to be operative.[7] However, this result can be rationalized considering that the fraction of unpaired electron delocalized from one copper atom on the oxygen atom occupying an axial position of the other copper ion is in an orbital orthogonal to the $x^2 - y^2$ magnetic orbital of the latter. This situation is analogous to that seen in Cu(hfac)$_2$TEMPOL[8] (hfac = hexafluoroacetylactonato, TEMPOL = 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-*N*-oxy) and in Cu(pacTEMPOL)$_2$[9] (pacTEMPOL = bis(1-oxy-2,2,6,6-tetramethylpiperidin-4-yl)pivaloylacetato) where the unpaired electron on the radical is in an orbital similarly oriented with respect to the copper magnetic orbital: in both cases the coupling was reported to be ferromagnetic.

Experimental Section

The title compound was kindly supplied by Prof. P. Orioli, University of Firenze.

The EPR spectra were recorded with a Bruker ER200 spectrometer, equipped with an Oxford Instruments continuous-flow ESR10 cryostat. Q-Band spectra were recorded at room temperature on a Varian E9 spectrometer. The magnetic susceptibilities were measured by an ac mutual-inductance technique at nearly zero field.[10] The sample is immersed in liquid helium, and the temperature is measured by means of a germanium-resistance thermometer calibrated against the vapor pressure of He. Each data point is calibrated by measuring against CMN.

Acknowledgment. The work in Chicago was supported by the Solid State Chemistry Program of the Division of Materials Research of the National Science Foundation, Grant No. DMR-8211237.

Registry No. [Cu(ATP)(bpy)]$_2$, 97373-98-3.

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Coordination Chemistry of Samarium(II). X-ray Crystal Structures of SmI$_2$(NCCMe$_3$)$_2$ and SmI$_2$[O(CH$_2$CH$_2$OMe)$_2$]$_2$. The First Example of a Bent M—N≡C Structure

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Received December 14, 1984

Oxygen- and nitrogen-donor ligands are ubiquitous in trivalent lanthanide metal chemistry, and numerous structurally characterized compounds that incorporate these ligand types are known.[2] In contrast, very few soluble, well-characterized, compounds of the lanthanide elements in the divalent state have been reported [only three for Sm(II): the Sm(C$_5$Me$_5$)$_2$ derivatives[3]]. Except for a few compounds incorporating the sterically demanding ligand N(SiMe$_3$)$_2$,[4] we are unaware of structurally characterized coordination compounds of any of the divalent lanthanide metal ions that contain simple oxygen- and nitrogen-donor ligands. Herein, we report the synthesis and X-ray crystal structures of two Sm(II) derivatives: SmI$_2$(NCCMe$_3$)$_2$ (**1**) and SmI$_2$[O(CH$_2$CH$_2$OMe)$_2$]$_2$ (**2**). As detailed below, these present several interesting structural features, including a unique bent M—N≡C structure for **1**. The latter is of particular interest in view of the isoelectronic relationship between R—C≡N and N≡N. In addition, the preparation and characterization of soluble compounds are important for the elaboration of the chemistry of divalent lanthanide metal ions. We also note here that SmI$_2$ in oxygen-donor solvents has been used extensively as a reducing agent in organic chemistry,[5] and **1** and **2** represent the first well-characterized derivatives of SmI$_2$.

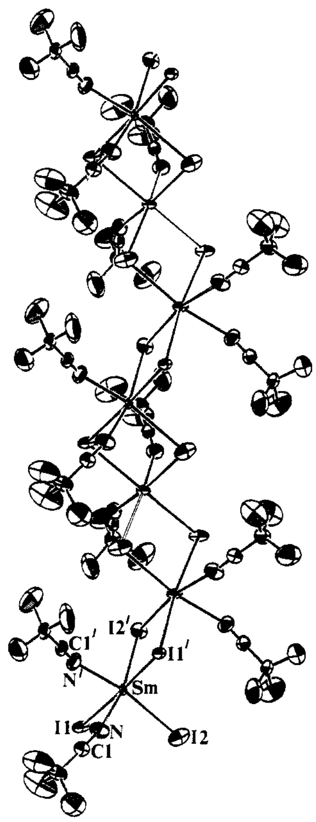

Figure 1. ORTEP drawing of **1**.

