

962. *The Nitrate Group as a Ligand in Some Amine Oxide Complexes.*

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The nitrates of manganese(II), cobalt(II), nickel(II), and copper(II) form complex compounds with either two or six moles of pyridine *N*-oxide, yielding, respectively, $[M(C_5H_5NO)_2(NO_3)_2]$ or $[M(C_5H_5NO)_6](NO_3)_2$. Infra-red studies indicate that the nitrate group is ionic and lies outside the coordination sphere in the $[M(C_5H_5NO)_6](NO_3)_2$ series, while it is co-ordinated to the metal ion in the $[M(C_5H_5NO)_2(NO_3)_2]$ complexes. The results indicate that, in the latter series of complexes, the nitrate group behaves as a bidentate chelating ligand; this is confirmed by a comparison of the spectral and magnetic properties of the two series of complexes.

IN this Paper, we report a study of some amine oxide complexes of several first-row transition-metal ions as the nitrate salts. The metals used were manganese(II), cobalt(II), nickel(II), and copper(II). Complexes of the type $[M(C_5H_5NO)_6](NO_3)_2$, where C_5H_5NO is pyridine *N*-oxide, have been prepared for each of these metals, and have been shown to be similar to the complexes $[M(C_5H_5NO)_6](ClO_4)_2$, reported earlier.¹ Evidence is presented that the former series of complexes is correctly formulated as involving ionic nitrate.

Recent interest²⁻⁷ in complexes of covalent molecular oxides, which also contain co-ordinated nitrate, prompted us to search for a series of pyridine *N*-oxide complexes having co-ordinated nitrate. We have prepared the series $[M(C_5H_5NO)_2(NO_3)_2]$, where M is Mn, Co, Ni, or Cu, and we show below that the nitrate is bidentate in these complexes.

We also report several complexes of cobalt with trimethylamine *N*-oxide. This ligand is bulkier than is pyridine *N*-oxide; whereas octahedral $[Co(C_5H_5NO)_6](NO_3)_2$ can be prepared, we find that only the tetrakis complex $[Co(Me_3NO)_4](NO_3)_2$, which is probably tetrahedral, can be prepared. We have also studied the complex $[Co(Me_3NO)_2(NO_3)_2]$.

¹ R. L. Carlin, *J. Amer. Chem. Soc.*, 1961, **83**, 3773.

² B. M. Gatehouse, S. E. Livingstone, and R. S. Nyholm, *J.*, 1957, 4222.

³ E. Bannister and F. A. Cotton, *J.*, 1960, 2276.

⁴ D. K. Straub, R. S. Drago, and J. T. Donoghue, *Inorg. Chem.*, 1962, **1**, 848.

⁵ J. T. Donoghue and R. S. Drago, *Inorg. Chem.*, 1963, **2**, 572.

⁶ F. A. Cotton and R. H. Soderberg, *J. Amer. Chem. Soc.*, 1963, **85**, 2402.

⁷ F. A. Cotton, D. M. L. Goodgame, and R. H. Soderberg, *Inorg. Chem.*, 1963, **2**, 1162.

Several trimethylamine *N*-oxide complexes were prepared earlier,⁸ but we find the reported magnetic behaviour to be in error.

EXPERIMENTAL

Reagents.—All metal salts were reagent grade, and were used without further purification. Pyridine *N*-oxide was obtained commercially (K and K) in a very impure form. It was purified by vacuum sublimation. Trimethylamine oxide dihydrate was also obtained commercially (Eastman), and was used without further purification.

