Research Article

Synthesis and Structural Study of Tris(μ -pyrazolyl)hexakis(pyrazole)dicobalt(III) Nitrate

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The new $(\text{Hpyz})_3\text{Co}(\mu_2\text{-pyz})_3\text{Co}(\text{Hpyz})_3^{3+}$ complex has been isolated as the nitrate salt through a reaction of Co(II) nitrate, Hpyz (pyrazole), triethylamine, and oxygen. The salt crystallizes in the monoclinic space group $P2_1/m$ with $a = 12.5977(3)$ Å, $b = 15.3387(4)$ Å, $c = 14.0800(3)$ Å, $\beta = 93.0868(15)^\circ$, and $D_{\text{calc}} = 1.464$ g/cm³ at 150(1) K. The complex, with pseudo-octahedral coordination about the equivalent cobalt centers, has shorter Co–N distances for the bridging anionic pyz ligands as compared to the neutral Hpyz ligands, with the averages being 1.918(2) and 1.966(4), respectively. The Co–Co separation is 3.568 Å, reflecting the absence of any significant metal-metal interaction.

1. Introduction

Although numerous approaches for the syntheses of heterobimetallic complexes have been developed, most of these either involve organometallic complexes or utilize ligands such as bridging phosphides, which could be detrimental to potential catalytic applications [1]. It would therefore appear advantageous to construct the heterobimetallic species using more traditional coordination chemistry. Ligands such as 1,8-naphthyridine or pyridazine could potentially be utilized, but their lack of negative charge appears often to lead to the more strongly Lewis acidic metal ion abstracting the ligand from the weaker acid [2, 3]. Hence, more basic species such as the pyrazolyl ion, $1,2\text{-C}_3\text{N}_2\text{H}_3^-$ (**1**, Figure 1), appear more useful for the stabilization of the desired bimetallics. Indeed, we recently reported a cobalt/ruthenium complex [1] in which the two metal centers were united via three μ_2 -pyrazolyl anions. Though other heterobimetallics had been isolated previously with this same linking agent [4–7], they had all been organometallic complexes. Herein we report a homobimetallic complex involving two cobalt centers, linked by three μ_2 -pyrazolyl ligands, that was isolated as part of our general bimetallic studies.

2. Materials and Methods

2.1. Synthesis. All reactions were carried out in Schlenk apparatus under a nitrogen atmosphere. THF was dried by distillation from sodium benzophenone ketyl under nitrogen. All reagents were obtained commercially.

Hexakis(pyrazole)tris(μ_2 -pyrazolyl)dicobalt(III) nitrate, $[(\text{Hpyz})_3\text{Co}(\mu_2\text{-pyz})_3\text{Co}(\text{Hpyz})_3](\text{NO}_3)_3$, **2** $[\text{NO}_3]_3$.

To a solution of 1.00 g (14.7 mmol) of pyrazole and 0.63 mL (4.5 mmol) of NEt_3 in 10 mL of THF was added dropwise 5 mL of a THF solution containing 0.45 g (1.5 mmol) of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Upon mixing, much pink crystalline solid precipitated from the light red solution over the course of several minutes. The mixture was then stirred at room temperature, while oxygen was bubbled through at the rate of 2.2 L/h. After two days, all solids had dissolved into the solution, which became dark red. It was then syringed to one side of an H-shaped tube having diphenylmethane in the other end. The solution slowly evaporated to yield a crop of red, rod-shaped crystals (yield: 0.061 g, 8.9%). Their quality was satisfactory for an X-ray diffraction study.

Anal. Calc. for $\text{C}_{27}\text{H}_{33}\text{O}_9\text{N}_{21}\text{Co}_2$: C, 35.50; H, 3.64; N, 32.20. Found: C, 36.23; H, 3.79; N, 32.07. ^1H NMR (300 MHz,

FIGURE 1

CDCl₃, ppm): 8.15 (m, 12H, H1, 1',3,3',4,4',6,6',7,7',9,9'), 6.71 (d, 6H, $J = 1.7$ Hz, H2,2',5,5',8,8'), 6.38 (d, 6H, $J = 2.5$ Hz, H10, 10',12,12',14,14'), 6.20 (t, 3H, $J = 2.5$ Hz, H11,13,15). Additional peaks, of variable intensity, due to THF were present at 1.85 and 3.75 ppm. However, peaks due to free pyrazole were not present, indicating that the pyrazole incorporation does not always occur, but perhaps it might lead to enhanced crystalline quality. The analytical data show high carbon and hydrogen but low nitrogen content relative to the simple salt (lacking THF and uncoordinated pyrazole), suggesting the presence of some residual THF in the lattice. The analytical data are in better accord with the addition of one-quarter of a molecule of THF in the sample, which had been dried and shipped under vacuum. With the inclusion of 0.25 THFs per dimetallic unit, the calculated values would be C, 36.10; H, 3.79; N, 31.57.

