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Bimetallic Reactivity. On the Use of Oxadiazoles as Binucleating Ligands

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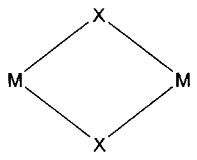
Two (1,3,4)-oxadiazole ligands have been prepared. In one case the oxadiazole ring is flanked by two *o*-aniline groups, and in the other case it is an extension of the first where the amines are condensed with 2-picolyl groups. A monometallic copper(II) complex of the former has been prepared, and its crystal structure was determined. A number of bimetallic copper(II), cobalt(II), and nickel(II) complexes of the di-deprotonated latter ligand were prepared and isolated. The crystal structure of the cobalt(II) complex bearing two acetate bridges is reported. The work demonstrates that the seldom-employed oxadiazole ring can be used effectively for generating bimetallic complexes.

Introduction

Generally, bimetallic complexes are formed by bridging ligands. The bridging ligands can consist of one atom, X, or two atoms, Y−Y, and with these combinations, four-, five-, or six-membered metallo-ring systems can be formed. Such rings are shown as **1**, **2**, and **3**, where the bridges may or may not be part of a complex binucleating ligand. The four-membered rings, **1**, are strained because the internal bond angles are different from those associated with the constituent atoms. The five- and six-membered rings, **2** and **3**, respectively, engender less strain because the atoms are allowed to adopt more closely their natural bond angles. These considerations bear on the construction of binucleating ligands because if the bridging ligand is part of the binucleating ligand structure, the strain of the bridge ring will usually be transmitted to other parts of the complexed ligand. Because the systems **2** and **3** are less strained, the two sites of the binucleating ligand complex will be less prone to transmit the effect of changes at one site to the other. Such strain factors are germane to the question of designing systems where the task of the metals is to act cooperatively. As we have demonstrated[1] in some bimetallic systems, oxidation of one metal leads to the deactivation of the other to oxidation principally because of mechanical coupling,[1] a conformational strain effect that couples the two sites. To obviate this mutual deactivation, we sought bimetallic complexes where mechanical coupling between the sites would be minimized. A properly designed system bearing the ring bridge, **2**, presented such a prospect. The nature of the Y−Y bridge, however, is important in decoupling the two metal sites when this bridge is part of the binucleating ligand. It appeared that properly constructed ligands bearing azole or azolate bridges would provide the least strained systems.



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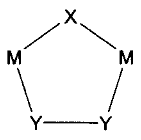

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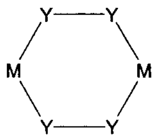

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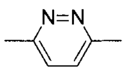
We considered the three bridging azole or azolate ligands **4**, **5**, and **6**. The bridging fragments **4** and **5** have been used extensively[2] for the syntheses of multimetallic complexes. The (1,3,4)-oxadiazole, **6**, bridge has received much less attention. We are aware of only three reports of attempts to use oxadiazole as a binucleating ligand.[3−5] In all cases, the ligand was **7**, but in every case only monometallic complexes were isolated and attempts to prepare bimetallic species failed. Molecular models indicate that the five-membered chelate rings that are formed



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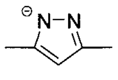

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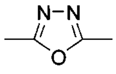

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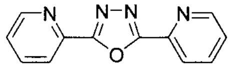

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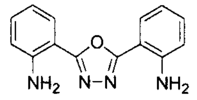
by **7** are strained and that six-membered chelate rings are required for strain-free coordination. Consequently, the systems reported here contain adjacent six-membered chelate rings.

Experimental Section

General Procedures and Methods. All reagents were obtained from commercial suppliers and used without further purification. 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. Elemental analyses were performed by Desert Analytics Laboratory, Arizona. Magnetic susceptibilities were measured at 25 °C on powdered samples 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. ^{1}H NMR and ^{13}C NMR spectra were recorded on either a Bruker DRX400 or a DMX500 Fourier transform spectrometer. Chemical shifts (δ) are given in ppm, coupling constants (J) in hertz. All of the aromatic signals show long-range coupling that ranges from $J = 1.0$ to $J = 1.7$ Hz. Consequently, the quoted coupling constants are difficult to determine precisely. Melting points are uncorrected. Acetonitrile was dried over CaH_2, THF was dried over potassium/benzophenone ketyl, and ethyl ether was dried over sodium/benzophenone ketyl.

