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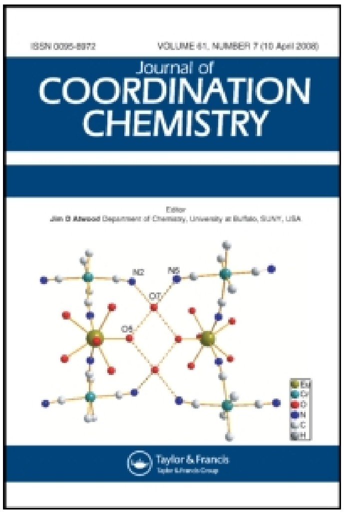

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Synthesis and Characterization of the Cobalt Complexes of New BF_2^+ Bridged, Anthracene Substituted Bis(a-Dioxime) Macrocycles

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SYNTHESIS AND CHARACTERIZATION OF THE COBALT COMPLEXES OF NEW BF_2^+ BRIDGED, ANTHRACENE SUBSTITUTED BIS(α-DIOXIME) MACROCYCLES

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The synthesis, characterization and structure are described for new cobalt complexes, with a BF_2^+ bridged, bis(α-dioxime) ligand, based upon a sterically demanding framework derived from an anthracene Diels–Alder adduct. The ligand provides a deep cleft within which axial ligands and/or O_2 can bind. The crystal structures of the bis- and mono(BF_2^+) bridged complexes have space groups $P2_1/c$ and $P\bar{1}$, respectively, with unit cell dimensions $a = 12.662(2)$ Å, $b = 16.430(3)$ Å, $c = 10.438(3)$ Å, $\beta = 103.51(2)°$, $a = 12.046(1)$ Å, $b = 17.596(3)$ Å, $c = 9.939(1)$ Å, $\alpha = 105.15(1)°$, $\beta = 102.87(1)°$, and $\gamma = 78.13(1)$, respectively. For both complexes $Z = 2$ and the residuals R and R_w were 0.070, 0.104, and 0.059, 0.075, respectively. ESR studies show that the cobalt(II) complexes have a strong tendency to bind two axial nitrogen bases, adopting a coordination number of six. The dioxygen affinity of the new cobalt(II) dioxygen carrier is limited by the competition between axial base binding and O_2 binding. This extends the understanding of correlations between electrode potentials and O_2 affinities and possible sources of apparent contradictions.

Keywords: Cobalt complex, macrocycle, dioxygen binding, ESR study, X-ray crystal structure

INTRODUCTION

Dioxygen binding has been the focus of considerable interest in recent years and this laboratory has been extensively involved in the design, synthesis and characterization of a number of classes of compounds which have been shown to reversibly bind dioxygen.[1]

Recently we have been exploring a group of macrocyclic dioximato complexes of cobalt in which the original bridging protons of the bis-dioxime[2] system have been replaced by BF_2^+ groups.[3] This substitution has enhanced markedly the stability of the dioxygen adduct by removing the labile acidic protons from the ligand.[4]

In the course of the studies on the variation of the dioxime ligand structure, we have been exploring those factors that determine the dioxygen affinity and the resistance toward irreversible oxidation of the dioxygen carriers. Since a common first step of irreversible oxidation processes is formation of a dimeric μ-peroxo complex, the

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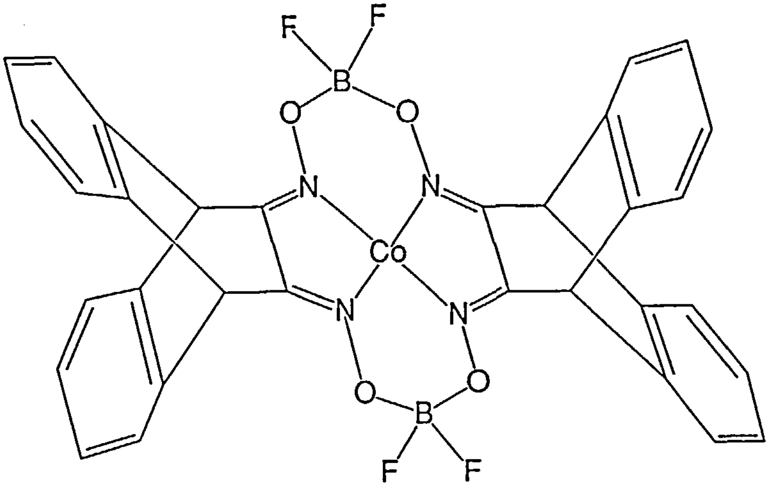
presence of bulky substitutents on the ligand should enhance stability of the system by keeping metal centres separated by a distance greater than that required for the μ-peroxo bridge. Many variations of this structural feature have been reported for iron and cobalt dioxygen carriers[1,5] and the specific component of the structure, that is used here as the source of steric bulk, was employed in a distinctly different macrocycle by Baldwin and Huff in the first so-far undisputed report of a non-porphyrin synthetic iron(II) dioxygen carrier.[6] Both ligands contain two 9,10-dihydroanthracene substituted units whose bulk extends above and below the coordination plane (structure 1). As proposed by the earlier investigators, this should protect both faces of the macrocycle without hindering access of the dioxygen or an axial base to the metal centre. Our new cobalt complexes provide the opportunity to study the benefits of this structural feature in detail. Structure 1 shows the new bis(α-dioxime) macrocyclic ligand as its cobalt complex. Here we report the synthesis, characterization, redox, and O_2 binding properties of the cobalt complexes of BF_2^+ linked bis(anthracenedioximato) ligand systems.



EXPERIMENTAL

The syntheses of organic compounds and cobalt(III) complexes were performed in the laboratory atmosphere and when necessary, under a blanket of nitrogen. The oxygen sensitive complexes of cobalt(II) were prepared and handled in a Vacuum Atmospheres glove box containing dry nitrogen gas and having less than 4 ppm of oxygen. Solvents used in the synthesis of cobalt(II) complexes were dried using standard techniques, distilled under nitrogen, and degassed under vacuum prior to use.

Physical Measurements

Elemental analyses were performed by Galbraith Laboratories, Inc. Knoxville, Tennessee. Mass spectra were obtained using either electron impact (EI) on a Nermag R10-10 quadrupole GC/MS system or fast atom bombardment (FAB) techniques on a ZAB HS mass spectrometer. Infrared spectra were obtained for KBr pellets on a Perkin-Elmer 1610 FTIR spectrometer (4000–400 cm^{-1}) calibrated with polystyrene and band positions are reported in cm^{-1}. NMR spectra were recorded on a Varian XL-300 spectrometer operating at 299.943 MHz (^{1}H) or 75.429 MHz (^{13}C). Chemical shifts are reported in ppm relative to tetramethylsilane by direct resonance assignments in deuterated solvents. ^{13}C NMR spectra were recorded using broadband decoupling and assignments were facilitated using the attached proton test (APT) method.

Electron spin resonance (ESR) spectra were obtained using a Varian E-112 spectrometer operating in the X-band and the magnetic field was calibrated with external DPPH ($g = 2.0036$). ESR spectra were collected, in 500 discrete points, on an IBM PC microcomputer *via* a locally made interface. Simulations of the ESR spectra were performed on an IBM AT personal computer or an IBM PS/2 Model 80 microcomputer using a program written in Pascal by one of the authors (PC). The spin-Hamiltonian parameters were obtained by fitting of the calculated spectra by means of the Marquardt[7] method using the residual square sum of the first derivative spectrum as an optimized function.

Cyclic voltammetry experiments were performed using a Princeton Applied Research potentiostat (model 173) and universal programmer (model 175), the output being recorded directly to paper using a Houston Instruments 200 chart recorder. The working electrode was a 3 mm diameter vitreous carbon disc, sealed into Kel F (Bioanalytical System Inc.), the secondary/counter electrode was a platinum gauze and the reference electrode was a silver wire. All electrode potentials were measured *versus* ferrocene, which was used as an internal standard. The supporting electrolyte was 0.1 M tetrabutylammonium tetrafluoroborate (Southwestern Analytical Chemicals Inc.), which was recrystallized from aqueous ethanol and dried *in vacuo*. All electrochemical experiments were performed in a nitrogen atmosphere glovebox.

Spectrophotometric studies of the interaction of cobalt(II) complex with dioxygen were conducted using a 1 cm gas-tight quartz cell, fitted with a gas inlet and a bubbling tube. Spectra were recorded on a Varian 2300 spectrophotometer.

Syntheses

Tetrachloroethylene Carbonate (1)[8]

Into a 1 dm^3 3-necked round-bottomed flask, fitted with a gas inlet, reflux condenser and a thermometer, were placed 88 g (1 mol) of ethylene carbonate and 400 cm^3 of dry carbon tetrachloride. The vessel was placed in a Rayonet photochemical reactor, where irradiation with light of wavelength 3000 Å and bubbling chlorine gas through the solution continued for 22 hrs at 85°C. At the end, the reaction mixture was filtered and carbon tetrachloride was removed leaving an oily residue. This was distilled under reduced pressure giving a dense colourless liquid. Yield: 190 g (84%). IR: 1885 (C=O); ^{1}H NMR (CDCl$_3$): no signal; ^{13}C NMR (CDCl$_3$): 143.1 (*C*=O), 113.8 (*C*Cl$_2$).

