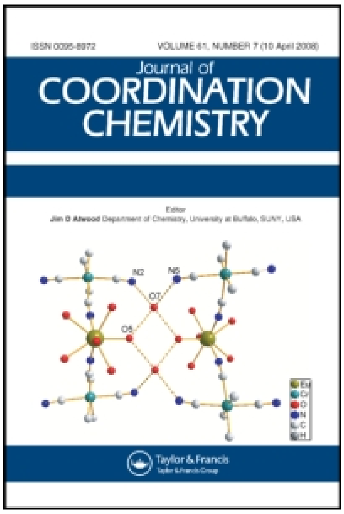

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

PENTAGONAL BIPYRAMIDAL COMPLEXES OF Co(II) WITH SINGLY- AND DOUBLY-DEPROTONATED2',2''-(2,6-PYRIDINDIYLDI-ETHYLIDENE)DIOXAMOHYDRAZIDE The Crystal Structure of [Diaqua-2',2''-(2,6-Pyridindiyldiethylidene) Dioxamohydrazidecobalt(II)] Hexahydrate

Ivana Ivanović[a]; Katarina Andjelković[a]; Vladimir Beljanski[a]; Bogdan V. Prelesnik[b]; Vukadin M. Leovac[c]; Mirijana Momirović[d]
[a] Faculty of Chemistry, University of Belgrade, Belgrade, Yugoslavia [b] Laboratory of Condensed Matter Physics, Institute of Nuclear Sciences, Belgrade, Yugoslavia [c] Institute of Chemistry, Faculty of Sciences, Novi Sad, Yugoslavia [d] Institute of General and Physical Chemistry, Belgrade, Yugoslavia

To cite this Article Ivanović, Ivana , Andjelković, Katarina , Beljanski, Vladimir , Prelesnik, Bogdan V. , Leovac, Vukadin M. and Momirović, Mirijana(1997) 'PENTAGONAL BIPYRAMIDAL COMPLEXES OF Co(II) WITH SINGLY- AND DOUBLY-DEPROTONATED2',2''-(2,6-PYRIDINDIYLDI-ETHYLIDENE)DIOXAMOHYDRAZIDE The Crystal Structure of [Diaqua-2',2''-(2,6-Pyridindiyldiethylidene) Dioxamohydrazidecobalt(II)] Hexahydrate', Journal of Coordination Chemistry, 42: 4, 335 — 342

To link to this Article: DOI: 10.1080/00958979708022862

URL: http://dx.doi.org/10.1080/00958979708022862

J. Coord. Chem., 1997, Vol. 42, pp. 335–342
Reprints available directly from the publisher
Photocopying permitted by license only

PENTAGONAL BIPYRAMIDAL COMPLEXES OF Co(II) WITH SINGLY- AND DOUBLY-DEPROTONATED 2′,2‴-(2,6-PYRIDINDIYLDI-ETHYLIDENE)DIOXAMOHYDRAZIDE

The Crystal Structure of [Diaqua-2′,2‴-(2,6-Pyridindiyldiethylidene) Dioxamohydrazidecobalt(II)] Hexahydrate

IVANA IVANOVIĆ[a], KATARINA ANDJELKOVIĆ[a],* VLADIMIR BELJANSKI[a], BOGDAN V. PRELESNIK[b], VUKADIN M. LEOVAC[c] and MIRIJANA MOMIROVIĆ[d]

[a]*Faculty of Chemistry, University of Belgrade, P.O.B. 158, 11001 Belgrade, Yugoslavia;* [b]*Laboratory of Condensed Matter Physics, Institute of Nuclear Sciences "Vinca" P.O.B. 522, 11000 Belgrade, Yugoslavia;* [c]*Institute of Chemistry, Faculty of Sciences, Trg D. Obradovica 3, 21000 Novi Sad, Yugoslavia;* [d]*Institute of General and Physical Chemistry, P.O.B. 551, 11000 Belgrade, Yugoslavia*

(Received 24 October 1996)

This paper reports the first Co(II) complexes with a singly- and doubly-deprotonated H_2L ligand (H_2L = 2′,2‴-(2,6-pyridindiyldiethylidene)dioxamohydrazide belonging to the planar pentadentate class. The complexes were characterized by elemental analysis, thermal analysis, IR spectroscopy, molar conductivity and magnetic susceptibility measurements. The crystal structure of $[Co(L)(H_2O)_2]\cdot 6H_2O$ complex has been determined. The pentagonal bipyramidal geometry present in the previously synthesized complex $[Co(H_2L)(H_2O)(MeOH)](ClO_4)_2$, wherein the ligand is present in a neutral form, has been preserved around Co(II).