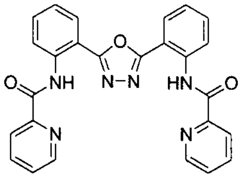
***N,N*-Bis(2-aminobenzoyl)hydrazine (8).** **8** was prepared by modification of the literature procedure.[6] To a suspension of isatoic anhydride (16.13 g, 0.1 mol) in absolute ethanol (80 mL) at 25 °C was added hydrazine monohydrate (2.43 mL, 0.05 mol) dropwise over 5 min. The mixture was brought to reflux and was refluxed for 1 h during which time the solid dissolved and a new precipitate formed. The mixture was slowly cooled to room temperature, then was kept at 5 °C for 1 h. Pale-gray crystals were collected and washed with cold ethanol, ether, and pentane. They were recrystallized from hot DMF−water to afford pure product as a light-brown solid (7.2 g, 53% yield). ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 10.04$ (s, 2H), 7.60 (d, 2H, $J = 7.4$ Hz), 7.18 (t, 2H, $J = 7.7$ Hz), 6.73 (d, 2H, $J = 7.9$ Hz), 6.51 (t, 2H, $J = 7.5$ Hz), 6.43 (s, 4H).

2,2′-(1,3,4)Oxadiazole-2,5-diyl-bis-aniline (oxan, 9). **9** was prepared by a modification of the literature procedure.[6] A mixture of **8** (7.2 g, 26.64 mmol) and polyphosphoric acid (18.5 mL) was heated to 160 °C. A light-brown thick solution was formed in 30 min. It was kept at 160 °C for 2 h, then was slowly cooled to 50 °C. Then 100 mL of an ice−water mixture was carefully added to the solution. A yellow precipitate formed immediately. It was collected via filtration and washed with water. The filtrate was adjusted with 15% NaOH solution to pH 5. The precipitated solid was collected, washed with water, combined with the main crop, and recrystallized from hot DMF−water. Light-brown needles of **9** were obtained. These were washed with water and dried under vacuum (5.7 g, 85%). Mp, 228−230 °C. Lit. mp, 228−230 °C. Selected IR bands (mineral oil, cm^{-1}): 3463, 3429, 3376, 3334, 1619, 1534, 1496, 1316, 1257, 1158, 740, 707. ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 7.86$ (d, 2H, $J = 7.9$ Hz), 7.27 (t, 2H, $J = 7.6$ Hz), 6.91 (d, 2H, $J = 8.3$ Hz), 6.77 (s, 4H), 6.70 (t, 2H, $J = 7.5$ Hz).^{13}C NMR (400 MHz, DMSO-d_6): $\delta = 162.33$, 147.82, 132.46, 127.86, 115.87, 115.60, 103.98 Hz.



oxan

9



oxanpy(H)$_2$

10

***N,N*-Dipicolylamide-2,2′-(1,3,4)oxadiazole-2,5-diyl-bis-aniline (oxanpyH$_2$, 10).** To a suspension of oxan (0.5 g, 2 mmol) and picolinic acid (0.75 g, 6 mmol) in dry pyridine (5 mL) was added triphenyl phosphite (1.1 mL, 4 mmol).[7] The mixture was kept at 50 °C for 15 h and was then refluxed for 1 h. More triphenyl phosphite (0.55 mL, 2 mmol) was added, and the refluxing was continued for 3 more hours. The solvent was removed in vacuo. The white residue was suspended in benzene and filtered. It was washed successively with cold benzene, water, ether, and pentane. It was dried under vacuum to afford a pure product as a white crystalline solid (0.68 g, 74%). It can be recrystallized by vapor diffusion of ether into chloroform solution. Mp, 249−251 °C. Selected IR bands (mineral oil, cm^{-1}): 1683, 1584, 1538, 1441, 1303, 744. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 12.86$ (s, 2H), 9.06 (d, 2H, $J = 8.5$ Hz), 8.84 (d, 2H, $J = 4.7$ Hz), 8.34 (d, 2H, $J = 7.8$ Hz), 8.17 (d, 2H, $J = 7.9$ Hz), 7.94 (t, 2H, $J = 7.7$ Hz), 7.64 (dd, 2H, $J = 7.9$ Hz, $J = 8.5$ Hz), 7.55 (dd, 2H, $J = 4.7$ Hz, $J = 7.6$ Hz), 7.29 (t, 2H, $J = 7.6$ Hz). ^{13}C NMR (400 MHz, C_6D_6): $\delta = 163.85$, 162.84, 150.38, 148.36, 138.03, 137.46, 133.01, 128.28, 126.49, 123.64, 122.89, 121.33, 111.44 Hz. Anal. Calcd for $C_{26}H_{18}N_6O_3$: C, 67.53; H, 3.92; N, 18.17. Found: C, 67.60; H, 3.69; N, 18.18.

