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Contribution from the Departments of Chemistry, Lafayette College, Easton, Pennsylvania 18042,
and University of Arkansas, Fayetteville, Arkansas 72701

Six-Coordinate Complexes with 1,10-Phenanthroline Ligands in the Trans Configuration. Preparation of *trans*-Bis(1,10-phenanthroline)ruthenium(II) Complexes and Crystal Structure of *trans*-Bis(1,10-phenanthroline)bis(pyridine)ruthenium(II) Hexafluorophosphate

P. BONNESON,[1a] J. L. WALSH,*[1a] W. T. PENNINGTON,[1b] A. W. CORDES,[1b] and B. DURHAM[1b]

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The complex *trans*-$[\mathrm{Ru(phen)_2(OH_2)_2}](\mathrm{PF_6})_2$ (phen = 1,10-phenanthroline) has been prepared by photolysis of the cis complex in aqueous $\mathrm{HPF_6}$ solution. Subsequent thermal substitution with appropriate ligands yielded *trans*-$[\mathrm{Ru(phen)_2(CH_3CN)(OH_2)}](\mathrm{PF_6})_2$, *trans*-$[\mathrm{Ru(phen)_2(CH_3CN)_2}](\mathrm{PF_6})_2$, and *trans*-$[\mathrm{Ru(phen)_2(py)_2}](\mathrm{PF_6})_2$ (py = pyridine) with complete retention of the stereochemistry. Photolysis of the trans complexes results in efficient rearrangement to the cis geometry. *trans*-$[\mathrm{Ru(phen)_2(py)_2}](\mathrm{PF_6})_2$ is triclinic, in space group $P\bar{1}$, with a = 10.316 (1) Å, b = 10.877 (2) Å, c = 8.775 (1) Å, α = 89.09 (1)°, β = 97.66 (1)°, γ = 118.45 (2)°, Z = 1, and R = 0.047 for 1731 observed reflections. The ruthenium ion lies on a center of inversion with the 1,10-phenanthroline ligands tilted and slightly bowed away from each other, thus minimizing the α-hydrogen interactions.

Introduction

The chemistry of 1,10-phenanthroline (phen) complexes of ruthenium is often very similar to that of the corresponding 2,2′-bipyridyl complexes (bpy). Phenanthroline, however, is structurally more rigid; thus complexes whose reactivity are influenced by the chelate's ability to distort could provide a situation where marked differences are observed in the chemistry of 2,2′-bipyridine and 1,10-phenanthroline complexes. Such a situation arises with *trans*-$\mathrm{Ru(N{-}N)_2L_2}^{2+}$ (N–N = 2,2′-bipyridine or 1,10-phenanthroline and L = monodentate ligand), where significant distortion of the chelate or of the coordination sphere must occur to prevent excessive steric interaction between hydrogens on opposing N–N ligands.[2]

A number of *trans*-$\mathrm{Ru(bpy)_2L_2}^{2+}$ complexes have been prepared and structurally characterized.[3-5] Within this series two general types of distortion that minimize steric interactions have been observed. In one type, exemplified by $\mathrm{Ru(bpy)_2(OH)(H_2O)}^{2+}$ and designated as the "twisted configuration", the bpy ligands remain nearly planar but twist out of the equatorial plane of the octahedrally coordinated metal to form a flattened-tetrahedral arrangement of N atoms. In the second type, called the "bowed configuration", the octahedral coordination geometry is maintained but the bipyridine moieties are bent in such a way to minimize the opposing hydrogen interactions. The complexes *trans*-$[\mathrm{Ru(bpy)_2L_2}](\mathrm{PF_6})_2$, where L = pyridine and triphenylphosphine, are examples of this type of distortion. Other trans complexes of 2,2′-bipyridine and 1,10-phenanthroline are known and can be classified as either bowed or twisted.[6-12] These include four-coordinate and tetragonally distorted six-coordinate metal complexes such as complexes with the formulation $\mathrm{M(phen)_2}^{2+}$, where M = Pd and Pt, which exist in the twist configuration. An eight-coordinate complex $[\mathrm{Sr(phen)_2(OH_2)_4}](\mathrm{ClO_4})_2\cdot2\mathrm{phen}$ is the only undistorted example[13] and underlines the importance of the steric interaction under consideration. In this case the coordinated phenanthrolines are both flat and coplanar but the M–N distances are such that no hydrogen–hydrogen interactions are expected.

In this report a general prepraration for the previously unknown series of complexes $\mathrm{Ru(phen)_2L_2}^{2+}$ is described. A single-crystal X-ray structure determination has been performed on the bis pyridine complex, and this analysis indicates still a third possible mode of distortion for the relief of α-hydrogen interaction.

Experimental Section

Equipment. UV–visible absorption spectra were obtained on a Varian DMS-90 spectrophotometer. Electrochemical measurements were carried out at 22 ± 2 °C in acetonitrile with 0.1 M tetraethylammonium perchlorate as supporting electrolyte. Photolyses were performed in glass vessels with a 450-W medium-pressure mercury lamp or a 275-W sunlamp. Infrared spectra were recorded on a Perkin-Elmer Model 299 or Model 283 spectrometer either as a mull with Nujol or as a KBr pellet. NMR spectra were recorded on a Varian EM-360A or a JEOL FX 900 spectrometer.