Keywords: pentagonal bipyramidal complexes; cobalt(II); pentadentates; X-ray structure

---

*Author for correspondence

INTRODUCTION

So far, fifteen Co(II) complexes [2-4] with pentagonal bipyramidal geometry (PBP) have been synthesized. The last among them was $[Co(H_2L)(H_2O)(MeOH)](ClO_4)_2$ [1], where H_2L is 2′,2‴-(2,6-pyridindiyldiethylidene)dioxamohydrazide. In all the fifteen complexes mentioned, the planar pentadentate ligands have been coordinated in a neutral form.

It has been considered significant to investigate the changes that would possibly accrue from the ligand's single or double deprotonation. This has been addressed for the first time through the synthesis of $[Co(HL)(H_2O)_2]ClO_4$ and $[Co(L-)(H_2O)_2]\cdot 6H_2O$ complexes and an X-ray crystal structure analysis of the latter.

It should be noted that in the literature there are only three cases describing the behaviour of the first transition series metal complexes of pentagonal bipyramidal structure, in the course of a chelate ligand deprotonation. The first was a description of a tetrameric structure of pentacoordinated copper(II) [5]. The second was an octahedral Zn(II) [6, 7] dimeric structure while the third concerned a Mn(II) [8] complex where, despite deprotonation, the ligand remained planar and the complex maintained PBP geometry. In all three examples, however, the ligand appears to have a dianionic form.

The sole example of a singly-deprotonated ligand structure that maintained PBP geometry is the Cr(III) complex with 2,6-diacethylpyridinesemicarbazone [9]. Our work has revealed that in case of Co(II), the PBP structure remains unchanged after double deprotonation, as well as in the case when the complex has been singly deprotonated.

EXPERIMENTAL

$[Co(L)(H_2O)_2]\cdot 6H_2O$

Here 2 cm^3 of NH_4OH solution was added to a solution of $[Co(H_2L)(H_2O-)(MeOH)](ClO_4)_2$ [1] (0.64 g, 1 mmol) in water (45 cm^3). The mixture was gently heated for 10 minutes. During this process the colour changed from orange to dark red. After 24h at room temperature, prismatic single crystals suitable for X-ray crystal structure analysis were obtained. Yield: 0.44g, 83%. *Anal.*: calcd. for $CoC_{13}H_{29}N_7O_{12}$: C, 29.21; H, 5.43; N, 18.35%. Found: C, 29.27; H, 5.57; N, 18.13%.

$[Co(HL)(H_2O)_2]ClO_4$

In this synthesis, 2 cm^3 of NH_4OH solution was added dropwise to a solution of $[Co(H_2L)(H_2O)(MeOH)](ClO_4)_2$ [1] (0.64 g, 1 mmol) in absolute methanol (50

TABLE I Crystal data and data collection details for $[Co(L)(H_2O)_2]\cdot 6H_2O$.

Formula	$C_{13}H_{29}N_7O_{12}Co$	λ(Å)	0.71073
M	534.4	μ(MoKα)/mm^{-1}	0.83
Crystal system	triclinic	Scan mode	$\omega/2\Theta$
Space group	$P\bar{1}$ (no 2)	2 Θ range (°)	4-52
a/Å	8.947(1)	data collcd.	4319
b/Å	10.474(1)	independent reflexions having $I > 3\sigma(I)$	3421
c/Å	13.846(1)		
α/°	107.79(2)		
β/°	94.12(2)		
γ/°	69.94(5)		
V/Å^3	1129.5(5)	R	0.038
F(000)	558	R_w[a]	0.039
Z	2		
D_x/M gm^{-3}	1.57		

[a] $W = 1/\sigma^2(F_o)$.

cm^3), with gentle heating. During this process, tiny orange crystals were precipitated. The solid was recrystallized from water. Yield: 0.32 g, 61%.