[Cu(oxan)Cl$_2$]·DMF (11). To a solution of oxan (300 mg, 1.19 mmol) in DMF (3 mL) was added a solution of copper chloride hydrate (289 mg) in DMF (5 mL). The dark brown-green solution was stirred for 18 h. Then ethanol (3 mL) was added followed by ether (15 mL). Dark-green crystals started forming. The mixture was kept at 5 °C for 3 h. The green solid was filtered, washed with ether, and dried in air (506 mg, 93% yield). It was dissolved in DMF (5 mL) and vapor-diffused with acetonitrile over 4 days. Dark blocks suitable for X-ray crystallography were formed. They were washed with ether and dried under vacuum (320 mg, 59%). Selected IR bands (mineral oil, cm^{-1}): 3452, 3348, 3147, 1653, 1620, 1540, 1319, 1257. Absorption spectrum [λ_{max} in nm (ϵ in L mol^{-1}cm^{-1}), DMF solution]: 275 (12 140), 367 (21 480), 402 (sh, 386). Anal. Calcd for $C_{17}H_{19}N_5OCuCl_2$: C, 44.40; H, 4.17; N, 15.23; Cl, 15.42. Found: C, 44.46; H, 4.26; N, 15.17; Cl, 14.69.

[Cu(oxanpy)Cu(μ-O)] (12). OxanpyH$_2$ (**10**) (0.46 g, 1 mmol) was dissolved in DMF (30 mL) with heating to 80 °C. The solution was cooled to room temperature. DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) (0.55 mL, 3.5 mmol) was added followed by water (0.36 mL, 20 mmol) and DMF (10 mL). To this clear solution was added a solution of copper trifluoromethanesulfonate (0.73 g, 2 mmol) in DMF (5 mL). The clear dark-green solution became turbid within 3 min. The mixture was heated at 90 °C for 1 h. A light-brown suspension was formed after 30 min of heating. It was cooled to room temperature. The solid was collected and was washed with DMF (9 mL), ether (15 mL), and hexane (15 mL) and was dried under vacuum. Brownish-green powder was obtained (0.54 g, 90% yield). Selected IR bands (mineral oil, cm^{-1}): 1580, 1565, 1533, 1346. Anal. Calcd for $C_{26}H_{16}N_6O_4Cu_2$: C, 51.74; H, 2.67; N, 13.92. Found: C, 51.45; H, 2.68; N, 13.71.

[Cu(oxanpy)Cu(μ-OH)]BF$_4$ (13). To a suspension of oxanpyH$_2$ (0.23 g, 0.5 mmol) in DMF (8 mL) was added DBU (164 μL, 1.05 mmol) followed by a solution of $Cu(BF_4)_2$ (334 mg, 77%, 1.0 mmol) in DMF (2 mL). A green solution formed and became turbid after 4 min of stirring. After the mixture was stirred for 3 h, acetone (20 mL) was added and the suspension was stirred further for 30 min. The solid was collected and washed successively with acetone (15 mL), methanol (2 mL), acetone (5 mL), ether, and finally hexane. It was dried under vacuum to afford a greenish powder (0.29 g). It was recrystallized by slow vapor diffusion of acetone into DMF solution. The product was obtained as a yellowish-green crystalline solid (70 mg, 20%). Selected IR bands (mineral oil, cm^{-1}): 1620, 1601, 1576, 1547, 1338, 756. Absorption spectrum [λ_{max} in nm (ϵ in L mol^{-1}cm^{-1}), DMF solution]: 267 (51 450), 289 (36 000 sh), 366 (35 200), 579 (254). Anal. Calcd for $C_{26}H_{17}N_6O_4BF_4Cu_2$: C, 45.17; H, 2.48; N, 12.16. Found: C, 45.24; H, 2.71; N, 12.36.

