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N-Acyl Isocyanide Complexes of Iron(II) Porphyrins: Analogy between the Bonding Properties of *N*-Acyl Isocyanides and Carbon Monoxide

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The bonding properties of *N*-acyl isocyanides (RC(=O)NC; R = Ph, *t*-Bu) in ferrous porphyrin complexes have been studied. The hexacoordinate complexes Fe^{II}(porphyrin)$(CNCOR)_2$, with porphyrin = TPP, TTP, or DPDME,[1] and the pentacoordinate complexes Fe(TPP)(CNCOPh) and Fe(TPP)(CNCO-*t*-Bu) have been prepared. NMR studies show that both mono- and bis(*N*-acyl isocyanide) adducts are diamagnetic. The comparison of IR and Mössbauer data indicates a great similarity between the bonding properties of the *N*-acyl isocyanide and carbon monoxide ligands. The mixed hexacoordinate complexes (P)Fe(CNCOPh)L (L = pyridine, *N*-methylimidazole, 4-cyanopyridine, and tetrahydrothiophene) have been obtained from (P)Fe$(CNCOPh)_2$ complexes by displacement of the *N*-benzoyl isocyanide ligand upon addition of 1 equiv of L, providing models for isocyanide binding to myoglobin.

Introduction

Much attention has been given to studies of the binding of small diatomic ligands (O_2, CO, and NO) to hemoproteins.[2] In particular, considerable work has been devoted to carbon monoxide complexation in comparing the coordination properties of metalloporphyrins with hemoproteins.[3] More recently, some effort has been focused on these ligands, especially by the use of ^{13}C NMR spectroscopy.[3] The choice of the isocyanide alkyl chain can be varied to study steric hindrance between the bound ligand molecule and the protein residue at the sixth coordination position of the heme iron atom.[2,4] Unfortunately, complexed alkyl isocyanides are poor probes to test electronic modification around the iron atom in porphyrin chemistry.[6] This behavior is mainly due to the lower π-accepting ability of the alkyl isocyanides compared to that of carbon monoxide.[7]

We recently demonstrated that the bonding properties of the isocyanide ligand can be greatly modified by conjugating the multiple C–N bond with a carbonyl group in position α to the nitrogen.[8] Such *N*-acyl isocyanide derivatives RC(=O)NC[9] are interesting for two main reasons:

First, they exhibit good π-accepting character and, consequently, display features in common with carbon monoxide,[10] a ligand frequently used as a probe for the study of the environment of the heme in hemoproteins.

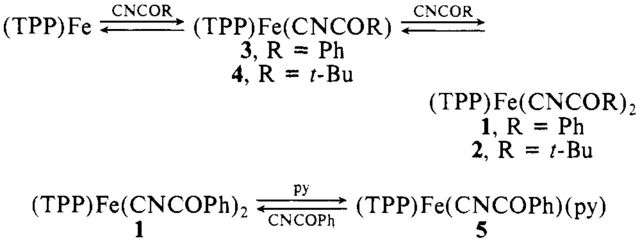
Second, the choice of the R group provides an opportunity to study steric interactions between the ligand and the protein environment.

We now want to describe the preparation of iron porphyrin *N*-acyl isocyanide complexes and their study by various spectroscopic methods. This work, which shows a striking analogy between the bonding properties of *N*-acyl isocyanides and carbon monoxide as ligands of ferrous porphyrins, has been reported in a preliminary communication.[11]

