Mendeleev Commun., 2003, 13(5), 202–204

New polydentate Schiff bases and their cobalt complexes

Natalia E. Borisova,[a] **Yuri A. Ustynyuk,***[a] **Marina D. Reshetova,**[a] **Grigory G. Aleksandrov,**[b] **Igor L. Eremenko**[b] **and Ilya I. Moiseev**[b]

[a] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119992 Moscow, Russian Federation.*
Fax: +7 095 939 2677; e-mail: yust@nmr.chem.msu.su
[b] *N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation.*
Fax: +7 095 954 1279; e-mail: ilerem@igic.ras.ru

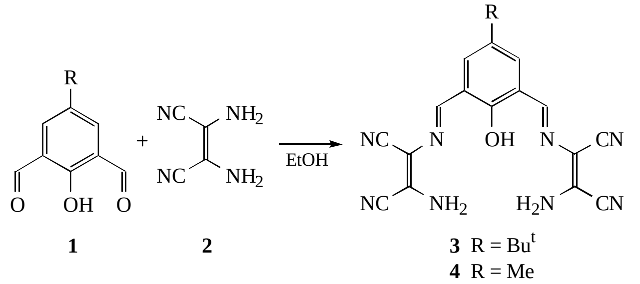
10.1070/MC2003v013n05ABEH001777

The condensation of 2,6-diformyl-4R-phenols (R = Me, Bu^t) 1 with 2,3-diaminomaleodinitrile 2 in the absence of metal ions affords new polydentate acyclic [1+2] Schiff bases 4 and 5, which form binuclear and tetranuclear cobalt complexes.

As a rule, the condensation of 2,6-diformyl-4-alkylphenols **1** with diamines in the presence of metal ions, which act as template agents, affords mono- or binuclear metal complexes with [2+2]-macrocyclic Schiff bases.[1,2] In the absence of metal ions, aliphatic α,ω-diamines react with **1** to form only oligomeric products.[3,4] The condensation of **1** with *o*-phenylenediamine and its derivatives bearing substituents at the aromatic ring occurs more complicatedly and is accompanied by the reduction of two of the four C=N bonds in the [2+2]-macrocycle to CH_2NH fragments.[4,5]

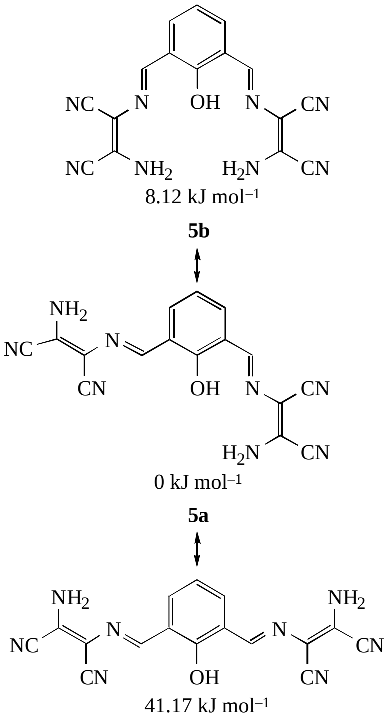
2,3-Diaminomaleodinitrile **2**, in which the nucleophilicity of amino groups is substantially diminished due to conjugation with the electron-withdrawing CN groups, reacts with **1** in the presence of copper ions to form binuclear complexes of macrocyclic Schiff bases, whose structures were postulated from the elemental analysis and IR spectroscopic data.[6]

We studied the reactions of **1** with **2** in boiling anhydrous ethanol in the absence of metal ions and found that they give only acyclic [1+2]-condensation products **3** and **4** in 75% yield† regardless of the ratio between the reactants (1:2 or 1:1) (Scheme 1).



Scheme 1

Compounds **3** and **4** are yellow amorphous substances, which are soluble in DMSO and ethyl acetate and insoluble in nonpolar solvents. They were characterised by NMR spectroscopy, mass spectrometry, IR spectroscopy and elemental analysis.



