Bimetallic Reactivity. One-site Addition Two-metal Oxidation Reactions Using a Di-Co(II) Complex of a Binucleating Ligand with 5- and 6-Coordinate Sites

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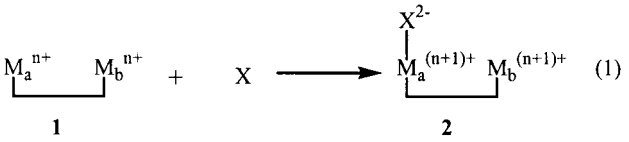
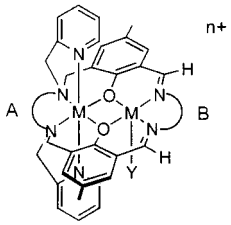
The preparation of an unsymmetrical binucleating ligand bearing a bridging oxadiazole ring flanked on one side by three ligands and on the other by four ligands is described. When bound to two metals, the ligand forms complexes where the metals are in 5- and 6-coordinate sites after the incorporation of an exogenous bridging ligand. A di-Co^{2+} complex of this ligand has been prepared containing a hydroxide bridge. The complex is readily oxidized to the di-Co^{3+} state by outer sphere electron transfer with ferrocenium ions. Addition of Br_2 or NO_2^+ to the di-Co^{2+} complex leads to the rapid formation of the di-Co^{3+} bromo or nitro complexes, respectively. The ligand characteristics which allow for double oxidation with ferrocenium ions and for the one-site addition two-metal oxidations with Br_2 and NO_2^+ are discussed in terms of mechanical coupling between the two metal sites.

Introduction

Multimetallic complexes have been the subject of numerous investigations, which have ranged from studies of their physical properties to searches for unique reactivity patterns.[1−4] Among the more appealing prospects is the possibility of deploying the reducing power of multiple metals to reduce substrates bound to one of the metals. For a bimetallic complex, such reactions can be referred to as "one-site addition two-metal oxidation reactions" and are illustrated in eq 1 for the bimetallic complex **1** using a two-electron oxidant, X, to give the double oxidized product, **2**.



Our previous work on bimetallic reactivity concerned the two bimetallic complexes, **3** and **4**.[5]



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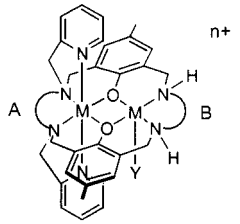

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The two complexes, **3** and **4**, bear the metal ions in 5- and 6-coordinate sites so that the substrate is directed to the 5-coordinate site. The chelate links, A and B, can be any combination of two and three methylene groups. Whereas Co^{2+} in the 6-coordinate site of **3** and **4** is readily oxidized to Co^{3+} in monometallic complexes and the Co^{2+} salen-like site of **3** is oxidized by O_2,[6] the di-Co^{2+} bimetallic complex of **3** is unreactive to O_2 or ferrocenium (fc^+) ions. The di-Co^{2+} complex of **4** is somewhat more reactive, either one or the other of the Co^{2+} ions in the two sites can be raised to the Co^{3+} state, but once one site is oxidized, the other site becomes deactivated to oxidation. This oxidative deactivation was ascribed principally to mechanical coupling, a phenomenon associated with conformational changes in the ligand which lead to ligand geometries unfavorable to metal oxidation.[5] Mechanical coupling in **3** and **4** is probably exacerbated by the macrocyclic framework and by the presence of a four-membered bridge, **5**. Other bridges,[7] such as **6** and **7**, would be expected to impose less strain, and we chose **7** for the system described here, which uses the oxadiazole bridge.

The ligand oxapymeH_2, **8**, was prepared, and one-site addition two-metal oxidation reactions of its di-Co^{2+} complex, **9**, were

(1) Suzuki, M.; Furutachi, H.; Okawa, H. *Coord. Chem. Rev.* **2000**, *200−202*, 227.
(2) Vigato, P. A.; Tamburini, S.; Fenton, D. E. *Coord. Chem. Rev.* **1990**, *106*, 25.
(3) Zanello, P.; Tamburini, S.; Vigato, P. L.; Mazzocchin, G. A. *Coord. Chem. Rev.* **1987**, *77*, 165.
(4) Gruber, S. J.; Harris, C. M.; Sinn, E. *Inorg. Chem.* **1968**, *7*, 268.
(5) (a) Fraser, C.; Johnston, L.; Rheingold, A. L.; Haggerty, B. S., Williams, C. K.; Whelan, J.; Bosnich, B. *Inorg. Chem.* **1992**, *31*, 1835. (b) Fraser, C.; Ostrander, R.; Rheingold, A. L.; White, C.; Bosnich, B. *Inorg. Chem.* **1994**, *33*, 324. (c) Fraser, C.; Bosnich, B. *Inorg. Chem.* **1994**, *33*, 338. (d) McCollum, D. G.; Hall, L.; White, C.; Ostrander, R.; Rheingold, A. L.; Whelan, J.; Bosnich, B. *Inorg. Chem.* **1994**, *33*, 924. (e) McCollum, D. G.; Fraser, C.; Ostrander, R.; Rheingold, A. L.; Bosnich, B. *Inorg. Chem.* **1994**, *33*, 2383. (f) McCollum, D. G.; Yap, G. P. A.; Rheingold, A. L.; Bosnich, B. *J. Am. Chem. Soc.* **1996**, *118*, 1365. (g) McCollum, D. G.; Yap, G. P. A.; Liable-Sands, L.; Rheingold, A. L.; Bosnich, B. *Inorg. Chem.* **1997**, *36*, 2230. (h) Bosnich, B. *Inorg. Chem.* **1999**, *38*, 2554.
(6) (a) Floriani, C.; Calderazzo, F. *J. Chem. Soc. A*: **1969**, 946. (b) Gall, R. S.; Schaefer, W. P. *Inorg. Chem.* **1976**, *15*, 2758.
(7) Steel, P. J. *Coord. Chem. Rev.* **1990**, *106*, 227.

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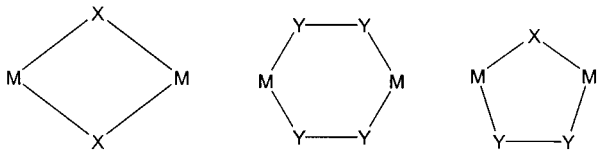
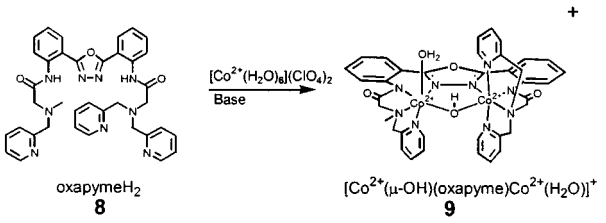


5 **6** **7**

investigated using the two-electron oxidants, Br_2 and NO_2^+.



oxapymeH$_2$ **8** $[Co^{2+}(\mu\text{-OH})(\text{oxapyme})Co^{2+}(H_2O)]^+$ **9**

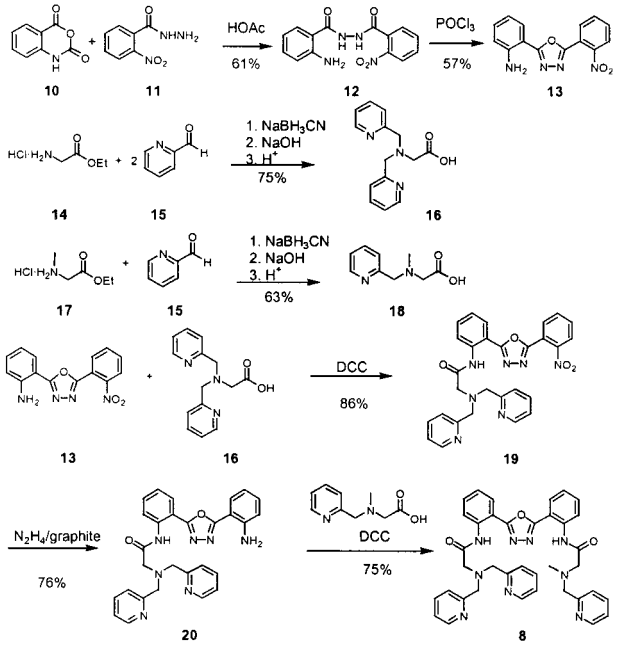
Ligand **8**, was selected for the following reasons. The oxadiazole[8] ring with the flanking *o*-aniline residues is readily prepared. To obtain nearly strain-free coordination, a six-membered chelate ring is required to flank the two oxadiazole bridging nitrogen atoms. To ensure that all six non-pyridine nitrogen atoms lie in one plane, five-membered chelate rings are required to emanate from the aniline nitrogen atoms. As a result of this planar nitrogen array, the terminal 2-methylene-pyridine groups will coordinate perpendicularly to this plane. With this combination of chelate ring sizes and the overall geometry, a single atom bridge such as OH^- is likely to be stable. The rigidity provided by the oxadiazole bridge and the presence of an exogenous OH^- bridge should conspire to minimize mechanical coupling between the two metal sites. The bond contraction which occurs when one metal is oxidized is likely to be localized to this site because the OH^- bridge can adjust its position without involving the binucleating ligand and the rigid oxadiazole ring is unlikely to transmit conformational changes from one site to the other.

