in which it has been simplified that diffusion coefficients remain constant in the course of redox processes. On the basis of the anodic shifts of the first and second processes ($\Delta E_1 = 0.04$ V and $\Delta E_2 = 0.17$ V), we obtain $K_1 \simeq 5K_2$ and $K_2 \simeq 8 \times 10^2 K_3$. These results, although roughly computed, are in agreement with the view that oxidation processes remove electrons able to be involved in stabilizing π back-donation toward CO.[20,21] It seems noteworthy that the loss of the two electrons from the HOMO level causes that $K_3 \simeq 2.5 \times 10^{-4} K_1$.

Acknowledgment. We thank the Italian Ministry of Education for financial support. We also thank Professor F. A. Cotton for making the results cited in ref 12 available to us.

Registry No. 1^{2+}, 108149-50-4; 1^+, 108149-51-5; 1, 108149-48-0; 1^-, 108149-52-6; 2, 108149-49-1; $Rh_2(form)_2(O_2CCF_3)_2(H_2O)_2$, 105164-41-8; Rh, 7440-16-6; CO, 630-08-0.

Supplementary Material Available: Cyclic voltammograms of 1 and $Rh_2(form)_2(O_2CCF_3)_2(H_2O)_2$ in CH_2Cl_2 solvent (Figure 6) and a list of temperature factors (Table V) (2 pages); a listing of calculated and observed structure factors (4 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Biochemistry, James Cook University of North Queensland, Townsville, Queensland 4811, Australia, and Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973

Mode of Coordination of Tris(2-pyridyl)methanol to Ruthenium(II): Synthetic, Spectral, and Structural Studies of the Bis(ligand) Species

F. Richard Keene,*[1] David J. Szalda,*[2] and Tracy A. Wilson[1]

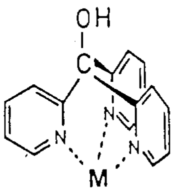
Received September 4, 1986

Two forms of the cation bis[tris(2-pyridyl)methanol]ruthenium(II) have been isolated—a yellow species, $[Ru((py)_3COH)_2]^{2+}$ (**2**), and an orange form in which one ligand is deprotonated, $[Ru((py)_3COH)((py)_3CO^-)]^+$ (**1**). The pK_a for the ligand deprotonation is 3.78 (±0.02) in aqueous 0.1 M KNO_3 at 25.0 °C. X-ray structural determinations show coordination occurs in an (N,N′,N″)(N,N′,O) mode for both complexes, with the coordinated oxygen atom being the site of the acid/base reactivity. The deprotonated species (**1**) has a plane of symmetry with Ru-N bond lengths in the range 2.040-2.063 Å. The nondeprotonated form (**2**) has Ru-N bond lengths in the range 2.046-2.058 Å, except for an abnormally short Ru-N bond (2.023 (2) Å) trans to the coordinated Ru-OH. Additionally, in **2** the plane of symmetry is lost. In aqueous solution the redox potentials for the Ru(III)/Ru(II) couples are 0.40 (**2**) and 0.25 V (**1**) vs. SSCE. The electronic and ^{13}C NMR spectra are also reported. Crystals of the deprotonated form, $[Ru((py)_3COH)((py)_3CO)]Br \cdot 2C_2H_5OH$ (**1a**), are monoclinic, space group $P2_1/m$, with $a = 8.096$ (2) Å, $b = 13.584$ (2) Å, $c = 15.204$ (2) Å, $\beta = 101.96$ (1)°, $V = 1635$ (1) Å^3, and $Z = 2$. Crystals of $[Ru((py)_3COH)_2](CH_3SO_4)_2$ (**2a**) are triclinic, space group $P\bar{1}$, with $a = 13.517$ (3) Å, $b = 14.458$ (2) Å, $c = 9.727$ (2) Å, $\alpha = 104.72$ (2)°, $\beta = 108.56$ (2)°, $\gamma = 92.41$ (2)°, $V = 1727$ (3) Å^3, and $Z = 2$.

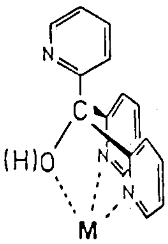
Introduction

The ligation of a number of tripodal π-acceptor tridentates to a variety of metal centers has been reported. Canty et al.[3-6] have used a wide range of ligands XY_3 (X = CH, COH; Y = 2-pyridyl, 1-pyrazolyl, *N*-methylimidazol-2-yl) to impose unusual coordination geometries on metal centers such as Hg(II) and Au(III). White and Faller[7] and Szalda and Keene[8] have isolated complexes of cobalt with tris(2-pyridyl)methanol and tris(2-pyridyl)methane, and Boggess and co-workers[9-11] have reported studies of a number of complexes of first-row transition metals with ligands of the type $(2\text{-py})_3X$ (X = N, P, As, P=O, CH, COH). The zinc complexes of the trisubstituted methanols have also been noted[12] as models for the enzyme carbonic anhydrase.

Tris(2-pyridyl)methanol has been shown to be ambiguous with regard to its mode of coordination, with ligation occurring via three py N atoms (N,N′,N″), structure A, or via two py N atoms and the deprotonated alcohol O (N,N′,O⁻), structure B. For the



$(py)_3COH$-*N*,*N*′,*N*″
A



$(py)_3CO(H)$-*N*,*N*′,*O*
B

bis(ligand)cobalt(III) species, two linkage isomers were isolated:[8] viz. the symmetrical bis(N,N′,N″) form and the (N,N′,N″)(N,N′,O⁻) species. As part of our current general study of complexes of tripodal π-acceptor ligands with metals in Groups 8-10, we now report synthetic and structural studies of the corresponding bis(ligand)ruthenium(II) complex, which have realized only the unsymmetric (N,N′,N″)(N,N′,O⁻) form and its nondeprotonated analogue (N,N′,N″)(N,N′,O).

Experimental Section

Physical Measurements. Electronic spectra were recorded on a Cary 219 spectrophotometer, and NMR spectra were recorded with a Bruker AM-300 spectrometer (Me_2SO-d_6 solution; Me_4Si reference).

Electrochemical measurements were made by using a Bioanalytical Systems (BAS) CV-27 voltammograph, with cyclic voltammograms

---

(1) James Cook University of North Queensland.
(2) Brookhaven National Laboratory. Permanent address: Baruch College, New York, NY 10010.
(3) Canty, A. J.; Chaichit, N.; Gatehouse, B. M.; George, E. E.; Hayhurst, G. *Inorg. Chem.* **1981**, *20*, 2414-2422.
(4) Canty, A. J.; Chaichit, N.; Gatehouse, G. M.; George, E. E. *Inorg. Chem.* **1981**, *20*, 4293-4300.
(5) Canty, A. J.; Minchin, N. J.; Healy, P. C.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1982**, 1795-1802.
(6) Canty, A. J.; Patrick, J. M.; White, A. H. *Inorg. Chem.* **1984**, *23*, 3827-3830.
(7) White, D. L.; Faller, J. W. *Inorg. Chem.* **1982**, *21*, 3119-3122.
(8) Szalda, D. J.; Keene, F. R. *Inorg. Chem.* **1986**, *25*, 2795-2799.
(9) Boggess, R. K.; Zatko, D. A. *Inorg. Chem.* **1976**, *15*, 626-630.
(10) Boggess, R. K.; Boberg, S. J. *J. Inorg. Nucl. Chem.* **1980**, *42*, 21-26.
(11) Boggess, R. K.; Hughes, J. W.; Chew, C. W.; Kemper, J. J. *J. Inorg. Nucl. Chem.* **1981**, *43*, 939-945.
(12) Brown, R. S.; Huguet, J. *Can. J. Chem.* **1980**, *58*, 889-901.