Materials. The complexes *cis*-$\mathrm{Ru(phen)_2Cl_2\cdot2H_2O}$,[14] $\mathrm{Ru(phen)_2CO_3\cdot2H_2O}$,[15] *cis*-$[\mathrm{Ru(phen)_2(py)_2}](\mathrm{PF_6})_2$[16] (py = pyridine), and *cis*-$[\mathrm{Ru(phen)_2(CH_3CN)_2}](\mathrm{PF_6})_2$[17] were prepared by methods described for the corresponding 2,2′-bipyridyl complexes. Other materials were reagent grade and used as received. Elemental analyses were performed by Integral Microanalytical Laboratories, Raleigh, NC, and Air Products Corp., Trexlertown, PA.

***trans*-$[\mathrm{Ru(phen)_2(OH_2)_2}](\mathrm{PF_6})_2$.** One hundred milliliters of 3% $\mathrm{HPF_6}$ was added to 0.263 g of $\mathrm{Ru(phen)_2CO_3\cdot2H_2O}$ and the solution was stirred for 15 minutes. After it was filtered, the solution was irradiated for 2.5 h with a 450-W mercury lamp. The product, which precipitated during photolysis, was collected by filtration and washed twice with water and three times with diethyl ether; yield 0.254 g (68%). Anal. Calcd for $\mathrm{RuC_{24}H_{20}N_4O_2P_2F_{12}}$: C, 36.61; H, 2.56; N, 7.12. Found: C, 36.26; H, 2.45; N, 6.95.

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Table I. Summary of Crystallographic Data

formula: $RuC_{34}H_{26}N_6P_2F_{12}$
fw: 909.7
space group: $P\bar{1}$
V = 857.5 Å^3
Z = 1
D(calcd) = 1.76 g cm^{-3}
μ(Cu Kα) = 56.76 cm^{-1}
a = 10.316 (1) Å
b = 10.887 (2) Å
c = 8.775 (1) Å
α = 89.09 (1)°
β = 97.66 (1)°
γ = 118.45 (2)°
radiation: Cu Kα (λ = 1.5418 Å)
diffractometer: manual unit, GE XRD-5 quarter circle
no. of reflctns used for unit cell detn: 15 (2θ = 60–85°)
data set, 2θ max: 100°
scan type: θ–2θ
scan speed: 2°/min
scan width: 2°
bkgd measmt: 10 s stationary, each end of scan
total no. of reflctns collected: 1754
unique data used with $I > 3\sigma(I)$: 1731
no. of parameters refined: 256
range of abs cor: 0.51–0.78
weighting scheme: $w = 1/(2F_{min} + F_o + 2F_o^2/F_{max})$
$R(F)$, $R_w(F)$: 0.047, 0.062
std dev of observn of unit wt: 0.55
cryst faces, face-to-center dist: (100), $(\bar{1}00)$, 0.045 mm; $(\bar{1}07)$, $(10\bar{7})$, 0.094 mm; (010), $(0\bar{1}0)$, 0.126 mm; $(\bar{1}10)$, $(1\bar{1}0)$, 0.126 mm

***cis*-[Ru(phen)$_2$(OH$_2$)$_2$](PF$_6$)$_2$.** Three milliliters of water and 5 mL of 30% HPF$_6$ were added to 120 mg of Ru(phen)$_2$CO$_3$·2H$_2$O. After 5 min of stirring, the solution was filtered and the remaining solid was washed several times with water. The solution and washings were combined, and the volume was reduced on a rotary evaporator. The product was collected by filtration, dissolved in warm water, and precipitated by adding 0.5 mL of 60% HPF$_6$ and reducing the volume. The resulting product was collected, washed twice with water, and air-dried; yield 96 mg (56%). Anal. Calcd for $RuC_{24}H_{20}N_4O_2P_2F_{12}\cdot H_2O$: C, 35.01; H, 2.94; N, 6.80. Found: C, 34.78; H, 2.88 N, 6.76.

***trans*-[Ru(phen)$_2$(py)$_2$](PF$_6$)$_2$.** After *trans*-[Ru(phen)$_2$(H$_2$O)$_2$](PF$_6$)$_2$ (48 mg) was dissolved in 15 mL of acetone, 10 mL of pyridine was added and the solution was heated gently for 1 h. The solution was placed in a freezer overnight. Bright red crystals were obtained by filtering and washing once with pyridine and three times with diethyl ether; yield 26 mg (47%). Anal. Calcd for $RuC_{34}H_{26}N_6P_2F_{12}$: C, 44.89; H, 2.89; N, 9.24. Found: C, 44.86; H, 2.81; N, 9.21.

***trans*-[Ru(phen)$_2$(CH$_3$CN)(H$_2$O)](PF$_6$)$_2$.** Acetonitrile (5 mL) was added to 0.129 g of *trans*-[Ru(phen)$_2$(H$_2$O)$_2$](PF$_6$)$_2$. After it was stirred for about 1 min, the solution was filtered and poured into diethyl ether. The product was collected by filtration, washed twice with diethyl ether, and air-dried; yield 0.126 g (96%). Anal. Calcd for $RuC_{26}H_{21}N_5OP_2F_{12}$: C, 38.53; H, 2.62; N, 8.64. Found: C, 37.76; H, 2.64; N, 8.53.