Results and Discussion

1 was obtained as dark green crystals by the reaction of SmI$_2$ with Me$_3$CCN at 25 °C. An X-ray crystal structure of **1** revealed the geometry around each samarium to be a distorted octahedron, the ligating atoms being the two nitrogens and the four bridging iodides. All the iodide ions are bridging, and this results in infinite chains of repeating unit SmI$_2$(NCCMe$_3$)$_2$, with an average Sm–I distance of 3.242 (1) Å (Figure 1). The samarium lies on a twofold axis that generates a complete monomeric unit; in addition, a twofold axis passes through both unique iodide ions, thus generating the bridging iodide polymeric structure of **1**. The two nitrile ligands have a cis configuration with Sm–N distances of 2.596 (8) Å.

The most remarkable structural feature of **1** is the Sm—N≡C angle of 151.3 (6)°.[6] Crystal structures of nitrile adducts of the actinides,[7] the transition metals,[8] and the main-group elements[9]

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Table I

	compd 1	compd 2
	A. Crystal Data	
empirical formula	$C_{10}H_{18}SmI_2N_2$	$C_{12}H_{28}SmI_2O_6$
fw	570.43	672.56
$F(000)$	780	732
cryst dimens, mm	0.21 × 0.50 × 0.67	0.22 × 0.25 × 0.68
peak width at half-height, deg	1.10	1.30
Mo Kα radiation: λ, Å	0.71073	0.71073
temp, °C	21 (1)	21 (1)
space group	hexagonal $P3_121$	monoclinic $P2_1/n$
cell dimens		
a, Å	11.518 (3)	8.674 (1)
b, Å		9.726 (3)
c, Å	12.424 (13)	13.086 (3)
β, deg		104.0 (3)
vol, $Å^3$	1427 (2)	1071.4 (8)
Z	3	2
density (calcd), g/cm^3	1.99	2.084
abs coeff (μ), cm^{-1}	62.9	56.2
	B. Intensity Measurements	
instrument	Enraf-Nonius CAD4 diffractometer	
monochromator	graphite cryst, incident beam	
attenuator	Zr foil, factor 20.6	
takeoff angle, deg	2.8	
detector aperture, mm	2.0–2.5, horizontal; 4.0, vertical	
cryst–detector dist, cm	21	
scan type	ω–θ	
scan rate, deg/min (in ω)	1–5	
scan width, deg	1.1 + 0.347 tan θ	1.3 + 0.347 tan θ
max 2θ, deg	53.2	47.2
no. of reflns measd	2502 total, 2009 unique	1820 total, 1594 unique
corrections	Lorentz-polarization	
linear decay	from 0.969 to 1.136 on *I*	from 1.000 to 1.099 on *I*
refln averaging	agreement on *I* = 3.0%	agreement on *I* = 5.0%
empirical abs	from 0.53 to 1.00 on *I*	from 0.43 to 1.00 on *I*
	C. Structure Solution and Refinement	
solution	Patterson method	
hydrogen atoms	not included	included at fixed $B = 5.0$ $Å^2$
minimization function	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	
least-squares weights	$4F_o^2/\sigma^2(F_o^2)$	
anamalous dispersion	all non-hydrogen atoms	
no. of reflns included	1810 with $F_o^2 > 3.0\sigma(F_o^2)$	1402 with $F_o^2 > 2.0\sigma(F_o^2)$
params refined	70	139
unweighted agreement factor	0.037	0.037
weighted agreement factor	0.054	0.047
esd in observn of unit weight	1.61	1.58
convergence, largest shift	0.00σ	0.34σ
high peak in final diff map, e/$Å^3$	1.92 (17)	1.13 (12)
computer hardware	VAX-11/750	PDP-11/34a
computer software	SDP-PLUS (Enraf-Nonius & B. A. Frenz Associates, Inc.)	

are known, but in no case does the M—N≡C angle deviate from the ideal value of 180° by more than 8°.[10] The N≡C—CMe_3 angles in **1** are an unremarkable 178.8 (7)°. The N≡C bond lengths of 1.178 (14) Å are long, although not outside the range observed for other nitrile complexes. The IR spectrum of **1** in the form of a Nujol mull exhibits a $\bar{\nu}$(CN) value of only 15 cm^{-1} greater than that observed for free $NCCMe_3$ (2231 cm^{-1}). The corresponding CH_3CN complex, prepared in an analogous manner, shows two IR bands whose $\bar{\nu}$(CN) values are very close to those

Table II. Bond Distances (Å) and Bond Angles (deg) for **1**[a]

