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The Copper(II) Nitrate-Pyridine System¹

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The copper(II) nitrate-pyridine system has been reinvestigated. Contrary to previous reports, only three complexes have been found to exist in the solid state, and these are formulated as $[\text{Cu}(\text{py})_2(\text{NO}_3)_2]$, $[\text{Cu}(\text{py})_4(\text{NO}_3)_2]$, and $[\text{Cu}(\text{py})_6(\text{NO}_3)_2] \cdot 2\text{py}$. The three complexes form a reversible system, transitions occurring by the addition or removal of pyridine. Thermal, magnetic, conductometric, and spectral data are given.

Introduction

Pyridine complexes of anhydrous copper(II) nitrate having the general formula $\text{Cu}(\text{py})_x(\text{NO}_3)_2$ ($x = \text{integer}$) have been reported by a number of workers, but there appears to be some confusion as to which compositions actually exist. The compounds reported are: $\text{Cu}(\text{py})_7(\text{NO}_3)_2$,³ $\text{Cu}(\text{py})_6(\text{NO}_3)_2$,^{3,4} $\text{Cu}(\text{py})_5(\text{NO}_3)_2$,³ $\text{Cu}(\text{py})_4(\text{NO}_3)_2$,³⁻⁵ $\text{Cu}(\text{py})_3(\text{NO}_3)_2$,^{4,6} and $\text{Cu}(\text{py})_2(\text{NO}_3)_2$.⁴ Two compounds, $\text{Cu}(\text{py})_7(\text{NO}_3)_2$ and $\text{Cu}(\text{py})_6(\text{NO}_3)_2$, are somewhat doubtful since they were based solely upon vapor pressure measurements without analytical substantiation. Mitra and Sinha also failed to reproduce the $\text{Cu}(\text{py})_3(\text{NO}_3)_2$ and $\text{Cu}(\text{py})_2(\text{NO}_3)_2$ compounds reported by the earlier workers and reported that $\text{Cu}(\text{py})_4(\text{NO}_3)_2$ decomposed by "attack of the nitrate ion on the pyridine molecule." It thus seemed pertinent to reinvestigate the copper(II) nitrate-pyridine system to ascertain which compounds actually exist.

The several reported pyridine complexes of copper(II) nitrate offer a variety of possible stereochemical arrangements of the ligands about the copper, further complicated by the range of functional possibilities for the nitrate group. Studies have shown that the nitrate group can function as an ionic species,⁷ a monodentate ligand,⁸ or a bidentate ligand.⁹ The nitrate group is also known to function as a bridging group.¹⁰ These stereochemical possibilities have also been considered.

Experimental Section

Materials.—Methanol was dried by distilling CP reagent from magnesium activated with iodine. CP pyridine was distilled from potassium hydroxide and stored over barium oxide. Silver nitrate and copper dust were dried over sulfuric acid. A solution of copper(II) nitrate in methanol was prepared by allowing 10 g of copper dust to react with a solution of 20 g of silver nitrate in 150 ml of methanol.¹¹ The reaction mixture was shaken until the filtrate gave a negative Ag^+ test, about 4 hr. The reaction

mixture was filtered to remove suspended solids, and the filtrate was stored in a closed system until used.

The compound $\text{Cu}(\text{py})_4(\text{NO}_3)_2$ was prepared by slowly adding 50 ml of pyridine to the warm methanol solution of copper(II) nitrate. Violet crystals precipitated almost immediately. The product was recrystallized by adding 25 ml of pyridine to the solid and by adding warm methanol until the solid was completely dissolved. Violet crystals separated on cooling. These were collected on a sintered-glass filter, pressed to remove as much solvent as possible, and evacuated over silica gel for 3 hr to remove residual solvent.

Anal. Calcd for $\text{Cu}(\text{py})_4(\text{NO}_3)_2$: Cu, 12.61; py, 62.78. Found: Cu, 12.55; py, 62.61.

Identification of the Compounds Present in the System.—The interrelationship between the compounds was determined in part by thermogravimetric analysis. Small samples were analyzed in a nitrogen atmosphere using a thermal balance constructed by Kingston,¹² based on a model described by Wendlandt.¹³

(1) Two samples (I and II) of the 4-pyridine compound were thermally decomposed by heating at a constant rate of 1°/min. Sample I started to lose weight at 76° and continued until a total weight loss of 31.2% had occurred. At 160°, decomposition of the sample took place with formation of a blue oil, which did not crystallize on cooling. The weight loss corresponded to formation of $\text{Cu}(\text{py})_2(\text{NO}_3)_2$, for which the weight loss would be 31.4%.

