palladium acetate (Scheme 1). To the best of our knowledge, there has been no report of a palladium(II)–alkali metal(I) complex based on salophen-type ligands. Furthermore, **3** was revealed as an unusual metal-mediated electron

delocalised complex. Some literature systems related to the present one have been demonstrated to act as an electron reservoir.<sup>7,8</sup>

We now report our finding for the two related compounds of the macrocyclic palladium(II)–sodium(I) complexes, **2** possessing two perchlorate anions and **3** with neutral charge.

Compound **1** was obtained in highest yield by the reaction of barium perchlorate–crown ether derivative complex, [BaLH<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> with sodium sulfate (ESI †). The reaction of **1** with palladium acetate afforded the mixture of **2** and **3** in *ca.* 80 and 10% yield, respectively. The compounds **1**, **2** and **3** were fully characterised by NMR, IR, mass and microanalysis. ‡ The microanalysis data for **1** confirmed the stoichiometry of this product to be 1 : 2 : 2 (ligand : Na<sup>+</sup> : ClO<sub>4</sub><sup>-</sup>). The <sup>1</sup>H NMR spectra of **2** and **3** (Fig. 1) together with their 2D (COSY) NMR spectra (ESI †) provide the evidence of the formation of those compounds. The proton signals of the salophen unit (from *g* to *l*) in **2** shifted significantly to a higher field than those in **3**, while the chemical shift changes for the others (from *a* to *f*) in **2** and **3** are not remarkable. This is due to the difference of electrical environments between neutral- (**2**) and negative-charged (**3**) forms of the salophen unit with palladium cation. In IR spectra, **2** exhibited a strong band at 1095 cm<sup>-1</sup> due to a perchlorate ion, but **3** shows no band corresponding to the perchlorate ion. We prepared the single crystals of **2** and **3** suitable for X-ray analyses by slow evaporation from acetonitrile/acetone and dichloromethane solutions, respectively. §



Scheme 1 Reagents and condition: i, dichloromethane, Pd(OAc)<sub>2</sub>.

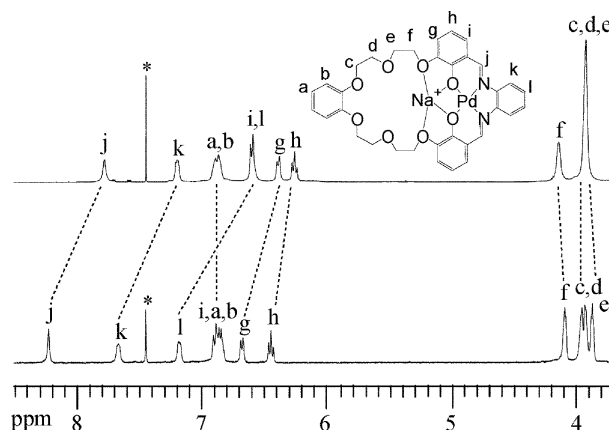
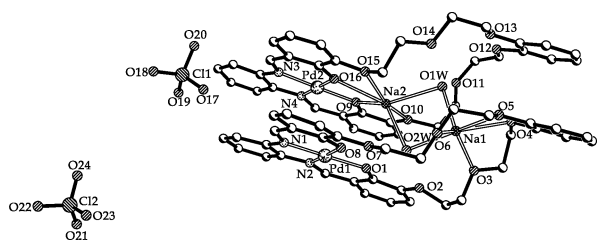


Fig. 1 Comparison of <sup>1</sup>H NMR spectra in CDCl<sub>3</sub>/CD<sub>3</sub>CN (2 : 1) of (a) **2** and (b) **3**. The signal labeled with an asterisk represents CHCl<sub>3</sub>.

The structure of **2** (Fig. 2), [Pd<sub>2</sub>Na<sub>2</sub>L<sub>2</sub>(μ-OH<sub>2</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>(CH<sub>2</sub>Cl<sub>2</sub>)<sub>3</sub> contains two stair-shaped macrocyclic dinuclear palladium(II)–sodium(I) complexes in parallel, which are connected by two bridging water molecules, forming a unique dimeric complex. The layered structure permits weak face-to-face π–π interactions between aromatic groups, with the

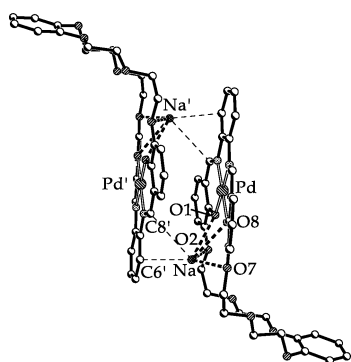
† Electronic supplementary information (ESI) available: Synthetic procedures for **1**; molecular structure of [BaLH<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>]; partial COSY-NMR spectra of **2** and **3**; molecular structures of **2** and **3**; packing structure of **3**; and comparison of UV-visible spectra of **2** and **3**. See <http://www.rsc.org/suppdata/dt/b4/b402507e/>



