

The Structure of Carbonatobis(2,2'-bipyridine)ruthenium(II) Tetrahydrate

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(Received 18 December 1980; accepted 12 June 1981)

Abstract

[Ru(C₁₀H₈N₂)₂CO₃].4H₂O is monoclinic, space group C2/c, with $a = 15.775$ (3), $b = 19.738$ (4), and $c = 7.1467$ (15) Å, $\beta = 96.42$ (2)°, $U = 2211.3$ (8) Å³, $Z = 4$. The final R value is 0.040 for 1552 independent reflections. The crystal structure consists of a monomeric complex with a bidentate carbonato ligand and four water molecules. The complex molecule has twofold symmetry.

Introduction

Carbonatobis(2,2'-bipyridine)ruthenium(II) tetrahydrate was synthesized as a starting material for preparing bis(2,2'-bipyridine)ruthenium(II) derivatives (Johnson, Sullivan, Salmon, Adeyemi & Meyer, 1978; Tanaka, Nagai, Miki, Mizumachi & Ishimori, 1979). There are many metal-carbonato complexes, and a variety of coordination behaviour is found for the carbonato ligand in the complexes. In our previous paper (Tanaka *et al.*, 1979), it was proposed that the carbonato ligand in the title complex is bidentate on the basis of the IR absorption. Also, we have been interested in the high lability of the carbonato ligand. An X-ray structure analysis of this complex was made to determine specific structural details.

Experimental and structure determination

The single crystal for X-ray analysis was prepared as described in the literature (Tanaka *et al.*, 1979). A well formed pillar-shaped crystal with dimensions 0.2 × 0.15 × 0.2 mm was used in this work.

X-ray diffraction data were collected on a Rigaku four-circle automatic diffractometer with graphite-monochromatized Mo $K\alpha$ radiation within the range $2\theta < 55^\circ$. Intensities were not corrected for absorption ($\mu = 0.748$ mm⁻¹). The usual Lorentz and polarization corrections were applied and 1552 independent reflec-

tions with $|F| > 3\sigma(F)$ were used in the calculations. The structure was solved by the heavy-atom method and was refined by the block-diagonal least-squares method with anisotropic temperature factors. Unit weight was given to all reflections. The two O atoms of the water molecules and all H atoms of the bipyridine rings, which were derived from the difference Fourier synthesis, were included in the final refinement with anisotropic and isotropic temperature factors, respectively. The final value of R was 0.040. Atomic parameters are given in Table 1. Selected interatomic

Table 1. Atomic parameters

Positional parameters are multiplied by 10⁴ for Ru, O, N, and C atoms and by 10³ for H atoms. The atom-numbering scheme is shown in Fig. 1.

	x	y	z	B_{eq}^*/B (Å ²)
Ru†	0	2033 (0)	2500	3.5 (0)
O(1)	498 (3)	2932 (2)	1544 (7)	6.9 (1)
O(2)†	0	3921 (4)	2500	14.6 (5)
O(3)	763 (4)	3869 (4)	-1363 (11)	12.9 (3)
O(4)	1150 (4)	4759 (4)	4404 (17)	19.8 (5)
N(1)	986 (2)	2007 (2)	4610 (6)	3.6 (1)
N(2)	753 (2)	1327 (2)	1499 (6)	3.4 (1)
C(1)	1657 (3)	1613 (3)	4278 (8)	3.6 (1)
C(2)	2379 (3)	1552 (3)	5585 (8)	4.5 (2)
C(3)	2400 (4)	1915 (3)	7242 (9)	5.4 (2)
C(4)	1732 (4)	2316 (3)	7582 (9)	5.3 (2)
C(5)	1033 (3)	2361 (3)	6246 (9)	4.7 (2)
C(6)	1539 (3)	1241 (3)	2493 (7)	3.4 (1)
C(7)	2146 (3)	840 (3)	1812 (8)	4.3 (2)
C(8)	1959 (4)	483 (3)	157 (9)	5.4 (2)
C(9)	1141 (4)	531 (4)	-773 (9)	5.5 (2)
C(10)	573 (3)	959 (3)	-80 (8)	4.5 (2)
C(11)†	0	3282 (5)	2500	8.6 (4)
H(2)	287 (3)	128 (3)	518 (7)	4.5 (1.2)
H(3)	289 (3)	186 (3)	817 (7)	5.5 (1.6)
H(4)	171 (3)	259 (3)	869 (7)	4.8 (1.2)
H(5)	54 (3)	265 (2)	631 (7)	3.8 (1.1)
H(7)	262 (3)	78 (3)	254 (8)	4.9 (1.2)
H(8)	241 (3)	23 (3)	-31 (8)	6.0 (1.6)
H(9)	97 (4)	29 (3)	-209 (8)	7.4 (1.5)
H(10)	1 (3)	103 (2)	-69 (7)	4.3 (1.2)

$$* B_{eq} = \frac{1}{3} \sum_i \sum_j \beta_{ij} a_i^* \cdot a_j^*$$

† Multiplicity 0.5.

