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Citation: *Journal of Applied Physics* **90**, 1436 (2001); doi: 10.1063/1.1372660

View online: <http://dx.doi.org/10.1063/1.1372660>

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# Electronic structure of polycrystalline polyamine copper dinitrate complexes investigated by photoacoustic and electron paramagnetic resonance spectroscopy

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(Received 29 November 2000; accepted for publication 28 March 2001)

Photoacoustic and electron paramagnetic resonance (EPR) spectroscopies have been applied to resolve the electronic structure in powder polycrystalline samples of three biogenic polyamine copper complexes, spermine copper dinitrate, aqua norspermine copper dinitrate, and homospermine copper dinitrate. The fine structure of the intense absorption band in the photoacoustic spectra is assigned to the  $d-d$  transitions between the crystal field split levels of copper ions, that cannot be discriminated in the UV/vis solution absorption spectra. Combination with the EPR results allows one to probe the variation of the electronic properties and bonding interaction at the copper site, consistent with the structural data for the crystalline complexes and further supports the reliability of the photoacoustic method to resolve the  $d-d$  transition band. A dominant contribution of the in-plane ligand field due to equatorial nitrogen atoms is deduced for the complexes of polyamines with copper salts. © 2001 American Institute of Physics.  
[DOI: 10.1063/1.1372660]

## I. INTRODUCTION

Polyamines, which occur as natural elements of most living organisms, play a major role in many biological processes, including the structural conformation and stabilization of nucleic acids.<sup>1-3</sup> The widespread presence of polyamines, which under physiological ionic conditions are positively charged, and the diversity of their interaction with other bioligands and metal ions, has been the stimulus of intensive investigations of their complexes.<sup>4,5</sup> The centers of polyamine interaction with other biomolecules have been considered as potential coordination sites of metal ions present in living cells, while biogenic amines have been simultaneously regarded as an interfering factor in complex formation of metals with nucleic acids.<sup>5</sup> Considerable research effort has been recently devoted to precise structural and spectroscopic investigations of different crystalline complexes of biogenic amines with salts of bivalent copper to

define the conformation and interaction of polyamine cations.<sup>6-8</sup> Determination of the electronic properties and their variation in polyamine metal complexes thus becomes essential for a better understanding of their action on the molecular level and the establishment of firm correlations with their biological function.

Nevertheless, a serious limitation appears because transitions between the crystal field energy levels of copper ions, that carry information on the coordinate ligand field, are only weakly allowed and often appear as an unresolved band in electronic spectroscopy experiments conventionally carried out in solution. Moreover, accurate information on the crystal field symmetry and ground state magnetic properties of copper ions provided by electron paramagnetic resonance (EPR)<sup>9</sup> is difficult to exploit for investigation of the metal-ligand interaction when the excited states are not determined. Photoacoustic spectroscopy (PAS) relying on thermal and elastic wave generation by absorption of an intensity modulated light beam has been long considered a sensitive, non-invasive method for the spectroscopic study of solid samples with respect to conventional spectroscopic techniques.<sup>10</sup> Al-

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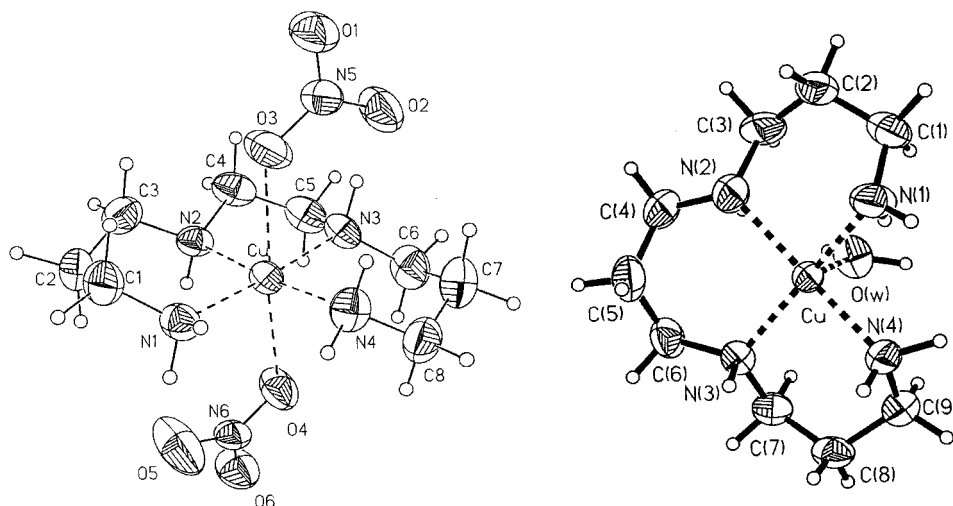