Anal.: calcd. for $CoC_{13}H_{18}N_7O_{10}Cl$: C, 29.63; H, 3.42; N, 18.61%. Found: C, 29.52; H, 3.56; N, 18.53%.

Measurements

IR spectra were run on a Perkin Elmer FT-IR 1726 spectrophotometer using KBr discs. Thermal analyses were carried out with a Du Pont 9900 instrument, with a 910 differential scanning calorimeter and a 951 thermogravimeter analyzer module. Heating rate: 10°/min in nitrogen atmosphere. Molar conductance of DMF solutions (1×10^{-3} mol dm^{-3}) was measured at room temperature on a Jenway 4009 digital conductivity meter.

Magnetic moments were determined (291K) using a magnetic susceptibility balance (MSB-MK1), manufactured by Sherwood Scientific Ltd. The susceptibility was corrected for diamagnetic contributions.

X-ray Crystal Structure Analysis

Intensities were measured on dark red single crystal of dimensions $0.25\times0.30\times0.45$ mm with an Enraf Nonius CAD-4 diffractometer equipped with a graphite monochromator and Mo anticathode. Unit cell parameters were determined from 25 high angle reflections. A summary of crystal data and experimental details is listed in Table I. Data were corrected for Lorenz polarization, decay and extinction, but no absorption correction was applied. The phase problem was solved by a Patterson synthesis and the structure was refined

TABLE II Positional and thermal parameters of non-hydrogen atoms of $[Co(L)(H_2O)_2]\cdot 6H_2O$.

Atom	*x/a*	*y/b*	*z/c*	$B_{eq}/Å^2$
Co	−0.01354(4)	0.25041(4)	0.24541(3)	2.209(7)
O1	0.1891(2)	0.2985(2)	0.3234(2)	2.94(5)
OW1	−0.0419(3)	0.1921(2)	0.3865(2)	3.13(5)
O2	0.1796(2)	0.0493(2)	0.1917(2)	3.04(5)
OW2	0.0370(3)	0.2970(3)	0.1095(2)	4.41(6)
OW3	0.2934(3)	0.4075(3)	0.9445(3)	6.9(1)
O3	0.2859(2)	0.5945(2)	0.4747(2)	3.40(5)
O4	0.2310(3)	−0.3038(2)	0.0436(2)	4.24(6)
OW4	0.4551(3)	0.0428(2)	0.3195(2)	4.17(6)
OW5	0.2321(3)	0.9736(2)	0.6233(2)	4.66(6)
OW6	0.0492(4)	0.7831(3)	0.3391(2)	5.43(7)
OW7	−0.0107(3)	0.6310(3)	0.1363(3)	6.72(9)
OW8	0.2432(3)	0.9580(3)	0.4110(2)	5.49(7)
N1	−0.0095(3)	−0.0517(2)	0.1160(2)	2.81(6)
N2	−0.1101(3)	0.0881(2)	0.1550(2)	2.66(5)
N3	−0.2705(3)	0.3476(2)	0.2356(2)	2.55(5)
N4	−0.0874(3)	0.4773(2)	0.3324(2)	2.57(5)
N5	0.0264(3)	0.5338(2)	0.3838(2)	2.75(5)
N6	0.4309(3)	0.3607(3)	0.4269(2)	3.36(6)
N7	0.4093(3)	−0.2006(3)	0.1213(2)	3.36(7)
C1	−0.3395(3)	0.4876(3)	0.2754(2)	2.70(6)
C2	−0.2312(3)	0.5621(3)	0.3325(2)	2.77(6)
C3	−0.2880(4)	0.7195(3)	0.3801(3)	4.18(9)
C4	0.1624(3)	0.4272(3)	0.3732(2)	2.43(6)
C5	0.2996(3)	0.4694(3)	0.4304(2)	2.54(6)
C6	0.1366(3)	−0.0541(3)	0.1396(2)	2.42(6)
C7	0.2640(3)	−0.1998(3)	0.0968(2)	2.78(7)
C8	−0.2591(3)	0.1149(3)	0.1394(3)	2.78(7)
C9	−0.3331(4)	0.0057(4)	0.0845(3)	3.99(8)
C10	−0.3536(3)	0.2669(3)	0.1804(2)	2.74(7)
C11	−0.5143(3)	0.3280(4)	0.1625(3)	3.52(8)
C12	−0.5859(4)	0.4728(4)	0.2040(3)	3.85(8)
C13	−0.5006(4)	0.5548(3)	0.2612(3)	3.41(8)

