Contribution from the Departments of Chemistry, The University of North Carolina at Charlotte,
Charlotte, North Carolina 28223, and North Carolina State University, Raleigh, North Carolina 27650

A Rhenium(I) Bipyrimidine Tricarbonyl Complex Containing Methyl Viologen as the Sixth Ligand: NMR and Structural Results

Linda N. Winslow,[†] D. Paul Rillema,*[,†] Jane H. Welch,[‡] and Phirtu Singh[‡]

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The structural properties of the $[Re(bpm)(CO)_3(MeQ)]^{2+}$ cation were investigated in solution by proton and ^{13}C NMR. The assignments of the resonances were made by comparison to those of the uncoordinated ligands bpm (2,2′-bipyrimidine) and MeQ (*N*-methyl-4,4′-bipyridinium ion). Two distinct ^{13}C resonances were found for "two equivalent" sites of the bipyrimidine ligand. A crystal structure of the PF_6^- salt revealed that the geometry of the cation was facial and the reason for the two resonances was a 9° twist of the pyrimidine rings from planarity. The crystal structure also revealed a 38° twist between the py and Me-py components of the MeQ ligand, a Re–N(bpm) bond distance of 2.17 Å, and a Re–N(MeQ) bond distance of 2.21 Å.

Introduction

Work in our laboratories has centered on the design and synthesis of potential solar energy catalysts.[1-7] In this respect, we have reported the preparation and properties of mixed-metal complexes containing up to four metal centers held together by bidentate bridging ligands.[1,3,4] These complexes contained ruthenium(II),[1] platinum(II),[3,4] and rhenium(I).[8] We have extended our work to the design and synthesis of molecules containing electron acceptor or donor groups for charge separation studies.

The rhenium(I) tricarbonyl molecule reported here, $[Re(bpm)(CO)_3MeQ]^{2+}$, represents our first success in that direction. The molecule contains the electron donor core "$Re(bpm)(CO)_3$", where bpm is 2,2′-bipyrimidine, and the electron acceptor unit MeQ, where MeQ is the *N*-methyl-4,4′-bipyridinium ion (Figure 1). The idea of using molecular systems, such as this one, is not without precedence. Recently, Meyer and co-workers[9] reported the synthesis and photophysical properties of $[Re(bpy)(CO)_3MeQ]^{2+}$, where bpy is 2,2′-bipyridine, and $[Re(bpy)(CO)_3BzQ]^{2+}$, where BzQ is the *N*-benzyl-4,4′-bipyridinium ion. The appearance of a weak, red-shifted emission was attributed to electron-transfer quenching involving the charge-separated intermediate $[Re^{II}(bpy)(CO)_3BzQ^-]^{2+}$ induced photochemically.

In this report, we focus on the structural aspects of the $[Re(bpm)(CO)_3MeQ]^{2+}$ ion and the implications of the structure on charge separation. The ^{13}C NMR spectrum led us to conclude that the pyrimidine rings of 2,2′-bipyrimidine were not equivalent and prompted an X-ray structure investigation to determine the reason for this unexpected observation.

Experimental Section

Materials. $Re(CO)_5Cl$ was purchased from Pressure Chemical Co. The ligand 2,2′-bipyrimidine was purchased commercially and used without further purification. The $(MeQ)PF_6$ compound was a gift from Tom Meyer's research group at The University of North Carolina at Chapel Hill. Acetonitrile was HPLC grade and was dried over 4-Å molecular sieves before use. The other reagents were purchased as reagent grade chemicals and were used without further purification. Elemental analyses were carried out by Atlantic Microlab, Inc., Norcross, GA.

Preparation of Compounds. $Re(bpm)(CO)_3Cl$. This compound was prepared by a modification of the procedure reported by Vogler and Kisslinger.[10] A slurry of $Re(CO)_5Cl$ (1.00 g, 2.77 mmol) in 250 mL of methanol was stirred while a solution of 2,2′-bipyrimidine (1.16 g, 7.31 mmol) in 50 mL of methanol was added. The mixture was heated to reflux for 16 h, during which time the mixture turned orange and a golden precipitate formed. The solid was collected by vacuum filtration and dried. The yield was 1.29 g (92%). Anal. Calcd for $ReC_{11}H_6N_4O_3Cl$: C, 28.48; H, 1.30; N, 12.08; Cl, 7.64. Found: C, 28.21; H, 1.39; N, 11.98; Cl, 7.77.