	Distances		
Sm–I1	3.260 (1)	C1–C2	1.442 (14)
Sm–I2	3.225 (1)	C2–C3	1.45 (2)
Sm–N	2.596 (8)	C2–C4	1.52 (2)
N–C1	1.178 (14)	C2–C5	1.49 (2)
	Angles		
I1–Sm–I1	173.04 (2)	Sm–I2–Sm	92.90 (2)
I1–Sm–I2	87.75 (1)	Sm–N–C1	151.3 (6)
I1–Sm–I2	96.68 (1)	N–C1–C2	178.8 (7)
I2–Sm–I2	101.07 (10)	C1–C2–C3	111 (1)
I1–Sm–N	83.9 (2)	C1–C2–C4	112 (1)
I1–Sm–N	90.6 (2)	C1–C2–C3	109.0 (8)
I2–Sm–N	92.1 (2)	C3–C2–C4	108.8 (9)
I2–Sm–N	166.8 (2)	C3–C2–C5	114 (1)
N–Sm–N	74.7 (3)	C4–C2–C5	101 (1)
Sm–I1–Sm	91.60 (2)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

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(10) Except for two Cu(I) compounds[11] with chelating dinitriles that exhibit M—N≡C angles of 169°. This has been ascribed to the rigidity of the particular N≡C—C frameworks.[8,11a] Side-on nitrile–metal interactions have been proposed for several metal–nitrile complexes,[8] on the basis of low $\bar{\nu}$(CN) values in these compounds. However, there are no structurally characterized side-on-bonded nitrile complexes, and in several cases, the low $\bar{\nu}$(CN) values have been ascribed to other factors (see text and ref 12).

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Table III. Bond Distances (Å) and Bond Angles (deg) for **2**[a]

Distances							
Sm–I	3.265 (1)	O2–C4	1.423 (10)	C2–H2A	1.16 (7)	C4–H4B	0.80 (7)
Sm–O1	2.720 (4)	O2–C5	1.402 (10)	C2–H2B	0.96 (7)	C5–H5A	0.78 (7)
Sm–O2	2.676 (4)	O3–C6	1.447 (10)	C3–H3A	1.29 (6)	C5–H5B	0.99 (7)
Sm–O3	2.701 (4)	C1–H1A	0.78 (6)	C3–H3B	0.94 (7)	C6–H6A	1.07 (7)
O1–C1	1.411 (10)	C1–H1B	1.01 (7)	C4–C5	1.488 (13)	C6–H6B	1.04 (7)
O1–C2	1.442 (9)	C1–H1C	1.34 (7)	C4–H4A	1.32 (7)	C6–H6C	0.97 (8)
O2–C3	1.418 (9)	C2–C3	1.462 (12)				

Angles					
I–Sm–O1	84.4 (1)	Sm–O3–C6	121.6 (5)	H3A–C3–H3B	118 (5)
I–Sm–O1	95.6 (1)	C5–O3–C6	111.3 (8)	O2–C4–C5	105.4 (7)
I–Sm–O2	98.0 (1)	O1–C1–H1A	152 (6)	O2–C4–H4A	112 (3)
I–Sm–O2	82.0 (1)	O1–C1–H1B	102 (4)	O2–C4–H4B	126 (5)
I–Sm–O3	83.3 (1)	O1–C1–H1C	91 (3)	C5–C4–H4A	112 (3)
I–Sm–O3	96.7 (1)	H1A–C1–H1B	103 (7)	C5–C4–H4B	106 (5)
O1–Sm–O2	59.0 (2)	H1A–C1–H1C	90 (6)	H4A–C4–H4B	95 (6)
O1–Sm–O2	121.0 (2)	H1B–C1–H1C	113 (5)	O3–C5–C4	107.8 (6)
O1–Sm–O3	113.3 (2)	O1–C2–C3	108.4 (5)	O3–C5–H5A	124 (6)
O1–Sm–O3	66.7 (2)	O1–C2–H2A	106 (3)	O3–C5–H5B	108 (4)
O2–Sm–O3	121.5 (2)	O1–C2–H2B	119 (4)	C4–C5–H5A	113 (6)
O2–Sm–O3	58.5 (2)	C3–C2–H2A	123 (3)	C4–C5–H5B	104 (4)
Sm–O1–C1	123.1 (6)	C3–C2–H2B	101 (4)	H5A–C5–H5B	97 (7)
Sm–O1–C2	119.6 (4)	H2A–C2–H2B	102 (5)	O3–C6–H6A	117 (4)
C1–O1–C2	113.4 (8)	O2–C3–C2	106.7 (6)	O3–C6–H6B	94 (4)
Sm–O2–C3	111.8 (4)	O2–C3–H3A	102 (3)	O3–C6–H6C	111 (5)
Sm–O2–C4	110.8 (4)	O2–C3–H3B	111 (5)	H6A–C6–H6B	99 (5)
C3–O2–C4	113.5 (6)	C2–C3–H3A	104 (3)	H6A–C6–H6C	100 (5)
Sm–O3–C5	121.4 (5)	C2–C3–H3B	114 (4)	H6B–C6–H6C	136 (6)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