0020-1669/87/1326-2211$01.50/0

output to a Linseis LY-1800 X-Y recorder. Both platinum and glassy-carbon working electrodes were used, and all potentials are reported relative to a saturated sodium chloride calomel electrode (SSCE).

The pK_a measurements were made by using an automated titration system, which has been described earlier.[13] Determinations were made at 25.0 °C in 95% methanol/0.1 M tetraethylammonium perchlorate by titration with tetraethylammonium hydroxide and in aqueous 0.1 M KNO_3 by titration with KOH.

Elemental analyses were carried out by the Canadian Microanalytical Service, New Westminster, Canada.

Materials. $[Ru(H)(CO_2CH_3)(PPh_3)_3]$ was purchased from Strem Chemicals, and $[Ru(H)(OH_2)_2(CH_3OH)(PPh_3)_2]BF_4$[14] and tris(2-pyridyl)methanol[8,15] were prepared by literature methods.

Syntheses. [Tris(2-pyridyl)methanol][tris(2-pyridyl)methoxo]ruthenium(II) Tetrafluoroborate Dihydrate, $[Ru((py)_3COH)((py)_3CO)]BF_4 \cdot 2H_2O$. Freshly prepared $[Ru(H)(OH_2)_2(CH_3OH)(PPh_3)_2]BF_4$ (0.39 g, 0.50 mmol) was added to thoroughly degassed (N_2) AR methanol (30 mL), tris(2-pyridyl)methanol (0.39 g; 1.5 mmol) was added, and the mixture was refluxed for ca. 18 h (until the sparingly soluble precursor complex had dissolved). The orange solution was cooled and filtered and the solvent evaporated off; the residue was triturated three times with dry ether, filtered, and washed with ether. Recrystallization was achieved from methanol/ether. Yield: 0.30 g; 84%. Anal. Calcd for $RuC_{32}H_{25}N_6O_2BF_4 \cdot 2H_2O$: C, 51.3; H, 3.90; N, 11.2. Found: C, 50.9; H, 3.81; N, 10.9.

[Tris(2-pyridyl)methanol][tris(2-pyridyl)methoxo]ruthenium(II) bromide, $[Ru((py)_3COH)((py)_3CO)]Br$, was prepared by dissolving the tetrafluoroborate salt in 2-butanone and precipitation by the addition of tetra-*n*-butylammonium bromide. The bromide was filtered and washed with 2-butanone and ether. Yield: >90%.

[Tris(2-pyridyl)methanol][tris(2-pyridyl)methoxo]ruthenium(II) Bromide–Bis(ethanol), $[Ru((py)_3COH)((py)_3CO)]Br \cdot 2C_2H_5OH$ (1a). $[Ru((py)_3COH)((py)_3CO)]Br$ (0.037 g) was dissolved in ethanol (4 mL) containing 2 drops of 2,6-lutidine. Dry diethyl ether was layered on top of this solution, and the solution was left undisturbed in the dark for several days. The resultant orange crystals were collected and washed with ether.

Bis[tris(2-pyridyl)methanol]ruthenium(II) Bis(methyl sulfate), $[Ru((py)_3COH)_2](CH_3SO_4)_2$ (2a). $[Ru((py)_3COH)((py)_3CO)]Br$ (0.040 g, 57 μmol) was dissolved in methanol (4 mL) and Ag_2SO_4 (0.010 g; 32 μmol) added. The mixture was stirred in the dark for 30 min and filtered, 2 drops of concentrated H_2SO_4 were added, and dry ether was layered on top of the solution. After several days, the resultant yellow crystals of the methyl sulfate salt[16] were collected and washed with ether.

Collection and Reduction of X-ray Data. [Tris(2-pyridyl)methanol-*N*,*N′*,*N″*][tris(2-pyridyl)methoxo-*N*,*N′*,*O*]ruthenium(II) Bromide–Bis(ethanol) (1a). This compound crystallized as red-orange prisms. The crystals slowly lost solvent so they were coated with petroleum jelly and enclosed in Lindemann glass capillary tubes. A preliminary X-ray study indicated the crystals had monoclinic symmetry and symmetric absences $0k0$, $k = 2n + 1$, consistent with the space groups $P2_1$ (No. 4, C_2^2)[17a] and $P2_1/m$ (No. 10, C_{2h}^1).[17b] The structure was originally solved in space group $P2_1$, but because the cation exhibited mirror symmetry the space group was changed to $P2_1/m$ for the final refinement. The successful refinement of the structure confirmed that $P2_1/m$ is the correct space group.

The crystal used for data collection was a prism of dimensions 0.220 × 0.425 × 0.500 mm^3 and faces (001) and $(00\bar{1})$, (100) and $(\bar{1}00)$, and (100) and $(\bar{1}00)$, respectively. Crystal data and details of the data collection and reduction are given in Table I.

Bis[tris(2-pyridyl)methanol-(*N*,*N′*,*N″*)(*N*,*N′*,*O*)]ruthenium(II) Bis(methyl sulfate) (2a). The crystals were yellow prisms. They were coated with petroleum jelly and sealed in Lindemann glass capillary tubes. These crystals showed $\bar{1}$ Laue symmetry consistent with the triclinic space groups $P1$ (No. 1, C_1^1)[17c] and $P\bar{1}$ (No. 2, C_i^1).[17d]

The crystal used for data collection had dimensions 0.176 × 0.400 × 0.500 mm^3 and faces $(\bar{1}10)$ and $(1\bar{1}0)$, (110) and $(\bar{1}\bar{1}0)$, and $(01\bar{2})$ and $(0\bar{2}1)$, respectively. Crystal data and details of the data collection and reduction are given in Table I.