2.2. X-Ray Crystallography. Single crystals of the compound were examined under Paratone oil, and a suitable crystal was selected for data collection. It was transferred to a Nonius Kappa CCD diffractometer where it was held in place on a glass fiber through the use of a cold nitrogen stream. The programs COLLECT, DENZO-SMN, and SCALEPAC [8] were used for unit cell determination and data collection and processing. SIR97 [9] was used to solve the structure, while SHELXL-97 [10] was used for refinements, based on published scattering factors [11, 12]. All of the nonhydrogen atoms could be refined anisotropically, except for the two highly disordered THF molecules. Hydrogen atoms were allowed to ride on their attached carbon atoms, and the former were assigned isotropic thermal parameters based upon those of the latter. Key experimental details are given in Table 1, while pertinent bonding parameters are listed in Table 2. An ORTEP representation of the molecule is given in Figure 1.

The CCDC deposition 810359 contains the full crystallographic information for this structure. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

3. Results and Discussion

3.1. Synthesis. The combination of Co(II) nitrate with pyrazole in THF, in the presence of triethylamine as a proton acceptor and oxygen as an oxidizing agent, led to the isolation of the $(\text{Hpyz})_3\text{Co}(\mu_2\text{-pyz})_3\text{Co}(\text{Hpyz})_3^{3+}$ ion, as the nitrate salt. The yield, though unoptimized, was rather low at 8.9%,

TABLE 1: Crystal and experimental data.

Empirical formula	C ₄₂ H ₆₁ Co ₂ N ₂₃ O ₁₂
Formula weight	1198.00
Temperature (K)	150(1) K
Wavelength (Å)	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/m$
Unit cell dimensions	
<i>a</i>	12.5977(3)
<i>b</i>	15.3387(4)
<i>c</i>	14.0800(3)
β (°)	93.0868(15)
Volume (Å ³)	2716.76(11)
<i>Z</i>	2
D_{calcd} (g cm ⁻³)	1.351
$\mu(\text{MoK}\alpha)$ (mm ⁻¹)	0.691
<i>F</i> (000)	1248
θ range (°)	2.2–27.5
	–16 ≤ <i>h</i> ≤ 16
Limiting indices	–19 ≤ <i>k</i> ≤ 18
	–18 ≤ <i>l</i> ≤ 18
Reflections collected/unique	11053/6431
Completeness (%)	99.5%
Goodness of fit on F^2	1.036
<i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0512$, $wR_2 = 0.1305$
<i>R</i> indices (all data)	$R_1 = 0.0755$, $wR_2 = 0.1455$
$(\Delta\rho)_{\text{max, min}}$	0.664, –0.522
<i>R</i> (int)	0.0303

FIGURE 2

but conceivably it could be improved with some effort. The diamagnetic complex exhibited a ¹H NMR spectrum consistent with the result of the X-ray diffraction study.

3.2. Structural Description. The structure of the Co₂(μ₂-C₃N₂H₃)₃(C₃N₂H₄)₆ complex trication (2) is presented in Figures 2 and 3. The complex is diamagnetic and contains two low spin Co(III) centers, each with pseudo-octahedral

TABLE 2: Selected bond lengths (Å) and angles (°) for $[(\text{Hpyz})_3\text{Co}(\mu_2\text{-pyz})_3\text{Co}(\text{Hpyz})_3](\text{NO}_3)_3$.

Co–N1	1.973(2)	N1–N2	1.345(3)
Co–N3	1.966(2)	N3–N4	1.353(3)
Co–N5	1.960(2)	N5–N6	1.339(3)
Co–N7	1.913(2)	N7–N7'	1.372(4)
Co–N9	1.919(2)	N8–N8'	1.369(4)
Co–N11	1.921(2)	N9–N9'	1.366(4)
N10–O1	1.259(5)	N10–O2	1.232(3)
N11–O3	1.278(5)	N11–O4	1.234(3)
N12–O5	1.268(5)	N12–O6	1.225(3)
Bond angles			
N1–Co–N3	90.18(9)	Co–N1–N2	122.4(2)
N1–Co–N5	89.59(9)	Co–N3–N4	122.9(2)
N1–Co–N7	92.44(9)	Co–N5–N6	122.7(2)
N1–Co–N8	87.45(9)	Co–N1–C1	132.1(2)
N1–Co–N9	175.99(9)	Co–N3–C4	131.1(2)
N3–Co–N5	89.79(9)	Co–N5–C7	130.8(2)
N3–Co–N7	87.26(9)	O1–N10–O2	118.8(2)
N3–Co–N8	176.70(9)	O2–N10–O2'	122.4(4)
N3–Co–N9	92.51(9)	O3–N11–O4	119.2(2)
N5–Co–N7	176.42(9)	O4–N11–O4'	121.6(4)
N5–Co–N8	92.49(9)	O5–N12–O6	118.3(2)
N5–Co–N9	87.44(9)	O6–N12–O6'	123.4(5)
N7–Co–N8	90.54(9)	N8–Co–N9	89.98(9)
N7–Co–N9	90.66(9)

FIGURE 3: Molecular structure of the 2 trications, showing the 30% probability ellipsoids. The nitrate ions are not included.