Scheme 2

The theoretical study of model compound **5** containing no alkyl substituent by the DFT (gradient corrected functional PBE, TZ2p basis set[7]) showed three minima on the potential energy surface (PES) of this compound. *cis*,*trans*-Conformer **5a** is most thermodynamically favourable. *cis*,*cis*-Conformer **5b** lies higher in energy by 8.12 kJ mol^{-1}. *trans*,*trans*-Conformer **5c** is least stable. According to this, the coexistence of the *cis*,*trans*- and *cis*,*cis*-conformers in a solution can be expected for **3** and **4** (Scheme 2).

The reaction of two equivalents of cobalt(II) trimethylacetate with **3** in ethyl acetate at room temperature affords black-violet amorphous binuclear complex **6**‡ (Scheme 3), which is poorly

---

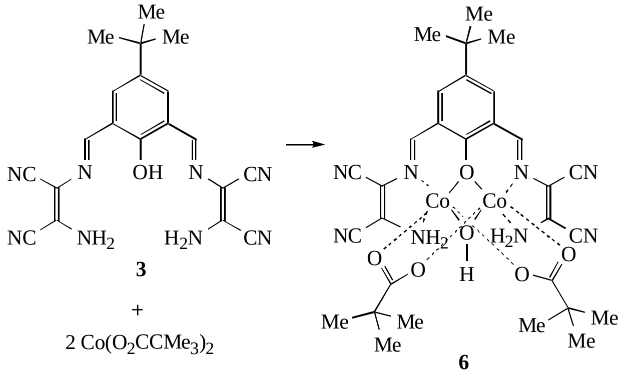
† *Synthesis of* **3** *and* **4**. Compounds **1** (0.84 mmol) and **2** (1.68 mmol) in hot anhydrous ethanol (25 ml) were refluxed for 3 h. The precipitate formed was filtered off, the filtrate was halved by evaporation and cooled, and an additional portion of the precipitate was filtered off. The yield was 70–75%.

3: mp 282–284 °C. ^{1}H NMR ([$^2H_6$]DMSO) δ: 1.30 (s, 3Me), 8.06 (br. s, $2NH_2$), 8.08 (s, 2CH), 8.65 (s, 2CH=N), 11.35 (s, OH). ^{13}C NMR ([$^2H_6$]DMSO) δ: 31.06, 34.22, 102.81, 113.92, 114.45, 120.85, 126.41, 130.69, 142.57, 154.32, 156.37. MS, *m/z*: 386 [100%, (M)$^+$]. IR (oil, ν/cm^{-1}): 1620 (C=N, CH), 2216, 2245 (C≡N), 3200, 3330, 3470, 3630 (NH, OH). Found (%): C, 61.92; H, 4.52; N, 28.72. Calc. for $C_{20}H_{18}N_8O$ (%): C, 62.17; H, 4.69; N, 28.99.

4: decomp. > 290 °C. ^{1}H NMR ([$^2H_6$]DMSO) δ: 2.27 (s, Me), 7.86 (s, CH), 7.96 (br. s, $2NH_2$), 8.44 (s, 2CH=N), 11.15 (br. s, OH). ^{13}C NMR ([$^2H_6$]DMSO) δ: 19.92, 102.81, 113.79, 114.46, 121.22, 126.45, 128.83, 133.96, 153.49, 156.32. MS, *m/z*: 344 [13%, (M)$^+$], 237 [20%, (M – 107)$^+$] 53 [100%, (NCCNH)$^+$]. IR (oil, ν/cm^{-1}): 1620 (C=N, CH), 2220, 2250 (C≡N), 3230, 3350, 3430 (NH, OH). Found (%): C, 58.88; H, 3.41; N, 32.26. Calc. for $C_{17}H_{12}N_8O$ (%): C, 59.30; H, 3.51; N. 32.54.

