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### THE AUTOXIDATION REACTION PATHWAY OF THE COBALT(II) COMPLEX OF 2,6-BIS(2-(3,6-DIAZAHEXYL))PYRIDINE THROUGH FORMATION OF A COBALT DIOXYGEN COMPLEX INTERMEDIATE. EFFECT OF LIGAND CONFORMATION ON THE REACTION PRODUCT

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## COMMUNICATION

# THE AUTOXIDATION REACTION PATHWAY OF THE COBALT(II) COMPLEX OF 2,6-BIS(2-(3,6-DIAZAHXYL))PYRIDINE THROUGH FORMATION OF A COBALT DIOXYGEN COMPLEX INTERMEDIATE. EFFECT OF LIGAND CONFORMATION ON THE REACTION PRODUCT

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In a previous study<sup>1</sup> it was proposed that the conformations of pyridyl-containing pentamines in the coordination sphere of peroxo-bridged binuclear cobalt dioxygen complexes have a profound effect on the reaction pathways and mechanisms of redox rearrangements of such complexes. Thus the binuclear monobridged cobalt dioxygen complexes having 1,9-bis(2-pyridyl)-2,5,8-triazanonane (PYDIEN)<sup>2</sup> and 1,11-bis(2-pyridyl)-2,6,10-triazaundecane (PYDPT)<sup>3</sup> as ligands undergo oxidative dehydrogenation under mild conditions, in accordance with the fact that the aliphatic polyamine bridges in these complexes have conformations that allow the facile formation of imine double bonds conjugated with the terminal pyridine rings.<sup>2-5</sup> The analogous dioxygen complex, containing the pentamine 2,6-bis(2-(3,6-diazahexyl)pyridine (EPYDEN) as the coordinated ligand, does not undergo oxidative dehydrogenation under the same conditions. On that basis it was suggested<sup>1</sup> that of the two possible conformers of this dioxygen complex, it must have the structure indicated by **1**, in which the aliphatic side chains are folded in a manner that makes it impossible to form conjugated imine groups by oxidative dehydrogenation.

In order to confirm the suggested structure, attempts have recently been made to crystallize the binuclear cobalt dioxygen complex containing the ligand EPYDEN for X-ray structure determination. A solution of 1.2 mmol EPYDEN.4HCL and 1.2 mmol CoI<sub>2</sub> in 5.0 cm<sup>3</sup> of water was prepared under a dioxygen atmosphere. The pH was adjusted to 5.6 with 2M aqueous KOH solution and was maintained at 15° for an extended period. After 2.5 days the dark red crystals that formed were filtered off and washed with ethanol (yield 7%). Further crystallization occurred on slow evaporation of the filtrate at ambient room temperature. The yield of the second batch was 52%. A crystal structure was carried out on a crystal taken from the first crop of product.

The crystalline complex thus obtained turned out to be not the dioxygen complex that had been expected, but the iodide substitution product, 3S-2,6-bis(2-(3,6-diazahexyl))pyridine cobalt(III) iodide. Details of the crystal and molecular structure of this new complex will be reported elsewhere.<sup>6</sup> The cobalt atom is octahedrally coordinated by five nitrogen atoms of the EPYDEN ligand and the sixth position located *trans* to the pyridyl nitrogen is occupied by an iodide. The remaining iodides