Dichlorovinylene Carbonate (2)

The procedure described by Scharf[8] was adopted and modified. In a 1 dm^3 3-necked round-bottomed flask, equipped with a reflux condenser and mechanical stirrer, was placed 135 g (0.6 mol) of tetrachloroethylene carbonate and 400 cm^3 of dry diethyl ether. The solution was stirred and warmed until the boiling point was reached and then 4 cm^3 of dimethylformamide (DMF) was added. Heating was stopped and 130 g (2 mol) of zinc–copper couple (prepared according to the method of LeGoff[9]) was added portion-wise over a period of 3 hours with vigorous stirring. The reaction mixture was then warmed and stirred for an additional 17 hours. Thereafter, the excess of zinc couple was removed by filtration (CAUTION! PYROPHORIC!) and the ether filtrate was dried (magnesium sulphate) and filtered through Celite. Solvent was removed and the oily orange residue was distilled under reduced pressure to give a colourless liquid (CAUTION! LACHRYMATOR!) which crystallized below room temperature. Yield: 80 g (86%). IR: 1925, 1875 and 1835 (C=O), 1680 (C=O); ^{1}H NMR ($CDCl_3$): no signals; ^{13}C NMR ($CDCl_3$): 146.8 (*C*=O), 125.5 (*C*=C); MS (EI): 154 ($m^{+\cdot}$).

Anthracene/Dichlorovinylene Carbonate Cycloaddition Compound (3)

This product was obtained according to the literature method[10]. The product was recrystallized twice from dioxane giving the cycloaddition adduct 3, yield 81%. M.Pt. 216–218°C (Lit.[10] 218°C). IR: 1805, 1845 and 1875 (C=O); ^{1}H NMR ($CDCl_3$): 7.26–7.41 (m, 8H, Ar*H*), 4.94 (s, 2H, C*H*); ^{13}C NMR ($CDCl_3$): 148.0 (*C*=O), 136.0 (C_{Ar}), 135.5 (C_{Ar}O), 128.7 (C_{Ar}H), 128.4 (C_{Ar}H), 126.6 (C_{Ar}H), 126.5 (C_{Ar}H), 104.0 (Cl–*C*–O), 57.8 (*C*H); MS (EI): 154 ($m^{+\cdot}$).

9,10-Dihydro-9,10-ethanoanthracene-11,12-dione (4)

Prepared according to the method of Scharf *et al.*[10] A solution of 18 g (0.054 mole) of 3 in 270 cm^3 of dioxane, 120 cm^3 of water and 5 cm^3 of concentrated HCl was heated at reflux for 12 hours. After cooling to room temperature, the solution was extracted several times with 100 ml of ether until no yellow colour came into the ether layer. The combined extracts were dried (magnesium sulphate) and filtered. The solvent was removed and the crude yellow-orange product was recrystallized from benzene. Yield: 10.5 g (83%). M.Pt. 199°C (Lit.[10] 198°C). Anal.: calc. for $C_{16}H_{10}O_2$: C, 82.01; H, 4.31%. Found: C, 82.51; H, 4.50%. IR: 1755 and 1735 (C=O); ^{1}H NMR ($CDCl_3$): 7.30–7.44 (m, 8H, Ar*H*), 4.96 (s, 2H, C*H*); ^{13}C NMR ($CDCl_3$): 183.7 (*C*=O), 134.6 (C_{Ar}), 129.2, 126.1 (C_{Ar}H), 59.7 (*C*H); MS (EI): 234 ($m^{+\cdot}$).

9,10-Dihydro-9,10-ethanoanthracene-11,12-dione Dioxime; AnthraGlyox (5)

4.68 g (20 mmol) of the α-diketone 4, 8.34 g (120 mmol) of hydroxylamine hydrochloride, 8.29 g (60 mmol) of potassium carbonate and 340 cm^3 of methanol was placed in a 500 cm^3 flask and heated at reflux with stirring for 30 hours. At the end of that time, the boiling solution was filtered through Celite and the methanol was removed under reduced pressure. The white residue was stirred with 100 cm^3 of water for 30 minutes, filtered, washed several times with 10 cm^3 portions of water and dried under vacuum. The white product was recrystallized from aqueous methanol and dried *in vacuo*. Yield: 4.7 g (87%). M.Pt. 250°C (dec.). Anal.: calc. for $C_{16}H_{12}N_2O_2$: C, 72.77; H, 4.58; N, 10.60%. Found: C, 72.81; H, 4.72; N, 10.56%. IR: 2900–3500 (OH), 1620 (C=N); ^{1}H NMR (d_8-THF): 10.4 (s, 2H, O*H*) 7.1–7.4 (m, 8H, Ar*H*) 6.0 (s, 2H, C*H*); ^{13}C NMR (d_8-THF): 150.3 (*C*=N), 141.4 (C_{Ar}), 127.5, 125.2 (C_{Ar}H), 45.7 (*C*H); MS (EI): 264 ($m^{+\cdot}$), 247 {$(m\text{-}OH)^{+\cdot}$}, 230 {$(m\text{-}2OH)^{+\cdot}$}.

Chloro(pyridine)bis-(9,10-dihydro-9,10-ethanoanthracene-11,12-dione dioxamato) cobalt(III), [Co(AnthraGlyoxH)$_2$(py)Cl] (6)

To a hot solution of 2.64 g (10 mmol) of dioxime 5 and 1.19 g (5 mmol) of cobalt chloride hexahydrate in 150 cm^3 of 95% ethanol, 0.79 g (10 mmol) of pyridine was added. The reaction mixture was stirred for a few minutes, cooled to room temperature and a stream of air was then allowed to agitate the solution for 45 minutes. The reaction mixture was kept at room temperature for 3 hours whereupon the product crystallized from the solution. The brown solid was collected, washed with ethanol and dried *in vacuo*. Yield: 1.6 g (50%). Anal.: calc. for $C_{37}H_{27}N_5O_4CoCl{\cdot}C_2H_5OH$: C, 62.78; H, 4.46; N, 9.39%. Found: C, 62.85; H, 4.62, N, 9.31%. IR: 3450 (OH), 1610 (C=N); ^{1}H NMR (d_6-DMSO):[11] 7.65 (d, 2H, py*H*), 7.54 (m, 4H, Ar*H*), 7.51 (t, 1H, py*H*) 7.32 (m, 4H, Ar*H*), 7.18 (m, 4H, Ar*H*), 7.05 (t, 2H, py*H*), 6.98 (m, 4H, Ar*H*), 5.89 (s, 4H, C*H*); ^{13}C NMR (d_6-DMSO):[11] 154.2 (*C*=N), 149.4 (C_{Ar}H), 139.6 (C_{Ar}), 139.4 (C_{Ar}), 127.3 (C_{Ar}H), 127.1 (C_{Ar}H), 125.9 (C_{Ar}H), 124.6 (C_{Ar}H), 45.4 (*C*H); MS (FAB): 699 ($m^{+\cdot}$), 585 {$(m{-}py{-}Cl)^{+\cdot}$}.

Chloro(pyridine)-{1,1,8,8-tetrafluoro-4,5,11,12-di(9',10'-dihydro-9'-anthracene)-2,7,9,14-tetraoxa-3,6,10,13-tetraaza-1,8-dibora-cyclotetradeca-3,5,10,12-tetraene}-cobalt(III), [Co(AnthraGlyoxBF$_2$)$_2$(py)Cl] (7)

1.4 g (2 mmol) of 6 was added to 200 cm^3 of freshly distilled acetonitrile and the resulting suspension was brought to reflux under an atmosphere of nitrogen. To this suspension 1 cm^3 (8 mmol) of boron trifluoride etherate was added slowly with stirring which converted the suspension to a red solution within 15 minutes. The solvent was removed under reduced pressure and the residue was dissolved in 30 cm^3 of acetonitrile and evaporated to dryness. The last step was repeated twice. Finally the residue was dissolved in 10 cm^3 of acetonitrile and allowed to stand at 0°C for 3 hrs, whereupon the product crystallized from solution. The product was collected by filtration, washed with acetonitrile, and dried under vacuum. Recrystallization from CH_2Cl_2/CH_3OH (96/4) resulted in orange-red crystals. Yield: 1.3 g (85%). Anal.: calc. for $C_{37}H_{25}N_5O_4B_2F_4CoCl$: C, 55.85; H, 3.17; N, 8.80%. Found: C, 55.67; H, 3.31; N, 8.88%. ^{1}H NMR (d^6-DMSO): 7.80 (m, 4H, Ar*H*), 7.69 (m, 4H, Ar*H*), 7.45 ppm (m, 4H, Ar*H*), 7.31 (m, 4H, Ar*H*) 7.12 (t, 1H, py*H*), 6.78 (t, 2H, py*H*), 6.40 (s, 4H, C*H*) 6.23 (d, 2H, py*H*); ^{13}C NMR (d_6-DMSO): 162.4 (*C*=N), 145.9, 140.9 (C_{Ar}), 137.7, 137.2, 129.1, 128.5, 126.3, 126.2, 126.1 (C_{Ar}H), 45.9 (*C*H); MS (FAB): 662 {$(m{-}py{-}Cl{-}F)^{+\cdot}$}, 614 {$(m{-}py{-}Cl{-}3F{-}B)^{+\cdot}$}; visible spectrum (acetonitrile): λ_{max} 495 nm.