FIG. 1. Local crystal structure of copper in Spn323 (left) and Spn333 (right) complexes, with the thermal ellipsoids at 50% probability.

though PAS has been successfully applied to determine the crystal field energy spectrum and to study nonradiative de-excitation processes of transition metal ions in various hosts,<sup>11–14</sup> its utilization on polycrystalline powder samples of hydrate isomers and polyamine copper complexes has been only recently shown to trace the crystal field bands of  $\text{Cu}^{2+}$ , which otherwise become indistinguishable in the solution absorption spectra.<sup>15,16</sup> In particular, PAS combined with EPR and optical spectroscopies has been successfully applied to resolve the electronic properties of  $\text{Cu}^{2+}$  ions in three polycrystalline polyamine complexes with  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , namely, aqua spermine copper sulfate trihydrate (Spm343), norspermine copper sulfate trihydrate (Spm333), and homospermine copper sulfate dihydrate (Spm)323.<sup>16</sup> In this respect, it becomes of great interest to study a series of slightly different polyamine copper complexes both to assess the potential of PAS to determine the crystal field transitions of  $\text{Cu}^{2+}$  ions for powder samples, as well as to explore the correlation of the spectral electronic features with metal coordination and to provide a better understanding of the bonding interaction at the metal site.

In this work, three polyamine copper dinitrate complexes have been prepared and investigated by photoacoustic and EPR spectroscopy in combination with the crystal structure determination and conventional UV/vis solution spectra. PAS is shown to probe successfully in the solid state the variation of the weakly allowed  $d-d$  transitions from the crystal field split energy levels of  $\text{Cu}^{2+}$  and, combined with EPR and simple crystal field analysis, to provide a meaningful description of the electronic structure and bonding interaction of the metal complexes with polyamines.

## II. EXPERIMENT

Three complexes, spermine copper dinitrate



aqua norspermine copper dinitrate



and homospermine copper dinitrate



designated hereafter as Spn343, Spn333, and Spn323, have been prepared by slow evaporation of methanol from the appropriate solution of the corresponding polyamine complexes with  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , previously described in Ref. 6. The crystal structure of only two complexes, which were obtained in single crystal form, namely, Spn323 (Ref. 6) and Spn333,<sup>17</sup> has been determined by x-ray diffraction and IR spectroscopy. Figure 1 shows the local environment of the copper site in Spn323 and Spn333. In both structures, copper is coordinated by four equatorial nitrogen atoms from the amino groups, leading to the formation of tricyclic chelated complexes. One oxygen atom provided by the water molecule, which is axial with respect to the mean plane of the nitrogen atoms, coordinates copper in Spn333, forming a complex with coordination number 5. The  $\text{NO}_3^-$  anion, contrary to the  $\text{SO}_4^{2-}$  anion studied previously,<sup>7,8</sup> is strictly planar and can easily adjust to the structure of the complex. This is the case for the Spn323 complex, in which two  $\text{NO}_3^-$  groups are in the coordination sphere of a copper ion, although with substantially longer bonds. The corresponding bond lengths are presented in Table I for both complexes. For Spn323 the four Cu–N bond lengths are consistently shorter compared to those of Spn333. This might be related to the axial water molecule, which pulls the Cu atom out of the  $\text{N}_4$  plane ( $\sim 0.257 \text{ \AA}$ ) towards the O atom, stretching the Cu–N bonds, and distorts their arrangement in the Spn333 complex.<sup>6</sup>

The PA spectra of the three complexes in powder form were recorded at room temperature in the range of 300–800 nm, using a homemade single beam spectrometer.<sup>18</sup> The excitation source is a 1000 W arc xenon lamp coupled with a

TABLE I. Cu–N and Cu–O bond lengths (in  $\text{\AA}$ ) for the Spn323 and Spn333 complexes.