Table I. Proton NMR Properties of Compounds[a]

compd	bpm	MeQ
$[MeQRe(bpm)(CO)_3](PF_6)_2$	7.92 (dd, *J* = 5, 5), 9.30 (dd, *J* = 1.9, 5), 9.49 (dd, *J* = 1.9, 5)	4.32 (s), 7.73 (d, *J* = 6.6), 8.17 (d, *J* = 6.6), 8.55 (d, *J* = 6.6), 8.70 (d, *J* = 6.6)
bpm	7.52 (t, *J* = 6), 8.97 (d, *J* = 6)	
$(MeQ)PF_6$		4.33 (s), 7.79 (dd, *J* = 4.8, 1.2), 8.30 (d, *J* = 6.6), 8.71 (d, *J* = 6.6), 8.85 (dd, *J* = 4.8, 1.2)

[a] Chemical shifts are given in ppm and *J* values in Hz.

Table II. ^{13}C NMR Resonances of Compounds

compd	bpm	MeQ	CO
$[MeQRe(bpm)(CO)_3](PF_6)_2$	125.5, 125.7, 161.6, 161.8, 162.4	48.7, 110.6, 126.4, 145.0, 146.5, 151.6, 154.1	194.6, 194.7
bpm	121.8 (C-5),[a] 158.1 (C-4,6), 163.5 (C-2)		
$(MeQ)PF_6$		48.7, 122.6, 126.4, 142.1, 147.1, 152.0, 154.4	

[a] These assignments were made as follows: The quaternary carbon atom shows the weakest ^{13}C resonance and is the furthest downfield; C-4 and C-6 are equivalent and are located next to a ring nitrogen and appear downfield of the C-5 carbon resonance, located at the smallest shift.

$[Re(bpm)(CO)_3MeQ](PF_6)_2$. A solution of $Re(bpm)(CO)_3Cl$ (1.00 g, 2.16 mmol) and silver hexafluorophosphate (0.55 g, 2.16 mmol) in 200 mL of acetone was heated to reflux for 15 h and filtered to remove the silver chloride formed. $(MeQ)PF_6$(0.68 g, 2.16 mmol) was added, and the solution was heated for 24 h. After it was cooled, the orange solution was further concentrated by partial removal of the solvent by rotary evaporation. Adding ether and cooling to 0 °C produced analytically pure microcrystals of the product. Two additional crops of material were obtained, giving a total yield of 1.6 g (84%). Anal. Calcd for $ReC_{22}H_{17}N_6P_2F_{12}$: C, 29.71; H, 1.93; N, 9.45. Found: C, 29.70; H, 1.85; N, 9.41.

Crystals suitable for X-ray analyses were grown from a 50/50 (v/v) mixture of acetonitrile and toluene.

Physical Measurements. NMR Spectra. NMR spectra were recorded in deuterated acetonitrile with a 300-MHz General Electric QE-300 NMR spectrometer. Chemical shifts are reported in ppm downfield from

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[†] The University of North Carolina at Charlotte.

[‡] North Carolina State University.

(1) Sahai, R.; Morgan, L.; Rillema, D. P. *Inorg. Chem.* **1988**, *27*, 3495.
(2) Rillema, D. P.; Tighdiri, D. G.; Jones, D. S.; Keller, C. D.; Worl, L. A.; Meyer, T. J.; Levy, H. A. *Inorg. Chem.* **1987**, *26*, 578.
(3) Sahai, R.; Rillema, D. P. *J. Chem. Soc., Chem. Commun.* **1986**, 1133.
(4) Sahai, R.; Rillema, D. P. *Inorg. Chim. Acta* **1986**, *118*, L32.
(5) Allen, G.; Rillema, D. P.; Meyer, T. J.; White, R. P. *J. Am. Chem. Soc.* **1984**, *106*, 2613.
(6) Rillema, D. P.; Allen, G.; Meyer, T. J.; Conrad, D. *Inorg. Chem.* **1983**, *22*, 1617.
(7) Rillema, D. P.; Mack, K. B. *Inorg. Chem.* **1982**, *21*, 3849.
(8) Sahai, R.; Rillema, D. P.; Shaver, R.; Van Wallendael, S.; Jackman, D. C. *Inorg. Chem.*, in press.
(9) Sullivan, B. P.; Abruna, H. D.; Finklea, H. O.; Salmon, D. J.; Nagle, J. K.; Meyer, T. J.; Sprintschnik, H. *Chem. Phys. Lett.* **1978**, *58*, 389. Westmoreland, T. D.; LeBozec, H.; Murray, R. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 5952.
(10) Vogler, A.; Kisslinger, J. *Inorg. Chim. Acta* **1986**, 193.