Table 2. *Interatomic distances (Å) within a molecule*

Estimated standard deviations are given in parentheses.

Ru—O(1)	2.087 (5)	O(1)—C(11)	1.297 (7)
Ru—N(1)	2.042 (4)	O(2)—C(11)	1.261 (13)
Ru—N(2)	2.013 (4)		
N(1)—C(1)	1.356 (6)	N(2)—C(6)	1.369 (6)
C(1)—C(2)	1.395 (7)	C(6)—C(7)	1.373 (7)
C(2)—C(3)	1.381 (9)	C(7)—C(8)	1.380 (9)
C(3)—C(4)	1.362 (9)	C(8)—C(9)	1.387 (8)
C(4)—C(5)	1.378 (8)	C(9)—C(10)	1.364 (9)
C(5)—N(1)	1.357 (7)	C(10)—N(2)	1.346 (7)
C(2)—H(2)	1.01 (5)	C(7)—H(7)	0.87 (5)
C(3)—H(3)	0.96 (5)	C(8)—H(8)	0.96 (6)
C(4)—H(4)	0.96 (5)	C(9)—H(9)	1.06 (6)
C(5)—H(5)	0.97 (5)	C(10)—H(10)	0.96 (5)
C(1)—C(6)	1.466 (7)	H(2)—H(7)	2.12 (7)

Table 3. *Interatomic distances (Å) in the crystal*

Estimated standard deviations are given in parentheses.

O(1)—O(1 ⁱⁱ)	2.195 (6)	H(3)—H(4 ⁱⁱⁱ)	2.52 (7)
O(1)—O(2 ⁱⁱ)	2.239 (8)	H(4)—H(4 ⁱⁱⁱ)	2.96 (7)
O(1)—H(5 ⁱⁱⁱ)	2.53 (4)	H(5)—H(5 ⁱⁱⁱ)	2.55 (7)
O(1)—H(3 ⁱⁱⁱ)	2.57 (5)	H(7)—H(8 ⁱⁱⁱ)	2.56 (8)
O(3)—H(4)	2.94 (5)	H(8)—C(7 ⁱ)	2.94 (5)
O(3)—H(5)	2.93 (4)	H(9)—C(7 ⁱ)	3.06 (6)
O(3)—O(4)	2.82 (1)	H(9)—C(8 ⁱ)	3.05 (6)
O(3)—O(2 ⁱⁱ)	3.134 (8)	H(9)—C(9 ⁱ)	3.13 (6)
O(3)—O(3 ⁱⁱ)	2.750 (9)	H(9)—H(9 ⁱⁱ)	3.06 (8)
O(3)—H(5 ⁱⁱⁱ)	3.17 (5)	H(9)—H(10 ⁱⁱⁱ)	2.55 (7)
O(3)—H(7 ⁱⁱⁱ)	2.86 (5)	H(10)—N(1 ⁱⁱ)	2.66 (5)
O(4)—O(2 ⁱⁱ)	2.706 (9)	H(10)—C(1 ⁱⁱ)	3.14 (5)
O(4)—H(2 ⁱⁱⁱ)	2.57 (5)	H(10)—C(5 ⁱⁱ)	3.10 (5)
O(4)—H(7 ⁱⁱⁱ)	2.96 (5)	H(10)—C(9 ⁱⁱ)	3.10 (5)
O(4)—H(8 ^{iv})	2.48 (5)	H(10)—C(10 ⁱⁱ)	3.06 (5)
		H(10)—H(10 ⁱⁱ)	2.58 (7)

Symmetry operations: Roman superscripts refer to atoms in the following positions: (i) $x, -y, \frac{1}{2} + z$; (ii) $-x, y, \frac{1}{2} - z$; (iii) $\frac{1}{2} - x, \frac{1}{2} - y, -z$; (iv) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

distances and bond angles are tabulated in Tables 2, 3, and 4.* Fig. 1 shows the molecule and Fig. 2 the packing.

