Articles

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Structural Characterization of the Product of Oxidation of a Macrocyclic Cobalt(II) Complex in Pyridine Solution

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The macrocyclic cobalt(II) complexes [CoL^1] and [CoL^2] (L^{1}H$_2$ = 5,14-dihydrodibenzo[*b*,*i*][1,4,8,11]tetraaza[14]annulene; L^{1}H$_2$ = 2,3,11,12-tetramethyl-5,14-dihydrodibenzo[*b*,*i*][1,4,8,11]tetraaza[14]annulene) react with dioxygen in pyridine solution to give the bis(pyridine) adducts of the corresponding Co(III) complexes. Good-quality crystals of [CoL^2(py)$_2$]BF$_4$·py were obtained from a pyridine–toluene solution. [CoL^2(py)$_2$]BF$_4$·py crystallizes in the monoclinic space group $P2_1/n$ with a = 16.402 (4) Å, b = 19.889 (4) Å, c = 11.214 (4) Å, β = 105.19 (3)°, V = 3530 Å^3, and Z = 4. Structure refinement based on 1745 unique data [$F_o > 3\sigma(F_o)$] gave R (R_w) = 10% (8%). The coordination environment of the cobalt atom is octahedral CoN$_6$ (four nitrogens of the macrocycle and two pyridine molecules); L^2 assumes a saddle shape with bending in two perpendicular directions; the pyridine ligands are parallel to the short and long axes of the macrocycle (the angle between them is 90.7°). L^{1}H$_2$ crystallizes in the monoclinic space group $P2_1/c$ with a = 9.096 (4) Å, b = 10.648 (4) Å, c = 14.915 (5) Å, β = 95.93 (3)°, V = 1437 Å^3, and Z = 4. The L^{1}H$_2$ structure shows only minor deviations from planarity.

Introduction

For several years we have been studying the interactions of macrocyclic Co(II) and Fe(II) complexes with nitrogenous bases and with proteins.[2–4] During the course of this work, we found that [CoL^1] and [CoL^2] (Figure 1) react reversibly with dioxygen in the presence of bases such as pyridine and imidazole.[5] In each case the EPR spectrum of the dioxygen adduct disappears rapidly when water or excess base is added, thereby indicating that some sort of irreversible oxidation of the complex has taken place. Since it is important for us to know for our biological studies whether L^1 or L^2 itself is oxidized in this reaction, as has been reported by Goedken for the analogous complex [CoL^3],[6] we have determined the structures of L^{1}H$_2$ and the product obtained from the reaction of [CoL^2] with O$_2$ in excess pyridine.

Experimental Section

The ligand L^{1}H$_2$ was prepared as described by Hiller,[7] and L^{2}H$_2$ was prepared by a similar procedure. The ligands were purified by vacuum sublimation at 250 °C. [CoL^2] was prepared by Lin's method.[8] The complex was purified by vacuum sublimation at 280 °C.

Good-quality crystals of L^{1}H$_2$ (structure I) were obtained by sublimation as dark red plates. A single crystal of dimensions 0.37 × 0.30 × 0.10 mm was mounted on a Philips PW 1100/20 four-circle diffractometer, and accurate cell parameters were derived from 25 carefully centered reflections. Crystal data, measurement conditions, and refinement details are given in Table I. Intensities of 2551 reflections were measured, and these were reduced to structure factors after applying background, Lorentz, and polarization corrections.

The structure was solved by SHELX77.[9] All non-hydrogen atoms were located and refined anisotropically. The hydrogen atoms were located from difference Fourier maps and refined isotropically in one block. Statistical weights were introduced into the final refinement stage. Careful examination of the last difference map clearly suggests that the two hydrogens that are bonded to the nitrogen atoms are distributed equally among all four nitrogen sites.

Table I. Crystal Data, Measurement Conditions, and Refinement Details

	I	II
formula unit	$C_{18}H_{16}N_4$	$[C_{32}H_{32}N_6Co]BF_4\cdot C_5H_5N$
fw	288.3	725.5
$F(000)$	608	1504
a, Å	9.096 (4)	16.402 (4)
b, Å	10.648 (4)	19.889 (4)
c, Å	14.915 (5)	11.214 (4)
β, deg	95.93 (3)	105.19 (4)
D_{measd}, g cm^{-3}		1.368
D_{calcd}, g cm^{-3}	1.333	1.365
Z	4	4
space group	$P2_1/c$	$P2_1/n$
V, Å^3	1437	3530
radiation	Cu Kα	Mo Kα
μ, cm^{-1}	4.66	5.69
scan mode	$\omega/2\theta$	$\omega/2\theta$
scan speed, deg ω min^{-1}	3	1.5
scan width, deg ω	1.20	1.1
angular range in 2θ, deg	5–126	5–45
bkgd time at each side of the peak, s	10	10
no. of unique reflcns	2315	4204
cutoff criterion	$F_o > 1.5\sigma(F_o)$	$F_o > 3\sigma(F_o)$
no. of reflcns at the final refinement stage	1694	1745
R^a	0.07	0.10
$R_w{}^b$	0.088	0.08
weighting scheme w	$1.300/(\sigma^2(F_o) + 0.007F_o{}^2)$	$1.458/\sigma^2(F_o)$

[a] $R = \sum||F_o| - K|F_c||/\sum|F_o|$. [b] $R_w = \sum w^{1/2}||F_o| - K|F_c||/\sum w^{1/2}|F_o|$.