***trans*-[Ru(phen)$_2$(CH$_3$CN)$_2$](PF$_6$)$_2$.** *trans*-[Ru(phen)$_2$(H$_2$O)$_2$](PF$_6$)$_2$ was prepared from 0.130 g of Ru(phen)$_2$CO$_3$ as described above. The product was dissolved in acetonitrile and refluxed under nitrogen for 2 h. The solution was added to a large excess of diethyl ether. The resulting precipitate was collected by filtration, washed twice with diethyl ether, and air-dried; yield 0.141 g (72%). Anal. Calcd for $RuC_{28}H_{22}N_6P_2F_{12}$: C, 40.33; H, 2.60; N, 10.08. Found: C, 40.05; H, 2.57; N, 10.06.

X-ray Measurements. Crystallographic data for *trans*-[Ru(phen)$_2$(py)$_2$](PF$_6$)$_2$ are summarized in Table I. Periodic measurements of three check reflections during data collection showed one abrupt change of 2.5% in intensity, which was attributed to instrument instability; a simple scaling factor was used to compensate for the event. Ten of the 1741 observed reflections were removed due to obvious human errors in the manual data collection. All non-hydrogen atoms were found on a Fourier map phased by a Ru atom at the origin. Least-squares refinements used anisotropic temperature factors for non-hydrogen atoms and fixed isotropic temperature factors (B = 5.0 Å^2) for hydrogen atoms. All hydrogen atoms were located on difference maps. In the final full-matrix least-squares refinement all hydrogen atoms, except the two α-hydrogen atoms of the phenanthroline ligand, which were refined, were held in fixed positions (C–H = 0.95 Å). The largest peak on the final difference map, near the ruthenium atom, had a magnitude of 0.73 e/Å^3. There were also several peaks near the hexafluorophosphate anion which suggested an orientational disorder; however, no rational scheme for the disorder was apparent. Neutral-atom scattering factors[18] were used for all atoms; anomalous dispersion corrections were made for ruthenium and phosphorus.[18] The weighting scheme gave a final refinement that showed no dependence of $\Delta F/\sigma$ on either F or θ. The constrained hydrogen atom positions, the anisotropic thermal parameters, and the structure factor tables are available as supplementary material.

Table II. Positional Parameters for [Ru(phen)$_2$(py)$_2$](PF$_6$)$_2$

atom	x/a	y/b	z/c	B_{equiv},[a] Å^2
Ru1	0.0	0.0	0.0	2.60 (3)
N2	0.0494 (5)	−0.0777 (5)	−0.1886 (5)	3.1 (2)
N3	0.0544 (5)	0.1648 (5)	−0.1492 (5)	3.1 (2)
N4	0.2281 (5)	0.0940 (4)	0.0842 (5)	2.9 (2)
C5	0.0273 (7)	−0.2041 (7)	−0.2231 (7)	4.2 (3)
C6	0.0874 (8)	−0.2351 (7)	−0.3416 (7)	4.8 (3)
C7	0.1693 (7)	−0.1311 (8)	−0.4306 (7)	4.8 (4)
C8	0.1871 (7)	0.0023 (7)	−0.4058 (7)	3.8 (3)
C9	0.2624 (7)	0.1159 (8)	−0.4991 (7)	4.9 (3)
C10	0.2678 (8)	0.2401 (8)	−0.4771 (8)	4.7 (3)
C11	0.1958 (6)	0.2624 (7)	−0.3607 (7)	3.6 (3)
C12	0.1888 (7)	0.3858 (7)	−0.3407 (7)	4.4 (3)
C13	0.1100 (7)	0.3940 (6)	−0.2319 (8)	4.4 (3)
C14	0.0432 (7)	0.2811 (6)	−0.1398 (7)	3.9 (3)
C15	0.1284 (6)	0.1548 (6)	−0.2624 (6)	2.9 (3)
C16	0.1245 (6)	0.0244 (6)	−0.2852 (6)	3.0 (3)
C17	0.3086 (6)	0.2327 (6)	0.1171 (7)	3.6 (3)
C18	0.4569 (7)	0.2977 (7)	0.1707 (8)	4.7 (3)
C19	0.5300 (7)	0.2198 (8)	0.1934 (8)	4.9 (3)
C20	0.4493 (7)	0.0783 (8)	0.1592 (8)	4.9 (4)
C21	0.3009 (7)	0.0201 (6)	0.1053 (7)	3.9 (3)
P22	0.3153 (2)	0.6379 (2)	0.2303 (3)	6.3 (1)
F23	0.4730 (6)	0.7405 (7)	0.1966 (7)	9.7 (3)
F24	0.2528 (8)	0.6942 (8)	0.0837 (9)	13.0 (5)
F25	0.313 (1)	0.5299 (7)	0.110 (1)	15.1 (6)
F26	0.3777 (8)	0.580 (1)	0.365 (1)	16.3 (6)
F27	0.305 (1)	0.7471 (9)	0.320 (1)	20.5 (8)
F28	0.1544 (8)	0.531 (1)	0.254 (2)	19.7 (8)
H29	−0.04 (1)	−0.27 (1)	−0.17 (1)	
H30	−0.01 (1)	0.288 (9)	−0.06 (1)	

[a] $B_{equiv} = {}^4/_3(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab\cos\alpha + \beta_{13}ac\cos\beta + \beta_{23}\cos\gamma)$.