[Co(oxanpy)Co(μ-OAc)$_2$]·CH$_2$Cl$_2$ (14). To a suspension of oxanpyH$_2$ (0.27 g, 0.6 mmol) in deaerated DMF (10 mL), DBU (196 μL, 1.26 mmol) was added. The reaction mixture was flushed with N_2 for 10 min before solid cobalt acetate tetrahydrate (0.306 g, 1.23 mmol)

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was added in one portion. An orange solution formed and became turbid within minutes. It was stirred for 3 h at room temperature. The yellow solid was collected under N_2, washed with deaerated DMF (8 mL) and ether (6 mL), and dried under vacuum. A yellow-orange powder (310 mg) was obtained. It was recrystallized by slow vapor diffusion of ether (deaerated) into CH_2Cl_2 solution (deaerated, 25 mL). Two types of crystals formed, brown blocks and yellow needles. The blocks (260 mg, 55%) were manually separated from the needles. Both the blocks and needles were analyzed. The blocks, which contain CH_2Cl_2 of crystallization, were used for X-ray diffraction. The needles do not contain any solvent of crystallization. Selected IR bands (needles, mineral oil, cm^{-1}): 1620, 1601, 1576, 1547, 1338, 756. Absorption spectrum [needles, λ_{max} in nm (ϵ in L $mol^{-1}cm^{-1}$), deaerated CH_2Cl_2 solution]: 284 (68 100), 384 (18 167), 504 (106 sh), 640 (30). Anal. Calcd for $C_{31}H_{24}N_6O_7Cl_2Co_2$ (blocks): C, 47.65; H, 3.10; N, 10.76. Found: C, 47.37; H, 3.71; N, 10.65. Anal. Calcd for $C_{30}H_{22}N_6O_7Co_2$ (needles): C, 51.73; H, 3.19; N, 12.07. Found: C, 51.60; H, 3.08; N, 11.94.

[Ni(oxanpy)Ni(μ-OAc)$_2$]·2DMF (15). A solution of nickel acetate tetrahydrate (118 mg, 0.47 mmol) in dry DMF (3 mL) was added to a stirred suspension of oxanpyH_2 (100 mg, 0.216 mmol) in dry DMF (1 mL). A clear dark-green solution formed and was stirred for 3 h at room temperature. Then ether (30 mL) was slowly added. Greenish-brown crystals started forming. The mixture was kept at 5 °C for 3 h. The solid was collected, washed with ether, and dried in air (160 mg, 88%). It was recrystallized by slow vapor diffusion of ether into a DMF solution. Greenish-brown crystals were collected, washed with DMF, and were dried in vacuo (113 mg, 62% yield). Selected IR bands (mineral oil, cm^{-1}): 1677, 1614, 1587, 1547, 1330, 1258, 1226, 1166, 755. Absorption spectrum [λ_{max} in nm (ϵ in L $mol^{-1}cm^{-1}$), DMF solution]: 263 (66 230), 377 (18 620), 575 (58), 816 (34). Anal. Calcd for $C_{36}H_{36}N_8O_9Ni_2$: C, 51.38; H, 4.27; N, 13.17. Found: C, 51.37; H, 4.28; N, 13.31.

Crystallographic Structural Determination. Crystal, data collection, and refinement parameters are given in Table 2. Suitable crystals for data collection were selected and mounted with epoxy cement on the tip of a fine glass fiber. All data were collected at 173(2) K with a Siemens P4/CCD diffractometer with graphite-monochromated Mo Kα X-radiation (λ = 0.710 73 Å).

The systematic absences in the diffraction data for **14** are uniquely consistent with the reported space group, and the centrosymmetric option for **11** was verified by the results of refinement. Structure **14** was solved using direct methods and structure **11** by the heavy-atom Patterson method. Both structures were completed by subsequent difference Fourier syntheses and refined by full-matrix least-squares procedures. Structure **14** cocrystallized with one molecule of methylene chloride per dicobalt complex. Structure **11** cocrystallized with dimethylformamide, which resides in proximity to the coordinated amine group (O(2)−N(1) = 2.79(4) Å). The four amine protons of **11** were located from the electron difference map and allowed to refine. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms, with the exception of the amine protons of **14**, were treated as idealized contributions.