Table I. Experimental Details of the X-ray Diffraction Study of $[Ru((py)_3COH)((py)_3CO)]Br \cdot 2C_2H_5OH$ (**1a**) and $[Ru((py)_3COH)_2](CH_3SO_4)_2$ (**2a**)

(A) Crystal Parameters[a] at 22 °C

	1a	**2a**
a, Å	8.096 (2)	13.517 (3)
b, Å	13.584 (2)	14.458 (2)
c, Å	15.204 (2)	9.727 (2)
α, deg	90.0	104.72 (2)
β, deg	101.96 (1)	108.56 (2)
γ, deg	90.0	92.41 (2)
V, $Å^3$	1635 (1)	1727 (3)
Z	2	2
mol wt	798.70	849.85
space group	$P2_1/m$	$P\bar{1}$
ρ(exptl), g cm^{-3}	1.57[b]	1.65[c]
ρ(calcd), g cm^{-3}	1.621	1.634

(B) Measurement of Intensity Data

	1a and **2a**
instrument	Enraf-Nonius Cad 4 diffractometer
radiation	Mo Kα (λ = 0.70926 Å) graphite monochromatized
2θ limits	2–55°
scan type	θ(crystal)–2θ(counter)
stds	3 reflcns measd after each 1 h of exposure, with no systematic variations

(C) Treatment of Intensity Data[d]

	1a	**2a**
redcn to prelim F_o and $\sigma(F_o)$	correction for background, attenuators, and Lorentz–polarization effects of monochromatized X-radiation in the usual manner	
abs cor	$\mu = 18.17\ cm^{-1}$	$\mu = 6.34\ cm^{-1}$
transmissn coeff		
max	0.6859	0.8969
min	0.4792	0.7837
obsd data	7670 obsd data combined to yield 3617 unique data with a $R_{av} = 0.0041$ of which 2825 having $F_0 > 3\sigma(F_o)$ were used in the refinement	7969 obsd data of which 5962 having $F_o > 3\sigma(F_o)$ were used in the refinement

[a] From a least-squares fit to the setting angles of 25 reflections with 2θ > 20°. [b] Using carbon tetrachloride and hexane. [c] Using carbon tetrachloride and bromoform. [d] Data reduction and corrections performed by using the program KAPPA and the absorption correction computed by using ABSOR, both part of the CRYSNET system at Brookhaven National Laboratory.

Determination and Refinement of Structures. Both structures were solved by heavy-atom Patterson and Fourier[18] methods. Anisotropic temperature factors were used for all non-hydrogen atoms. Corrections for anomalous dispersion[19] effects were included for all atoms. The locations of the hydrogen atoms on the pyridine rings were calculated (C–H bond lengths of 0.95 Å). These hydrogen atoms were allowed to "ride"[18] on the atom to which they were attached.

For $[Ru((py)_3COH)((py)_3CO)]Br \cdot 2C_2H_5OH$ (1a) the alcoholic hydrogen on the $(py)_3COH$-*N*,*N′*,*N″* ligand was located on a difference Fourier map and fixed at that position. A common isotropic temperature factor for all the hydrogen atoms refined to a value of $U = 0.055$ (5) $Å^2$. The hydrogen atoms on the ethanol solvent molecules were not included in the refinement. The quantity $\sum w(|F_o| - |F_c|)^2$ where $w = 1.4332/(\sigma^2(F_o) + 0.002504(F_o)^2)$ was minimized in the least-squares refinement. During the final least-squares cycle, the largest parameter shift was less

---

(13) Adam, K. R.; Leong, A. J.; Lindoy, L. F.; Lip, H. C.; Skelton, B. W.; White, A. H. *J. Am. Chem. Soc.* **1983**, *105*, 4645–4651.

(14) Young, R. J.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1976**, 719–725.

(15) Wibaut, J. P.; de Jonge, A. P.; Van der Voort, H. G. P.; Otto, H. L. *Recl. Trav. Chim. Pays-Bas* **1951**, *70*, 1054–1060.

(16) The methyl sulfate anion is formed by the reaction of the solvent with sulfuric acid under the anhydrous conditions.

(17) *International Tables for X-Ray Crystallography*, 3rd ed.; Kynoch: Birmingham, U.K., 1969; Vol. I: (a) p 79; (b) p 91; (c) p 74; (d) p 75.

(18) Except where otherwise noted, all calculations were performed by using SHELX-76: Sheldrick, G. M. In *Computing in Crystallography*; Schenk, H., Olthof-Hazekamp, R., van Koningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp 34–42.

(19) (a) Neutral-atom scattering factors were taken from: *International Critical Tables for X-Ray Crystallography*; Kynoch: Birmingham, U.K., 1974; Vol. IV, p 99. (b) Anomalous dispersion effects were taken from: Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891–1898.

Table II. $[Ru((py)_3COH)((py)_3CO)]Br\cdot 2C_2H_5OH$ Atomic Coordinates[a]

atom	*x*	*y*	*z*
Ru	−0.02705 (7)	0.2500	0.81196 (4)
N(1)	−0.1233 (5)	0.1468 (3)	0.7153 (3)
C(12)	−0.0669 (6)	0.1597 (4)	0.6384 (3)
C(13)	−0.1133 (7)	0.0984 (4)	0.5662 (4)
C(14)	−0.2185 (9)	0.0200 (5)	0.5718 (5)
C(15)	−0.2775 (9)	0.0060 (5)	0.6505 (5)
C(16)	−0.2271 (7)	0.0702 (4)	0.7203 (4)
N(3)	0.1018 (9)	0.2500	0.4917 (5)
C(32)	0.1688 (10)	0.2500	0.5785 (5)
C(33)	0.3388 (12)	0.2500	0.6106 (7)
C(34)	0.4440 (14)	0.2500	0.5509 (8)
C(35)	0.3767 (13)	0.2500	0.4607 (7)
C(36)	0.2092 (13)	0.2500	0.4347 (6)
O(1)	0.1512 (6)	0.2500	0.7341 (3)
C(1)	0.0529 (9)	0.2500	0.6461 (5)
N(4)	0.0920 (5)	0.1477 (3)	0.9013 (3)
C(42)	0.0949 (6)	0.1572 (4)	0.9894 (3)
C(43)	0.1754 (7)	0.0890 (4)	1.0517 (4)
C(44)	0.2591 (8)	0.0102 (4)	1.0228 (4)
C(45)	0.2593 (7)	0.0022 (4)	0.9317 (4)
C(46)	0.1755 (7)	0.0703 (4)	0.8746 (4)
N(5)	−0.2140 (7)	0.2500	0.8840 (4)
C(52)	−0.1765 (8)	0.2500	0.9742 (5)
C(53)	−0.3019 (9)	0.2500	1.0252 (5)
C(54)	−0.4698 (10)	0.2500	0.9815 (6)
C(55)	−0.5084 (9)	0.2500	0.8899 (6)
C(56)	−0.3791 (9)	0.2500	0.8435 (5)
O(2)	0.0201 (6)	0.2500	1.1118 (3)
C(2)	0.0103 (9)	0.2500	1.0187 (4)
Br	0.40808 (14)	0.2500	0.22082 (8)
O(3)	0.6167 (19)	0.0556 (9)	0.2495 (9)
C(3)	0.745 (4)	0.068 (2)	0.3171 (13)
C(4)	0.814 (9)	0.129 (3)	0.299 (4)

[a] Numbers in parentheses are errors in the last significant digit(s).

