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First binuclear complex of an *N*,*N*′,*N*″,*N*‴-tetraalkyl 2,5-diamino-1,4-benzoquinonediimine†

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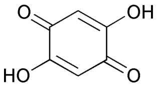
A new method for the synthesis of *N*,*N*′,*N*″,*N*‴-tetraalkyl 2,5-diamino-1,4-benzoquinonediimines is described together with the structure of a binuclear Pt(II) complex with such a bridging ligand which provides an extended π-system.

The coordination complexes derived from 2,5-dihydroxy-1,4-benzoquinone **1** display many interesting features and possess a rich redox chemistry. Indeed, the deprotonated, enolate form of **1** can react with metal ions to form dinuclear complexes of particular interest owing to the specific electronic properties induced by the quinone system.[1–3] The related 2,5-diamino-1,4-benzoquinonediimines **2a**,**b** could give access to a wider range of metal complexes because of the suitable overlap between the nitrogen and metal orbitals.



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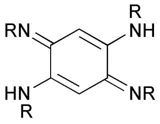
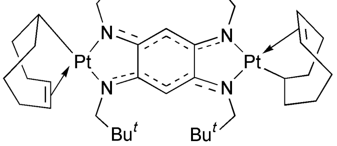


2a: R = alkyl
2b: R = H

Such compounds are expected to increase the scope of bonding patterns and electronic delocalization compared to other bridging nitrogen ligands such as terpyridine systems,[4] Creutz–Taube species[5] and *p*-benzoquinonediimine-bridged ligands.[6,7] The direct use of **2b** has been shown to be unsuitable since coordination of metal fragments renders the benzoquinonediimine bridge more susceptible to nucleophilic attack.[8] In contrast, *N*-substitution by electron-donating groups should lead to more stable complexes toward dioxygen and/or water. Since ligands of type **2a** are only accessible by self-condensation of aniline and/or 1,4-diaminobenzene,[9–12] one faces considerable limitations in the nature of the substituents on both types of nitrogen atoms. Here we describe a new strategy to access such ligands and demonstrate their ability to function as bridging chelates in dinuclear chemistry.

Compound **3**·4 HCl was first reacted smoothly in MeCN and excess NEt_3 at room temperature with trimethylacetyl chloride (4 equiv.) to afford **4** which is almost insoluble in most solvents so that only characterization in the solid state is reported (Scheme 1).‡ Reduction of **4** with $LiAlH_4$ in CCl_4 did not lead to the corresponding tetraamino derivative **5** but to yellow **6** which is formed in 18% yield during aerobic work-up. A single crystal X-ray analysis (Fig. 1) established its *p*-benzoquinonediimine form.§ The C(2)–C(3′) bond length of 1.508(3) Å is indicative of the lack of conjugation between the two halves of this 12π electron system[13] and is even slightly longer than the corresponding distance in Bandrowski's base [1.485(6) Å].[14] The π-electron conjugation is thus confined to the upper and lower halves of the ligand. A fast intramolecular double proton transfer involving two tautomers generates in solution a structure of higher symmetry, which accounts for the NMR data.[15]‡

The metallation reaction of **6** with $[PtCl_2(cod)]$ (2 equiv.) at room temperature in CH_2Cl_2 required basic conditions and afforded **7** (*ca*. 15% yield) the ^1H NMR spectrum of which revealed no NH resonances. The molecular structure of **7** was elucidated by X-ray crystallography (Fig. 2).§