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

Results

Ligand Synthesis. The two ligands investigated here are **9** and **10**. Two aspects of these ligands are noteworthy. First, the oxadiazoles bear aromatic substituents, which provide stability to the oxadiazole ring that otherwise is prone to nucleophilic attack at the imine carbon atoms. Second, the chelate rings associated with the bridging ligand are six-membered, the least strained ring. The syntheses of the two ligands **9** and **10** followed modifications of known procedures (Scheme 1). Isatoic anhydride was reacted with hydrazine hydrate in ethanol to give **8**, which after recrystallization was converted to the oxadiazole ligand oxan, **9**.[6] Reaction of **9** with picolinic acid in dry pyridine in the presence of triphenyl phosphite gave oxanpy(H)$_2$ as a white crystalline solid.

Scheme 1. Synthesis of oxan and oxanpyH_2

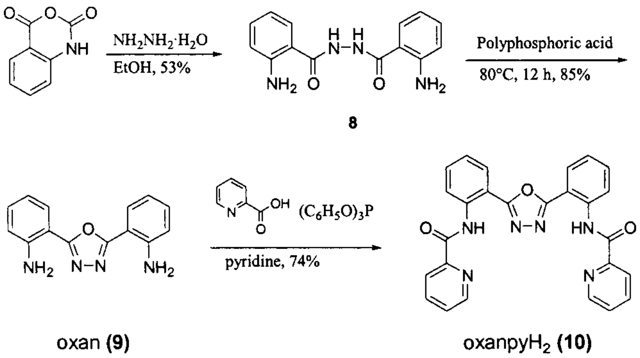

Table 1. Physical Properties of oxan and oxanpy Complexes

complex	color	solid-state magnetic moment (μ_B)$_{25°C}$	conductivity, Ω^{-1} mol^{-1} cm^2 (solvent)
[Cu(oxan)Cl_2]·DMF	dark-brown	1.73	27 (DMF)
[Cu(oxanpy)Cu(μ-O)]	brown-green	2.14	insoluble
[Cu(oxanpy)Cu(μ-OH)]BF_4	olive-green	1.66	67 (DMF)
[Co(oxanpy)Co(μ-OAc)$_2$]	yellow	5.96	3 (CH_2Cl_2)
[Ni(oxanpy)Ni(μ-OAc)$_2$]	green-brown	4.51	2 (DMF)

Complexes. Some of the complexes that were prepared with the oxan and oxanpy ligands are listed in Table 1, together with some of their physical properties. An outline of the preparation of the complexes is shown in Scheme 2. The oxan ligand with varying equivalents of $CuCl_2$ in DMF formed a dark-brown solution. Addition of ethanol followed by diethyl ether always precipitated the monometallic complex irrespective of the equivalents of $CuCl_2$ that were present. The formation of the monometallic complex is consistent with the results reported for the ligand **7**. Whether the isolation of the monometallic complex of oxan is a reflection of the instability of the bimetallic species or is merely a consequence of solubility has not been pursued. The solid-state magnetic moment is representative of an $S = {}^1/_2$ system, but the conductivity in DMF solution suggests some dissociation of the chloro ligands.

The Cu^{2+}, Co^{2+}, and Ni^{2+} complexes formed by the oxanpy ligand are bimetallic (Table 1). The oxo-bridged complex, [Cu(oxanpy)Cu(μ-O)], is insoluble in all solvents, protic and aprotic, that were tried, and as a result, preparation of the soluble hydroxo-bridged complex [Cu(oxanpy)Cu(μ-OH)]BF_4 requires some care. The latter was prepared by the addition of 2 equiv of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) to deprotonate the ligand. Addition of more than 2 equiv of DBU led to the precipitation of the μ-oxo complex. Even when the μ-hydroxy complex is allowed to stand in methanol solution at 25 °C, the μ-O complex begins to slowly precipitate from solution. The μ-OH complex is stable in aprotic solvents such as acetone or DMF. Curiously, addition of acid to a methanol suspension of the insoluble μ-O complex does not result in the detectable formation of the μ-OH complex.

