It would therefore be of some interest to study such a complex by neutron diffraction to see the extent of the elongation and of the deviation from planarity of the ethylene moiety.

Safety Notes. Perchlorate salts of metal complexes with organic ligands are potentially explosive. In general, when noncoordinating agents are required, every attempt should be made to substitute anions such as the fluoro sulfonates for the perchlorates. If a perchlorate must be used, only small amounts of material should be prepared and this should be handled with great caution.

Acknowledgment. We thank Dr. M. S. Lehmann and J. Archer for advice during the experiment and Prof. G. Ferraris for useful discussion. We are indebted to the CSI Piemonte, Torino, Italy, for financial support to carry out the computer calculations.

Registry No. $[Pt(C_2H_4)Cl(Me_2NCH_2CH_2NMe_2)](ClO_4)$, 71639-56-0.

Supplementary Material Available: A listing of anisotropic thermal parameters (2 pages). Ordering information is given on any current masthead page.

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Anisotropic Exchange in Transition-Metal Dinuclear Complexes. 8.[1] Bis(μ-pyridine *N*-oxide)bis[dichloro(dimethyl sulfoxide)copper(II)]

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Received October 28, 1985

Single-crystal EPR spectra of bis(μ-pyridine *N*-oxide)bis[dichloro(dimethyl sulfoxide)copper(II)], $[Cu(pyO)Cl_2(Me_2SO)]_2$, were recorded at room temperature at both X- and Q-band frequencies. They are typical of a triplet with $g_{xx} = 2.069$ (2), $g_{yy} = 2.077$ (2), $g_{zz} = 2.337$ (2), $D_{x'x'} = 0.0898$ (6), $D_{yy} = 0.0373$ (5), and $D_{z'z'} = -0.1271$. The z and z' axes make an angle of 28.7 (5)°, while the x' direction makes an angle of 82.0 (2)° with the copper–copper direction. The overall appearance of the **D** tensor is indicative of a relevant exchange contribution, and the observed deviation of the z' axis from the z direction suggests a sizable, essentially exchange-determined D_{yz} component of the zero-field-splitting tensor. The polycrystalline-powder EPR spectra of the manganese(II)-doped compound show the presence of exchange-coupled copper(II)–manganese(II) pairs and are characteristic of a quintet state.

Introduction

In the course of a systematic study on the relationships between anisotropic exchange and structural parameters in dinuclear copper(II) complexes,[3-9] we have shown that for bis(μ-oxo)-bridged complexes that have magnetic orbitals lying on the same plane, the interaction between the ground xy and the excited $x^2 - y^2$ orbital is dominant and ferromagnetic in nature.[1,3-5] This result found an independent check from Russian authors.[10]

We also found that, for this class of complexes, the intensity of the interaction tends to decrease as the metal–metal distance increases.[1,5] These data were interpreted within the scheme of the ferromagnetic interactions between the xy and $x^2 - y^2$ orbitals.

Looking for systems at the long edge of available copper–copper distances, we found in the literature bis(μ-pyridine *N*-oxide)bis[dichloro(dimethyl sulfoxide)copper(II)], $[Cu(pyO)Cl_2(Me_2SO)]_2$,[11] which contains the usual dinuclear units, with a copper–copper distance of 3.342 (3) Å, which, to our knowledge, is the largest reported thus far for bis(μ-oxo)-bridged complexes. Since no EPR spectra were available, we decided to characterize this complex in order to compare its spectromagnetic properties to those of structurally similar systems.

We obtained also manganese(II)-doped samples, whose polycrystalline-powder EPR spectra show evidence of a substantial copper(II)–manganese(II) coupling.

Experimental Section

The title compound, $[Cu(pyO)Cl_2(Me_2SO)]_2$, was prepared by recrystallizing the anhydrous pyridine *N*-oxide complex $[Cu(pyO)Cl_2]_2$ in dimethyl sulfoxide, according to the reported procedure.[11] EPR suitable single crystals were oriented with a Philips PW 1100 diffractometer. They were found to correspond to the reported structure with prominent (100) and ($\bar{1}$00) faces.

