

# First structural characterization of an eight-coordinate cobalt(II) complex containing five-membered chelate rings: evidence for d-orbital $\sigma$ -stabilization energy favoring eight- over six-coordination at cobalt(II) ions

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For the first time, an eight-coordinate cobalt(II) complex is presented where only five-membered chelate rings are formed with the coordinated ligand; evidence is put forward that in addition to reasons of the tetraazamacrocyclic nature of the ligand 2,11-diaza-[3.3](2,6)pyridinophane (L), eight-coordination at cobalt(II) ions is, to some extent, favored with respect to six-coordination by the presence of d-orbital  $\sigma$ -stabilization energy as calculated by angular overlap methods.

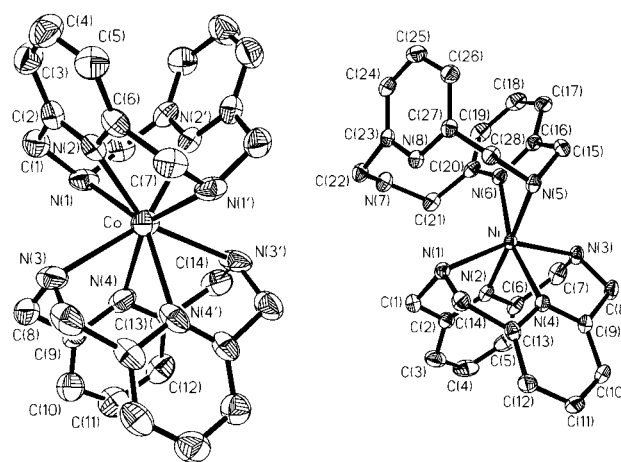
Structurally established eight-coordination at a cobalt ion is very rare and, to our knowledge, has only been reported for  $[\text{Co}(\text{NO}_3)_4]^{2-}$  ions where the oxygen donor atoms assume a dodecahedral arrangement.<sup>1</sup> The existence of eight-coordinate cobalt(II) ions has also been implied to exist, without any structural proof, in another cobalt complex containing the ligand 1,8-naphthyridine.<sup>2</sup> Here we introduce the first structural characterization of an eight-coordinate cobalt(II) complex in which the ligand forms only five-membered instead of four-membered chelate rings with the metal ion and, further, we present evidence that eight-coordination at cobalt(II) ions is favored, to some extent, by d-orbital  $\sigma$ -stabilization energy as calculated by angular overlap methods.<sup>3</sup>

In a recent publication<sup>4</sup> we demonstrated that eight-coordinate iron(II) and -(III) complexes can be obtained with the tetraazamacrocyclic ligand 2,11-diaza-[3.3](2,6)pyridinophane (L). In these complexes the metal ion is positioned in a sandwich-like fashion between the two ligand moieties. We showed that a distorted dodecahedral coordination geometry is achieved because of the *syn* boat–boat conformation of the two coordinated macrocyclic ligands.

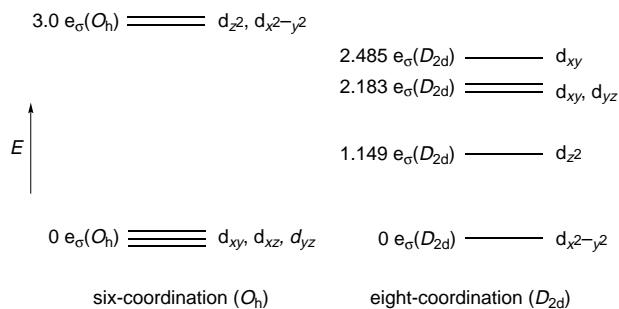
The lilac cobalt(II) complex  $[\text{CoL}_2]^{2+}$  was prepared by the addition of 1 equiv. of cobalt(II) perchlorate to a methanolic solution containing 2 equiv. of the tetraazamacrocyclic ligand. Upon recrystallization from acetonitrile–diethyl ether, the complex was isolated either directly as the perchlorate salt  $[\text{CoL}_2][\text{ClO}_4]_2$  **1** or, after a preceding metathesis with sodium tetraphenylborate, as the tetraphenylborate salt  $[\text{CoL}_2][\text{BPh}_4]_2 \cdot \text{Et}_2\text{O}$  **2**. Analogous procedures render the violet nickel(II) complexes  $[\text{NiL}_2][\text{ClO}_4]_2 \cdot \text{MeCN}$  **3** and  $[\text{NiL}_2][\text{BPh}_4]_2$  **4**.