Hexakis(pyridine N-Oxide)metal(II) Dinitrates.—Hydrated manganese(II), cobalt(II), or nickel(II) nitrate was dissolved in warm absolute ethanol. Upon addition of excess of pyridine *N*-oxide, also in warm ethanol, there was an immediate colour change in the solution, which, on cooling, gradually deposited crystals of the complex. These were filtered off and dried in a vacuum at 60°. The copper complex was similarly prepared from anhydrous copper(II) nitrate (from the reaction of equivalent amounts of copper and silver nitrate in methanol). The preparation of the hexakis(pyridine *N*-oxide)-cobalt(II) and -nickel(II) ions has been previously reported.^{1,9}

Bis(pyridine N-Oxide)dinitratometal(II).—Hydrated manganese(II), cobalt(II), or copper(II) nitrate was dissolved in absolute ethanol. The addition of two equivalents of pyridine *N*-oxide caused an immediate colour change. The copper complex was precipitated almost immediately; the addition of a small quantity of ether was necessary to accelerate the precipitation of the other complexes. The complexes were filtered off and dried in a vacuum at 60°.

The cobalt complex contained 4 mols. of water: upon heating in a vacuum, the orange-pink colour changed to deep rose. The nickel complex was similarly prepared from anhydrous nickel(II) nitrate (from the reaction of the hydrated salt with 2,2-dimethoxypropane¹⁰). The pyridine *N*-oxide used was also treated with 2,2-dimethoxypropane in ethanol.

The preparation of the cobalt(II) complex has been reported by Issleib and Kreibich.⁸ The copper(II) complex had been prepared previously.¹¹

*Bis(trimethylamine Oxide)dinitratocobalt(II).*⁸—Anhydrous cobalt nitrate (from the reaction of the hydrated salt with 2,2-dimethoxypropane) was mixed with trimethylamine oxide (similarly made anhydrous), both in absolute ethanol, blue-purple crystals being immediately precipitated. These were filtered off and dried in a vacuum at 60°. Care was taken throughout to exclude moisture, since these crystals are extremely deliquescent.

Tetrakis(trimethylamine Oxide)cobalt(II) Nitrate.—This was prepared by the reaction of trimethylamine oxide dihydrate (2.0 g.) with hydrated cobalt(II) nitrate (2.0 g.) in acetone-ethanol (3:1). (This is the method reported by Issleib for the bis-complex, [Co(Me₃NO)₂(NO₃)₂].⁸) The lavender-coloured precipitate, which was formed immediately on mixing the reactants, was filtered off. The compound did not look homogeneous; on attempting to recrystallize it from acetonitrile, a grey-blue residue, which has not been further investigated, and a deep purple solution were obtained. Addition of ether to the solution caused precipitation of deep purple crystals. From its analysis, this complex was concluded to be [Co(Me₃NO)₄](NO₃)₂.

*Tetrakis(trimethylamine Oxide)cobalt(II) Perchlorate.*⁸—Stoichiometric amounts of cobalt(II) perchlorate hexahydrate and trimethylamine oxide dihydrate, both in absolute ethanol, were mixed together. The deep purple complex obtained was filtered off and dried in a vacuum.

The solubilities of all the above complexes are fairly similar. They all decompose in water. They are all soluble in ethanol, acetonitrile, and *NN*-dimethylformamide; the five cobalt complexes slowly decompose in the last two solvents. They are all very slightly soluble in tetrahydrofuran, methylene dichloride, nitroethane, and benzene. In a number of cases, the compounds react with non-aqueous solvent, as can be seen from a comparison of their solution and reflectance spectra.

The analyses, colours, and melting points are listed in Table 1.

Physical Measurements.—Reflectance spectra were recorded on a Cary 14 spectrophotometer with reflectance attachment, using magnesium carbonate as the reference, and are summarized

⁸ K. Issleib and A. Kreibich, *Z. anorg. Chem.*, 1962, **313**, 338.

⁹ J. V. Quagliano, J. Fujita, G. Franz, D. H. Phillips, J. A. Walmsley, and S. Y. Tyree, *J. Amer. Chem. Soc.*, 1961, **83**, 3770.

¹⁰ K. Starke, *J. Inorg. Nuclear Chem.*, 1959, **11**, 77.

¹¹ R. L. Carlin, unpublished work.

TABLE 1.

Analyses, colours, and melting points of the compounds studied.