Sample II was heated to 76° and maintained at that temperature until weight loss was complete. The loss in weight of 31.2% was accompanied by a color change from violet to light blue. The isothermal decomposition curve for $\text{Cu}(\text{py})_4(\text{NO}_3)_2$ is shown in Figure 1.

The formation of $\text{Cu}(\text{py})_2(\text{NO}_3)_2$ in the decompositions was verified by comparison of the X-ray powder diffraction pattern with that of an analyzed sample, prepared by thermal decomposition of $\text{Cu}(\text{py})_4(\text{NO}_3)_2$ at 68° and 2 mm until constant weight was obtained.

Anal. Calcd for $\text{Cu}(\text{py})_2(\text{NO}_3)_2$: Cu, 18.37; py, 45.47. Found: Cu, 18.33; py, 45.48.

(2) A sample of $\text{Cu}(\text{py})_4(\text{NO}_3)_2$ was placed in a desiccator over pyridine at room temperature for 24 hr. The compound added two moles of pyridine to form purple $\text{Cu}(\text{py})_6(\text{NO}_3)_2$.

Anal. Calcd for $\text{Cu}(\text{py})_6(\text{NO}_3)_2$: Cu, 9.60; py, 71.57. Found: Cu, 9.64; py, 71.41.

(3) A thermogram of $\text{Cu}(\text{py})_6(\text{NO}_3)_2$ indicated loss in weight at 34°, at which point the heating rate was set to zero. A total weight loss of 23.7% corresponded to the calculated loss of 23.9% for formation of $\text{Cu}(\text{py})_4(\text{NO}_3)_2$. The isothermal decomposition curve for $\text{Cu}(\text{py})_6(\text{NO}_3)_2$ is shown in Figure 1. The X-ray pattern agreed with that of the analyzed sample.

(4) A sample of $\text{Cu}(\text{py})_2(\text{NO}_3)_2$ was placed in an Abderhalden drying apparatus over pyridine at 56° for 24 hr. The color

(1) Taken in part from the Ph.D. theses of Richard V. Biagetti and William G. Bottjer.

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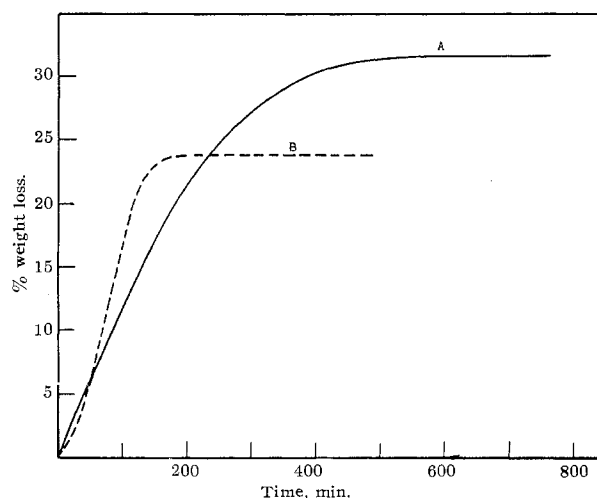


Figure 1.—Isothermal decomposition of $\text{Cu}(\text{py})_x(\text{NO}_3)_2$ complexes: A, $\text{Cu}(\text{py})_4(\text{NO}_3)_2$ at 76° ; B, $\text{Cu}(\text{py})_6(\text{NO}_3)_2$ at 34° .

change reversed from light blue to violet, and X-ray diffraction identified the product as $\text{Cu}(\text{py})_4(\text{NO}_3)_2$.

Analysis.—Copper was determined by weighing as $\text{Cu}(\text{py})_2\text{-(SCN)}_2$.¹⁴ Pyridine was determined by potentiometric titration of the complexes with perchloric acid in glacial acetic acid.

X-Ray Powder Patterns.—These were taken with a 57.3-mm camera, using iron or copper radiation. The solid samples were mounted in 0.3-mm capillaries.