Results and Discussion

Photolysis of a concentrated solution of *cis*-Ru(phen)$_2$(H$_2$O)$_2^{2+}$ in aqueous HPF$_6$ results in the production of *trans*-Ru(phen)$_2$(H$_2$O)$_2^{2+}$, which readily precipitates as the hexafluorophosphate salt. In dilute solution without excess PF$_6^-$, spectral changes suggest that a photostationary state with approximately equal concentrations of the cis and trans isomers is obtained. The trans isomer is thermally unstable in aqueous solution and completely converts to the cis isomer in about 8 h at room temperature.

Both *cis*- and *trans*-Ru(phen)$_2$(H$_2$O)$_2^{2+}$ will undergo facile replacement of aquo ligands by solvent when placed in pyridine or acetonitrile solution. In each case complete retention of geometric configuration is observed. In acetonitrile, substitution for the first aquo ligand appears to be complete upon mixing and the intermediate *trans*-[Ru(phen)$_2$(CH$_3$CN)(H$_2$O)](PF$_6$)$_2$ can be isolated. The second step is complete in about 2 h at room temperature. Photolysis of *trans*-Ru(phen)$_2$(py)$_2^{2+}$ in pyridine or of *trans*-Ru(phen)$_2$(CH$_3$CN)$_2^{2+}$ in acetonitrile results in rapid and quantitative conversion to the corresponding cis complexes. The above results are remarkably similar to those reported for the *trans*-Ru(bpy)$_2$L$_2^{2+}$ complexes.[3,4]

The structure of *trans*-[Ru(phen)$_2$(py)$_2$](PF$_6$)$_2$ has been confirmed by single-crystal X-ray analysis and is described

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[18] "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Table III. Selected Bond Distances (Å) and Angles (deg) for *trans*-$[Ru(phen)_2(py)_2](PF_6)_2$

Ruthenium Inner Coordination Sphere			
Ru1-N2	2.096 (5)	Ru1-N4	2.097 (5)
Ru1-N3	2.100 (5)		
N2-Ru1-N3	78.09 (6)	N3-Ru1-N4	86.61 (6)
N2-Ru1-N4	86.83 (6)		
Phenanthroline Ligand			
N2-C5	1.317 (9)	C10-C11	1.427 (9)
N2-C16	1.371 (8)	C11-C12	1.39 (1)
N3-C14	1.330 (9)	C11-C15	1.397 (9)
N3-C15	1.365 (7)	C12-C13	1.36 (1)
C5-C6	1.40 (1)	C13-C14	1.40 (1)
C6-C7	1.36 (1)	C15-C16	1.418 (9)
C7-C8	1.39 (1)	C5-H	0.9 (1)
C8-C9	1.42 (1)	C14-H	1.01 (9)
C8-C16	1.390 (8)	H(C5)-H(C14′)	2.0 (1)
C9-C10	1.34 (1)		
Ru1-N2-C5	130.78 (8)	C5-N2-C16	116.4 (6)
Ru1-N2-C16	112.73 (7)	C14-N3-C15	116.7 (6)
Ru1-N3-C14	130.36 (8)	N2-C5-C6	123.8 (6)
Ru1-N3-C15	112.40 (7)	C7-C8-C9	123.7 (6)
N2-C16-C8	123.2 (6)	C7-C8-C16	117.9 (5)
N2-C16-C15	116.3 (6)	C10-C11-C12	123.3 (6)
N2-C5-H(C5)	113 (6)	C12-C11-C15	118.4 (4)
C6-C5-H(C5)	123 (6)	N3-C14-C13	123.6 (6)
N3-C14-H(C14)	117 (6)	N3-C15-C11	122.8 (6)
C13-C14-H(C14)	119 (6)	N3-C15-C16	116.8 (6)
Pyridine Ligand			
N4-C17	1.344 (9)	C19-C20	1.37 (1)
C17-C18	1.36 (1)	C20-C21	1.36 (1)
C18-C19	1.38 (1)	N4-C21	1.335 (8)
Ru1-N4-C17	121.34 (8)	N4-C17-C18	123.1 (6)
Ru1-N4-C21	121.88 (8)	N4-C21-C20	123.2 (6)
C17-N4-C21	116.8 (6)		
Hexafluorophosphate Ion			
P22-F23	1.539 (8)	P22-F26	1.538 (9)
P22-F24	1.605 (9)	P22-F27	1.49 (1)
P22-F25	1.583 (9)	P22-F28	1.55 (1)