Pyridine-1,1,8,8,-tetrafluoro-4,5,11,12-di(9',10'-dihydro-9',10'-anthracene)-2,7,9,14-tetraoxa-3,6,10,13-tetraaza-1,8-dibora-cyclotetradeca-3,5,10,12-tetraene-cobalt(II), [Co(AnthraGlyoxBF$_2$)$_2$(py)] (8)

A solution of 0.5 g (0.6 mmol) of 7 in 40 cm^3 of acetonitrile was mixed with a solution of 82.4 mg (0.3 mmol) of tetrabutylammonium borohydride in 10 cm^3 of acetonitrile in a nitrogen atmosphere. The colour turned green and then within 10 s changed to brown. After 30 minutes stirring, the solution volume was reduced to 10 cm^3 and a yellow-orange product was collected and recrystallized from dichloromethane/toluene. Yield 0.3 g (62%). Anal.; calc. for $C_{37}H_{25}N_5O_4B_2F_4Co$: C, 58.45; H, 3.29; N, 9.22%. Found: C, 58.90; H, 3.24; N, 8.67%. MS (FAB): 681 {$(m{-}py)^{+\cdot}$}, 662 {(m–py–F)$^{+\cdot}$}; visible spectrum (acetonitrile/toluene): λ_{max} 450 nm; visible spectru (acetonitrile/pyridine, 95/5): λ_{max} 470 nm.

X-Ray Analyses

Crystals of [Co(AnthraGlyoxBF$_2$)$_2$(py)$_2$] and [Co(AnthraGlyox)$_2$BF$_2$(py)$_2$] for ray analysis were obtained from a solution of [Co(AnthraGlyoxBF$_2$)$_2$(py)] in 90/ pyridine/acetonitrile. The former were obtained in an inert atmosphere enclosu while the latter were formed upon slow evaporation of solvent in air. Crystal da and details of the parameters associated with data collection for both [Co(Anthr GlyoxBF$_2$)$_2$(py)$_2$] and [Co(AnthraGlyox)$_2$BF$_2$(py)$_2$] are summarized in Table All measurements were made on a Rigaku AFC5R diffractometer with graphi monochromated CuKα radiation. Cell constants and orientation matrixes for da collection, obtained from a least-squares refinement using the setting angles of carefully centred reflections in the ranges $50.00 < 2\theta < 70.00°$ a $60.00 < 2\theta < 70.00°$, corresponded to a triclinic cell for [Co(Anthra lyox)$_2$BF$_2$(py)$_2$] and a monoclinic cell for [Co(AnthraGlyox-BF$_2$)$_2$(py)$_2$], respe ively. The data were collected at room temperature using the θ–2θ scan technique t maximum 2θ value of 112.5°. The intensities of three representative reflections, wh were measured after every 150 reflections, remained constant throughout da collection indicating crystal and electronic stability in both cases (no decay correcti was applied). The data were corrected for Lorentz and polarization effects.

The structures were solved by direct methods. the function minimized w $\Sigma w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$. The non-hydrogen atoms were refin anisotropically. Hydrogen atoms were refined isotropically for [Co(AnthraGlyox BF$_2$(py)$_2$]. In the case of [Co(AnthraGlyoxBF$_2$)$_2$(py)$_2$], hydrogen atoms we refined with assigned isotropic thermal parameters which were 20% greater than t $B_{equivalent}$ values of the atoms to which they were bonded.

Neutral atom scattering factors were taken from Cromer and Weber.[12] Anom lous dispersion effects were included in F_{calc},[13] the values for $\Delta f'$ and $\Delta f''$ were tho of Cromer.[14] All calculations were performed using the TEXSAN[15] crystallograp software package of the Molecular Structure Corporation.

It is to be noted that both complexes contain disordered solvent molecules in t crystal lattice, pyridine in the case of [Co(AnthraGlyox)$_2$BF$_2$(py)$_2$] and acetonitr in the case of [Co(AnthraGlyoxBF$_2$)$_2$(py)$_2$].

Final atomic coordinates are listed in Table II for [Co(AnthraGlyoxBF$_2$)$_2$(py and Table V for [Co(AnthraGlyox)BF$_2$(py)$_2$].

RESULTS AND DISCUSSION

Synthesis and Characterization of Co(AnthraGlyoxBF$_2$)$_2$(py)

The multistep synthesis of this compound involves preparation of the α-dioxi ligand and consecutive synthesis of the cobalt(III) complex of that parent dioxi [Co(AnthraGlyoxH)$_2$(py)(Cl)], followed by substitution of bridging protons BF$_2^+$ and reduction to the desired cobalt(II) derivative.

The method of preparation of 9,10-dihydro-9,10-ethanoanthracene-11,12-dio which is a precursor of the α-dioxime, is shown in Scheme I. This is the meth described by Scharf and Kuesters,[6] which was modified in order to obtain lar

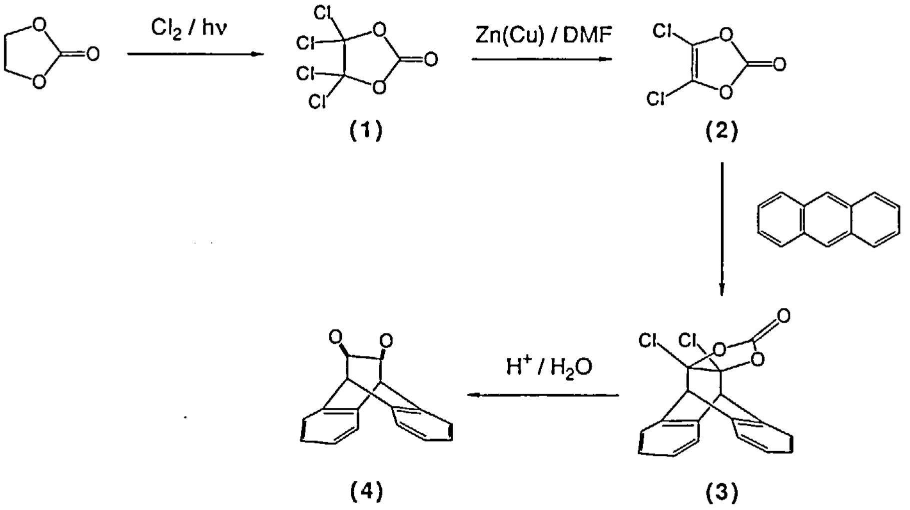
TABLE I
Crystal data and structure analysis parameters for [Co(AnthraGlyoxBF$_2$)$_2$(py)$_2$]*CH$_3$CN (9) and [Co(AnthraGlyox)$_2$BF$_2$(py)$_2$]*0.75py (10).

	9	10
Empirical Formula	$CoC_{44}H_{33}N_7O_4B_2F_4$	$CoC_{45.75}H_{45.75}N_{6.75}O_4BF_2$
Formula Weight	880.34	860.99
Crystal Colour, Habit	brown, prism	red, prism
Crystal Dimensions (mm)	0.2 × 0.2 × 0.5	0.3 × 0.2 × 0.2
Crystal System	monoclinic	triclinic
No. Reflections Used for Unit Cell Determination (20 range)	25 (60.0–70.0°)	25 (50.0–70.0°)
Omega Scan Peak Width at Half-height	0.42	0.42
Lattice Parameters:	a = 12.662(2) A°	a = 12.046(1) A°
	b = 16.430(3) Å	b = 17.596(3) Å
	c = 10.438(3) A°	c = 9.939(1) Å
	α = 90°	α = 105.15(1)°
	β = 103.51(2)°	β = 102.87(1)°
	γ = 90°	γ = 78.13(1)°
	V = 2120(1) Å^3	V = 1957.9(5) Å
Space Group	$P2_1/c$ (#14)	$P\bar{1}$ (#2)
Z	2	2
D_{calc}	1.38 g/cm^3	1.46 g/cm^3
F_{000}	902	899
$\mu_{(CuK\alpha)}$	38.94 cm^{-1}	39.17 cm^{-1}
Diffractometer	Rigaku AFC5R	
Radiation	CuKα (λ = 1.54178 Å)	
Take-off Angle	6°	
Scan Rate	16.0°/min (in omega)	8.0°/min (in omega)
Scan Width	(1.15 + 0.30 tanθ)°	(1.10 + 0.3 tanθ)°
No. of Reflections Measured:		
Total	3100	5435
Unique	2917 (R_{int} = .033)	5137 (R_{int} = .018)
Correction	Lorentz-polarization Absorption	
Transmission factors	0.49–1.00	0.92–1.00
Structure Solution	Direct Methods	
Hydrogen Atoms Treatment	Refined	
Refinement	Full-matrix least-squares	
Function minimized	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	
Least-squares Weights	$4F_o^2/\sigma^2(F_o^2)$	
Anomalous Dispersion	All non-hydrogen atoms	
No. Observations ($I > 3\sigma(I)$)	1926	4858
No. Variables	301	638
Reflection/Parameter Ratio	6.40	7.61
Residuals: R; R_w	0.070; 0.104	0.059; 0.075
Goodness of Fit	1.66	1.34
Max Shift/Error in Final Cycle	4.30	3.40
Maximum Peak in Final Diff. Map	1.18 e$^-$/Å^3	0.85 e$^-$/Å^3
Minimum Peak in Final Diff. Map	−0.49 e$^-$/Å^3	−0.31 e$^-$/Å^3