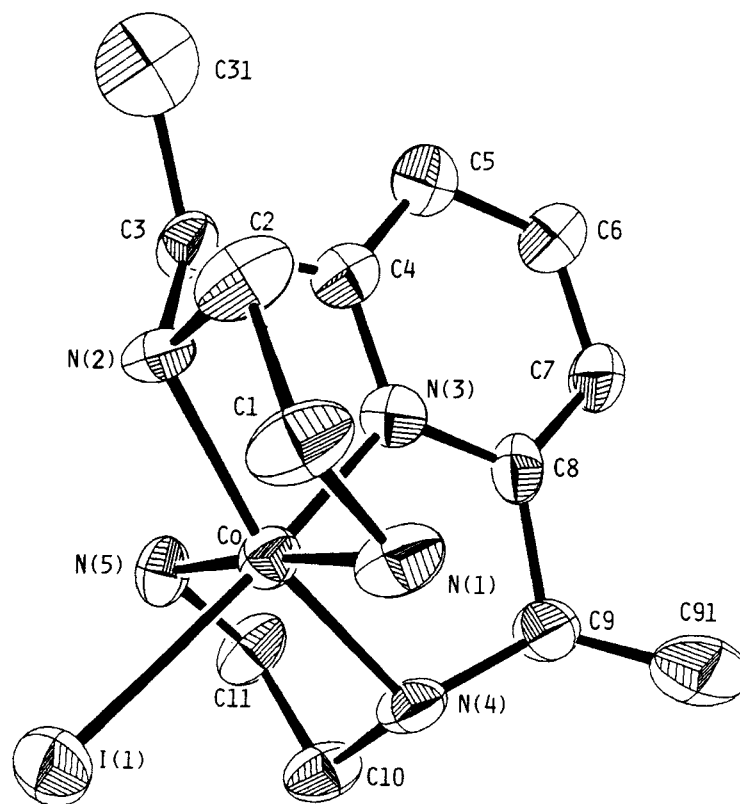
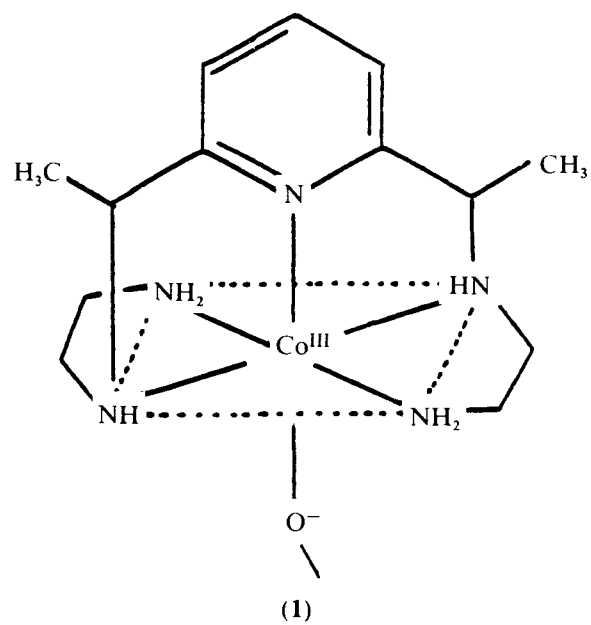


FIGURE 1 ORTEP drawing of the cation.

TABLE I  
Selected Bond Distances in Angstrom Units.

Atom 1	Atom 2	Distance <sup>a</sup>
Co	N(1)	1.981(8)
Co	N(2)	1.999(8)
Co	N(3)	1.868(8)
Co	N(4)	1.982(8)
Co	N(5)	1.981(8)
Co	I(1)	2.613(2)

<sup>a</sup>Numbers in parentheses are estimated standard deviations.

and water molecules form an intermolecular hydrogen bonding network throughout the structure.<sup>7</sup>

An ORTEP diagram of the iodo cobalt(III) complex, together with the numbering scheme employed, is given in Figure 1. Atoms I(2), I(3), O(1) and O(2) are located in the lattice. A good least-squares plane is found in the structure through the pyridine ring. Selected bond lengths and angles for the coordination sphere are listed in Table I and Table II, respectively.

Inspection of the Co-N bond lengths, Table I, shows considerable shortening of the Co-N(3) distance. The shortening compared to the other Co-pyridine N distances (Table III) is between 0.034 Å to 0.172 Å. The significant deviations from 109.56 degrees of most of the tetrahedral angles seem to provide an indication of steric strain. Distortions from octahedral geometry about the cobalt atom are observed for the angles formed between the cobalt atom and nitrogens N(3) and N(4), as well as N(2) and N(3). These distortions are probably the result of the requirement of the aromatic ring, which forces the angles Co-N(3)-C8, Co-N(3)-C4, N(3)-C4-C3, and N(3)-C8-C9 to be as close to 120° as possible. All bond angles forming the 5-membered chelate rings designated by the atoms Co-N(2)-C3-C4-N(3) and Co-N(4)-C9-C9-N(3) are less than the theoretical bond angles with the exception of the bond angle between Co-N(4)-C9. For the binuclear monobridged cobalt dioxygen complexes having 1,9-bis(2-pyridyl)-2,5,8-triazanonane (PYDIEN) or 1,11-bis(2-pyridyl)-2,6,10-triazaundecane (PYDPT) as ligands which undergo facile oxidative dehydrogenation, the strained tetrahedral bond angles that are converted to trigonal bond angles are 118.2° and 112.6°, respectively. The bond angle of 118.2° for the tetrahedral angle is approximately the same as the analogous trigonal bond angle in 2,12-bis(2-pyridyl)-3,7,11-triazatrideca-2,11-diene(methyl)cobalt(III) diiodide dihydrate.<sup>12</sup> Thus the distortion of tetrahedral bond angles toward the trigonal value plays an important role in the lowering of the energy of the reaction pathway for dehydrogenation of the amine ligand to the imine.