0020-1669/89/1328-1596$01.50/0

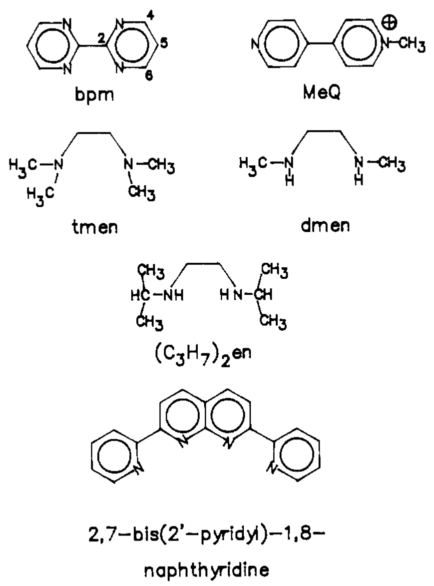

Figure 1. Structures of the ligands 2,2'-bipyrimidine (bpm), *N*-methyl-4,4'-bipyridinium ion (MeQ^+), *N*,*N*,*N'*,*N'*-tetramethylethane-1,2-diamine (tmen), *N*,*N'*-dimethylethane-1,2-diamine (dmen), *N*,*N'*-diisopropylethane–1,2-diamine ($(C_3H_7)_2en$), and 2,7-bis(2-pyridyl)-1,8-naphthyridine.

tetramethylsilane. Results of proton spectra are summarized in Table I; ^{13}C spectral results are summarized in Table II.

Collection and Reduction of X-ray Data. X-ray data were collected on a Nicolet R3 m/μ diffractometer using the θ–2θ method. A total of 4773 reflections were recorded to a 2θ value of 45°. Data were corrected for Lorentz and polarization effects. An empirical absorption correction was made by using the ψ scan method because of the large absorption coefficient (41.1 cm^{-1}). An extinction correction was made (SEC = 10^{-7}). Atomic scattering factors for all atoms were made from ref 11. The rhenium atom was located by direct methods of the crystallographic program package SHELXTL.[12] The remaining non-hydrogen atoms were found by conventional difference Fourier techniques to give a trial structure. The structure was refined by the block-diagonal least-squares technique using SHELXTL on the Data General Microelipse computer. The non-hydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms were placed 0.96 Å away from attached carbon atoms and were not refined. The single-crystal X-ray crystallographic analysis data are given in Table III.

IR Spectra. Infrared spectra were recorded in acetonitrile with a Mattson FTIR spectrometer.

Results

NMR Spectra. The ^1H NMR spectrum of $[Re(bpm)(CO)_3MeQ]^{2+}$ in CD_3CN contained seven sets of resonances in the aromatic region and a singlet at 4.32 ppm downfield from tetramethylsilane due to the methyl group of the *N*-methylbipyridinium ligand (Table I). All of the resonances can be assigned to either the bipyrimidine or the MeQ ligand by comparison to the spectra of the uncoordinated ligands. Only two resonances are observed for uncoordinated bipyrimidine, a doublet located at 8.97 ppm and a triplet located at 7.52 ppm. The doublet is attributed to protons on the C-4 and C-6 carbon atoms (see Figure 1 for the numbering system) on each ring, which are coupled by 6 Hz to the C-5 protons; the triplet is attributed to protons on the C-5 carbon atoms, which are coupled by 6 Hz to protons located on the C-4 and C-6 carbon atoms. Upon coordination to the metal, the C-4 and C-6 protons on each ring no longer are magnetically equivalent and, therefore, exhibit different chemical shifts (9.30 and 9.49 ppm). The C-5 resonance shifts downfield to 7.92 ppm and is a doublet of doublets, verifying the nonequivalence of the C-4 and C-6 protons. The remaining resonances are readily assigned to the MeQ ligand, which are not shifted significantly from those of the uncoordinated ligand.