The structure determinations<sup>†</sup> of both cobalt complexes unambiguously establish eight-coordination at the cobalt(II) ions. The coordination geometry around the cobalt(II) ion in **2** (Fig. 1) is best described as a distorted dodecahedron. Thus, the two diazapyridinophane ligands form a torsional angle of approximately  $70^\circ$  and there are substantial differences in lengths ( $> 0.1 \text{ \AA}$ ) observed between the two crystallographically distinct  $\text{Co}-\text{N}_{\text{py}}$  and the two  $\text{Co}-\text{N}_{\text{amine}}$  bonds, respectively. In contrast, in **1** (structure not shown) the cobalt ion is located in a nearly perfect dodecahedral coordination environment (torsional angle of  $90^\circ$ ), providing the complex with  $D_{2d}$  overall symmetry. The average  $\text{Co}-\text{N}_{\text{py}}$  and  $\text{Co}-\text{N}_{\text{amine}}$  bond lengths in **1** (which are approximately the same as the average bond lengths in **2**) are  $2.308 \pm 0.002$  and  $2.389 \pm 0.005 \text{ \AA}$ , respectively; the average  $\text{N}_{\text{py}}-\text{Co}-\text{N}_{\text{py}}$  and  $\text{N}_{\text{amine}}-\text{Co}-\text{N}_{\text{amine}}$

angles, defined by the  $\text{Co}-\text{N}$  bonds to the same ligand moiety, are determined to be  $72.96$  and  $132.61^\circ$ , respectively. The magnetic moment of the solid cobalt(II) complex **2**,  $4.45 \mu_{\text{B}}$ , is considerably lower than that of an octahedral cobalt(II) complex<sup>5</sup> but similar to that of cobalt(II) complexes with a tetrahedral<sup>5</sup> or a dodecahedral coordination geometry<sup>2,6</sup> around the metal ion. Because the magnetic moment scarcely changes upon dissolving the complex in dimethyl sulfoxide ( $4.41 \mu_{\text{B}}$ ) and because eight-coordinate cobalt complexes are obtained in the solid state irrespective of the counter anions used in the preparation, it is difficult to imagine that the coordination number eight at the cobalt ion is just the result of some solid state effect and that it prevails only in the solid state. Thus, this study demonstrates that coordination number eight can be readily achieved with the 'relatively small', late first row transition metal ion cobalt in the moderately low +2 oxidation state. In the two previously investigated cobalt complexes where eight-coordination is observed or assumed, the ligands have rather small chelate bites forming four-membered chelate rings, whereby the interaction of the two donor atoms of a