Results

Preparation of (*N*-Acyl isocyano)iron(II) Porphyrin Complexes. Reduction under argon of the chloro(*meso*-tetraphenylporphyrinato)iron(III) complex by zinc amalgam to (*meso*-tetraphenylporphyrinato)iron(II) [(TPP)Fe^{II}][12] followed by addition of an excess of benzoyl isocyanide (3–4 equiv)[9] in CH_2Cl_2 and subsequent addition of methanol affords a high yield of the hexacoordinate complex (TPP)Fe$(CNCOPh)_2$ (**1**) (85%). For the preparation of the other hexacoordinate complex, (TPP)Fe^{II}(CNCO-*t*-Bu)$_2$ (**2**), with tert-butyl isocyanide,[9] the same procedure can be used. However, if only 1 equiv of *N*-acyl isocyanide is added to (TPP)Fe^{II}, the formation in solution of the pentacoordinate species (TPP)Fe(CNCOPh) (**3**) and (TPP)Fe(CNCO-*t*-Bu) (**4**) can be followed by IR spectroscopy (see Table I). Both complexes **3** and **4** can be precipitated by addition of MeOH but are contaminated by a small amount of the hexacoordinate derivatives **1** and **2**, respectively (Scheme I). Attempts to grow crystals suitable for X-ray crystallography of pentacoordinate complexes were unsuccessful.

Scheme I



$$\mathrm{(TPP)Fe} \xrightleftharpoons{\mathrm{CNCOR}} \underset{\substack{\mathbf{3},\ R = Ph\\ \mathbf{4},\ R = t\text{-}Bu}}{\mathrm{(TPP)Fe(CNCOR)}} \xrightleftharpoons{\mathrm{CNCOR}} \underset{\substack{\mathbf{1},\ R = Ph\\ \mathbf{2},\ R = t\text{-}Bu}}{\mathrm{(TPP)Fe(CNCOR)_2}}$$

$$\underset{\mathbf{1}}{\mathrm{(TPP)Fe(CNCOPh)_2}} \xrightleftharpoons[\mathrm{CNCOPh}]{\mathrm{py}} \underset{\mathbf{5}}{\mathrm{(TPP)Fe(CNCOPh)(py)}}$$

Mixed coordinate complexes have been prepared by addition of 1 equiv of a base (pyridine, *N*-methylimidazole, 4-cyanopyridine, and tetrahydrothiophene) at room temperature under argon. Such preparation allows the respective formation of (TPP)Fe(CNCOPh)(py) (**5**), (TPP)Fe(CNCOPh)(*N*-MeIm) (**6**), (TPP)Fe(CNCOPh)(4-CNpy) (**7**), and (TPP)Fe(CNCOPh)(THT) (**8**), which have been characterized by IR (Table I) and ^1H NMR spectroscopy (Table II).

The above described methods are general and have been used for the preparation of (DPDME)Fe$(CNCOR)_2$ complexes and (DPDME)Fe(CNCOR)L complexes, with R = Ph or *t*-Bu and L = pyridine (respectively complexes **11**–**14**; Table II). In the case where the porphyrin is DPDME, however, the reduction of Fe(III) to Fe(II) has to be carried out with sodium dithionite in an CH_2Cl_2/H_2O system.[13] These complexes have been identified

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(1) Abbreviations: TPP, *meso*-tetraphenylporphyrinate; TTP, *meso*-tetratolylporphyrinate; DPDME, deuteroporphyrinate dimethyl ester.

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Table I. UV-Visible and IR Spectroscopy Results for (TPP)Fe(CNCOR), $(TPP)Fe(CNCOR)_2$, and (TPP)Fe(CNCOR)(L) Complexes

complex	no.	UV-vis[a] λ, nm (ε, mM^{-1} cm^{-1})	IR[b] ν_{CN}, cm^{-1}	ν_{CO}, cm^{-1}
$(TPP)Fe(CNCOR)_2$				
R = Ph	**1**	428 (430); 553 (11); 593 (6)	2040	1710
R = *t*-Bu	**2**	430 (405); 552 (11); 593 (7)	2045	1745
(TPP)Fe(CNCOR)				
R = Ph	**3**	410; 518[c]	1970	1675
R = *t*-Bu	**4**[d]		1970	1720
(TPP)Fe(CNCOPh)L				
L = py	**5**	424 (430); 534 (10)	1980	1690
L = *N*-MeIm	**6**	428 (400); 539 (10)	1975	1690
L = 4-CNpy	**7**	424 (410); 532 (11)	2020	1700
L = THT	**8**	428 (360); 542 (30)	1990	1685
$(TTP)Fe(CNCOPh)_2$	**9**	431 (320); 553 (14); 597 (7)	2040	1700
(TTP)Fe(CNCOPh)py	**10**	427 (499); 529 (22)	1975	1685
$(TPP)Fe(CO)_2$[e]				2042
(TPP)Fe(CO)[e]				1973
$(TPP)Fe(CN\text{-}t\text{-}Bu)_2$[f]			2129	

[a] Deaerated toluene solution (25 °C). [b] Nujol; ±5 cm^{-1}. [c] **3** was obtained as a mixture with **1**; ε was not determined. [d] λ not determined. [e] Reference 3d. [f] Reference 14.