‡ *Synthesis of* **6**. A solution of **3** (386 mg, 1 mmol) in boiling ethyl acetate (30 ml) was added to cobalt trimethylacetate (522 mg), and the resulting solution was cooled to room temperature. After a day, **6** was filtered off (70 mg). An additional portion of the substance can be isolated as a black powder after additional evaporation of the reaction mixture. The overall yield of **6** was 450 mg (76%), mp > 350 °C. ESI-MS, *m/z*: 518.2 $(LCo_2O)^+$, 444.2 $(LCo^+H)^+$. IR (oil, ν/cm^{-1}): 1610 (C=N, CH), 2190, 2245 (C≡N), 3350, 3600 (NH, OH). Found (%): C, 50.85; H, 4.71; N, 14.71. Calc. for $C_{30}H_{36}N_8O_6Co_2\cdot 0.5C_5H_{10}O_2$ (%): C, 50.49; H, 5.28; N, 14.49.

Synthesis of **7**. Recrystallization of complex **6** (70 mg) from hot DMF gave **7** (65 mg, 80%), mp > 350 °C. ESI-MS, *m/z*: 522.0 $(LCo_2OH + 3H)^+$, 444.2 $(LCo^+H)^+$, 385.3 $(L – H)^-$. Found (%): C, 47.92; H, 4.07; N, 17.80. Calc. for $C_{50}H_{52}N_{16}O_8Co_4$ (%): C, 48.32; H, 4.37; N, 18.03.



Scheme 3

soluble in most organic solvents but soluble in ethanol and DMF. The structure of **6** was established by mass spectrometry and IR spectroscopy and confirmed by elemental analysis data. In the ESI mass spectra, complex **6** gives no peak due to the molecular ion. Fragmentation occurs similarly to that observed previously in the FAB spectra of complexes of this type with the elimination of trimethylacetate extra-ligands.[8,9]

According to the DFT calculations, triplet state **6a** corresponds to the global minimum on the PES of **6** (Figure 1). The metal atoms in this triplet state are localised in the cavity of the almost planar polydentate ligands in the octahedral environment formed by two iminic and two aminic nitrogen atoms in the *cis*-positions, phenolic oxygen atom, oxygen atom of the μ^2-hydroxy group in the basal plane, and oxygen atoms of two μ^2-trimethylacetate ligands in apical positions in the *trans*-position to each other. The local minimum of singlet complex **6b** lies by 68.95 kJ mol^{-1} higher in energy. In this complex, one of the metal atoms exists in the octahedral environment, and the second atom is in the tetragonal-pyramidal environment. One of the trimethylacetate extra-ligands is bidentate-bridging, and the second extra-ligand is monodentate-terminal.

After recrystallization of **6** from DMF, two bridging bidentate trimethylacetate ligands eliminate from two molecules of **6** as trimethylacetic acid molecules due to the deprotonation of two NH_2 groups, and tetranuclear complex **7** forms as black-violet crystals.[‡]