Results

1. Ligand Synthesis. The synthetic procedure for the preparation of **8** is outlined in Scheme 1. Isatoic acid anhydride, **10**, was condensed with *o*-nitrobenzohydrazine, **11**, in acetic acid to give the hydrazide, **12**, which, in turn, was converted to the oxadiazole, **13**, by reaction with phosphoryl chloride. The two pyridine-containing arms of the binucleating ligand, **16** and **18**, were prepared by reductive amination of ethyl glycine hydrochloride, **14**, or ethyl sarcosine hydrochloride, **17**, with pyridine-2-carboxaldehyde, **15**. Coupling of **13** and **16** with DCC (dicyclohexylcarbodiimide) gave **19**. Reduction of the nitro group of **19** provided limited options; catalytic hydrogenation could lead to unwanted over-reduction, and conventional metal/acid reductions led to the formation of insoluble complexes. The hydrazine/graphite method[9] worked well provided the addition of hydrazine was controlled to suppress hydrazine attack at the oxadiazole ring. The product, **20**, is a crystalline solid, which was coupled with **18** using DCC to give the desired ligand, **8**, as a white crystalline solid. The synthetic procedure is technically simple, efficient, and multigram quantities of the ligand can be obtained.

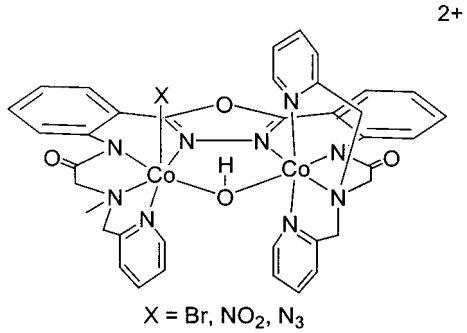
(8) Incarvito, C.; Rheingold, A. L.; Qin, C. J.; Gavrilova, A. L.; Bosnich, B. *Inorg. Chem.* **2001**, *40*, 1386.
(9) Han, B. H.; Shin, D. H.; Cho, S. Y. *Tetrahedron Lett*. **1985**, *26*, 6233.

Scheme 1



2. Complexes. The complex, $[Co^{2+}(\mu\text{-OH})(\text{oxapyme})Co^{2+}(H_2O)]ClO_4$, was prepared by sequential addition of 2 and then 1 equiv of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) to an acetonitrile solution of $[Co(H_2O)_6](ClO_4)_2$ and the ligand, oxapyme(H)$_2$. The light yellow solid slowly precipitates over 15 h to give nearly a quantitative yield of the product. We found that the successful isolation of the product is critically dependent on the counterion, the solvent, and the amount of DBU added. The complex, $[Co(\mu\text{-OH})(\text{oxapyme})Co(H_2O)]ClO_4$, is very sensitive to O_2 in CH_3CN, DMF (dimethylformamide), and methanol solutions. As a solid, it slowly turns brown when exposed to O_2. Its visible and near-IR electronic absorption spectrum shows a d−d absorption at 1015 nm (ϵ, 12 L mol^{-1} cm^{-1}). It is a 1:1 electrolyte in DMF solutions (Λ_M, 122 cm^2 Ω^{-1} mol^{-1}) and has a solid-state magnetic moment of 6.01 μ_B at 20 °C, indicating that both Co^{2+} ions are high-spin but are antiferromagnetically coupled.

In addition to this di-Co^{2+} complex, a number of di-Co^{3+} complexes were isolated and characterized. Their preparation will be described presently, but it is convenient to present their physical properties now. The di-Co^{3+} complexes are of the type **21**.



X = Br, NO_2, N_3

21

All three complexes show clean but complex ^{1}H NMR spectra in CD_3CN solutions and are consistent with the structure **21**. Perhaps the most notable feature of these spectra is the position of the proton of the μ-OH group. A sharp ^{1}H NMR signal is

Table 1. The Co^{2+}/Co^{3+} Redox Potentials of the Di-Co^{3+} Complexes, **21**, in Acetonitrile Solutions[a]

	5-coordinate site		6-coordinate site	
complex	$E_{1/2}$ (V)	ΔE (V)	$E_{1/2}$ (V)	ΔE (V)
$[Co(\mu\text{-OH})(oxapyme)CoN_3](PF_6)_2$	−0.01	0.138	−0.280	0.125
$[Co(\mu\text{-OH})(oxapyme)CoBr]Br_2$	+0.108	irr.	−0.291	0.152
$[Co(\mu\text{-OH})(oxapyme)CoNO_2](PF_6)_2$	−0.03	0.99	−0.320	0.140

[a] Supporting electrolyte, $TBAPF_6$ (0.1 M); scan rate, 50 $mVsec^{-1}$; glassy carbon working electrode; Ag/AgCl reference electrode.

Table 2. Crystallographic Data for $[Co(\mu\text{-OH})(oxapyme)CoN_3](PF_6)_2\cdot 3CH_3CN$ (**27**)

compound	**27**
formula	$C_{43}H_{43}Co_2F_{12}N_{15}O_4P_2$
fw	1241.72
space group	$P2_1/n$
a, Å	12.371(14)
b, Å	23.92(3)
c, Å	33.29(3)
β, deg	100.42(2)
V, Å^3	9686(18)
Z, Z'	8, 2
cryst color, habit	red plate
D(calc), g cm^{-3}	1.703
μ(Mo Kα), cm^{-1}	8.59
temp, K	173(2)
diffractometer	Siemens P4/CCD
radiation	Mo Kα ($\lambda = 0.71073$ Å)
$R(F)$, %[a]	9.50
$R(wF^2)$, %[a]	22.61

[a] Quantity minimized $= R(wF^2) = \sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]^{1/2}$; $R = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c)|$. $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + \max(F_o, 0)]/3$.

observed for the bromo perchlorate, the nitro hexafluorophosphate, and the azido hexafluorophosphate complexes at −1.69, +0.57, and −2.01 ppm, respectively. These values vary slightly with counterion and when the complexes are transferred to $(CD_3)_2SO$ solutions, but the shifts are mainly controlled by the nature of the X group in **21**. Addition of D_2O to CD_3CN solutions of the complexes causes slow proton exchange which can be accelerated by the addition of a base such as DBU, which, when in excess, appears to remove the proton to give the μ-oxo complex. All three complexes are 2:1 electrolytes in CH_3CN solutions consistent with their formulation.

Cyclic voltammetry of the $[Co(\mu\text{-OH})(oxapyme)Co(H_2O)]ClO_4$ complex gave neither cathodic nor anodic peaks in acetonitrile solution, but useful redox potentials could be obtained for the di-Co^{3+} complexes, **21**. These are listed in Table 1.

The potentials are assigned to the respective sites on the assumption that the 6-coordinate site will show less variation than the other site. If this redox partitioning is correct, the 6-coordinate site stabilizes Co^{3+} more than the X-ligand containing site. Other physical properties of these complexes are given in the Experimental Section.

3. Crystal Structure. It proved difficult to obtain crystals suitable for X-ray diffraction of the bromo and nitro complexes with a variety of counterions, although all gave what appeared to be well-formed crystals. Eventually, conditions were found which produced crystals of $[Co(\mu\text{-OH})(oxapyme)CoN_3](PF_6)_2\cdot 3CH_3CN$ from CH_3CN solutions by diffusion with MeOH. These crystals were suitable, but the scattering was weak. Crystallographic data are listed in Table 2 and selected bond lengths and angles are provided in Table 3. The structure is illustrated in Figure 1. Hydrogen atoms were not located. The overall structure is as expected, (Co(1)) occupies the 6-coordinate ligand site, and the 5-coordinate site contains (Co(2)) with the azido ligand. Two crystallographically independent molecules are found in the unit cell and have slightly different parameters. Those provided in Table 3 refer to one of the molecules. The metal−ligand bond lengths and angles are unexceptional. The metal−metal distance is 3.355(5) Å and the metal−μ-O−metal angle is 118.86(5)°. Because of the metal−metal separation and the structure, parallel ligands on each metal which lie perpendicular to the approximate ligand plane encompassing the oxadiazole ring tend to be in close contact. Thus, the two pyridine ligands bearing (N(2) and N(9)) experience steric interaction. The carbon atoms (C(12) and C(36)) are separated by only 3.377(5) Å. This contact may cause the chelate ring containing (C(30) and C(29)) to twist out of the mean molecular plane. The neighboring contacts of the type described may put limits on the substituents which can be placed at (C(12) and C(36)). Although hydrogen atoms were not located, the orientation of the μ-OH proton can give rise to "up−down" isomerism. The solution ^1H NMR spectra, however, show

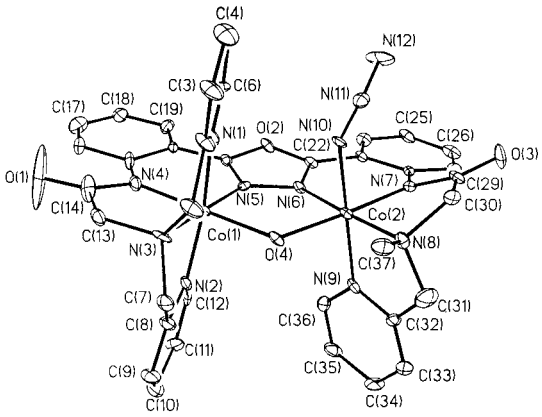


Figure 1. ORTEP diagram of $[Co(\mu\text{-OH})(oxapyme)CoN_3](PF_6)_2\cdot 3CH_3CN$ (**27**). Thermal ellipsoids are at 30% probability. Hydrogen atoms, counterions, and solvent molecules are removed for clarity.

