

Copper(II) Complexes of 2-Dimethylamino-3-picoline *N*-Oxide (3MDM) and 2-Diethylamino-3-picoline *N*-Oxide (3MDE)

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Abstract

Copper(II) complexes with 2-dimethylamino-3-picoline *N*-oxide (3MDM) and 2-diethylamino-3-picoline *N*-oxide (3MDE) have been prepared from the following salts: tetrafluoroborate, nitrate, chloride and bromide. Solids of the general formula $[\text{CuL}_2](\text{BF}_4)_2$ and $[\text{CuLX}_2]$ where L = 3MDM and 3MDE and X = NO_3 , Cl and Br were characterized using spectral methods (*i.e.*, IR, UV–Vis and ESR). Both of these *N*-oxides coordinate as bidentate ligands via the *N*-oxide oxygen and the amine nitrogen in all of the complexes. The steric effect of the diethylamino group is larger compared to the dimethylamino in the four pairs of complexes involving the different anions. Considerable distortion compared to the complexes of the analogous pyridine *N*-oxide ligands also occurs due to the ring methyl group.

Introduction

2-Aminopyridine *N*-oxide [1], 2-alkylaminopyridine *N*-oxides [2], 2-aminopicoline *N*-oxides [3–6] and 2-alkylaminopicoline *N*-oxides [7, 8] coordinate to copper(II) in all but a few compounds [8] as monodentate ligands via the *N*-oxide oxygen. In contrast, 2-dialkylaminopyridine *N*-oxides [9, 10] have been shown to coordinate exclusively as bidentate ligands via the *N*-oxide oxygen and the amine nitrogen. Recently, our laboratory made the first study of the copper(II) complexes of a 2-dialkylaminopicoline *N*-oxide, 2-dimethyl-6-picoline *N*-oxide (6MDM), and found that it also coordinates as a bidentate ligand [7]. The Cu(II) complexes of this ligand along those of with 2-dimethylaminopyridine *N*-oxide (DM) [9] and 2-diethylaminopyridine *N*-oxide (DE) [10] are the only examples having pyridine *N*-oxide ligands with 2-dialkylamino groups that

have been studied. There are variations in the spectral properties of the complexes of the different ligands prepared with the same Cu(II) salts and this has prompted us to extend our studies to new examples of this structural type. We have selected 2-dimethylamino-3-picoline *N*-oxide (3MDM) and 2-diethylamino-3-picoline *N*-oxide (3MDE) (Fig. 1) because of the possible steric effect that the methyl group in the 3-position of the ring will have on the complexes of these two ligands. We can find no indication that either of the ligands or any of the complexes have been previously prepared or studied.

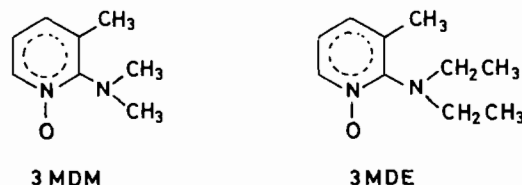


Fig. 1. 2-Dimethylamino-3-picoline *N*-oxide (3MDM) and 2-diethylamino-3-picoline *N*-oxide (3MDE).

Experimental

Both ligands were prepared by amination of 2-chloro-3-picoline *N*-oxide in a steel bomb at a temperature of 140 °C for a period of 48 h with the desired secondary amine. The 2-chloro-3-picoline *N*-oxide was prepared by oxidation of 2-chloro-3-picoline with peracetic acid following the method of Katritzky [11]. 2-Chloro-3-picoline was prepared from 2-amino-3-picoline (Aldrich) following the procedure described by Jovanovic [12].

The copper(II) complexes were isolated from anhydrous ethanol solution, washed with anhydrous ether and stored in a vacuum desiccator over calcium sulfate. Approximate magnetic susceptibility values were obtained with a Johnson Matthey, Inc. balance and the other methods of characterization were the same as previous studies from this laboratory [2].

