Inorganica Chimica Acta, 210 (1993) 173–176

The X-ray structure analysis of bis-2,2′,*N,N*′-bipyridyl ketone cobalt(III) nitrate dihydrate

Shaun O. Sommerer*
Division of Science, The Pennsylvania State University at Erie, The Behrend College, Station Road, Erie, PA 16563-1200 (USA)

John David Baker
USDA/ARS, 1700 SW 23 Rd. Dr., Gainesville, FL32608 (USA)

William P. Jensen and Abdul Hamza
Department of Chemistry, South Dakota State University, Brookings, SD 57007 (USA)

Robert A. Jacobson
Ames Laboratory, Iowa State University, Ames, IA 50011 (USA)

(Received March 5, 1993; revised May 12, 1993)

Abstract

An X-ray structural analysis of bis-2,2′,*N,N*′-bipyridyl ketone cobalt(III) nitrate dihydrate, $CoC_{22}H_{20}N_4O_4^+ \cdot NO_3^- \cdot 2H_2O$, $M_r = 559.38$ g/mol, $P\bar{1}$, $a = 8.862(2)$, $b = 16.195(3)$, $c = 8.772(2)$ Å, $\alpha = 103.54(2)$, $\beta = 95.74(3)$, $\gamma = 105.07°$, $V = 1164.4(4)$ Å^3, $Z = 2$, $D_x = 1.595$ g/cm^3, Mo Kα radiation ($\lambda = 0.71073$ Å), $\mu = 7.8$ cm^{-1} and $R = 0.079$, revealed a Co(III) cation in a slightly distorted octahedral environment. The structure reveals that the ligand di-2-pyridyl ketone (dpk) has undergone a hydration reaction across the ketone double bond and one of the hydrate oxygen atoms coordinated to the metal forming a tridentate chelate. This new Co(dpk-hydrate)$_2^+$ complex displays the least distorted geometry yet reported for either 1:1 or 1:2 (metal:ligand) complexes. A geometry optimization using the INDO model Hamiltonian as implemented in the program ZINDO was performed on the title complex with the Co^{3+} modeled as a singlet. The result of the computation corroborates the geometry of the title complex as that expected for Co^{3+}.

Introduction

There has been extensive study directed towards understanding the chemistry of transition metal complexes of 2,2′-bipyridine and bipyridine-like molecules due to their potential in electron transfer processes and photocatalysis [1]. A particularly interesting molecule in this category is the ligand di-2-pyridyl ketone (dpk) which has been confirmed by X-ray structural studies to undergo hydration to form a diol function replacing the ketone when in aqueous media and in the presence of a transition metal cation [2].

The hydration reaction (depicted in Fig. 1) is unusual since ketones are not normally hydrated to any appreciable extent in aqueous media, unless flanked by very strong electron withdrawing groups such as Cl or F. By coordinating through the two pyridine nitrogen atoms and one oxygen atom from the newly formed diol, the ligand becomes tridentate rather than bidentate as might be expected. A prominent feature of these structures is the highly distorted octahedral coordination environment assembled around the metal center when two dpk-hydrate ligands are coordinated. Off-axial angles ranging from 12.5° [1d] to 31° [2] have been reported for the intersection of the M–O vector with the line normal to the equatorial plane.

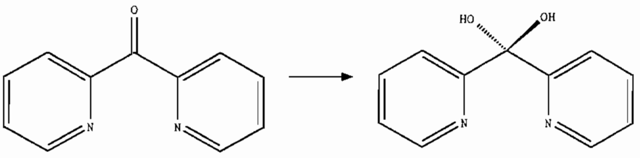

Fig. 1. dpk and dpk-hydrate.

We report here the isolation and three-dimensional structure of a new Co(dpk-hydrate)$_2^+$ complex which displays the smallest off-axis distortion yet reported for either 1:1 or 1:2 (metal:ligand) complexes. In addition, we report the results of a ZINDO geometry optimization of the complex which corroborates the geometry of the title complex as that expected for Co^{3+} low spin.

