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A Study of the Electronic Structure of 2-(Dialkylamino)-1,3-dimethyl-1,3,2-diazaphospholanes and Related Molecules

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Ultraviolet photoelectron spectroscopy has been employed to study the electronic structure of several diazaphospholanes and related molecules. These molecules contain two nitrogen lone-pair basis orbitals oriented such that their interaction with the phosphorus lone-pair basis orbital is of π type. The third nitrogen lone-pair basis orbital (exocyclic nitrogen) is orthogonal to the other three. A series of interaction parameters have been derived to assist in PES band assignments which are consistent with dynamic NMR data and PES of acyclic aminophosphines studied earlier in these laboratories and elsewhere. The current data suggest that the HOMO for the (dialkylamino)diazaphospholanes has partial phosphorus lone-pair character in contrast to the HOMO for the acyclic aminophosphines which has only nitrogen lone-pair character.

Introduction

There has been considerable interest in the electronic structure of aminophosphines in recent years, particularly as regards the orientation and interaction of the nitrogen and phosphorus lone pairs.¹⁻¹² Structures A–D show a series of



possible conformations that these aminophosphines could assume; of course there are an infinite number of intermediate conformations possible as well. While NMR provides timeaveraged spectra which complicate conformational analyses unless the molecules can be frozen out into their lowest energy conformers at low temperatures,^{9,12} ultraviolet photoelectron spectroscopy does not suffer from this limitation. The rapid time scale of the Franck-Condon ionization process observed in photoelectron spectroscopy permits observation of the spectrum of the predominant conformer or conformers of a molecule, even though the molecule may contain quite low rotational barriers. Thus if well-resolved spectra for which band assignments are definitive can be obtained, predominant gas-phase conformations can be studied. This is particularly true for molecules such as aminophosphines which contain interacting "lone-pair" orbitals. Nevertheless, there currently exists a lively controversy concerning the predominant conformation of acyclic tris(dialkylamino)phosphines.

Vilkov and co-workers employed electron diffraction in a study of tris(dimethylamino)phosphine.² Their interpretation concluded that the molecule has a C_3 axis of symmetry but no symmetry plane. This interpretation has been questioned by several groups of photoelectron spectroscopists. Cowley and co-workers concluded that the molecule is best represented by conformation B, i.e., C_s symmetry.³ Later Lappert and collaborators suggested that D (C_{3v} symmetry) was a preferred model.⁴ More recently, work in these laboratories⁸ on several (dialkylamino)phosphines has confirmed the Cowley model B but questions the photoelectron band assignments proposed³ earlier. Yarbrough and Hall have since suggested that their

photoelectron spectral data on the chromium pentacarbonyl complex of tris(dimethylamino)phosphine confirms the early band assignments of Cowley.¹⁰ However, in fairness it must be pointed out that upon complexation of the phosphorus lone pair with $Cr(CO)_5$, distortion of the geometry at phosphorus and drastically altered orbital interactions would be expected. Very recently Cowley and co-workers¹¹ have studied the X-ray crystal structure of the iron tricarbonyl complex of tris(dimethylamino)phosphine and performed STO-3G ab initio MO calculations on $(H_2N)_3P$. This work suggests that the Vilkov C_3 conformation and conformation B are very close in energy and both substantially lower in energy than conformers A, C, or D. A similar ab initio calculation on tris(dimethyl-amino)phosphine should be illuminating.

The lively controversy discussed above has led to studies of the electronic structure of other aminophosphines for which the conformation has definitely been established by NMR or by tying the molecule into a particular cyclic conformation. In this respect several groups are currently attempting to synthesize model compounds which can be proven to have the various conformations A–D. Cowley and co-workers have reported already the electronic structures of a series of caged aminophosphines for which model A must apply.⁷ The current paper will report the photoelectron spectra and assigned electronic structure of a series of diazaphospholanes (1a-c)which closely resemble model C and two related compounds (2 and 3).