TABLE II  
Selected Bond Angles in Degrees.<sup>a</sup>

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
N(1)	Co	N(2)	86.5(3)	Co	N(2)	C3	106.2(8)
N(1)	Co	N(4)	91.0(4)	N(3)	C3	C4	105.9(8)
N(2)	Co	N(3)	81.6(4)	C(3)	C4	N(3)	112.5(9)
N(3)	Co	N(4)	84.1(4)	C(4)	N(3)	Co	119.2(9)
N(4)	Co	N(5)	86.4(4)	Co	N(4)	C9	111.4(9)
C4	C3	C31	114.4(9)	N(4)	C9	C8	109.4(8)
C8	C9	C91	112(1)	C(9)	C8	N(3)	113.8(9)
				C(8)	N(3)	Co	117.9(9)

<sup>a</sup>Numbers in parentheses are estimated standard deviations.

TABLE III  
 Co-Pyridine N Bond Distances.

Complex <sup>a</sup>	Bond Distance.
[Co(PYDIEN)]O <sub>2</sub> <sup>b</sup>	1.902(8)
	1.910(7)
[Co(PYDPT)]O <sub>2</sub> <sup>c</sup>	1.948(9)
	1.928(7)
	1.945(8)
Co(PYDIEN)NO <sub>2</sub> <sup>d</sup>	1.982(9)
	1.941(4)
Co(PYDIEN)Cl <sup>e</sup>	1.962(5)
	1.97(1)
Co(PYDPT)Cl <sup>f</sup>	1.95(1)
	1.97(1)
Co(TRIEN)(PY)Cl <sup>g</sup>	1.95(1)
	2.004(6)
Co(DMPY=DPT)(CH <sub>3</sub> ) <sup>h</sup>	2.04(1)
	1.95(1)

<sup>a</sup>Abbreviations: TRIEN = triethylenetetramine; PY = pyridine; DMPY = DPT = 2,12bis(2-pyridyl)-3,7,11-triazatrideca-2,11-diene. <sup>b</sup>Ref. 4. <sup>c</sup>Ref. 5. <sup>d</sup>Ref. 8. <sup>e</sup>Ref. 9. <sup>f</sup>Ref. 10. <sup>g</sup>Ref. 11. <sup>h</sup>Ref. 12.

The iodide complex (Figure 1) was isolated from the reaction mixture in which the binuclear dioxygen complex was first formed, which was then subjected to the expected metal-centred redox rearrangement reaction.<sup>1</sup> This reaction has been shown to produce the inert cobalt(III) complex of the ligand and hydrogen peroxide, and is hydroxide ion-catalyzed at high pH<sup>13</sup>. Thus it would not be surprising that conversion of the binuclear dioxygen complex to the inert Co(III) mononuclear analog by peroxide displacement would also be catalyzed by iodide ion. Such a reaction therefore represents a new type of substitution reaction of cobalt dioxygen complexes, and warrants further investigation.

On the basis of the substitution reactions that have been carried out on Co(III) complexes, it is highly probable that the conformation of the pentamine, EPYDEN in Figure 1 is the same as that of the cobalt dioxygen complex from which it was formed.<sup>14</sup> Thus the present results confirm the previous prediction<sup>1</sup> that the folding of the aliphatic diamine chains of the EPYDEN structure provides a sufficient barrier for the formation of conjugated double bonds to prevent the oxidative dehydrogenation reaction that readily takes place with the analogous ligands PYDIEN and PYDPT.

#### SUPPLEMENTARY MATERIAL

A table of calculated and observed structure factors and additional details on the crystal structure of the iodide complex (Figure 1) may be obtained from P.R. Rudolf, Department of Chemistry, Texas A and M University, College Station, Texas 77843.

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