Compound	Colour	M. p.		Analysis		
				C	H	N
[Mn(C ₅ H ₅ NO) ₂ (NO ₃) ₂] ...	Pale yellow	204—206°	Calc.	32.6	2.7	
			Found	32.6	2.75	
[Mn(C ₅ H ₅ NO) ₆](NO ₃) ₂ ...	Deep yellow	159—161	Calc.	48.3	4.0	14.95
			Found	48.3	4.2	14.1
[Co(C ₅ H ₅ NO) ₂ (NO ₃) ₂] ...	Deep rose	178—180	Calc.	32.2	2.7	15.0
			Found	32.05	3.0	14.9
[Co(C ₅ H ₅ NO) ₆](NO ₃) ₂ ...	Bright red	166—168	Calc.	47.8	4.0	14.9
			Found	47.6	4.3	14.7
[Ni(C ₅ H ₅ NO) ₂ (NO ₃) ₂] ...	Light green	230—232	Calc.	32.2	2.7	15.0
			Found	31.9	3.2	14.5
[Ni(C ₅ H ₅ NO) ₆](NO ₃) ₂ ...	Yellow-green	185—187	Calc.	47.8	4.01	
			Found	47.0	3.9	
[Cu(C ₅ H ₅ NO) ₂ (NO ₃) ₂] ...	Turquoise	157—159	Calc.	31.8	2.7	
			Found	32.55	2.8	
[Cu(C ₅ H ₅ NO) ₆](NO ₃) ₂ ...	Yellow-green	145—147	Calc.	47.5	4.0	14.8
			Found	47.8	4.15	14.6
[Co(Me ₃ NO) ₂ (NO ₃) ₂] ...	Blue-purple	170—172	Calc.	21.6	5.45	16.8
			Found	20.7	5.7	16.4
[Co(Me ₃ NO) ₄](NO ₃) ₂ ...	Deep purple	201—203	Calc.	29.8	7.5	17.4
			Found	30.6	7.7	17.5
[Co(Me ₃ NO) ₄](ClO ₄) ₂ ...	Deep purple	>200°	Calc.	25.8	6.5	10.0
			Found	25.9	7.0	10.0

TABLE 2.

Electronic spectra.

Compound	Medium	$\lambda_{\max.}$ (in Å) ($\epsilon_{\max.}$)	Onset of charge transfer (Å)
[Mn(C ₅ H ₅ NO) ₂ (NO ₃) ₂]	Solid	3750, 4800sh, 6500sh	5800
	MeCN	3800 (190)	4400
[Co(C ₅ H ₅ NO) ₆](NO ₃) ₂	Solid	3900, 5100sh, 5500, 12,300	4650
	MeOH	5200 (25)	
[Co(C ₅ H ₅ NO) ₂ (NO ₃) ₂]	Solid	3600, 5350, 6800sh, 12,700	4250
	MeOH	5200 (28)	
[Ni(C ₅ H ₅ NO) ₆](NO ₃) ₂	Solid	4000, 7200, 7800sh, 12,500	5500
	MeCN	3850 (77)	5000
	MeOH	3800 (25), 7300 (4), 12,500 (5)	
[Ni(C ₅ H ₅ NO) ₂ (NO ₃) ₂]	Solid	3600, 6800, 7500sh, 12,000	5200
	EtOH	3500 (27), 7100 (7)	
[Cu(C ₅ H ₅ NO) ₆](NO ₃) ₂	Solid	8400, 10,000sh, 13,000sh	5000
[Cu(C ₅ H ₅ NO) ₆](ClO ₄) ₂	Solid	8200, 10,200sh	5000
[Cu(C ₅ H ₅ NO) ₄](ClO ₄) ₂	Solid	7000, 10,500sh	4800
[Cu(C ₅ H ₅ NO) ₂ (NO ₃) ₂]	Solid	7200, 8500, 12,000sh	5000
	MeCN	8750 (84)	
	*	7750 (40)	
[Co(Me ₃ NO) ₄](NO ₃) ₂	Solid	5700, 10,900, 13,500	
	MeCN	5800 (250)	
[Co(Me ₃ NO) ₄](ClO ₄) ₂	Solid	5800, 11,100, 13,750	
	MeCN	5700 (200)	
[Co(Me ₃ NO) ₂ (NO ₃) ₂]	Solid	4800, 5400, 6000sh, 8000sh, 13,000	3800