Both of these complexes have magnetic moments lower than the expected spin-only values, indicating antiferromagnetic coupling. The μ-OH complex in DMF displays a molar conductivity consistent with a 1:1 electrolyte.[8] The analogous Co^{2+} and Ni^{2+} complexes were prepared from the metal acetates. Both are nonelectrolytes and have magnetic moments lower than

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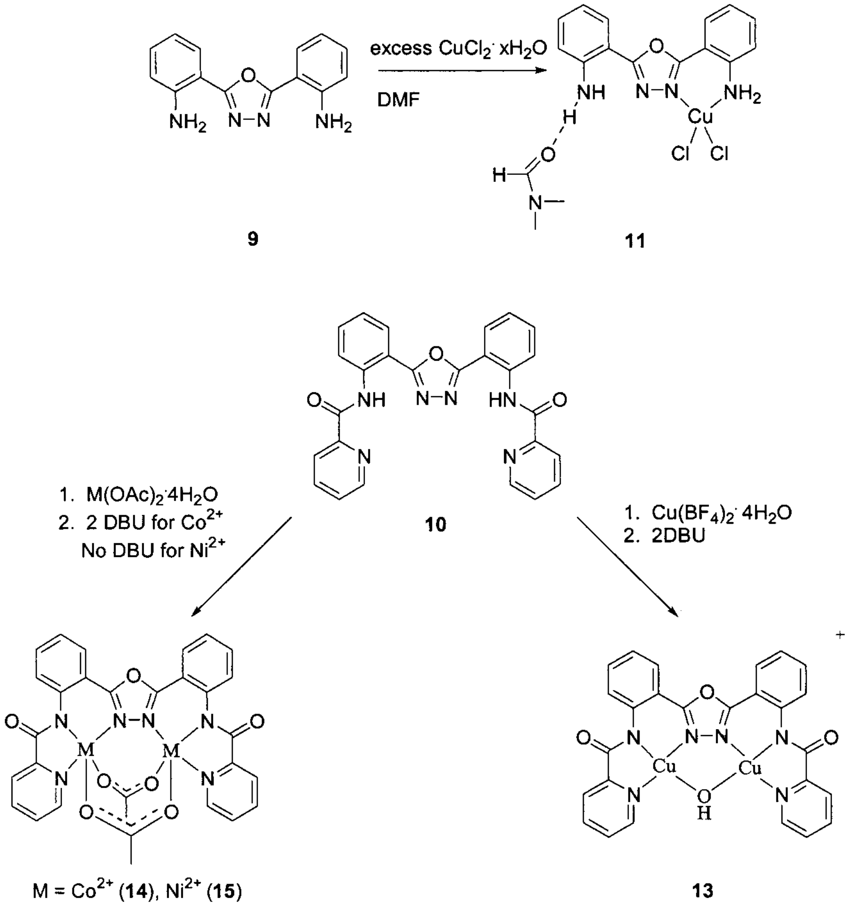
Scheme 2



the expected spin-only values for high-spin complexes. The conductivity indicates that the acetate ions are coordinated to the metals. The cobalt complex is sensitive to dioxygen in solution but is moderately stable in the solid state in air. None of the complexes gave reversible cyclic voltammetry waves under a variety of conditions.

Crystal Structures. Crystal structures of the [Cu(oxan)Cl_2]·DMF and [Co(oxanpy)Co(μ-OAc)$_2$]·CH_2Cl_2 were determined. Crystallographic data for these complexes are provided in Table 2, and selected bond lengths and angles are listed in Tables 3 and 4. The Cu^{2+} (Cu(1)) in [Cu(oxan)Cl_2]·DMF (Figure 1) is square planar, as expected, but the bond length of Cu(1)−Cl(1) is longer than that of Cu(1)−Cl(2). The dimethylformamide (DMF) solvate forms a hydrogen bond with one of the protons of the neighboring nitrogen atoms (N(1)). The other amine nitrogen atom (N(4)) is oriented so that one of its hydrogen atoms may form a hydrogen bond to N(3) of the oxadiazole group.

The [Co(oxanpy)Co(μ-OAc)$_2$] complex forms two types of crystals when crystallized from CH_2Cl_2/ether: yellow needles and brown blocks. The latter is a CH_2Cl_2 solvate, for which the structure is reported, and the former is devoid of solvate. The crystal structure is shown in Figure 2 where the Co^{2+} ions are in a distorted trigonal bipyramidal geometry. The oxadiazole and pyridine nitrogen atoms represent the axial positions of the trigonal bipyramid. The metal−metal distance, Co(1)−Co(2), is 3.781 Å. The other bond lengths and angles are unexceptional.