for free CH_3CN. This contrasts sharply with substantial increases in $\bar{\nu}$(CN) upon coordination that are observed for the majority of the nitrile complexes.[7-9] However, in several transition metal–nitrile complexes, the $\bar{\nu}$(CN) values have been found to remain virtually unchanged or are lower than that observed for the corresponding free nitriles and this has been ascribed to significant "back-bonding" between the metal d orbitals and the π^* orbitals of the nitriles in these compounds.[12] Depending on the symmetry, this type of overlap would be expected to decrease in compounds containing bent M—N≡C structures and, in any case, d_π–p_π interactions would not be possible for d^0-Sm(II) compounds (the 4f electrons are too well shielded by 5s and 5p electrons for any f_π–p_π interactions to take place). On the other hand, given the highly reducing nature of Sm(II) [$E°_{Sm(III)/Sm(II)} = -1.55$ V[13]], the bent M—N≡C structure of **1** and the low $\bar{\nu}$(CN) values for **1** and the corresponding CH_3CN complex are strongly reminiscent of the bent M—NO structures formed in some transition metal–nitrosyl complexes and may possibly have similar bonding origins[14] (in bending the nitrosyls, electron-rich systems avoid placing excess electrons into strongly antibonding orbitals but at the expense of decreasing M—NO π-bonding).

2 was synthesized as dark brown crystals by the reaction of SmI_2 with diglyme at 25 °C. An X-ray crystal structure of **2** indicated an eight-coordinate, monomeric structure (in contrast to a six-coordinate, polymeric structure for **1**; see above). The atoms in the coordination sphere of samarium are the six oxygens and the two iodides, which have a trans configuration. The molecular geometry is best described as a distorted hexagonal bipyramid (Figure 2). The samarium sits on an inversion center. The Sm–I bond distances are 3.265 (1) Å and the average Sm–O bond distance is 2.699 (4) Å.

Experimental Section

The reagent grade solvents were appropriately dried and deoxygenated prior to their use. All reactions were carried out either on a high-vacuum line or in a N_2-filled drybox.

SmI_2 was synthesized by a published procedure.[5b]

$SmI_2(NCCMe_3)_2$ (1). A 0.5-g portion of SmI_2 was stirred in 30 mL of Me_3CCN at 25 °C for 4 h. The solution was then filtered and the filtrate concentrated to 15 mL. On standing, dark green crystals deposited.

$SmI_2[O(CH_2CH_2OMe)_2]_2$ (2). A 0.5-g portion of SmI_2 was stirred in 30 mL of diglyme at 25 °C for 4 h. The solution was then filtered and the residue redissolved in 25 mL of THF. This solution on standing overnight at −15 °C deposited dark brown crystals.

Structure Determination. Data relating to the determination of the crystal structures of **1** and **2** are summarized in Table I. For **1**, the space group was determined to be either $P3_121$ (No. 152)[15] or $P3_221$ (No. 154).[15] Final anisotropic convergence in each space group using a unit weighing scheme was achieved ($P3_121$ $R_1/R_2 = 0.039/0.042$, esd = 2.139; $P3_221$ $R_1/R_2 = 0.044/0.045$, esd = 2.332). This showed that $P3_121$ was the proper choice of the space group.

The structure was solved by using the Patterson heavy-atom method, which revealed the positions of the Sm and I atoms. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were not included in the calculations for compound **1** but were included with fixed isotropic thermal parameters for compound **2**. The standard deviation on intensities, $\sigma(F_o^2)$, is defined as

$$\sigma^2(F_o^2) = [S^2(C + R^2B) + (pF_o^2)^2]/Lp^2$$

where S is the scan rate, C is the total integrated peak count, R is the ratio of scan time to background counting time, B is the total background count, Lp is the Lorentz–polarization factor, and the parameter p is a factor introduced to downweight intense reflections. Here p was set to 0.055 for **1** and 0.050 for **2**.