by full-matrix least-squares methods and difference Fourier syntheses. All H atoms were found in the difference Fourier map and were refined isotropically. Computer programs used were from the SDP system [13] on a PDP 11/73 computer. Positional parameters of non-hydrogen atoms are given in Table II.

RESULTS AND DISCUSSION

Complexes $[Co(L)(H_2O)_2]\cdot 6H_2O$ and $[Co(HL)(H_2O)_2]ClO_4$ were obtained by heating aqueous or methanolic solutions of $[Co(H_2L)(H_2O)(MeOH)](ClO_4)_2$, respectively, in the presence of ammonia. The existence of crystalline and coordinated water molecules in $[Co(L)(H_2O)_2]\cdot 6H_2O$ has been confirmed by thermal analysis performed in a nitrogen steam. It has been observed that crystalline water (endothermic) loss starts at room temperature and ends at 71°C when the endothermic loss of coordinated water commences and continues to 165°C. At 363°C, the organic ligand decomposes.

Considerable numbers of water molecules and hydrogen bonds present in the crystal structure of $[Co(L)(H_2O)_2]\cdot 6H_2O$ lead to an extremely wide and intense band in the IR spectrum from 3150 to 3500 cm^{-1}. This impairs any observation of an (N-H) band; this band is present in H_2L and $[Co(H_2L)(H_2O)(MeOH)](ClO_4)_2$ [1] IR spectra.

In the IR spectra of both deprotonated complexes, there is no splitting of the "amide I band", as in the case of the IR spectrum of $[Co(H_2L)(H_2O)(MeOH)](ClO_4)_2$ [1]. This indicates that symmetrical Co-O bonds exist in the deprotonated complexes. Further comparison of the IR spectra of deprotonated complexes with IR spectra of $[Co(H_2L)(H_2O)(MeOH)](C_1O_4)_2$ [1], shows that in both cases an extremely strong band is present at 1559 cm^{-1}. This band is ascribed to ν(C=N) in the deprotonated ligand form [5, 8, 10, 11]. This band, as well as ones at 1370 and 1372 cm^{-1}, respectively, being characteristic of δ(NCO) [10], indicates that the amide oxygen is coordinated in an enolic [10], or more precisely, α-oxyazine form (>C=N-N=Cl-O$^-$), resulting from deprotonation. Additional confirmation of charge delocalization and coordination of the α-oxyazine oxygen atom is in the existence of a very strong band at 1289 cm^{-1} in $[Co(L)(H_2O)_2]\cdot 6H_2O$, and a strong band at 1293 cm^{-1} in $[Co(HL)(H_2O)]ClO_4$, corresponding to the ν(C-O) vibration of the α-oxyazine fragment [12]. The only significant difference in the IR spectra of these two complexes is in the presence of a band at 1089 cm^{-1} in the spectrum of $[Co(HL)(H_2O)]ClO_4$, resulting from the ClO_4^- ion.

The non-electrolyte nature of $[Co(L)(H_2O)_2]\cdot 6H_2O$ was confirmed by the low molar conductivity ($\lambda_{M(DMF)} = 2.8\ \Omega^{-1}\ cm^2mol^{-1}$) and the value of $\lambda_{M(DMF)} = 23.2\ \Omega^{-1}cm^2mol^{-1}$ for $[Co(HL)(H_2O)]ClO_4$ suggested a 1:1 electrolyte. Similarities of IR spectra and magnetic susceptibilities of $[Co(L)(H_2O)_2]\cdot 6H_2O$ (μ_{eff} = 4.13 BM) and $[Co(HL)(H_2O)_2]ClO_4$ (μ_{eff} = 4.12 BM) complexes, show that PBP geometry persists in both complexes.