	Cu–N(1)	Cu–N(2)	Cu–N(3)	Cu–N(4)	Cu–O(1)	Cu–O(2)
Spn323	2.015(4)	2.033(4)	2.038(4)	1.995(4)	2.440(4)	2.646(4)
Spn333	2.060(5)	2.076(4)	2.052(3)	2.041(4)	2.253(4)	...

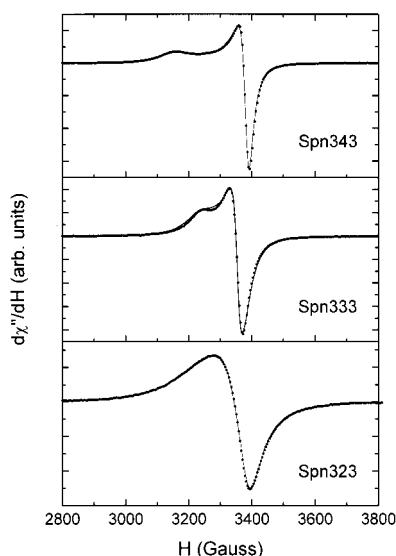


FIG. 2. X-band EPR powder spectra of  $\text{Cu}^{2+}$  ions, experiment (circles) and simulation (lines), of the polyamine copper complexes at room temperature.

1/4 m ORIEL monochromator with a band pass width of 5 nm at 500 nm. The intensity of the light, modulated with a mechanical chopper at 10 Hz, is directed into a photoacoustic cell equipped with a TREVI EM27 microphone. The amplitude and phase of the photoacoustic signal are then processed using a dual SR830 lock-in amplifier and a computer-controlled acquisition system. The signal-to-noise ratio of a single measurement, which is approximately 10 for the whole measuring system, is increased at least to 50 after averaging 20 runs at the same wavelength of incident light. The PA spectrum of highly absorbing carbon black is used as a standard to recalibrate the final spectrum and to eliminate contributions from the spectral response of the optical apparatus. In the case of thermally thick samples, where the thermal diffusion length is shorter than the sample thickness, the photoacoustic signal is approximately proportional to the absorption coefficient of the sample and saturation is avoided provided that the optical length is larger than the thermal diffusion length.<sup>19</sup>

The EPR spectra were recorded with a conventional X-band ( $\nu=9.76$  GHz) Bruker E500 spectrometer employing magnetic field modulation of 100 kHz, at room temperature. The EPR measurements were performed on fine powder samples (20 mg), sealed in quartz tubes of cylindrical shape, while the resonance line positions and their linewidths were measured with nuclear resonance probes. The UV/vis measurements were performed on a Hitachi-2000 double beam

spectrometer at room temperature, in methanol solution, for 0.1% concentration of the complexes investigated.

### III. RESULTS AND DISCUSSION

#### A. EPR measurements

Figure 2 shows the EPR spectra for the three polyamine complexes at room temperature. In all cases, an intense anisotropic powder spectrum typical for  $\text{Cu}^{2+}$  ions is observed, most clearly resolved for the Spn343 complex. The MONOQ simulation program for spin  $S=1/2$  (Ref. 20) was used to reliably determine the principal  $g$  values allowing for a  $g$  tensor of rhombic symmetry with anisotropic linewidths  $w_i$  ( $i=x, y, z$ ) and the presence of strain producing inhomogeneous broadening. The values of the EPR parameters obtained for the three samples are presented in Table II, and the simulated EPR spectra in comparison with the experimental ones, are shown in Fig. 2. The hyperfine structure of copper isotopes is found to be suppressed for all complexes, as is often observed for concentrated copper compounds where exchange narrowing is effective, and thus it was not taken into account. For all cases,  $g$  anisotropy is present along the three principal axes, although essential differences exist among the three compounds. Considerable in-plane anisotropy of the  $g$  tensor is deduced only for the Spn323 complex, where copper lies in a distorted sixfold coordination, whereas a substantial reduction is inferred for the other two complexes, most pronounced for Spn343. The presence of water in the coordination sphere of copper in Spn333 seems to reduce the in-plane anisotropy, in accord with our previous result for aqua spermine copper sulfate trihydrate (Spm343), which has one axially coordinated water molecule.<sup>16</sup> Accordingly, it may be suggested that the Spn343 complex, whose crystal structure is presently unknown, might also have one water molecule coordinated to the  $\text{Cu}^{2+}$  ion. On the other hand, Spn333 exhibits a smaller  $g_z$  value, implying a relatively increased crystal field strength and/or covalency with the equatorial ligands.