Mixtures of $[Cu(pyO)Cl_2]_2$ and its manganese(II) analogue in a molar ratio of 2:1 in favor of copper were dissolved in dimethyl sulfoxide, yielding single crystals of the doped complex. The analysis of the metals was in agreement with the calculated value for the copper (calcd, 20.65%; found, 20.40%), and indicated a manganese percent rate of 2%. The crystals were revealed to have the same lattice parameters as for the copper(II) pure dimer, having well-developed (011) and (0$\bar{1}\bar{1}$) faces, but the crystal had a very unusual appearance, with two zones of different color, without showing any evidence of gemination.

Polycrystalline-powder and single-crystal EPR spectra were recorded with a Varian E9 spectrometer equipped with standard X- and Q-band facilities. The symmetry properties of the crystals were used to check the alignment of the magnetic field.

Results and Discussion

Polycrystalline-powder EPR spectra of $[Cu(pyO)Cl_2(Me_2SO)]_2$ at both X- and Q-band frequencies at room temperature are shown in Figure 1. They are typical of a triplet state split in the zero field by about 0.10–0.15 cm^{-1}. When the sample is cooled down to liquid-nitrogen temperature the spectrum disappears, and only

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Table I. Principal Values and Directions[a] of **g** and **D** Tensors for $[Cu(pyO)Cl_2(Me_2SO)]_2$

g_{xx}	g_{yy}	g_{zz}	$D_{x'x'}$[b]	$D_{y'y'}$[b]	$D_{z'z'}$[b]
2.069 (2)	2.077 (2)	2.337 (2)	0.0898 (6)	0.0373 (5)	-0.1271 (5)
0.914 (3)	-0.0 (1)	0.404 (4)	0.927 (3)	0.364 (7)	0.090 (2)
0.2 (1)	-0.74 (5)	-0.656 (3)	0.376 (6)	-0.865 (3)	-0.335 (2)
0.3 (1)	0.67 (5)	-0.676 (3)	-0.044 (3)	0.344 (2)	-0.9378 (7)

[a] The principal directions are given by their direction cosines referred to the orthogonal cyrstal axes a^*, b, and c. [b] In cm^{-1}.

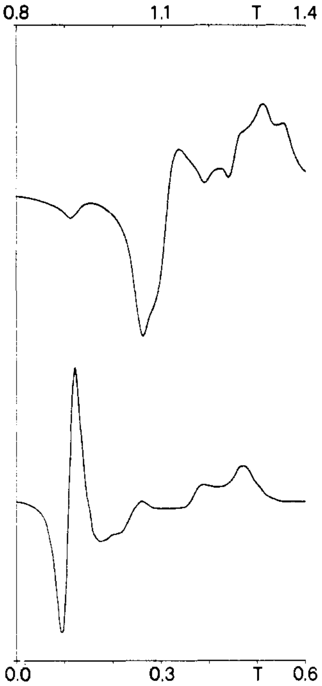

Figure 1. Polycrystalline-powder EPR spectra of $[Cu(pyO)Cl_2(Me_2SO)]_2$ at room temperature: lower trace, X-band frequency; upper trace, Q-band frequency.

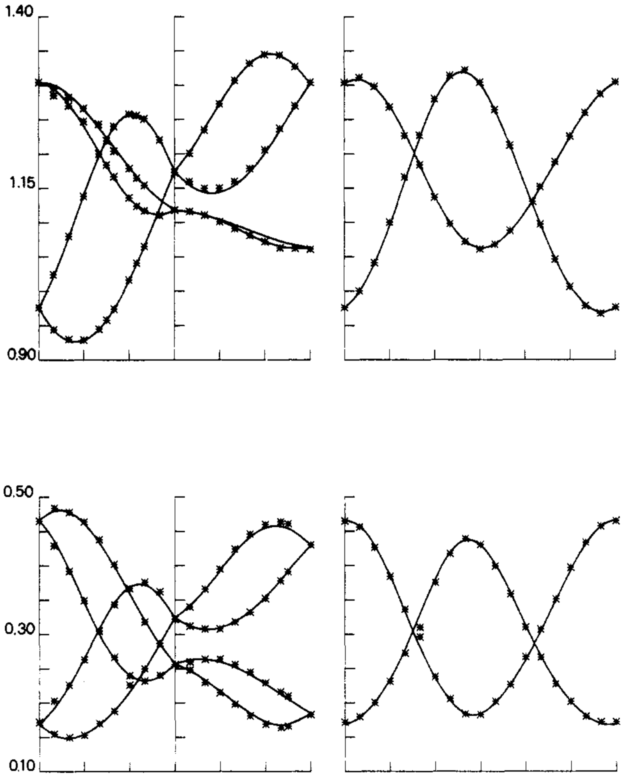

Figure 2. Angular dependence of the transition fields (in T) for $[Cu(pyO)Cl_2(Me_2SO)]_2$: lower trace, X-band frequency; upper trace, Q-band frequency.