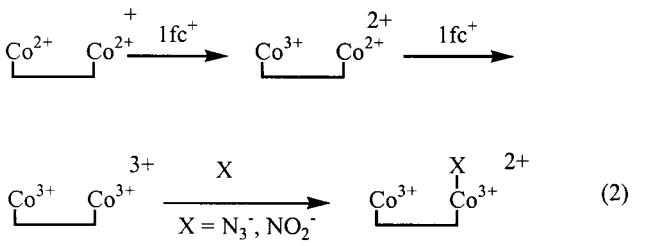
Table 3. Selected Bond Lengths and Angles for $[Co(\mu\text{-OH})(oxapyme)CoN_3](PF_6)_2\cdot 3CH_3CN$

Bond Lengths (Å)			
Co(1)−N(5)	1.873(5)	Co(2)−N(6)	1.837(5)
Co(1)−N(4)	1.916(5)	Co(2)−N(8)	1.921(6)
Co(1)−O(4)	1.921(5)	Co(2)−N(10)	1.930(5)
Co(1)−N(3)	1.927(5)	Co(2)−N(7)	1.931(5)
Co(1)−N(2)	1.932(5)	Co(2)−N(9)	1.965(5)
Co(1)−N(1)	1.949(5)	Co(2)−O(4)	1.964(4)
		Co(1)- - -Co(2)	3.355(5)

Angles (Deg)			
N(5)−Co(1)−N(4)	91.3(2)	N(6)−Co(2)−N(8)	176.59(19)
N(5)−Co(1)−O(4)	86.99(18)	N(6)−Co(2)− N(10)	90.0(2)
N(4)−Co(1)−O(4)	178.33(18)	N(8)−Co(2)−N(10)	89.2(2)
N(5)−Co(1)−N(3)	176.8(2)	N(6)−Co(2)−N(7)	91.2(2)
N(4)−Co(1)−N(3)	90.4(2)	N(8)−Co(2)−N(7)	85.6(2)
O(4)−Co(1)−N(3)	91.28(19)	N(10)−Co(2)−N(7)	91.9(2)
N(5)−Co(1)−N(2)	98.4(2)	N(6)−Co(2)−N(9)	95.1(2)
N(4)−Co(1)−N(2)	89.6(2)	N(8)−Co(2)−N(9)	85.9(2)
O(4)−Co(1)−N(2)	90.52(19)	N(10)−Co(2)−N(9)	174.1(2)
N(3)−Co(1)−N(2)	84.3(2)	N(7)−Co(2)−N(9)	90.9(2)
N(5)−Co(1)−N(1)	94.1(2)	N(6)−Co(2)−O(4)	87.56(18)
N(4)−Co(1)−N(1)	89.1(2)	N(8)−Co(2)−O(4)	95.68(18)
O(4)−Co(1)−N(1)	91.1(2)	N(10)−Co(2)−O(4)	85.88(19)
N(3)−Co(1)−N(1)	83.2(2)	N(7)−Co(2)−O(4)	177.48(19)
N(2)−Co(1)−N(1)	167.50(18)	N(9)−Co(2)−O(4)	91.39(19)
		Co(1)−O(4)−Co(2)	118.86(5)

only one signal for this proton, indicating a single isomer or a fast exchange of isomers.

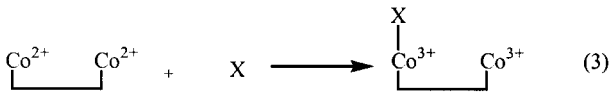
4. Oxidation with Ferrocenium Ions. Addition of 1 equiv of fc^+ to an acetonitrile solution of $[Co^{2+}(\mu\text{-OH})(\text{oxapyme})Co^{2+}(H_2O)]^+$ leads to the immediate decoloration of the fc^+ ion. We have been unable to isolate this product in a pure state because of its instability. On the basis of the fc^+ stoichiometry and the redox potentials (Table 1), the product is believed to be a mixed valence complex where the Co^{3+} is in the 6-coordinate site. Addition of either one more equivalent of fc^+ to this mixed valence species or two equivalents of fc^+ to the di-Co^{2+} complex leads to the immediate formation of a di-Co^{3+} species. Addition of N_3- or NO_2- to solutions of the fc^+ formed di-Co^{3+} species gave the $[Co^{3+}(\mu\text{-OH})(\text{oxapyme})Co^{3+}(N_3)]^{2+}$ or $[Co^{3+}(\mu\text{-OH})(\text{oxapyme})Co^{3+}(NO_2)]^{2+}$ ions in high yield. The initial di-Co^{3+} complex formed from the addition of 2 equiv of fc^+ was isolated in >90% purity, as estimated by its ^1H NMR spectrum, but attempts to purify the complex, believed to be the $[Co^{3+}(\mu\text{-OH})(\text{oxapyme})Co^{3+}(H_2O)]^{3+}$ ion, led to slow decomposition. These results are summarized in eq 2.



(2)

The oxidation reactions of $[Co^{2+}(\mu\text{-OH})(\text{oxapyme})Co^{2+}(H_2O)]^+$ with fc^+ are in sharp contrast to the results obtained for **3** and **4**, where oxidative deactivation was observed. The results suggest that one-site addition two-metal oxidations may be possible with this system using suitable two-electron oxidants.

5. One-site Addition Two-metal Oxidation Reactions. The one-site addition two-metal oxidation reaction for the $[Co^{2+}(\mu\text{-OH})(\text{oxapyme})Co^{2+}(H_2O)]^+$ ion is represented in eq 3, where X is a two-electron oxidant.



(3)

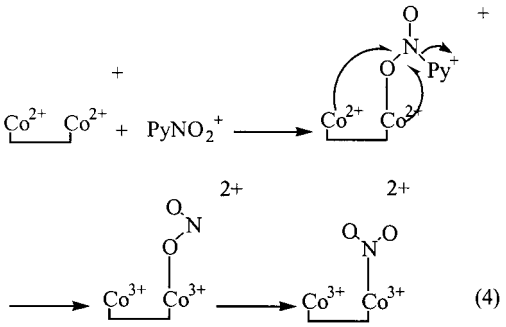
A number of two-electron oxidation substrates were investigated. These included the oxo-transfer reagent iodosobenzene, NO^+, NO_2^+, and Br_2. Iodosobenzene proved to be unreactive. Whereas NO^+ did react with the complex, the reaction led to complex, intractable mixtures of products which did not appear to contain the desired di-Co^{3+}−nitrosyl product. The reactions with NO_2^+ and Br_2 were clean, and the products were unambiguously identified.

Addition of one equivalent of Br_2 to the bimetallic complex $[Co^{2+}(\mu\text{-OH})(\text{oxapyme})Co^{2+}(H_2O)]ClO_4$ in acetonitrile solution at 25 °C led to the immediate formation of a red-brown solution. From this solution was isolated, in nearly quantitative yield, the di-Co^{3+} complex, $[Co^{3+}(\mu\text{-OH})(\text{oxapyme})Co^{3+}Br]^{2+}$, as either the ClO_4^- or PF_6^- salts. As expected, the product is diamagnetic, displays a sharp unshifted ^1H NMR spectrum, and behaves as a typical, stable Co^{3+} complex. The complexes **3** and **4**, by contrast, produce ill-defined products when reacted with Br_2 under similar conditions.

An analogous reaction occurs when the $[Co^{2+}(\mu\text{-OH})(\text{oxapyme})Co^{2+}(H_2O)]ClO_4$ complex in acetonitrile solution at −40 °C is allowed to react with 1 equiv of *N*-nitropyridinium tetrafluoroborate ($pyNO_2^+BF_4^-$).[10] Upon addition of $pyNO_2^+$, a rapid color change occurs from light yellow to a deep brown. From this solution, a nearly quantitative yield of the nitro complex, $[Co^{3+}(\mu\text{-OH})(\text{oxapyme})Co^{3+}(NO_2)](ClO_4)_2$, is isolated. The product is identical to the compound prepared from double fc^+ oxidation of $[Co^{2+}(\mu\text{-OH})(\text{oxapyme})Co^{2+}(H_2O)]ClO_4$ followed by the addition of NO_2^- ions described earlier.

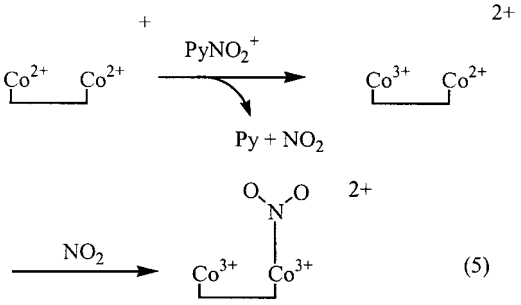
6. Mechanism of One-site Addition Two-metal Oxidation Reactions. Unlike the cases of the bimetallic complexes **3** and **4**, the $[Co^{2+}(\mu\text{-OH})(\text{oxapyme})Co^{2+}(H_2O)]^+$ ion undergoes the desired one-site addition two-metal oxidation reactions. Specifically, the results show that such reactions are thermodynamically allowed for the present system, but these observations do not speak to the mechanism of reaction.