* In NN-Dimethylformamide solution.

in Table 2. Infrared absorption spectra (KBr discs and Nujol mulls) were obtained with a Perkin-Elmer Infracord spectrophotometer equipped with a rock-salt prism, and are listed in Table 3. Magnetic-susceptibility measurements were made with a Gouy balance, the calibrant being Hg[Co(SCN)₄]. The cobalt complexes were studied over a temperature range, and the results fitted to the Curie-Weiss equation:

$$\mu = 2.84 [Z_m^{\text{corr.}} (T - 0)]^{\frac{1}{2}}$$

The diamagnetic corrections were calculated by using Pascal's constants. The magnetic data are summarized in Table 4.

TABLE 3.

Infrared spectra.

Metal	Medium	[M(C ₅ H ₅ NO) ₂ (NO ₃) ₂] complexes.			
		Frequencies (cm. ⁻¹)			
Mn	Nujol	1499s, sh	1290s, b	1031m, sp	782s, sh
			1260s, sh	1024m, sp	
Co	KBr *	1480s, sp		1025m, sp	785m, sh
	Nujol	1490s, sh	1290s, sp	1025m, sp	782m, sh
Ni	Nujol		1260m, sh		
		1490s, sh	1290s, br	1040w, sh	785m, sh
Cu	KBr	1480s, shp	1290s, sp	1020s, sp	780s, sp
			1255m, sh		
[Co(Me ₃ NO) ₂ (NO ₃) ₂]	Nujol	1480s, sh	1290s, br	1020s, sp	780s, sp
	KBr *	1600m, shp	1290m, sh	1005m, sp	
	Nujol	1600m, sp	1290m, sh	1010m, sp	
Assignment		Asym. NO ₂ str.	Sym. NO ₂ str.	NO str.	Non-plane Deform.
Range †		1531—1481	1290—1253	1034—970	800—781
[M(C ₅ H ₅ NO) ₆](NO ₃) ₂ complexes.					
Mn	Nujol	1350s, b	1040w	838m, sh	735m, sh
Co	Nujol			825m, sh	
		1350s, b	1050w, sh	830s, br	
Ni	KBr	1350s, sp	1050w	840s, sp	710w, sh
				831m, sh	
Cu	Nujol	1350s, b	1050w	840s, sp	710w
				825m, sh	
[Co(Me ₃ NO) ₄](NO ₃) ₂	KBr	1390s, sp	1045w, sp	832s, br	710w
		1350br, sh		832m, sp	
Assignment		Asym. NO ₂ str.	N—O str.	NO ₂ Deform.	Planar rocking
Range †		1390—1350	1050	836—815	720

* Strong 1390 cm.⁻¹ band, plus change in colour of KBr disc, suggests halide ion replacing NO₃ in co-ordination sphere. † According to Gatehouse *et al.*²

TABLE 4.

Corrected magnetic moments at 297°K.

Compound	Diamagn. corr. × 10 ⁶ (c.g.s.u.)	μ (B.M.)	θ (°K)
[Mn(C ₅ H ₅ NO) ₂ (NO ₃) ₂]	84	5·86	
[Co(C ₅ H ₅ NO) ₂ (NO ₃) ₂]	83	4·92 (4·58 ⁸)	-36
[Ni(C ₅ H ₅ NO) ₂ (NO ₃) ₂]	83	3·12	
[Cu(C ₅ H ₅ NO) ₂ (NO ₃) ₂]	83	1·90 (1·89 ⁹)	
[Co(Me ₃ NO) ₄](NO ₃) ₂	243	4·64	-13
[Co(Me ₃ NO) ₄](ClO ₄) ₂	269	4·75 (4·12 ⁹)	-14
[Co(Me ₃ NO) ₂ (NO ₃) ₂]	147	4·91 (4·39 ⁸)	-2