Magnetic Susceptibilities.—Magnetic moments, μ_{eff} , of the solids were determined at 23.5° by the Gouy method. The values are listed in Table I and have been corrected for the diamagnetic susceptibilities of the ligands in the usual way.^{15,16}

TABLE I
PROPERTIES OF COPPER(II) NITRATE-PYRIDINE COMPLEXES

Compd	Color	μ_{eff} , BM	Molar conductance, $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$	
			In DMF	In CH_3NO_2
$\text{Cu}(\text{py})_2(\text{NO}_3)_2$	Light blue	1.99	134	18
$\text{Cu}(\text{py})_4(\text{NO}_3)_2$	Violet	1.88	145	26
$\text{Cu}(\text{py})_6(\text{NO}_3)_2$	Purple	1.89	134	32
$[\text{Sn}(\text{C}_9\text{H}_6\text{NO})_2]$	2.3	4.4
$[(\text{CH}_3)_4\text{N}]\text{I}$	88	118

Spectral Measurements.—Infrared spectra of the solids as mulls in Nujol and Halocarbon oil and as solutions in chloroform were taken in the $4000\text{--}650\text{-cm}^{-1}$ range with a Perkin-Elmer Model 21 recording spectrophotometer. In the $650\text{--}400\text{-cm}^{-1}$ range, spectra of the mulls in Nujol were obtained using a Perkin-Elmer Model 337 grating infrared spectrophotometer. The infrared spectra are summarized in Table II.

Visible spectra of solutions in chloroform were obtained with a Beckman DU spectrophotometer. Spectra of the solids were taken with a Cary Model 14 recording spectrophotometer. These are shown in Figures 2 and 3.

Conductivity Measurements.—These were made at 25° using a Wheatstone bridge circuit with a conventional cell. Nitromethane and N,N-dimethylformamide (DMF) were purified prior to use and had specific conductances of approximately $2 \times 10^{-7} \text{ohm}^{-1} \text{cm}^{-1}$. The cell was calibrated with aqueous potassium chloride. Solutions were $10^{-3} M$. Bis(8-quinolinolato)tin(II), $[\text{Sn}(\text{C}_9\text{H}_6\text{NO})_2]$,¹⁷ and tetramethylammonium

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TABLE II NITRATE ABSORPTION BANDS OF $\text{Cu}(\text{py})_x(\text{NO}_3)_2$ COMPLEXES		
Compd	Medium	Frequencies, cm^{-1} ^{a,b,c}
$\text{Cu}(\text{py})_2(\text{NO}_3)_2$	Solid in Nujol and Halo-carbon oil	1477–1468 vs, b; ^d NO_2 asym str (ν_4)
		1282–1268 vs, b; ^d NO_2 sym str (ν_1)
	Soln in CHCl_3	1024 m, shp; NO str (ν_2)
		804 m, shp; nonplanar def (ν_6)
		1482 s, b; NO_2 asym str (ν_4)
		1275 s, b; NO_2 sym str (ν_1)
$\text{Cu}(\text{py})_4(\text{NO}_3)_2$	Solid in Nujol and Halo-carbon oil	1405 vs, b; NO_2 asym str (ν_4)
		1300 vs, b; NO_2 sym str (ν_1)
	Soln in CHCl_3	1028 m, shl; NO str (ν_2)
		816 m, shp; nonplanar def (ν_6)
$\text{Cu}(\text{py})_6(\text{NO}_3)_2$	Solid in Nujol and Halo-carbon oil	1390 vs, b; NO_2 asym str (ν_4)
		1300 vs, b; NO_2 sym str (ν_1)
	Soln in CHCl_3	1400 vs, b; NO_2 asym str (ν_4)
		1300 vs, b; NO_2 sym str (ν_1)
		1030 vs, shl; NO str (ν_2)
		816 m, shp; nonplanar def (ν_6)

^a s, strong; m, medium; v, very; shp, sharp; b, broad; shl, shoulder. ^b Assignments are according to Gatehouse, *et al.*¹⁸ ^c Because of the limited solubility of the compounds and absorption due to chloroform, only the NO_2 stretching vibrations have been assigned to the spectra in chloroform. ^d Absorption bands are doublets.