---

*Author to whom correspondence should be addressed.

0020-1693/93/$6.00

Experimental

Preparation of Co(dpk-hydrate)$_2^+$

The title compound was prepared by mixing 0.44 mmol [Co(NH$_3$)$_4$CO$_3$]NO$_3$ with 1.1 mmol DPK in 75 ml water. After several weeks red–orange crystals began to form upon slow evaporation of the solvent. Crystals of a size suitable for X-ray analysis were harvested when the solution was reduced to 1/4 the original volume.

X-ray crystallography

An irregular crystal approximately 0.2×0.2×0.3 mm suitable for diffraction studies was mounted on the end of a glass fiber. All subsequent measurements were made using a Rigaku AFC6-R diffractometer with graphite-monochromated Mo Kα radiation (λ=0.71073 Å). The cell dimensions were determined by a least-squares refinement of 25 automatically centered reflections. The intensity data were collected using a 2θ–ω scan technique from 2 to 50° in 2θ and data was collected for $h=-9$ to 9, $k=0$ to 19 and $l=-10$ to 10. Two standard reflections were measured every 98 reflections to monitor for decomposition during the X-ray analysis. An analysis of the standards showed no sign of crystal decay. No absorption correction was made. The pertinent crystal details are given in Table 1.

TABLE 1. Summary of crystal details

Molecular formula	$C_{22}H_{20}N_4O_4Co^+ \cdot NO_3^- \cdot 2H_2O$
M_r	559.4
Color, habit	red–orange, irregular
Crystal size (mm)	0.2×0.2×0.3
Crystal system	triclinic
a (Å)	8.862(2)
b (Å)	16.195(3)
c (Å)	8.772(2)
α (°)	103.54(2)
β (°)	95.74(3)
γ (°)	105.07(2)
V (Å^3)	1164.4(4)
Space group	$P\bar{1}$
Z	2
D_{calc} (g cm^{-3})	1.595
μ (cm^{-1})	7.8
Final Δ-map (e Å^{-3})	+/−0.860
Measured reflections	4197
Independent reflections	3906
Reflections with $I_{net} > 2.5\sigma(I_{net})$	2567
Parameters refined	337
Final shift/error ratio	0.003
R, R_w where $w = 1/\sigma^2(F_o)$[a]	0.079, 0.090

[a] $R = \sum \frac{|(|F_o| - |F_c|)|}{(|F_c|)}$, $R_w = \left[\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w |F_o|^2} \right]^{1/2}$.

Structure refinement

The data reduction, structure solution and final refinement were performed using the NRCVAX (PC-Version) [3] package of programs. The Co atom and all non-hydrogen atoms were located by the heavy-atom method (Patterson syntheses) and refined anisotropically by full-matrix least-squares. The hydrogen atoms were located using a difference electron density map and refined isotropically. The model converged to R=0.079 and R_w=0.090 for 2567 observed reflections. The final positional parameters are given in Table 2. The final bond distances involving the non-hydrogen atoms and bond angles are listed in Table 3.