Taking the $pyNO_2^+$ reaction as an example, two possible mechanisms can be envisioned, a quasiconcerted process or a stepwise radical pathway. The quasiconcerted process is outlined in eq 4.



(4)

This mechanism assumes that $pyNO_2^+$ adds first to the 5-coordinate site, and after successive electron transfers and the loss of pyridine, the nitrito complex is formed which converts to the nitro product.[11−13] In acetonitrile solution, nitration reactions using $pyNO_2^+$ appear to occur by the $pyNO_2^+$ ion and not by the free NO_2^+ ion.[10] The alternative stepwise mechanism is outlined in eq 5.



(5)

In this mechanism, the powerful[14] one-electron oxidizing agent, $pyNO_2^+$, oxidizes the Co^{2+} in the 6-coordinate site to give the mixed valence complex with the release of NO_2 (in equilibrium with N_2O_4).[15] The NO_2 then adds to the Co^{2+} in the 5-coordinate site to give the nitro product. In this stepwise

(10) Olah, G. A.; Narang, S. C.; Olah, J. A.; Pearson, R. L.; Cupas, C. A. *J. Am. Chem. Soc.* **1980**, *102*, 3507.
(11) Jackson, W. G.; Lawrence, G. A.; Lay, P. A.; Sargeson, A. M.; *J. Chem. Soc., Chem. Commun.* **1982**, 70.
(12) Murmann, R. K.; Taube, H. *J. Am. Chem. Soc.* **1956**, *78*, 4886.
(13) (a) Basolo, F.; Hammaker, G. S. *Inorg. Chem.* **1962**, *1*, 1. (b) Jackson, W. G.; Lawrence, G. A.; Lay, P. A.; Sargeson, A. M. *Inorg. Chem.* **1980**, *19*, 904.
(14) Lee, K. Y.; Kuchynka, D. J.; Kochi, J. K. *Inorg. Chem.* **1990**, *29*, 4196.
(15) Lee, K. Y.; Amatore, C.; Kochi, J. K. *J. Phys. Chem.* **1991**, *95*, 1285.

process, it is assumed that the more readily oxidized 6-coordinate site (see Table 1) is oxidized first and that the thermodynamically more stable mixed valence complex is formed before NO_2 addition. We are, however, unaware of any reported example of NO_2 addition to a Co^{2+} complex to give a $Co^{3+}-$nitro complex. Even at −40 °C, the $pyNO_2^+$ reaction appears to be complete upon mixing, and because of this we have employed an indirect method to ascertain the mechanism.

Addition of ∼2 equiv of NO_2 to the mixed valence complex $[Co^{3+}(\mu\text{-OH})(oxapyme)Co^{2+}(H_2O)]^{2+}$, in acetonitrile solution at −40 °C, gave a quantitative yield of $[Co^{3+}(\mu\text{-OH})(oxapyme)\text{-}Co^{3+}(NO_2)]^{2+}$. This experiment demonstrates that the second step of the stepwise mechanism shown in eq 5 is possible. Although this observation does not establish that a stepwise mechanism operates, the result is consistent with such a mechanism. At −40 °C in acetonitrile solution, both the NO_2^+ reaction with the di-Co^{2+} complex and the NO_2 reaction with the $Co^{3+}-Co^{2+}$ mixed valence species appear to occur upon mixing. If the one electron oxidation of the di-Co^{2+} complex is fast with NO_2^+, the overall rate of the reaction would be consistent with the stepwise process. The results, of course, do not exclude the operation of a very rapid quasiconcerted mechanism. The Br_2 reaction with the di-Co^{2+} complex also occurs upon mixing. The mechanism of this reaction was not investigated, but it also could be a stepwise radical process.

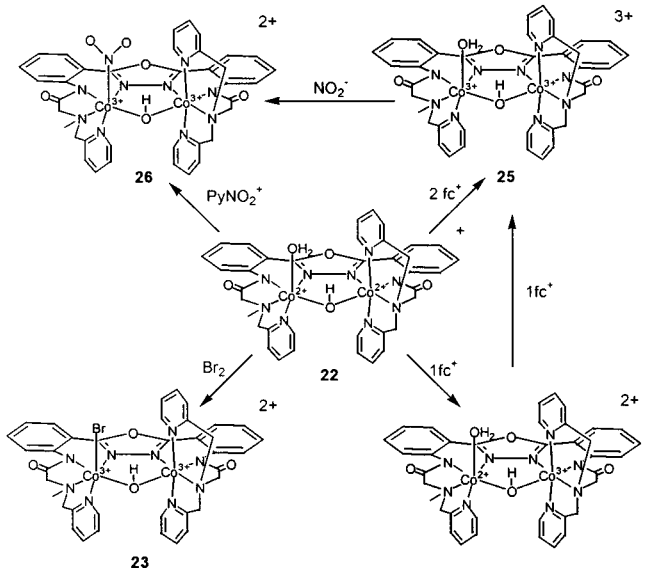
The $[Co^{3+}(\mu\text{-OH})(oxapyme)Co^{3+}(NO_2)]^{2+}$ ion does not show any IR bands in the 1110−1050 cm^{-1} region expected for a nitrito NO stretch;[16] the IR region where nitro bands would be expected is obscured by other absorptions. We conclude that the complex is most probably a nitro complex. It is interesting to note in this context that addition of 1 equiv of $pyNO_2^+$ to an acetonitrile solution of $[Co^{2+}(\mu\text{-OH})(oxapyme)Co^{2+}(H_2O)]ClO_4$ at −40 °C generates a visible absorption spectrum, within 1 min of mixing, which is almost identical to that observed for the independently prepared $[Co^{3+}(\mu\text{-OH})(oxapyme)Co^{3+}(NO_2)]^{2+}$ ion. This indicates that the $pyNO_2^+$ reaction leads directly to the nitro complex, provided that the nitrito to nitro isomerism does not occur on this time scale.

The reaction of 2 equiv of tetra-*n*-butylammonium bromide with the $[Co^{3+}(\mu\text{-OH})(oxapyme)Co^{3+}(H_2O)]^{3+}$ ion, in acetonitrile solution at 25 °C, leads to the complete formation of the $[Co^{3+}(\mu\text{-OH})(oxapyme)Co^{3+}Br]^{2+}$ ion within 1 min of mixing as judged by a comparison with the visible absorption spectrum of an independently prepared sample of the bromo complex. This result indicates that the Br_2 oxidation of $[Co^{2+}(\mu\text{-OH})\text{-}(oxapyme)Co^{2+}(H_2O)]^+$ and the Br^- substitution of $[Co^{3+}(\mu\text{-}OH)(oxapyme)Co^{3+}(H_2O)]^{3+}$ occur on similar time scales. Consequently, it is not possible to distinguish between an outer sphere radical process and an inner sphere electron transfer process for the Br_2 reaction with the $[Co^{2+}(\mu\text{-OH})(oxapyme)\text{-}Co^{2+}(H_2O)]^+$ ion.

Discussion

The oxidation reactions which $[Co(\mu\text{-OH})(oxapyme)Co\text{-}(H_2O)]ClO_4$ undergoes are illustrated in Scheme 2. It is clear from these results that the Co^{3+} state in both sites is readily accessible, and the results are in sharp contrast to previous work on the bimetallic complexes, **3** and **4**, where pronounced oxidative deactivation is observed. The fc^+ reactions show that outer sphere electron transfer can cause sequential oxidation of the metals in the two sites. Consequently, a strong one-electron oxidant such as NO_2^+ and possibly Br_2 could also engage in outer sphere electron transfer. This is probably the case for the one-site addition two-metal oxidation reactions observed here. Irrespective to the precise mechanisms of these reactions, the transformations shown in Scheme 2 establish that one-site addition two-metal oxidation reactions are thermodynamically accessible. As was supposed in the initial design of the ligand, it is probable that the rigid oxadiazole bridge serves to localize conformational changes, which ensue upon metal oxidation, to the site of oxidation. In the case of **4**, for example, oxidation of one metal causes deactivating conformational rearrangements which are transmitted to the other site. The design elements which were incorporated into the present binucleating system may serve to identify the features which are necessary to design systems which can engage in multielectron reactions.