**Fig. 2** The molecular structure of **2** (solvent molecules and hydrogen atoms are not shown for clarity). Selected bond lengths (Å) and angles (°): Na(1)–O(3) 2.366(6), Na(1)–O(4) 2.542(7), Na(1)–O(5) 2.569(7), Na(1)–O(6) 2.381(7), Na(1)–O(1W) 2.376(7), Na(1)–O(2W) 2.325(7), Na(2)–O(9) 2.596(6), Na(2)–O(10) 2.759(8), Na(2)–O(15) 2.758(6), Na(2)–O(16) 2.593(6), Na(2)–O(1W) 2.758(7), Na(2)–O(2W) 2.799(8); O(2W)–Na(1)–O(1W) 88.4(3), O(3)–Na(1)–O(6) 129.7(3), O(4)–Na(1)–O(5) 60.9(2), O(16)–Na(2)–O(9) 62.0(2), O(15)–Na(2)–O(10) 165.3(2), O(1W)–Na(2)–O(2W) 72.3(2).

centroid-to-centroid distances of 3.7–4.0 Å. Two non-coordinating perchlorate ions were found in the outer sphere of the complex. Each palladium centre has a distorted square planar array of two N and two phenolate O atoms from the salophen cavity in a *cis* arrangement. However, two sodium atoms have quite different coordination environment. Na(1) is coordinated to four ether O atoms in the opposite side of the salophen moiety from one macrocycle in a bent arrangement, with the two ether O donors remaining uncoordinated. The Na(1) coordination is completed by two Na(1)–O bonds [Na(1)–O(1W) 2.376(7), Na(1)–O(2W) 2.325(7) Å], from two bridging water molecules, in such a way that the Na(1) shows six-coordination with an irregular geometry. Na(2) atom is bounded by two phenolate O and two ether O atoms closed to the salophen unit as well as two bridging water molecules such that the overall coordination geometry about the Na(2) is also six-coordinate. Intermetallic distances of Pd(1) ⋯ Na(2) (3.599(3) Å) and Pd(2) ⋯ Na(2) (3.669(3) Å) are slightly shorter than the sum of van der Waals radii of “Pd + Na” (3.90 Å).<sup>9</sup> The Na–O bond distances and angles are similar to those of [Co(salophen)Na(THF)]<sub>2</sub> complex.<sup>8a</sup> The Na(2) atom is displaced 0.368(4) Å out of the plane of the salophen unit with two ring O atoms, which dictates that the Na(2)–O(1W) bond distance (2.758(7) Å) is shorter than the Na(2)–O(2W) bond distance (2.799(8) Å). In addition, the molecular conformation is stabilized by formation of several hydrogen bonds (2.85(1)–3.05(1) Å) between two water molecules and ring O atoms.

Interestingly, an X-ray analysis reveals that **3** (Fig. 3), [Pd<sub>2</sub>Na<sub>2</sub>(L<sup>-</sup>)<sub>2</sub>](CH<sub>3</sub>CN)<sub>2</sub>(C<sub>3</sub>H<sub>6</sub>O)<sub>2</sub> is a dimer of a hetero-binuclear complex with an imposed inversion symmetry. The non-planar skeleton of the macrocycle in **3** can be denoted as an approximate L-shape. In **3**, no anion was found. As suggested in Scheme 1, the crystal structure of **3** provides an



**Fig. 3** The molecular structure of **3** (solvent molecules and hydrogen atoms are not shown for clarity). Selected bond lengths (Å) and angles (°): Na ⋯ O(1) 2.943(2), Na ⋯ O(2) 3.103(3), Na ⋯ O(7) 3.077(3), Na ⋯ O(8) 3.005(3), Na ⋯ C(6') 3.515(3), Na ⋯ C(8') 3.320(3); O(1)–Na–O(8) 54.38(5), O(2)–Na–O(7) 128.30(8) [symmetry operation:  $-x, 2-y, 1-z$ ].

unusual electron delocalisation<sup>10</sup> of the salophen unit by metal-mediated electron transfer. Some related literature systems show that the new C–C single bond was formed by the metal-assisted long-range electron transfer without chemical reactions during the reaction, which has the means of storing and releasing electrons in a reversible manner.<sup>7</sup> In our system, the metal-mediated electron transfer in complex **3** appears to be neither the metal nor the formation of the C–C single bond, but rather the salophen unit of the ligand.

