

# Unprecedented amido-bridged dinuclear mixed-valence cobalt complexes: first structure of a dinuclear $\mu$ -OMe Co(II)/Co(III) complex

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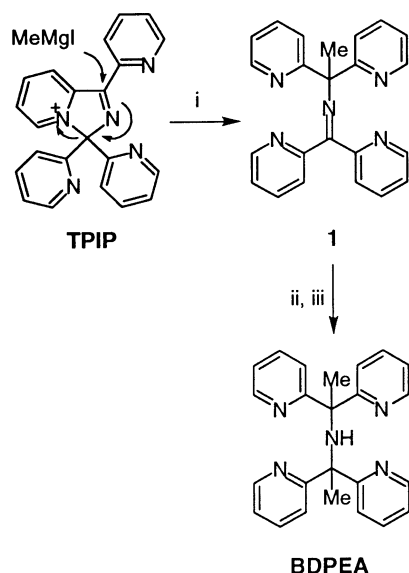
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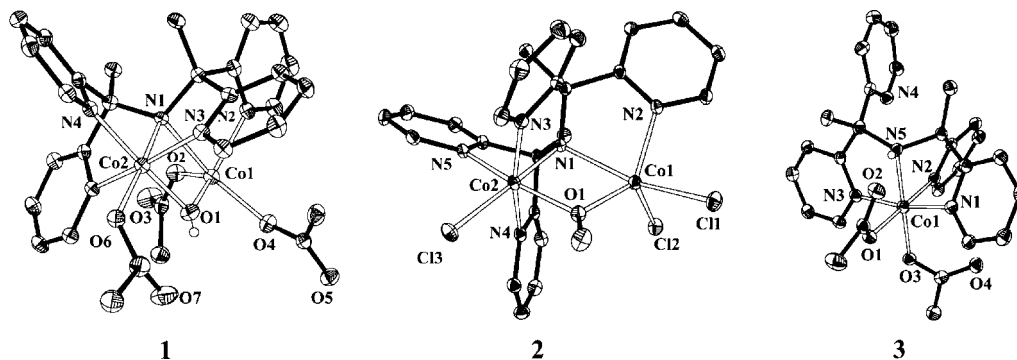
**The complexation of the pentadentate ligand bis[1,1-di(2-pyridyl)ethyl]amine (BDPEA), by cobalt(II) salts leads to novel Co(II)/Co(III) mixed-valence complexes: the secondary amine of the starting BDPEA is deprotonated, leading to a dinucleating bridging amido ligand.**

First-row transition metal complexes with aromatic nitrogen-containing ligands constitute a wide field of research relevant to biomimetic catalysts.<sup>1</sup> With this in mind, we have focused our interest on the development of new tetrapyridyl ligands. The first generation is represented by bis[di(2-pyridyl)methyl]amine (BDPMA), which exhibits two rather fragile benzylic C–H bonds.<sup>2</sup> In the presence of redox-active metallic salts, oxidative degradation of the ligand leads to the cationic compound 1,3,3-tris(2-pyridyl)-3*H*-imidazo[1,5-*a*]pyridin-4-ium (TPIP).<sup>3</sup> Starting from TPIP, and taking into account the high reactivity of the imidazolium ring of TPIP towards nucleophiles, we were able to synthesize a new robust tetrapyridyl ligand, namely bis[1,1-di(2-pyridyl)ethyl]amine (BDPEA) (Scheme 1), representing the second generation of this family of ligands.<sup>4</sup> BDPEA has the same coordination sites as BDPMA, but the fragile benzylic H atoms are substituted by more stable methyl groups. Complexation of BDPEA with MnCl<sub>2</sub>, FeCl<sub>3</sub> or CuCl<sub>2</sub> in stoichiometric amounts generates mononuclear complexes, in which BDPEA always acts as a tetradentate ligand *via* the secondary amine and three pyridine nitrogen atoms.<sup>5</sup>