Table II. ^1H NMR Data for (P)Fe(CNCOR)L Complexes[a]

	porphyrin							
		Ph			CNCOPh			
complex	pyr	ortho	ortho′	meta and para	ortho	meta	para	CNCO-*t*-Bu
1	8.79	8.03		7.74	7.25	6.97	7.07	
2	8.78	8.15		7.80				−0.45
3	8.80	8.19	7.98	7.75	6.91	7.18	7.27	
4	8.84	8.15		7.80				−0.68
5[b]	8.70	8.06	7.97	7.68	6.92	7.25	7.35	
6[c]	8.67	8.05	7.98	7.67	6.92	7.16	7.25	
11	9.04	*d*	*d*	*d*	7.36	6.96		
13	9.00	*e*	*d*	*e*	6.85	7.24	7.35	

[a] 0.05 M in deaerated CD_2Cl_2, 0 °C, in ppm, Me_4Si reference. [b] py: 2.12, 5.42, 6.24 ppm. [c] *N*-MeIm: 0.85, 1.58, 2.12, 4.92 ppm. [d] H_{meso}: 9.77, 9.79, 9.82, 9.91 ppm. CH_2: 3.26, 4.31 ppm. CH_3: 3.57, 3.60, 3.63, 3.66 ppm. [e] H_{meso}: 9.72, 9.75, 9.79, 9.85 ppm. CH_2: 3.22, 4.28 ppm. CH_3: 3.51, 3.57, 3.62, 3.64 ppm. Data for py were not determined.

Table III. UV-Visible and IR Spectroscopy Results for $Fe(DPDME)(CNCOR)_2$ and Fe(DPDME)(CNCOR)L Complexes

complex	no.	UV-vis[a] λ, nm (ε, mM^{-1} cm^{-1})	IR (CNCOR)[b] ν_{CN}, cm^{-1}	ν_{CO}, cm^{-1}
$Fe(DPDME)(CNCOC_6H_5)_2$	**11**	415 (211); 534 (21)	2015	1695
$Fe(DPDME)(CNCO\text{-}t\text{-}Bu)_2$	**12**	414 (200); 535 (24)	2020	1725
$Fe(DPDME)(CNCOC_6H_5)(py)$	**13**	411 (271); 523 (44)	1955	1675
Fe(DPDME)(CNCO-*t*-Bu)(py)	**14**	410 (310); 525 (41)	1960	1700

[a] Deaerated toluene solution (25 °C). [b] Nujol; ±5 cm^{-1}.

by mass spectrometry and IR and ^1H and ^{13}C NMR spectroscopy (Tables I-III).

IR Spectroscopy. The IR spectra of the new complexes (Tables I and III) are similar to those of (TPP)Fe and (TPP)FeCl,[15] but they all exhibit two major additional bands, an intense band between 1950 and 2100 cm^{-1} and a weaker band between 1650 and 1750 cm^{-1}. The former is located in the $\nu_{C\equiv N}$ region, and the preparation of ^{13}C-labeled $^{13}CNCOPh$ can be used for a definitive assignment of this band. For example, in the IR spectrum of $(TPP)Fe(^{12}CNCOPh)_2$ the band assigned to $\nu_{C\equiv N}$ vibration is at 2040 cm^{-1}. Accordingly, this band exhibits a 40-cm^{-1} shift to lower frequencies for $(TPP)Fe(^{13}CNCOPh)_2$. The second band, at 1710 cm^{-1} in complex **1**, can be assigned to the $\nu_{C=O}$ stretching vibration of the *N*-acyl isocyanide.