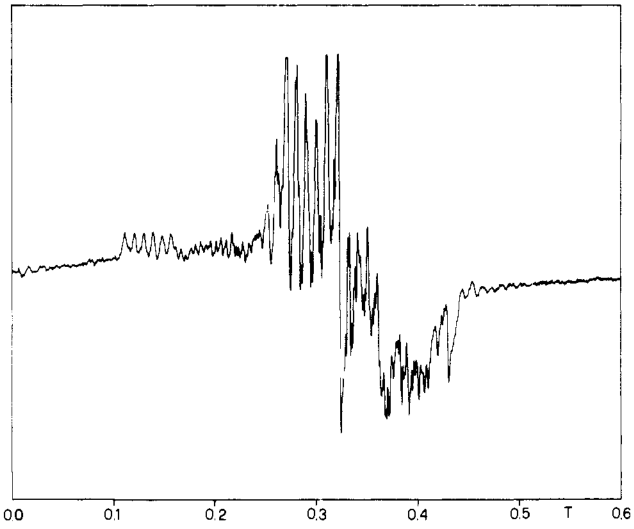

Figure 3. Polycrystalline-powder EPR spectra of $[(Cu,Mn)(pyO)Cl_2(Me_2SO)]_2$ at 77 K at X-band frequency.

the signals of at least two "monomeric" impurities are left. The most intense of them has $g_\parallel = 2.41$, $g_\perp = 2.08$, and $A_\parallel = 130 \times 10^{-4}$ cm^{-1}.

Single-crystal spectra were recorded at room temperature at both X- and Q-band frequencies by rotating around the a^*, b, and c crystal axes. The angular dependence of the transition fields is shown in Figure 2. The experimental points were fit with the procedure previously described.[4] Since the crystals are monoclinic, there is ambiguity in the determination of the spin-Hamiltonian tensors[12] and two different sets of eigenvectors corresponding to the same eigenvalues were obtained. However one choice yields **g** and **D** tensors that do not compare well with those previously reported for similar complexes[13,14] and do not fit well in the molecular frame; therefore, we will use only the other one. The principal **g** and **D** values and directions thus obtained are shown in Table I.

Polycrystalline-powder EPR spectra of manganese(II)-doped $[Cu(pyO)Cl_2(Me_2SO)]_2$, recorded at 77 K (Figure 3), are indicative of the presence of exchange-coupled copper(II)–manganese(II) pairs diluted in a diamagnetic host material and are characteristic of a quintet ($S = 2$) state as previously observed for copper(II)–manganese(II) heterodinuclear units in $[Cu(pyO)Cl_2(H_2O)]_2$.[14-16] No evidence of the $S = 3$ state was observed: the room-temperature polycrystalline-powder spectrum shows the superimposed features of the pure copper–copper dimer and of the quintet state of the copper(II)–manganese(II) pairs. The hyperfine structure from the manganese nuclei is clearly observed in the low-field transitions, while the hyperfine splitting due to the copper nuclei remains completely unresolved. In the high-field region of the spectra many overlapping bands make the spectra more difficult to read. In spite of this we can assign the lowest field features, characterized by a well-resolved manganese(II) hyperfine, to the first parallel transition, the fourth one being the very weak sextet at fields higher than 0.5 T. So we

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Table II. Principal Values of the **D** Tensor for $[Cu(pyO)Cl_2(H_2O)]_2$, $[Cu(pyO)Cl_2(pyO)]_2$, and $[Cu(pyO)Cl_2(Me_2SO)]_2$

	$[Cu(pyO)Cl_2$-$(H_2O)]_2$	$[Cu(pyO)Cl_2$-$(pyO)]_2$	$[Cu(pyO)Cl_2$-$(Me_2SO)]_2$
r^a	3.272	3.306	3.342
ϑ^b	26	23	28.7 (5)
$D_{x'x'}{}^c$	0.081 (2)	0.09	0.0898 (6)
$D_{y'y'}{}^c$	0.022 (2)	0.05	0.0373 (5)
$D_{z'z'}{}^c$	−0.103 (2)	−0.14	−0.1271 (4)