**Scheme 1** Synthesis of BDPEA from TPIP. (i) MeMgI. (ii) MeMgI. (iii) H<sub>2</sub>O–H<sup>+</sup>.

In order to synthesise a monomeric cobalt–BDPEA complex, we reacted BDPEA with Co(OAc)<sub>2</sub> or CoCl<sub>2</sub> salts in 1 : 1 molar ratios in a MeCN–MeOH mixture. Subsequent crystallisation in a methyl *tert*-butyl ether (MTBE) atmosphere gave single crystals and the X-ray analysis indicated the unexpected formation of amido-bridged dinuclear cobalt complexes.<sup>†</sup> For the first time, we observed the deprotonation of the central amine of the BDPEA ligand during complexation with cobalt(II) ions. In all previously obtained complexes, BDPEA behaves as a neutral mononucleating ligand.<sup>5</sup> The X-ray structure of complex **1** (Fig. 1) shows that the anionic [BDPEA]<sup>–</sup> behaves as a bridging pentadentate ligand between the two cobalt centers.<sup>‡</sup> The Co1 center exhibits a distorted trigonal bipyramidal geometry. One pyridine atom (N2), one oxygen atom of an acetato ligand (O2), and the bridging hydroxo (O1) are in the equatorial positions, while another acetate oxygen atom (O4) and the bridging deprotonated nitrogen atom of the [BDPEA]<sup>–</sup> ligand (N1) are in axial positions (N1–Co1–O4 161.4°). The geometric environment of the second cobalt atom (Co2) is completely different and is best described as a distorted octahedron. Co2 is coordinated by three pyridyl N atoms (N3, N4, N5), one oxygen atom of an acetato ligand (O6) and the bridging amido (N1) and hydroxo (O1) ligands. Examining the coordination spheres in more detail, the asymmetric nature of the bridging atoms is remarkable (Co1–N1 2.283(3) and Co2–N1 1.896(3) Å; Co1–O1 1.928(3) and Co2–O1 1.871(3) Å). There are also significant differences in the Co–O<sub>Ac</sub> (Co1: 1.968(2) and 2.033(3); Co2: 1.955(2) Å) and the Co–N<sub>py</sub> (Co1: 2.054(3); Co2: 1.913–1.927 Å) distances, and in any case the bond lengths around the Co2 center are shorter than around Co1. The geometrical parameters of the metal centers are in good agreement with a mixed valence Co(II)/Co(III) complex: Co1 has a +2 oxidation state with a high-spin configuration and Co2 is a low-spin cobalt(III) ion. The structural parameters evidence a localized mixed-valence molecule in the solid state (Class I).<sup>6</sup> Complex **1** provides a rare example of a trapped-valence dinuclear Co(II)/Co(III) complex<sup>7,8</sup> and constitutes the first example of an amido-bridged dinuclear mixed-valence cobalt complex.<sup>9</sup> The structural motif of [Co<sup>II</sup>Co<sup>III</sup>–(BDPEA<sup>–</sup>)(OCH<sub>3</sub>)Cl<sub>3</sub>] (**2**) (see Fig. 1) is identical to that of complex **1**, the three acetato ligands are replaced by chloro ligands and a  $\mu$ -methoxo ligand takes the place of the hydroxo group present in **1**. We again found the same significant differences in the coordination spheres of the metal centers as observed in **1**. **2** represents the first example of a methoxo-bridged dinuclear Co(II)/Co(III) complex. The reproducible obtention of these new mixed-valence complexes was inherent to the use of cobalt itself and did not depend on the anions of the metal salt, Co(OAc)<sub>2</sub> for complex **1** and CoCl<sub>2</sub> for complex **2**, used in their preparation.



**Fig. 1** Crystal structure of complexes 1–3. Selected bond lengths (Å) for **1**: Co1–N1: 2.283(3); Co1–N2: 2.054(3); Co1–O1: 1.928(3); Co1–O2: 1.968(2); Co1–O4: 2.033(3); Co2–N1: 1.896(3); Co2–N3: 1.913(3); Co2–N4: 1.927(3); Co2–N5: 1.914(3); Co2–O1: 1.871(3); Co2–O6: 1.955(2). H atoms and a water molecule are omitted for clarity. For **2**: Co1–N1: 2.265(2); Co1–N2: 2.071(2); Co1–O1: 1.974(2); Co1–Cl1: 2.383(1); Co1–Cl2: 2.296(1); Co2–N1: 1.894(2); Co2–N3: 1.931(2); Co2–N4: 1.926(2); Co2–N5: 1.932(1); Co2–O1: 1.916(2); Co2–Cl3: 2.275(1). H atoms and a methanol molecule are omitted for clarity. For **3**: Co1–N1: 1.912(5); Co1–N2: 1.904(5); Co1–N3: 1.916(5); Co1–N5: 1.932(5); Co1–O1: 1.912(4); Co1–O3: 1.913(4). H atoms, a noncoordinated acetate and four water molecules are omitted for clarity.