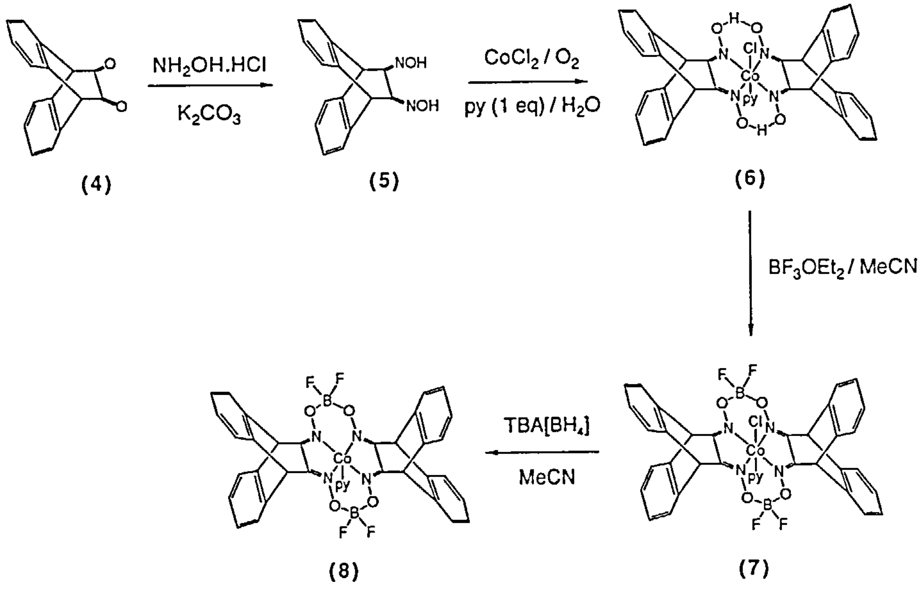
TABLE II
Positional parameters for [Co(AnthraGlyoxBF$_2$)$_2$(py)$_2$] (9).

atom	*x/a*	*y/b*	*z/c*
Co	1/2	1/2	1/2
F1	0.3119(4)	0.4591(3)	0.8085(5)
F2	0.3469(4)	0.5762(3)	0.7073(5)
O1	0.6926(4)	0.5459(3)	0.4111(5)
O2	0.4786(4)	0.4753(3)	0.7670(5)
N1	0.6470(5)	0.5246(4)	0.5123(6)
N2	0.5427(5)	0.4985(4)	0.6828(6)
N3	0.4684(5)	0.6405(4)	0.4992(6)
C1	0.7994(9)	0.7745(6)	0.837(1)
C2	0.7138(7)	0.6761(6)	0.9441(8)
C3	0.853(1)	0.4175(6)	0.970(1)
C4	0.947(2)	0.3801(8)	0.971(2)
C5	1.003(1)	0.3980(9)	0.882(2)
C6	0.968(1)	0.4557(7)	0.783(1)
C7	0.8291(7)	0.7151(6)	0.7576(9)
C8	0.7404(9)	0.7550(6)	0.927(1)
C9	0.8173(7)	0.5616(5)	0.6888(8)
C10	0.7097(7)	0.5262(5)	0.8687(8)
C11	0.7986(7)	0.6344(5)	0.7734(8)
C12	0.7414(6)	0.6156(5)	0.8679(7)
C13	0.8692(8)	0.4946(6)	0.784(1)
C14	0.8120(8)	0.4755(6)	0.878(1)
C15	0.7054(6)	0.5443(5)	0.6306(8)
C16	0.6436(7)	0.5156(4)	0.7314(7)
C17	0.5114(8)	0.6880(7)	0.598(1)
C18	0.4991(8)	0.7711(6)	0.601(1)
C19	0.437(1)	0.8092(7)	0.496(1)
C20	0.390(1)	0.7641(7)	0.391(1)
C21	0.409(1)	0.6798(6)	0.397(1)
B	0.3620(9)	0.4941(7)	0.718(1)
C1S	0.8658	0.1560	0.9932
C2S	0.8886	0.1661	0.8901
N3S	0.9033	0.1861	0.7751
H1	0.8231	0.8303	0.8257
H2	0.6750	0.6624	1.0123
H3	0.8172	0.3995	1.0335
H4	0.9857	0.3415	1.0240
H5	1.0773	0.3747	0.8699
H6	1.0041	0.4717	0.7108
H7	0.8740	0.7285	0.6962
H8	0.7195	0.7990	0.9779
H9	0.8553	0.5747	0.6244
H10	0.6718	0.5124	0.9308
H17	0.5510	0.6620	0.6782
H18	0.5318	0.8030	0.6755
H19	0.4234	0.8660	0.4946
H20	0.3464	0.7886	0.3146
H21	0.3757	0.6478	0.3190

quantities of the product. Exhaustive chlorination of the readily accessible ethylene carbonate results in tetrachloroethylene carbonate (**1**) which loses chlorine upon reaction with a zinc–copper couple in ether in the presence of catalytic amounts of dimethylformamide to give dichlorovinylene carbonate (**2**). **2** reacts with anthracene to give the Diels–Alder adduct (**3**) which readily hydrolyses to the required α-diketone (**4**). Reaction of the α-diketone with excess hydroxylamine hydrochloride in the presence of a proton scavenger (potassium carbonate) produces the dioxime (**5**) in high yield.



Scheme I



Scheme II

The complex [Co(AnthraGlyoxBF$_2$)$_2$py] was prepared as illustrated in Scheme II. The synthetic procedure for [Co(AnthraGlyoxH)$_2$(py)(Cl)] (6) was adapted from that for the parent compound in this family, [Co(MeGlyoxH)$_2$(py)(Cl)].[2a] It was necessary to use the exact stoichiometric amount of pyridine because the presence of excess base in the reaction mixture has been reported to yield a complex from which one of the linking protons (between pairs of oxime oxygens) has been removed and which contains two axially bound nitrogen base molecules.[2a] It was also necessary to perform this reaction in the presence of water.

The template synthesis of the macrocyclic Co(III) complex [Co(AnthraGlyoxBF$_2$)$_2$(py)(Cl)] (7) was performed by adding boron trifluoride etherate to a refluxing acetonitrile solution containing the proton-linked precursor 6. The bridging protons were replaced by BF_2^+ groups and the single mole of axial base, pyridine, was retained, according to both ^{1}H and ^{13}C NMR spectra, and elemental analysis. That distinguished this system from those previously reported,[4] where the axial pyridine was replaced by an acetonitrile solvent molecule. The mass spectrum (FAB) of the complex supports the structure of the macrocycle; however the peak at 662 amu does not confirm the presence of the pyridine.

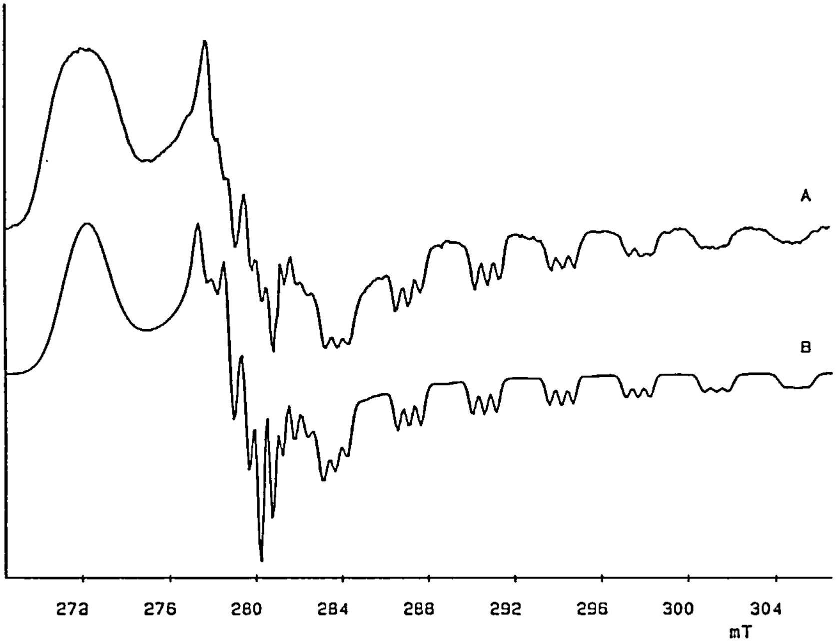


FIGURE 1 ESR spectrum of [Co(AnthraGlyoxBF$_2$)$_2$py] (8) in frozen toluene/dichloromethane solution, T = 77 K; A) experimental; B) stimulated.