Experimental Section

Materials. Compounds **1a**-c were prepared by reacting 2chloro-1,3-dimethyl-1,3,2-diazaphospholane with a 2 molar excess of the appropriate dialkylamine in dry ether under nitrogen.¹³ After filtration and removal of the solvent, the resulting liquids were distilled: **1a** bp 30-32 °C (1.8 mm); **1b** bp 59 °C (2.4 mm); **1c** bp 70-72 °C (0.5 mm). Compound **3** was prepared by reacting 2-chloro-1,3-dimethyl-1,3,2-diazaphospholane with an excess of methanol in the presence of triethylamine in dry ether under nitrogen. The product was distilled; bp 77-78 °C (40 mm). Compound **2** was prepared by reacting an equimolar mixture of *sym*-dimethylethylenediamine with 2,2-dimethoxypropane in benzene in the presence of a small amount of acetone. Purification was accomplished by distillation (bp 120-140 °C; atmospheric pressure) followed by gas chromatography. The ¹³C and ¹H NMR spectra and mass spectra of these compounds were in accord with the structures. All compounds were handled carefully

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Figure 1. Photoelectron spectra of three diazaphospholanes. Excitation source was the He I resonance line.

Table I. The "Lone-Pair" Ionization Potentials for Some Diazaphospholanes and Related Molecules^{α}

| I_1 | I_2 | I_3 | I_4 |
|-------|---|--|---|
| 7.61 | 7.80 | 8.68 | 9.91 |
| 7.50 | 7.73 | 8.50 | 9.81 |
| 7.40 | 7.65 | 8.37 | 9.75 |
| 7.85 | 8.22 | | |
| 8.12 | 8.41 | 9.69 | 10.58 |
| | <i>I</i> ₁ 7.61 7.50 7.40 7.85 8.12 | $\begin{array}{ccc} I_1 & I_2 \\ \hline 7.61 & 7.80 \\ \hline 7.50 & 7.73 \\ \hline 7.40 & 7.65 \\ \hline 7.85 & 8.22 \\ \hline 8.12 & 8.41 \end{array}$ | $\begin{array}{cccccc} I_1 & I_2 & I_3 \\ \hline 7.61 & 7.80 & 8.68 \\ \hline 7.50 & 7.73 & 8.50 \\ \hline 7.40 & 7.65 & 8.37 \\ \hline 7.85 & 8.22 \\ \hline 8.12 & 8.41 & 9.69 \end{array}$ |

^a All ionization potentials are in electronvolts.

in view of a previous toxicity warning.13

Photoelectron Spectra. The photoelectron spectra discussed in this work were measured on a Perkin-Elmer PS 18 instrument equipped with a heated inlet probe. All samples were purified by extensive pumping on an external vacuum line linked directly to the inlet system of the spectrometer. Care was exercised to maintain minimal contact of the samples with air during transfer to the vacuum line. The data presented here represent an average of those for at least four runs for each compound. Argon and xenon were always employed as internal calibrants. The resolution of the spectrometer during this work was ca. 35 meV.

Results

The photoelectron spectra of 1a, 1b, and 1c are shown in Figure 1. The "lone-pair" ionization energies measured for these three diazaphospholanes along with those of two related molecules 2 and 3 are given in Table I. The photoelectron spectra of 2 and 3 are shown in Figure 2.

Discussion

While it might be desirable to base an interpretation of the PES of the diazaphospholanes upon rigorous molecular orbital calculations, this is not possible at the current time because of the complexity of the molecules. Calculations of the ab initio type would require a prohibitive amount of computer time due to the extensive basis set necessary, and the semiempirical MINDO/3 SCF procedure available in our laboratories is not parameterized for phosphorus-nitrogen interactions. Therefore, we have chosen to base our interpretation on crude HMO/PMO-type arguments. Although these sim-



Figure 2. Photoelectron spectra of molecules 2 and 3. Excitation source was the He I resonance line.



Figure 3. Possible orbital correlation diagrams for molecule 1a.

ple-minded arguments are not theoretically rigorous, they have worked well in the past for complex molecules,¹⁴ and we have employed them successfully already for a series of acyclic aminophosphines.⁸ Cowley and co-workers have used similar arguments for their PES interpretations as well.^{3,7}

Low-temperature ¹³C and ¹⁵N NMR results obtained in these laboratories have established conclusively that the lowest energy conformation of 1a-c is that shown below with the exocyclic nitrogen lone-pair basis orbital orthogonal to the other nitrogen and phosphorus lone-pair basis orbitals in close approximation to the model C depicted in the Introduction.