Crystals of [CoL^2(py)$_2$]BF$_4$·py (structure II) were grown by dissolving [CoL^2] in a 1:1 mixture of pyridine and toluene that was allowed to evaporate slowly in air. In the presence of NaBF$_4$, good-quality, dark blue prisms were obtained. A single crystal of dimensions 0.17 × 0.17 × 0.22 mm was placed in a thin-walled capillary and mounted on the four-circle diffractometer. Crystal data, measurement conditions, and refinement details are summarized in Table I. Intensities of 4204 reflections were collected, and these were reduced to structure factors after applying background, Lorentz, and polarization corrections. An absorption correction was not made.

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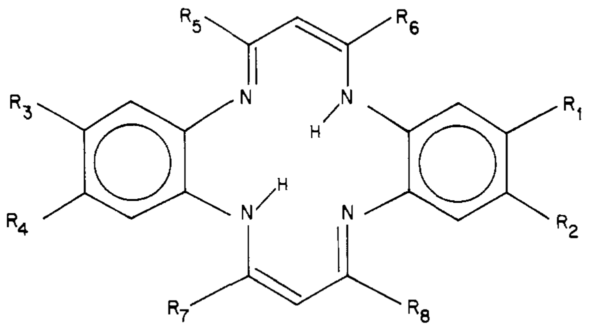

Figure 1. Drawing of the macrocycle: L^1H_2 = 5,14-dihydrodibenzo[*b*,*i*][1,4,8,11]tetraaza[14]annulene ($R_1 = R_2 = R_3 = R_4 = R_5 = R_6 = R_7 = R_8$ = H); L^2H_2 = 2,3,11,12-tetramethyl-5,14-dihydrodibenzo[*b*,*i*][1,4,8,11]tetraaza[14]annulene ($R_1 = R_2 = R_3 = R_4 = CH_3$; $R_5 = R_6 = R_7 = R_8$ = H); L^3H_2 = 6,8,15,17-tetramethyl-5,14-dihydrodibenzo[*b*,*i*][1,4,8,11]tetraaza[14]annulene ($R_1 = R_2 = R_3 = R_4$ = H; $R_5 = R_6 = R_7 = R_8 = CH_3$).

Calculations were performed with the SHELX77 package.[9] Scattering factor tables for C, N, B, and F were taken from Cromer and Mann,[10] for H from Stewart, Davidson, and Simpson,[11a] and for Co from ref 11b. The cobalt atom was located by direct methods, and the light atoms were located by successive difference Fourier maps. Isotropic refinement of these atoms gave $R = 0.24$. At this stage, the maps revealed one BF_4^- ion and a pyridine molecule of solvation. These were introduced and refined isotropically ($R = 0.157$). However, their high temperature factors and apparent geometric distortions suggested that they were disordered and should be treated in an unconventional way. After the atoms of the complex were refined anisotropically ($R = 0.14$), it was realized that the tetrahedron of fluorines around the B atom has two different orientations. Hence, an idealized geometry for each tetrahedron was calculated, and both were refined as rigid bodies while the position of the B atom was kept fixed. The temperature factors of each fluorine having an occupancy of 0.5 were allowed to refine isotropically. The pyridine molecule of solvation was initially refined as a benzene ring with separate isotropic temperature factors. However, one of the carbon atoms refined with remarkably lower temperature factors relative to the other five. This atom was replaced by nitrogen, which then refined and yielded more reasonable values. The calculated positions of 32 hydrogens of the complex cation were introduced, and the structure was further refined with an $F_o > 3\sigma(F_o)$ cutoff. Finally, all atoms of the complex cation were refined anisotropically in one block with statistical weights. The remaining atoms were refined isotropically in a separate block (BF_4^- and pyridine were allowed to shift as rigid bodies, and the hydrogens were refined in the normal way). Structure refinement converged to $R = 0.10$. Residual electron densities of ~0.7 e Å^{-3} in the difference maps around the B atom were not considered important for further treatment.

Final positional and equivalent thermal parameters for structures I and II are presented in Tables II and III. Observed and calculated structure factors for both structures together with anisotropic thermal parameters (Tables S1 and S2) are given in the supplementary material.

Results and Discussion

A stereo drawing of L^1H_2 is displayed in Figure 2. Interatomic distances and angles are listed in Table IV. The ligand is essentially planar (the largest displacement from the mean molecular plane being 0.06 Å).[12] The small deviations from planarity indicate a slight twisting of the ligand around an axis directed along the N1–N3 vector of two molecular positions obtained by bisecting the ligand along the N2–N4 vector. It is reasonable to assume that this distortion arises from the van der Waals repulsion of hydrogen atoms HN2 and HN4, where d(NH2–NH4) = 2.15 Å. As a result, the molecule adopts point group C_2 rather than C_{2h} with the 2-fold axis perpendicular to the molecular plane.