The preparation of the Co(II) complex was accomplished by reducing [Co(AnthraGlyoxBF$_2$)$_2$(py)(Cl)] with 0.5 mol of tetrabutylammonium borohydride at ambient temperature in an inert atmosphere. Upon addition of the reducing agent, the transient formation of a blue-green species is observed. This change is due to formation of cobalt(I), which undergoes further reaction with Co(III) to form the desired Co(II) complex (8). Electrochemical studies using [Co^{III}(AnthraGlyoxBF$_2$)$_2$(py)(Cl)] in acetonitrile support this conproportionation process. The fast atom bombardment mass spectrum shows a peak at 681 amu due to [Co(Anthra-

$GlyoxBF_2)_2{}^+$] ion and another at 662 amu attributed to loss of one fluorine atom. Unlike other complexes from this family, this species retains the mole of pyridine, which was present in the parent Co(III) complex; in related complexes, the pyridine is replaced by two moles of acetonitrile (solvent).[4] This finding, based on elemental analysis, was confirmed by the ESR spectrum in a frozen toluene/dichloromethane solution (Figure 1). The spectrum clearly shows the cobalt(II) ion to be low spin, having an unpaired electron occupying the molecular orbital with a major contribution from the $d_z{}^2$ metal orbital, and only one axially bound nitrogeneous base to be present.The spectrum can be reproduced by computer simulation assuming orthorhombic symmetry of both g and A^{Co} tensors and axial symmetry for A^N with the following spin-Hamiltonian parameters: $g_1 = 2.36$, $g_2 = 2.20$, $g_3 = 2.008$, $A_1 = 0\,cm^{-1}$, $A_2 = 0.0012\,cm^{-1}$, $A_3 = 0.0082\,cm^{-1}$, $A^N{}_{\parallel} = A^N{}_{\perp} = 0.0013\,cm^{-1}$. Mag netic moment measurements in solution, as determined by the Evans method,[16] support the low spin character of the cobalt ion at room temperature. The observed magnetic moment values of 2.18 B.M. in chloroform, 2.20 B.M. in acetone and 2.35 B.M. in pyridine are somewhat above that expected for one unpaired electron, possibly due to some population of low lying excited states (quartets).

Formation and X-ray Structures of Bis-pyridine Adducts

Addition of a 10-fold excess of pyridine to the toluene-dichloromethane solution of $[Co(AnthraGlyoxBF_2)_2(py)]$ resulted in changes in the frozen solution ESR spectrum of the complex. The five-line superhyperfine splitting, observed on several high-field hyperfine lines (Figure 2), is due to the presence of the two pyridine nitrogens coordinated to the cobalt ion. The spectrum was simulated assuming orthorhombic symmetry of g and A^{Co} tensors, axial symmetry of the A^N, coaxiality of both hyperfine tensors and magnetic equivalence of both axial nitrogen nuclei. The following parameters produced the best fit: $g_1 = 2.23$, $g_2 = 2.15$, $g_3 = 2.027$, $A_1{}^{Co} = 0.0040\,cm^{-1}$, $A_2{}^{Co} = 0.0055\,cm^{-1}$, $A_3{}^{Co} = 0.0068\,cm^{-1}$, $A^N{}_{\parallel} = 0.0014\,cm^{-1}$, $A^N{}_{\perp} = 0\,cm^{-1}$.

The formation of $[Co(AnthraGlyoxBF_2)_2(py)_2]$ and its presence in the solid state was confirmed by X-ray crystallography. The dark brown, paramagnetic crystals were obtained from 90/10 pyridine/acetonitrile solution in the protective atmosphere of a glove box. The crystals decomposed readily by losing solvent from the lattice, so it was necessary to protect them by a layer of a mineral oil. The molecules of acetonitrile trapped in the crystal are disordered, a fact which strongly affected the overall quality of the data. The results of the refined structure determination are represented by the ORTEP drawing in Figure 3. Tables II to IV give positional parameters, calculated bond distances and selected bond angles.

The molecule is highly symmetric and possesses a cobalt(II) ion located at the centre of inversion. Consequently, only half of the geometric parameters are independent. The four nitrogens of the equatorial ligand and cobalt ion occupy a common plane. However, the organic part of the ligand deviates slightly from planarity in the vicinity of the donor atoms having an N(1)–C(15)–C(16)–N(2) torsion angle of −4(1)°. As a result of a compromise between the repulsive interaction of the pyridines and fluorine atoms on one side and the ligand's aromatic rings on the other, the plane established by the base molecules does not bisect any of the two N–Co–N bond angles. The projection of the N(3)–C(17) pyridine bond on the N(1)–Co–N(2) plane makes an N(1)–Co bond angle of 63°.

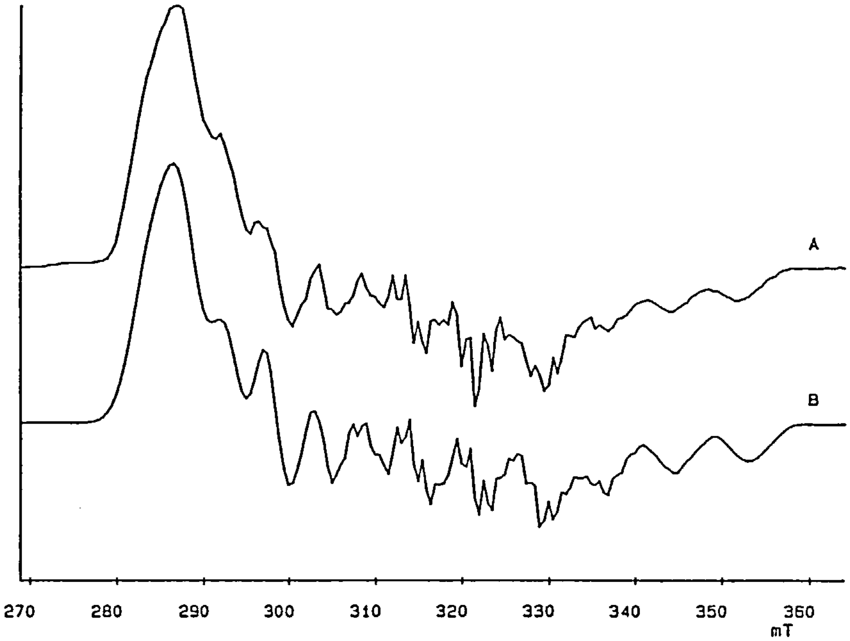


FIGURE 2 ESR spectrum of [Co(AnthraGlyoxBF$_2$)$_2$(py)$_2$] (9) in frozen toluene/dichloromethane solution, T = 77 K; A) experimental; B) simulated.

TABLE III
Selected interatomic distances (in Å) for [Co(AnthraGlyoxBF$_2$)$_2$(py)$_2$] (9).

atom pair	distance	atom pair	distance
Co–N2	1.866(6)	C3–C14	1.37(1)
Co–N2′	1.866(6)	C4–C5	1.32(2)
Co–N1	1.879(7)	C5–C6	1.40(2)
Co–N1′	1.879(7)	C6–C13	1.40(1)
Co–N3	2.342(7)	C7–C11	1.40(1)
Co–N3′	2.342(7)	C9–C15	1.47(1)
F1–B	1.39(1)	C9–C13	1.52(1)
F2-B	1.36(1)	C9–C11	1.54(1)
O1–N1	1.366(8)	C10–C16	1.50(1)
O1–B	1.52(1)	C10–C12	1.52(1)
O2–N2	1.385(8)	C10–C14	1.52(1)
O2–B	1.48(1)	C11–C12	1.39(1)
N1–C15	1.30(1)	C13–C14	1.39(1)
N2–C16	1.29(1)	C15–C16	1.49(1)
N3–C17	1.31(1)	C17–C18	1.38(1)
N3–C21	1.32(1)	C18–C19	1.35(1)
C1–C8	1.37(1)	C19–C20	1.35(1)
C1–C7	1.39(1)	C20–C21	1.41(1)
C2–C8	1.36(1)	C2–C12	1.37(1)
C3–C4	1.34(2)		

TABLE IV
Selected interatomic angles (deg) for [Co(AnthraGlyoxBF$_2$)$_2$(py)$_2$] (9).

N2–Co–N2′	180.00	C8–C1–C7	121(1)
N2–Co–N1	83.6(3)	C8–C2–C12	120.6(9)
N2–Co–N1′	96.4(3)	C4–C3–C14	121(1)
N2–Co–N3	91.4(3)	C5–C4–C3	121(1)
N2–Co–N3′	88.6(3)	C4–C5–C6	123(1)
N2–Co–N1	96.4(3)	C5–C6–C13	116(1)
N2–Co–N1′	83.6(3)	C1–C7–C11	118.1(9)
N2–Co–N3	88.6(3)	C2–C8–C1	120(1)
N2–Co–N3′	91.4(3)	C15–C9–C13	106.0(7)
N1–Co–N1′	180.00	C15–C9–C11	102.2(7)
N1–Co–N3	87.4(2)	C13–C9–C11	106.6(7)
N1–Co–N3′	92.6(2)	C16–C10–C12	101.3(6)
N1′–Co–N3	92.6(2)	C16–C10–C14	105.8(7)
N1′–Co–N3′	87.4(2)	C12–C10–C14	107.8(7)
N3–Co–N3′	180.00	C12–C11–C7	119.9(8)
N1–O1–B	113.1(6)	C12–C11–C9	114.4(7)
N2–O2–B	113.9(6)	C7–C11–C9	125.6(8)
C15–N1–O1	117.4(7)	C2–C12–C11	120.0(8)
C15–N1–Co	115.2(6)	C2–C12–C10	126.3(8)
O1–N1–Co	126.4(5)	C11–C12–C10	113.6(7)
C16–N2–O2	118.8(6)	C14–C13–C6	121(1)
C16–N2–Co	115.1(5)	C14–C13–C9	114.2(8)
O2–N2–Co	125.9(5)	C6–C13–C9	125(1)
C17–N2–C21	113.7(8)	C3–C14–C13	119(1)
C17–N3–Co	123.0(6)	C3–C14–C10	127(1)
C21–N3–Co	123.3(6)	C13–C14–C10	114.1(8)
N1–C15–C9	135.3(8)	N1–C15–C16	112.1(7)
C9–C15–C16	112.6(7)	N2–C16–C15	113.7(7)
N2–C16–C10	133.2(8)	C15–C16–C10	113.0(7)
N3–C17–C18	125.3(9)	C19–C18–C17	120(1)
C20–C19–C18	118(1)	C19–C20–C21	118(1)
N3–C21–C20	125(1)	F2–B–F1	112.8(8)
F1–B–O2	104.5(7)	F1–B–O1	104.2(7)
F2–B–O2	110.2(7)	F2–B–O1	109.5(7)
O2–B–O1	115.5(7)		