Diazaphospholanes

Table II

| | eq set 1 | eq set 2 |
|--------------------|-------------|-------------|
| N _o ' | -8.68 | -8.68 |
| No | -8.70 | -8.70 |
| P | -7.92^{a} | -7.92^{a} |
| BNN | -0.90 | -1.09 |
| β_{NP}^{π} | -0.31 | -0.12 |

^a Assumed.

Given that the conformational model for 1a-c is C, the crude MO diagrams shown in Figure 3 can be constructed. The origin of the difference between the two diagrams is in the placement of the phosphorus basis orbital P_0 relative to the nitrogen basis orbitals N_0 . In other words, does the first ionization band in the PES correspond to ionization of a molecular orbital which has some phosphorus lone-pair character or does it correspond to ionization of an MO with only nitrogen lone-pair character? There is no doubt that the third ionization band in the PES of 1a must be assigned to the exocyclic nitrogen lone pair which does not interact with the other basis orbitals to a first approximation because of its orthogonality. Earlier work in these laboratories⁸ on several acyclic tris(dialkylamino)phosphines established that the N_0 basis orbital should lie at ca. -8.74 eV for tris(dimethylamino)phosphine. I_3 for the cyclic phospholane **1a** is 8.68 eV, establishing a value of -8.68 eV for the basis orbital N_0' ; none of the other ionization potentials for 1a are close to the expected N_0' value. Once the assignment for I_3 is established, I_4 must necessarily correspond to ionization of an MO which is composed of the symmetric combination of P_0 and the two endocyclic N_0 basis orbitals. This leaves I_1 and I_2 to be assigned to ionization of either the antisymmetric combination of P_0 with the N_0 's or the antisymmetric combination of the two N_0 basis orbitals. The latter molecular orbital has no phosphorus lone-pair character because P_0 does not mix with the antisymmetric combination of the two N_0 's due to symmetry. Unfortunately the sets of eq 1 and 2 in Figure 3 contain one more unknown than there are equations. Therefore, in order to solve for the various parameters given the experimental ionization energies, one must arbitrarily choose a value for one of them. Because our dynamic NMR studies¹² showed very little difference in phosphorus coupling constants throughout the series **1a**-c, we can assume that the geometry about phosphorus varies little throughout the series. This, in turn, might indicate that the basis orbital P_0 would change negligibly for the three molecules since the alkyl substituent is only altered at the exocyclic nitrogen. Thus we have chosen to assign a value of -7.92 eV to P_0 for all three molecules; this was the P_0 value experimentally deduced for tris(dimethylamino)phosphine in our earlier study⁸ of model B compounds.

If we evaluate the various parameters (eV) by using the experimental ionization energies in Table I, we find for **1a** the values given in Table II.

Neither of these sets of parameters seems completely unreasonable for **1a**. However, the β_{NN}^{μ} for **1a** evaluated from equation set 2 is almost as large in magnitude as was the case for β_{NN}^{σ} for tris(dimethylamino)phosphine (-1.15 eV).⁸ Orbital overlap should be considerably more efficient for the N_0 basis orbitals in the acyclic compound than for **1a** because the interaction is more σ in character for the acyclic aminophosphine but μ for the cyclic **1a**. Thus, it would seem that equation set 1 provides a more reasonable interpretation of our data than does equation set 2 although we cannot completely reject the equation 2 parameters. This means that the highest occupied molecular orbital of **1a** is predicted to have phosphorus lone-pair character. This is interesting in that we have postulated that the HOMO for the acyclic tris(dialkylamino)phosphines does *not* have phosphorus lone-pair

Table III. Values of Interaction Parameters for the Diazaphospholanes^{α}

| molecule | No | N ₀ ' | P ₀ | β _{NN} ^μ | β_{NP}^{π} |
|----------|-------|------------------|--------------------|------------------------------|--------------------|
| 1a | -8.70 | -8.68 | -7.92 ^b | -0.90 | -0.31 |
| 1b | -8.56 | -8.50 | -7.92 ^b | -0.83 | -0.42 |
| 1c | -8.44 | -8.37 | -7.92 ^b | -0.79 | -0.52 |

^a All values are in eV. ^b Assumed from the data for tris(dimethylamino)phosphine.

character.⁸ Rather for the acyclic molecules the HOMO consists entirely of the interaction of two nitrogen lone pairs in a near end-on σ manner, with the second highest MO corresponding to a π interaction between the phosphorus lone-pair basis orbital and the remaining nitrogen one. Although relative intensities of PES bands usually cannot be employed in assignments due to our lack of knowledge about relative cross sections for ionization of various types of MO's and to our general use of spectrometers which analyze electrons given off normal to the excitation source only,¹⁵ it is noteworthy that the intensity pattern for the first two bands in the PES of the acyclic molecules as compared to the cyclic ones inverts.