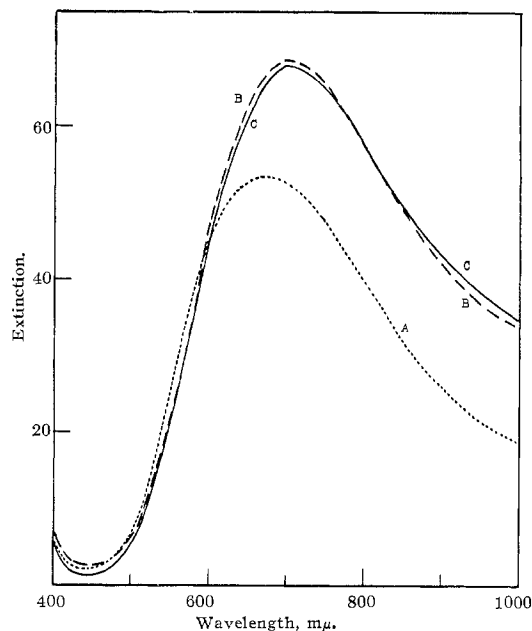


Figure 2.—Electronic absorption spectra of $\text{Cu}(\text{py})_x(\text{NO}_3)_2$ complexes in CHCl_3 : A, $\text{Cu}(\text{py})_2(\text{NO}_3)_2$; B, $\text{Cu}(\text{py})_4(\text{NO}_3)_2$; C, $\text{Cu}(\text{py})_6(\text{NO}_3)_2$.

iodide were used as standard nonelectrolyte and 1:1 electrolyte, respectively. The results are summarized in Table I.

Other Measurements.—Attempts to determine molecular weights of the complexes failed because the compounds were either not sufficiently soluble in or were decomposed by solvents appropriate for these measurements.

Results

From the data assembled it is evident that there are only three stable pyridine complexes of anhydrous copper(II) nitrate, as summarized in Table I.

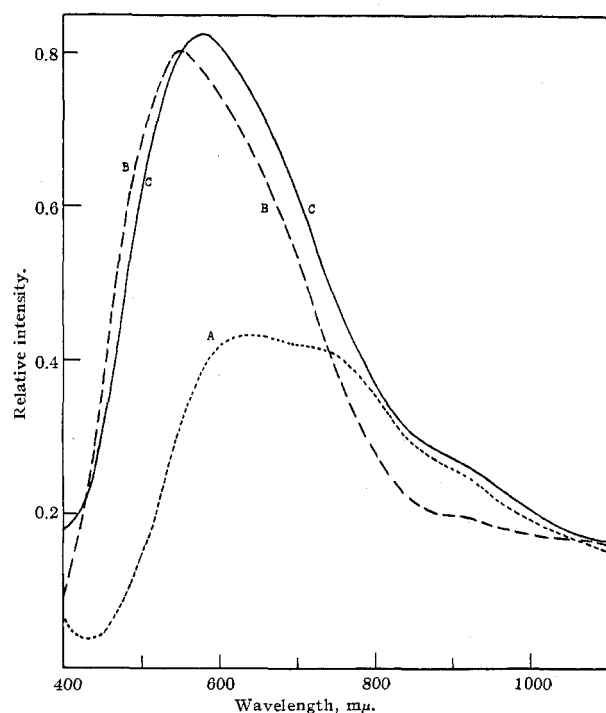
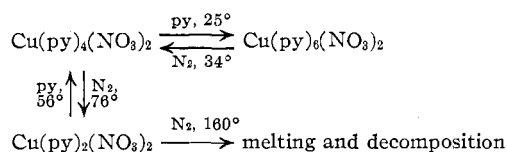


Figure 3.—Reflectance spectra of $\text{Cu}(\text{py})_x(\text{NO}_3)_2$ complexes: A, $\text{Cu}(\text{py})_2(\text{NO}_3)_2$; B, $\text{Cu}(\text{py})_4(\text{NO}_3)_2$; C, $\text{Cu}(\text{py})_6(\text{NO}_3)_2$.

The reactions involving the removal and addition of pyridine are reversible, as shown in the scheme



The temperature stated for conversions are those at which the reactions were studied and do not imply a limitation. Conversion of $\text{Cu}(\text{py})_2(\text{NO}_3)_2$ to $\text{Cu}(\text{py})_4(\text{NO}_3)_2$, for example, should proceed at any temperature between 34 and 76°.