Calculations were performed on the FACOM 230-75 computer of this Institute using the UNICS III program system (Sakurai & Kobayashi, 1979). The drawings were prepared by ORTEP (Johnson, 1965).

Description and discussion of the structure

Many structural studies have been reported on a variety of complexes which contain the CO_3^{2-} group. In these complexes, the carbonate ion is coordinated to a

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36212 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Bond angles (°) with estimated standard deviations in parentheses*

O(1)—Ru—N(1)	88.8 (2)	Ru—O(1)—C(11)	90.4 (5)
O(1)—Ru—N(2')	164.5 (2)	O(1)—C(11)—O(1')	115.6 (8)
O(1)—Ru—O(1')	63.5 (2)	O(1)—C(11)—O(2)	122.2 (4)
O(1)—Ru—N(1')	93.6 (2)	Ru—N(1)—C(1)	115.5 (3)
O(1)—Ru—N(2)	102.3 (2)	Ru—N(1)—C(5)	126.0 (3)
N(1)—Ru—N(2')	98.7 (2)	Ru—N(2)—C(6)	116.0 (3)
N(1)—Ru—N(1')	177.1 (2)	Ru—N(2)—C(10)	126.5 (3)
N(1)—Ru—N(2)	79.3 (2)		
N(2)—Ru—N(2')	92.4 (2)		
N(1)—C(1)—C(2)	121.8 (5)	N(2)—C(6)—C(7)	121.0 (5)
C(1)—C(2)—C(3)	118.0 (5)	C(6)—C(7)—C(8)	120.5 (5)
C(2)—C(3)—C(4)	120.6 (5)	C(7)—C(8)—C(9)	118.2 (6)
C(3)—C(4)—C(5)	119.3 (6)	C(8)—C(9)—C(10)	118.9 (6)
C(4)—C(5)—N(1)	121.8 (5)	C(9)—C(10)—N(2)	123.6 (5)
C(5)—N(1)—C(1)	118.5 (4)	C(10)—N(2)—C(6)	117.5 (4)
N(1)—C(1)—C(6)	114.5 (4)	N(2)—C(6)—C(1)	114.1 (4)
C(2)—C(1)—C(6)	123.7 (5)	C(7)—C(6)—C(1)	124.9 (4)
C(1)—C(2)—H(2)	117 (3)	C(6)—C(7)—H(7)	117 (4)
C(3)—C(2)—H(2)	125 (3)	C(8)—C(7)—H(7)	122 (4)
C(2)—C(3)—H(3)	118 (3)	C(7)—C(8)—H(8)	118 (3)
C(4)—C(3)—H(3)	122 (3)	C(9)—C(8)—H(8)	124 (3)
C(3)—C(4)—H(4)	125 (3)	C(8)—C(9)—H(9)	121 (3)
C(5)—C(4)—H(4)	116 (3)	C(10)—C(9)—H(9)	119 (3)
C(4)—C(5)—H(5)	126 (3)	C(9)—C(10)—H(10)	123 (3)
N(1)—C(5)—H(5)	112 (3)	N(2)—C(10)—H(10)	114 (3)

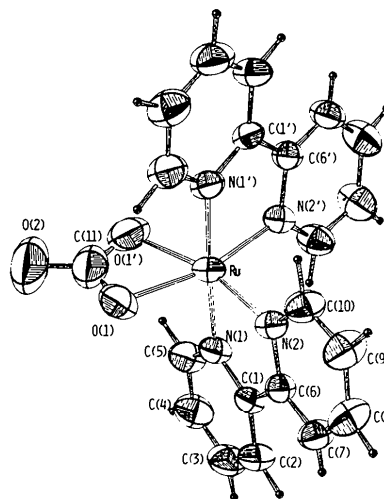
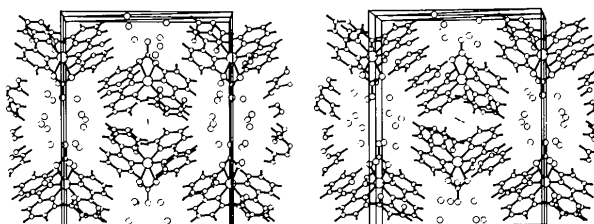


Fig. 1. View of the complex molecule.

Fig. 2. Stereoscopic drawing of the packing viewed along c .

transition metal as a uni- or bidentate ligand in monomeric complexes, and as a bridging multidentate ligand in polymeric compounds. The crystal structure of carbonatobis(bipyridine)ruthenium(II) tetrahydrate consists of a monomeric complex with a bidentate carbonato ligand and four water molecules.