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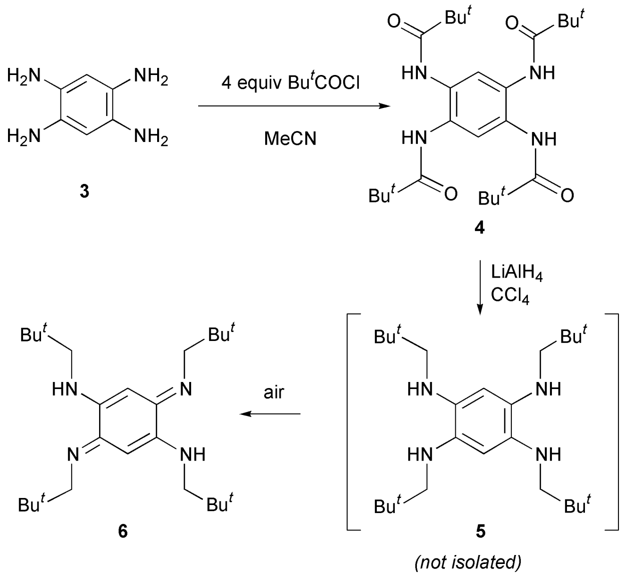
The molecule is centrosymmetric and the dianion-derived from **6** chelates each of the two Pt centres, thus acting as a tetradentate bridging ligand. The coordination geometry around the platinum centre is square planar, with the metal being only slightly out the molecular plane. The Pt atom completes its coordination with a Pt–C(19) σ-bond [2.12(1) Å] and a Pt–olefinic π-bond [with Pt–C distances of 2.17(2) and 2.140(9) Å]. Accordingly, the Pt···C(18) separation of 2.677(1) is non-bonding. The most striking feature of **7** is that electronic delocalization of the π-system occurs, in contrast to **6**, and is confined to the upper and lower halves of the ligand, as shown by the C(1)–C(2) bond length of 1.53(1) Å. The delocalization pathway also differs from that in complexes where the metal centres are linked by substituted *p*-benzoquinonediimines.[6,7] This important feature may be of wider occurrence in such systems than previously believed.[16,17] The molecular structure of **7** indicates that π-backbonding from the Pt orbitals into a π* orbital of the quinonediimine is occurring: the N(1)=C(1), C(1)–



Scheme 1 Synthesis of **6** from **3**.

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† Dedicated to Professor B. T. Heaton on the occasion of his 60th birthday, with our warmest congratulations and best wishes.

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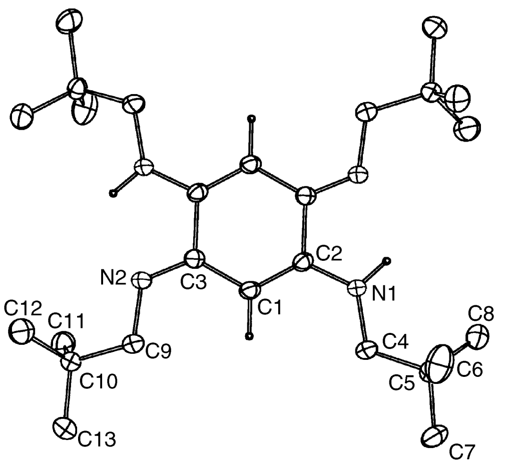

Fig. 1 View of the structure of **6** in the crystal. Selected bond lengths (Å) and bond angles (°): C(1)–C(2) 1.358(4), C(1)–C(3) 1.437(3), C(2)–C(3′) 1.508(3), C(2)–N(1) 1.346(3), C(3)–N(2) 1.286(3); C(2)–N(1)–C(4) 124.7(2), C(3)–N(2)–C(9) 120.1(2), C(2)–C(1)–C(3) 121.9(2), C(1)–C(2)–C(3′) 120.8(2), C(1)–C(2)–N(1) 125.7(2), C(1)–C(3)–N(2) 127.7(2), C(3′)–C(2)–N(1) 113.5(2).