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TABLE I. Colors, Partial Elemental Analyses, Molar Conductivities and Approximate Magnetic Susceptibilities of Some Copper(II) Complexes of 2-Dimethylamino-3-picoline *N*-Oxide (3MDM) and 2-Diethylamino-3-picoline *N*-Oxide (3MDE)

Compound	Color	Found (calculated) (%)		Λ_M^a	μ (BM)
		C	H		
[Cu(3MDM) ₂](BF ₄) ₂ ·H ₂ O	violet	33.7(34.3)	3.6(4.6)	230 ^b	1.9
[Cu(3MDE) ₂](BF ₄) ₂ ·H ₂ O	rose	38.4(39.0)	5.1(5.6)	242 ^b	1.7
[Cu(3MDM)(NO ₃) ₂]	blue	27.9(28.3)	3.5(3.6)	72 ^b	2.1
[Cu(3MDE)(NO ₃) ₂]	blue	32.8(32.7)	4.6(4.4)	88 ^b	1.5
[Cu(3MDM)Cl ₂]	bright green	33.4(33.5)	3.9(4.2)	35 ^c	1.8
[Cu(3MDE)Cl ₂]	dark green	38.3(38.2)	5.1(5.1)	20 ^c	1.7
[Cu(3MDM)Br ₂] ^d	brown	25.4(25.6)	3.1(3.2)	37 ^c	1.7

^aohm⁻¹ cm² mol⁻¹. ^bca. 10⁻³ M CH₃CN. ^cca. 10⁻³ M DMF. ^d%N 7.6(7.5).

TABLE II. Infrared Assignments (cm⁻¹) for the Copper(II) Complexes of 2-Dimethylamino-3-picoline *N*-Oxide (3MDM) and 2-Diethylamino-3-picoline *N*-Oxide (3MDE)

Compound	$\nu(\text{NO})$	$\delta_a(\text{CNC})$	$\delta_s(\text{CNC})$	$\delta(\text{NO})$	$\nu(\text{CuO})$	$\nu(\text{CuN})$	$\nu(\text{CuX})$
3MDM	1267s	1055s	946sh	(822sh)			
3MDE	1275s	1079s	960s	(818sh)			
[Cu(3MDM) ₂](BF ₄) ₂	1245s	^a	913m	812m	410m	365m	
[Cu(3MDE) ₂](BF ₄) ₂	1230s	^a	930w	834m	392m	338m	
[Cu(3MDM)(NO ₃) ₂]	1241s	997sh	909m	810m	374m	364s	326m
[Cu(3MDE)(NO ₃) ₂]	1222sh	1028sh	925w	828m	396m	345s	302m
[Cu(3MDM)Cl ₂]	1235s	1009m	913m	821m	371m	342m	(345s)
[Cu(3MDE)Cl ₂]	1228s	1027s	930sh	808m	309m	342m	302sh
[Cu(3MDM)Br ₂]	1231s	998s	910m	811s	398m	339s	296m
[Cu(3MDE)Br ₂]	1230s	1027s	937sh	810m	387m	338m	298m
	1211sh				374m	339s	296m
	1231s	998s	910m	811s	393s	339s	270s
	1230s	1027s	937sh	810m	396m	338m	230s
							265m
							225m

^aObscured by $\nu_3(\text{BF}_4)$.

Results and Discussion

The unique solids isolated with each ligand and the different copper(II) salts are shown in Table I along with their colors, partial elemental analyses, molar conductivities and approximate magnetic susceptibilities. The colors are similar to the analogous compounds formed with DM [9] and DE [10] and again show variation with alkyl substitution on the amine function. The first two compounds listed in Table I involve *N*-oxide oxygen and amine nitrogen coordination of the ligand and not the polyatomic anions, which is consistent with their 1:2 electrolytic nature [13]. The remaining compounds behave as non-electrolytes and therefore also involve coordination of the anions along with the bidentate ligand. Approximate magnetic susceptibility measurements indicate all of the compounds prepared in this study are monomeric.

In Table II we have compiled the assignments of the infrared bands most useful for establishing the coordination mode of the ligands. Bands associated with the water molecules of the two tetrafluoroborate solids indicate them to be lattice water rather than coordinated water. The $\nu(\text{NO})$ band is difficult to assign in the spectra of both ligands since there are two strong bands in the region generally associated with this mode. These bands are at 1267 and 1241 cm⁻¹ for 3MDM and at 1275 and 1246 cm⁻¹ for 3MDE. We have assigned the higher energy band to $\nu(\text{NO})$ in each case based on this band being found at higher energy for 3MA (3MA = 2-amino-3-picoline *N*-oxide) [3], 3MMH (3MMH = 2-methylamino-3-picoline *N*-oxide) [8] and 3MEH (3MEH = 2-ethylamino-3-picoline *N*-oxide) [8] than the analogous 2-substituted pyridine *N*-oxides [1, 2]. In the spectra of all the complexes there is no band in the 1270 cm⁻¹ region and the band originally in the 1245 cm⁻¹

region of the ligands' spectra may be combined with the $\nu(\text{NO})$ bands assigned in Table II. The shift to lower energy, confirming coordination by the *N*-oxide oxygen [14], is comparable in magnitude (*i.e.*, 35–45 cm^{-1}) to that for previously studied copper(II) complexes of 2-dialkylaminopyridine *N*-oxides [7, 9, 10].