The coordination geometry around Ru is a highly distorted octahedron. The Ru atom and non-coordinated O(2) and C(11) of the carbonato ligand are on a crystallographic twofold axis along the *b* axis. Thus, the molecule has twofold symmetry. The carbonato group is distorted from D_{3h} symmetry as a result of its coordination to Ru. In some carbonate salts, for example CaCO_3 (Sass, Vidale & Donohue, 1957), $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ (Dickens & Brown, 1970), and $\text{CaNa}_2(\text{CO}_3)_2 \cdot n\text{H}_2\text{O}$ (Dickens & Brown, 1969), the carbonate ion weakly interacts with other atoms and maintains nearly D_{3h} symmetry. An average C—O bond length in these compounds is in the range 1.28–1.29 Å. In the present work, the coordinated-oxygen O(1)—C(11) bond length (1.297 Å) slightly increases while the non-coordinated-oxygen O(2)—C(11) length (1.261 Å) clearly decreases. The O(1)—C(11)—O(1') bond angle opposite the shorter O(2)—C(11) bond becomes narrow (115.6°). These features in the bond lengths and angles are generally found in similar carbonate complexes. O(1)—Ru—O(1') of 63.5° is one of the most distorted angles observed yet in the carbonate complexes. The carbonato ligand in this complex is labile in solution and this should be due to the highly strained four-membered ring.

The Ru—N distances are somewhat shorter than the corresponding distances of 2.056 Å in $[\text{Ru}(\text{bpy})_3][\text{PF}_6]_2$ (Rillema, Jones & Levy, 1979). The Ru—N bond lengths *trans* to the N of the bipyridine and *trans* to the O of the carbonato ligand are 2.042 (3) and 2.013 (4) Å, respectively. There is a small difference in length. Also, in similar complexes (Freeman & Robinson, 1965; Gene & Snow, 1971; Kaas & Sørensen, 1973; Hennig, Sieler, Benedix, Kaiser, Sjölin & Lindqvist, 1980), these two kinds of metal—N bond lengths do not differ significantly and no clear influence of the carbonato ligand is found except in $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{Br}$ (Barclay & Hoskins, 1962). The N—Ru—N angle of 79.3 (2)° for the chelating bipyridine is in agreement with the value of 78.7° found in $[\text{Ru}(\text{bpy})_3][\text{PF}_6]_2$. The bond lengths and angles in the bipyridine moiety are quite similar to those in $[\text{Ru}(\text{bpy})_3][\text{PF}_6]_2$ and *trans*- $[\text{Ru}(\text{bpy})_2(\text{OH})_2(\text{OH})][\text{ClO}_4]_2$ (Durham, Wilson, Hodgson & Meyer, 1980). Table 5 gives the equations for the least-squares planes and the deviations of the atoms from them. Equatorial planes 1 and 3 form an angle of 8.9°. The two pyridyl rings (planes 5 and 6) mutually twist about the C(1)—C(6) axis, and make an angle of 7.4° which agrees with a mean value of 8° for the related complexes (Durham *et al.*, 1980). The deviations of the

atoms in plane 5 from plane 6 indicate that in addition to the twist these two planes also incline to each other about the C(1)—C(6) axis.

The torsion angles C(5)—N(1)—C(1)—C(6) and C(10)—N(2)—C(6)—C(1) are 178.8 (5) and -174.8 (4)°, respectively. The mean deviation of the atoms in plane 6 *trans* to the carbonato is larger than that in plane 5 *trans* to the bipyridine. The distance between H(2) and H(7) is 2.12 (7) Å.

Water molecules occupy the vacancy which is surrounded by the carbonato complex molecules and extends along the crystallographic *c* axis. From the interatomic distances in Table 3, it can be considered that the water molecules interact with each other and with the carbonato oxygens and the hydrogens in the bipyridines through hydrogen bonds and van der Waals contacts.