A stereo drawing of the distorted octahedral $[CoL^2(py)_2]^+$ complex is shown in Figure 3. Interatomic distances and angles are listed in Table V. The cobalt atom and the four macrocycle-nitrogen atoms are nearly coplanar with two short in-plane Co–N distances (1.86 Å; N2 and N4) and two longer distances (1.92 Å; N1 and N3). The bond distances to the pyridine nitrogen atoms are longer still, being 1.97 and 2.01 Å to N5 and N6, respectively.

Table II. Final Fractional Atomic Coordinates and Equivalent Temperature Factors for Structure I[a]

atom	*x*	*y*	*z*	U_{eq}, Å^2
N(1)	7370 (2)	3531 (2)	8565 (2)	544 (6)
N(2)	5298 (3)	5142 (2)	7884 (2)	557 (5)
N(3)	3532 (3)	4293 (2)	9186 (2)	551 (6)
N(4)	5583 (3)	2639 (2)	9836 (2)	576 (7)
C(1)	7717 (3)	4280 (3)	7835 (2)	513 (7)
C(2)	9062 (4)	4254 (3)	7449 (2)	644 (9)
C(3)	9301 (4)	5021 (3)	6737 (3)	723 (10)
C(4)	8211 (4)	5833 (3)	6387 (2)	703 (9)
C(5)	6884 (4)	5885 (3)	6756 (2)	642 (9)
C(6)	6623 (3)	5123 (3)	7477 (2)	519 (7)
C(7)	4172 (4)	5926 (3)	7684 (2)	625 (8)
C(8)	2928 (4)	5936 (3)	8121 (2)	666 (9)
C(9)	2641 (4)	5160 (3)	8842 (2)	628 (8)
C(10)	3191 (3)	3543 (3)	9914 (2)	536 (7)
C(11)	1874 (4)	3588 (3)	10319 (2)	657 (9)
C(12)	1630 (4)	2808 (4)	11015 (2)	750 (10)
C(13)	2679 (4)	1949 (4)	11330 (3)	762 (10)
C(14)	3994 (4)	1886 (3)	10946 (2)	703 (9)
C(15)	4255 (3)	2672 (3)	10247 (2)	548 (7)
C(16)	6761 (4)	1914 (3)	10073 (2)	680 (9)
C(17)	8046 (4)	1952 (3)	9670 (2)	731 (9)
C(18)	8315 (4)	2741 (3)	8955 (2)	632 (8)
atom	*x*	*y*	*z*	U_{iso}, Å^2
HN(2)	520 (4)	456 (3)	836 (2)	8 (1)
HN(4)	573 (3)	317 (3)	939 (2)	9 (1)
H(2)	981 (3)	368 (3)	773 (2)	7 (1)
H(3)	1024 (4)	495 (3)	648 (2)	8 (1)
H(4)	841 (4)	642 (3)	588 (2)	10 (1)
H(5)	610 (3)	646 (3)	650 (2)	8 (1)
H(7)	430 (3)	652 (3)	720 (2)	8 (1)
H(8)	218 (4)	651 (3)	792 (2)	9 (1)
H(9)	162 (4)	529 (3)	908 (2)	9 (1)
H(11)	118 (3)	416 (3)	1006 (2)	6 (1)
H(12)	72 (3)	288 (3)	1129 (2)	7 (1)
H(13)	247 (4)	142 (4)	1182 (3)	10 (1)
H(14)	475 (3)	127 (3)	1117 (2)	8 (1)
H(16)	665 (3)	127 (3)	1054 (2)	8 (1)
H(17)	890 (4)	139 (3)	994 (2)	9 (1)
H(18)	933 (4)	269 (3)	874 (2)	8 (1)

[a] Coordinates and U_{eq} for non-hydrogen atoms are $\times 10^4$. Hydrogen coordinates and U_{iso} are $\times 10^3$ and $\times 10^2$, respectively. Esd's are in parentheses.

The pyridine ligands are parallel to the short and long axes of the macrocyclic ligand with an angle of 90.7° between them. This arrangement optimizes the bonding interactions of the two π-acceptor ligands with the occupied dπ orbitals that are axially oriented (d_{xz}, d_{yz}). A similar axial-ligand conformation has been observed[13] in the structure of bis(pyridine)(hemiporphyrazinato)nickel(II).

The tetraaza[14]annulene ligand undergoes severe distortions from planarity in $[CoL^2(py)_2]^+$. The displacements of the carbon atoms from the plane defined by the four macrocycle-nitrogen atoms make the ligand saddle-shaped with bending in two perpendicular directions (Figure 4). The bending along the long axis is directed downward from the upper pyridine ring, and upward along the short axis away from the lower pyridine ring. This distortion can be attributed to nonbonded repulsions involving the pyridine hydrogens (attached to C23, C27, C28, and C32) and the macrocycle-carbon atoms.