Neutral-atom scattering factors were taken from Cromer and Waber.[15] Anomalous dispersion effects were included in F_c;[16] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[17] Only the 1810 reflections having intensities greater than 3.0 times their standard deviation were used in the refinements (1402 reflections having intensities greater than $2.0(\sigma(I))$ for compound **2**). The final cycle of refinement included 70 variable parameters (139 parameters for **2**) and converged with the largest parameter shift being 0.00 times the esd (0.34 for **2**) with unweighted and weighted agreement factors of

$$R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.037 \quad (0.037 \text{ for } \mathbf{2})$$

$$R_2 = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2} = 0.054 \quad (0.047 \text{ for } \mathbf{2})$$

---

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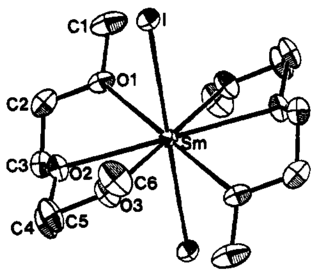

Figure 2. ORTEP drawing of **2**.

Table IV. Positional Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	B, Å^2
		A. Compound **1**		
Sm	0.10866 (4)	0.000	0.333	3.801 (9)
I1	0.000	−0.25167 (5)	0.167	5.19 (2)
I2	0.000	0.13855 (6)	0.167	8.17 (3)
N	0.3320 (7)	0.0883 (8)	0.2282 (7)	8.5 (2)
C1	0.4018 (8)	0.0721 (8)	0.1681 (8)	6.3 (2)
C2	0.4896 (7)	0.0548 (9)	0.0954 (7)	7.2 (2)
C3	0.609 (1)	0.074 (2)	0.150 (1)	19.2 (6)
C4	0.531 (1)	0.150 (2)	0.000 (1)	16.1 (5)
C5	0.412 (1)	−0.078 (2)	0.041 (2)	21.8 (5)
		B. Compound **2**		
Sm	0.000	0.000	0.000	3.060 (9)
I	0.19296 (7)	0.27325 (5)	−0.04404 (4)	5.53 (1)
O1	−0.1994 (6)	0.1836 (6)	0.0584 (4)	5.9 (1)
O2	0.0120 (6)	0.0463 (6)	0.2033 (4)	5.3 (1)
O3	0.2669 (6)	−0.0473 (6)	0.1516 (4)	5.8 (1)
C1	−0.258 (1)	0.301 (1)	−0.001 (1)	9.8 (3)
C2	−0.202 (1)	0.1949 (9)	0.1677 (7)	6.6 (2)
C3	−0.1415 (9)	0.0668 (9)	0.2209 (6)	5.7 (2)
C4	0.101 (1)	−0.058 (1)	0.2678 (5)	6.5 (2)
C5	0.267((1)	−0.040 (1)	0.2587 (8)	7.5 (3)
C6	0.423 (1)	−0.019 (1)	0.135 (1)	8.9 (3)
H1A	−0.301 (7)	0.337 (7)	−0.054 (5)	*
H1B	−0.187 (7)	0.376 (6)	0.038 (5)	*
H1C	−0.396 (8)	0.292 (7)	0.027 (5)	*
H2A	−0.326 (8)	0.239 (7)	0.168 (5)	*
H2B	−0.133 (9)	0.260 (7)	0.211 (5)	*
H3A	−0.108 (8)	0.098 (7)	0.319 (5)	*
H3B	−0.207 (9)	−0.010 (7)	0.199 (6)	*
H4A	0.046 (8)	−0.182 (7)	0.239 (5)	*
H4B	0.106 (8)	−0.070 (7)	0.329 (5)	*
H5A	0.315 (9)	0.014 (7)	0.298 (6)	*
H5B	0.323 (8)	−0.123 (6)	0.293 (5)	*
H6A	0.505 (8)	−0.103 (7)	0.146 (5)	*
H6B	0.463 (9)	0.030 (7)	0.207 (5)	*
H6C	0.417 (9)	0.002 (7)	0.062 (6)	*

[a] Asterisks indicate that the atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

The standard deviation of an observation of unit weight was 1.61 (1.58 for **2**). The highest peak in the final difference Fourier had a height of 1.92 (17) e/Å^3 (1.13 (12) e/Å^3 for **2**).[18] Plots of $\sum w(|F_o| - |F_c|)^2$ vs. $|F_o|$, reflection order in data collection, $(\sin\theta)/\lambda$, and various classes of indices showed no unusual trends.

The bond distances and bond angles for **1** and **2** are given in Tables II and III, respectively. The positional parameters are given in Table IV.