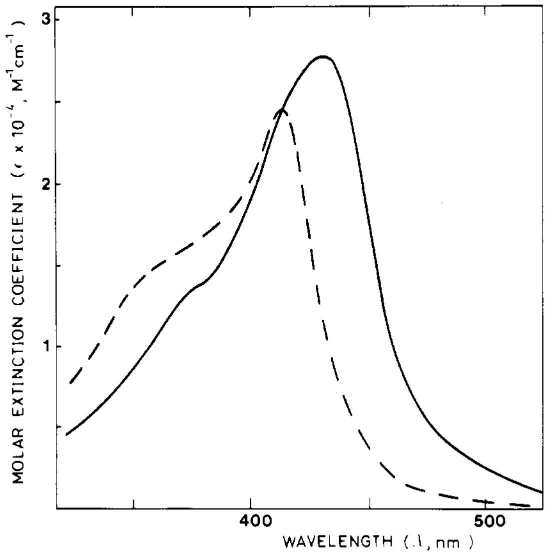


Figure 1. Visible spectra of the cations $[Ru((py)_3COH)((py)_3CO)]^+$ (**1**) in 0.2 M phosphate buffer at pH 7 (—) and $[Ru((py)_3COH)_2]^{2+}$ (**2**) in 0.1 M HCl (--).

than 0.08 of its standard deviation. The final R_1[20] value was 0.056. The final weighted discrepency index R_2[20] was 0.069. A final difference Fourier map revealed peaks of 1–1.6 e/Å^3 near the bromide and ruthenium atoms. Other peaks were less than 0.5 e/Å^3. The final non-hydrogen atomic parameters are reported in Table II.

For $[Ru((py)_3COH)_2](CH_3SO_4)_2$ (2a) the space group was assumed to be $P\bar{1}$, and the successful refinement of the structure confirmed the correctness of this assignment. A common isotropic temperature factor for the pyridine hydrogen atoms refined to a value of $U = 0.059$ (4) Å^2. The positional and isotropic temperature factors for the alcoholic hydrogen atoms on the ligands were refined (Table S1). The hydrogen atoms on the anions were not located. The quantity $\sum w(|F_o| - |F_c|)^2$ where $w = 0.3307/(\sigma^2(F_o) + 0.004(F_o)^2)$ was minimized in the least-squares refinement. During the final least-squares cycle the largest parameter shift was less than 0.42 of its error. The final R_1[20] was 0.053. The final weighted discrepency index R_2[20] was 0.072. A final difference Fourier map revealed a peak of ca. 1.8 e/Å^3 near one of the anions, indicating some positional disorder, but no disordered model for this anion could be determined. Several peaks of about 1 e/Å^3 were also observed near the ruthenium atoms. The final non-hydrogen atomic positions are listed in Table III.

Table III. $[Ru((py)_3COH)_2)](CH_3SO_4)_2$ Atomic Coordinates[a]

atom	*x*	*y*	*z*
Ru	0.22998 (3)	0.14745 (2)	0.40747 (4)
N(1)	0.1468 (3)	0.2401 (3)	0.5094 (4)
C(12)	0.1588 (3)	0.3305 (3)	0.4966 (5)
C(13)	0.1081 (4)	0.4020 (4)	0.5562 (6)
C(14)	0.0408 (5)	0.3801 (4)	0.6288 (7)
C(15)	0.0259 (5)	0.2881 (5)	0.6380 (7)
C(16)	0.0800 (4)	0.2198 (4)	0.5783 (6)
N(2)	0.3585 (3)	0.2508 (3)	0.5316 (4)
C(22)	0.3452 (4)	0.3392 (3)	0.5142 (5)
C(23)	0.4252 (4)	0.4164 (4)	0.5860 (6)
C(24)	0.5218 (4)	0.4004 (4)	0.6764 (7)
C(25)	0.5356 (4)	0.3113 (5)	0.6929 (7)
C(26)	0.4533 (4)	0.2375 (4)	0.6208 (6)
N(3)	0.2516 (4)	0.5138 (3)	0.4424 (7)
C(32)	0.2154 (4)	0.4266 (3)	0.3447 (7)
C(33)	0.1594 (5)	0.4139 (5)	0.1937 (8)
C(34)	0.1471 (6)	0.4966 (6)	0.1456 (10)
C(35)	0.1854 (7)	0.5845 (6)	0.2423 (13)
C(36)	0.2365 (6)	0.5903 (5)	0.3887 (13)
C(1)	0.2339 (4)	0.3420 (3)	0.4102 (5)
O(1)	0.2064 (2)	0.2525 (2)	0.2882 (4)
N(4)	0.0950 (3)	0.0571 (3)	0.2694 (4)
C(42)	0.0938 (4)	−0.0390 (3)	0.2377 (5)
C(43)	0.0033 (4)	−0.1019 (4)	0.1493 (6)
C(44)	−0.0874 (4)	−0.0657 (4)	0.0883 (6)
C(45)	−0.0862 (4)	0.0339 (4)	0.1185 (6)
C(46)	0.0060 (4)	0.0920 (3)	0.2081 (6)
N(5)	0.3115 (3)	0.0589 (3)	0.2946 (4)
C(52)	0.2860 (4)	−0.0378 (3)	0.2578 (5)
C(53)	0.3376 (4)	−0.1005 (4)	0.1808 (6)
C(54)	0.4179 (4)	−0.0652 (4)	0.1420 (6)
C(55)	0.4448 (4)	0.0339 (4)	0.1831 (6)
C(56)	0.3909 (4)	0.0927 (4)	0.2582 (6)
N(6)	0.2508 (3)	0.0578 (3)	0.5408 (4)
C(62)	0.2319 (4)	−0.0390 (3)	0.4796 (5)
C(63)	0.2429 (4)	−0.1020 (4)	0.5673 (6)
C(64)	0.2735 (4)	−0.0663 (4)	0.7206 (6)
C(65)	0.2946 (4)	0.0324 (4)	0.7847 (6)
C(66)	0.2833 (4)	0.0911 (4)	0.6933 (5)
C(2)	0.1981 (4)	−0.0753 (3)	0.3063 (5)
O(2)	0.1862 (4)	−0.1759 (3)	0.2702 (5)
S(1)	0.14385 (12)	−0.31425 (10)	−0.13736 (16)
O(11)	0.2564 (5)	−0.3319 (6)	−0.0514 (8)
O(12)	0.1091 (4)	−0.2638 (5)	−0.0240 (6)
O(13)	0.0882 (5)	−0.3991 (5)	−0.2260 (9)
O(14)	0.1568 (9)	−0.2533 (7)	−0.2224 (13)
C(11)	0.3212 (8)	−0.3585 (9)	−0.1524 (15)
S(2)	0.39127 (12)	0.28945 (10)	0.09600 (17)
O(21)	0.3735 (8)	0.3873 (6)	0.0571 (12)
O(22)	0.4403 (5)	0.2349 (5)	0.0068 (8)
O(23)	0.2905 (3)	0.2425 (3)	0.0807 (5)
O(24)	0.4511 (6)	0.3368 (6)	0.2452 (8)
C(21)	0.3170 (11)	0.3860 (9)	−0.0869 (11)

[a] Numbers in parentheses are errors in the last significant digit(s).