The $\delta(\text{NO})$ mode in both of the ligands is difficult to assign because of the presence of other ligand bands, so the energies that we have assigned should be taken as tentative. However, this band often undergoes only small shifts in energy upon complexation because of two opposing effects [15]. It is noteworthy that the energy of this band is highest for the most sterically hindered Cu(II) center, $[\text{Cu}(\text{3MDE})_2](\text{BF}_4)_2$, and next highest for another Cu(II) center that would have high steric requirements, $[\text{Cu}(\text{3MDE})(\text{NO}_3)_2]$. Just as was found for other dialkylaminopyridine *N*-oxide complexes when compared to their analogous alkylaminopyridine *N*-oxide complexes [2, 7, 9, 10], the $\nu(\text{CuO})$ bands are found at considerably lower energy for these complexes than for the complexes prepared with 3MMH and 3MEH [8], 2-methylamino-3-picoline *N*-oxide and 2-ethylamino-3-picoline *N*-oxide, respectively.

Coordination by the amine nitrogen is confirmed by the shift to lower energy of both of the $\delta(\text{CNC})$ bands [16] in the complexes of both ligands. As was found for the complexes of DM [9] and DE [10], the asymmetrical bending mode is shifted to a greater extent than is the lower energy symmetrical bending mode. The more sterically hindered 3MDE ligand has both of these bands at higher energy than their position in the spectrum of 3MDM. Also indicative of coordination of the amine nitrogen of both ligands is a band in the 338–365 cm^{-1} region of the spectra of all the complexes which we have assigned to $\nu(\text{CuN})$ [17].

At lower energy in the spectra of the four halo complexes are two bands assignable to $\nu(\text{CuX})$ [18] consistent with the *cis* arrangement of the two halo

ligands in these apparently planar Cu(II) complexes. The energies of these bands are consistent with the 4-coordinate nature of these complexes [19]. Similarly, both solids prepared with copper(II) nitrate have two bands assigned to $\nu(\text{CuO})$ of the nitrate ligand. Since the separation of the two bands assignable to $\nu_1 + \nu_4$ in the 1700–1800 cm^{-1} is about 40 cm^{-1} suggesting bidentate coordination [20] in both solids, it appears that the two bands are due to equatorial and axial coordination of the nitrate ligands. Both tetrafluoroborate solids have bands at *ca.* 1055 and 527 cm^{-1} assignable to ν_3 and ν_4 , respectively, and confirming the non-coordination of these ions.

These infrared assignments along with the results of the electronic (Table III) and electron spin resonance (Table IV) spectra will now be discussed for the individual compounds. Also, the spectral properties of the present complexes will be compared to those prepared with related ligands [1–10].

[Cu(3MDM)₂](BF₄)₂ and [Cu(3MDE)₂](BF₄)₂

Since there is no indication of coordination of the tetrafluoroborate anions, both of these complexes can be expected to have a *trans* arrangement of the two bidentate ligands analogous to the violet $[\text{Cu}(\text{DM})_2](\text{ClO}_4)_2$ (DM = 2-dimethylaminopyridine *N*-oxide) [21]. Both the perchlorate and tetrafluoroborate solids of DM were violet while those of DE (DE = 2-diethylaminopyridine *N*-oxide) were rose [9, 10] just as is the situation for these two solids. We have not attempted to prepare complexes with copper(II) perchlorate because of the explosive nature of $[\text{Cu}(\text{6MDM})_2](\text{ClO}_4)_2$ (6MDM = 2-dimethylamino-6-picoline *N*-oxide) [7] as well as $[\text{Cu}(\text{DM})_2](\text{ClO}_4)_2$ [22]. The infrared spectra of both of these solids suggested 'semi-coordination' of the perchlorate anions [23].