The parameters determined in this work for 1a are quite reasonable when compared with those evaluated earlier⁸ for tris(dimethylamino)phosphine. The N_0 (-8.70 eV) and N_0' (-8.68 eV) values for **1a** are in close accord with N_0 (-8.74 eV) for the acyclic aminophosphine. The β values are quite different, however, as expected because, as noted above for 1a, in the cyclic molecule the endocyclic basis orbitals N_0 are interacting with each other in a μ fashion, whereas the corresponding interaction for the acyclic molecule is more a σ one. This is reflected in a larger interaction in the acyclic case $(\beta_{NN})^{\sigma}$ = -1.15 eV as compared to β_{NN}^{μ} = -0.90 eV). The β_{NP}^{π} interaction, on the other hand, is larger for the cyclic molecule (-0.31 eV) than for the acyclic one (-0.01 eV). This, of course, implies that the phosphorus and two nitrogens are closer to being coplanar for the cyclic compound than for the acyclic one; i.e., the phosphorus basis orbital overlaps with the N_0 basis orbitals more efficiently for the former.

The comparison of the parameters calculated for 1a-c given in Table III is informative. The exocyclic nitrogen basis orbital energy shifts from -8.68 eV for 1a to -8.37 eV for 1c. This is to be expected since the isopropyl group is a more proficient electron-releasing substituent than is the methyl group. The other observations (less negative β_{NN}^{μ} , more negative β_{NP}^{π} and less negative N_0 for 1c as compared to 1a) can only be rationalized in terms of a slight change in geometry of the ring. We believe that the most reasonable explanation of our data is that the large, bulky isopropyl groups are causing the ring to adopt a conformation which is more planar for 1c than for 1a. Increased planarity of the ring for 1c would decrease the μ -type overlap between the N_0 basis orbitals and thus lead to a less negative β_{NN}^{μ} . Molecular models show that increased planarity of the ring also leads to more efficient π overlap of the N_0 and P_0 basis orbitals and hence to a more negative $\beta_{\rm NP}^{\pi}$; the N_0 basis orbitals should also assume more p character as ring planarity increases, which could explain the decrease in magnitude of N_0 in passing from 1a to 1c. It should be emphasized, however, that our NMR results show conclusively that the ring does not achieve complete planarity in 1c and that there can be very little change in geometry at phosphorus. It is seen in Table III that the values of the various parameters for 1b are intermediate between those of 1a and 1c as would be expected.

Now let us consider the PES data for the two related molecules 1,2,2,3-tetramethyl-1,3-diazacyclopentane (2) and 2-methoxy-1,3-dimethyl-1,3,2-diazaphospholane (3) (Figure 2; Table I). For 2 the two ionization bands in the low-energy region of the PES at 7.85 and 8.22 eV must represent the



Figure 4. Possible orbital correlation diagrams for molecule 3.

interaction of the two nitrogen lone-pair basis orbitals. The much less negative apparent $\beta_{NN}{}^{\mu}$ for 2 (-0.19 eV) than for 1a (-0.90 eV) could be indicative of more planarity in the ring of 2 than of 1a; it could be also a result of near pyramidal nitrogens in 2 as opposed to near planar ones in 1a. An equally reasonable explanation for the low value of β_{NN}^{μ} for 2 could be that it represents a substantial through-bond interaction as well as a through-space one for this molecule. The PES results of Heilbronner et al.¹⁵ and Nelson and Buschek¹⁶ have shown that through-bond interactions between nitrogen lone pairs can be rather large for dimethylene bridges when the lone-pair axes are parallel to the σ -bonding axis of the bridge. Such through-bond interaction through a dimethylene bridge would tend to raise the symmetric combination of N_0 basis orbitals relative to the antisymmetric combination (opposite to the through-space interaction). Since the nitrogens in 2 must be more pyramidal than the near planar nitrogens in 1a, the lone-pair basis orbitals in 2 are more nearly parallel to the σ axis of the dimethylene bridge in 2 than in 1a for which they are almost orthogonal. Thus through-bond interaction should be much more significant for 2 than for 1a and tend to reduce the value of the β_{NN} . The very low N_0 for 2 (-8.04 eV) as compared to 1a (-8.70 eV) can be attributed in part to a greater stabilizing inductive effect on the ionic state caused by $C(CH_3)_2$ in 2 as compared to $PN(CH_3)_2$ in 1a.