The $[CoL^2(py)_2]^+$ complex is readily obtained from the aerial oxidation of $[CoL^2]$ in excess pyridine. The structural data confirm that $[CoL^2]$ is oxidized at the metal center; that is, the

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Table III. Final Fractional Atomic Coordinates and Equivalent Temperature Factors for Structure II[a]

atom	x	y	z	U_{eq}, Å^2	atom	x	y	z	U_{eq}, Å^2
Co	5974 (1)	3651 (1)	2632 (3)	41 (1)	C(14)	6293 (12)	5636 (11)	1742 (21)	51 (7)
N(1)	5939 (10)	2997 (8)	1364 (18)	48 (6)	C(15)	6160 (11)	5020 (10)	2244 (23)	39 (7)
N(2)	5949 (10)	2905 (8)	3616 (17)	44 (5)	C(16)	5860 (13)	4344 (10)	409 (25)	56 (8)
N(3)	5991 (10)	4316 (9)	3874 (16)	42 (6)	C(17)	5796 (11)	3766 (11)	−293 (16)	52 (6)
N(4)	6015 (10)	4391 (8)	1620 (18)	43 (5)	C(18)	5846 (13)	3122 (11)	169 (20)	54 (8)
N(5)	7215 (8)	3625 (8)	3144 (16)	43 (4)	C(19)	6415 (11)	517 (10)	1054 (18)	69 (6)
N(6)	4704 (7)	3663 (10)	2156 (12)	45 (4)	C(20)	6433 (11)	428 (10)	3768 (19)	75 (7)
C(1)	6063 (13)	2340 (11)	1861 (22)	46 (8)	C(21)	6593 (11)	6774 (10)	4604 (19)	69 (7)
C(2)	6187 (11)	1752 (11)	1273 (19)	48 (6)	C(22)	6515 (13)	6875 (8)	1897 (21)	71 (8)
C(3)	6250 (14)	1122 (11)	1860 (26)	56 (8)	C(23)	7627 (12)	3599 (11)	4342 (20)	59 (6)
C(4)	6305 (14)	1094 (11)	3054 (26)	57 (8)	C(24)	8479 (14)	3591 (11)	4734 (18)	61 (7)
C(5)	6180 (13)	1649 (11)	3725 (19)	53 (7)	C(25)	8961 (11)	3635 (11)	3926 (27)	68 (9)
C(6)	6057 (10)	2264 (9)	3083 (22)	37 (7)	C(26)	8552 (12)	3652 (11)	2685 (19)	53 (6)
C(7)	5753 (12)	2945 (10)	4679 (23)	55 (7)	C(27)	7691 (11)	3662 (10)	2330 (15)	45 (5)
C(8)	5655 (12)	3542 (11)	5336 (18)	63 (7)	C(28)	4236 (16)	3128 (11)	1948 (20)	61 (8)
C(9)	5803 (12)	4196 (10)	4892 (21)	47 (7)	C(29)	3355 (17)	3143 (10)	1687 (23)	71 (9)
C(10)	6185 (11)	4963 (12)	3494 (22)	46 (8)	C(30)	2978 (12)	3753 (15)	1666 (21)	83 (8)
C(11)	6278 (11)	5543 (11)	4196 (19)	45 (6)	C(31)	3450 (14)	4317 (11)	1848 (23)	70 (8)
C(12)	6431 (12)	6157 (10)	3731 (27)	55 (9)	C(32)	4307 (12)	4279 (10)	2105 (20)	57 (7)
C(13)	6445 (12)	6193 (12)	2461 (27)	64 (9)					