RESULTS AND DISCUSSION

Gatehouse, Livingstone, and Nyholm have listed the infrared absorption frequencies for ionic nitrate as well as for the co-ordinately bound nitrate-group.² For the latter, they assumed that the nitrate-group donates through one oxygen atom; the observed frequencies change little when the nitrate-group behaves as a bidentate or bridging ligand co-ordinating through two oxygen atoms. It has been pointed out⁷ that it is not in general possible to distinguish between mono- and bi-dentate co-ordinated nitrate ions on the basis of the number or positions of the observed infrared bands alone. Band positions alone in the spectrum of co-ordinated nitrate groups are insufficient to enable one to distinguish between the two possible modes of co-ordination. An interesting example is the complex [Co(Ph₃PO)₂(NO₃)₂], which exhibits the characteristic frequencies of the co-ordinated nitrate-group.³ On this basis, it was concluded that the nitrate was co-ordinated by way of one oxygen atom, and that the metal ion was in tetrahedral co-ordination. A later structural determination showed that two oxygen atoms from each nitrate group were bound to the central metal ion.⁶

Quagliano and his co-workers have made assignments for the significant infrared absorption bands of a number of pyridine *N*-oxide complexes.^{12a} This has enabled us to decipher those bands which correspond to the nitrate-group and those which correspond to the N-O group from the co-ordinated pyridine *N*-oxide molecules. The assignments for the nitrate group are given in Table 3. These results show that the behaviour of the nitrate group can be established. In compounds of the type $[M(C_5H_5NO)_6](NO_3)_2$, the nitrate group is ionic and lies outside the co-ordination sphere. In compounds of the type $[M(C_5H_5NO)_2(NO_3)_2]$, the nitrate group is co-ordinated to the metal ion. The infrared assignments for the trimethylamine oxide ligand in its complexes can be established by comparison with the perchlorate complexes. The nitrate group in $[Co(Me_3NO)_4](NO_3)_2$ is ionic and therefore lies outside the co-ordination sphere. In the $[Co(Me_3NO)_2(NO_3)_2]$ complex, the nitrate group behaves as a ligand co-ordinating to the metal ion. The shift of the nitrate absorption from 1390 cm^{-1} in the ion, to 1290 cm^{-1} , in the co-ordinated nitrate-group, is associated with a lowering of the symmetry of the nitrate molecule.²

The additional evidence for the existence of bidentate chelate or bridging nitrate is derived from a comparison of the electronic spectra of the complexes of each metal ion in the range 3000–20,000 Å. If the nitrate is bidentate, the $[M(C_5H_5NO)_2(NO_3)_2]$ complexes should have an octahedral configuration somewhat similar to that of the $[M(C_5H_5NO)_6](NO_3)_2$ complexes. If the nitrate is monodentate, the spectra should be significantly different, corresponding to either a tetrahedral or a square-planar configuration for the $[M(C_5H_5NO)_2(NO_3)_2]$ complexes. The magnetic susceptibilities of the compounds also confirm the respective configurations. An attempt to correlate electronic spectra with infrared spectra for co-ordinated anions has been published.^{12b} The most prominent spectral feature for the manganese complexes reported here is the intense charge-transfer band at *ca.* 3800 Å; a similar band was reported¹ for $[Mn(C_5H_5NO)_6](ClO_4)_2$. We attribute the weak, structured absorption in the visible region to the tail of the charge-transfer peak; none of the anticipated spin-forbidden bands has been observed. Since the magnetic behaviour of manganese complexes is not diagnostic of their stereochemistry, we are unable to assign a geometry to $[Mn(C_5H_5NO)_2(NO_3)_2]$ on the basis of its magnetic moment. The infrared spectra, however, indicate that the compound involves co-ordinated nitrate; it is probably similar to the other compounds reported here.