The crystal structure of **7**[§] is formed of neutral tetranuclear complexes (Figure 2) and solvate dimethylformamide molecules bound by hydrogen bonds and van der Waals interactions. In turn, the centrosymmetric tetranuclear complex consists of two $[(\mu\text{-L})Co_2(\mu_3\text{-OH})(\mu\text{-piv})]$ fragments (L = **3**-2H) bound to each other by the (μ-L) and (μ_3-OH) groups. In the binuclear fragment, the pairs of cobalt atoms are bound by the bridging (μ-piv), (μ_3-OH), and μ-L ligands. The Co–O bond lengths involving the pivalate [1.913, 1.934(5) Å] and μ_3-hydroxy [*cf.* 1.855(5) Å] bridges are usual for the bi- and polynuclear cobalt trimethylacetate complexes.[10] The polydentate coordination of the ligand in the binuclear fragments resulted in the formation of two five-membered and two six-membered metallocycles with somewhat different characters of distortion of their planarity. In combination with the hydroxy group and bridging pivalates, this coordination provides a distorted pentacoordination of the metal atoms in the binuclear fragments, which is supplemented to octahedral for the Co(1) atom by O(2a) and for the Co(2) atom by N(1a), *i.e.*, by the oxygen and nitrogen atoms of an adjacent binuclear fragment shifted from the initial posi-tion by the crystallographic symmetry centre. The centrosym-metric character of the tetranuclear complex determines the planarity of the Co_4 fragment, which is an almost regular rhombus with the internal sharp angle [Co(1)Co(2)Co(1a)] close to 60°. The lengths of the rhombus sides Co(1)···Co(2) and Co(1)···Co(2a) are equal to 2.751(1) and 2.836(1) Å, respec-tively. The plane drawn through the atoms of four joint metallo-cycles of ligand L forms a dihedral angle of 122.8° with the plane of the metallic rhombus. The asymmetric coordination [in fact, chemically equivalent N(1) and N(4) atoms coordinate two and one metal atoms, respectively] results in some difference in the distortion of planarity of the metallocycles: the N(3)C(11)–C(12)N(4)Co(2) five-memebred metallocycle is almost planar (mean deviation, m.d. = 0.02 Å), and for analogous N(1)C(1)–C(2)N(2)Co(1) the distortion of planarity is much greater (m.d. = 0.09 Å). The dihedral angle between these planes is equal to 155.7°. The distortions in planarity of the six-mem-bered metallocycles (m.d. = 0.06 Å) are also great, and the angle between them equals 166.4°.

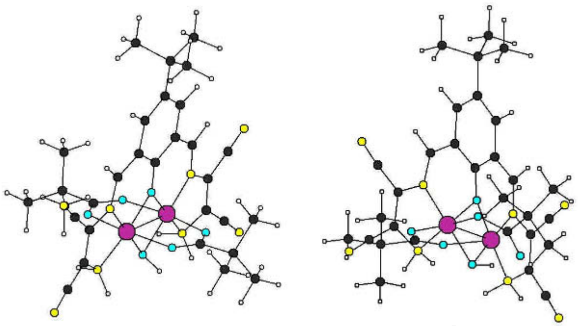


Figure 1 Structures of triplet **6a** and singlet **6b** complexes according to the density functional calculations.

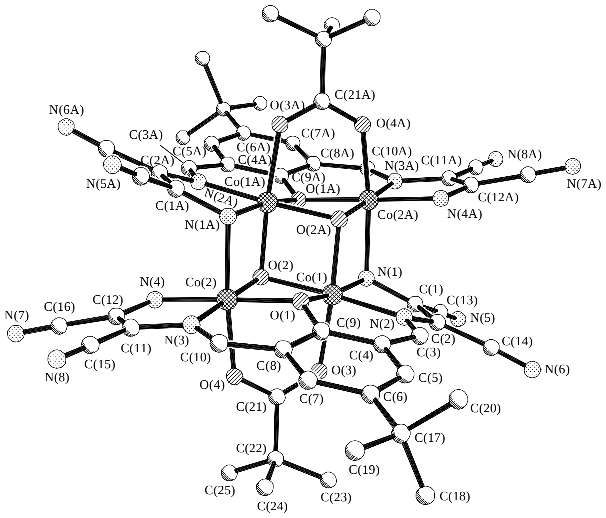


Figure 2 Structure of tetranuclear complex **7** according to the X-ray diffraction data.