The equatorial Co–N distance of 1.87 Å is similar to that found in other low-spin Co(II) 14-membered macrocycles containing four imine donors.[17,18] The Co–N (pyridine) bonds (2.34 Å) are considerably longer than the Co–N equatorial bonds. This axial elongation is a result of the Jahn–Teller effect observed in low-spin d^7 complexes.[17–20] An additional elongation (about 0.05 Å) due to axial-equatorial ligand–ligand repulsion may be inferred when comparing with the Co–O bond distances found in complexes having two axial O-ligands (water, methanol).[17,18]

An identical pyridine/acetonitrile solution to that producing the crystals of [Co(AnthraGlyoxBF$_2$)$_2$(py)$_2$] was left on the benchtop, and this resulted in the slow growth of another kind of crystal. These crystals were red, diamagnetic (no ESR signal) and apparently stable to solvent loss from the crystal lattice. Their FAB mass spectrum displayed no peaks at 681 or 662 Daltons, features characteristic of [Co(AnthraGlyoxBF$_2$)$_2$(py)] and [Co(AnthraGlyoxBF$_2$)$_2$(py)$_2$]. Instead, a group of

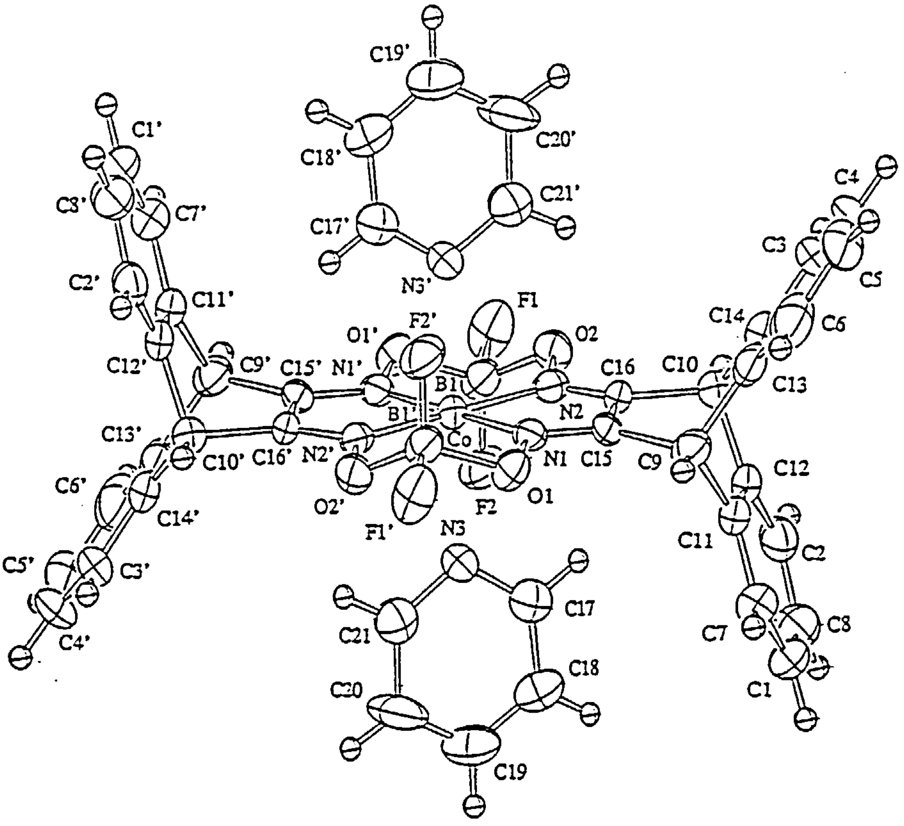


FIGURE 3 ORTEP drawing and atom numbering of [Co(AnthraGlyoxBF$_2$)$_2$(py)$_2$] (9).

ions was observed with maximum intensity at 614 Daltons. This is consistent with loss of a fluorine atom from an adduct bearing a single bridging BF$_2$.

The X-ray crystal structure of this complex is shown by the ORTEP drawing in Figure 4, which clearly exhibits the absence of one of the bridging BF$_2^+$ groups. In Tables V to VII are shown the positional parameters of the atoms, and selected bond distances and bond angles.

The molecule has no symmetry elements. Its pyridine ligands are *trans* to each other but they are not coplanar and their Co–N bonds are not mutually collinear. The two Co–N(pyridine) distances are slightly different from each other, but they are close and within 0.01 Å of the equatorial ones. However, the four equatorial Co–N bonds are all distinct. The lack of axial elongation, the diamagnetism and the charge balance all indicate the presence of cobalt(III) in this molecule. The complex is a product of oxidation and hydrolysis processes, which are the results of the prolonged contact of the solution with atmospheric moisture and oxygen. These processes may be similar to those proposed by Schrauzer^2 for decomposition of [Co(Me$_2$-GlyoxH)$_2$(py)$_2$] in the presence of oxygen and trace amounts of water, which lead to the formation of the cobalt(III) anhydrobase complex [Co(Me$_2$Glyox)$_2$H(py)$_2$].

TABLE V
Positional parameters for [Co(AnthraGlyox)$_2$BF$_2$(py)$_2$] 10).

atom	x/a	y/b	z/c
Co	0.25318(6)	0.21175(4)	0.14459(7)
F1	0.3172(3)	0.3860(2)	0.5813(3)
O1	0.2418(3)	0.1815(2)	−0.1619(3)
O2	0.3033(3)	0.3646(2)	0.3441(3)
N1	0.2478(3)	0.2328(2)	−0.0434(4)
N2	0.2676(3)	0.3234(2)	0.2084(4)
N3	0.0818(3)	0.2263(2)	0.1059(4)
C1	0.0436(5)	0.5270(3)	−0.1942(6)
C2	0.1123(4)	0.4533(3)	−0.2279(6)
C3	0.5199(5)	0.4353(3)	0.1241(6)
C4	0.6130(5)	0.4079(4)	0.0522(8)
C5	0.5990(5)	0.3617(4)	−0.0827(8)
C6	0.4933(5)	0.3415(4)	−0.1506(7)
C7	0.1394(5)	0.5464(3)	0.0478(6)
C8	0.0563(5)	0.5726(3)	−0.0573(6)
C9	0.2781(4)	0.3472(3)	−0.1398(5)
C10	0.3046(4)	0.4361(3)	0.1182(5)
C11	0.1958(4)	0.4268(3)	−0.1222(5)
C12	0.2094(4)	0.4731(3)	0.0147(5)
C13	0.3995(4)	0.3663(3)	−0.0832(5)
C14	0.4140(4)	0.4137(3)	0.0542(5)
C15	0.2584(4)	0.3071(3)	−0.0310(4)
C16	0.2731(4)	0.3560(3)	0.1090(4)
C17	0.0290(4)	0.1995(3)	−0.0278(5)
C18	−0.0890(5)	0.2026(3)	−0.0644(6)
C19	−0.1561(5)	0.2319(4)	0.0380(7)
C20	−0.1020(5)	0.2569(4)	0.1755(7)
C21	0.0159(5)	0.2539(3)	0.2054(6)
F1′	0.1440(3)	0.3661(2)	0.4416(3)
O1′	0.2940(3)	0.2598(2)	0.4631(3)
O2′	0.2227(3)	0.0524(2)	−0.0175(3)
N1′	0.2654(3)	0.2047(2)	0.3394(4)
N2′	0.2366(3)	0.0991(2)	0.1050(4)
N3′	0.4189(3)	0.1815(2)	0.1457(4)
C1′	0.4439(5)	−0.0644(3)	0.5828(6)
C2′	0.3819(4)	0.0115(3)	0.5947(6)
C3′	−0.0193(4)	0.0116(3)	0.2527(6)
C4′	−0.1079(5)	0.0419(4)	0.3283(7)
C5′	−0.0900(5)	0.0973(4)	0.4541(8)
C6′	0.0166(5)	0.1248(3)	0.5076(6)
C7′	0.3520(4)	−0.1015(3)	0.3390(6)
C8′	0.4306(5)	−0.1202(4)	0.4578(7)
C9′	0.2276(4)	0.1113(3)	0.4777(5)
C10′	0.1941(4)	0.0050(3)	0.2377(5)
C11′	0.3047(4)	0.0308(3)	0.4787(5)
C12′	0.2883(4)	−0.0256(3)	0.3516(5)
C13′	0.1048(4)	0.0923(3)	0.4320(5)
C14′	0.0868(4)	0.0359(3)	0.3048(5)
C15′	0.2457(4)	0.1378(3)	0.3509(4)
C16′	0.2284(4)	0.0793(3)	0.2205(5)