atom	x	y	z	U_{iso}, Å^2	atom	x	y	z	U_{iso}, Å^2
N(7)	2604 (8)	767 (9)	2305 (12)	132 (7)	H(18)	586 (6)	278 (5)	−24 (9)	1 (3)
C(33)	2717 (8)	1345 (9)	3034 (12)	133 (8)	H(191)	696 (5)	37 (4)	176 (9)	2 (3)
C(34)	3493 (8)	1467 (9)	3879 (12)	147 (9)	H(192)	620 (7)	58 (6)	30 (11)	5 (4)
C(35)	4156 (8)	1012 (9)	3995 (12)	153 (10)	H(193)	601 (5)	11 (4)	97 (8)	1 (3)
C(36)	4044 (8)	433 (9)	3268 (12)	140 (9)	H(201)	702 (8)	33 (6)	384 (12)	10 (5)
C(37)	3267 (8)	309 (9)	2422 (12)	144 (9)	H(202)	570 (8)	5 (7)	288 (14)	11 (6)
B	852 (5)	3249 (4)	2463 (8)	144 (12)	H(203)	624 (8)	34 (6)	398 (13)	6 (5)
F(1)′	545 (5)	3643 (4)	1442 (8)	190 (14)	H(211)	677 (10)	730 (8)	410 (17)	24 (7)
F(2)′	219 (5)	2848 (4)	2648 (8)	148 (15)	H(212)	704 (9)	675 (7)	505 (13)	12 (6)
F(3)′	1149 (5)	3651 (4)	3477 (8)	152 (10)	H(213)	612 (8)	688 (6)	483 (12)	8 (5)
F(4)′	1497 (5)	2857 (4)	2285 (8)	123 (9)	H(221)	691 (12)	704 (8)	241 (19)	22 (8)
F(1)″	954 (5)	3521 (4)	1390 (8)	87 (7)	H(222)	615 (10)	710 (8)	166 (16)	15 (7)
F(2)″	577 (5)	3736 (4)	3130 (8)	130 (9)	H(223)	710 (10)	691 (7)	127 (16)	16 (7)
F(3)″	269 (5)	2741 (4)	2189 (8)	132 (14)	H(23)	727 (6)	363 (6)	498 (10)	6 (4)
F(4)″	1610 (5)	2998 (4)	3145 (8)	230 (17)	H(24)	891 (6)	352 (5)	577 (10)	6 (4)
H(2)	605 (7)	186 (5)	64 (10)	5 (4)	H(25)	961 (5)	365 (5)	414 (8)	3 (3)
H(5)	645 (7)	169 (5)	473 (10)	4 (4)	H(26)	883 (5)	351 (5)	199 (8)	1 (3)
H(7)	569 (6)	257 (5)	513 (10)	3 (4)	H(27)	730 (4)	365 (4)	144 (7)	0 (2)
H(8)	561 (8)	355 (7)	605 (12)	11 (5)	H(28)	439 (6)	270 (5)	180 (10)	6 (4)
H(9)	564 (5)	454 (4)	538 (8)	0 (3)	H(29)	316 (6)	274 (5)	153 (10)	2 (4)
H(11)	648 (8)	541 (6)	516 (12)	10 (5)	H(30)	242 (9)	360 (8)	125 (14)	20 (6)
H(14)	625 (5)	567 (4)	53 (8)	0 (3)	H(31)	308 (7)	465 (6)	183 (11)	8 (4)
H(16)	608 (6)	477 (5)	12 (10)	5 (4)	H(32)	460 (6)	474 (5)	236 (9)	3 (4)
H(17)	571 (7)	382 (5)	−121 (11)	8 (4)					

[a] Coordinates and U_{eq} for the cation are ×10^4 and ×10^3, respectively. Coordinates and U_{iso} for the pyridine solvate and BF_4^- are ×10^4 and ×10^3, respectively. Hydrogen coordinate and U_{iso} are ×10^3 and ×10^2, respectively. Esd's are in parentheses.

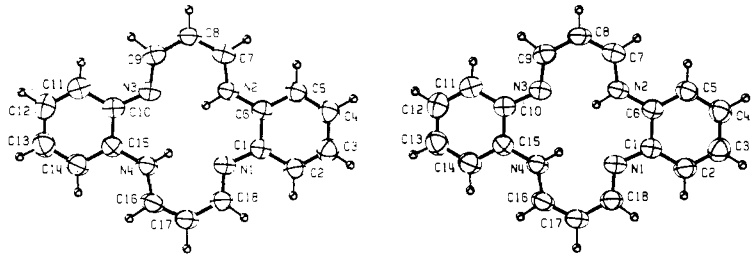

Figure 2. Stereoview of L^1H_2.

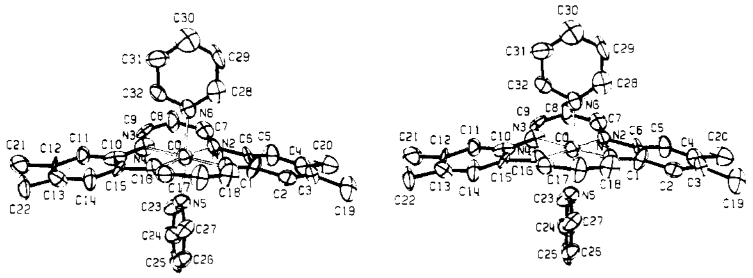

Figure 3. Stereoview of $[CoL^2(py)_2]^+$.

Table IV. Molecular Bond Lengths (Å) and Angles (deg) for Structure I[a]

N(1)–C(1)	1.411 (3)	C(13)–C(14)	1.381 (5)
N(1)–C(18)	1.296 (3)	C(14)–C(15)	1.376 (4)
N(2)–C(6)	1.405 (3)	C(16)–C(17)	1.369 (5)
N(2)–C(7)	1.331 (3)	C(17)–C(18)	1.400 (4)
N(3)–C(9)	1.299 (3)	N(2)–HN(2)	0.95 (3)
N(3)–C(10)	1.407 (3)	N(4)–HN(4)	0.90 (3)
N(4)–C(15)	1.410 (3)	C(2)–H(2)	0.98 (2)
N(4)–C(16)	1.338 (4)	C(3)–H(3)	0.98 (3)
C(1)–C(2)	1.405 (4)	C(4)–H(4)	1.01 (3)
C(1)–C(6)	1.403 (3)	C(5)–H(5)	0.99 (2)
C(2)–C(3)	1.375 (5)	C(7)–H(7)	0.98 (3)
C(3)–C(4)	1.377 (4)	C(8)–H(8)	0.94 (3)
C(4)–C(5)	1.379 (5)	C(9)–H(9)	1.04 (3)
C(5)–C(6)	1.387 (4)	C(11)–H(11)	0.93 (2)
C(7)–C(8)	1.363 (4)	C(12)–H(12)	0.96 (3)
C(8)–C(9)	1.402 (4)	C(13)–H(13)	0.96 (3)
C(10)–C(11)	1.398 (4)	C(14)–H(14)	0.99 (3)
C(10)–C(15)	1.395 (3)	C(16)–H(16)	0.99 (3)
C(11)–C(12)	1.365 (5)	C(17)–H(17)	1.03 (3)
C(12)–C(13)	1.369 (5)	C(18)–H(18)	1.01 (3)