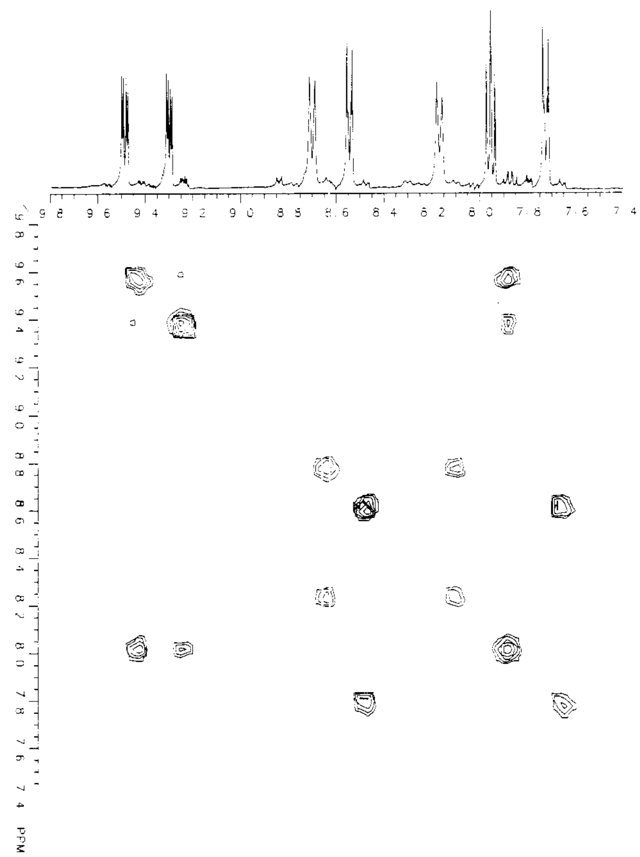

Figure 2. 2-D ^1H NMR spectrum (COSY) of $[Re(bpm)(CO)_3(MeQ)]^{2+}$.

Table III. Single-Crystal X-ray Crystallographic Analysis

	Crystal Parameters		
formula	$ReC_{22}H_{17}N_6O_3P_2F_{12}\cdot CH_3CN$	crystallizn medium	acetonitrile/toluene
mol wt	930.59	cryst size, mm	0.6 × 0.7 × 0.1
cell dimens	a = 41.19 (1) Å	cryst habit	thin plate
	b = 11.263 (2) Å	space group	$C2/c$
	c = 14.582 (2) Å	molecule/unit cell	8
	β = 102.94 (2)°	calcd density	1.79
V	6594 (2) Å	$F(000)$	3424 e
	Data Collection Parameters		
temp	298 K		
2θ range	3–45°		
scan type	θ		
scan speed	variable, 4–29.3°/min		
octants collected	hkl, $hk\bar{l}$		
bkgd measurement	$^1/_2$ of total scan time at beginning and end of each scan		
linear abs coeff	41.1 cm^{-1}		
	Refinement Parameters[a]		
final R indices	R = 0.074, R_w = 0.094		
goodness of fit	1.88		
largest shift/end	0.06		
data/param ratio	8.6		

[a] The data fit criteria (based on reflections having $I > 2\sigma(I)$) were $R = \sum||F_o - F_c||/F_o = 0.075$, $R_w = [\sum w(\Delta F)^2/\sum F_o]^{0.5} = 0.094$, GOF $= \sum(w[||F_o| - |F_c||^2/[N_o - N_v])^{0.5} = 1.30$, and $w = 1/(\sigma_F^2 + 0.002F^2)$.

A 2-D H NMR (COSY) study shown in Figure 2 unambiguously confirmed these assignments. The two resonances downfield are weakly coupled to each other and strongly coupled to the resonances at 7.92 ppm, confirming their assignments as the C-4 and C-6 hydrogen atoms of the bipyrimidine ligand. Furthermore, the remaining four doublets were found to consist of two sets of two coupled doublets as expected from the structure of the MeQ ligand.

The ^{13}C spectrum of $[Re(bpm)(CO)_3MeQ]^{2+}$ in CD_3CN consisted of two downfield resonances located at 194.7 and 195.6

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(11) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 71–102.

(12) "SHELXTL"; X-ray Instruments Group, Nicolet Instrument Corp., Madison, WI 53711.

Table IV. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$)