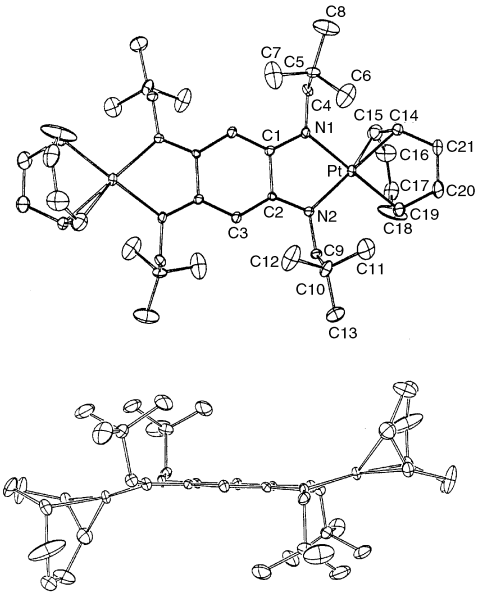

Fig. 2 Top- and side-views of the structure of **7** in the crystal. Selected bond lengths (Å) and bond angles (°): Pt–N(1) 2.082(7), Pt–C(14) 2.140(9), Pt–C(15) 2.17(2), Pt–C(19) 2.12(1), N(1)–C(1) 1.33(1), C(1)–C(2) 1.53(1), C(1)–C(3′) 1.40(1), C(2)–C(3) 1.37(1), C(2)–N(2) 1.33(1); N(1)–Pt–N(2) 78.2(3), N(1)–Pt–C(19) 174.2(4), N(2)–Pt–C(19) 99.6(3), C(14)–Pt–C(15) 36.4(4), Pt–N(1)–C(1) 114.5(6), N(1)–C(1)–C(2) 113.5(7), N(1)–C(1)–C(3′) 127.6(7), N(2)–C(2)–C(3) 127.1(7), C(1)–C(2)–C(3) 117.5(7).

C(3′), C(3′)=C(2′) and C(2′)–N(2′) bonds of the bridge show alternating lengthening and shortening relative to those of the free ligand (Table 1). Such differences are also observed in *p*-benzoquinonediimine systems.[7] Complex **7** is the first example of a binuclear complex bridged with ligands of type **2a** and extends previous results on related mononuclear complexes.[18,19] The electronic spectrum of **7** reveals a metal-to-ligand charge transfer (MLCT) absorption at λ_{max} = 504 nm.

Table 1 Comparison of interatomic distances (Å)

	C=N	C–C	C=C	C–N
6	1.286(3)	1.437(3)	1.358(4)	1.346(3)
7	1.33(1)	1.37(1)	1.40(1)	1.33(1)

Further studies on the electronic properties of **7** and analogous molecules are in progress as well as the synthesis of potential new mixed-valence dimers based on **6**.

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Notes and references

‡ *Selected data*: for **4**: MS(EI) *m/z* 474 (M$^+$); Anal. Calc. for $C_{26}H_{42}N_4O_4$: C, 65.78; H, 8.92; N, 11.81. Found: C, 66.31; H, 8.85; N, 11.86%. For **6**: NMR ($CDCl_3$): δ_H 1.00 (36H, s, CH_3), 2.95 (8H, s, CH_2), 5.16 (2H, s, Ph-H), 6.75 (2H, s, NH); δ_C 27.8 (CMe_3), 31.9 (CMe_3), 57.7 (CH_2N), 83.9 (C=C), 150.1 (C=N). UV–VIS (CH_2Cl_2): λ_{max} = 340 nm (intraquinone transition).

§ *Crystal data*: for **6**: $C_{26}H_{48}N_4$, M = 416.70, triclinic, space group $P\bar{1}$; a = 5.8950(7), b = 9.4081(9), c = 12.695(2) Å, α = 85.059(5), β = 77.180(5), γ = 88.044(5)°, V = 683.9(2) Å^3, Z = 1, μ(Mo-Kα) = 0.060 mm^{-1}, T = 173 K, 1384 data with $I > 3\sigma(I)$, final R = 0.051, R_w = 0.071, GOF = 1.126.

For **7**: $C_{42}H_{70}N_4Pt_2$, M = 1021.23, monoclinic, space group $P2_1/c$; a = 9.829(1), b = 22.615(1), c = 10.618(1) Å, β = 117.474(5)°, V = 2094.0(6) Å^3, Z = 2, μ(Mo-Kα) = 6.705 mm^{-1}, T = 173 K, 3184 data with $I > 3\sigma(I)$, final R = 0.047, R_w = 0.068, GOF = 1.289. Although the cod-derived ligands are disordered in the solid state structure, their $\sigma + \pi$-type bonding with the metals was unambiguously established.

CCDC 182/1814. See http://www.rsc.org/suppdata/cc/b0/b005952h/ for crystallographic files in .cif format.

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