The crystal structure of $[Co(L)(H_2O)_2]\cdot 6H_2O$ consists of $[Co(L)(H_2O)_2]$ units, where L exists in a doubly deprotonated form. Packing in the crystal is achieved by a complex network of weak hydrogen bonds of OW···OW, OW···O and OW···N type. Figure 1 presents a view of the complex molecule with the atom numbering scheme.

The cobalt atom exhibits PBP coordination geometry with a N_3O_4 donor set. The five equatorially disposed N_3O_2 atoms making up a pentagonal girdle of four fused five-membered chelate rings are nearly co-planar, and the apical positions of the polyhedron are occupied by two water oxygens. The metal atom is shifted from the least-squares plane of the girdle by 0.03 Å towards the OW2 oxygen atom.

The neutrality of the complex is achieved by deprotonation of H_2L. If compared with the structure of $[Co(H_2L)(H_2O)(MeOH)]^{2+}$, where H_2L appears in its neutral form, the molecular structure of $[Co(L)(H_2O)_2]$ looks more natural, since the charge balance is attained inside the molecule and no further demands for molecular structure stabilization are necessary. Comparison of $[Co(L)(H_2O)_2]$ and $[Co(H_2L)(H_2O)(MeOH)]^{2+}$ gives some interesting information about the influence of different forms of the ligand on the shape of polyhedron around the metal. Looking to Table III it is evident that Co-O1 and Co-O2 distances in the basal plane of the pentagonal bipyramid differ only slightly. In $[Co(H_2L)(H_2O)(MeOH)]^{2+}$, corresponding Co-O distances of 2.177 and 2.325 Å are somewhat different. On the other hand, Co-N distances in the complex containing the neutral ligand are very close to those found in the neutral complex.

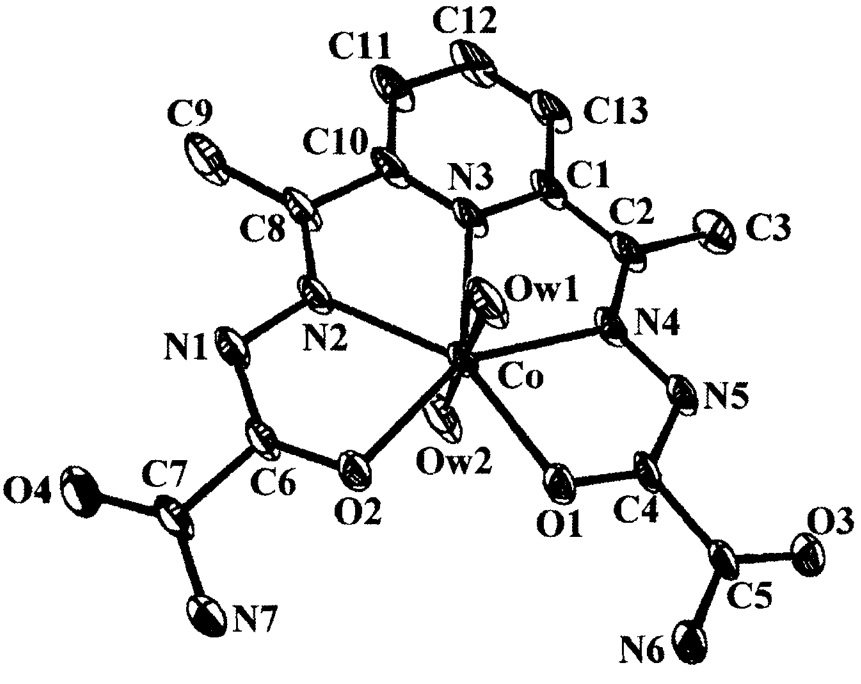

FIGURE 1 Molecular structure of $[Co(L)(H_2O)_2]$ with numbering scheme for atoms. Thermal ellipsoids are drawn at the 50% probability level.