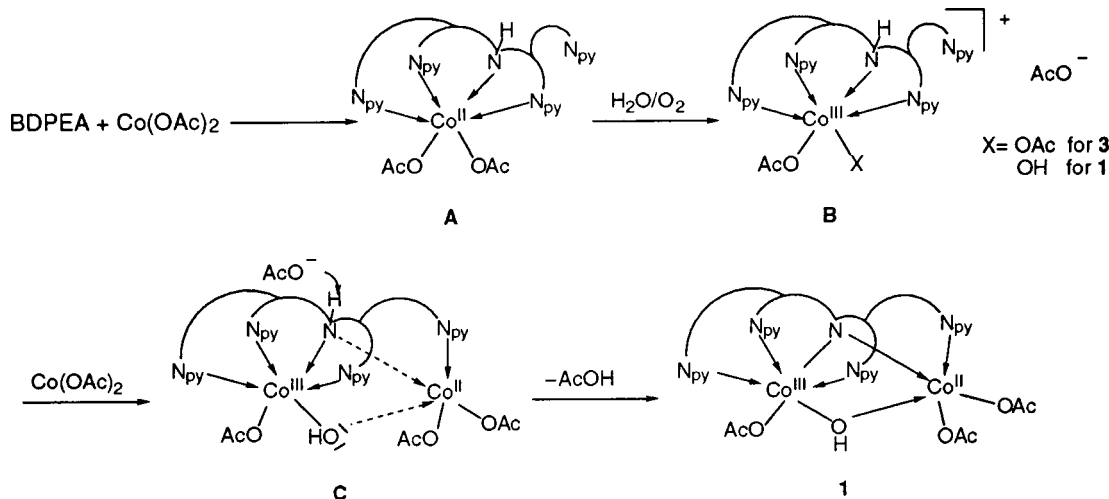
We observed that reaction of equimolar ratios of a cobalt salt and BDPEA gave mixed-valence complexes with a metal : ligand ratio of 2 : 1. Our target was the preparation of a mononuclear BDPEA–cobalt complex, so, we reacted one equivalent of cobalt(II) acetate with two equivalents of BDPEA. Crystallisation led to the more ‘traditional’ mononuclear complex **3** in 55% yield.<sup>†</sup> The crystal structure of **3** (Fig. 1) evidenced a distorted octahedral environment around the metal center.<sup>‡</sup> As expected, the cobalt ion is coordinated by the secondary amine and three pyridine nitrogen atoms of BDPEA. The coordination sphere is completed by two monodentate acetate groups. A third acetate ion and four molecules of water are present in the asymmetric unit of the lattice. The short distances between the cobalt and the oxygen and nitrogen atoms of the ligands are in good agreement with a cobalt complex in the oxidation state +3, which is confirmed by the presence of the third non-coordinated acetate ion.

At room temperature, the X-band EPR spectrum of a crystalline sample of **1** showed a broad, poorly resolved signal at  $g = 2$ . Variable-temperature magnetic susceptibility studies were performed on crystalline samples of **1** and **2**. For **1** the effective magnetic moment ( $\mu_{\text{eff}}$ ) per dinuclear complex decreased from 3.40  $\mu_{\text{B}}$  at 300 K to 2.07  $\mu_{\text{B}}$  at 3 K, for **2** it decreased from 4.12  $\mu_{\text{B}}$  (300 K) to 1.35  $\mu_{\text{B}}$  (1.97 K). The 300 K values are near to that expected for a high-spin ( $S = 3/2$ ) Co(II) ion in a trapped mixed-valence complex. The temperature dependence of  $\mu_{\text{eff}}$  is probably mainly due to a low thermal transition from high spin to low spin ( $S = 1/2$ ) and perhaps to weak intermolecular antiferromagnetic interactions

between Co<sup>II</sup> centers, through a hydrogen bond lattice.<sup>10</sup> No evident characteristic band or shoulder (see ref. 9) in the visible spectra of **1** and **2** can be attributed to the trigonal bipyramidal Co(II). Surprisingly, no EPR signal of cobalt was detectable in a CH<sub>2</sub>Cl<sub>2</sub> solution of **1** at 273 or 95 K. We have no rational explanation for this phenomenon and measurements at 4 K will be carried out later.

In conclusion, the tetrapyridyl ligand BDPEA and Co(II) salts provided mixed valence dinuclear complexes **1** and **2**. Compound **2** represents the first example of a methoxy-bridged dinuclear Co(II)/Co(III) complex. It seems reasonable to consider the mononuclear species **A** (Scheme 2) as the first possible intermediate on the way to **1**, because BDPEA behaves generally as a mononucleating tetradentate ligand. Facile air oxidation leads to a second intermediate **B** (isolated as complex **3**). The formation of this latter complex not being complete (55% with respect to the starting cobalt amount for **3**), an excess of the cobalt salt probably interacts with the fourth pyridine of BDPEA, giving rise to the dinuclear compound **C**, stabilized through bridging interactions between the amine nitrogen and the hydroxo group and the Co(II) ion. Subsequent deprotonation of the secondary amine (by the acetate anion or by the free ligand in excess in the medium, with the pyridines acting as proton sponges) affords the mixed-valence neutral complexes **1** or **2**. We were able to synthesise the mononuclear complex **3** by reaction of cobalt(II) with two equivalents of BDPEA. The potential catalytic activities of complexes **1** to **3** are currently under investigation.