Results and Discussion

The ruthenium(II) complex containing two tris(2-pyridyl)methanol ligands was synthesized by using the $[Ru(H)(OH_2)_2(CH_3OH)(PPh_3)_2]BF_4$ precursor, in a manner analogous to the synthesis of $[Ru(py)_6]^{2+}$ developed by Templeton.[21] The orange cation thus obtained was found (microanalysis, ion-exchange

---

(20) $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

(21) Templeton, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 4906–4917.

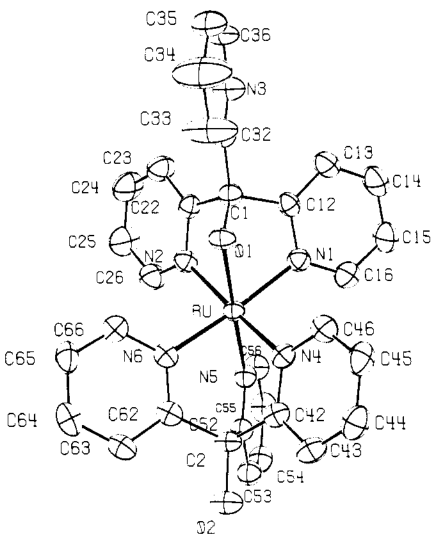


Figure 2. ORTEP drawing of a single molecule of the cation [Ru((py)$_3$COH)((py)$_3$CO$^-$)]$^+$ showing the atom-labeling scheme used. The thermal ellipsoids are at the 50% probability level. The molecule lies on a crystallographic mirror plane that contains the ruthenium, the uncoordinated pyridine ring (N(3)–C(36)), a coordinated pyridine ring (N(5)–C(56)), the coordinated methoxy group (C(1) and O(1)) and the uncoordinated alcohol group (C(2), O(2), H(2)). The pyridine rings labeled N(2)–C(26) and N(6)–C(66) are related to the pyridine rings N(1)–C(16) and N(4)–C(46) respectively by the mirror plane (x, $^1/_2 - y$, z). Hydrogen atoms have been omitted for clarity.

Table IV. Bond Distances (Å) and Angles (deg) for [Ru((py)$_3$COH)((py)$_3$CO)]Br·2C$_2$H$_5$OH

	Ruthenium–Ligand Distances		
Ru–O(1)	2.047 (5)	Ru–N(4)	2.040 (4)
Ru–N(1)	2.063 (4)	Ru–N(5)	2.044 (6)
	Ruthenium–Ligand Angles		
O(1)–Ru–N(1)	78.2 (1)	N(1)–Ru–N(5)	99.8 (2)
O(1)–Ru–N(4)	95.3 (1)	N(1)–Ru–N(6)	173.5 (2)
O(1)–Ru–N(5)	177.2 (2)	N(4)–Ru–N(5)	86.7 (2)
N(1)–Ru–N(2)	85.6 (2)	N(4)–Ru–N(6)	85.9 (2)
N(1)–Ru–N(4)	93.9 (2)		

chromatography) to have a +1 charge by virtue of deprotonation of one of the ligands. A yellow form of the cation (charge +2) could be obtained by protonation of the orange form. The visible spectra of the two complexes are shown in Figure 1.

Alternative synthetic methods using [RuCl$_5$(OH$_2$)]$^{2-}$ or [Ru(DMF)$_6$]$^{2+}$ as precursors have also realized the same coordination mode of the ligand.[22]

Description of the Structures. A view of the [Ru((py)$_3$COH)((py)$_3$CO)]$^+$ cation (**1**) and the atom-labeling scheme used are shown in Figure 2. The neutral tris(2-pyridyl)methanol ligand is coordinated to the ruthenium by its three pyridyl nitrogens (N,N′,N″; A), while the anionic tris(2-pyridyl)methoxide ligand is coordinated through two pyridyl nitrogens and the methoxide oxygen (N,N′,O$^-$; B). Complex **1** contains a crystallographic mirror plane (see Figure 2). The neutral ligand (N,N′,N″-coordinated) has an average Ru–N bond distance of 2.042 (6) Å (Table IV) while the anionic ligand (N,N′,O$^-$-coordinated) has a somewhat longer average Ru–N bond distance of 2.063 (4) Å indicating some bond stretching as a result of the oxygen coordination. The average Ru–N(pyridyl) bond length reported in [Ru(bpy)$_3$]$^{2+}$[23] is 2.056 Å. The Ru–O bond length is 2.047 (5) Å, which is normal for a Ru(II)–O$^-$ bond.[24]

A view of the [Ru((py)$_3$COH)$_2$]$^{2+}$ cation (**2**) and the atom-labeling scheme used are presented in Figure 3. In this case the complex contains two neutral tris(2-pyridyl)methanol ligands, one ligand coordinated to the ruthenium(II) by its three pyridyl nitrogens while the other is coordinated by two pyridyl nitrogen atoms and the nondeprotonated oxygen of the alcohol. For the two ligands, the average Ru–N bond length is 2.053 (6) Å, except for the Ru–N(6) bond (trans to Ru–O(1)), which is abnormally short (2.023 (4) Å; Table V). The Ru–O bond length is 2.111 (4) Å; the average Ru–O bond length in Ru(OH$_2$)$_6$$^{2+}$ is 2.12 (2) Å.[25]

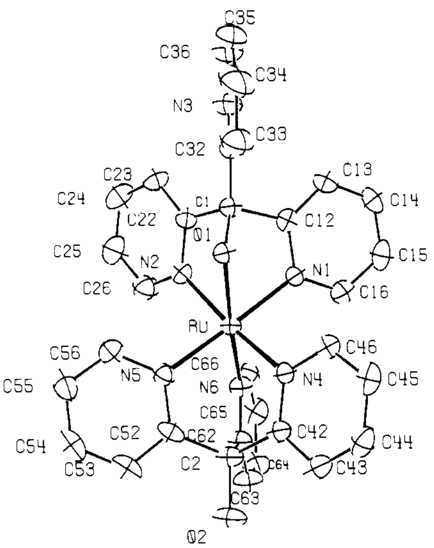


Figure 3. ORTEP drawing of the [Ru((py)$_3$COH)$_2$]$^{2+}$ cation with the atom-labeling scheme. The thermal ellipsoids are at the 50% probability level. Atom O(1) is protonated, but all the hydrogen atoms have been omitted for clarity. The pyridine rings containing N(3) and N(6) are 13.6° for coplanar.