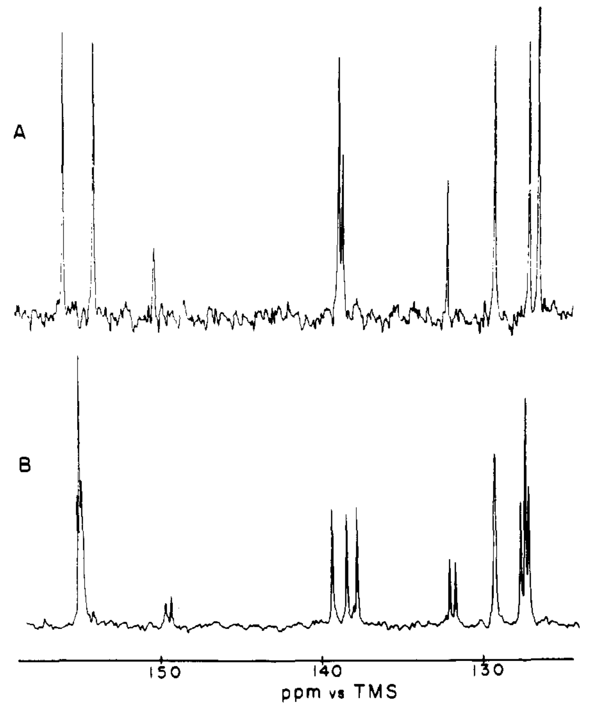

Figure 1. Aromatic region of the ^{13}C NMR spectra of (A) *trans*- and (B) *cis*-$[Ru(phen)_2(py)_2](PF_6)_2$ in CD_3CN.

below. The geometry of the cis and trans isomers of $Ru(phen)_2L_2^{2+}$ complexes, however, can be easily assigned from the phenanthroline portion of the proton or ^{13}C NMR spectra. The latter is particularly useful with complexes containing additional aromatic ligands as illustrated in Figure 1 for the difficult case of $Ru(phen)_2(py)_2^{2+}$. In general, the trans complexes yield spectra in which the halves of the 1,10-phenanthroline ligand appear equivalent. The spectra are thus similar to that of free 1,10-phenanthroline.[19] Cis complexes, on the other hand, yield spectra in which the halves of the 1,10-phenanthroline are nonequivalent and two sets of slightly different aromatic resonances are observed.

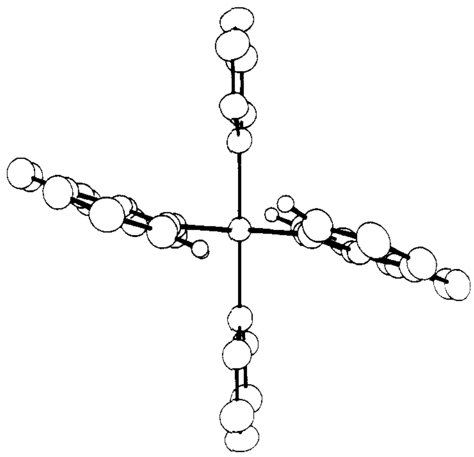

Figure 2. ORTEP drawing of the *trans*-$Ru(phen)_2(py)_2^{2+}$ cation.

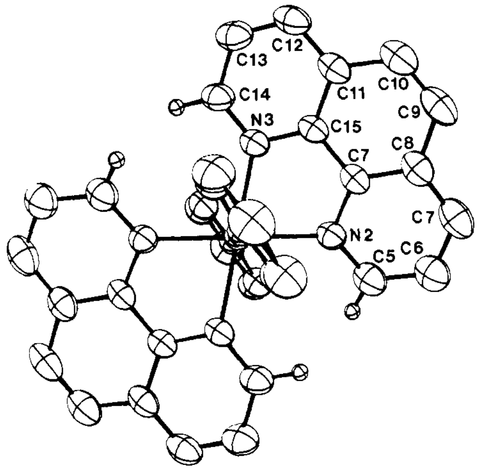

Figure 3. Atom-numbering scheme used for the *trans*-$Ru(phen)_2(py)_2^{2+}$ cation.

Structurally, the $Ru(phen)_2(py)_2^{2+}$ cation is unique among other trans-phenanthroline complexes. In particular, $Ru(phen)_2(py)_2^{2+}$ undergoes a new type of distortion to relieve the problem of the close approach of the α-hydrogen atoms on opposing phenanthroline ligands. This new distortion can be described as a "tilt" displacement of the phenanthroline ligands such that both nitrogen atoms of each ligand are displaced 0.12 Å from the idealized equatorial plane of the RuN_6 octahedron. This gives an angle between the N(py)–Ru–N(py) axis and the RuN_4 (phenanthroline N atoms) plane of 85.8 (2)°. The phenanthroline ligands are then tilted by a rotation of 15.6 (2)° about their N–N vectors, as shown in Figure 2. This configuration gives an interligand α-hydrogen separation (H(C25)–H(C14′)) of 2.0 (1) Å. The phenanthroline ligand has larger deviations from planarity (mean 0.08 Å, maximum 0.17 Å) than the phenanthroline ligands in the Pt, Pd, and Hg cations $M(phen)_2^{2+}$ (mean 0.013–0.028 Å).[6,7,13] These latter ions all accommodate the H atom steric problem by undergoing a "twist" distortion and thus lie on twofold axes whereas the $Ru(phen)_2(py)_2^{2+}$ cation is located on a crystal-

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[19] Miller, J. D.; Prince, R. H. *J. Chem. Soc. A* **1969**, 519.