TABLE 2. Atomic positional and isotropic equivalent thermal parameters

	x/a	y/b	z/c	B_{iso}[a]
Co1	0	0	0	1.82(9)[b]
Co2	1	1/2	1/2	1.87(9)
O1	0.4019(8)	0.0968(4)	−0.1304(8)	2.7(4)
O2	0.2231(7)	0.0319(4)	0.0177(7)	2.0(3)
O3	0.9736(7)	0.5276(4)	0.3041(7)	2.2(3)
O4	0.7550(8)	0.5130(4)	0.1173(8)	2.9(3)
N1	−0.0276(10)	−0.1132(5)	0.0424(9)	2.4(4)
N2	−0.0060(9)	0.0501(5)	0.2198(8)	1.8(4)
N3	0.8472(9)	0.3914(5)	0.3841(9)	2.1(4)
N4	0.8281(9)	0.5501(5)	0.5372(10)	2.4(4)
C1	0.0660(13)	−0.1671(7)	0.0221(12)	2.8(6)
C2	0.0197(15)	−0.2489(7)	0.0483(13)	3.5(6)
C3	−0.1238(15)	−0.2776(7)	0.0994(12)	3.6(6)
C4	−0.2213(13)	−0.2212(6)	0.1226(12)	2.8(5)
C5	−0.1666(12)	−0.1393(6)	0.0936(11)	2.1(5)
C6	0.2473(12)	0.0642(6)	−0.1147(11)	2.2(5)
C7	−0.1436(12)	0.0088(6)	0.2585(11)	2.1(5)
C8	−0.1801(13)	0.0341(7)	0.4079(11)	2.7(5)
C9	−0.0712(14)	0.1044(8)	0.5168(12)	3.3(6)
C10	0.0692(14)	0.1446(7)	0.4759(12)	3.3(5)
C11	0.0990(12)	0.1153(7)	0.3277(11)	2.5(5)
C12	0.8235(13)	0.3089(7)	0.4099(13)	2.9(6)
C13	0.7168(14)	0.2368(7)	0.3085(12)	3.1(5)
C14	0.6303(13)	0.2458(7)	0.1787(14)	3.5(6)
C15	0.6507(12)	0.3284(7)	0.1512(12)	2.7(5)
C16	0.7603(12)	0.3994(6)	0.2611(11)	2.0(4)
C17	0.8096(13)	0.4978(6)	0.2617(11)	2.5(5)
C18	0.7464(12)	0.5472(6)	0.3960(11)	2.3(5)
C19	0.6225(13)	0.5858(7)	0.3881(12)	2.8(5)
C20	0.5907(14)	0.6292(8)	0.5297(15)	4.0(7)
C21	0.6753(14)	0.6314(8)	0.6728(13)	3.8(6)
C22	0.7939(13)	0.5910(7)	0.6714(11)	2.8(5)
W1	0.4671(10)	0.0307(6)	0.2291(9)	4.8(5)
W2	1.1864(11)	0.5918(6)	0.1268(9)	5.3(5)
NO31	0.5562(15)	0.2010(8)	0.6270(13)	4.7(6)
ONN1	0.5435(14)	0.2742(7)	0.7114(13)	7.3(7)
ONN2	0.4434(13)	0.1554(8)	0.5276(13)	8.0(7)
ONN3	0.6749(14)	0.1842(9)	0.6542(15)	9.5(9)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid. [b] In this and subsequent Tables e.s.d.s in the least significant figure are given in parentheses.

TABLE 3. Bond distances (Å) and angles (°)