^{a} Copper–copper distance, in Å. ^{b} Angle between g_{zz} and $D_{z'z'}$, in deg. ^{c} In cm^{-1}

obtain $|D_{z'z'}| = 0.0424$ cm^{-1}, greater than those previously observed for analogous bis(*μ*-pyridine *N*-oxide)–copper(II)–manganese(II) dimers,[14–16] and $g_{z'} = 1.97$. We assign the features around 0.203 and 0.47 T respectively to a perpendicular component of the zero-field-splitting tensor, obtaining $g_{x'} = 1.98$ and $E/D = 0.11$. From the polycrystalline-powder EPR spectra it is not possible to obtain direct information on the principal directions of the **g**, *D*, and hyperfine tensors or on their mutual positions. The principal values of the g tensor of the copper(II)–manganese(II) pair, deduced from the reported formula[17,18] by using the $\mathbf{g}_{Cu}$ tensor obtained for the copper–copper dimers and an isotropic $\mathbf{g}_{Mn}$ tensor $g_{x,Mn} = g_{y,Mn} = g_{z,Mn} = 2.,00$ for the manganese ion, are $g_x = 1.990$ $g_y = 1.989$, and $g_z = 1.946$, slightly different from those experimentally obtained. In particular $g_{z'}$, the g value observed along the $D_{z'z'}$ direction, is greater and $g_{\perp'}$ is lower than the expected g_z and $g_\perp$ respectively. This suggests that the **g** and **D** tensors are not collinear as they were observed in $[Cu(pyO)Cl_2(H_2O)]_2$, for which single-crystal data are available.[14,16]

We tried to obtain single-crystal data for $[(Cu,Mn)(pyO)Cl_2(Me_2SO)]_2$, but we had some problems. The host lattice is monoclinic, with two dimers *per* unit cell, and the spectra recorded with the static magnetic field in a plane containing the *b* crystal axis must show two magnetically nonequivalent sites. We recorded single-crystal spectra of copper(II)–manganese(II) pairs in different single crystals, but we never succeeded in finding the required symmetry properties of the spectra or in observing two equivalent dimeric units, as required when the static magnetic field lies along the unique axis. This must be due to the fact that the presence of manganese(II) induces much distortion in the host lattice,[16] and so it is not possible to use the known structure of the $[Cu(pyO)Cl_2(Me_2SO)]_2$ to correlate the principal directions of the **g** and **D** tensors with the molecular frame and we gave up the single-crystal analysis.

The principal values and directions of the **g** tensor of the copper(II) pairs are in good agreement with the structural data.[11] In fact the largest g value, $g_{zz} = 2.337$ (2), is found roughly parallel to the long Cu–O(Me$_2$SO) bond, and also the actual value compares well with the values expected for square-pyramidal copper(II) complexes.[13,19,20] The in-plane g values are, as usual, determined with much less accuracy.

The **D** tensor has its largest value, $D_{z'z'}$, along a direction that makes an angle of 28.7 (5)° with g_{zz}, while the second largest component, $D_{x'x'}$ is essentially in the CuOOCu plane and roughly orthogonal to the copper–copper direction r. In fact $D_{x'x'}$ makes an angle of 82.0 (2)° with r, and of 14 (1)° with the line connecting the two bridging oxygen atoms. If we simplify to some extent, we may say that the **D** tensor has two principal axes in the plane defined by g_{zz} and r, the actual directions being rotated from this by 28.7 (5)°. This result is similar to that previously reported for bis(*μ*-pyridine *N*-oxide)bis[dichloro(pyridine *N*-oxide)copper(II)], $[Cu(pyO)Cl_2(pyO)]_2$,[13] and for bis(*μ*-pyridine *N*-oxide)bis[dichloroaquocopper(II)], $[Cu(pyO)Cl_2(H_2O)]_2$,[14,16] for which the corresponding rotation angles were 23 and 26°, respectively. The principal D values of the three complexes are compared in Table II.