The $\nu_{C\equiv N}$ stretching frequency of RCONC is lowered upon coordination of the isocyanide of iron(II) porphyrins, decreasing from 2100 cm^{-1} for the free ligand[9] to about 2040 cm^{-1} in $(P)Fe^{II}(CNCOR)_2$ and to about 1970 cm^{-1} in $(P)Fe^{II}(CNCOR)$ and $(P)Fe^{II}(CNCOPh)(L)$ [1980 cm^{-1} for **5** (L = py) and 1990 cm^{-1} for *8* (L = THT)], and by the basicity of the porphyrin (2040 cm^{-1} for **1** (TPP) to 2015 cm^{-1} for **11** (DPDME).

Mass Spectrometry. We never observed the molecular peaks corresponding to (P)Fe(CNCOR)L, either with L = CNCOR or L = base, but the successive appearance of the peaks corresponding to axial ligands and then the peak corresponding to (P)Fe when the temperature was increased from 30 to 200 °C (both with TPP and with DPDME) was observed.

^1H NMR Spectroscopy. The ^1H NMR spectrum of $(TPP)Fe(CNCOPh)_2$ (**1**) displays two groups of signals corresponding respectively to the porphyrin ring protons [8.79 (pyr), 8.03 (O–Ph), and 7.74 ppm (Ph meta and para hydrogens)] and to the ligand [7.25 (Ph ortho hydrogen), 6.97 and 7.07 ppm (Ph meta and para hydrogens)]. The chemical shift of the former are very similar to those of $(TPP)Fe(py)_2$[3d] and are expected for diamagnetic iron(II) porphyrin derivatives. The ^1H NMR spectrum of (TPP)Fe(CNCOPh)(py) (**5**) displays also signals corresponding to the porphyrin ring protons expected for a diamagnetic species (see Table II). These signals are not modified upon addition of 1–2 equiv of pyridine, indicating that the equilibrium is completely shifted to the hexacoordinate complex:

$$(TPP)Fe(CNCOPh) + py \rightleftharpoons (TPP)Fe(CNCOPh)(py)$$

This is due to the high concentration of complex **5** used for the

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Table IV. ^{13}C NMR Data for (TPP)Fe(CNCOPh)L Complexes[a,b]

	$\delta(^{13}C)$								
	(porphyrin)			phenyl ring			CNCOPh[c]		
complex	C_α	C_β	C_{meso}	C_q	C_o	$C_{m,p}$	CN	C_q, C_o	$C_{m,p}$
1	145.7	134.4	120.5	142.8	133.9	129.4, 128.6	171.9	132.9, 131.3	126.9, 125.8
3	146.4	134.4		142.5	134.1	129.3, 128.5	190.7	134.0, 133.5	127.0, 125.6
5[d]	145.6	134.5	119.9	142.6	134.7	128.7, 127.6	186.2	134.4, 133.8	127.0, 126.9
6[e]	145.8	134.3	120.0	143.1	134.5	128.6, 127.5	188.3	133.8, 133.3	127.3, 126.8

[a] 0.01 M in deaerated CD_2Cl_2, at 20 °C, Me_4Si reference. [b] ^{13}C NMR signals for the (DPDME)Fe complexes are given in Experimental Section. [c] δ(CO) of the ligand was not determined. [d] $\delta(^{13}C)$ for py: 146.1, 136.7, 121.7. [e] $\delta(^{13}C)$ for NMeIm: 129.3, 126.6, 118, 32.3.

NMR experiment. The positions of the two groups of signals corresponding to phenyl ortho (6.92 ppm) and meta and para (7.30 ppm) hydrogens of CNCOPh are found to be inversed. Now, the ortho protons are more shielded than the meta and para protons. This may be due to the ring current shifts, which depend on the distance of the proton to the porphyrin plane. The signals corresponding to bound pyridine are similar to those of $(TPP)Fe(py)_2$. The NMR characteristics of the other *N*-acyl isocyanide complexes are very similar, as indicated in Table II.