Scheme 2



Experimental Section

General. Infrared spectra were recorded on a Nicolet 20SXB FTIR spectrometer, using Nujol mulls on NaCl disks for solid samples. Electronic absorption spectra were obtained with a Perkin-Elmer Lambda 6 UV/VIS Spectrophotometer and Cary 14DS UV/VIS/NIR spectrophotometer. Electronic absorption spectra at −40 °C were obtained using a CCD array spectrophotometer. Cyclic voltammetric measurements were carried out at 25 °C in dry acetonitrile under argon using a BAS 100 electrochemical analyzer (Bioanalytical Systems Inc.). The supporting electrolyte was tetrabutylammonium hexafluorophosphate ($TBAPF_6$, 0.1 M). A three-electrode assembly consisting of a platinum disk working electrode, a platinum auxiliary electrode, and a Ag/AgCl reference electrode was used. Elemental analyses were performed by Desert Analytics Laboratory, Arizona. Magnetic susceptibility was measured on a powdered sample using a Johnson Matthey magnetic susceptibility balance. Conductance measurements were made at 25 °C in dry acetonitrile using 1.0×10^{-3} M samples and a YSI Scientific Model 35 conductance meter. The ^1H NMR and ^{13}C NMR spectra were recorded either on Bruker DRX400 or DMX500 Fourier transform spectrometers. Chemical shifts (δ) are given in ppm and coupling constants (J) in Hertz. Melting points are uncorrected. All preparations of Co(II) complexes were conducted under N_2 using deaerated solvents and standard Schlenk techniques. Acetonitrile was dried over CaH_2, THF was dried over potassium/benzophenone ketyl, and ethyl ether was dried over sodium/benzophenone ketyl. TLC was carried out on precoated silica gel (Whatman, PE SIL G/UV). Silica gel 60 Å (Merck, 230−400 mesh) was used for flash chromatography.

Ligand Synthesis. 2-Amino-benzoic acid *N′*-(2-nitro-benzoyl)-hydrazide (12). Isatoic anhydride (5.21 g, 30.65 mmol) and *o*-

(16) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds,* 4th ed.; John Wiley & Sons: New York, 1986; p 224.

nitrobenzohydrazide (5.66 g, 30.65 mmol) were suspended in glacial acetic acid (15 mL). The suspension was immersed in an oil bath preheated to 140 °C. A clear brown solution formed within 5 min, which started to form a precipitate after 15 min of heating. The suspension was kept at 120 °C for 1 h, after which time it solidified. It was cooled to room temperature, and 40 mL of ethanol was added. The mixture was sonicated and then refluxed for 30 min. The yellow solid was filtered, thoroughly washed with ethanol and hexane, and dried in air to give the product (5.63 g, 61% yield). Mp 217−218 °C. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 10.53 (s, 1H), 10.33 (s, br, 1H), 8.08 (d, 1H, J = 8.07 Hz), 7.86 (t, 1H, J = 7.38 Hz), 7.76 (m, 2H), 7.62 (d, 1H, J = 8.04 Hz), 7.18 (t, 1H, J = 7.93 Hz), 6.72 (d, 1H, J = 7.79 Hz), 6.53 (t, 1H, J = 7.91 Hz), 6.47 (s, br, 2H).

2-[5-(2-Nitro-phenyl)-[1,3,4]oxadiazol-2-yl]-phenylamine (13). 12 (3.3 g, 10.9 mmol) was suspended in phosphoryl chloride (15 mL) and was slowly heated to reflux over 40 min. During the warming period, the mixture turned into a thick white paste and then dissolved into a brown solution. It was refluxed for 4 h, after which time the phosphoryl chloride was removed under vacuum, and to the resulting black oily residue was carefully (violent fuming!) added water (25 mL) while it was still hot. After sonication, a brown crystalline precipitate formed. The suspension was neutralized with concentrated aqueous ammonia over the period of 2 h. The precipitate was filtered, washed with water, and was recrystallized from hot DMF solution by addition of water. The resulting brown solid was passed through a short silica gel column (16 g) with methylene chloride. The resulting yellow solid was recrystallized from methylene chloride−hexane to afford analytically pure product as yellow needles (1.72 g, 57% yield). Mp 174−176 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.19 (m, 2H), 7.94 (m, 2H), 7.64 (d, 1H, J = 9.37 Hz), 7.30 (t, 1H, J = 8.41 Hz), 6.93 (d, 1H, J = 8.32 Hz), 6.78 (s, br, 2H), 6.69 (t, 1H, J = 7.46 Hz). Anal. Calcd for $C_{14}H_{10}N_4O_3$: C, 59.58; H, 3.57; N, 19.85. Found: C, 59.26; H, 3.42; N, 19.73.

(Bis-pyridine-2-ylmethyl-amino)-acetic acid (16). Ethyl glycine hydrochloride (0.5 g, 3.58 mmol) was dissolved in methanol (5 mL) and cooled to 0 °C. To this solution was added pyridine-2-carboxaldehyde (0.75 mL, 7.88 mmol). Then solid sodium cyanoborohydride (0.39 g, 5.82 mmol) was slowly added to this solution at 0 °C. The resulting orange suspension was stirred at room temperature for 18 h. Then 1 mL of HCl (12.1 N) was carefully added to it, and the suspension was stirred for 30 min, whereafter all of the solvent was removed under vacuum. The solid residue was neutralized with saturated sodium bicarbonate solution and extracted into methylene chloride. After the organic layer was dried over $MgSO_4$, the solvent was removed under vacuum to afford 1 g of a red oil, which was chromatographed on silica gel (20 g) with 2% triethylamine in ethyl acetate as the eluant. Pure ester was obtained as an orange oil (0.82 g, 80% yield). ^{1}H NMR (C_6D_6, 500 MHz): δ 8.44 (d, 2H, J = 5.95 Hz), 7.50 (m, 2H), 7.12 (t, 2H, J = 7.43 Hz), 6.62 (t, 2H, J = 6.00 Hz), 4.12 (s, 4H), 3.89 (q, 2H, J = 6.96 Hz), 3.44 (s, 2H), 0.88 (t, 3H, J = 7.17 Hz). To the obtained ester (0.82 g, 2.9 mmol) 1 N NaOH solution (3 mL) was added at room temperature. The resulting orange suspension was stirred for 1 h and washed with benzene (10 mL). The aqueous layer was neutralized with 1N HCl (3 mL) and stirred at room temperature for 30 min. It was washed with methylene chloride (10 mL), and the aqueous solution was evaporated to dryness in vacuo. The residue was slurried with absolute ethanol (5 mL) and sonicated. The precipitate of NaCl was removed by filtration, and the filtrate was concentrated under vacuum. The residue was dissolved in methylene chloride (15 mL) and dried over magnesium sulfate. The product (pure by ^{1}H NMR spectroscopy) was obtained upon filtration and evaporation of the solvent (0.7 g, 75% overall yield). ^{1}H NMR (D_2O, 400 MHz): δ 8.35 (dd, 2H, J = 4.35 and 1.46 Hz), 7.75 (td, 2H, J = 7.88 and 1.78 Hz), 7.31 (m, 4H), 4.26 (s, 4H), 3.57 (s, 2H).

(Methyl-pyridine-2-ylmethyl-amino)-acetic acid (18). Ethyl sarcosine hydrochloride (12.28 g, 80 mmol) was dissolved in methanol (400 mL), at 0 °C, and pyridine-2-carboxaldehyde (8.36 mL, 88 mmol) in methanol (40 mL) was added. Solid sodium cyanoborohydride (4.34 g, 68.9 mmol) was added slowly to the solution at 0 °C. The clear yellow solution was stirred at room temperature for 18 h. Then 16.2 mL of HCl (12.1 N) was carefully added at room temperature, and the yellow suspension was stirred for 2 h until the bubbling subsided. The solvent was removed under vacuum, and the residue was basified with saturated aqueous sodium bicarbonate and extracted with methylene chloride. After the organic layer was dried over magnesium sulfate and evaporated in vacuo, the resulting orange oil (14.8 g) was chromatographed on silica gel (250 g) with 2% triethylamine in ethyl acetate as an eluant. The ester was obtained as a pale yellow oil (10.56 g, 63% yield). ^{1}H NMR (DMSO-d_6, 500 MHz): δ 8.46 (d, 1H, J = 5.04 Hz), 7.75 (td, 1H, J = 7.67 and 1.49 Hz), 7.43 (d, 1H, J = 7.88 Hz), 7.24 (t, 1H, J = 5.07 Hz), 4.08 (q, 2H, J = 7.19 Hz), 3.75 (s, 2H), 3.33 (s, 2H), 2.28 (s, 3H), 1.18 (t, 3H, J = 7.05 Hz). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 170.34, 158.77, 148.98, 148.30, 122.81, 122.50, 61.87, 59.67, 57.42, 41.52, 14.04. To this ester (10.56 g, 50.76 mmol) at 0 °C was added 1 N NaOH solution (56 mL). The orange suspension was stirred for 3 h at room temperature, was washed with benzene (200 mL), and was neutralized with 1 N HCl (56 mL). After being stirred for 30 min, the solution was washed with methylene chloride (200 mL), and the aqueous phase was evaporated under vacuum to dryness. The residue was slurried with absolute ethanol, sonicated, and filtered. The filtrate was evaporated to give a yellow oil (9.1 g, 63% overall yield), which was found by ^{1}H NMR spectroscopy to be the pure product. ^{1}H NMR (D_2O, 400 MHz): δ 8.45 (d, 1H, J = 4.86 Hz), 7.78 (td, 1H, J = 7.74 and 1.69 Hz), 7.41 (d, 1H, J = 7.85 Hz), 7.34 (m, 1H), 4.33 (s, 2H), 3.63 (s, 2H), 2.76 (s, 3H).