	x	y	z	U^a
Re	952 (1)	524 (1)	−473 (1)	52 (1)
P(1)	2703 (1)	−5028 (3)	6496 (3)	78 (1)
F(1)	2589 (2)	−4315 (8)	7319 (7)	114 (4)
F(2)	2808 (3)	−5678 (7)	5666 (8)	134 (5)
F(3)	3046 (3)	−4423 (10)	6779 (9)	157 (6)
F(4)	2598 (3)	−3949 (12)	5817 (8)	169 (6)
F(5)	2327 (4)	−5483 (17)	6101 (12)	249 (12)
F(6)	2779 (5)	−6092 (12)	7130 (11)	236 (10)
P(2)	883 (1)	5236 (4)	−401 (2)	87 (2)
F(7)	720 (3)	4021 (8)	−186 (7)	143 (5)
F(8)	828 (4)	4907 (11)	−1462 (7)	168 (6)
F(9)	526 (4)	5746 (11)	−715 (11)	180 (8)
F(10)	1037 (3)	6415 (11)	−632 (8)	163 (6)
F(11)	874 (4)	5622 (10)	630 (8)	163 (7)
F(12)	1202 (4)	4611 (14)	−118 (17)	270 (13)
C(1)	722 (3)	1686 (10)	−1369 (7)	64 (4)
O(1)	581 (2)	2329 (8)	−1914 (5)	94 (4)
C(2)	573 (3)	−517 (9)	−891 (8)	66 (5)
O(2)	358 (2)	−1106 (9)	−1157 (6)	95 (4)
C(3)	1134 (3)	−130 (9)	−1453 (7)	63 (4)
O(3)	1253 (3)	−517 (8)	−2043 (7)	97 (4)
N(1)	1207 (2)	−777 (7)	578 (6)	51 (3)
C(4)	1035 (3)	−1367 (9)	1122 (7)	61 (4)
C(5)	1173 (3)	−2231 (9)	1737 (7)	64 (4)
C(6)	1498 (2)	−2595 (8)	1811 (6)	52 (3)
C(7)	1682 (3)	−1980 (9)	1269 (8)	64 (4)
C(8)	1525 (2)	−1103 (9)	661 (8)	63 (4)
C(9)	1647 (3)	−3598 (9)	2437 (7)	59 (4)
C(10)	1446 (4)	−4552 (9)	2535 (9)	73 (5)
C(11)	1574 (4)	−5469 (10)	3082 (9)	79 (6)
N(2)	1894 (3)	−5493 (7)	3549 (7)	74 (4)
C(12)	2092 (4)	−4587 (9)	3458 (10)	79 (5)
C(13)	1972 (3)	−3617 (11)	2884 (9)	81 (5)
C(14)	2021 (5)	−6538 (14)	4092 (11)	123 (8)
N(3)	800 (2)	1394 (6)	698 (5)	50 (3)
C(15)	501 (2)	1311 (10)	912 (7)	59 (4)
C(16)	431 (3)	1977 (11)	1637 (8)	73 (5)
C(17)	667 (3)	2690 (11)	2120 (7)	70 (4)
N(4)	966 (2)	2806 (7)	1929 (5)	57 (3)
C(18)	1020 (2)	2116 (8)	1220 (6)	47 (3)
C(19)	1344 (2)	2234 (8)	965 (6)	47 (3)
N(5)	1363 (2)	1666 (6)	164 (5)	50 (3)
C(20)	1654 (3)	1801 (10)	−121 (7)	64 (4)
C(21)	1911 (3)	2440 (10)	397 (8)	70 (4)
C(22)	1866 (3)	2930 (10)	1225 (8)	75 (5)
N(6)	1587 (2)	2834 (7)	1508 (6)	59 (3)
C(23)	142 (4)	2479 (19)	6018 (11)	107 (7)
C(24)	132 (5)	3703 (15)	6169 (16)	141 (10)
N(7)	165 (4)	1455 (17)	5923 (11)	134 (8)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

ppm arising from the carbonyl ligands, eleven resonances in the aromatic region (110–165 ppm), and one methyl resonance at 48.7 ppm (Table II). Six resonances in the aryl region of the ^{13}C NMR spectrum were assigned to the *N*-methylbipyridinium ligand by comparison to the free ligand, leaving five resonances assignable to the bipyrimidine ligand. The C-2, C-4, and C-6 carbon resonances (162.4, 161.8, and 161.5 ppm) were shifted only slightly from the free ligand values and were readily assigned. However, the ^{13}C resonances of the C-5 carbon atoms appear as two distinct resonances located at 125.5 and 125.7 ppm.