The overall appearance of the **D** tensors of these pyridine *N*-oxide-bridged complexes is similar to those reported for other bis(*μ*-oxo)-bridged copper(II) complexes,[1,3–5] in the sense that they all have sizable exchange contributions, with the largest D values roughly orthogonal to the copper–copper direction, as expected for a dominant xy–$x^2 - y^2$ interaction. Now the actual principal directions leave some unresolved problems, however; in fact they are not parallel to g_{zz}, as expected on the basis of the above model, but are rotated from that direction by an angle that is much larger than the experimental error. In all the other similar complexes investigated so far $D_{z'z'}$ has always been found to be very close to g_{zz}.[1,3–5,8,9] Since the experimental **D** tensor is given by the sum of two contributions, $\mathbf{D}^{dip}$, determined by the magnetic dipolar interaction, and $\mathbf{D}^{ex}$, determined by the exchange interaction,[21] it is the latter that must be responsible for the observed rotation of the principal directions. $\mathbf{D}^{dip}$ in fact can be calculated with reasonable accuracy[22] and is expected to have its largest component parallel to the copper–copper direction, the second one being parallel to g_{zz}. Therefore inclusion of the dipolar interaction can only change the D values parallel to z and y, respectively, but not rotate the tensor, contrary to what was previously suggested.[13] Since these complexes possess inversion centers, it is also not possible to attribute the observed directions to a strong antisymmetric exchange interaction,[23,24] as was suggested for an analogous copper(II)–manganese(II) pair.[23] Therefore the inescapable conclusion is that the exchange tensor has a sizable D_{yz} component.[6] This can be estimated from the experimental zero-field-splitting tensors through the relations

$$\begin{aligned} D_{zz} &= (\cos^2 \vartheta)D_{z'z'} + (\sin^2 \vartheta)D_{y'y'} \\ D_{yy} &= (\sin^2 \vartheta)D_{z'z'} + (\cos^2 \vartheta)D_{y'y'} \qquad (1) \\ D_{yz} &= (\sin (2\vartheta/2))(D_{z'z'} - D_{y'y'}) \end{aligned}$$

Using the experimental $D_{z'z'}$, $D_{y'y'}$, and ϑ values, we calculate $D_{yz} = -0.0692$ cm^{-1} for $[Cu(pyO)Cl_2(Me_2SO)]_2$, $D_{yz} = -0.0493$ cm^{-1} for $[Cu(pyO)Cl_2(H_2O)]_2$, and $D_{yz} = -0.0683$ cm^{-1} for $[(Cu(pyO)Cl_2(pyO)]_2$. Having assumed that D_{yz} is essentially exchange-determined, we may express it as previously reported. Assuming for the sake of simplicity that the ground state is to a good approximation represented by the two xy magnetic orbitals, D_{yz} is expressed as[25,26]

$$D_{yz} = -\tfrac{1}{4}\Delta g_z\ \Delta g_y\ J_{xy,yz,x^2-y^2,xy} \qquad (2)$$

where $\Delta g_z = g_z - 2.0023$, $\Delta g_y = g_y - 2.0023$ and $J_{xy,yz,x^2-y^2,xy} = \langle xy_A,yz_B|H_{ex}|x^2 - y_B,xy_A\rangle$, where B and A refer to the two copper centers, respectively. Using (2) and the experimental data, $J_{xy,yz,x^2-y^2,xy}$ is estimated to be on the order of 10 cm^{-1}. This seems to be an interesting result, since in general these parameters are completely neglected probably because they are very difficult to estimate, since they cannot be obtained from the analysis of either homo- or heterodinuclear species.

The sign of the J parameter is determined by the sign choice for $D_{z'z'}$ and $D_{y'y'}$. With our sign choice $J_{xy,yz,x^2-y^2,xy}$ is positive. It must be also recalled here that parameters of a very similar form, namely $J_{gA,eB,eB,gA}$, where g and e indicate the ground function and one excited function, respectively, on center A or B, are present in the expression for the antisymmetric exchange vector, $\vec{d}$.[23] It would be desirable to have more experimental data

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available to learn how to evaluate these kind of parameters.

The overall symmetry of the **D** tensor is compatible with C_s, the plane passing for the copper atoms, or, including the crystal C_i symmetry, with the C_{2h} point group. Indeed xy is antisymmetric referred to the plane and yz and $x^2 - y^2$ are symmetric, so that $J_{xy,yz,x^2-y^2,xy}$ is totally symmetric as required. The question still to be answered is why D_{yz} becomes so important for the pyridine *N*-oxide complexes, while for all the other members of the series its effect is much less evident. The best explanation we can find is that $J_{xy,yz,x^2-y^2,xy}$ does not vary much as the metal–metal distances decrease, so that D_{yz} does not vary appreciably. Since its value is determined essentially from the rotation of the principal D axes from the g_{zz} direction, keeping D_{yz} constant and increasing $|D_{z'z'}|$ and $|D_{yy}|$ yield progressively smaller angles, which eventually fall within experimental indetermination. Beyond the bis(μ-oxo)-bridged series, relevant deviations of the $D_{z'z'}$ axis from the g_{zz} direction were determined also for 1,3-bis(μ-azido)bis(1,1,4,7,7-pentamethyldiethylenetriamine)copper(II) bis(tetraphenylborate), where the diagonal values were slightly smaller than in the present case ($D = 0.0854$ cm^{-1}).