2-(Bis-pyridin-2-ylmethyl-amino)-*N*-{2-[5-(2-nitro-phenyl)-[1,3,4]-oxadiazol-2-yl]-phenyl}-acetamide (19). To a solution of **13** (8.4 g, 29.78 mmol) in dry methylene chloride (210 mL) was added a solution of **16** (10.71 g, 41.7 mmol) in dry methylene chloride (60 mL). To this solution at 0 °C, DCC (dicyclohexylcarbodiimide, 8.6 g, 41.7 mmol) was added in small portions. The orange solution became cloudy within 5 min. The suspension was stirred overnight at room temperature by which time it had become dark brown. It was filtered, washed with methylene chloride, and the filtrate was evaporated under vacuum to afford 21 g of a black residue, which was chromatographed on silica gel (440 g in 2 columns) with 5% triethylamine in ethyl acetate as an eluant, and methylene chloride as a loading solvent. The product was obtained as a dark oil (14.6 g). It can be crystallized by addition of ethanol followed by hexane to afford a cream powder (13.36 g, 86% yield). Mp 131−132 °C. ^{1}H NMR (C_6D_6, 500 MHz): δ 11.87 (s, 1H), 9.21 (d, 1H, J = 8.91 Hz), 8.40 (d, 2H, J = 5.79 Hz), 7.91 (d, 2H, J = 7.48 Hz), 7.62 (dd, 1H, J = 7.97 and 1.41 Hz), 7.55 (dd, 1H, J = 7.18 and 1.27 Hz), 7.44 (td, 2H, J = 7.68 and 1.50 Hz), 7.27 (dd, 1H, J = 8.01 and 0.9 Hz), 7.14 (m, 1H), 6.95 (t, 1H, J = 7.48 Hz), 6.83 (t, 1H, J = 7.9 Hz), 6.71 (m, 3H), 3.99 (s, 4H), 3.64 (s, 2H). ^{13}C NMR (C_6D_6, 125 MHz): δ 170.63, 164.69, 160.08, 158.77, 149.25, 148.85, 139.26, 136.37, 133.22, 132.40, 132.31, 130.83, 128.30, 124.38, 124.08, 122.99, 122.18, 121.27, 117.80, 110.21, 61.37, 60.07. Anal. Calcd for $C_{28}H_{23}N_7O_4$: C, 64.48; H, 4.45; N, 18.80. Found: C, 64.58; H, 4.29; N, 18.70.

***N*-{2-[5-(2-Amino-phenyl)-[1,3,4]oxadiazol-2-yl]-phenyl}-2-(bis-pyridin-2-ylmethyl-amino)-acetamide (20).** To a solution of **19** (10.14 g, 19.46 mmol) in dry dioxane (34 mL), at 50 °C under N_2 atmosphere, was added 1-2 μ graphite (5.4 g) followed by hydrazine monohydrate (1.88 mL, 38.9 mmol). The resulting black suspension was refluxed for 18 h under N_2. After being cooled to 30 °C, it was filtered through Celite (30 g), and the solid was washed with excess of methylene chloride. The solvent was removed under vacuum, and the solid residue was recrystallized twice from ethanol−hexane to afford analytically pure product as an off-white powder (7.26 g, 76% yield). Mp 153−154 °C. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 11.64 (s, 1H), 8.61 (d, 1H, J = 8.41 Hz), 8.44 (dd, 2H, J = 4.86 and 1.58 Hz), 8.16 (dd, 1H, J = 7.91 and 1.60 Hz), 7.92 (dd, 1H, J = 7.98 and 1.49 Hz), 7.85 (d, 2H, J = 7.88 Hz), 7.67 (td, 2H, J = 8.52 and 1.75 Hz), 7.56 (t, 1H, J = 7.21 Hz), 7.32 (m, 2H), 7.20 (m, 2H), 6.95 (d, 1H, J = 7.96 Hz), 6.88 (s, 2H), 6.73 (t, 1H, J = 7.79 Hz), 3.92 (s, 4H), 3.49 (s, 2H). Anal. Calcd for $C_{28}H_{25}N_7O_2$: C, 68.42; H, 4.98; N, 19.95. Found: C, 67.96; H, 5.05; N, 19.80.

2-(Bis-pyridin-2-ylmethyl-amino)-*N*-[2-(5-{2-[2-(methyl-pyridin-2-ylmethyl-amino)-acetylamino]-phenyl}-[1,3,4]oxadiazol-2-yl)-phenyl]-acetamide (oxapyme(H)$_2$) (8). To a solution of **20** (6.97 g, 14.19 mmol) in dry methylene cholride (50 mL) was added a solution of **18**

(5.11 g, 28.38 mmol) in dry methylene chloride (135 mL). DCC (5.86 g, 28.38 mmol) was added to this solution in small portions at 0 °C. A bright red turbid mixture formed within 5 min. It was stirred for 18 h at room temperature, was filtered, and was washed with methylene chloride. The solvent was removed under vacuum to afford a brown residue (14 g), which was chromatographed on silica gel (250 g) with 3% triethylamine in ethyl acetate as an eluant and methylene chloride as a loading solvent. Upon removal of the solvent, the product was obtained as a yellowish solid (9 g). It was recrystallized from hot benzene−hexane to afford white crystals of analytically pure ligand (6.9 g, 75% yield). Mp 136−137 °C. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 11.81 (s, 1H), 11.76 (s, 1H), 8.45 (d, 1H J = 8.86 Hz), 8.77 (d, 1H, J = 8.93 Hz), 8.45 (d, 2H, J = 5.58 Hz), 8.42 (d, 1H, J = 5.46 Hz), 8.16 (dd, 1H, J = 8.29 and 1.44 Hz), 8.12 (dd, 1H, J = 7.86 and 1.45 Hz), 7.71 (d, 2H, J = 8.00 Hz), 7.57 (m, 6H), 7.29 (m, 2H), 7.06 (m, 3H), 3.96 (s, 4H), 3.69 (s, 2H), 3.47 (s, 2H), 3.29 (s, 2H), 2.34 (s, 3H). ^{13}C NMR (CD_2Cl_2, 125 MHz): δ 171.05, 170.98, 163.28, 163.11, 158.58, 158.30, 149.46, 149.44, 149.36, 149.34, 138.59, 138.54, 136.66, 133.24, 133.21, 128.69, 128.62, 123.91, 123.78, 123.49, 122.53, 122.44, 121.56, 121.54, 111.49, 111.35, 63.87, 61.96, 61.26, 58.88, 43.88. Anal. Calcd for $C_{37}H_{35}N_9O_3$: C, 67.97; H, 5.39; N, 19.28. Found: C, 67.61; H, 5.25; N, 19.24.

Syntheses of the Complexes. [Co(μ-OH)(oxapyme)Co(H_2O)]ClO_4 (22). The ligand oxapyme(H_2) (0.98 g, 1.5 mmol) was suspended in dry acetonitrile (30 mL) under N_2, and DBU (0.47 mL, 3 mmol) was added. To the resultant white suspension was added $Co(ClO_4)_2 \cdot 6H_2O$ (1.13 g, 3.075 mmol) in dry acetonitrile (4 mL) to give a dark red-brown solution. After stirring the solution for 10 min under N_2 at 25 °C, more DBU (0.26 mL, 1.65 mmol) was added, whereupon a dark yellow-brown solution formed. A yellow solid started to precipitate upon stirring the solution for 10 min. The mixture was continuously stirred for 15 h. The yellow solid was collected and washed with dry and deaerated acetonitrile (4 mL). Finally, the solid was dried under argon. The solid was stored in a drybox filled with argon (1.31 g, 97% yield). Λ_M = 122 cm^2 Ω^{-1} mol^{-1} (deaerated CH_3CN). μ_{eff} (20 °C) = 6.01 μ_B. UV−Vis−NIR [λ_{max} in nm (ϵ in L mol^{-1} cm^{-1}) in DMF]: 369 (11406), 1015 (11). IR: 3582 (H_2O), 1096, 1085 (ClO_4). Anal. Calcd for $C_{37}H_{36}ClCo_2N_9O_9$: C, 49.61; H, 4.01; N, 13.94. Found: C, 49.31; H, 3.97; N, 13.95.