New polydentate Schiff bases **3** and **4** also readily form binuclear copper and nickel complexes. Their structures and properties will be described elsewhere. Since **3** and **4** contain

---

[§] *Crystallographic data for* **7**. $C_{50}H_{52}N_{16}O_8Co_4\cdot6(C_3H_7NO)$, M = 1679.37, $F(000)$ = 1752, monoclinic system, at T = 110 K a = 11.280(3), b = = 15.948(3), c = 21.882(5) Å, V = 3927(2) Å^3, space group $P2_1/c$, Z = 2, d_{calc} = 1.420 g cm^{-3}, μ = 0.905 mm^{-1}. Intensities of 15430 reflections [7317 with $I \geq 2\sigma(I)$, of which 4271 (R_{int} = 0.0395) are independent] were measured using a Bruker AXS SMART 1000 CCD three-circle diffractometer at 180 K (graphite-monochromated Mo$K\alpha$ radiation, λ = = 0.7107 Å, ω scan mode, $2 \leq 2\theta \leq 60°$). Software: SMART[11] for collecting frames of data, indexing, integration of intensity of reflections and scaling; SADABS[11] for empirical absorption correction. The structure was solved by direct methods using the SHELXS97 program and refined against F^2 in the anisotropic approximation for non-hydrogen atoms using the SHELXL97 package.[11] The H atoms were located on the difference electron density map and refined in the rider approximation. The final R_1 values are 0.0677 [$wR_2(F^2)$ = 0.1395] for 4271 reflections, GOOF = 0.999.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 208871. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2003.

four CN groups with coordination ability and accessible to various chemical transformations, more complicated supramolecular assemblies can be developed from these ligands and their complexes.

This work was supported by the Russian Foundation for Basic Research (grant nos. 02-03-32101 and 03-03-06588mac).

References

1 P. Guerriero, S. Tamburini and P. A. Vigato, *Coord. Chem. Rev.*, 1995, **139**, 17.

2 H. Okawa, H. Furutachi and D. Fenton, *Coord. Chem. Rev.*, 1998, **174**, 51.

3 H. Adams, N. A. Bailey, D. E. Fenton, S. Moss, C. O. Rodriguez de Barbarin and G. Jones, *J. Chem. Soc., Dalton Trans.*, 1986, 693.

4 Yu. Tian, J. Tong, G. Frenzen and J. Sun, *J. Org. Chem.*, 1999, **64**, 1442.

5 Yu. A. Ustynyuk, N. E. Borisova, V. M. Nosova, M. D. Reshetova, S. S. Talismanov, S. E. Nefedov, G. G. Alexandrov, I. L. Eremenko and I. I. Moiseev, *Izv. Akad. Nauk, Ser. Khim.*, 2002, 454 (*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 488).

6 L. K. Thompson, S. K. Mandal, S. S. Tandon, J. N. Bridson and M. K. Park, *Inorg. Chem.*, 1996, **35**, 3117.

7 D. N. Laikov, *Chem. Phys. Lett.*, 1997, **281**, 151.

8 K. Brychcy, K. Drager, K.-J. Jens, M. Tilset and U. Behrens, *Chem. Ber.*, 1994, **127**, 465.

9 K. Brychcy, K.-J. Jens, M. Tilset and U. Behrens, *Chem. Ber.*, 1994, **127**, 991.

10 M. A. Golubnichaya, A. A. Sidorov, I. G. Fomina, M. O. Ponina, S. M. Deomidov, S. E. Nefedov, I. L. Eremenko and I. I. Moiseev, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 1773 (*Russ. Chem. Bull.*, 1999, **48**, 1773).

11 (*a*) *SMART (control) and SAINT (integration) software*, version 5.0, Bruker AXS Inc., Madison, WI, 1997; (*b*) G.M.Sheldrick, *SADABS, program for scaling and correction of area detector data*, University of Göttingen, 1997 (based on the method of R. H. Blessing, *Acta Crystallogr., A*, 1995, **51**, 33); (*c*) G. M. Sheldrick, *SHELXS97. Program for the Solution of Crystal Structures*. University of Göttingen, Germany, 1997; (*d*) G. M. Sheldrick, *SHELXL97. Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, 1997.

Received: 24th April 2003; Com. 03/2103