IR Spectra. Carbonyl stretching frequencies for [Re(bpm)(CO)$_3$MeQ]$^{2+}$ were determined in acetonitrile. The vibrations were observed at 2030 and 1940 cm^{-1}. In comparison, the CO band maxima for *fac*-ClRe(bpy)(CO)$_3$ were observed at 2027 and 1926 cm^{-1} in CH_2Cl_2.[13]

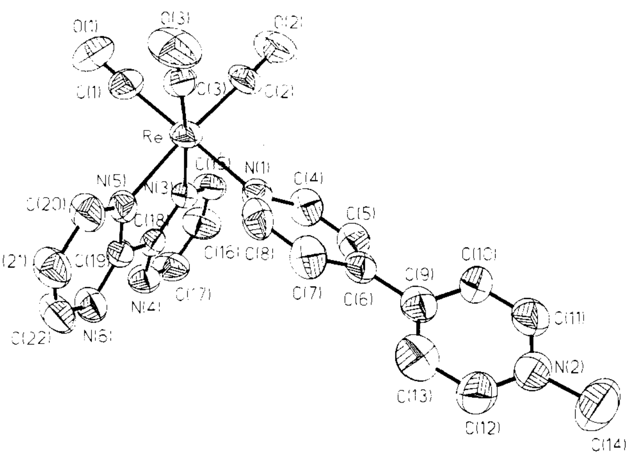

Figure 3. ORTEP drawing of the cation [Re(bpm)(CO)$_3$(MeQ)]$^{2+}$.

Table V. Selected Bond Distances (Å) and Angles (deg)

Re–C(1)	1.941 (10)	C(6)–C(9)	1.495 (13)
Re–C(3)	1.905 (12)	N(5)–C(20)	1.362 (14)
Re–N(3)	2.180 (8)	N(2)–C(14)	1.451 (17)
Re–C(2)	1.940 (12)	N(3)–C(15)	1.340 (13)
Re–N(1)	2.210 (8)	C(17)–N(4)	1.329 (14)
Re–N(5)	2.161 (7)	C(18)–(19)	1.471 (14)
		C(22)–N(6)	1.308 (15)
C(1)–Re–C(2)	87.7 (4)	C(1)–Re–C(3)	88.3 (4)
C(2)–Re–C(3)	87.4 (5)	C(1)–Re–N(1)	178.4 (4)
C(2)–Re–N(1)	92.3 (4)	C(3)–Re–N(1)	93.3 (4)
C(1)–Re–N(3)	92.4 (4)	C(2)–Re–N(3)	99.5 (4)
C(3)–Re–N(3)	173.1 (4)	N(1)–Re–N(3)	86.0 (3)
C(1)–Re–N(5)	96.0 (4)	C(2)–Re–N(5)	172.9 (4)
C(3)–Re–N(5)	98.7 (4)	N(1)–Re–N(5)	83.8 (3)
N(3)–Re–N(5)	74.4 (3)	Re–C(1)–O(1)	177.2 (9)
Re–C(2)–O(2)	177.7 (12)	Re–C(3)–O(3)	178.4 (10)
Re–N(1)–C(4)	120.1 (6)	Re–N(1)–C(8)	123.3 (7)
C(4)–N(1)–C(8)	116.4 (8)	Re–N(3)–C(18)	116.7 (7)
Re–N(3)–C(15)	126.3 (6)	Re–N(5)–C(19)	117.7 (6)
C(17)–N(4)–C(18)	115.0 (8)	C(19)–N(5)–C(20)	115.7 (8)
Re–N(5)–C(20)	126.4 (6)	C(19)–N(6)–C(22)	117.0 (9)

X-ray Structure. The single-crystal X-ray crystallographic analysis positional parameters are given in Table IV. Figure 3 shows an ORTEP drawing of the cation, and Table V contains selected bond distances and angles. Each asymmetric unit contained one acetonitrile solvate molecule (C(23), C(24), N(7)).

The average Re–C(CO) bond distance is 1.92 Å, the average Re–N(bpm) bond distance is 2.17 Å, and the Re–N(MeQ) bond distance is 2.21 Å. The C–C bond distances for the bridgehead carbon atoms of 4,4′-bipyridine (1.49 Å) are similar to the ones for 2,2′-bipyrimidine (1.47 Å). For bipyrimidine, bond distances between coordinated nitrogen atoms and the closest nonbridgehead carbon atoms are longer than comparable bond distances for noncoordinated nitrogen atoms and their closest nonbridgehead carbon atom. For example, this difference is 0.054 Å between N(5)–C(20) and N(6)–C(22). The PF_6 ions have nearly octahedral symmetry with an average P–F distance of 1.55 Å.