C(1)–N(1)–C(18)	121.5 (2)	C(7)–C(8)–C(9)	126.3 (3)
C(6)–N(2)–C(7)	126.0 (2)	N(3)–C(9)–C(8)	124.3 (2)
C(9)–N(3)–C(10)	122.0 (2)	N(3)–C(10)–C(11)	125.5 (2)
C(15)–N(4)–C(16)	126.7 (2)	N(3)–C(10)–C(15)	116.9 (2)
N(1)–C(1)–C(2)	125.3 (2)	C(11)–C(10)–C(15)	117.6 (2)
N(1)–C(1)–C(6)	116.7 (2)	C(10)–C(11)–C(12)	121.5 (3)
C(2)–C(1)–C(6)	118.0 (2)	C(11)–C(12)–C(13)	120.3 (3)
C(1)–C(2)–C(3)	121.2 (3)	C(12)–C(13)–C(14)	119.5 (3)
C(2)–C(3)–C(4)	120.1 (3)	C(13)–C(14)–C(15)	120.7 (3)
C(3)–C(4)–C(5)	119.9 (3)	N(4)–C(15)–C(10)	117.1 (2)
C(4)–C(5)–C(6)	120.9 (3)	N(4)–C(15)–C(14)	122.5 (2)
N(2)–C(6)–C(1)	116.8 (2)	C(10)–C(15)–C(14)	120.4 (2)
N(2)–C(6)–C(5)	123.3 (2)	N(4)–C(16)–C(17)	124.3 (3)
C(1)–C(6)–C(5)	119.8 (2)	C(16)–C(17)–C(18)	125.2 (3)
N(2)–C(7)–C(8)	123.7 (2)	N(1)–C(18)–C(17)	124.9 (3)

[a] Esd's are in parentheses.

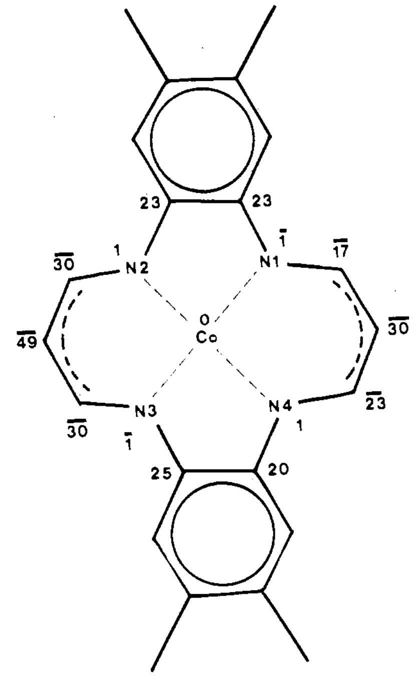

Figure 4. Displacements from the mean molecular plane of L^2 in $[CoL^2(py)_2]^+$.

Table V. Molecular Bond Lengths (Å) and Angles (deg) for Structure II[a]

Co–N(1)	1.92 (1)	C(4)–C(5)	1.38 (3)
Co–N(2)	1.85 (1)	C(4)–C(20)	1.53 (3)
Co–N(3)	1.92 (1)	C(5)–C(6)	1.41 (2)
Co–N(4)	1.87 (1)	C(7)–C(8)	1.43 (3)
Co–N(5)	1.97 (1)	C(8)–C(9)	1.44 (3)
Co–N(6)	2.01 (1)	C(10)–C(11)	1.38 (3)
N(1)–C(1)	1.41 (2)	C(10)–C(15)	1.40 (3)
N(1)–C(18)	1.33 (3)	C(11)–C(12)	1.38 (3)
N(2)–C(6)	1.44 (2)	C(12)–C(13)	1.43 (4)
N(2)–C(7)	1.32 (3)	C(12)–C(21)	1.55 (3)
N(3)–C(9)	1.28 (3)	C(13)–C(14)	1.35 (3)
N(3)–C(10)	1.42 (3)	C(13)–C(22)	1.51 (3)
N(4)–C(15)	1.42 (2)	C(14)–C(15)	1.39 (3)
N(4)–C(16)	1.32 (3)	C(16)–C(17)	1.38 (3)
N(5)–C(23)	1.34 (2)	C(17)–C(18)	1.38 (2)
N(5)–C(27)	1.35 (2)	C(23)–C(24)	1.35 (2)
N(6)–C(28)	1.30 (2)	C(24)–C(25)	1.35 (3)
N(6)–C(32)	1.38 (2)	C(25)–C(26)	1.38 (3)
C(1)–C(2)	1.38 (3)	C(26)–C(27)	1.36 (2)
C(1)–C(6)	1.38 (3)	C(28)–C(29)	1.40 (3)
C(2)–C(3)	1.41 (3)	C(29)–C(30)	1.36 (3)
C(3)–C(4)	1.32 (4)	C(30)–C(31)	1.35 (3)
C(3)–C(19)	1.57 (3)	C(31)–C(32)	1.36 (2)