The electronic spectra of the present solids suggests stronger bonding for 3MDE compared to 3MDM just as was found for DE in comparison to DM. Both of these diethyl complexes have two d–d

TABLE III. Electronic Spectral Assignments (cm^{-1}) of the Copper(II) Complexes of 2-Dimethylamino-3-picoline *N*-Oxide (3MDM) and 2-Diethylamino-3-picoline *N*-Oxide (3MDE)

Compound	O → Cu(II)	X → Cu(II)	d–d
$[\text{Cu}(\text{3MDM})_2](\text{BF}_4)_2$	27400		19460
$[\text{Cu}(\text{3MDE})_2](\text{BF}_4)_2$	a		21570; 18550sh
$[\text{Cu}(\text{3MDM})(\text{NO}_3)_2]$	26180		16580; 14930sh
$[\text{Cu}(\text{3MDE})(\text{NO}_3)_2]$	26320		16390; 14750sh
$[\text{Cu}(\text{3MDM})\text{Cl}_2]$	28900		12840
$[\text{Cu}(\text{3MDE})\text{Cl}_2]$	27170		13850
$[\text{Cu}(\text{3MDM})\text{Br}_2]$	29850	21190	12270
$[\text{Cu}(\text{3MDE})\text{Br}_2]$	25590	21650	12800

^aObscured by $\pi \rightarrow \pi^*$ (and shoulder presumably due to $n \rightarrow \pi^*$) at *ca.* 38000 cm^{-1} (32570 cm^{-1}).

TABLE IV. Electron Spin Resonance Parameters of some Copper(II) Complexes of 2-Dimethylamino-3-picoline *N*-Oxide (3MDM) and 2-Diethylamino 3-picoline *N*-Oxide (3MDE)

Compound	Temperature	g_1 or g_{\parallel}	g_2	g_3 or g_{\perp}	g_{av}
Solid state spectra					
[Cu(3MDM) ₂](BF ₄) ₂	RT ^a	2.207 $A_{\parallel} = 196$ G		2.015	2.079
[Cu(3MDE) ₂](BF ₄) ₂	77 K RT	2.172 $A_{\perp} = 160$ G	2.064	2.048 2.023	2.086
[Cu(3MDM)(NO ₃) ₂]	77 K RT	(2.241) 2.231		2.042 2.067	(2.108) 2.122
[Cu(3MDE)(NO ₃) ₂]	77 K RT	2.239 2.222	2.121	2.064 2.060	2.122 2.134
[Cu(3MDM)Cl ₂]	77 K RT	2.220 2.286	2.112	2.059 2.060	2.130 2.135
[Cu(3MDE)Cl ₂]	77 K RT	2.288 2.242	2.096	2.057 2.064	2.134
[Cu(3MDM)Br ₂]	77 K RT	2.229 2.239	2.089	2.063 2.062	2.127 2.121
[Cu(3MDE)Br ₂]	77 K RT	2.234 2.233	2.077	2.059 2.050	2.117 2.120
	77 K	2.236	2.074	2.049	2.120
Solution spectra					
[Cu(3MDM) ₂](BF ₄) ₂	RT	$A_o = 66$ G			$g_o = 2.120$
	77 K	2.232 $A_{\parallel} = 175$ G		2.054	2.113

^aRoom temperature

bands in their spectrum and the average energy of these two band maxima is higher than the maximum of the d-d band in the spectra of the respective dimethyl ligands. We interpret this to be due to the larger diethylamino function blocking axial interaction of either *N*-oxide oxygens of ligands on adjacent copper(II) centers or the tetrafluoroborate anions. The appearance of two distinct peaks assignable to d-d transitions has been attributed to 4-coordinate, planar Cu(II) centers [24]. The ESR spectrum of [Cu(3MDE)₂](BF₄)₂ indicates it to have a rhombic distortion although the highest *g*-value features in the spectra of both of these solids are difficult to assign accurately because of interference from the more intense low *g*-value signal. Dissolution of the violet [Cu(3MDM)₂](BF₄)₂ in acetonitrile gives a blue solution indicating solvent interaction with the CuO₂N₂ chromophore in the axial positions. This axial coordination is accompanied by the expected change in the ESR spectrum (*i.e.*, shifts to higher values by g_{\parallel} , g_{\perp} , and g_{av}) when an essentially square planar complex becomes 6-coordinate.

In contrast, the two metal-ligand stretching frequencies are considerably lower in energy for the complex prepared with 3MDE than for the one prepared with 3MDM which is similar to the relationship found for the analogous DE and DM complexes.