Our interpretation of the PES of molecule 3 is presented in Figure 4. While oxygen introduces the complication of an extra lone-pair basis orbital, one of the O_0 basis orbitals has always been observed to have considerably more "s character" than the other¹⁷ and hence does not interact appreciably with other high-energy lone-pair basis orbitals. Thus only one band in the low-ionization-energy region of the PES of 3 can correspond primarily to ionization of an oxygen "lone pair". This band is most certainly I_4 at 10.58 eV. A similar band is observed in the PES of 4 at 10.63 eV, which must also cor-



| | eq set 1 | eq set 2 |
|--------------------|-------------|-------------|
| N _o | -8.70^{a} | -8.70^{a} |
| P_0° | -8.82 | -8.82 |
| O_0 | -10.58 | -10.58 |
| β_{NN}^{μ} | -0.29 | -0.58 |
| β_{NP}^{π} | -0.70 | -0.41 |

^a Assumed.

respond to ionization of a molecular orbital which is primarily O_0 in character.¹⁸ Cowley and co-workers^{7,19} have shown that the O_0 basis orbital is in the range 10.1–11.0 eV for a variety of other phosphites. Any interaction between O_0 and N_0 or P_0 should be very small because of the large energy separation between O_0 and N_0 or P_0 . Thus it makes little difference in the interpretation of the PES of 3 what conformation 3 adopts about the exocyclic P-O bond. We do not have dynamic NMR data yet for 3, but a similar exocyclic conformation for 3 to that of 1a seems reasonable. If we assume that the high-energy O_0 basis orbital is orthogonal to P_0 ,²⁰ I_4 becomes O_0 (-10.58 eV), and our interpretation is similar to that for 1a. Just as for the 1a-c series, there are two sets of equations which can be fitted to the experimental PES data for 3; these are presented in Figure 4. For both sets of equations I_4 must correspond to ionization of the high-energy O_0 basis orbital and I_3 to ionization of an orbital representing the symmetric combination of the N_0 and P_0 basis orbitals. The other two low-energy ionization bands in the PES of 3 (I_1 and I_2) can be assigned either to ionization of the orbital representing the antisymmetric combination of P_0 with the symmetric combination of the two N_0 basis orbitals or to ionization of the orbital representing the antisymmetric combination of the two N_0 's. The P_0 basis orbital does not mix with the latter combination due to symmetry. The assignments for 3 are less certain than those for 1a-c and 2. The N_0 value for 3 will certainly shift from the value for 1a due to the substitution of the more electronegative oxygen moiety for nitrogen at phosphorus. However, the band assignment problem is again complicated by the presence of one more unknown than there are equations such that one parameter must be assumed. Since the major molecular modification occurs at phosphorus for 3, we have chosen to assign N_0 a value of -8.70 eV as for 1a. The values of the parameters (eV), which result from the two sets of equations shown in Figure 4, are given in Table IV. We believe that equation set 1 can be rejected on the grounds that $\beta_{\rm NN}^{\mu}$ is too small and $\beta_{\rm NP}^{\pi}$ is too large. These parameters are completely out of line when compared to the analogous ones for **1a-c** and the acyclic aminophosphines studied earlier.⁸ The parameters evaluated from equation set 2 are more reasonable because β_{NN}^{μ} is now larger in magnitude than is β_{NP}^{π} in accord with all of our previous observations. The high negative value of P_0 for 3 (-8.82 eV) reflects the substantial inductive effect caused by the highly electronegative oxygen. It should be noted that for our assignments the HOMO of 3 has only nitrogen lone-pair character as was the case for the acyclic aminophosphines studied earlier in these laboratories,⁸ but in contrast to 1a-c for which we postulate nitrogen and phosphorus lone-pair character in the HOMO.