The bond angles in Table V clearly indicate that the CO ligands are linearly coordinated. The bond angles between adjacent CO carbon atoms are less than 90° (87–88°) and between adjacent nitrogen atoms of the heterocyclic ligands are greater than 90°. There is a difference between bond angles of coordinated CO ligands and the coordinated nitrogen atoms of the pyrimidine components of the bipyrimidine ring. These are C(1)–Re–N(5) = 96° and C(3)–Re–N(5) = 99° compared to C(2)–Re–N(3) = 99° and C(1)–Re–N(3) = 92°. Within the MeQ ligand, the angle between the normal to the plane of the $CH_3NC_5H_5$ unit and the coordinated C_5H_5N component is 36°. Carbon atoms labeled C(21) and C(16) i n the ORTEP drawing, the C-5 carbon atoms in Figure 1, lie +0.2 and −0.6 Å, respectively, with respect to the plane through C(3), C(2), and Re. Normals to the plane of each pyrimidine ring intersect at a 9° angle, which appears as a twist from planarity.

Discussion

The [Re(bpm)(CO)$_3$(MeQ)]$^{2+}$ ion exhibited unique structural properties that warrant further discussion. The ^{13}C NMR

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(13) Giordano, P. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 2888.

spectrum indicated that the C-5 carbon atoms (Figure 1) of the pyrimidine rings were not equivalent, which suggested meridional geometry for the complex ion. The IR evidence based on C=O vibrations, however, indicated that the complex ion had facial geometry by comparison to other known tricarbonylrhenium(I) complexes. This ruled out the meridional possibility. By means of an X-ray diffraction study, the origin of the difference in the C-5 carbon atoms was traced to a twist of the pyrimidine rings of the bipyrimidine ligand.

A comparison of Re–N(bpm) and Re–N(MeQ) bond distances to those of rhenium(I) tricarbonyl complexes is of interest.[14–21] Ligands associated with these complexes are illustrated in Figure 1. The reported average Re–N bond distances vary from 2.13 Å for $[Re(CO)_3(CH_3CN)_3]^{2+}$ to 2.26 Å, for both Re(tmen)$(CO)_3X$, where tmen is *N*,*N*,*N'*,*N'*-tetramethylene-1,2-diamine and X = F[14] and Br,[19] and $Re(NHR_2)_2(CO)_3Br$,[16] where NHR_2 is a dialkylamine and R = CH_3 and C_2H_5. The average bond distance in $Re(bpy)(CO)_3PO_2F_2)$,[17] where bpy is 2,2′-bipyridine, was 2.14 Å, while it was 2.22 Å for $Re(dmen)(CO)_3Br$,[12] where dmen is *N*,*N'*-dimethylethane-1,2-diamine. The diisopropylethanediamine analogue $Re((C_3H_7)_2en)(CO)_3Cl$[21] exhibited an average Re–N bond length of 2.24 Å. One other compound merits comment. The complex bromotricarbonyl(2,7-bis(2-pyridyl)-1,8-naphthyridine)rhenium(I)[15] contained a Re–N("py") bond length of 2.19 Å and a Re–N("naphthyridine") bond length of 2.21 Å. The tmen, dmen, $(C_3H_7)_2$en, and NHR_2 ligands are saturated amine systems which contain nitrogen donor atoms that can only form σ bonds. The other ligands bpy, bpm, CH_3CN, MeQ, and "naphthyridine" contain nitrogen donors that can both σ and π bond. On the basis of these arguments, it appears Re–N bond lengths fall into two categories. σ-bonded systems fall in the range 2.22–2.26 Å, whereas systems in which π bonding plays a role fall in the range 2.13–2.21 Å. The differences within each grouping may be due, in part, to steric factors. The order from the longest Re–N bond distance to the shortest for the systems discussed here is Re–N(en) > Re–N("py") > Re–N(bpm) > Re–N(bpy) > Re–N(CH_3CN).

The bond distances between rhenium and coordinated nitrogen donors for $[Re(bpm)(CO)_3(MeQ)]^{2+}$ were different for the bpm and MeQ ligands. The average Re–N(bpm) bond distance was 2.17 Å; the Re–N(MeQ) bond distance was 2.21 Å. The difference in bond distances cannot be related to σ–donor strength. The pK_a of pyrimidinium is 1.3,[22] whereas the pK_a of pyridinium is 5.23,[23] indicating MeQ is the stronger σ donor. This difference in bond lengths could be related to steric factors. However, it is more likely due to more extensive π bonding between the dπ orbitals of rhenium with the empty π^* orbitals of bipyrimidine than with the empty π^* orbitals of MeQ.