Co1–O2	1.890(6)	Co2–N3	1.900(8)
Co1–N1	1.914(7)	Co2–N4	1.926(8)
Co1–N2	1.921(7)	O3–C17	1.388(12)
O1–C6	1.370(12)	O4–C17	1.408(11)
O2–C6	1.393(11)	N3–C12	1.374(12)
N1–C1	1.346(12)	N3–C16	1.312(12)
N1–C5	1.351(13)	N4–C18	1.356(13)
N2–C7	1.347(13)	N4–C22	1.315(12)
N2–C11	1.312(13)	C12–C13	1.348(16)
C5–C6	1.548(16)	C6–C7	1.528(16)
C1–C2	1.362(16)	C13–C14	1.365(16)
C2–C3	1.392(18)	C14–C15	1.385(15)
C3–C4	1.407(15)	C15–C16	1.382(14)
C4–C5	1.384(13)	C16–C17	1.537(13)
C17–C18	1.504(14)	C18–C19	1.401(13)
C19–C20	1.373(16)	C20–C21	1.383(17)
C7–C8	1.377(13)	C21–C22	1.373(15)
C8–C9	1.372(16)	NO31–ONN1	1.281(16)
C9–C10	1.367(17)	NO31–ONN2	1.202(17)
C10–C11	1.354(15)	NO31–ONN3	1.170(17)
Co2–O3	1.882(6)		
O2–Co1–N1	97.1(3)	O3–Co2–N4	83.3(3)
O2–Co1–N2	97.0(3)	N3–Co2–N4	88.3(3)
N1–Co1–N2	88.8(3)	Co2–O3–C17	100.8(5)
Co2–N3–C12	128.4(7)	Co1–O2–C6	102.3(5)
Co2–N3–C16	112.8(6)	Co1–N1–C1	129.4(7)
C12–N3–C16	118.7(8)	O3–C17–C18	106.0(8)
Co1–N1–C5	110.7(6)	Co2–N4–C18	109.4(6)
C1–N1–C5	119.9(8)	Co2–N4–C22	129.9(7)
Co1–N2–C7	110.3(6)	C18–N4–C22	120.3(8)
Co1–N2–C11	130.0(7)	N3–C12–C13	120.8(9)
C7–N2–C11	119.7(8)	C12–C13–C14	119.9(10)
N1–C1–C2	120.5(10)	C13–C14–C15	120.3(10)
C1–C2–C3	120.6(10)	C14–C15–C16	116.7(9)
C2–C3–C4	119.1(9)	N3–C16–C15	123.5(9)
C3–C4–C5	117.0(10)	N3–C16–C17	107.9(8)
N1–C5–C4	122.7(9)	C15–C16–C17	128.6(8)
O3–C17–O4	113.0(8)	O3–C17–C16	106.1(8)
O1–C6–O2	116.0(8)	O4–C17–C16	113.9(8)
O4–C17–C18	110.2(8)	C16–C17–C18	107.3(8)
N4–C18–C17	109.7(8)	N4–C18–C19	121.5(9)
C17–C18–C19	128.8(9)	N2–C7–C8	122.0(9)
C18–C19–C20	117.1(9)	C19–C20–C21	120.5(9)
C7–C8–C9	117.1(10)	C20–C21–C22	119.4(9)
C8–C9–C10	119.8(9)	N4–C22–C21	121.3(9)
C9–C10–C11	120.1(10)	ONN1–NO31–ONN2	116.5(13)
N2–C11–C10	121.2(10)	ONN1–NO31–ONN3	117.5(13)
O3–Co2–N3	82.4(3)	ONN2–NO31–ONN3	126.0(14)

Geometry optimization of Co(dpk-hydrate)$_2$$^+$

Due to the previous success in dealing with transition metal compounds, the INDO model Hamiltonian [4] as implemented in the program ZINDO [5], was used for a geometry optimization of the title complex.

The geometry optimization was performed using the parameters appropriate for the structure [5b]. The BFGS quasi-Newton update technique [6] was used for the geometry optimization and was considered converged when the norm of the gradient was less than 1.0×10^{-3} hartree/bohr. A restricted Hartree-Fock determinant was used and the self-consistent-field calculation was continued until successive cycles yielded differences in energy of less than 1.0×10^{-10} hartree.

Discussion

Structure

The ORTEP representation of the title complex, Fig. 2, shows two hydrated-dpk ligands coordinated to the cation in a tridentate mode. Note that labeling for the second molecule has been removed for clarity. The geometry about the metal ion can be described as a somewhat distorted octahedron though it is clearly not as distorted as previously reported 1:2 complexes [1d, 2]. The angle made by the off-axis coordination of the oxygen atom with the line normal to the equatorial plane is 8.0°, the smallest angle reported to date.

The metal–ligand bond distances are unusual in that the axial bonds (Co–O av. = 1.886 Å) are shorter than the equatorial bonds (Co–N av. = 1.915 Å) Furthermore, the entire coordination sphere in this species appears to be held much closer to the Co center than any of the previously reported 1:2 complexes of this type [1d, 2].