#### B. UV/vis solution spectra

Figure 3 shows the UV/vis absorption spectra in methanol solution for the compounds studied. An intense absorption band is detected at 272, 278, and 282 nm for Spn323, Spn333, and Spn343, respectively, which is consistent with the metal–ligand charge transfer transitions occurring at relatively high energies.<sup>21</sup> At lower energy, a much weaker absorption band is detected for all three complexes, at 538 nm for Spn323, at 590 nm for Spn333, and at 554 nm for

TABLE II. EPR parameters for the three copper complexes derived from the simulated EPR powder spectra.

	$g_x$	$g_y$	$g_z$	$w_x$ (MHz)	$w_y$ (MHz)	$w_z$ (MHz)	$c_{1x}$	$c_{2y}$	$c_{3z}$
Spn343	2.0530	2.0580	2.2060	50	68	175	...	...	...
Spn333	2.0737	2.0854	2.165	115	48	165	...	...	0.0015
Spn323	2.0620	2.0950	2.1770	115	187	400	...	...	...

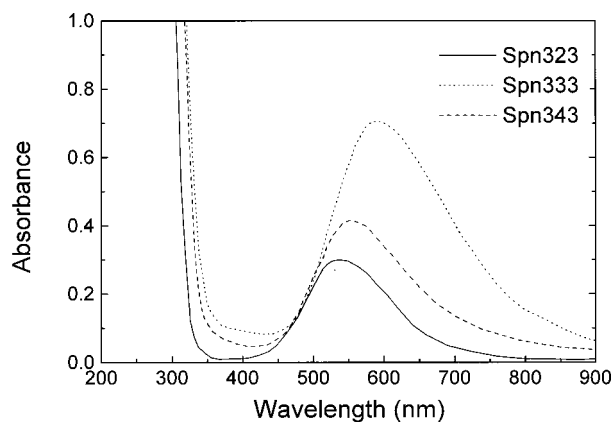


FIG. 3. UV/vis absorption spectra in methanol solution (0.1% mole concentration) of the Spn323, Spn333, and Spn343 complexes.

Spn343. The corresponding peak wavelength ( $\lambda_0$ ) complies with the expected energy range for the  $\text{Cu}^{2+}d-d$  transitions in polyamine copper complexes with fourfold nitrogen coordination in the equatorial plane.<sup>4,5</sup> In the low crystal field symmetry of the copper site in the polyamine complexes, three nominally forbidden  $d-d$  transitions become weakly allowed through the admixture with the ligand orbitals. Both the decreasing order of the peak wavelengths and, most importantly, their absolute values for the present polyamine copper dinitrate complexes (Spn333>Spn343>Spn323) are almost identical to those of the analogous sulfate complexes (Spn333>Spn343>Spn323).<sup>16</sup> This indicates that despite the presence of small, although essential, differences in the crystal structure and copper coordination for the sulfate and nitrate complexes, the crystal field band detected in the solution spectra is mainly determined by the polyamine type and hardly probes the structurally induced modifications of the electronic structure anticipated in the solid state.

### C. Photoacoustic spectra and electronic properties

On the other hand, the photoacoustic spectra of the three polyamine complexes in powder form reveal an intense and broad absorption band in the visible range, with a weakly resolved fine structure, as shown in Fig. 4. The wavelength peak position and width variation for the three compounds are close to those of the unresolved crystal field transition band derived from the solution spectra (Fig. 3), although the PA absorption band extends to higher wavelengths. The overall splitting of PA spectra, assumed to be the linewidth of the absorption band at its half height, is 232 nm for Spn343, 239 nm for Spn323, and 245 nm for Spn333 and correlates well with the  $g$ -tensor axial anisotropy, defined as  $g_z - g_x$ , derived from the EPR spectra (Table II). The same correlation was previously observed for the polyamine sulfate complexes,<sup>16</sup> which can plausibly be expected in view of the close relationship between the principal  $g$  values and the crystal field split energy levels. However, comparison with the latter PA spectra shows that the fine structure splitting of the PA band is significantly obscured in the present case by the overlap of the individual  $d-d$  transitions. To decompose the corresponding peaks, line shape analysis with a Gaussian