^{13}C NMR Spectroscopy. The ^{13}C NMR spectrum of complex **5** displays seven signals corresponding to the porphyrin ring carbons whose chemical shifts are similar to those of $TPPH_2$. Their assignments were done according to previous work,[16,17] and the chemical shifts are also indicative of the diamagnetism of complex [5] (Table IV). The other signals corresponding to bound ligands (CNCOPh and pyridine) are also reported in Table IV together with the signals of complexes **1**, **3**, and **6**.

The sensitivity of the *N*-acyl isocyanide ligand to electronic variation around the iron atom is underlined by the following NMR results:

(1) Comparison of ^{13}CNCOPh chemical shifts for complex [5] (186.2 ppm) with those for complex **13**, (DPDME)Fe(CNCOPh)(py) (190.7 ppm), reveals a marked cis effect. It was previously reported that variation of porphyrin did not cause any significant difference in the ^{13}C shift of alkyl isocyanide bonded to iron(II) porphyrin[6].

(2) When one of the isocyanide ligands in complex **1** is replaced by pyridine (complex **5**), the shift from 171.9 to 186.2 ppm indicates also a strong trans effect.

Discussion

The above mentioned results show the analogy between the two ligands CO and CNCOPh:

(1) CNCOR like CO allows pentacoordination.

(2) Decrease of the $\nu_{C\equiv N}$ stretching frequency from that of the free ligand (ν_{CNCOPh} = 2100 cm^{-1}) to 2040 cm^{-1} for **1** and 1970 cm^{-1} for **3** follows the same order and is of comparable magnitude to the decrease of the CO stretching frequency from that of the free ligand (ν_{CO} = 2143 cm^{-1}) to 2042 cm^{-1} for $(TPP)Fe(CO)_2$ and 1973 cm^{-1} for (TPP)Fe(CO)[3d] (Table I).

(3) The ^{13}C chemical shift of ^{13}CNCOPh is very sensitive to variations of the charge density on metal atom (cis and trans effect), even more sensitive than the chemical shift of ^{13}CO.[8]

The similarity of the π-acceptor ability of CO and CNCOPh are confirmed by the analogy of Mössbauer data of their complexes. Both isomer shift and quadrupole splitting are very close. The results summarized in Table V agree with those for iron(II) low-spin complexes. When compared to those for other isocyanide ligands such as alkyl isocyanides, the isomer shift increases, CNCO-*t*-Bu (complex **2**) < $\mathrm{CN}\overline{\mathrm{CH(CH_2)_4CH_2}}$, with decreasing π-acceptor ability (Table V).[18] As expected, a large quadrupole splitting is found for pentacoordinate species both with the *N*-acyl isocyanide adduct (TPP)Fe(CNCO-*t*-Bu) (ΔE_q = 1.48 mm/s) and with the carbonyl adduct (TPP)Fe(CO) (ΔE_q = 1.13 mm/s).[19]

Table V. Mössbauer Data for Isocyanide and Carbonyl Complexes of Iron(II) Porphyrins

complex	*T*, K	δ[a]	ΔE_q[b]	Γ[c]	ref
1	298	0.16	0.26	0.23	*d*
2	80	0.26	0.14[f]	0.33	*d*
4	80	0.50	1.48	0.27	*d*
5	298	0.19	0.58	0.25	*d*
6	80	0.41	0.62	0.34	*d*
7	80	0.26	0.31	0.30	*d*
8	80	0.28	0.80	0.27	*d*
$(TPP)Fe[CN(c\text{-}Hx)]_2$	80	0.31	0.23	0.26	*d*
(TPP)Fe(CO)	298	0.17	1.13		*e*
$(TPP)Fe(CO)_2$	298	0.19	0.27	0.26	*e*

[a] Isomer shift in mm/s relative to that of metallic iron (298 K); ±0.01 mm/s. [b] Quadrupole splitting; ±0.02 mm/s. [c] Line width in mm/s at half-maximum. [d] This work. [e] Reference 19. [f] Unresolved doublet.