Table IV. Best Planes Data

A. Displacements from Best Planes (Å)[a]

atom	plane 1	plane 2	plane 3	plane 4	plane 5	plane 6	plane 7	plane 8
Ru1	−0.503	0.0*	0.281	0.342	−0.292	0.359	−0.354	−0.464
N2	−0.083 (4)*	0.0*	0.021 (5)*	−0.180 (4)	−0.025 (5)*	−0.022 (4)	0.191 (4)	−0.003 (4)*
N3	−0.050 (4)*	0.0*	−0.267 (5)	0.011 (4)*	0.277 (5)	−0.058 (4)	−0.015 (4)*	0.003 (4)*
C5	0.107 (6)*	0.200 (7)	−0.044 (7)*	−0.481 (6)	0.033 (7)*	−0.212 (6)	0.498 (6)	0.202 (6)
C6	0.175 (7)*	−0.036 (7)	−0.015 (7)*	−0.608 (6)	0.010 (7)*	−0.251 (7)	0.642 (6)	0.299 (7)
C7	0.086 (6)*	−0.453 (6)	0.038 (7)*	−0.461 (6)	−0.028 (7)*	−0.134 (6)	0.502 (6)	0.224 (6)
C8	−0.021 (6)*	−0.589 (6)	0.012 (6)*	−0.235 (5)	0.006 (6)*	−0.026 (6)*	0.270 (5)	0.103 (6)
C9	−0.031 (6)*	−0.933 (6)	−0.026 (7)*	−0.156 (6)	0.059 (7)	0.012 (6)*	0.198 (6)	0.107 (6)
C10	−0.043 (7)*	−0.962 (7)	−0.143 (7)	−0.029 (6)*	0.184 (7)	0.023 (7)*	0.064 (6)	0.080 (7)
C11	−0.022 (6)*	−0.624 (6)	−0.258 (6)	0.006 (5)*	0.291 (6)	−0.027 (6)*	0.013 (5)*	0.072 (6)
C12	0.066 (6)*	−0.543 (6)	−0.480 (7)	0.036 (6)*	0.520 (7)	−0.118 (6)	−0.026 (6)*	0.144 (6)
C13	0.157 (7)*	−0.137 (7)	−0.652 (7)	−0.010 (6)*	0.685 (7)	−0.238 (7)	0.005 (6)*	0.207 (7)
C14	0.110 (6)*	0.139 (6)	−0.553 (7)	−0.036 (6)*	0.571 (7)	−0.219 (6)	0.024 (6)*	0.148 (6)
C15	−0.087 (5)*	−0.356 (5)	−0.148 (5)	0.004 (5)*	0.166 (5)	0.009 (5)*	0.008 (5)*	−0.007 (5)*
C16	−0.089 (5)*	−0.342 (5)	−0.010 (5)*	−0.115 (5)	0.020 (5)*	0.012 (5)*	0.134 (5)	0.007 (5)*
H(C5)	0.30 (9)	0.61 (9)	−0.2 (1)	−0.71 (9)	0.2 (1)	−0.42 (9)	0.72 (9)	0.38 (9)
H(C14)	0.17 (9)	0.43 (9)	−0.68 (9)	−0.06 (8)	0.69 (9)	−0.30 (9)	0.04 (8)	0.19 (9)

B. Dihedral Angles (deg)

planes	angle	planes	angle	planes	angle	planes	angle
1-2	15.6 (2)	2-3	15.7 (2)	3-5	0.6 (2)	4-8	4.5 (3)
1-3	5.6 (2)	2-4	15.8 (2)	3-6	5.5 (2)	5-6	5.8 (3)
1-4	4.9 (2)	2-5	16.3 (2)	3-7	10.8 (2)	5-7	11.1 (2)
1-5	5.9 (2)	2-6	14.2 (2)	3-8	6.5 (3)	5-8	6.6 (3)
1-6	1.4 (2)	2-7	16.3 (2)	4-5	10.7 (2)	6-7	5.5 (2)
1-7	5.2 (2)	2-8	16.5 (3)	4-6	5.0 (2)	6-8	2.5 (4)
1-8	1.2 (2)	3-4	10.4 (2)	4-7	0.6 (2)	7-8	4.7 (2)

[a] Asterisks denote the atoms included in the calculation of the plane.