TABLE V (continued)

atom	*x/a*	*y/b*	*z/c*
C17′	0.4529(4)	0.1210(3)	0.0402(5)
C18′	0.5669(5)	0.0965(3)	0.0297(7)
C19′	0.6496(5)	0.1335(4)	0.1278(7)
C20′	0.6154(5)	0.1959(4)	0.2349(7)
C21′	0.4995(4)	0.2189(3)	0.2412(5)
B	0.2645(5)	0.3435(4)	0.4565(6)
N1S	0.7802	0.3095	0.5971
C2S	0.6831	0.3313	0.5769
C3S	0.8258	0.3995	0.5128
C4S	0.6369	0.3963	0.5172
C5S	0.8484	0.3388	0.5687
C6S	0.7247	0.4306	0.4855
N1S′	0.6634	0.4308	0.4944
C2S′	0.6305	0.3654	0.5621
C3S′	0.7199(1)	0.3079	0.6015
C4S′	0.8336	0.3076	0.5993
C5S′	0.8673	0.3692	0.5305
C6S′	0.7774	0.4281	0.4791
H1	−0.015(5)	0.556(3)	−0.250(6)
H2	0.102(4)	0.421(3)	−0.319(5)
H3	0.521(4)	0.476(3)	0.228(5)
H4	0.689(5)	0.421(3)	0.100(6)
H5	0.653(5)	0.351(3)	−0.129(6)
H6	0.484(4)	0.312(3)	−0.225(5)
H7	0.156(4)	0.576(3)	0.144(5)
H8	0.005(4)	0.627(3)	−0.031(5)
H9	0.270(4)	0.314(3)	−0.227(5)
H10	0.313(3)	0.471(2)	0.210(4)
H17	0.081(5)	0.170(4)	−0.108(7)
H18	−0.124(5)	0.189(3)	−0.169(6)
H19	−0.248(5)	0.246(3)	0.020(6)
H20	−0.147(5)	0.286(4)	0.252(7)
H21	0.055(4)	0.278(3)	0.303(6)
H1′	0.501(5)	−0.077(3)	0.675(6)
H2′	0.392(4)	0.048(3)	0.681(5)
H3′	−0.034(4)	−0.027(3)	0.163(5)
H4′	−0.188(5)	0.023(3)	0.289(6)
H5′	−0.152(6)	0.116(4)	0.495(7)
H6′	0.039(5)	0.163(3)	0.601(6)
H7′	0.343(4)	−0.141(3)	0.247(5)
H8′	0.474(5)	−0.177(3)	0.453(6)
H9′	0.236(3)	−0.151(2)	0.567(4)
H10′	0.186(4)	−0.031(3)	0.155(5)
H17′	0.392(4)	0.094(3)	−0.034(5)
H18′	0.585(5)	0.052(3)	−0.042(6)
H19′	0.730(6)	0.109(4)	0.121(7)
H20′	0.666(5)	0.226(3)	0.309(6)
H21′	0.466(4)	0.269(3)	0.324(5)

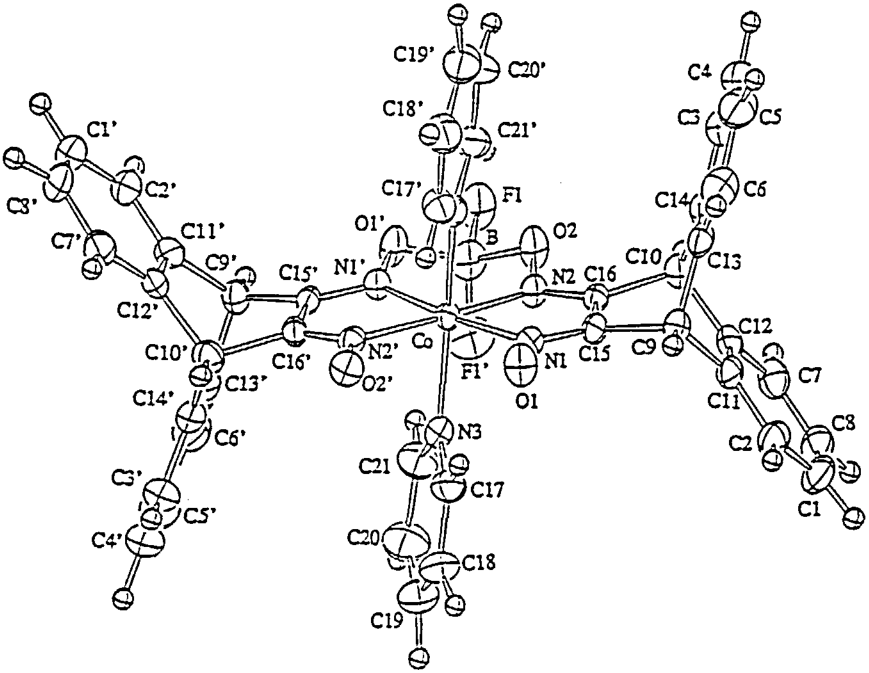


FIGURE 4 ORTEP drawing and atom numbering of [Co(AnthraGlyox)$_2$BF$_2$(py)$_2$] (10).

Electrochemical Properties and Dioxygen Binding

The *quasi*-reversible Co(II)/Co(I) couple at $E_{1/2} = -0.94$ V *vs* ferrocene, with peak separation $\Delta E_p = 80$ mV, is the only electrochemical process which could be observed for [Co(AnthraGlyoxBF$_2$)$_2$(py)] in methylene chloride solution. The additon of pyridine did not affect this process but resulted in the appearance of an irreversible Co(III)/Co(II) couple at about −0.09V with $\Delta E_p = 200$ mV. In acetonitrile solution, in addition to the Co(II)/Co(I) couple at $E_{1/2} = -0.90$ V with $\Delta E_p =$ 75 mV another *quasi*-reversible couple was observed at $E_{1/2} = -1.98$ V with $\Delta E_p =$ 115 mV, which is most likely due to the ligand reduction. Two new peaks are formed, one on the anodic scan at 0.44 V and another, cathodic at −0.09 V, which are due to an irreversible Co(III)/Co(II) process. Upon addition of pyridine both peaks were shifted toward more negative potentials, 0.05 V and −0.24 V, respectively, but the couple remained irreversible ($\Delta E_p = 290$ mV).

The lack of, or strongly irreversible character of, the Co(III)/Co(II) couple in the system under study prevents detailed discussion of the Co(II) ion's ability to donate an electron. The electrochemical potential of this process has been correlated with the dioxygen affinity in the cobalt Schiff base complexes[20] and since then has been widely believed to be a good indicator of oxygen carrying ability of the metal complexes.

Comparison of [Co(AnthraGlyoxBF$_2$)$_2$] with [Co(Me$_2$GlyoxBF$_2$)$_2$][4] reveals only small differences in electrochemical behaviour. The Co(III)/Co(II) couple for the dimethylglyoxamato complex also shows irreversible character in acetonitrile having peaks at 0.24 V and 0.64 V, which upon addition of pyridine are shifted negatively forming a *quasi*-reversible couple ($\Delta E_p = 100$ mV) at 0.04 V *vs* ferrocene.[4] These data

TABLE VI

Selected interatomic distances (in Å) for [Co(AnthraGlyox)$_2$BF$_2$(py)$_2$] (**10**).

atom pair	distance	atom pair	distance
Co-N2	1.932(4)	C6-C13	1.377(7)
Co-N1'	1.944(4)	C7-C8	1.379(7)
Co-N3'	1.956(4)	C7-C12	1.392(7)
Co-N2'	1.961(4)	C9-C13	1.518(7)
Co-N1	1.983(4)	C9-C15	1.519(6)
Co-N3	1.989(4)	C9-C11	1.534(6)
F1-B	1.364(6)	C10-C16	1.509(6)
O1-N1	1.282(4)	C10-C12	1.521(7)
O2-N2	1.374(4)	C10-C14	1.525(7)
O2-B	1.458(6)	C11-C12	1.385(6)
N1-C15	1.310(6)	C13-C14	1.396(7)
N2-C16	1.285(5)	C15-C16	1.427(6)
N3-C21	1.336(6)	C17-C18	1.380(7)
N3-C17	1.346(6)	C18-C19	1.369(8)
C1-C8	1.380(8)	C19-C20	1.376(8)
C1-C2	1.390(7)	C20-21	1.378(8)
C2-C11	1.388(7)	C9'-C15'	1.524(6)
C3-C14	1.387(7)	C9'-C13'	1.526(7)
C3-C4	1.398(8)	C9'-C11'	1.528(7)
C4-C5	1.369(9)	C10'-C16'	1.510(6)
C5-C6	1.372(9)	C10'-C14'	1.523(7)
F1'-B	1.408(7)	C10'-C12'	1.535(7)
O1'-N1'	1.377(4)	C11'-C12'	1.391(7)
O1'-B	1.456(7)	C13'-C14'	1.394(7)
O2'-N2'	1.276(4)	C15'-C16'	1.433(6)
N1'-C15'	1.286(6)	C17'-C18'	1.371(7)
N2'-C16'	1.312(5)	C18'-C19'	1.367(8)
N3'-C21'	1.343(6)	C19'-C20'	1.381(8)
N3'-C17'	1.352(6)	C20'-C21'	1.382(7)
C1'-C8'	1.368(8)	C1'-C2'	1.379(8)
C2'-C11'	1.381(7)	C3'-C14'	1.378(7)
C3'-C4'	1.379(8)	C4'-C5'	1.374(9)
C5'-C6'	1.408(9)	C6'-C13'	1.380(7)
C7'-C12'	1.387(7)	C7'-C8'	1.406(8)

show that [Co(Me$_2$GlyoxBF$_2$)$_2$] has a more positive potential for the Co(III)/Co(I couple than [Co(AnthraGlyoxBF$_2$)$_2$] and one could therefore expect a high dioxygen affinity for the latter.