[Co(μ-OH)(oxapyme)CoBr]$(ClO_4)_2 \cdot 2H_2O$ (23). Complex **22** (0.18 g, 0.20 mmol) was dissolved in dry acetonitrile (120 mL) at 25 °C to give a light orange solution after 1.5 h of stirring. Bromine (10.3 μL, 0.2 mmol) was added to the solution via a syringe in one portion to give a red−brown solution immediately. The solution was stirred for 30 min, and then the solvent was evaporated. The resultant light-brown solid was slurried in methanol (5 mL), was filtered, was washed with methanol (2 × 2 mL) then ether, and was dried under vacuum (0.14 g, 64% yield). The ^{1}H NMR spectrum indicated that the compound was pure. The solid was dissolved in acetonitrile (1 mL) and added to the $NaClO_4$ (0.2 g) solution in methanol (10 mL). The precipitated yellow−brown solid was collected by filtration, and the procedure was repeated one more time. The yellow−brown solid (0.11 g) was recrystallized from a mixture of dry acetonitrile (2 mL) and methanol (2 mL) by vapor diffusion of methanol. The product was obtained as dark-brown needlelike crystals. Λ_M = 249 cm^2 Ω^{-1} mol^{-1} (CH_3CN). ^{1}H NMR (400 MHz, CD_3CN): δ 8.94 (1 H, d, J = 8.86 Hz), 8.79 (1 H, d, J = 8.89 Hz), 8.57 (1 H, d, J = 8.04), 8.53 (1 H, d, J = 8.04 Hz), 8.00 (1 H, t, J = 6.88 Hz), 7.86 (1 H, d, J = 5.74 Hz), 7.67−7.52 (7 H, m), 7.38−7.33 (3 H, m), 7.26−7.22 (2 H, m), 7.16 (1 H, t, J = 6.77 Hz), 7.05 (1 H, t, J = 6.77 Hz), 5.51 (1 H, d, J = 17.08 Hz), 5.44 (1 H, d, J = 15.76 Hz), 5.07 (1 H, d, J = 15.97 Hz), 4.89 (1 H, d, J = 17.08 Hz), 4.68 (1 H, d, J = 16.19 Hz), 4.35 (1 H, d, J = 17.77 Hz), 4.25 (1 H, d, J = 16.01 Hz), 4.05 (1 H, d, J = 17.60 Hz), 4.03 (1 H, d, J = 17.75 Hz), 3.34 (1 H, d, J = 17.62 Hz), 3.25 (3 H, s), −1.69 (1 H, s). ^{13}C NMR (400 MHz, CD_3CN): δ 178.45, 165.97, 165.39, 162.69, 161.88, 160.03, 153.40, 153.22, 151.99, 148.07, 145.97, 142.73, 142.19, 142.05, 137.64, 136.96, 130.18, 129.42, 129.00, 128.59, 128.38, 128.16, 126.86, 126.14, 125.69, 124.63, 123.84, 123.49, 118.51, 108.42, 107.14, 72.46, 70.06, 69.71, 69.68, 69.12, 55.47. Anal. Calcd for $C_{37}H_{38}BrCl_2Co_2N_9O_{14}$: C, 40.35; H, 3.48; N, 11.45, Br, 7.25. Found: C, 40.51; H, 3.58; N, 11.62, Br, 6.76.

[Co(μ-OH)(oxapyme)CoBr]$Br_2 \cdot 5H_2O$ (24). The bromide salt of the bromo complex was obtained by loading the complex **23** (0.21 g, 0.91 mmol) onto an Amberlite 401−10N anion-exchange resin column (Br^- form, generated with saturated NaBr aqueous solution followed by eluting with water (4 column volumes) and methanol (4 column volumes)). The complex was eluted with methanol (50 mL). The eluant was evaporated to dryness, and the resulting solid was redissolved in methanol (3 mL). The solution was left overnight to give dark brown blocks (0.1 g, 45% yield). UV−Vis [λ_{max} in nm (ϵ in L mol^{-1} cm^{-1}) in CH_3CN]: 241 (58320), 301 (sh, 22538), 317 (sh, 18220), 381 (sh, 11530), ∼620 (sh, 318), ∼700 (sh, 210). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.84 (1 H, d, J = 8.77 Hz), 8.74 (1 H, d, J = 9.52 Hz), 8.72 (1 H, d, J = 8.71 Hz), 8.68 (1 H, d, J = 8.01 Hz), 8.12−8.06 (2 H, m), 7.93 (1 H, d, J = 5.63 Hz), 7.88 (1 H, d, J = 5.76 Hz), 7.78−7.69 (3 H, m), 7.57−7.53 (2 H, m), 7.41−7.29 (5 H, m), 7.13 (1 H, t), 7.08 (1 H, t), 5.97 (1 H, d, J = 16.94 Hz), 5.57 (1 H, d, J = 15.78 Hz), 5.15 (1 H, d, J = 15.93 Hz), 5.00 (1 H, d, J = 16.94 Hz), 4.83 (1 H, d, J = 15.77 Hz), 4.60 (1 H, d, J = 18.13 Hz), 4.45 (1 H, d, J = 15.98 Hz), 4.22 (1 H, d, J = 17.62 Hz), 4.18 (1 H, d, J = 17.89 Hz), 3.40 (3 H, d, J = 17.80 Hz), 3.25 (1 H, s), − 1.75 (1 H, s). Anal. Calcd for $C_{37}H_{44}Br_3Co_2N_9O_9$: C, 39.81; H, 3.97; N, 11.29. Found: C, 39.25; H, 3.73; N, 11.05.

[Co(μ-OH)(oxapyme)Co(H_2O)]$(PF_6)_2ClO_4$ (25). The complex **22** (0.180 g, 0.20 mmol) was dissolved in dry acetonitrile (120 mL) to give light orange solution after stirring for 1.5 h. A solution of $fcPF_6$ (0.136 g, 0.41 mmol) in dry acetonitrile (3 mL) was added to it to immediately give a greenish solution. After stirring the solution for 1 h, the solvent was evaporated. The solid was then slurried in dry ether (200 mL) to remove the ferrocene. The solid was collected, was washed with dry ether and hexane, and was dried under vacuum. A greenish−brown powder (0.26 g, quantitative yield) was isolated which was >90% pure by NMR. The complex slowly decomposed when attempts were made to recrystallize it from acetonitrile and ether. This material was used for preparation of the di-Co^{3+} complexes which follow. IR: 1087 (ClO_4^-), 840 (PF_6^-). ^{1}H NMR (400 MHz, CD_3CN): δ 8.91 (1 H, d, J = 8.83 Hz), 8.70 (1 H, d, J = 8.86 Hz), 8.62 (2 H, d, J = 8.53 Hz), 8.09 (1 H, t, J = 7.65 Hz), 7.87 (1 H, d, J = 5.69 Hz), 7.82−7.63 (5 H, m), 7.58 (1 H, t, J = 7.25 Hz), 7.46−7.39 (5 H, m), 7.29 (1 H, d, J = 7.79 Hz), 7.19 (1 H, t, J = 6.75 Hz), 7.08 (1 H, t, J = 6.75 Hz), 5.55 (1 H, d, J = 16.40 Hz), 5.48 (1 H, d, J = 16.03 Hz), 5.17 (1 H, d, J = 16.78 Hz), 4.93 (1 H, d, J = 16.44 Hz), 4.73 (1H, d, J = 16.56 Hz), 4.42 (1 H, d, J = 16.81 Hz), 4.36 (1 H, d, J = 17.81 Hz), 4.14 (1 H, d, J = 17.49 Hz), 4.04 (1 H, d, J = 17.83 Hz), 3.54 (1 H, d, J = 17.51 Hz), 3.18 (3 H, s), − 1.10 (1 H, s).

[Co(μ-OH)(oxapyme)Co(NO_2)]$(PF_6)_2$ (26). Complex **25** (0.26 g, 90% pure, 0.196 mmol) was dissolved in dry acetonitrile (4 mL) and added to a solution of $NaNO_2$ (2.1 mmol, 14.9 mg) in methanol (5 mL) and dry acetonitrile (5 mL). The red−brown solution was stirred at 25 °C overnight. The solution was reduced to ∼2 mL volume and added to a solution of NH_4PF_6 (1.6 mmol, 0.26 g) in methanol (5 mL). After removing the solvent, the resultant solid was slurried in methanol (5 mL), was collected, and was washed with methanol (4 mL). The solid was redissolved in dry acetonitrile (4 mL), and the solution was added to a solution of NH_4PF_6 (0.26 g, 1.6 mmol) in methanol (5 mL). After removing the solvent, the solid was slurried in water (5 mL). The solid was collected and washed with water (2 × 3 mL), methanol (2 × 3 mL), ether (2 × 5 mL), and pentane (2 × 5 mL). The pale yellow−green powder was dried under vacuum (0.17 g, 94% yield). The complex was pure by ^{1}H NMR spectroscopy. The solid was recrystallized from a mixture of dry acetonitrile (1 mL) and methanol (4 mL) by diffusion with methanol for 2 days to give a crystalline solid (60 mg, 33% yield). The ^{1}H NMR spectrum of the solid in deuterated acetonitrile shows a signal at 0.57 ppm which can be slowly exchanged by deuterium oxide. Λ_M = 256 cm^2 Ω^{-1} mol^{-1} (CH_3CN). UV−Vis [λ_{max} in nm (ϵ in L mol^{-1} cm^{-1}) in CH_3CN]: 302 (21172), 313 (shoulder, 19990), 376 (9746), 415 (12027), ∼496 (shoulder, 840), 580 (470). IR: 1640, 1619, 1603, 1584, 1545, 1461, 1377, 1366, 1352, 1317, 1313, 1300, 1265, 1167, 844 (PF_6^-), 768, 746, 722, 705. ^{1}H NMR (400 MHz, CD_3CN): δ 8.94 (1 H, d, J = 8.81 Hz), 8.80 (1 H, d, J = 8.91 Hz), 8.52−8.50 (2 H, m), 8.04 (1 H, d, J = 7.92 Hz), 7.75 (1 H, d, J = 7.75 Hz), 7.69−7.62 (4 H, m), 7.56−7.51 (2 H, m), 7.42−7.33