coordination. In each of the outermost parts of the molecule, three neutral pyrazole ($\text{C}_3\text{N}_2\text{H}_4$) ligands each coordinates via a single nitrogen center to the cobalt center, while the three deprotonated pyrazolyl ligands ($\text{C}_3\text{N}_2\text{H}_3$) bind both cobalt centers simultaneously. A crystallographically imposed mirror plane of symmetry passes through C11, C13, and C15, rendering the two metal coordination spheres equivalent. The Co–N distances for the bridging, anionic

ligands average 1.918(2) Å, shorter than those for the neutral ligands (1.966(4) Å). A more favorable interaction for the anionic form is reasonable and reflects the fact that the Co(III) centers are better able to compete with each other than with a proton. The coordinations of the three central ligands to two metal centers also lead to an increase in their N–N distances, to an average of 1.369(2) Å from the 1.346(4) Å in the protonated ligands. The Co–Co separation is 3.568 Å, clearly providing no suggestion whatsoever of any metal–metal bonding. A related Co–Ru bimetallic was found to have a separation of 3.666(2) Å [1].

Additional asymmetry about the cobalt ions is induced due to the presence of the differing ligands. The N–Co–N angles involving the neutral ligands coordinating through N1, N3, and/or N5 average 89.8(2)°, while those between the anionic ligands average 90.4(2)°. The nine remaining N–Co–N' angles fall into three sets, each angle involving one terminal and one bridging ligand. The formally trans values average 176.4(2)°, while the other two sets average 92.5(2)° and 87.4(6)°. The larger three of these involve N1/N7, N3/N9, and N5/N8. The slight differences in angles could possibly be induced by C (or N)–H/ π interactions between pyrazoles and/or pyrazolyl ligands.

A more substantial asymmetry may be observed about the coordinated nitrogen atoms of the uncharged pyrazole ligands. Thus, the Co–N–N angles about N(1, 3, and 5) average 122.7(2)°, while the corresponding Co–N–C angles average 131.3(4)°. Such distortions have been observed in related complexes [1].

The three independent nitrate ions are each bisected by a mirror plane passing through the nitrogen atom and one of the oxygen atoms (O2, O4, or O6). As a result, the nitrate ions are rigorously planar. Interestingly, the N–O distances for the bonds residing on the mirror planes are slightly longer relative to the others, with the respective averages being 1.268(6) Å versus 1.230(3) Å. Similarly, the O–N–O angles that are bisected by a mirror plane are slightly larger than the others, with averages of 122.5(5)° and 118.8(3)°. This asymmetry may be attributed to hydrogen bonding interactions that utilize equivalent N–H bonds from pyrazoles on opposite cobalt ions. Thus, O1 interacts with N4–H4 and N4'–H4', O3 interacts with N2–H2 and N2'–H2', and O5 interacts with N6–H6 and N6–H6'. Each independent half-dimetallic unit is accompanied by an uncoordinated pyrazole and one and a half independent THF molecules, but the THF molecules suffer from an extremely severe disorder, rendering their structural parameters meaningless.

Some useful comparisons may be made with a series of divalent, di- and polymetallic analogues derived from substituted pyrazoles. Thus, with 3,5-dimethylpyrazole (Hdmpz), both zinc [13] and cobalt [14] form dimeric complexes of the type (Hdmpz)(dmpz)M(μ_2 -dmpz)₂M(dmpz)(Hdmpz), in which the metal ions are four coordinate (pseudo-tetrahedral). For the M=Co complex, the average Co–N distance for the bridging anionic ligands is 1.993(3) Å, about 0.075 Å longer than for the six-coordinate Co(III) dimetallic described herein, reflecting the greater importance of differing spin states as compared to coordination numbers in determining the relative Co–N bond distances. The longer Co–N distances in the divalent complex lead to an increased Co–Co separation, 3.777 Å, while in a trimetallic Co(II) species, a separation of 3.627 Å was found. An interesting mixed valence (Co(II,III)) complex having six-coordinate metals held together via three triazole/triazolate ligands has a Co–Co separation of 3.653 Å [15]. Conceivably, the polymetallic Co(II) complexes [14] could serve as useful precursors to Co(III) analogues.

Notably, a Co(py₃)₃ species is known in which pseudo-octahedral coordination is achieved via the formation of a one-dimensional polymer [16]. The structure was determined from powder data, and thus not all of the bonding parameters could be obtained accurately. Nonetheless, the Co–Co separation of 3.5526(2) Å and the Co–N bond distance of 1.95 Å are in reasonable accord with the values observed herein.

4. Conclusions

The homobimetallic [(Hpyz)₃Co]₂(μ_2 -pyz)₃³⁺ complex has been isolated as the nitrate salt from the reaction of Co(II) nitrate with pyrazole, triethylamine, and oxygen in THF solution. The metal-metal separation indicates no significant interaction, as expected. Given the fact that Ru(Hpyz)₄(pyz)₂ can be used to form a heterobimetallic Co/Ru complex, deprotonation of the dicobalt complex could also make it amenable to the introduction of one or more metal ion(s) as well.

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