Registry No. [Cu(pyO)Cl_2(Me_2SO)]$_2$, 57063-89-5; Mn, 7439-96-5.

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Palladated Azobenzenes and Regiospecific Aromatic Metaloxylation

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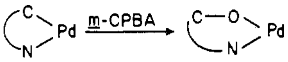
Received October 28, 1985

Three groups of ortho-palladated azobenzenes (**4**, **8**, and **9**) and their high-yield regiospecific oxidation (called aromatic metaoxylation, Ar–Pd → Ar–OPd) by *m*-chloroperbenzoic acid (*m*-CPBA) in acetonitrile solution are described. Schematically, the metaloxylation reaction is



the product being an azophenol chelate (**5**, **6**, **10**, **11**). Several modes of binding—bidentate N,O and C,N and tridentate C,N,O—of *o*-hydroxyazobenzenes to palladium(II) are characterized. The C,N,O mode occurs in **8**. The Pd–O bond in **8** can be reversibly cleaved by acids, resulting in sharp color changes that are useful for indicator action in acid–base titrations in acetonitrile. The tridentate binding of the organic ligands in **8** and **9** (C,N,S mode) is unequivocally revealed by their ^{1}H NMR spectra. The oxidation of **4** by *m*-CPBA is complicated by the formation of two products: **5** and **6**. The oxidation of **8b** furnishes **11** while **9** yields **10**. A notable feature is that the metaloxylation reaction is very much faster than the possible oxidation of other centers (e.g. pyridine in **8b** or SR″ in **9**). In all cases the identity of the metaloxylated product has been established by its independent synthesis from preformed (by nonoxidative routes) hydroxyazobenzenes and palladium(II) salts. The reaction **9c** → **10c** has been kinetically characterized (295.8 K), affording the rate law d[**10c**]/d*t* = *k*[**9c**]^2[*m*-CPBA] with $k = 3.02 \times 10^4$ M^{-2} s^{-1}. It is proposed that an adduct (**13**) consisting of two **9c** molecules bridged (at palladium(II) centers) by a peroxo oxygen of *m*-CPBA is formed as a reactive intermediate, which decomposes in the rate-determining step to afford **10c**. The key step is the heterolytic dissociation of the O–O bond, allowing insertion of oxygen into the Pd–C bond of one **9c** molecule.

Introduction

The regiospecific oxidation of the aromatic C–H function to the C–OH function, reaction 1, is of considerable import in chemistry.[1,2] In Nature this reaction is a useful tool for imparting

$$\text{Ar–H} \rightarrow \text{Ar–OH} \qquad (1)$$

$$\text{Ar–M} \rightarrow \text{Ar–OM} \qquad (2)$$

desirable properties such as biological activity and water solubility to organic compounds.[3] The associated enzymes (monooxygenases) often have a metal (usually copper or iron) at the active site for binding and activating[4-11] dioxygen, the natural oxidant. This work stems from our interest[12] in reaction 2, which can be considered as the organometallic analogue of the aromatic

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(4) In order to buttress this, a variety of synthetic metal-containing hydroxylating reagents[1,2] have been examined, such as those of Fenton (Fe^{2+}, H_2O_2),[5] Brackman and Havinga (Cu^{2+}, amine, H_2O_2),[6] Udenfriend (Fe^{2+}, edta, ascorbic acid, O_2),[7] and Hamilton (Fe^{3+}, catechol, H_2O_2).[1,8] Aromatic hydroxylation of copper(I) complexes of *m*-xylyl binucleating ligands by dioxygen is reported.[9] Macrocyclic polyamine complexes of nickel(II) can mediate aromatic hydroxylation:[10] Palladium(II) and platinum(II) complexes of azo ligands provide interesting cases of aromatic hydroxylation.[11]

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