While a rhombic distortion, in part, would explain this trend, it is unexpected that the bonding in the complexes with reduced axial interactions would be weaker, particularly when the d-d band energies suggest stronger bonding. Careful inspection of the lower energy portion of the spectra shows a band present in 3MDE solid's spectrum at 470 cm⁻¹ which is not present in the spectrum of the 3MDM solid, but this band is also present in the spectrum of Cu(3MDE)Cl₂. This latter result suggests that the band is more likely due to a deformation of the ethyl groups than to Cu-ligand stretching modes since $\nu(\text{CuO})$ is found at nearly the same energy in the spectrum of Cu(3MDE)Cl₂ as it is in the spectrum of Cu(3MDM)Cl₂. Therefore, we see no alternative bands for assignment to either $\nu(\text{CuO})$ or $\nu(\text{CuN})$ and assume that these bands are lower in energy than would be expected due to combination with other bands of the complexes when the diethylamino function is present in bis complexes.

[Cu(3MDM)(NO₃)₂] and [Cu(3MDE)(NO₃)₂]

The infrared spectra of both complexes indicate the coordinated nitrate ligands to be bidentate and, since the *N*-oxide ligands are also bidentate in their coordination, the expected structure for both complexes is shown in Fig. 2. The appearance of two

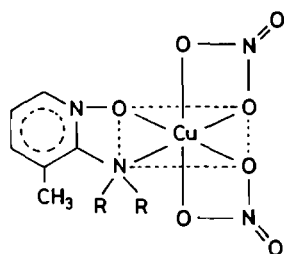


Fig. 2. Proposed structure of $[\text{Cu}(3\text{MMDM})(\text{NO}_3)_2]$ and $[\text{Cu}(3\text{MDE})(\text{NO}_3)_2]$.

bands assignable to $\nu(\text{CuO})$ for the nitrate ligands can be explained based on their required *cis* relationship as well as the axial–equatorial nature of their coordination. The lower energies of the Cu–ligand stretching frequencies for the 3MDE complex are probably due to the steric requirements of the larger diethylamino group. As with the previously discussed complex, this steric requirement also causes a rhombic distortion of $[\text{Cu}(3\text{MDE})(\text{NO}_3)_2]$ based on its ESR spectrum. The lower energy for the d–d bands of these two complexes compared to their tetrafluoroborate counterparts confirms the weaker crystal field for the nitrate ligand compared to the *N*-oxide ligands as well as the stronger axial interaction occurring in these complexes.

While both of these solids are blue as was $[\text{Cu}(\text{DE})(\text{NO}_3)_2]$, $[\text{Cu}(\text{DM})(\text{NO}_3)_2]$ was bright green with a single d–d band at considerably lower energy (*i.e.*, $14\,250\text{ cm}^{-1}$). The blue $[\text{Cu}(\text{DE})(\text{NO}_3)_2]$ had a single d–d band at $17\,250\text{ cm}^{-1}$ and a reversed ESR signal while both of these complexes have assignable shoulders on their d–d bands and typical $d_{x^2-y^2}$ ground state powder ESR spectra. Attempts to record solution ESR spectra for these compounds as well as the halide solids to be discussed next yielded a mixture of Cu(II) species indicating decomposition of desired Cu(II) center. The lower energy d–d bands as well as the shoulders suggests that the methyl group on the 3-position of the ring is also affecting the stereochemistry by weakening the axial bonding of chelating nitrate ligands in the present solids. The low values for g_{\parallel} and g_1 (Table IV) for the ESR

spectra are also consistent with decreased axial bonding. It should be noted that for the ligand 6MDM we were unable to isolate a nitrate solid of this stoichiometry, but, instead prepared the blue $[\text{Cu}(6\text{MDM})_2(\text{NO}_3)_2]$ with two bidentate *N*-oxide ligands and monodentate nitrate ligands.