The palladium atom in a distorted square planar array shows a very similar metal coordination environment to that of **2**. According to Fig. 3, the sodium atom is as far as 1.337(2) Å above the mean plane of four coordinating O atoms (O1, O2, O7, O8, average deviation: 0.0421 Å). It is quite surprising to see the floating of a metal cation above the macrocyclic plane. Thus, the Na atom coordination cannot be described simply in terms of a regular polyhedron. The Na atom involves two Na–O (ether) and two Na–O (phenolate) contacts (2.943(2)–3.103(3) Å), which are longer by *ca.* 0.4–0.5 Å than those of **2** but still lie within the sum of the van der Waals radii 3.80 Å.<sup>9</sup> The bond angles range (49.66(5)–128.30(8)°) between adjacent Na–O consistent with the unusual quadrupodal structure. The intermetallic distance of Pd ⋯ Na (3.939(2) Å) in **3** is longer than the sum of the van der Waals radii and also those of Pd(1) ⋯ Na(2) and Pd(2) ⋯ Na(2) in **2**. More interestingly, the long-range intermolecular interactions (3.319(3)–3.515(3) Å) of the sodium cation with the negatively charged salophen unit through the C atoms were observed in the packing structure, which are longer than those (2.8–3.1 Å) of the [Na{Nd(OC<sub>6</sub>H<sub>3</sub>Ph<sub>2</sub>-2,6)<sub>4</sub>}] complex<sup>11</sup> but less than the sum of the van der Waals radii 3.95–4.0 Å.<sup>9</sup> It is conceivable that the exceptional large dislocation of the Na atom as well as the elongation of Na–O distances in **3** are due to these interactions. UV-visible spectroscopy reveals a small difference of the charge-transfer band between **2** (477.4 nm) and **3** (483.0 nm) in MeCN (ESI†). These results suggest that the salophen unit has an electron, which is delocalised and reduction does not affect the oxidation state of the metal (remaining palladium(II)) but, rather, the ligand.

In conclusion, we have isolated and structurally characterised the two stable related compounds of palladium(II)–sodium(I) bifunctional complexes, **2** and **3**, with a crown ether macrocycle containing a salophen moiety. In particular, we were able to demonstrate that **3** is an interesting example of metal-mediated electron delocalisation. These results reveal that bifunctional complexes based on the salophen moiety might have the potential to act as an electron reservoir.

## Acknowledgement

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## Notes and references

‡ Selected data for **1**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/CD<sub>3</sub>CN = 1 : 2, 298 K): δ 14.22 (2 H, s, OH), 8.74 (2 H, s, CH=N), 7.43–7.37 (4 H, m, ArH), 7.15 (2 H, d, *J* = 8 Hz, ArH), 7.08 (2 H, d, *J* = 8 Hz, ArH), 6.98–6.95 (2 H, m, ArH), 6.93–6.89 (2 H, m, ArH), 6.89 (2 H, t, *J* = 8 Hz, ArH), 4.25 (4 H, m, CH<sub>2</sub>OAr), 4.14 (4 H, m, CH<sub>2</sub>OAr), 4.00 (4 H, m, CH<sub>2</sub>OCH<sub>2</sub>), 3.95 (4 H, m, CH<sub>2</sub>OCH<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>/CD<sub>3</sub>CN = 1 : 2, 298 K): δ 162.9, 151.9, 147.8, 146.1, 139.9, 128.0, 124.5, 121.9, 118.5, 118.2, 118.1, 115.9, 114.7, 68.5, 68.3, 68.1, 67.1; FAB MS: *m/z* 621 (M<sup>+</sup> – Na – 2ClO<sub>4</sub>, 55%); IR (KBr, cm<sup>-1</sup>): 3487m, 2923w, 1604s, 1435w, 1249s, 1195w, 1103vs (ClO<sub>4</sub><sup>-</sup>), 941w, 740s; Found: C, 48.24; H, 4.14; N, 3.68. Calc. for C<sub>34</sub>H<sub>34</sub>Cl<sub>2</sub>N<sub>2</sub>Na<sub>2</sub>O<sub>16</sub>: C, 48.41; H, 4.06; N, 3.32%.