Table V. Spectral and Redox Data for Bis(1,10-phenanthroline)ruthenium(II) Complexes

complex	UV-visible data[a] λ_{max}, nm ($10^{-3}\epsilon$, $M^{-1}\ cm^{-1}$)					redox data[b] $E_{1/2}$, V vs. SCE
cis-$Ru(phen)_2(OH_2)_2^{2+}$	469 (10.7)	264 (83)	223 (55)			...
trans-$Ru(phen)_2(OH_2)_2^{2+}$	500 (11.5)	266 (58)	225 (53)			...
trans-$Ru(phen)_2(OH_2)(CH_3CN)^{2+}$	467 (10.0)	264 (62)				1.08[c]
cis-$Ru(phen)_2(CH_3CN)_2^{2+}$	420 (8.6)	383 (9.4)	261 (65)			1.44
trans-$Ru(phen)_2(CH_3CN)_2^{2+}$	442 (11.0)	263 (58)				1.45
cis-$Ru(phen)_2(py)_2^{2+}$	445 (10.1)	414 (11.0)	316 (8.5)		265 (65)	1.29
trans-$Ru(phen)_2(py)_2^{2+}$	488 (12.0)	409 (6.4)	336 (7.8)	322 (7.5)	267 (48)	1.26

[a] In CH_3CN solution except for aquo complexes, for which water was used as a solvent. [b] In acetonitrile (0.1 M tetraethylammonium perchlorate) vs. saturated sodium chloride calomel electrode. [c] Solvent substitution for the aquo ligand occurs slowly.

lographic center of symmetry. The twist configuration, giving dihedral angles between MN_2 planes of 18.7–27.5°, apparently produces less deformation of the planar ligand than does the tilt arrangement. In terms of the pyramidalization and twist parameters used for the "bowed" and "twisted" cateogorization of distortions in bipyridyl complexes,[5] the more rigid phenanthroline ligands have, as expected, essentially no twisting about the C15–C16 bond (0.9 (9)°) and small pyramidalization parameters (4.1 (6)°) for C15 and C16.

The $Ru(phen)_2$ subunit has an approximate mirror plane of symmetry, which bisects the phenanthroline ligands; corresponding distances and angles for each half of the chelate are the same within 1.5 standard deviations. The pyridine ligands, however, are not consistent with this mirror since the plane of the pyridine ring makes an 84.7 (3)° angle with the pseudomirror. This orientation of the pyridine ring, with its best plane nearly parallel to the N–N vectors of the phenanthroline ligands, is similar to that found in *trans*-$[Ru(Me_2bpy)_2(py)_2](PF_6)_2$.

The Ru–N bond distances of 2.096 (5)–2.100 (5) Å in $Ru(phen)_2(py)_2^{2+}$ are equal to the Ru–N distances[5,20] found in *trans*-$Ru(bpy)_2(py)_2^{2+}$ and $Ru(NH_3)_6^{3+}$ and indicate little or none of the steric problem of the trans-phenanthroline ligands is relieved by Ru–N bond elongation. The small bite of the phenanthroline gives a N–Ru–N angle of 78.09°, which is typical of phenanthroline and bipyridine complexes. No unusual bond distances or angles are observed in the pyridine or hexaphosphate moieties.

Other structural indicators such as the visible spectra of the cis and trans isomers of $Ru(phen)_2L_2^{2+}$ (L = H_2O, CH_3CN, py) are distinctive but cannot be used alone in structural assignments. For each L, the absorbance maximum occurs at lower energy for the trans isomer than for the cis (Table V). The intense bands in the visible region have been assigned as metal-to-ligand charge-transfer bands by analogy to the case for the 2,2′-bipyridyl species.[21] The UV region is dominated by intraligand bands. The infrared spectra of *cis*- and *trans*-$Ru(phen)_2L_2^{2+}$ complexes provided no distinguishing criteria by which the geometry could be assigned. In particular, the CH stretching region (~3100 cm^{-1}), the ring deformation region (1400–1600 cm^{-1}), and the out-of-plane hydrogen motion (~725 cm^{-1}) for the 1,10-phenanthroline complexes showed only minor differences in band position and intensity for a given pair of isomers, but these differences are not consistent in comparing complexes with different L ligands.

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The metal–nitrogen stretching region provided no distinctive information with regard to geometric identity. Cyclic voltammetry indicates that the pyridine and acetonitrile complexes undergo reversible oxidation to the ruthenium(III) state and that both isomers exhibit essentially the same redox potential (Table V).

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Registry No. Ru(phen)$_2$CO$_3$, 71603-93-5; *cis*-[Ru(phen)$_2$(py)$_2$](PF$_6$)$_2$, 85370-13-4; *trans*-[Ru(phen)$_2$(py)$_2$](PF$_6$)$_2$, 85549-97-9; *cis*-[Ru(phen)$_2$(CH$_3$CN)$_2$](PF$_6$)$_2$, 85370-15-6; *trans*-[Ru(phen)$_2$(CH$_3$CN)$_2$](PF$_6$)$_2$, 85439-56-1; *trans*-[Ru(phen)$_2$(OH$_2$)$_2$](PF$_6$)$_2$, 85439-54-9; *cis*-[Ru(phen)$_2$(OH)$_2$](PF$_6$)$_2$, 85370-16-7; *trans*-[Ru(phen)$_2$(CH$_3$CN)(H$_2$O)](PF$_6$)$_2$, 85370-18-9.