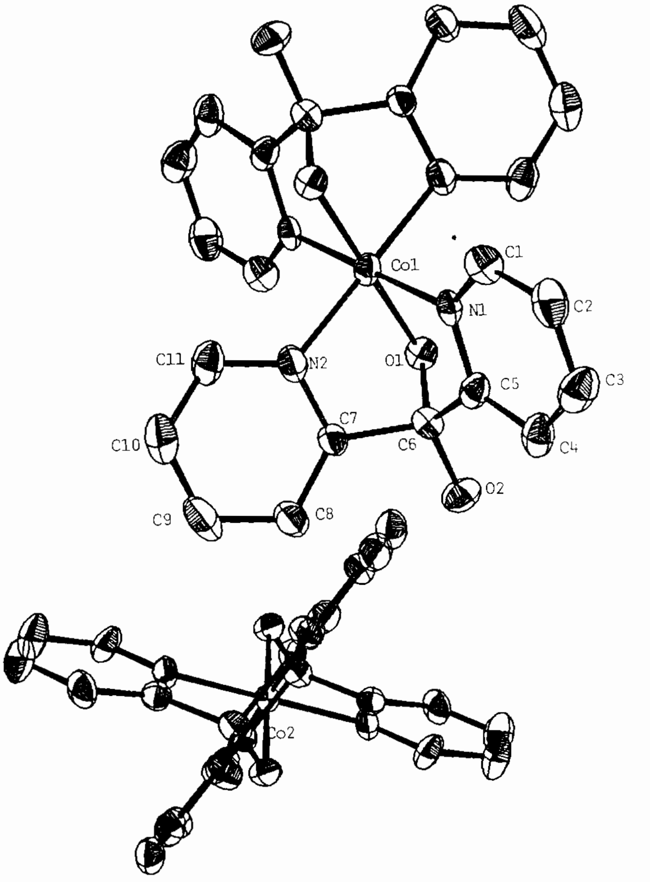

Fig. 2. ORTEP representation of title complex with ellipsoids drawn at the 50% probability level.

TABLE 4. Bond distances (Å) and angles (°) for the geometry optimized singlet Co(dpk-hydrate)$_2$$^+$

Co1–O2	1.897	Co1–N1	1.981
Co1–N2	1.978	O1–C6	1.388
O2–C6	1.388	N1–C1	1.380
N1–C5	1.354	N2–C7	1.380
N2–C11	1.354	C1–C2	1.881
C6–C5	1.488	C6–C7	1.499
C2–C3	1.388	C3–C4	1.399
C4–C5	1.386	C7–C8	1.406
C8–C9	1.388	C9–C10	1.398
C10–C11	1.386		
O2–Co1–N2	95.10	O2–Co1–N2	95.16
N1–Co1–N2	80.62	Co1–O2–C6	101.54
Co1–N1–C1	131.13	Co1–N1–C5	105.96
C1–N1–C5	121.63	Co1–N2–C7	105.85
Co1–N2–C11	131.02	C7–N2–C11	121.64
N1–C1–C2	121.43	C1–C2–C3	117.84
C2–C3–C4	121.09	C3–C4–C5	119.43
N1–C5–C4	118.48	O1–C6–O2	111.30
N2–C7–C8	118.45	C7–C8–C9	119.45
C8–C9–C10	121.11	C9–C10–C11	117.81