N(1)–Co–N(2)	84.1 (7)	N(2)–C(6)–C(5)	125 (2)
N(1)–Co–N(3)	178.7 (8)	C(1)–C(6)–C(5)	124 (1)
N(1)–Co–N(4)	94.8 (7)	N(2)–C(7)–C(8)	127 (1)
N(1)–Co–N(5)	91.6 (7)	C(7)–C(8)–C(9)	121 (1)
N(1)–Co–N(6)	89.0 (7)	N(3)–C(9)–C(8)	126 (1)
N(2)–Co–N(3)	96.8 (7)	N(3)–C(10)–C(11)	126 (2)
N(2)–Co–N(4)	178.6 (7)	N(3)–C(10)–C(15)	115 (2)
N(2)–Co–N(5)	89.3 (7)	C(11)–C(10)–C(15)	118 (2)
N(2)–Co–N(6)	89.1 (7)	C(10)–C(11)–C(12)	122 (2)
N(3)–Co–N(4)	84.3 (7)	C(11)–C(12)–C(13)	118 (2)
N(3)–Co–N(5)	89.4 (7)	C(11)–C(12)–C(21)	119 (2)
N(3)–Co–N(6)	90.1 (7)	C(13)–C(12)–C(21)	123 (1)
N(4)–Co–N(5)	89.9 (7)	C(12)–C(13)–C(14)	120 (2)
N(4)–Co–N(6)	91.6 (7)	C(12)–C(13)–C(22)	119 (2)
N(5)–Co–N(6)	178.3 (6)	C(14)–C(13)–C(22)	120 (2)
C(1)–N(1)–C(18)	122 (1)	C(13)–C(14)–C(15)	120 (2)
C(6)–N(2)–C(7)	121 (1)	N(4)–C(15)–C(10)	112 (1)
C(9)–N(3)–C(10)	124 (1)	N(4)–C(15)–C(14)	127 (2)
C(15)–N(4)–C(16)	122 (1)	C(10)–C(15)–C(14)	121 (2)
C(23)–N(5)–C(27)	117 (1)	N(4)–C(16)–C(17)	128 (2)
C(28)–N(6)–C(32)	118 (1)	C(16)–C(17)–C(18)	125 (2)
N(1)–C(1)–C(2)	128 (2)	N(1)–C(18)–C(17)	122 (1)
N(1)–C(1)–C(6)	117 (1)	N(5)–C(23)–C(24)	122 (1)
C(2)–C(1)–C(6)	115 (1)	C(23)–C(24)–C(25)	121 (2)
C(1)–C(2)–C(3)	122 (2)	C(24)–C(25)–C(26)	118 (2)
C(2)–C(3)–C(4)	119 (2)	C(25)–C(26)–C(27)	119 (1)
C(2)–C(3)–C(19)	115 (2)	N(5)–C(27)–C(26)	123 (1)
C(4)–C(3)–C(19)	125 (2)	N(6)–C(28)–C(29)	123 (2)
C(3)–C(4)–C(5)	123 (2)	C(28)–C(29)–C(30)	118 (2)
C(3)–C(4)–C(20)	122 (2)	C(29)–C(30)–C(31)	120 (2)
C(5)–C(4)–C(20)	115 (2)	C(30)–C(31)–C(32)	120 (2)
C(4)–C(5)–C(6)	116 (2)	N(6)–C(32)–C(31)	121 (1)
N(2)–C(6)–C(1)	110 (1)		

[a] Esd's are in parentheses.

product is a Co(III) species. The reaction takes place in two steps: Addition of pyridine to air-saturated solutions of [CoL] first produces the EPR-active dioxygen adduct $[CoL^2(py)O_2]$, which reacts with excess pyridine to give an EPR-silent complex that exhibits an electronic absorption spectrum that is slightly different from that of the dioxygen adduct.[5] The spectrum of the EPR-silent complex is identical with that measured on crystals containing $[CoL^2(py)_2]^+$ and with that of the product of oxidation of $[CoL^2]$ by Br_2 under N_2 in the presence of excess pyridine. Similar behavior is observed with imidazole as the base.

Oxidation of $[CoL^2(B)O_2]$ (B = pyridine, imidazole) also is rapid in the presence of water, resulting in Co(III) complexes that on the basis of their electronic absorption spectra may reasonably be formulated as $[CoL^2(B)H_2O]^+$. Preliminary studies indicate[3,4] that this type of reaction allows certain cobalt complexes to be attached to surface histidines of proteins. Investigations of the effects of driving force and reorganization energy on long-range electron transfer[14,15] could be greatly facilitated by the availability

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of a series of cobalt-substituted proteins.

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Supplementary Material Available: Tables S1 and S2, listing anisotropic thermal parameters (2 pages); tables of calculated and observed structure factors (21 pages). Ordering information is given on any current masthead page.