Discussion

This work illustrates that the oxadiazole fragment can be used for the formation of bimetallic complexes, which can incorporate acetate, hydroxide, and oxo supporting bridges between the two metals. One of the possible problems with using oxadiazole rings is the possible hydrolysis of the ring to give **16**[9] under basic conditions:

Table 2. Crystallographic Data for [Co(oxanpy)Co(μ-OAc)$_2$]·CH_2Cl_2 (**14**) and [Cu(oxan)Cl_2]·DMF (**11**)

	14	**11**
formula	$C_{31}H_{24}Cl_2Co_2N_6O_7$	$C_{17}H_{19}Cl_2CuN_5O_2$
fw	781.32	459.81
space group	$P2_1/c$	$P\bar{1}$
a, Å	10.8054(10)	10.4222(3)
b, Å	18.5327(17)	10.4310(4)
c, Å	15.7320(15)	11.3251(4)
α, deg		75.014(2)
β, deg	96.575(2)	63.130(2)
γ, deg		61.121(2)
V, Å^3	3129.7(5)	960.41(6)
Z, *Z*_	4, 1	2, 1
cryst color, habit	dark-red block	dark-green block
D(calcd), g cm^{-3}	1.658	1.590
μ(Mo Kα), cm^{-1}	12.90	14.38
temp, K	173(2)	173(2)
diffractometer	Siemens P4/CCD	Siemens P4/CCD
λ (Mo Kα), Å	0.710 73	0.710 73
R(*F*),[a] %	4.37	3.33
R(*wF*^{2}),[a] %	13.53	13.32

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

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[9] Lagrenee, M.; Sueur, S.; Wignacourt, J. P. *Acta Crystallogr.* **1991**, *C47*, 1158.

Table 3. Selected Bond Lengths and Angles for [Cu(oxan)Cl$_2$]·DMF

Bond Lengths (Å)			
Cu(1)−N(1)	2.0056(16)	Cu(1)−Cl(2)	2.2304(5)
Cu(1)−N(2)	2.0167(15)	Cu(1)−Cl(1)	2.3184(4)
Angles (deg)			
N(1)−Cu(1)−N(2)	86.96(6)	N(1)−Cu(1)−Cl(1)	88.69(5)
N(1)−Cu(1)−Cl(2)	173.36(5)	N(2)−Cu(1)−Cl(1)	150.94(5)
N(2)−Cu(1)−Cl(2)	94.02(4)	Cl(2)−Cu(1)−Cl(1)	93.583(17)

Table 4. Selected Bond Lengths and Angles for [Co(oxanpy)Co(μ-OAc)$_2$]·CH$_2$Cl$_2$

Bond Lengths (Å)			
Co(1)−O(1)	1.989(2)	Co(2)−O(4)	1.990(2)
Co(1)−O(3)	2.015(2)	Co(2)−O(2)	2.009(2)
Co(1)−N(1)	2.041(2)	Co(2)−N(2)	2.032(3)
Co(1)−N(3)	2.048(2)	Co(2)−N(4)	2.038(2)
Co(1)−N(5)	2.075(2)	Co(2)−N(6)	2.068(3)
Angles (deg)			
O(1)−Co(1)−O(3)	110.98(10)	O(4)−Co(2)−O(2)	118.82(10)
O(1)−Co(1)−N(1)	96.28(9)	O(4)−Co(2)−N(2)	95.26(10)
O(3)−Co(1)−N(1)	93.52(9)	O(2)−Co(2)−N(2)	91.17(9)
O(1)−Co(1)−N(3)	125.29(9)	O(4)−Co(2)−N(4)	128.84(10)
O(3)−Co(1)−N(3)	123.19(9)	O(2)−Co(2)−N(4)	111.95(9)
N(1)−Co(1)−N(3)	87.95(9)	N(2)−Co(2)−N(4)	89.43(10)
O(1)−Co(1)−N(5)	90.37(9)	O(4)−Co(2)−N(6)	92.64(10)
O(3)−Co(1)−N(5)	91.98(9)	O(2)−Co(2)−N(6)	89.16(9)
N(1)−Co(1)−N(5)	169.23(10)	N(2)−Co(2)−N(6)	170.79(10)
N(3)−Co(1)−N(5)	81.30(9)	N(4)−Co(2)−N(6)	81.92(10)
Metal−Metal Separation (Å)			
Co(1)−Co(2)		3.781	