Table 5. *Least-squares planes, with atomic deviations (Å), and dihedral angles (°)*

Plane 1: Ru, O(1), O(2), C(11), O(1')			
$-0.6188X - 0.7855Z = -1.2709$			
Ru	0.000	C(11)	0.000
O(1)	0.000	O(1')	0.000
O(2)	0.000		
Plane 2: Ru, N(1), N(2), C(1), C(6)			
$0.4771X + 0.7430Y - 0.4694Z = 2.0113$			
Ru	0.041 (1)	N(2)	-0.055 (4)
N(1)	-0.039 (4)	C(6)	0.040 (5)
C(1)	0.012 (5)		
Plane 3: Ru, N(2), N(2')			
$-0.4893X - 0.8721Z = -1.4505$			
Ru	0.000	N(2')	0.000
N(2)	0.000		
Plane 4: Ru, N(1'), N(2'), C(1'), C(6')			
$0.4771X - 0.7430Y - 0.4694Z = -3.8686$			
Ru	-0.041 (1)	C(1')	-0.012 (5)
N(1')	0.039 (4)	C(6')	-0.040 (5)
N(2')	0.055 (4)		
Plane 5: N(1), C(1), C(2), C(3), C(4), C(5)			
$0.4700X + 0.7711Y - 0.4295Z = 2.2138$			
N(1)	-0.007 (4)	C(3)	-0.001 (6)
C(1)	0.004 (5)	C(4)	-0.002 (6)
C(2)	0.000 (6)	C(5)	0.006 (6)
Plane 6: N(2), C(6), C(7), C(8), C(9), C(10)			
$0.3812X + 0.7622Y - 0.5233Z = 1.8195$			
N(2)	0.027 (4)	N(1)	-0.061
C(6)	-0.030 (5)	C(1)	-0.117
C(7)	0.006 (6)	C(2)	-0.299
C(8)	0.021 (6)	C(3)	-0.408
C(9)	-0.024 (7)	C(4)	-0.343
C(10)	0.000 (6)	C(5)	-0.158
Dihedral angles			
Plane	Angle (°)	Plane	Angle (°)
1-2	85.8 (2)	2-5	2.8 (2)
1-3	8.9 (2)	2-6	6.4 (2)
2-3	79.9 (2)	5-6	7.4 (2)
2-4	96.0 (2)		

Thanks are due to Miss K. Kobayashi for her assistance with the calculations and to Mr M. Tanaka for his helpful discussions.

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Acta Cryst. (1982). **B38**, 115–120

Beiträge zur Strukturchemie phosphorhaltiger Ketten und Ringe.

3.* 1,2,4,5-Tetra-*tert*-butyl-3,3,6,6-tetramethyl-1,2,4,5-tetraphospha-3,6-disilacyclohexan, $[\text{Me}_2\text{Si}(t\text{-BuP})_2]_2$, ein P_4Si_2 -Sechsring in der klassischen Wannenform

VON ROLAND FRÖHLICH UND KARL-FRIEDRICH TEBBE

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(Eingegangen am 23. Februar 1981; angenommen am 18. Mai 1981)

Abstract

The structure of $\{(\text{CH}_3)_2\text{Si}[(\text{CH}_3)_3\text{CP}]_2\}_2$, $\text{C}_{20}\text{H}_{48}\text{P}_4\text{Si}_2$, has been determined at room temperature by X-ray analysis. The compound crystallizes in the monoclinic space group $P2_1/n$ with $a = 9.170$ (5), $b = 27.716$ (8), $c = 11.840$ (3) Å, $\beta = 108.72$ (3)°, $V = 2850.0$ Å³, $D_c = 1.092$ Mg m⁻³, $Z = 4$. The structure was solved by direct and Fourier methods from diffractometer data and refined by blocked least squares to $R = 0.064$ for 2559 observed reflections. The main structural feature is a six-membered ring with the conformation of a nearly ideal boat. In contrast to the chair and even the twisted boat this rather unusual conformation is fixed by the constitution and configuration of the whole molecule, e.g. by the repulsion

of the all-*trans* substituted *tert*-butyl groups and by the repulsion of the lone pairs on the P atoms. The bond lengths in the ring are $d(\text{P}-\text{P}) = 2.192$ Å and 2.249 Å $\leq d(\text{P}-\text{Si}) \leq 2.279$ Å. The geometry of the methyl and *tert*-butyl substituents is quite normal. Some of the latter are slightly disordered.

Einleitung

Die Reihe der Heterocyclophosphane konnte unter Anwendung der Methode der $[2 + 1]$ -Cyclokondensation auf $\text{K}_2(t\text{-BuP})_2$ und XCl_2 kürzlich um entsprechende Phosphor-Dreiring-Verbindungen ergänzt werden (Übersicht in Baudler, 1980). Dabei treten manchmal auch die Dimeren als Nebenprodukte auf. Diese Folgereaktion wurde z.B. bei der Darstellung der Verbindung 1,2-Di-*tert*-butyl-3,3-dimethyl-1,2,3-diphosphasiliran beobachtet (Baudler & Jongebloed,

* Teil 2: Fehér, Fröhlich & Tebbe (1981b).