Supplementary Material Available: Listings of positional parameters for hydrogen atoms, anisotropic thermal parameters, and observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Laboratory for Research on the Structure of Matter,
University of Pennsylvania, Philadelphia, Pennsylvania 19104

Structural Characterization of 3′:2-[2′,4′-$C_2B_5H_6$][1,8,5,6-(η-C_5H_5)$_2$$Co_2C_2B_5H_6$]: A Coupled-Cage Cobaltacarborane Containing a Boron–Boron Linkage

ROBERT P. MICCICHE, JEFFREY S. PLOTKIN, and LARRY G. SNEDDON*[1]

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The molecular structure of 3′:2-[2′,4′-$C_2B_5H_6$][1,8,5,6-(η-C_5H_5)$_2$$Co_2C_2B_5H_6$] has been determined from the single-crystal X-ray diffraction data. In agreement with the structure previously proposed on the basis of the spectroscopic data, the compound was shown to be a two-cage complex consisting of a 1,8,5,6-(η-C_5H_5)$_2$$Co_2C_2B_5H_6$ cobaltacarborane unit linked to a 2′,4′-$C_2B_5H_6$ carborane cage by means of a two-center boron–boron single bond. The cage geometry of the 1,8,5,6-(η-C_5H_5)$_2$$Co_2C_2B_5H_6$ is based on a tricapped trigonal prism, while that of the 2′,4′-$C_2B_5H_6$ unit is based on a pentagonal bipyramid. Crystal data: space group $P\bar{1}$, $Z = 2$, $a = 9.155$ (3) Å, $b = 15.659$ (11) Å, $c = 7.142$ (2) Å, $\alpha = 99.64$ (4)°, $\beta = 101.11$ (3)°, $\gamma = 100.69$ (5)°, $V = 965$ (2) Å^3. The structure was refined by full-matrix least-squares methods to a final R of 0.047 and R_w of 0.047 for the 2085 reflections that had $F_o^2 > 3\sigma(F_o^2)$.

Introduction

The number and variety of multicage boron compounds have increased significantly in the last few years because of the development of new synthetic procedures for the formation of cage linkages. The availability of these compounds has now allowed initial investigations of the chemistry and properties of these unique species that have already demonstrated that these compounds will be an important area of future research. We, in particular, have become interested in the formation and properties of multimetal, multicage boron clusters and have already reported[2] that the reaction of (η-C_5H_5)Co(CO)$_2$ with an isomeric mixture of the coupled-cage carborane (2,4-$C_2B_5H_6$)$_2$ results in the formation of six isomeric cobaltacarboranes. Each of these complexes was proposed on the basis of spectroscopic data to be composed of a (η-C_5H_5)$_2$$Co_2C_2B_5H_6$ cobaltacarborane linked by means of a boron–boron single bond to a 2,4-$C_2B_5H_6$ carborane cage. We also demonstrated that at elevated temperatures these coupled cage complexes underwent three different types of reversible rearrangements until at 400 °C an equilibrium mixture of 12 different isomeric compounds was produced. We report here the structural characterization of one of these compounds.[3]

Experimental Section

Several crystals of the compound were grown over a 12-h period by evaporation of a dilute heptane solution. A very thin rectangular-shaped crystal, 0.484 × 0.125 × 0.030 mm, was selected for data collection, mounted on a glass fiber, and then transferred to the diffractometer. The Enraf-Nonius program SEARCH was used to obtain 25 reflections, which were then used in the program INDEX to obtain an orientation matrix for data collection. This orientation matrix was improved by the substitution of new reflections, and refined cell dimensions and their standard deviations were obtained from the least-squares refinement of these 25 accurately centered reflections. Crystal data: $Co_2C_{14}B_{10}H_{22}$, mol wt 416.31, space group $P\bar{1}$, $Z = 2$, $a = 9.155$ (3) Å, $b = 15.659$ (11) Å, $c = 7.142$ (2) Å, $\alpha = 99.64$ (4)°, $\beta = 101.11$ (3)°, $\gamma = 100.69$ (5)°, $V = 965$ (2) Å^3, ρ(calcd) = 1.433 g cm^{-3}. The mosaicity of the crystal was judged acceptable on the basis of several θ scans.

Collection and Reduction of Data. The diffraction data were collected at 295 K on an Enraf-Nonius four-circle CAD-4 diffractometer interfaced with a PDP 8/A computer, employing Mo Kα radiation from a highly oriented graphite-crystal monochromator. A combined $2\theta,\omega$-scan technique was used to record the intensities of all reflections for which $1.0 < 2\theta < 50°$. The raw intensities were corrected for Lorentz and polarization effects by using the Enraf-Nonius program DATARD. Of the 3395 measured intensities, 2085 had $F_o^2 > 3\sigma(F_o^2)$ and were used in the analysis.

Solution and Refinement of Structure. All calculations were performed on a PDP 11/60 computer using the Enraf-Nonius structure determination package.[4]

Normalized structure factors were calculated by using a K curve, and the intensity distribution statistics support a centrosymmetric space group. A three-dimensional Patterson synthesis gave the coordinates of the cobalt atoms. Full-matrix least-squares refinement of these coordinates, with use of preliminary scale and thermal parameters from the Wilson plot, followed by a subsequent Fourier map phased on these refined coordinates, led to the location of the remaining heavy atoms of the complex. Anisotropic least-squares refinement of these atoms followed by a difference Fourier synthesis resulted in the location

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[1] Alfred P. Sloan Foundation Fellow.

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[3] Compound II in ref 2.

[4] Enraf-Nonius Inc., Garden City Park, NY.

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