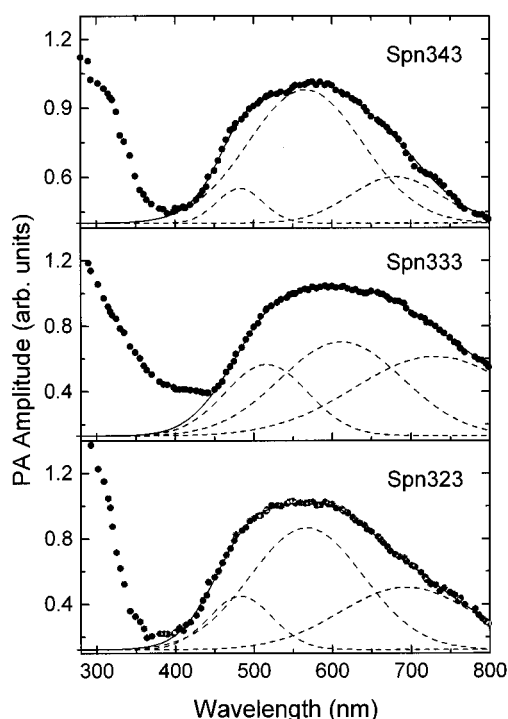


FIG. 4. Photoacoustic spectra of the powder Spn323, Spn333, and Spn343 samples at room temperature. Solid (sum) and dashed (components) lines show the best fit curves of the central absorption band with a Gaussian line shape.

profile was performed, showing that the broad PA spectrum can be accurately described with three individual absorption bands (Fig. 4). The wavelength values obtained, referred to as  $\lambda_1$ ,  $\lambda_2$ , and  $\lambda_3$ , along with the  $\lambda_0$  values determined from the solution spectra, are shown for all complexes in Table III. The corresponding values derived, applying the same procedure, from the PA spectra of the three polyamine sulfate complexes<sup>16</sup> are also included. It has to be noted that the latter values are generally close, within experimental error, to the previously cited ones, apart from the Spn323 case, where the PA spectrum exhibits significantly reduced resolution.<sup>16</sup> Comparison between the two sets of PA transitions for the nitrate and sulfate copper polyamine copper complexes shows that, although a similar trend in crystal field strength for the same polyamine ligand conformation can be deduced, distinct differences, practically hindered in the solution absorption spectra, occur in the electronic structure of the copper site in accord with the variation of the metal coordination and local structure in the crystalline complexes.

To exploit further the crystal field transitions for determination of the metal–ligand interaction of copper in the polyamine local environment and to indirectly assess the reliability of the PAS resolution, simple crystal field analysis of the  $\text{Cu}^{2+}$  ion is employed.<sup>22,23</sup> The ground state of  $\text{Cu}^{2+}$  ions in the low crystal field symmetry site of the polyamine complexes is a superposition of both the  $d(x^2-y^2)$  and  $d(3z^2-r^2)$  orbitals that belong to the same irreducible representation, namely,  $\alpha d(x^2-y^2) + \beta d(3z^2-r^2)$ , with the orthonormality condition  $\alpha^2 + \beta^2 = 1$ . The  $g$  values are

TABLE III. UV/vis and photoacoustic peak wavelengths along with the ground state coefficients and bonding parameters calculated from the EPR data for the polyamine copper complexes.