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**Scheme 2** Proposed mechanism for the formation of complex **1**.

## Notes and references

† Preparation and characterization of complexes 1–3. Complex 1: To 50 mg (0.13 mmol) of BDPEA dissolved in 2 mL of CH<sub>3</sub>CN was added a methanolic solution (2 mL) of Co(OAc)<sub>2</sub>·4H<sub>2</sub>O (33 mg, 0.13 mmol). After stirring for 30 min, the resulting red solution was exposed to a MTBE atmosphere. After two weeks, 39 mg (86%) of small red crystals of 1 were collected. Elemental analysis calc. for C<sub>30</sub>H<sub>32</sub>N<sub>5</sub>O<sub>7</sub>Co<sub>2</sub>·2H<sub>2</sub>O: C 49.46, H 4.98, N 9.61; found: C 49.38, H 4.93, N 10.07%; FAB-MS (MNBA–DMF) *m/z* (% abundance): 633 (8) [Co<sup>III</sup>(BDPEA<sup>−</sup>)(OH)(OAc)<sub>2</sub>]<sup>+</sup>, 574 (6) [Co<sup>II</sup>(BDPEA<sup>−</sup>)(OH)(OAc)]<sup>+</sup>, 558 (5) [Co<sup>III</sup>(BDPEA)(OAc)<sub>2</sub>]<sup>+</sup>, 499 (100) [Co<sup>II</sup>(BDPEA)(OAc)]<sup>+</sup>; IR (KBr):  $\tilde{\nu}$  = 1566 and 1382 cm<sup>−1</sup> (C=O); UV-Vis (MeOH):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 502 (250), 406 (sh, 358), 306 (sh, 6200), 264 (22 100), 208 nm (56 500 M<sup>−1</sup> cm<sup>−1</sup>).

Complex 2: This complex was prepared as described above for 1, using 83 mg of BDPEA (0.17 mmol) and 40 mg of CoCl<sub>2</sub>·4H<sub>2</sub>O (0.17 mmol). After one week, 11 mg (20%) of small red crystals of 2 were collected. Elemental analysis calc. for C<sub>25</sub>H<sub>25</sub>N<sub>5</sub>Cl<sub>3</sub>OCo<sub>2</sub>·CH<sub>3</sub>OH: C 46.77, H 4.38, N 10.49; found: C 46.61, H 4.12, N 10.50%; FAB-MS (MNBA–DMSO) *m/z* (% abundance): 599 (96) [Co<sup>II</sup>Co<sup>III</sup>(BDPEA<sup>−</sup>)(OCH<sub>3</sub>)Cl<sub>2</sub>]<sup>+</sup>, 568 (30) [Co<sup>II</sup>(BDPEA<sup>−</sup>)Cl<sub>2</sub>]<sup>+</sup>, 475 (100) [Co<sup>II</sup>(BDPEA)Cl]<sup>+</sup>.

Complex 3: 41 mg (0.11 mmol) of BDPEA and 14 mg (0.06 mmol) of Co(OAc)<sub>2</sub>·4H<sub>2</sub>O were dissolved separately in CH<sub>3</sub>CN (total volume of 2 mL). The resulting red solution was stirred for 30 min and then exposed to a MTBE atmosphere. After two weeks, 21 mg (55%) of small red crystals of 3 were collected. Elemental analysis calc. for C<sub>30</sub>H<sub>32</sub>N<sub>5</sub>O<sub>6</sub>Co·4H<sub>2</sub>O: C 52.25, H 5.85, N 10.16; found: C 52.09, H 5.63, N 10.68%; FAB-MS (MNBA–DMF) *m/z* (% abundance): 558 (4) [Co<sup>III</sup>(BDPEA)(OAc)<sub>2</sub>]<sup>+</sup>, 499 (100) [Co<sup>II</sup>(BDPEA)(OAc)]<sup>+</sup>; IR (KBr):  $\tilde{\nu}$  = 1561 and 1378 cm<sup>−1</sup> (C=O); UV-Vis (MeOH):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 496 (243), 404 (sh, 375), 314 (sh, 8000), 262 (30 900), 242 (38 300), 212 nm (66 200 M<sup>−1</sup> cm<sup>−1</sup>). We were not able to record NMR spectra due to paramagnetic influences during the experiments. The reason could be a slow degradation of the complex followed by reduction of the metal, because of the higher stability of cobalt(II) in a non-complexed form.