Finally, the stability of the Fe–CNCOPh bond was evaluated with both TPP and DPDME complexes by following the change in visible spectrum in an aerated solution. In oxygenated solvents like $CHCl_3$ or toluene, the $(P)Fe(CNCOPh)_2$ complexes are irreversibly oxidized to the μ-oxo dimer $[(P)Fe^{III}]_2O$. The half-lives of the $(P)Fe(CNCOPh)_2$ complexes in aerated toluene (10^{-4} M) depend on the nature of the porphyrin. They decrease from 4 h to < 1 min for P = DPDME to P = TPP. According to carbon monoxide complexation,[20] a more basic porphyrin (DPDME) increases the stability of the metal–isocyanide bond. All these results point to a great similarity among the coordinating properties of the CO and CNCOR ligands in $(TPP)Fe^{II}$ derivatives. It is noteworthy that an analogous similarity of the binding properties of *N*-acyl isocyanide and carbon monoxide has been reported in the case of chiral chromium complexes.[8]

Experimental Section

All preparations were performed in Schlenk tubes under dried, oxygen-free nitrogen or argon. Solvents were distilled from appropriate drying agents and stored under nitrogen. IR were recorded on a Unicam SP 1100 infrared spectrophotometer. ^{1}H NMR spectra were obtained at 80 MHz and proton-decoupled ^{13}C NMR spectra were obtained at 20 MHz in the pulse–Fourier transform mode with a Brucker WT 80DS spectrometer. Ultraviolet–visible spectra were recorded with a Jobin Yvon Hitachi spectrophotometer. Mössbauer spectra were recorded with a ^{57}Co(Rh) source, (15 mCi).

Elemental analyses were performed by the Service Central d'Analyses (CNRS) at Vernaison.

Reagents. (TPP)FeCl, (TTP)FeCl, and (DPDME)FeCl were prepared according to literature procedures.[21,22] The preparation of CNCOPh and CNCO-*t*-Bu was previously reported.[9]

Synthesis of Complexes 1 and 2. $(TPP)Fe(CNCO\text{-}t\text{-}Bu)_2$ (2). A solution of 0.1 g of (TPP)FeCl in 50 mL of toluene was reduced under argon by Zn–Hg amalgam. The solution was then evaporated under

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vacuum. A solution of an excess of CNCO-*t*-Bu (3-4 equiv) in 30 mL of CH_2Cl_2 was added at -40 °C to the $(TPP)Fe^{II}$ complex previously prepared. After a reaction time of 10 min, complex **2** was precipitated by addition of 60 mL of deaerated CH_3OH (yield 0.098, 78%). Mass spectrum, *m/e*: 668 [(TPP)Fe], 111 (CNCO-*t*-Bu).

Complex 1 was prepared as described above. Yield: 85%. Anal. Calcd for $C_{60}H_{38}N_6O_2Fe$: C, 77.41; H, 4.09; N, 9.03. Found: C, 77.82; H, 4.35; N, 8.71.[11]

Synthesis of Complexes 3 and 4. Both complexes were prepared as described above, except only 1 equiv of the N-functionalized isocyanide was added. As shown by IR spectroscopy, products obtained in crystalline form contain the pentacoordinate species ($\simeq$90%) contaminated with the hexacoordinate species.

General Procedure for Preparation of Complexes 5-8. Addition of a base L (1 equiv in CH_2Cl_2 (5 mL) to $(TPP)Fe(CNCOPh)_2$ (0.2 g) in CH_2Cl_2 (20 mL) under argon gave rapidly (5-20 mn) the expected complexes (TPP)Fe(CNCOPh)(L), which have been crystallized by CH_3OH addition (80 mL). **5**: yield 92%. Anal. Calcd for $C_{57}H_{38}N_6OFe$: C, 77.97; H, 4.33; N, 9.57. Found: C, 77.31; H, 4.21; N, 9.10). **6**: yield 83%; mass spectrum, *m/e* 668 [(TPP)Fe], 131 ($CNCOC_6H_5$), 79 (py). **7**: yield 78%; mass spectrum, *m/e* 668 [(TPP)Fe], 131 ($CNCOC_6H_5$), 104 (4-CNpy). **8**: yield 59%; mass spectrum, *m/e* 668 [(TPP)Fe], 131 ($CNCOC_6H_5$), 88 (THT); reaction time 4 h.