**2**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/CD<sub>3</sub>CN = 2 : 1, 298 K): δ 7.78 (2 H, s, CH=N), 7.19 (2 H, br, ArH), 6.89–6.87 (4 H, br, ArH), 6.61–6.59 (4 H, m, ArH), 6.38 (2 H, d, *J* = 8 Hz, ArH), 6.26 (2 H, d, *J* = 8 Hz, ArH), 4.14 (4 H, br, CH<sub>2</sub>OAr), 3.93 (12 H, br, CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>/CD<sub>3</sub>CN = 2 : 1, 298 K): δ 151.4, 147.2, 141.2, 126.6, 126.1,

120.9, 119.1, 114.7, 113.7, 113.0, 68.2, 67.6, 67.1, 66.0; FAB MS:  $m/z$  725 ( $M^+ - ClO_4$ , 38%), 702 ( $M^+ - NaClO_4$ , 7); IR (KBr,  $cm^{-1}$ ): 3464m, 2923w, 2877w, 1604s, 1442m, 1250s, 1095vs ( $ClO_4^-$ ), 933m, 740s; Found: C, 49.49; H, 4.08; N, 3.16. Calc. for  $C_{34}H_{32}ClN_2NaO_{12}Pd$ : C, 49.47; H, 3.91; N, 3.39%.

3:  $^1H$  NMR (400 MHz,  $CDCl_3/CD_3CN = 2 : 1$ , 298 K):  $\delta$  8.22 (2 H, s, CH=N), 7.74 (2 H, br, ArH), 7.18 (2 H, br, ArH), 6.88 (6 H, m, ArH), 6.67 (2 H, d,  $J = 8$  Hz, ArH), 6.44 (2 H, d,  $J = 8$  Hz, ArH), 4.09 (4 H, br,  $CH_2OAr$ ), 3.95–3.93 (8 H, m,  $OCH_2CH_2O$ ), 3.87 (4 H, br,  $CH_2OCH_2$ );  $^{13}C\{^1H\}$  NMR (100 MHz,  $CDCl_3/CD_3CN = 2 : 1$ , 298 K):  $\delta$  157.5, 155.3, 153.8, 153.5, 147.2, 132.4, 131.6, 126.1, 124.7, 120.7, 120.5, 119.7, 119.2, 74.1, 73.9, 73.7, 72.4; FAB MS:  $m/z$  725 ( $M^+$ , 60%), 702 ( $M^+ - Na$ , 27); IR (KBr,  $cm^{-1}$ ): 3502m, 2923w, 2869w, 1597s, 1427m, 1242s, 1188s, 1118m, 740s; Found: C, 54.92; H, 4.61; N, 4.23. Calc. for  $C_{34}H_{32}N_2NaO_8Pd \cdot H_2O$ : C, 54.88; H, 4.61; N, 3.76%.

§ X-ray analyses: intensity data from a Bruker SMART-CCD diffractometer, structure determination and refinement with SAINT<sup>12</sup> and SHELXTL<sup>13</sup> software packages, empirical absorption correction with SADABS<sup>14</sup> program.

Crystal data for 2:  $[Pd_2(C_{34}H_{32}N_2O_8)_2Na_2(H_2O)_2](ClO_4)_2(CH_2Cl)_3$ :  $C_{71}H_{74}Cl_6N_4Na_2O_{26}Pd_2$ ,  $M = 1941.72$ , monoclinic, space group  $P2_1/n$ ,  $a = 13.6945(7)$ ,  $b = 24.8174(13)$ ,  $c = 23.0266(12)$  Å,  $\beta = 92.322(1)^\circ$ ,  $V = 7819.4(7)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.649$  g  $cm^{-3}$ ,  $F(000) = 3944$ ,  $\mu(Mo-K\alpha) = 8.27$   $cm^{-1}$ ,  $T = 183(2)$  K, 60494 reflections measured, 19553 unique ( $R_{int} = 0.1128$ ),  $R_1 = 0.0865$  ( $I > 2\sigma(I)$ ),  $wR_2 = 0.2723$  (all data).

Crystal Data for 3:  $[Pd(C_{34}H_{32}N_2O_8)Na](CH_3CN)C_3H_6O$ :  $C_{39}H_{41}N_3NaO_9Pd$ ,  $M = 825.14$ , triclinic, space group  $P-1$ ,  $a = 11.3041(9)$ ,  $b = 12.1883(10)$ ,  $c = 15.3961(13)$  Å,  $\alpha = 73.037(2)$ ,  $\beta = 80.723(2)$ ,  $\gamma = 67.275(2)^\circ$ ,  $V = 1868.6(3)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.467$  g  $cm^{-3}$ ,  $F(000) = 850$ ,  $\mu(Mo-K\alpha) = 5.67$   $cm^{-1}$ ,  $T = 183(2)$  K, 14609 reflections measured, 9298 unique ( $R_{int} = 0.0193$ ),  $R_1 = 0.0363$  ( $I > 2\sigma(I)$ ),  $wR_2 = 0.1047$  (all data).

CCDC reference numbers 226722 (2) and 226723 (3). See <http://www.rsc.org/suppdata/dt/b4/b402507e/> for crystallographic data in CIF or other electronic format.

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