TABLE III Selected bond parameters for $[Co(L)(H_2O)_2]$

		Bond distances (Å)			
Co-O1	2.162(2)	Co-N3	2.184(2)	Co-OW1	2.150(3)
Co-O2	2.1671(16)	Co-N4	2.189(2)	Co-OW2	2.223(3)
Co-N2	2.171(2)				
		Bond Angles (°)			
O1-Co-O2	77.07(7)			N2-Co-N4	70.52(9)
O1-Co-N4	70.87(7)			N2-Co-OW1	88.54(10)
O1-Co-OW1	84.20(9)			N2-Co-OW2	92.9(11)
O1-Co-OW2	91.87(10)			N3-Co-OW1	92.38(9)
O2-Co-N2	70.96(8)			N3-Co-OW2	92.88(10)
O2-Co-OW1	88.45(8)			N4-Co-OW1	92.01(9)
O2-Co-OW2	87.24(9)			N4-Co-OW2	90.02(10)
N2-Co-N3	70.82(8)			OW1-Co-OW2	174.73(8)

Starting from the fact that the two halves of the doubly-deprotonated ligand are very similar, it follows that symmetrical distribution of charge supports a symmetrical distribution of bond lengths as found in $[Co(L)(H_2O)_2]$. Since in $[Co(H_2L)(H_2O)(MeOH)]^{2+}$ one could expect a similar situation, it follows that the difference in Co-O bond lengths is probably caused by external sources. In order to elucidate effects of external as well as internal factors on geometry, we are planning an X-ray structure analysis of the $[Co(HL)(H_2O)]ClO_4$ complex.

Since the literature does not offer much information on the structures of the first series complexes with deprotonated ligands of the planar pentadentates class, we are continuing further investigations in this area.

Supplementary Material

Table of bond distances and angles, atomic parameters, anisotropic thermal parameters and observed and calculated structure factors are available upon request from Katarina Andjelkovic, upon request.

Acknowledgements

The financial support of the Ministry for Science and Technology of the Republic of Serbia is gratefully acknowledged.

References

[1] K. Andjelković, I. Ivanović, B. V. Prelesnik, V. M. Leovac and D. Poleti, *Polyhedron*, in press.

[2] D. Belletti, M. Carcelli, C. Pelizzi and G. Pelizzi, *J. Crystallogr. Spectr. Res.*, **22**, 185, (1992).

[3] O. K. Kireeva, B. M. Bulychev, N. R. Streltsova, V. K. Belsky and A. G. Dunin, *Polyhedron* **11**, 1801, (1992).

[4] N. R. Streltsova, V. K. Belsky, B. M. Bulychev and O. K. Kireeva, *Inorg. Chim. Acta* **189**, 11, (1991).

[5] A. Mangia, C. Pelizzi and G. Pelizzi, *Acta Cryst.* **B30**, 2146, (1974).

[6] D. Wester and G. Palenik, *Inorg. Chem.* **15**, 755, (1976).

[7] C. Lorenzini, C. Pelizzi, G. Pelizzi and G. Predieri, *J. Chem. Soc., Dalton Trans.* 1349, (1983).

[8] C. Pelizzi, G. Pelizzi, G. Predieri and S. Resola, *J. Chem. Soc., Dalton Trans.* 1349, (1982).

[9] A. Bino, R. Frim and M. Van Genderen, *Inorg. Chim. Acta* **127**, 95, (1987).

[10] C. Lorenzini, C. Pelizzi, G. Pelizzi and G. Predieri, *J. Chem. Soc., Dalton Trans.* 721, (1983).

[11] F. A. El-Saied, A. M. Donia and S. M. Hamza, *Thermochim. Acta* **183**, 237, (1991).

[12] V. M. Leovac, I. Ivanović, K. Andjelković and S. Mitrovska, *J. Serb. Chem. Soc.* **60**, 1, (1995).

[13] B. A. Frenz, *Enraf Nonius: Structure Determination Package, Version 4. 2*, (Enraf-Nonius, Delft, The Netherlands, 1982).