The complex $\text{Cu}(\text{py})_7(\text{NO}_3)_2$ was reported as an unstable complex formed by absorption of pyridine by $\text{Cu}(\text{py})_6(\text{NO}_3)_2$.³ The tabulated data in the reference cited show a constant vapor pressure in going from a calculated composition of nine moles of pyridine per mole of $\text{Cu}(\text{NO}_3)_2$ to the compound $\text{Cu}(\text{py})_6(\text{NO}_3)_2$. The reason for formulating $\text{Cu}(\text{py})_7(\text{NO}_3)_2$ is obscure. Experiments indicate only very slight absorption of pyridine on $\text{Cu}(\text{py})_6(\text{NO}_3)_2$ at room temperature.

Mitra and Sinha³ reported $\text{Cu}(\text{py})_5(\text{NO}_3)_2$ as a stable intermediate. The isothermal decomposition of $\text{Cu}(\text{py})_6(\text{NO}_3)_2$ showed no inflection which would indicate formation of $\text{Cu}(\text{py})_5(\text{NO}_3)_2$. They also reported decomposition of the intermediate above 50°, but $\text{Cu}(\text{py})_4(\text{NO}_3)_2$ is stable up to 76°.

The compound $\text{Cu}(\text{py})_3(\text{NO}_3)_2$ was reported to have been prepared by partial decomposition of $\text{Cu}(\text{py})_4(\text{NO}_3)_2$, followed by repeated crystallizations,⁴ and by the heating of a saturated aqueous solution of copper(II) nitrate in the presence of excess pyridine at 70–80°.⁶ The isothermal decomposition curve of

$\text{Cu}(\text{py})_4(\text{NO}_3)_2$ shows no sharp change in slope to indicate formation of $\text{Cu}(\text{py})_3(\text{NO}_3)_2$. It is suggested that the reported compound may have been a mixture of $\text{Cu}(\text{py})_2(\text{NO}_3)_2$ and $\text{Cu}(\text{py})_4(\text{NO}_3)_2$. Comparison of X-ray powder patterns would have been desirable, but the experimental procedure outlined was not sufficiently detailed to allow replication of the synthesis. Similarly, Ragno's report on the synthesis of $\text{Cu}(\text{py})_3(\text{NO}_3)_2$ lacks detail, and an attempt to duplicate his synthesis was unsuccessful.

The infrared spectra of the compounds in the solid state and in chloroform solution (Table II) indicate that the nitrate groups are coordinated.^{8,18–21} The magnitude of splitting between ν_4 and ν_1 , ca. 100 cm^{-1} , for $\text{Cu}(\text{py})_4(\text{NO}_3)_2$ and $\text{Cu}(\text{py})_6(\text{NO}_3)_2$ is considerably less than the assignment quoted by Gatehouse, *et al.*, for coordinated nitrates. It has been suggested that the magnitude of splitting between ν_4 and ν_1 is a function of the degree of covalency of the nitrate group.^{20,21}

The infrared spectra of the solid complexes also show that all of the pyridine molecules are coordinated in the two complexes, $\text{Cu}(\text{py})_2(\text{NO}_3)_2$ and $\text{Cu}(\text{py})_4(\text{NO}_3)_2$, but not in $\text{Cu}(\text{py})_6(\text{NO}_3)_2$. Coordinated pyridine can be distinguished from uncoordinated pyridine by the presence of an absorption band at 600 cm^{-1} for free pyridine, which is shifted to 620–640 cm^{-1} when the pyridine is coordinated.²² The complexes $\text{Cu}(\text{py})_2(\text{NO}_3)_2$ and $\text{Cu}(\text{py})_4(\text{NO}_3)_2$ show absorption only at 640 cm^{-1} whereas $\text{Cu}(\text{py})_6(\text{NO}_3)_2$ shows absorption at both 600 and 640 cm^{-1} .

The interpretation of the conductance data is not straightforward. Conductance values in DMF are typical of 1:2 electrolytes.²³ However, the complexes, which are bluish, yield yellow solutions in DMF, indicating extensive solvation. A similar effect has been observed for the analogous dinitratobis(pyridine N-oxide)copper(II), $[\text{Cu}(\text{C}_5\text{H}_5\text{NO})_2(\text{NO}_3)_2]$, which gave an unexpected high conductivity in DMF even though the infrared spectrum indicated coordinated nitrate groups.²⁴ Extensive solvation was suggested.