‡ Crystal data for complexes 1–3. Reflections were collected at low temperatures using oil-coated shock-cooled crystals<sup>11</sup> on a STOE-IPDS diffractometer. The structures were solved by direct methods (SHELXS-97)<sup>12</sup> and refined using the least-squares method on  $F^2$ .<sup>13</sup>

Complex 1: C<sub>30</sub>H<sub>34</sub>Co<sub>2</sub>N<sub>5</sub>O<sub>8</sub>,  $M = 710.48$ , monoclinic,  $P2_1/n$ ,  $a = 11.450(2)$ ,  $b = 14.7600(10)$ ,  $c = 17.806(3)$  Å,  $\beta = 96.54(2)^\circ$ ,  $V = 2989.7(8)$  Å<sup>3</sup>,  $Z = 8$ ,  $\rho_c = 1.578$  Mg m<sup>−3</sup>,  $F(000) = 1468$ ,  $\lambda = 0.71073$  Å,  $T = 173(2)$  K,  $\mu(\text{Mo-K}\alpha) = 1.170$  mm<sup>−1</sup>, crystal size  $0.40 \times 0.30 \times 0.05$  mm,  $1.80^\circ \leq \theta \leq 24.13^\circ$ , 23 542 reflections (4726 independent,  $R_{\text{int}} = 0.0754$ ), largest electron density residue: 0.653 e Å<sup>−3</sup>,  $R_1$  [for  $F > 2\sigma(F)$ ] = 0.0418 and  $wR_2 = 0.1039$  (all data) with  $R_1 = \sum \|F_o| - |F_c| \| / \sum |F_o|$  and  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{0.5}$ .

Complex 2: C<sub>26</sub>H<sub>29</sub>Cl<sub>3</sub>Co<sub>2</sub>N<sub>5</sub>O<sub>2</sub>,  $M = 667.75$ , monoclinic,  $P2_1/n$ ,  $a = 9.8080(10)$ ,  $b = 16.784(2)$ ,  $c = 17.036(2)$  Å,  $\beta = 102.020(10)^\circ$ ,  $V = 2742.9(5)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho_c = 1.617$  Mg m<sup>−3</sup>,  $F(000) = 1364$ ,  $\lambda = 0.71073$  Å,  $T = 173(2)$  K,  $\mu(\text{Mo-K}\alpha) = 1.536$  mm<sup>−1</sup>, crystal size  $0.4 \times 0.4 \times 0.1$  mm,  $1.72^\circ \leq \theta \leq 24.25^\circ$ , 24 651 reflections (4257 independent,  $R_{\text{int}} = 0.0470$ ), 358 parameters, largest electron density residue: 0.349 e Å<sup>−3</sup>,  $R_1$  [for  $F > 2\sigma(F)$ ] = 0.0312 and  $wR_2 = 0.0742$  (all data).

Complex 3: C<sub>30</sub>H<sub>40</sub>CoN<sub>5</sub>O<sub>10</sub>,  $M = 689.60$ , triclinic,  $P\bar{1}$ ,  $a = 11.427(3)$ ,  $b = 12.785(3)$ ,  $c = 12.989(3)$  Å,  $\alpha = 66.80(3)$ ,  $\beta = 89.43(3)$ ,  $\gamma = 70.24(3)^\circ$ ,  $V = 1624.7(7)$  Å<sup>3</sup>,  $Z = 2$ ,  $\rho_c = 1.410$  Mg m<sup>−3</sup>,  $F(000) = 724$ ,  $\lambda = 0.71073$  Å,  $T = 173(2)$  K,  $\mu(\text{Mo-K}\alpha) = 0.591$  mm<sup>−1</sup>, crystal size  $0.4 \times 0.2 \times 0.1$  mm,  $1.91^\circ \leq \theta \leq 23.25^\circ$ , 11 111 reflections (4229 independent,  $R_{\text{int}} = 0.0755$ ), 483 parameters, largest electron density residue: 0.934 e Å<sup>−3</sup>,  $R_1$  [for  $F > 2\sigma(F)$ ] = 0.0622 and  $wR_2 = 0.1817$  (all data). CCDC reference number 440/218. See <http://www.rsc.org/suppdata/nj/b0/b007907n/> for crystallographic files in .cif format.

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