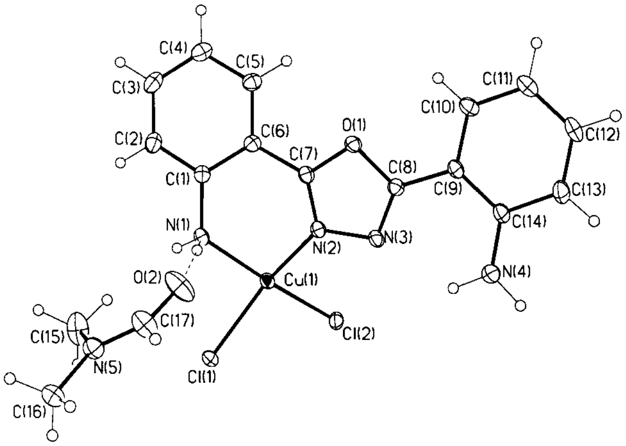
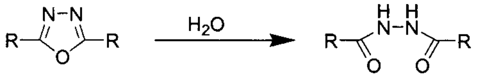


Figure 1. ORTEP diagram of [Cu(oxan)Cl$_2$]·DMF (**11**). Thermal ellipsoids are at 30% probability.



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During the course of this work, no such problems were encountered, although the complexes were not subjected to strong alkali. It appears, therefore, that the present oxadiazoles are stable to the normal conditions under which coordination chemistry is performed. Compared to the other 2-nitrogen bridging systems, **4** and **5**, the oxan, **9**, fragment is simple to prepare and to elaborate. The pyrazole bridging group **17**, related to oxan, carries with it synthetic difficulties when elaboration from the amino groups is attempted. It is known[10] that aldehydes and acyl chlorides give the products **18** and **19**.

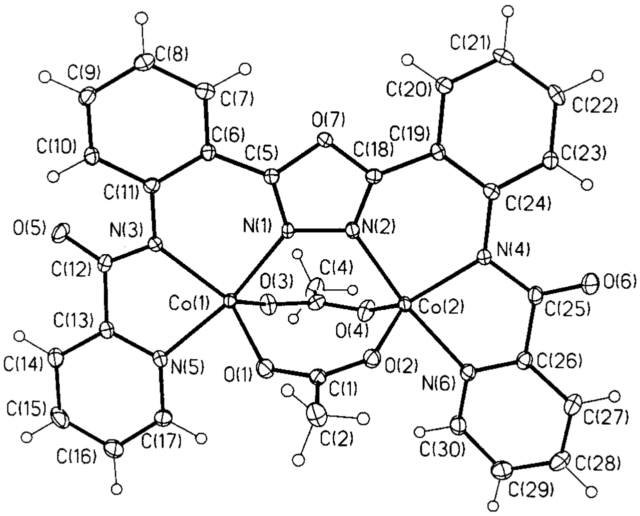
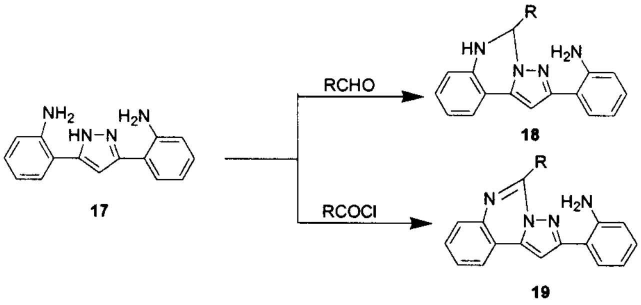


Figure 2. ORTEP diagram of [Co(oxanpy)Co(μ-OAc)$_2$]·CH$_2$Cl$_2$ (**14**). Thermal ellipsoids are at 30% probability, and the lattice solvent molecule is omitted for clarity.



Both of the products **18** and **19** are stable, and hence, the elaboration, such as in the preparation of oxanpyH$_2$, **10**, is not possible with **17**. Aside from the synthetic difficulties in preparing **17**, the reaction **17** → **19** was the other reason that led us to explore the coordination chemistry of oxadiazoles. We will report on the complexes of a more elaborate oxadiazole binucleating ligand shortly.

Acknowledgment. The work was supported by grants from the PRF, NSF, and NIH.

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

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(10) deStevens, G.; Blatter, H. M. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 159.