Complexes 9 and 10 were prepared as described above by using *meso*-tetratolylporphyrin instead of *meso*-tetraphenylporphyrin. **9**: yield 87%. **10**: yield 83%. Anal. Calcd for $C_{61}H_{46}N_6OFe$: C, 78.36; H, 4.96; N, 8.99. Found: C, 77.52; H, 4.93; N, 9.20.

Synthesis of Complex 11. A solution of 0.1 g of $(DPDME)Fe^{III}Cl$ in 50 mL of CH_2Cl_2/H_2O (4/1) was reduced under argon by sodium dithionite (10 min).[13] The solution was then decanted, and an excess of CNCOPh (3 equiv) in 30 mL of CH_2Cl_2 was added at 0 °C to the $(DPDME)Fe^{II}$ prepared. After the mixture was stirred for 10 min, the solution was concentrated to 10 mL of CH_2Cl_2. Addition of 40 mL of pentane yielded crystals of the expected complex $(DPDME)Fe^{II}(CNCOPh)_2$: yield 0.08 g; mass spectrum, *m/e* 586 [(DPDME)Fe], 131 (CNCOPh).

Complex 12 was prepared by the same procedure: yield 78% of $(DPDME)Fe(CNCO\text{-}t\text{-}Bu)_2$; mass spectrum, *m/e* 586 (DPDME), 111 (CNCO-*t*-Bu).

Synthesis of Complex 13. Addition of 1 equiv of pyridine (10 mg) in 10 mL of CH_2Cl_2 to $(DPDME)Fe(CNCOPh)_2$ (0.1 g) in 20 mL of CH_2Cl_2 under argon gave immediately the expected product (DPDME)Fe(CNCOPh)(py).

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Combined He I/He II Photoelectron Spectroscopic and Hartree-Fock-Slater Investigation of Electronic Structure and Bonding in Uranium Hexamethoxide

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The electronic structure of the uranium(VI) alkoxide $U(OCH_3)_6$ has been investigated by using a combination of He I/He II photoelectron spectroscopy and discrete variational (DV) Xα molecular orbital calculations. Good agreement is obtained between the experimental and calculated ionization energies. It is found that the low ionization energy features of the photoelectron spectra are due to varying degrees of donation of the oxygen lone pairs to the empty orbitals on the uranium atom and to the reduction of the molecular symmetry to C_i via bending of the U-O-C linkages. The methyl groups act as both σ and π donors to the oxygen 2p orbitals, increasing the overall donor strength of the alkoxide ligands.

Introduction

The bonding characteristics of actinide alkoxides[2] are of current interest for a number of reasons. First, M-OR functionalities are frequently endproducts in a variety of reactions involving organoactinide alkyls and hydrides,[3] and the driving force to produce such products is frequently unclear. Second, and closely connected with the first reason, molecular structural studies[3,4] have

Table I. Photoelectron Spectroscopic Data, Band Assignments, and Calculated Transition-State Ionization Energies of $U(OCH_3)_6$

band label	exptl IE,[a] eV	rel intens[b] He I	rel intens[b] He II	assignt	calcd IE, eV
a	8.80	1.00	1.00	$22a_g$	7.64
				$24a_u$	(7.69)[c]
				$21a_g$	(7.80)
a′	9.30	1.05	0.95	$23a_u$	(8.20)
				$20a_g$	(8.37)
b	9.95	1.10	1.75	$19a_g$	(8.77)
				$22a_u$	8.77
				$21a_u$	(9.22)
				$20a_u$	(9.33)
c	10.74	0.75	0.70	$18a_g$	9.70
				$17a_g$	(9.32)
d	12.79	0.50	0.45	$19a_u$	10.52
e	14.83	3.10	2.80	U-O and C-H σ bonds	

[a] Peak energies refer to centroids of Gaussian components. [b] Arbitrary units corrected for the analyzer transmission function. [c] Values in parentheses are estimated from ground-state values by using the energy shift of similar orbitals.

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