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Ruthenium(II) Solvento Complexes Containing the Tripod-like Ligands $MeC(CH_2EPh_2)_3$ (E = P or As) and Their Reactions with Carbon Monoxide. Crystal and Molecular Structure of $[Ru_2(\mu\text{-}Cl)_3(MeC(CH_2PPh_2)_3)_2][BPh_4]$

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Treatment of $[RuCl_2(DMSO)_4]$ with tripod [tripod = $MeC(CH_2EPh_2)_3$, E = P (triphos) or As (triars)] yields $[Ru_2(\mu\text{-}Cl)_3(tripod)_2]Cl$. In the case of triars the mononuclear intermediate $[RuCl_2(DMSO)(triars)]$ can be isolated. This condenses to the corresponding trichloro-bridged complex in MeOH. The chloride ligands of $[Ru_2(\mu\text{-}Cl)_3(tripod)_2]Cl$ can be abstracted by $AgCF_3SO_3$ in MeCN to yield $[Ru(MeCN)_3(tripod)](CF_3SO_3)_2$. When the chloride abstraction is carried out in DMSO and above 100 °C, the products are $[Ru(DMSO)_3(tripod)](CF_3SO_3)_2$, whereas if the reaction is carried out below 100 °C, the mixed-solvent complexes $[Ru(H_2O)(DMSO)_2(tripod)](CF_3SO_3)_2$ are obtained. Reaction of the DMSO complexes with carbon monoxide gives the dicarbonyl triflate complexes $[Ru(CF_3SO_3)(CO)_2(tripod)](CF_3SO_3)$. The X-ray diffraction study of a crystal of $[Ru_2(\mu\text{-}Cl)_3(tripod)_2][BPh_4]$ (orthorhombic, of space group *Pccn* and with a = 19.991 (8) Å, b = 18.388 (7) Å, c = 25.510 (10) Å, and Z = 4) is reported.

Introduction

Open sites in metal coordination spheres have long been recognized as essential features of reactive complexes. There has been a concentrated effort to synthesize and isolate complexes that either are coordinatively unsaturated and stabilized by bulky ligands[2] or possess potentially labile ligands such as phosphines,[3a] olefins,[3b] or solvent molecules.[3c] Some solvent-stabilized complexes have been shown to activate sp^3-hybridized C-H bonds.[4] Such novel reactivity has prompted a systematic search for similar compounds obtained by acidolysis of polyhydrides in suitable donor solvents.[5]

Our interest in solvento transition-metal complexes containing the facially coordinating tripod ligand [tripod = $(MeC(CH_2EPh_2)_3)$, E = P (triphos) or As (triars)] stems from preliminary studies in which it was found that $[Rh(MeCN)_3(triphos)](CF_3SO_3)_3$ catalyzed a number of reactions.[6] We have, therefore, extended this chemistry to include analogous complexes of ruthenium since coordinatively unsaturated $[RuHCl(PPh_3)_3]$[7] and $[RuCl_2(PPh_3)_3]$[8] are known to be active catalysts.

Ruthenium(II) complexes containing triphos have been previously reported in the literature,[9] but they contain coordinated carbon monoxide as they were prepared by using ruthenium carbonyl complexes as starting materials. Thus, other synthetic routes were required to obtain carbonyl-free species in general and solvento complexes in particular.

Preliminary to catalytic studies, we report herein the synthesis, isolation, and spectral and reactivity studies of complexes of the type $[Ru(solvent)_3(tripod)]^{2+}$.

Results

Synthesis and Reactivity Studies. Our initial efforts were directed toward the synthesis of $[Ru(MeCN)_3(tripod)]^{2+}$ using the method outlined by Crabtree and Pearman[10] for the synthesis of the cations $[Ru(MeCN)_3L_3]^{2+}$ (L = PMe_2Ph, $PMePh_2$), i.e., halogen abstraction from $[L_3Ru(\mu\text{-}Cl)_3RuL_3]^+$ in acetonitrile. Chatt et al.[11] reported that these binuclear complexes can be obtained by refluxing $RuCl_3 \cdot nH_2O$ ($n \sim 2$) with an excess of phosphine and with 2-methoxyethanol as a solvent. However, when triphos was used in this reaction, only moderate yields (ca. 40%) of the yellow product $[Ru_2(\mu\text{-}Cl)_3(triphos)_2]Cl$ (**1**) were obtained. The yields of **1** could be improved (ca. 60%) by reacting "ruthenium blue solutions"[12] in methanol with triphos (1 molar equiv) in 2-methoxyethanol. However, the method of choice, because of yield and ease of isolation, was the reaction of triphos with $[RuCl_2(DMSO)_4]$[13] in refluxing toluene, which gave ca. 80% yield (see eq 1). The $^{31}P\{^1H\}$ NMR spectrum of **1** shows a singlet at δ 36.0, consistent with a face-sharing bioctahedral structure with bridging chlorides. The X-ray analysis of $[Ru_2(\mu\text{-}Cl)_3(triphos)_2][BPh_4]$ is presented in a later section.

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