Conclusion

This paper has reported the PES of several aminophosphines which have been definitively established by dynamic ¹³C, and ¹⁵N, NMR studies to closely approximate conformation C (see Introduction).¹² Thus PES data are now available for aminophosphines having conformations A,⁷ B,^{3,8} and C, leaving only conformation D to be studied. The various parameters $(N_0', N_0, P_0, \beta_{NN}^{\mu}, \text{ and } \beta_{NP}^{\pi})$ evaluated in this work are consistent with those found earlier for three tris(dialkylamino)phosphines,⁸ and the trends in their values are consistent

(5,10,15,20-Tetraphenylporphyrin)iron(II)

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Paramagnetic Anisotropy, Average Magnetic Susceptibility, and Electronic Structure of Intermediate-Spin S = 1 (5,10,15,20-Tetraphenylporphyrin)iron(II)

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Measurements of average magnetic susceptibility and magnetic anisotropy on the single crystals of FeTPP in the 4-300 K temperature range are reported. These results together with the other existing evidence establish an S = 1 spin state for the iron(II) ion in FeTPP. It is shown that the experimental principal susceptibilities cannot be explained over the entire temperature region by a spin Hamiltonian formalism for the S = 1 ground state. A detailed ligand field calculation is presented which gives a satisfactory explanation of the magnetic data. The ligand field calculation indicates a d_{z^2} orbital lying lowest with ³A₂ as the ground state followed by ³E and ³B, in ascending order of energy. The best fit to the data is obtained only in the region where three states come close together.

Introduction

Iron(II) porphyrins are currently of much interest as they provide a model system to understand the properties of heme proteins.² Until recently iron(II) porphyrins were known to exist in either a low-spin (S = 0) or a high-spin (S = 2) state. No definite evidence of an intermediate-spin state (S = 1) was known among iron(II) porphyrins, though there had been speculation on the existence of such an unusual spin state in certain heme proteins.³ An intermediate-spin state is, however, definitely known to exist in the related iron(II) phthalocyanine, FePc.4,5

Magnetic moments of some iron(II) porphyrins have been measured at room temperature, but their high values $(4.75-4.85 \mu_B)$ have led earlier workers to ascribe them to a high-spin state.⁶⁻⁸ The first definite suggestion of an intermediate-spin state in iron(II) porphyrins came from the work of Collman et al.9 on (5,10,15,20-tetraphenylporphyrin)iron-(II), FeTPP. They prepared FeTPP by the chromous reduction of FeTPPCl, which gives a highly crystalline sample.¹⁰ On the basis of detailed molecular structure, room-temperature magnetic moment ($\simeq 4.4 \mu_{\rm B}$), and Mössbauer studies, they suggested an S = 1 spin state for FeTPP. The X-ray crystal structure of FeTPP shows a nearly square-planar geometry around the iron atom, as in FePc, with a very short Fe-N bond favoring strongly an S = 1 spin state.¹¹ Two recent isotropic proton-shift studies^{12,13} also indicate an S = 1 spin state for FeTPP.

Although these studies indicate that the ground state of FeTPP is a spin triplet (S = 1), our understanding of the electronic structure of ferrous ion in FeTPP that leads to this situation is still not clear. In particular the origin of the rather high magnetic moment associated with this spin state is still obscure. Speculations about the electron configuration corresponding to the ground state have been made from a consideration of Mössbauer⁹ and isotropic proton contact shift¹² measurements, but little information is available about the excited electronic states. Such information may be obtained from studies of the temperature dependence of the principal magnetic susceptibilities¹⁴ of FeTPP. We have therefore measured the average magnetic susceptibility and paramagnetic anisotropy of single crystals of FeTPP between 4.2 and 290 K. These results have been used to deduce the electronic structure of this iron(II) complex.

Experimental Section

Preparation of FeTPP. FeTPP was prepared by the method of Collman et al.⁹ All manipulations for the preparations were carried out in an inert atmosphere within a glovebox. Solvents used were deaerated. Crystals large enough for magnetic measurements were grown by seeding the small well-formed purple tetragonal crystals, obtained by the above method. The crystals were chemically analyzed. Anal. Calcd: C, 79.05; H, 4.2; N, 8.4. Found: C, 79.0; H, 4.1; N, 8.7. Their identity was also established by a spectroscopic method and finally by matching the unit cell dimensions by an X-ray method using rotation and Weissenberg photographs.

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