Table V. Bond Distances (Å) and Angles (deg) for [Ru((py)$_3$COH)$_2$](CH$_3$SO$_4$)$_2$

	Ruthenium–Ligand Distances		
Ru–N(1)	2.050 (4)	Ru–N(4)	2.046 (3)
Ru–N(2)	2.058 (3)	Ru–N(5)	2.058 (4)
Ru–O(1)	2.111 (4)	Ru–N(6)	2.023 (4)
	Ruthenium–Ligand Angles		
N(1)–Ru–N(2)	85.7 (1)	N(2)–Ru–N(6)	100.0 (2)
N(1)–Ru–O(1)	76.2 (2)	O(1)–Ru–N(4)	95.6 (1)
N(1)–Ru–N(4)	91.5 (1)	O(1)–Ru–N(5)	100.2 (2)
N(1)–Ru–N(5)	176.3 (2)	O(1)–Ru–N(6)	173.8 (1)
N(1)–Ru–N(6)	98.1 (2)	N(4)–Ru–N(5)	88.2 (1)
N(2)–Ru–O(1)	77.2 (1)	N(4)–Ru–N(6)	87.0 (1)
N(2)–Ru–N(4)	172.7 (2)	N(5)–Ru–N(6)	85.5 (2)
N(2)–Ru–N(5)	94.1 (2)		

Protonation of the tris(2-pyridyl)methoxide ligand in **1** occurs at the coordinated oxygen, rather than on the uncoordinated pyridine nitrogen, to give **2**. This protonation is accompanied by an increase in the Ru–O bond length of 0.064 Å between **1** and **2** and a corresponding decrease in the Ru–N bond length trans to the coordinated oxygen from 2.044 (6) to 2.023 (4) Å, which is significantly shorter than the other Ru–N bond distances. A similar feature has been observed in the structure of *cis*-[Ru(bpy)$_2$Cl$_2$]·3.5H$_2$O;[26] the Ru(II)–Cl bond lengths are relatively long, whereas the Ru–N bond lengths trans to Cl$^-$ are shorter (2.013 (2) Å) than those trans to the bpy N (2.054 (2) Å). This effect was attributed[26] to the importance of Ru → N(bpy) π-back-bonding where the trans ligand is not a back-bonding competitor for the electron density involving the same filled dπ orbitals; in the present case the effect of the –OH ligation in **2** is considered to be analogous to that of Cl$^-$. In the deprotonated complex **1**, the Ru–N bond in the trans position has the slightly longer bond

---

(22) Keene, F. R.; Stephenson, P. J., unpublished work.

(23) Rillema, D. P.; Jones, O. S.; Levy, H. A. *J. Chem. Soc., Chem. Commun.* **1979**, 849–851.

(24) Clegg, W. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 3112–3114.

(25) Bernhard, P.; Burgi, H.-B.; Hauser, J.; Lehmann, H.; Ludi, A. *Inorg. Chem.* **1982**, *21*, 3936–3941.

(26) Eggleston, D. S.; Goldsby, K. A.; Hodgson, D. J.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 4573–4580.

Table VI. Physical Characteristics of $[Ru((py)_3COH)((py)_3CO^-)]^+$ (1) and $[Ru((py)_3COH)_2]^{2+}$ (2)

	$[Ru((py)_3COH)((py)_3CO^-)]^+$	$[Ru((py)_3COH)_2]^{2+}$
electronic spectra	$\epsilon_{432} = 27800$ $\epsilon_{253} = 30500$ (0.2 M phosphate buffer, pH 7.0)	$\epsilon_{415} = 24700$ $\epsilon_{246} = 30600$ (0.1 M H_2SO_4)
^{13}C NMR spectra	bridgehead carbon atoms $\delta = 81.0, 90.0$ (Me_2SO-d_6 solvent; Me_4Si internal reference)	bridgehead carbon atoms $\delta = 81.1, 86.7$ (Me_2SO-d_6 solvent/ CF_3CO_2H; Me_4Si internal reference)
electrochemical chemical properties	$E_{1/2} = 0.25$ V ($\Delta E \approx 80$ mV) (0.05 M TRIS buffer/0.1 M KNO_3; glassy-carbon working electrode; sweep rate 100 mV/s; SSCE reference electrode)	$E_{1/2} = 0.40$ V ($\Delta E \approx 90$ mV) (0.05 M H_2SO_4; glassy-carbon working electrode; sweep rate 100 mV/s; SSCE reference electrode)
pK_a	3.86 ($\pm$0.01){95% MeOH/0.1 M Et_4NClO_4} 3.78 ($\pm$0.02){0.1 M KNO_3}	

length of 2.044 (6) Å. This observation may be rationalized in terms of σ-bonding effects if the energy of the e_g orbital of the metal corresponds more closely to the energy of the σ orbital of oxygen in O^- rather than the more stable –OH; in such a case, the strength of the Ru–O^- bond would be enhanced (compared with that of Ru–OH), with a resultant relative diminution of the strength of the trans Ru–N bond.

The possible role of π-bonding might also be considered in relationship to these structural observations. ^{13}C NMR data on uncoordinated tris(2-pyridyl)methanol and the tris(2-pyridyl)methoxide anion indicate a downfield shift in the resonance of the bridgehead carbon on deprotonation, consistent with a degree of delocalization in the anion in which the C–O bond may have some double-bond character.[27] Accordingly, when the anion is coordinated via the N,N′,O mode (B), $d\pi(Ru) \rightarrow \pi^*(ligand)$ back-bonding may occur, so that Ru–O^- is potentially a back-bonding competitor with the trans Ru–N bond, which therefore might be expected to have a longer bond length than in the nondeprotonated case. However, the –O^- ligand would be expected to function primarily as a π-donor, although this may not substantially influence the extent of back-bonding (and therefore, the bond length) of the trans Ru–N bond.[28] There is no structural evidence for multiple bond character in the C–O bond of coordinated tris(2-pyridyl)methoxo-*N,N′,O*⁻ since the bond length (1.408 (8) Å) is the same as the C–O bond length in the tris(2-pyridyl)methanol-*N,N′,N″* ligand in **2** (1.401 (8) Å) and **1** (1.395 (6) Å) (Tables S6 and S7). The X-ray data do indicate that in complex **2**, for the tris(2-pyridyl)methanol-*N,N′,O* ligand the attachment of the oxygen to both the proton and the metal weakens both the Ru–O and C–O bonds, increasing both bond lengths (0.064 and 0.047 Å, respectively) in comparison with the equivalent deprotonated ligand in **1**.

The ^{13}C NMR spectral studies reveal that the resonances due to the bridgehead carbon atom are virtually identical in free tris(2-pyridyl)methanol ($\delta = 81.4$) and in the neutral N,N′,N″-coordinated ligand (δ = ca. 81.1; Table VI and ref 27). For the neutral N,N′,O-coordinated ligand, the same resonance is shifted downfield ($\delta = 86.7$) and is shifted further downfield on ligand deprotonation ($\delta = 90.0$). The downfield shift observed for *both* of the N,N′,O-coordinated ligands relative to the free ligand reflects a complex metal/ligand electronic interaction in both species.