**Fig. 1** Perspective views of the complex cations  $[\text{CoL}_2]^{2+}$  and  $[\text{NiL}_2]^{2+}$  in **2** and **3**, respectively, showing thermal ellipsoids at 50% probability and the atom numbering scheme. The primed and unprimed atoms in **2** are related by a twofold rotation axis. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ): **2**:  $\text{Co}-\text{N}(1)$  2.316(2),  $\text{Co}-\text{N}(2)$  2.229(2),  $\text{Co}-\text{N}(3)$  2.438(3),  $\text{Co}-\text{N}(4)$  2.366(3);  $\text{N}(1)-\text{Co}-\text{N}(2)$  73.38(8),  $\text{N}(1)-\text{Co}-\text{N}(3)$  86.26(10),  $\text{N}(1)-\text{Co}-\text{N}(4)$  77.55(8),  $\text{N}(1)-\text{Co}-\text{N}(1')$  136.05(11),  $\text{N}(1)-\text{Co}-\text{N}(2')$  72.34(8),  $\text{N}(1)-\text{Co}-\text{N}(3')$  112.44(10),  $\text{N}(1)-\text{Co}-\text{N}(4')$  145.56(8),  $\text{N}(2)-\text{Co}-\text{N}(3)$  78.28(8),  $\text{N}(2)-\text{Co}-\text{N}(4)$  137.73(8),  $\text{N}(2)-\text{Co}-\text{N}(2')$  76.09(11),  $\text{N}(2)-\text{Co}-\text{N}(3')$  150.35(8),  $\text{N}(2)-\text{Co}-\text{N}(4')$  122.80(8),  $\text{N}(3)-\text{Co}-\text{N}(4)$  69.75(9),  $\text{N}(3)-\text{Co}-\text{N}(3')$  129.97(11),  $\text{N}(3)-\text{Co}-\text{N}(4')$  70.00(9),  $\text{N}(4)-\text{Co}-\text{N}(4')$  71.08(11). **3**:  $\text{Ni}-\text{N}(1)$  2.172(2),  $\text{Ni}-\text{N}(2)$  2.021(3),  $\text{Ni}-\text{N}(3)$  2.187(2),  $\text{Ni}-\text{N}(4)$  2.029(2),  $\text{Ni}-\text{N}(5)$  2.085(2),  $\text{Ni}-\text{N}(6)$  2.138(2);  $\text{N}(1)-\text{Ni}-\text{N}(2)$  79.45(9),  $\text{N}(1)-\text{Ni}-\text{N}(3)$  150.43(9),  $\text{N}(1)-\text{Ni}-\text{N}(4)$  78.46(9),  $\text{N}(1)-\text{Ni}-\text{N}(5)$  97.55(9),  $\text{N}(1)-\text{Ni}-\text{N}(6)$  116.19(9),  $\text{N}(2)-\text{Ni}-\text{N}(3)$  79.07(10),  $\text{N}(2)-\text{Ni}-\text{N}(4)$  84.34(10),  $\text{N}(2)-\text{Ni}-\text{N}(5)$  176.68(10),  $\text{N}(2)-\text{Ni}-\text{N}(6)$  102.38(10),  $\text{N}(3)-\text{Ni}-\text{N}(4)$  79.42(9),  $\text{N}(3)-\text{Ni}-\text{N}(5)$  104.24(10),  $\text{N}(3)-\text{Ni}-\text{N}(6)$  88.19(9),  $\text{N}(4)-\text{Ni}-\text{N}(5)$  96.50(10),  $\text{N}(4)-\text{Ni}-\text{N}(6)$  164.60(9),  $\text{N}(5)-\text{Ni}-\text{N}(6)$  77.60(9).



**Fig. 2** Energy diagrams for the d orbitals of a six-coordinate metal ion in an octahedral coordination geometry ( $O_h$ ) and of an eight-coordinate metal ion in a dodecahedral coordination geometry ( $D_{2d}$ ). The indicated energies of d orbitals are calculated by angular overlap methods<sup>3</sup> in units of  $e_\sigma = \beta S_R^2$ , assuming only  $\sigma$ -interactions between the metal ion and ligand donor atoms.

ligand with the metal ion is significantly favored by the spacial proximity of the donor atoms. In this study, for the first time, eight-coordination has been structurally established for a cobalt(II) ion where only five-membered chelate rings are present in the complex.

In contrast, the nickel(II) ion in **3**<sup>†</sup> is coordinated to all nitrogen donor atoms of one of the tetraazamacrocyclic ligands and to one each of the pyridine and amine nitrogen atoms of the second ligand (Fig. 1). Thus, the nickel ion assumes an octahedral coordination geometry which is also found in a preliminary structure determination of **4**.

Fig. 2 compares the energy levels obtained for an ideal octahedral and dodecahedral (using the angles within complex **1**) metal ion by angular overlap methods. With the assumption that  $\pi$  bonding can be neglected in these complexes, the dodecahedral site preference expressed as the difference in d-orbital  $\sigma$ -stabilization energies (calculated by angular overlap methods)<sup>3</sup> is:  $8 e_\sigma(D_{2d}) - 6 e_\sigma(O_h)$  for high-spin  $d^6$ ,  $6.85 e_\sigma(D_{2d}) - 6 e_\sigma(O_h)$  for high-spin  $d^7$  and  $4.67 e_\sigma(D_{2d}) - 6 e_\sigma(O_h)$  for a  $d^8$  metal ion. Considering that  $|e_\sigma(D_{2d})|$  is smaller than  $|e_\sigma(O_h)|$  owing to the larger M–N bond lengths in eight-coordinate complexes, eight- as well as six-coordination is possible for the cobalt(II) complex [depending on the relative magnitude of  $e_\sigma(D_{2d})$  with respect to  $e_\sigma(O_h)$ ], while only six-coordination is predicted to occur with nickel(II) ions according to angular overlap methods.<sup>‡</sup> Clearly, eight coordination at the cobalt(II) as well as at the iron(II) ion<sup>4</sup> is favored by the distinct