The cobalt(II) ion in weak octahedral fields usually absorbs in the 5000–6000 Å region; we find absorption in this region for both pyridine *N*-oxide complexes. Since $[Co(C_5H_5NO)_6](NO_3)_2$ is octahedral ($\mu = 4.77$ B.M.⁹), it is safe to conclude that the complex $[Co(C_5H_5NO)_2(NO_3)_2]$, whose spectrum is so similar, must also be essentially octahedral.* There is little difference between the intensities of the absorption bands of the two complexes as measured by means of their reflectance spectra. This suggests that the pyridine *N*-oxide and the nitrate group must be very close together in the spectrochemical series. Furthermore, the low intensities of these bands [ϵ 25–28 (in methanol)] support the assignment of octahedral geometry, which is also strongly supported by the large orbital contribution to the magnetic moment (Table 4).

It is interesting that $[Co(C_5H_5NO)_2(NO_3)_2]$ is the first, essentially octahedral nitrate-complex of cobalt which exhibits a magnetic moment consistent with the geometry. Thus, all previous complexes have been reported to have moments of the order of 4.55–4.65 B.M.^{4,5,7} Perhaps this can be attributed to the relative compactness and small size of the pyridine *N*-oxide ligand as compared with other ligands which have been used.

We have also examined several trimethylamine *N*-oxide complexes of cobalt(II).

* It is assumed throughout this Paper that bidentate nitrate has a configuration similar to that found in $[Co(Me_3PO)(NO_3)_2]$.⁴

¹² (a) S. Kida, J. V. Quagliano, J. A. Walmsley, and S. Y. Tyree, *Spectrochim. Acta*, 1963, **19**, 189; (b) B. J. Hathaway, D. G. Holah, and M. Hudson, *J.*, 1963, 4586.

We prepared $[\text{Co}(\text{Me}_3\text{NO})_4](\text{ClO}_4)_2$, since the perchlorate anion was expected to have minimal donor ability. The moment reported earlier for this compound (4.12 B.M.)⁸ is too low to be reasonable for cobalt complexes, and our value is more accurate. This compound is the first well-characterized tetrahedral cobalt complex with amine oxide ligands. The complexes $[\text{Co}(\text{Me}_3\text{NO})_4]\text{X}_2$ ($\text{X} = \text{NO}_3^-$ or ClO_4^-), which are both brilliant purple compounds, have similar spectra (Fig. 1). The absorption at 5700—5800 Å is at higher energy than is usually found for tetrahedral co-ordination. Also, this

FIG. 1. Reflectance spectra.
 A, $[\text{Co}(\text{Me}_3\text{NO})_4](\text{NO}_3)_2$.
 B, $[\text{Co}(\text{Me}_3\text{NO})_4](\text{ClO}_4)_2$.
 C, $[\text{Co}(\text{Me}_3\text{NO})_2](\text{NO}_3)_2$.

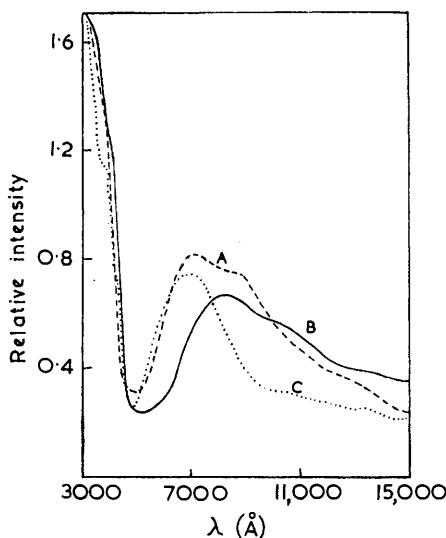
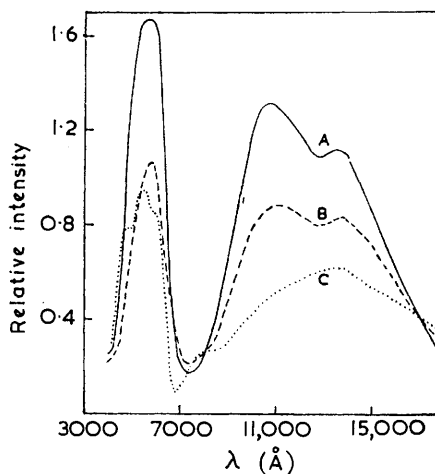


FIG. 2. Reflectance spectra.