The Ru–N bond lengths in both complexes **1** and **2** are more similar to those found in $Ru(bpy)_3^{2+}$, 2.056 Å,[23] than those found in $Ru(NH_3)_6^{2+}$, 2.144 Å,[29] and $Ru(py)_6^{2+}$, 2.12 Å.[21] This indicates the presence of π-back-bonding from the metal to the ligands in both **1** and **2** and, in comparison with $[Ru(py)_6]^{2+}$,[21] provides evidence for ligand delocalization in both tris(2-pyridyl)methanol and the corresponding methoxide in all observed coordination modes for the two ligands. Delocalization of back-bonded charge density in these tripodal ligands has been observed previously in Co(I) complexes.[8,9]

In the nondeprotonated species (**2**), the uncoordinated pyridine ring and the coordinated pyridine ring trans to –OH are 13.6° from being coplanar, while the pyridine rings trans to one another are 16.9 and 14.1° from being coplanar. In the cobalt(III) complex of the same ligand (in which both ligands are N,N′,N″-coordinated), the pyridine rings trans to one another are coplanar.[8] In both complexes, **1** and **2**, the bonds and angles within the pyridine rings are normal[8,30,31] (Tables S6 and S7). The bond distances and angles for the methyl sulfate anions in **2** are also similar to those reported.[32]

Comparisons with Other Structures. There are few reports of structural studies of complexes involving the title ligand, tris(2-pyridyl)methanol. Canty et al.[4] have reported a methylmercury(II) species, $[MeHg((py)_3COH)](NO_3)$, in which the ligand is tridentate with binding occurring via the three py N atoms; the coordination geometry is irregular with one Hg–N bond being significantly shorter than the other two. For the octahedral bis(ligand)cobalt(III) complex, two linkage isomers have been reported: an (N,N′,N″)(N,N′,O^-) form in which one ligand is deprotonated (and coordinated in the N,N′,O^- mode)[33] and the symmetrical bis(N,N′,N″) form in which both ligands are nondeprotonated.[8] Consequently, in the present study, structure **2** is the first example of N,N′,O-coordination of the nondeprotonated tris(2-pyridyl)methanol ligand. For the tris(2-pyridyl)methanol-*N,N′,N″* ligand in both complexes **1** and **2**, the angles Ru–N–C(2) and Ru–N–C(6) (see Figures 2 and 3) are approximately equal, as they are in the N,N′,N″-coordinated ligands in $Co((py)_3COH)_2^{3+}$.[8] However, for the N,N′,O-coordinated ligand in **1** and **2** these angles are asymmetric (113 (1) and 128 (1)°, respectively) as are the angles about the coordinated pyridyl nitrogens in $Co((py)_3N)_2^{2+}$ [31] and $Fe((py)_3N)_2^{3+}$.[30] In these two cases the asymmetric angles are a result of the shorter bridging C–N bond length of 1.44 (1) Å; for complexes **1** and **2** this distortion may also arise from steric constraints in coordination.

Physical Characteristics of $[Ru((py)_3COH)((py)_3CO)]^+$ (1) and $[Ru((py)_3COH)_2]^{2+}$ (2). The physical characteristics of the two forms of the cation are given in Table VI. Both species show an (N,N′,N″)(N,N′,O) coordination mode, differing according to the deprotonated (**1**) or nondeprotonated (**2**) state of the coordinated alcohol O atom. The ^{13}C NMR spectra (Me_2SO-d_6 solution) of the two species show complicated resonances in the region δ = 120–170 attributed to the pyridine C atoms, and the appearance of separate resonances for the two bridgehead carbon atoms (δ = 81.1 and 86.7 for **1**; δ = 81.0 and 90.0 for **2**) consistent with the nonsymmetric coordination of the two ligands. The preference of the metal center for N_5O- rather than N_6-coordination is unexpected, given the affinity of Ru(II) for unsaturated ligands such as pyridine.[34] The bis(ligand)ruthenium(II) species with other $(py)_3X$ ligands (X = CH, N, P, P=O) have been isolated and their structures determined;[35] since no unusual features are apparent in these N_6-coordinated species, the reason for N_5O-coordination of tris(2-pyridyl)methanol is unlikely to be steric

---

(27) ^{13}C NMR studies (Me_2SO-d_6 solvent) show the bridgehead carbon resonance of tris(2-pyridyl)methanol shifts downfield (δ = 81.4–83.4) on deprotonation by NaH.

(28) Adcock, P. A.; Keene, F. R.; Smythe, R. S.; Snow, M. R. *Inorg. Chem.* **1984**, *23*, 2336–2343.

(29) Stynes, H. C.; Ibers, J. A. *Inorg. Chem.* **1971**, *10*, 2304–2308.

(30) Kucharski, E. S.; McWhinnie, W. R.; White, A. H. *Aust. J. Chem.* **1978**, *31*, 53–56.

(31) Kucharski, E. S.; McWhinnie, W. R.; White, A. H. *Aust. J. Chem.* **1978**, *31*, 2647–2650.

(32) Munns, A. R. I.; Low, J. N.; Tollin, P.; Young, D. W. *Cryst. Struct. Commun.* **1981**, *10*, 1431–1434.

(33) Preliminary details of structure given in a footnote to ref 7.

(34) Taube, H. *Surv. Prog. Chem.* **1973**, *6*, 1–46.

(35) Keene, F. R.; Stephenson, P. J.; Tiekink, E. R. T.; Snow, M. R., unpublished work.

and may reflect a kinetic effect in the synthetic process.

The pK_a for the deprotonation is 3.78 (±0.02) in aqueous solution ($\mu = 0.1$; 25.0 °C). By comparison, the pK_a of coordinated 2-pyridinemethanol in the complex $[Ru(bpy)_2((py)CH_2OH)]^{2+}$ is 7.2 (±0.1) under the same conditions:[36] the higher acidity of coordinated tris(2-pyridyl)methanol probably reflects additional steric strain within the tripodal ligand. There is no evidence for protonation of the free py N atom in the N,N′,O-coordinated ligand even at pH ca. 1. The pK_a values of the free ligand $(py)_3COH$ in 95% methanol are 4.9 (±0.1) and 1.9 (±0.1), with the third value probably slightly lower than 1.5;[12] while the pK_a of the alcohol OH is significantly lowered by coordination to the positive metal center, the nonprotonation of the free py N is clearly unusual, since the pK_a values of the uncoordinated py N atoms in a number of polypyridyl-type ligands are actually raised by their coordination in a monodentate manner to Ru(II).[35,37] In the present case, one possibility is that in solution the coordinated –OH is hydrogen-bonded to the py N in the free ring, thereby forming a five-membered ring (–O(1)–H(1)···N(3)–C(32)–C(2)–, in the numbering scheme used in Figure 3) and inhibiting protonation of N(3). This is not the case for the solid state, however, where Figure 3 reveals that the free pyridine ring is rotated so that the nitrogen atom (N(3)) points away from the O(1)–H(1), and the –OH group is in fact hydrogen bonded to an oxygen atom of a methyl sulfate anion (Table S11).