The other structural feature of significance is the orientation of the two pyridine rings in the bipyrimidine ligand. The 38° angle has an important consequence for the design of donor/acceptor complexes. Meyer and co-workers[9] suggest charge separation can be achieved in $[Re(bpy)(CO)_3MeQ]^{2+}$ according to eq 1. According to eq 1, one pathway the excited electron may follow is to reside on the MeQ ligand but, in particular, to reside on the *N*-methyl-substituted pyridine, which has the more positive reduction potential. The 38° angle between the coordinated py component and the Me-py residue ensures that the direct communication between the π structure of the Me-py and py fragments of the MeQ ligand is broken, inhibiting back electron transfer between MeQ and rhenium. This break in communication, then, should allow one to generate these charge-separated intermediates on a detectable time scale.

$$[(bpy)Re^{I}(CO)_3(py\text{-}py\text{-}CH_3)]^{2+} \xrightarrow{h\nu} [(bpy)Re^{II}(CO)_3(py\text{-}py^{-}\text{-}CH_3)]^{2+*} \quad (1)$$

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Supplementary Material Available: Listings of bond lengths and bond angles, displacement parameters, and H atom positional and isotropic thermal parameters and a figure showing the unit cell packing (5 pages); a listing of observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

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(14) See Table I (Proton NMR Properties of Compounds) in: Horn, E.; Snow, M. R. *Aust. J. Chem.* **1984**, *37*, 35.

(15) Tikkanem, W.; Kaska, W. C.; Moya, S.; Layman, T.; Kane, R. *Inorg. Chim. Acta* **1983**, *76*, L29.

(16) Marchetti, F.; Calderazzo, F.; Vitali, D.; Mavani, I. P. *J. Chem. Soc., Dalton Trans.* **1981**, 2523.

(17) Horn, E.; Snow, M. R. *Aust. J. Chem.* **1980**, *33*, 2369.

(18) Abel, E. W.; Bhatti, M. M.; Hursthouse, M. B.; Malik, K. M. A.; Mazid, M. *J. Organomet. Chem.* **1980**, *197*, 345.

(19) Couldwell, M. C.; Simpson, J. *J. Chem. Soc., Dalton Trans.* **1979**, 1101.

(20) Chan, L. Y. Y.; Isaacs, E. E.; Graham, W. A. G. *Can. J. Chem.* **1977**, *55*, 111.

(21) Graham, A. J.; Akrigg, D.; Sheldrick, B. *Cryst. Struct. Commun.* **1977**, *6*, 577.

(22) Acheson, R. M. *An Introduction to the Chemistry of Heterocyclic Compounds*; Interscience: New York, 1960; p 299.

(23) *Handbook of Chemistry and Physics*, 42nd ed.; CRC: Boca Raton, FL, 1960; p 1750.

Notes

Contribution from the Department of Chemistry
and Rice Quantum Institute, Rice University,
P.O. Box 1892, Houston, Texas 77251

Infrared Spectroscopic Studies of the Reactions of Copper and Ammonia in Cryogenic Argon Matrices

David W. Ball,[†] Robert H. Hauge, and John L. Margrave*

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Recent work from our laboratory[1,2] has focused on the study of new oxidative-addition products from metal atoms and 2p hydrides in cryogenic matrices via FTIR spectroscopy. These products have the general formula HMX, where M is a first-row transition-metal atom and X is a member of the isoelectronic series CH_3/NH_2/OH/F. Our goal is to study the vibrational spectra of the entire array of these oxidative-addition products in order to elucidate what trends might exist in the H–M and M–X bond characteristics. To this end, we have recently studied the vibrational spectra of $HNiCH_3$,[1] $HNiNH_2$,[2] and HNiOH.[3]

Recent experiments on the reaction of Cu and diazomethane[4] have turned our interest to Cu as a reactant. This interest was bolstered by the reports by Ozin et al.[5,6] on the reactivity of Cu

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[†] Present address: Lawrence Berkeley Laboratory, University of California, Mail Stop 70A-1115, Berkeley, CA 94720.

(1) Chang, S.-C.; Hauge, R. H.; Margrave, J. L. *Inorg. Chem.* **1988**, *27*, 205.

(2) Ball, D. W.; Hauge, R. H.; Margrave, J. L. *High Temp. Sci.*, in press.

(3) Park, M.; Hauge, R. H.; Margrave, J. L. *High Temp. Sci.* **1988**, *25*, 1.

(4) Chang, S.-C.; Hauge, R. H.; Margrave, J. L. Unpublished results.

(5) Ozin, G. A.; McCaffrey, J. G.; Parnis, J. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1072 and references within.

0020-1669/89/1328-1599$01.50/0