- A, $[\text{Cu}(\text{C}_5\text{H}_5\text{NO})_2](\text{NO}_3)_2$.
 B, $[\text{Cu}(\text{C}_5\text{H}_5\text{NO})_6](\text{ClO}_4)_2$.
 C, $[\text{Cu}(\text{C}_5\text{H}_5\text{NO})_4](\text{ClO}_4)_2$.

peak does not show the fine-structure typical of tetrahedral cobalt(II); however, its intensity is high. The magnetic moments support a tetrahedral configuration, but it must be remembered that this criterion has not always proved reliable in the past.

We assign an essentially octahedral structure to $[\text{Co}(\text{Me}_3\text{NO})_2(\text{NO}_3)_2]$, primarily on the basis of its magnetic moment. The reflectance spectrum shows a peak at 4800—6000 Å with the fine-structure so common for tetrahedral co-ordination, but the peak is at higher energy than is usual for tetrahedral cobalt complexes. Spectral features such as these originally led to the assignment of a tetrahedral configuration to $[\text{Co}(\text{Ph}_3\text{PO})_2(\text{NO}_3)_2]$,³ but this compound has since been shown to be six-co-ordinate.⁷

The spectral and magnetic properties of both the pyridine *N*-oxide complexes of nickel(II) are readily assigned to an octahedral configuration. The spectra show the familiar double-peaked band at *ca.* 7000 Å (14,200 cm.⁻¹). The magnetic moment (312 B.M.) for [Ni(C₅H₅NO)₂(NO₃)₂] is appreciably lower than that (3·45 B.M.) reported for [Ni(Ph₃PO)₂(NO₃)₂]³ and [Ni(HMPA)₂(NO₃)₂]⁵ (HMPA = hexamethylphosphoramide), and indicates that [Ni(C₅H₅NO)₂(NO₃)₂] is more closely octahedral than are these last two compounds.

The assignment of stereochemistry to copper(II) from spectral and magnetic properties is not straightforward. The magnetic moment (1·90 B.M.) for [Cu(C₅H₅NO)₂(NO₃)₂] does not allow one to differentiate between the possible stereochemistries. However, the electronic spectrum (Fig. 2) of [Cu(C₅H₅NO)₂(NO₃)₂] resembles that of [Cu(C₅H₅NO)₆](ClO₄)₂, rather than that of [Cu(C₅H₅NO)₄](ClO₄)₂; the single, structureless peak in the spectrum of the last-mentioned compound suggests that it is probably square-planar. A planar structure has been assigned to [Cu(Me₃PO)₄](ClO₄)₂¹³ and to [Cu(Ph₃PO)₄](ClO₄)₂.¹⁴ We therefore suggest that [Cu(C₅H₅NO)₂(NO₃)₂] attains a six-co-ordinate structure by means of chelating nitrate groups.

Upon comparison of each pair of metal-pyridine *N*-oxide complexes, it is noticed that the electronic spectra are very similar, except that, in all cases, the spectra are shifted to slightly higher energy for the [M(C₅H₅NO)₂(NO₃)₂] complexes with respect to the [M(C₅H₅NO)₆](NO₃)₂ complexes. In comparison with other reported nitrate-complexes, the [M(C₅H₅NO)₂(NO₃)₂] complexes probably have a truer octahedral configuration, resulting from the compact size of the pyridine *N*-oxide ligands as well as from the similarity of chemical environment.

As was noted earlier,¹ all the pyridine *N*-oxide complexes have intense charge-transfer bands which overlap into the visible region.

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¹³ D. M. L. Goodgame and F. A. Cotton, *J.*, 1961, 2298.

¹⁴ E. Bannister and F. A. Cotton, *J.*, 1960, 1878.