The deprotonation is also associated with a color change of the complex from yellow to orange (see Table VI and Figure 1) and a cathodic shift in the redox potential of the Ru(III)/Ru(II) couple from 0.40 to 0.25 V. A reduction in redox potential is generally observed on lowering of the overall complex charge.[38] The potential of the Ru(III)/Ru(II) couple for the nondeprotonated species **2**, $E_{1/2} = 0.40$ V, compares with 0.62 V for $[Ru(bpy)_2((py)CH_2OH)]^{3+/2+}$[36] under the same conditions.

Studies of the photochemical properties of the ruthenium(II) complexes of a variety of tripodal π-acceptor ligands will be published subsequently, but preliminary measurements with the deprotonated complex **1** indicate a luminescence lifetime of ca. 1.4 ns.[39]

Acknowledgment. This work was performed at James Cook University of North Queensland (where it was supported by the Australian Research Grants Scheme) and at Brookhaven National Laboratory (which is operated under Contract No. DE-AC02-76CH00016 with the Department of Energy and supported by its Office of Basic Energy Sciences). D.J.S. thanks Baruch College for released time to do this research. Dr. P. Duckworth is thanked for useful comments on the manuscript, and the technical assistance of A. J. Leong (JCUNQ) with some of the pK_a measurements is gratefully acknowledged.

Registry No. **1a**, 108451-82-7; **2a**, 108451-84-9; $[Ru((py)_3COH)((py)_3CO)]BF_4$, 108451-80-5; $[Ru((py)_3COH)((py)_3CO)]Br$, 108451-81-6; $[Ru(H)(OH_2)_2(CH_3OH)(PPh_3)_2]BF_4$, 60020-13-5; tris(2-pyridyl)methanol, 73569-80-9.

Supplementary Material Available: Tables listing positional and isotropic thermal parameters for the refined hydrogen atoms in **2** (Table S1), anisotropic thermal parameters for the non-hydrogen atoms in **1** (Table S2) and **2** (Table S3), atomic coordinates for the hydrogen atoms in **1** (Table S4) and **2** (Table S5), bond distances and angles for **1** (Table S6) and **2** (Table S7), hydrogen bonding in **1** (Table S10) and **2** (Table 11), and best planes for **1** (Table S12) and **2** (Table S13) (19 pages); tables of observed and calculated structure factors for **1** (Table S8) and 2 (Table S9) (37 pages). Ordering information is given on any current masthead page.

---

(36) Ridd, M. J.; Keene, F. R.; Gakowski, D. J.; Sneddon, G. E., manuscript in preparation.

(37) Lavallee, D. K.; Fleischer, E. B. *J. Am. Chem. Soc.* **1972**, *94*, 2583–2599.

(38) Ridd, M. J.; Keene, F. R. *J. Am. Chem. Soc.* **1981**, *103*, 5733–5740 and references quoted therein.

(39) Winkler, J. R.; Keene, F. R., unpublished work.

Contribution from the Department of Chemistry,
Colorado State University, Fort Collins, Colorado 80523

A New Candidate for the Least Coordinating Anion: Preparation and Characterization of $[TlOTeF_5(mes)_2]_2\cdot mes$ (mes = Mesitylene) and $[Tl(mes)_2^+][B(OTeF_5)_4^-]$

Mark D. Noirot, Oren P. Anderson, and Steven H. Strauss*

Received February 24, 1987

The compounds $TlOTeF_5$, $[TlOTeF_5(mes)_2]_2\cdot mes$ (mes = mesitylene), and $[Tl(mes)_2^+][B(OTeF_5)_4^-]$ have been prepared and characterized by ^{19}F NMR and vibrational spectroscopy. In addition, the structures of the last two compounds have been determined by X-ray diffraction. The compound $[TlOTeF_5(mes)_2]_2\cdot mes$ crystallizes in the triclinic space group $P\bar{1}$. Unit cell parameters are $a = 11.048$ (3) Å, $b = 14.643$ (3) Å, $c = 16.345$ (4) Å, $\alpha = 102.43$ (2)°, $\beta = 99.10$ (2)°, $\gamma = 92.70$ (2)°, and $Z = 2$. The nearly centrosymmetric $[TlOTeF_5(mes)_2]_2$ dimer contains a nearly planar Tl_2O_2 core, with two $OTeF_5$ groups bridging the two thallium atoms. The mesitylene ligands are η^6-coordinated to the thallium atoms and make dihedral angles of 51.5 and 49.0° within each of the independent $Tl(mes)_2^+$ moieties. The compound $[Tl(mes)_2^+][B(OTeF_5)_4^-]$ crystallizes in the orthorhombic system, space group $Pbc2_1$. Unit cell parameters are $a = 10.659$ (3) Å, $b = 16.383$ (8) Å, $c = 20.165$ (6) Å, and $Z = 4$. The structure consists of a chain of $Tl(mes)_2^+$ cations and $B(OTeF_5)_4^-$ anions connected by extremely weak Tl···F interactions. The Tl–C distances within the $Tl(mes)_2^+$ cations of $[Tl(mes)_2^+][B(OTeF_5)_4^-]$ are substantially shorter than in $[TlOTeF_5(mes)_2]_2\cdot mes$. In all other respects, the $Tl(mes)_2^+$ moieties in these two compounds are structurally very similar. The $B(OTeF_5)_4^-$ anion is extremely weakly coordinated to Tl(I) in this salt, with four Tl···F contacts that range from 3.17 to 3.83 Å.

Introduction

We have been investigating the chemistry of the teflate[1] anion ($OTeF_5^-$) with respect to its use as a ligand for coordination and organometallc compounds. Complexes such as $Mn(CO)_5(OTeF_5)$,[2] $[AgOTeF_5(tol)_2]_2$ (tol = toluene),[3] $Fe(OTeF_5)_3$,[4] and $Pt(OTeF_5)_2(nor)$ (nor = norbornadiene)[5] reveal that the electronic and structural properties of teflate are quite different from those of any other anionic ligand including ClO_4^- and $CF_3SO_3^-$. We have also been exploring the use of $B(OTeF_5)_4^-$ as a potentially noncoordinating anion with which coordinatively unsaturated metal and non-metal cations could be isolated. Since the charge should

---

(1) Abbreviations: teflate = pentafluoroorthotellurate; teflic acid = pentafluoroorthotelluric acid; TPP = 5,10,15,20-tetraphenylporphyrinate dianion.

(2) Strauss, S. H.; Abney, K. D.; Long, K. M.; Anderson, O. P. *Inorg. Chem.* **1984**, *23*, 1994.

(3) Strauss, S. H.; Noirot, M. D.; Anderson, O. P. *Inorg. Chem.* **1985**, *24*, 4307.

(4) Strauss, S. H.; Miller, P. K., unpublished data, 1985.

(5) Colsman, M. R.; Manning, M. C.; Anderson, O. P.; Strauss, S. H., submitted for publication.

0020-1669/87/1326-2216$01.50/0 © 1987 American Chemical Society