Acknowledgment. Support of this research through a grant from the National Science Foundation (CHE-8312380) is gratefully acknowledged.

Registry No. **1**, 97316-33-1; **2**, 97316-34-2.

Supplementary Material Available: Tables of thermal parameters and structure factors for **1** and **2** (21 pages). Ordering information is given on any current masthead page.

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Basicity Constants of Iron(II) and Ruthenium(II) Complexes of 2,6-Dimethylpyrazine

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Received October 17, 1984

The pK_a of the coordinated pyrazine ion (pzH^+) has been used to estimate the back-bonding capability of a number of low-spin transition-metal complexes.[1,2] In this regard, the effective pK_a's of $[(CN)_5Ru(pzH)]^{2-}$ and $[(CN)_5Fe(pzH)]^{2-}$ have been recently determined by Johnson and Shepherd[3] as 0.4 and 0.065, respectively, being smaller than that for the coordinated pyrazine ligand ($pK_a = 0.6$). The extent of back-bonding in these complexes, based on MLCT and pK_a data, was reported to be 9% and 7%, respectively. However, as Johnson and Shepherd have pointed out, these data are not in harmony with the NMR results, which indicate that back-bonding to the pz ligand is more extensive for the $[(CN)_5Fe(pz)]^{3-}$ complex than for the $[(CN)_5Ru(pz)]^{3-}$ analogue.

In this work, we have extended the preceding basicity studies[3,4] to the 2,6-dimethylpyrazine (dmpz) complexes with $(CN)_5Fe^{3-}$, $(CN)_5Ru^{3-}$, and $(NH_3)_5Ru^{2+}$. Our choice was based on the fact that the dmpz ligand has a $pK_a = 1.9$,[5] comparable to that for the coordinated cyanide ligands in typical cyanoiron complexes.[4] Therefore, in contrast with the case of the pz complexes, the increase of basicity promoted by back-bonding interactions would be unambiguously detected by a preferential protonation of the dmpz ligand.

Experimental Section

Potassium hexacyanoruthenate(II) trihydrate (Alfa) and 2,6-dimethylpyrazine (Aldrich) were used as supplied. All other chemicals were reagent grade. The $[(NH_3)_5Ru(dmpz)](PF_6)_2$ and $K_3[Ru(CN)_5(dmpz)]$ complexes were synthesized according to literature procedures[1,3] for related compounds. Anal. Calcd for $RuC_6N_7H_{23}P_2F_{12}$: C, 12.33; N, 16.78; H, 3.96. Found: C, 12.2; N, 16.1; H, 4.1. Calcd for $K_3RuC_{11}N_7H_8(C_3H_6O)$: C, 32.67; N, 19.04; H, 2.74. Found: C, 33.2; N, 20.0; H. 3.0. The $[(CN)_5Fe(dmpz)]^{3-}$ complex was freshly prepared in aqueous solution by reacting $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ with at least 5 times excess of dmpz to prevent the dissociation of the coordinated ligand. The complex was also isolated as a hygroscopic solid by precipitating with ethanol. The analyses were consistent with the composition $Na_3[Fe(CN)_5dmpz]\cdot 3H_2O$. Anal. Calcd: C, 31.68; N, 23.50; H, 3.38. Found: C, 30.7; N, 22.8; H, 3.5.

The electronic spectra were recorded on a Cary 14 or 17 spectrophotometer fitted with thermostated cell compartments. Potentiometric and pH measurements were made with a digital Orion 801-A instrument, using a combined glass–Ag/AgCl microelectrode. Cyclic voltammetry was carried out with a Princeton Applied Research instrument, consisting of a 173 potentiostat and a 174 universal programmer. Platinum or gold disk electrodes were employed for the measurements, using the conventional Luggin capillary with the Ag/AgCl (1 M KCl) reference electrode in a nonisothermic arrangement. A platinum wire was used as the auxiliary electrode.

The pK_a's of the complexes were determined independently by spectrophotometry and cyclic voltammetry as a function of pH. Cells specially designed for the experiments were used, combining simultaneous pH measurements with absorption spectra, or cyclic voltammetry, under nitrogen atmosphere.

Results and Discussion

The spectrum of the $[(NH_3)_5Ru(dmpz)]^{2+}$ complex is shown in Figure 1A. The strong absorption at 460 nm ($\epsilon = 8.0 \times 10^3$ M^{-1} cm^{-1}) is assigned to a metal-to-ligand charge transfer (MLCT) transition. An additional band centered at 267 nm (ϵ

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