The interaction of [Co(AnthraGlyoxBF$_2$)$_2$(py)] with dioxygen was monitored b ESR spectroscopy. The solution of the complex in a frozen, air-saturated toluen dichloromethane mixture (80/20) showed a spectrum, the intensity of which w much lower than that obtained for an oxygen-free solution (Figure 1) in the g ≈ 2 region and had a new signal around g = 2.01, as is typical for oxygenated complexe The intensity ratio of the two signals was estimated by double integration. F [Co(AnthraGlyoxBF$_2$)$_2$(py)] the fraction of the oxygenated form was 75%, and the case of [Co(AnthraGlyoxBF$_2$)$_2$(py)$_2$] 50% of the complex was in the oxygenat form. For frozen acetonitrile solution, this fraction was only 30%. In both solven any addition of pyridine led to formation of the bis(pyridine) adduct (Figure 2), a this suppressed the oxygen carrying ability of the system. At 10-fold excess of pyridine *no* signal due to the dioxygen complex was observed, even after bubbling pure oxygen through the solution at low temperature. Under identical conditions for the solution with no extra base, *only* the oxygenated complex spectrum (Figure 5) was observed at 77K.

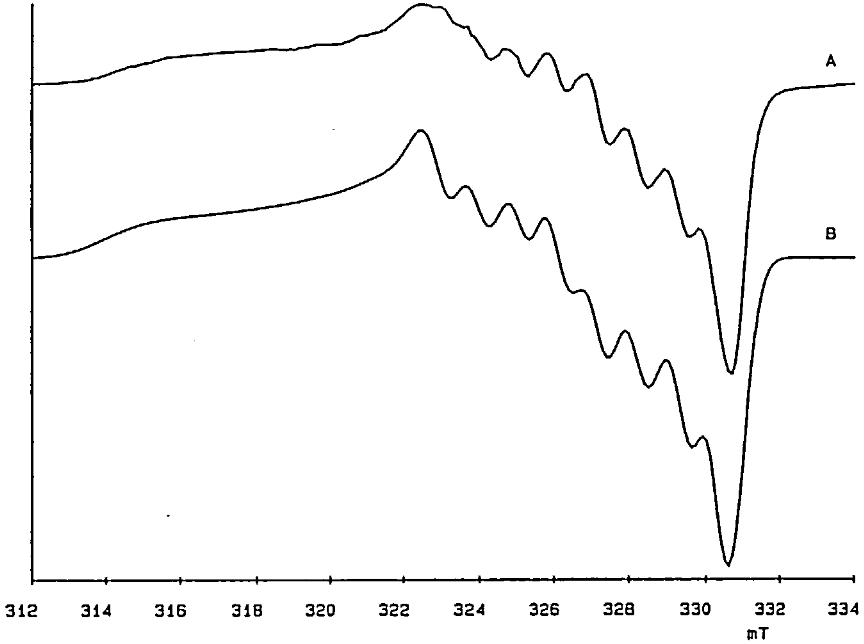


FIGURE 5 ESR spectrum of $[\mathrm{Co(AnthraGlyoxBF_2)_2py)(O_2)}]$ in frozen toluene/dichloromethane solution, $p_{O_2} = 760$ Torr, T = 77 K; A) experimental; B) simulated.

TABLE VII

Selected interatomic angles (deg) for $[\mathrm{Co(AnthraGlyox)_2BF_2(py)_2}]$ (10).

N2-Co-N1'	90.1(1)	N2-Co-N3'	91.6(2)
N2-Co-N2'	172.6(2)	N2-Co-N1	82.5(1)
N2-Co-N3	96.9(2)	N1'-Co-N3'	94.2(2)
N1'-Co-N2'	82.6(1)	N1'-Co-N1	172.4(2)
N1'-Co-N3	93.8(2)	N3'-Co-N2'	90.2(1)
N3'-Co-N1	84.3(1)	N3'-Co-N3	168.3(2)
N2'-Co-N1	104.8(2)	N2'-Co-N3	82.4(1)
N1-Co-N3	88.8(2)	O1-N1-Co	126.3(3)
C15-N1-Co	110.7(3)	N2-O2-B	116.3(3)
O1-N1-C15	122.8(4)	C16-N2-O2	115.8(4)
C16-N2-Co	113.8(3)	O2-N2-Co	127.8(3)
C21-N3-Co	124.5(3)	C17-N3-Co	117.8(3)
N1'-O1'-B	116.8(3)	C15'-N1-O1	117.2(4)
C15'-N1'-Co	113.6(3)	O1'-N1'-Co	129.2(3)
O2'-N2'-C16'	123.1(4)	O2'-N2'-Co	125.7(3)
C21'-N3'-Co	124.0(3)	C17'-N3'-Co	117.3(3)
F1-B-F1'	110.0(4)	F1-B-O1'	106.9(4)
F1-B-O2	106.5(4)	F1'-B-O1'	109.1(4)
F1'-B-O2	108.5(4)	O1'-B-O2	115.8(4)

The spectrum of the dioxygen complex was simulated using a model proposed by Smith and Pilbrow.[21] Monoclinic symmetry was assumed for the system, where the *A* tensor is rotated with respect to *g* with an angle of α about the *z* axis, which is common for both tensors. The following parameters gave the best fit: $g_x = 2.006$, $g_y = 2.069$, $g_z = 2.017$, $A_x = 0.0005\,\mathrm{cm}^{-1}$, $A_y = 0.0011\,\mathrm{cm}^{-1}$, $A_z = 0.0010\,\mathrm{cm}^{-1}$, $\alpha = 8°$.

Surprisingly, in liquid solution, the oxygen binding equilibrium is shifted strongly toward the deoxy complex. At a temperature near the freezing point of toluene, in a pure oxygen atmosphere, the oxygenated complex ratio was only 13%, giving an approximate value for the O_2 binding constant, K_{O_2}, of about 2×10^{-4} Torr^{-1} at about −90°C. Efforts to determine K_{O_2} more precisely using our well established electronic spectral method failed, giving values lower than the standard deviation. This very low dioxygen affinity is rather unexpected. For comparison, the K_{O_2} value for $[Co(Me_2GlyoxBF_2)_2]$ ranges from 1.8×10^{-3} at 0°C to 1.45×10^{-2} Torr^{-1} at −20°C,[4] and, as pointed out, the Co(III)/Co(II) redox potentials lead to the prediction that $[Co(AnthraGlyoxBF_2)_2]$ should have the higher dioxygen affinity.

The explanation lies in the relationship between the three equilibrium constants: K_B—the stability constant for binding the first axial ligand to give the 5-coordinate complex; K_{2B}—the stability constant for forming the bis(pyridine) adduct and K_{O_2} The absence of the ESR signal attributable to the dioxygen adduct in the case of the solution with a 10-fold excess of pyridine seems to indicate $K_{O_2} < K_{2B}$ and, possibly even $K_B \leqslant K_{2B}$. This is in contrast with $[Co(Me_2GlyoxBF_2)_2]$ for which only the mono-pyridine adduct was observed and the dioxygen binding experiments were conducted at 250-fold excess of pyridine.[4] It is suggested that this difference in behaviour arises because of the poor electron donor ability of the ligating nitrogen atoms of AnthraGlyox, which, in turn, is traceable to the electron withdrawing contributions of both the bridging BF_2 groups and the four benzene rings. The cobalt(II) complex displays its great tendency to accept the sixth Lewis base because of the resulting great need for electron density. Apparently the misleading electrochemical results actually reflect the difference in coordination numbers of the dominant species in solution.

The ligand developed for these studies was designed specifically to prevent μ-peroxo dimer formation by a BF_2-bridged bis(α-dioxime)cobalt(II) dioxygen carrier. Remarkably, the electronic factors appear to dominate and an exceptional competition between a second axial ligand and the O_2 molecule impairs the binding process. Clearly this phenomenon may occur with some generality and must be considered when evaluating correlations between the potentials of the metal ion couples and O_2 affinities. Unfortunately the present results mitigate against any inferences with respect to the success of the steric components in performing their proposed functions, *i.e.*, preventing the formation of μ-peroxo dimers.

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SUPPLEMENTARY MATERIALS

Tables of positional parameters, interatomic angles and distances, structural factor amplitudes and thermal parameters, and packing diagrams for both structures (78 pages) are available from DHB.

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