(4 H, m), 7.26−7.23 (2 H, m), 7.14 (1 H, t), 7.06 (1 H, t), 5.62 (1 H, d, $J = 16.90$ Hz), 5.43 (1 H, d, $J = 15.81$ Hz), 4.95 (1 H, d, $J = 15.84$ Hz), 4.93 (1 H, d, $J = 16.91$ Hz), 4.69 (1 H, d, $J = 15.78$ Hz), 4.35 (1 H, d, $J = 17.76$ Hz), 4.09 (1 H, d, $J = 17.50$ Hz), 4.05 (1 H, d, $J = 15.50$ Hz), 3.88 (1 H, d, $J = 17.64$ Hz), 3.26 (1 H, d, $J = 17.64$ Hz), 2.74 (3 H, s), 0.57 (1 H, s). ^{13}C NMR (400 MHz, CD_3CN): δ 178.49, 178.01, 165.611, 165.05, 162.40, 162.05, 159.54, 152.75, 151.97, 151.84, 148.15, 146.08, 142.82, 142.35, 142.18, 137.90, 137.22, 130.03, 129.44, 129.00, 128.51, 128.00, 127.61, 126.00, 125.81, 124.79, 123.97, 123.64, 118.49, 108.11, 106.73, 71.53, 69.58, 69.51, 69.33, 69.06, 52.00. Electrospray MS: m/z 416.1 $[M]^{2+}$.[17]Anal. Calcd for $C_{37}H_{34}Co_2F_{12}N_{10}O_6P_2$: C, 39.59; H, 3.05; N, 12.48. Found: C, 39.18; H, 2.95; N, 12.54.

[Co(μ-OH)(oxapyme)CoN$_3$](PF$_6$)$_2$·H$_2$O (27). The complex **25** (0.4 g, 90% pure, 0.3 mmol) was dissolved in dry acetonitrile (10 mL) followed by the addition of an NaN_3 (23.4 mg, 97% pure, 3.6 mmol) solution in methanol (10 mL) to give a dark brown solution immediately. The solution was stirred at 25 °C for 15 h. A NH_4PF_6 (0.39 g, 2.4 mmol) solution in methanol (10 mL) was added, and then the solvent was removed. The solid was slurried in methanol (10 mL), was collected, and was washed with methanol (2 mL). The solid was then dissolved in dry acetonitrile (6 mL) and filtered. The filtrate was added to a solution of NH_4PF_6 (0.39 g, 2.4 mmol) in methanol (10 mL). The solvent was then removed, and the solid was slurried in methanol (10 mL). The solid was collected and washed with methanol (3 × 2 mL), ether (3 × 4 mL), and pentane (3 × 4 mL). The pale yellow−brown solid was dried under vacuum (0.27 g). The ^{1}H NMR spectrum shows that the product is pure. The solid was then recrystallized from a mixture of dry acetonitrile (5 × 1 mL) and methanol (10 mL) by diffusion of methanol over 3 days to give thin dark brown plates (0.22 g, 65% yield). These crystals were found to be suitable for X-ray structure determination. $\Lambda_M = 240$ cm^2 Ω^{-1} mol^{-1} (CH_3CN). IR: 2027 (N_3); 844 (PF_6^-). UV−Vis [λ_{max} in nm (ϵ in L mol^{-1} cm^{-1}) in CH_3CN]: 302 (20297), 374 (shoulder, 8840), 414 (11461), 500 (shoulder, 880), ∼600 (shoulder, 293). ^{1}H NMR (400 MHz, CD_3CN): δ 8.84 (1 H, d, $J = 8.15$ Hz), 8.58 (2H, s), 8.43 (1 H, d, $J = 7.40$ Hz), 8.04−7.31 (15 H, m), 7.00 (1 H, t), 5.33 (1 H, d, $J = 15.00$ Hz), 5.16 (1 H, d, $J = 16.93$ Hz), 4.79−4. 73 (3 H, m), 4.61 (1 H, d, $J = 17.15$ Hz), 4.35 (1 H, d, $J = 17.56$ Hz), 4.18 (1 H, d, $J = 17.85$ Hz), 4.00 (1 H, d, $J = 16.51$ Hz), 3.63 (1 H, d, $J = 16.43$ Hz), 2.65 (3 H, s), − 2.01 (1 H, s). Anal. Calcd for $C_{37}H_{36}Co_2F_{12}N_{12}O_5P_2$: C, 39.10; H, 3.19; N, 14.79. Found: C, 38.80; H, 3.26; N, 15.28.

The Reaction of [Co(μ-OH)(oxapyme)Co(H$_2$O)](ClO$_4$) with PyNO$_2$BF$_4$. The complex **22** (0.271 g, 0.30 mmol) was dissolved in dry acetonitrile (180 mL). The light orange solution was then cooled to −40 °C in a dry ice−acetone bath. A solution of *N*-nitropyridinium tetrafluoroborate ($PyNO_2BF_4$, 63.6 mg, 0.33 mmol,) in dry acetonitrile (100 mL) at −40 °C was cannulated into the cobalt complex solution. A dark brown−yellow solution formed at once. The solution was stirred at −40 °C for 1 h and then concentrated to ∼2 mL. The solution was then added to a NH_4PF_6 (0.39 g, 2.4 mmol) solution in methanol (7 mL). After removing the solvent, the solid was slurried in methanol (10 mL), was filtered, and was washed with methanol (2 × 2 mL). The procedure was then repeated one more time. After washing the solid with methanol, ether (2 × 5 mL), and pentane (2 × 5 mL), the pale yellow−green solid was dried under vacuum (0.34 g, 100% yield). The product was identified as the [Co(μ-OH)(oxapyme)Co(NO_2)](PF$_6$)$_2$ complex by ^{1}H NMR spectroscopy (>95% purity). The complex was recrystallized from a mixture of dry acetonitrile (4 mL) and methanol (10 mL) by diffusion with methanol for 4 days to give a yellow−green crystalline solid (0.25 g, 74% yield). The product was pure by ^{1}H NMR spectroscopy.

The Reaction of [Co(μ-OH)(oxapyme)Co(H$_2$O)](PF$_6$)(ClO$_4$) with NO$_2$. The complex **22** (90 mg, 0.10 mmol) was dissolved in dry acetonitrile (60 mL), and a solution of $fcPF_6$ (33.1 mg, 0.1 mmol) in dry acetonitrile (3 mL) was added. An orange−brown solution formed at once. After stirring the solution for 1 h, the solvent was removed taking care to exclude O_2. The resultant solid was slurried with ether (360 mL) in the absence of O_2. After filtration, the solid was dried and redissolved in dry acetonitrile (20 mL) under N_2. The orange−brown solution was cooled to −40 °C, and 1 mL of a dry acetonitrile solution of NO_2 (0.11 M) was added. A greenish solution formed, and it was stirred at −40 °C for 30 min. An additional 1 mL of the NO_2 solution was then added, and the stirring was continued for a further 30 min before the solvent was removed. The solid was successively slurried with ether and methanol. It was collected and washed with methanol (2 × 2 mL), ether (2 × 4 mL), and pentane (2 × 4 mL). The solid was [Co(μ-OH)(oxapyme)Co(NO_2)](PF$_6$)ClO$_4$ (0.11 g, 100% yield), and ^{1}H NMR spectroscopy showed that it was >95% pure.

Crystallographic Structural Determination. Crystal, data collection, and refinement parameters are given in Table 2. A suitable crystal for data collection was selected and mounted with epoxy cement on the tip of a fine glass fiber. Data were collected at 173 K with a Siemens P4/CCD diffractometer with graphite-monochromated Mo Kα X-radiation ($\lambda = 0.71073$ Å).

The systematic absences in the diffraction data are uniquely consistent with the monoclinic space group $P2_1/n$. The structure was solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. The asymmetric unit contains two chemically equivalent but crystallographically independent molecules. One hexafluorophosphate counterion resides on a crystallographic inversion center. Complete resolution of the remaining $^1/_2PF_6^-$ counterion and lattice solvent was hindered by weak and diffuse data ($I/\Phi = 7.13$). The μ-hydroxy proton could not be located from the electron difference map and was omitted from the structure refinement. Squeeze/Platon[18] was applied to resolve six severely disordered molecules of acetonitrile within the asymmetric unit, which contains two crystallographically independent dications. Within the 2158.7 Å^3 void space occupied by solvent molecules and the unresolved anion, a total of 729 electrons was calculated. After correction for the unresolved counterion, a dication−solvent ratio of 1:3 was determined. In this treatment of solvent, the contributions of the solvent molecules are collective and not as individual atoms. Hence, the atom list does not contain the atoms of the solvent molecules. All non-hydrogen atoms were refined with anisotropic displacement coefficients and hydrogen atoms, with the exception noted, were treated as idealized contributions.

All software and sources of the scattering factors are contained in the SHELXTL (5.1) program library (G. Sheldrick, Siemens XRD, Madison, WI).

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Supporting Information Available: Detailed crystallographic data for the structure including tables of atomic coordinates, bond lengths, bond angles, anisotropic displacements, and hydrogen atom parameters in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org

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(17) Electrospray MS was obtained by Agilent Technologies, as a demonstration.

(18) PLATON, Spek, A. L., Acta Crystallogr. **1990**, *A46*, C34.