spacial properties of the tetraazamacrocyclic ligand **L**. However, in light of the finding that, in comparison with the cobalt(II) ion, the only slightly smaller nickel ion prefers octahedral over dodecahedral coordination geometry, evidence has been put forward that to some extent eight-coordination at iron(II) and cobalt(II) centres is stabilized with respect to six-coordination by electronic factors as illustrated by the d-orbital  $\sigma$ -stabilization energy calculated by angular overlap methods.

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## Footnotes and References

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<sup>†</sup> *Crystal data*: **1**:  $C_{28}H_{32}Cl_2CoN_8O_8$ , triclinic, space group  $P1$  (eightfold-primitive with the equivalent positions at  $x, y, z; 0.5 + x, y, 0.5 + z; 0.25 + x, 0.25 + y, 0.75 + z; 0.75 + x, 0.75 + y, 0.25 + z; 0.5 + x, 0.5 + y, 0.5 + z; x, 0.5 + y, z; 0.75 + x, 0.25 + y, 0.25 + z; 0.25 + x, 0.75 + y, 0.75 + z$ ),  $a = 23.162(5)$ ,  $b = 23.162(5)$ ,  $c = 11.380(4)$  Å,  $\alpha = 90.00$ ,  $\beta = 90.00$ ,  $\gamma = 90.00$ ,  $U = 6105(3)$  Å<sup>3</sup>,  $Z = 8$ ,  $D_c = 1.607$  g cm<sup>-3</sup>; 8938 unique reflections [6055 reflections with  $F_o > 4\sigma(F_o)$ ];  $T = 293$  K;  $\mu(\text{Mo-K}\alpha) = 8.03$  cm<sup>-1</sup>; 428 parameters;  $R = 0.0508$  [ $F_o > 4\sigma(F_o)$ ]. The crystal is a non-merohedral twin composed of four components.

**2**:  $C_{80}H_{82}B_2CoN_8O$ , monoclinic, space group  $C2/c$  (no. 15),  $a = 22.772(11)$ ,  $b = 15.050(2)$ ,  $c = 21.595(15)$  Å,  $\beta = 115.70(3)^\circ$ ,  $U = 6669(6)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.247$  g cm<sup>-3</sup>; 6847 unique reflections [4175 reflections with  $F_o > 4\sigma(F_o)$ ];  $T = 153$  K;  $\mu(\text{Mo-K}\alpha) = 3.11$  cm<sup>-1</sup>; 428 parameters;  $R = 0.0529$  [ $F_o > 4\sigma(F_o)$ ].

**3**:  $C_{30}H_{35}Cl_2N_9NiO_8$ , monoclinic, space group  $P2_1/n$  (no. 14),  $a = 11.216(3)$ ,  $b = 15.995(5)$ ,  $c = 17.981(5)$  Å,  $\beta = 92.23(3)^\circ$ ,  $U = 3223(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.606$  g cm<sup>-3</sup>; 7536 unique reflections [5665 reflections with  $F_o > 4\sigma(F_o)$ ];  $T = 153$  K;  $\mu(\text{Mo-K}\alpha) = 8.35$  cm<sup>-1</sup>; 464 parameters;  $R = 0.0456$  [ $F_o > 4\sigma(F_o)$ ]. CCDC 182/627.

<sup>‡</sup> The calculation of the ligand field stabilization energies for dodecahedral and octahedral high-spin metal ions with  $d^6$ ,  $d^7$  and  $d^8$  electron configurations shows that eight-coordination geometry is favored for a  $d^6$  metal ion, while six-coordination is preferred by  $d^8$  metal ions. For a  $d^7$  metal ion, the difference in ligand field stabilization energy between both geometries is small, but favors octahedral coordination geometry.

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