	$\lambda_0$ (nm)	$\lambda_1$ (nm)	$\lambda_2$ (nm)	$\lambda_3$ (nm)	$\alpha$	$\beta$	$k_1$	$k_{\perp}$
Spn343	554(3)	438(3)	566(3)	680(10)	0.9987	0.0498	0.68	0.82
Spm343 <sup>a</sup>	560(3)	498(3)	579(15)	690(100)	0.9991	0.0426	0.69	0.79
Spn333	590(3)	516(20)	610(100)	730(100)	0.9989	0.0458	0.58	0.93
Spm333 <sup>a</sup>	594(3)	570(10)	698(8)	795(7)	0.9921	0.1250	0.64	0.83
Spn323	536(4)	483(3)	567(15)	694(90)	0.9965	0.0838	0.62	0.96
Spm323 <sup>a</sup>	540(3)	486(4)	566(9)	670(100)	0.9978	0.0658	0.66	0.88

<sup>a</sup>Reference 16.

then given by  $g_z = 2 - 8\lambda_{so}k_1^2\alpha^2/E_{xy}$ ,  $g_x = 2 - 2\lambda_{so}k_2^2(\alpha - \sqrt{3}\beta)^2/E_{yz}$ ,  $g_y = 2 - 2\lambda_{so}k_3^2(\alpha + \sqrt{3}\beta)^2/E_{xz}$ , where  $\lambda_{so} = 828 \text{ cm}^{-1}$  is the spin-orbit coupling constant for free  $\text{Cu}^{2+}$ ,  $E_{ij}(i, j = x, y, z)$  is the relative energy of the  $d_{ij}$  level with respect to the ground one, and  $k_i(i = 1, 2, 3)$  are the combined orbital and spin-orbit reduction parameters yielding information on the bonding interaction. Assuming that the energy values of PAS lines  $\lambda_1$ ,  $\lambda_2$ , and  $\lambda_3$  correspond to the  $E_{xz}$ ,  $E_{yz}$ , and  $E_{xy}$  energies, respectively, and using the  $g$  values of the EPR spectra, the values of the  $\alpha, \beta, k_1, k_2 = k_3 = k_{\perp}$  parameters (this assumption is likely to be valid when departure from axial symmetry is not very large) are calculated, shown in Table III.

A number of conclusions may be deduced from these data. A small but considerable contribution of the  $d(3z^2 - r^2)$  orbital to the ground state, which is predominantly of  $d(x^2 - y^2)$  type, is immediately realized for all complexes, even in the case of Spn343, where the in-plane anisotropy of the  $g$  tensor is significantly reduced. The anisotropy in the bonding parameters  $k_1 < k_{\perp}$  for all complexes complies with a dominant in-plane bonding interaction of copper ions with the equatorial nitrogen and weaker out-of-plane bonding with the ligands along the  $z$  axis, the most substantial being that for the Spm343 complex where copper is axially coordinated with a water molecule. Comparison between the two norspermine complexes Spn333 and Spm333, where precise crystallographic data are available, shows that while the more symmetric arrangement of the equatorial nitrogen atoms in Spn333 indeed agrees with the smaller admixture of the  $d(3z^2 - r^2)$  orbital to the ground state, the bonding parameters ( $k_1, k_{\perp}$ ) vary consistently with the corresponding bond lengths for the two complexes. That is, the shorter the bond length is, the stronger is the covalent interaction and the deviation of  $k_i$  from the purely ionic value ( $k_j = 1$ ).<sup>23</sup> Accordingly, a consistent and meaningful picture of the electronic structure of copper in the polyamine environment can be inferred, which can be further supplemented by crystallographic and EPR studies, but it also corroborates the capability of PA spectroscopy to resolve the crystal field transitions in the polycrystalline state.

#### IV. CONCLUSIONS

We have shown that photoacoustic spectroscopy can be effectively exploited as a noninvasive sensitive method to

resolve the crystal field transitions of copper ions in powder polycrystalline samples of the biologically important polyamine complexes, which is not feasible using the conventional optical spectra obtained in solution. Line shape analysis of the broad absorption band and the fine structure observed in the PA spectra verifies the presence of three distinct  $d-d$  transitions anticipated for the low symmetry copper site in the polyamine complexes. Further substantiation of the assignment of the PAS lines is provided by the analysis of the energy spectrum along with the EPR results within the context of simple crystal field theory, which discloses a meaningful variation of the electronic structure and bonding interaction for the polyamine complexes investigated, consistent with crystallographic data on the local environment of copper ions. For the particular case of the dinitrate and sulfate copper complexes with biogenic amines, the dominant role of the equatorial field strength and bonding with the nitrogen atoms is inferred, while smaller out-of-plane bonding is traced with axially coordinated oxygen atoms.

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