$[\text{Cu}(3\text{MMDM})\text{Cl}_2]$ and $[\text{Cu}(3\text{MDE})\text{Cl}_2]$

Both $[\text{Cu}(\text{DM})\text{Cl}_2]$ and $[\text{Cu}(\text{DE})\text{Cl}_2]$ were blue while $[\text{Cu}(6\text{MDM})\text{Cl}_2]$ was a yellowish-green and the present compounds are green. Since all five of the solids behave as non-electrolytes, have $\nu(\text{CuCl})$ bands at energies expected for terminal, but not bridging chlorides, and have bidentate *N*-oxide ligands, all are considered to be 4-coordinate, monomeric complexes. Therefore, the color variations are due to differences in the stereochemistry of the 4-coordinate Cu(II) centers and the electronic and electron spin resonance spectral parameters are compiled for these five compounds in Table V. The presence of a methyl group on the pyridine *N*-oxide ring in either the 3- or 6-position must cause a distortion toward tetrahedral stereochemistry for these complexes. This is confirmed by the absence of a higher energy d–d band; the presence of a band in this energy region would be indicative of either planar or flattened tetrahedral stereochemistry [24, 25]. The more tetrahedral stereochemistry for the various picoline *N*-oxide complexes (*i.e.*, $[\text{Cu}(6\text{MDM})\text{Cl}_2]$ and the two solids of this study) is consistent with stronger coordinate bonds and each of the metal–ligand stretching frequencies is *ca.* 20 cm^{-1} higher energy than for the complexes of DM and DE [9, 10]. The rhombic distortion shown by the ESR spectrum is consistent with the other complexes of 3MDE of this study, all having this same distortion. Based on the metal–ligand stretching frequencies this distortion appears to weaken the copper–oxygen bond, but strengthen the copper–nitrogen and copper–chlorine bonds.

$[\text{Cu}(3\text{MMDM})\text{Br}_2]$

Although we were unable to prepare a compound from 3MDE and CuBr_2 that gave a plausible elemental analysis (low in C, H, and N), the spectral properties of the compound that we have isolated are either

TABLE V. A Comparison of Spectral Parameters of some Monomeric $[\text{Cu}(\text{NO})\text{Cl}_2]$ Chromophores

Compound	$\nu(\text{d-d}) (\text{cm}^{-1})$	g_{\parallel}	g_{av}	Reference
$[\text{Cu}(\text{DM})\text{Cl}_2]$	17240; 12660	2.223	2.096	9
$[\text{Cu}(6\text{MDM})\text{Cl}_2]$	12660	2.279	2.141	7
$[\text{Cu}(3\text{MMDM})\text{Cl}_2]$	12840	2.286	2.135	this work
$[\text{Cu}(\text{DE})\text{Cl}_2]$	17540; 13330	g_{iso}	2.107	10
$[\text{Cu}(3\text{MDE})\text{Cl}_2]$	13850	$g_1 = 2.242$	2.134	this work

similar to those of $[\text{Cu}(\text{3MDM})\text{Br}_2]$ or shifted in the manner expected based on the previously chloro complexes of these two ligands. The spectral differences are as follows: higher energy $\nu(\text{d-d})$ and rhombic ESR spectrum for $[\text{Cu}(\text{3MDE})\text{Br}_2]'$.

Like the chloro compounds, the bromo compounds prepared from ligands having a methyl group on the *N*-oxide ring are closer to a tetrahedral stereochemistry. Again, there is a color difference between $[\text{Cu}(\text{DM})\text{Br}_2]$ and the present compounds (*i.e.*, gold and brown, respectively). Also, there is a d-d band in the $16\,500\text{ cm}^{-1}$ energy region of $[\text{Cu}(\text{DM})\text{Br}_2]$, and considerably lower *g*-values for the DM compound [9] consistent with greater planarity. However, in contrast to $[\text{Cu}(\text{DE})\text{Cl}_2]$, $[\text{Cu}(\text{DE})\text{Br}_2]$ has spectral properties more like those of the present compounds indicating it to have considerably more tetrahedral distortion than its DM analogue.

Finally, a comparison of the spectral properties of $[\text{Cu}(\text{3MDM})\text{Br}_2]$ and $[\text{Cu}(\text{3MDM})\text{Cl}_2]$ show the two to be very similar. The $\nu(\text{CuBr})/\nu(\text{CuCl})$ ratio (*i.e.*, average of the two bands) being equal to 0.84 is indicative of their similarity of structure [26].

Conclusions

Both 3MDM and 3MDE coordinate solely as bidentate ligands via their *N*-oxide oxygen and amine nitrogen in all of the complexes of this study. Both impart considerably more steric requirements to their complexes than the analogous ring unsubstituted 2-dialkylaminopyridine *N*-oxides. This results in stronger planar bonding in the bis(ligand) complexes due to reduced interaction by the anions and to substantial tetrahedral distortion in the $\text{Cu}(\text{ON})\text{X}_2$ complexes. Both of these structural changes are greater for the larger 3MDE ligand.

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