The presence of a single NO_3^- anion in the asymmetric unit implies that each complex is formally 1+ ($Z=2$ for the unit cell) though the possibility does exist that an additional anion is present in the form of a deprotonated ligand or water molecule. We favor the former for the following reasons: first, the two uncoordinated H_2O molecules could have undergone deprotonation leaving an OH^- ion, but this is unlikely since the complex was isolated from an acidic solution (pH = 2–3). Second, there is no evidence of strong hydrogen bonding involving either of the uncoordinated water molecules as might be expected if either was in fact an OH^-. Third, the N_4O_2 coordination sphere presents a high field to the Co atom and hence would give rise to a low spin d^6 electron configuration for the Co [7]. In this configuration, the d_{z^2} orbital is vacant and can accept more electron density than if it were partially occupied. Donation of electron density by the axial oxygen atom would make the bonded hydrogen more 'protonic' and easily removed by a weak base. Each ligand would thereby take on a charge of 1− resulting in an overall charge of 1+ for each complex. Thus, a slightly more accurate description of the reaction would be a metal promoted hydration followed by deprotonation of the oxygen residing in the axial position.

The *R* value for the final model is slightly high. However, we believe this is due to the irregularity of the crystal used in the X-ray experiment since all peak scans were observed to be smooth and sharp.

Geometry optimization

Substantiating evidence for 3+ assignment for the Co was obtained from an INDO geometry optimization calculation of a Co(dpk-hydrate)$_2$$^+$ molecule. Due to low product yield, the quantity of material from which the crystal used in the structure determination was selected was not in sufficient amount or quality to perform magnetic studies upon. Hence, an INDO calculation was performed on the aforementioned molecule where the Co was modeled as a singlet d^6 and a proton was removed from each of the axial oxygens. The purpose of the calculation was to determine the geometry of the complex in a singlet spin state.

The bond distances and angles calculated for the singlet complex are tabulated in Table 4. The agreement of the bond distances within the coordination sphere determined for the singlet state are in excellent agreement with those observed in the solid state.

Conclusions

Complexes of dpk exhibiting the greatest distortions from octahedral geometry involve metals with a high number of d-electrons. The geometry computations suggest that the complex has a very soft potential energy surface as was exhibited by the slow convergence of the model to a minimum energy. Hence, it appears that the observed geometry of the Co–dpk complex may be most affected by the electronic configuration of the metal to which it is associated. In other words, the -OH function of dpk is quite facile and has a minor affect on the final observed geometry.

References

1 (a) A. Basu, T.G. Kasar and N.Y. Sapre, *Inorg. Chem., 27* (1988) 4539; (b) A. Basu, A.R. Saple and N.Y. Sapre, *J. Chem. Soc., Dalton Trans.,* (1987) 1797; (c) M.P. Suh, Y.-H. Oh and C.-H. Kwak, *Organometallics, 6* (1987) 411; (d) S. Sommerer, W.P. Jensen and R.A. Jacobson, *Inorg. Chim. Acta, 172* (1990) 3, and refs. therein.

2 S.L. Wang, J.W. Richardson, S.J. Briggs, R.A. Jacobson and W.P. Jensen, *Inorg. Chim. Acta, 111* (1986) 67.

3 E.J. Gabe, Y.L. Page, J.P. Charland, F.L. Lee and P.S. White, *J. Appl. Crystallogr., 22* (1989) 384.

4 J.A. Pople, D.L. Beveridge and P.A. Dobosh, *J. Chem. Phys., 47* (1967) 2026.

5 (a) J. Ridley and M.C. Zerner, *Theor. Chim. Acta, 32* (1973) 111; (b) A.D. Bacon and M.C. Zerner, *Theor. Chim. Acta, 53* (1979) 21; (c) W.P. Anderson, W.D. Edwards and M.C. Zerner, *Inorg. Chem., 25* (1986) 2728; (d) M.C. Zerner, G.H. Loew, R.F. Kirchner and U.T. Mueller-Westerhoff, *J. Am. Chem. Soc., 102* (1980) 589; (e) S.O. Sommerer, J.D. Baker, M.C. Zerner and G.J. Palenik, *Inorg. Chem., 31* (1992) 563.

6 J.D. Head and M.C. Zerner, *Chem. Phys. Lett., 122* (1985) 264.

7 F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry,* 5th edn., p. 733.