The conductance values in nitromethane are smaller than would be expected for electrolytes.^{25,26} They are, however, somewhat higher than expected for true nonelectrolyte behavior. Indications are that solvation occurs in this solvent also. The initially blue solutions slowly change to green, and this change is accompanied by an increase in conductivity. It is concluded that the compounds are nonelectrolytes but are readily susceptible to solvation.

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Discussion

Cu(py)₄(NO₃)₂.—Results have shown that this complex has coordinated nitrate groups and that all pyridines are coordinated. It is thus assigned an octahedral configuration having monodentate nitrate groups and should be represented as [Cu(py)₄(NO₃)₂], dinitratotetrakis(pyridine)copper(II).

Logan and Simpson have recently reported the infrared nitrate absorption frequencies of a tetrakis(pyridine) compound of copper(II) nitrate.²⁷ They report ν_4 at 1488 cm⁻¹ and ν_2 at 1008 cm⁻¹. The remaining nitrate assignments are similar to ours. Only a weak band was found by us near 1488 cm⁻¹, and this band has been assigned to pyridine. The possibility exists that the two compounds are structurally different since they were prepared by different synthetic methods.

Cu(py)₆(NO₃)₂.—The data for this complex show that the nitrate groups are coordinated and that both coordinated and uncoordinated pyridine are present. The ready loss of two moles of pyridine at 34° suggests that two of the six pyridine molecules are present as crystal pyridine and are not coordinated. The electronic spectra of Cu(py)₄(NO₃)₂ and Cu(py)₆(NO₃)₂ in chloroform (Figure 2) are identical within experimental error, indicating identity of the coordinated species. This compound is thus formulated as [Cu(py)₄(NO₃)₂]·2py, dinitratotetrakis(pyridine)copper(II)-bispyridine.

The reflectance spectra of Cu(py)₄(NO₃)₂ and Cu(py)₆(NO₃)₂ (Figure 3) have similar shapes, but the maximum for Cu(py)₆(NO₃)₂ (575 m μ) lies slightly higher than that for Cu(py)₄(NO₃)₂ (550 m μ). It is assumed that this is not indicative of differently coordinated species but is the result of a slight effect of the two molecules of crystal pyridine on the ligand field of the copper.

The coordination of two nitrate groups in preference to pyridine was unexpected but is probably associated with steric effects. Molecular models show that an octahedral arrangement of six pyridine molecules about

the metal atom is unfavorable. Although there are several reports of hexakis(pyridine)copper(II) complexes in the literature, there is no concrete evidence that these compounds actually contain six pyridine molecules coordinated to the copper.

Cu(py)₂(NO₃)₂.—This complex has coordinated nitrate groups and is formulated as [Cu(py)₂(NO₃)₂], dinitratobis(pyridine)copper(II).

The assignment of configuration is not unequivocal. The magnetic moment and the electronic spectra are significantly different from those for the Cu(py)₄(NO₃)₂ and Cu(py)₆(NO₃)₂ complexes, but these do not allow differentiation between possible configurations. The infrared spectrum does permit some tentative conclusions, in lieu of an X-ray structural study.

In the transition from Cu(py)₆(NO₃)₂ and Cu(py)₄(NO₃)₂ to Cu(py)₂(NO₃)₂, ν_4 is shifted to a higher frequency, from 1400 to *ca.* 1470 cm⁻¹, and ν_1 is shifted to a lower frequency, from 1300 to *ca.* 1275 cm⁻¹. Such an increase in splitting of the ν_4 and ν_1 frequencies has been related to a transition from a monodentate nitrate to a bidentate or bridging nitrate.^{27,28} Buffagni, *et al.*, have observed a larger splitting of these frequencies for bidentate nitrates in lutidine complexes of nickel(II) nitrate.^{8,9} Consequently, we have tentatively concluded that the larger splitting in the Cu(py)₂(NO₃)₂ complex is due to the presence of bidentate or bridging nitrate groups and that the complex should be assigned a six-coordinate configuration.

It may be significant that the reflectance spectrum for this complex is very similar to that of the corresponding bis(pyridine N-oxide) complex, to which has been assigned an octahedral configuration containing bidentate nitrate groups.⁷

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