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COPPER(II) COMPLEXES OF 2-CYCLOHEXYLAMINOPYRIDINE N-OXIDE

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Five copper(II) salts have been used to prepare complexes of 2-cyclohexylpyridine N-oxide. Their stoichiometries have been established by partial elemental analyses, and their ir, uv-vis- nir and esr spectra, along with other physical properties, are reported. The nature of these new compounds is compared to previously reported 2-alkylpyridine N-oxide copper(II) complexes.

INTRODUCTION

Copper(II) complexes of 2-aminopyridine N-oxide were initially prepared by Sigel and Brintzinger[1] and more fully characterized by Landers and Phillips[2] and in our laboratory.[3] Also, copper (II) complexes of 2-alkylaminopyridine N-oxides[4] (i.e., methyl- through the various butyl-groups), 2-dialkylaminopyriding N-oxide complexes,[5] the various 2-aminopicoline N-oxides,[6] and 2-alkyl-[7] and 2-dialkylaminopicoline N-oxides[8] have been prepared and spectrally characterized. However, to date, cycloalkylamino- derivatives have not been studied and complexes of 2- cyclohexylaminopyridine N-oxide (CH, Fig.1) prepared from various copper(II) salts are reported here.

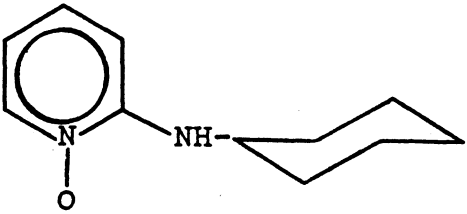

Fig. 1. 2-cycloaminopyridine N-oxide (CH).

EXPERIMENTAL

CH was prepared in the following manner: 5 g (0.03 mol) of 2- chloropyridine N-oxide hydrochloride (Aldrich) was heated at 140°C in a steel bomb for three days with an excess (i.e., 25 ml) of 2-cyclohexylamine (Aldrich) and 15 ml of deionized water. The contents of the bomb were transferred to a beaker using methanol and stirred with 5 g of sodium carbonate for several hours. Volatile materials were removed with a rotatory evaporator. The resulting residue was extracted with absolute ethanol, filtered and the ethanol removed; this procedure was repeated using ethyl acetate. Light brown crystals (m.pt. = 76°C) slowly formed on drying on a warm plate which yielded a positive (i.e., blue) iron(III) test.[1]

Complexes were prepared in refluxing ethanol with the following stoichiometric ratios of CH to copper salt: $Cu(BF_4)_2$, 4 : 1 and $Cu(NO_3)_2$, $CuCl_2$, and $CuBr_2$, 2 : 1. An aqueous solution of copper(II) acetate was used for the preparation of [Cu(CH–H)$_2$]. Partial elemental analyses were performed by Micro-Analysis, Inc., of Wilmington, DE, USA. Infrared (Perkin-Elmer 783) and electronic spectra (Perkin-Elmer 330) were recorded as nujol mulls and e.s.r. spectra (Varian E-104) were calibrated with DPPH.

RESULTS AND DISCUSSION

The colours, partial elemental analyses, molar conductivities and magnetic susceptibilities are given in Table 1. In contrast to dialkylaminopyridine N-oxides[5], which coordinate via both the pyridine N-oxide oxygen and amino nitrogen as bidentate ligands,[5] the alkylaminopyridine N-oxides studied to date[4] coordinate to copper(II) via only the N-oxide oxygen. Consistent with this is the isolation of the green $[Cu(CH)_4](BF_4)_2$ which likely contains a CuO_4 chromophore. The two complexes prepared from copper(II) halides are polymeric and involve coordination of both halogen and oxygen donors. Coordination of the nitrogen of 2- alkylaminopyridine N-oxides does occur on deprotonation,[9] which is most easily accomplished by refluxing an aqueous solution of the desired N-oxide with copper(II) acetate.

TABLE 1
COLOURS, PARTIAL ELEMENTAL ANALYSES, AND MAGNETIC MOMENTS OF THE COPPER(II) COMPLEXES OF 2-CYCLOHEXYLAMINOPYRIDINE N-OXIDE, CH

Compound	Colour	% Found (% Calcd)			μ*	Λ_M**
		C	H	N		
$[Cu(CH)_4](BF_4)_2 \cdot H_2O$	green	51.3 (51.6)	6.4 (6.5)	11.3 (10.9)	2.5	288
$[Cu(CH)_2(NO_3)_2]$	olive green	45.8 (46.2)	5.3 (5.6)	— —	2.1	62
$\{Cu(CH)Cl_2\}_x$	red brown	41.4 (40.4)	4.9 (4.9)	8.2 (8.6)	1.0	41
$Cu_3(CH)_4Br_6$	brown	36.9 (36.8)	4.2 (4.2)	7.1 (7.8)	0	69
$[Cu(CH-H)_2]$	brown	59.6 (59.2)	7.0 (6.8)	12.5 (12.6)	1.6	<10

*B.M.; **$ohm^{-1}cm^2mol^{-1}$; *ca.* 10^{-3} M CH_3CN.

The infrared spectrum of CH shows ν(NH) as a medium intensity band at 3245 cm^{-1} and δ(NH) as a strong band at 1623 cm^{-1}. In the spectra of the complexes the former is shifted to above 3300 cm^{-1} and the latter to above 1630 cm^{-1} confirming that the nitrogen is not coordinated to copper(II) in the first four complexes of Table 1. Although pyridine N-oxide has ν(NO) = 1242 cm^{-1},[10] 2-alkylaminopyridine N-oxides have this band below 1220 cm^{-1} because of the oxygen's involvement in intermolecular hydrogen bonding.[11] For CH, ν(NO) is assigned at 1212 cm^{-1}, and shifted on complexation to *ca.* 1190 cm^{-1} in the spectra of the first four complexes. [Cu(CH–H)$_2$] shows this band at 1173 cm^{-1} consistent with the greater shift observed for deprotonated 2-aminopyridine N-oxides.[6,7,9] Bands in the 390–410 cm^{-1} region of the spectrum of the five complexes are assignable to ν(CuO).[4,12] In the spectrum of [Cu(CH-H)$_2$) ν(CuN) is assigned to a strong band at 330 cm^{-1}.[9,13] A strong band at 340 cm^{-1} in the spectrum of [Cu(CH)$_2$(NO$_3$)$_2$] is assignable to ν(CuO) of nitrato ligands[14] and ν(CuCl) and ν(CuBr) are found as medium bands at 334 cm^{-1} and 258 cm^{-1} in the spectra of the halo complexes.[15]

The n→π band for the N-oxide function in CH is at 29,760 cm^{-1} and shifts to energies of 32,000–34,000 cm^{-1} in the complexes consistent with the coordination of the N-oxide oxygen. Additional band(s) in the spectra of the complexes at 26,000–28,000 cm^{-1} are due to oxygen (i.e., N-oxide) to copper(II) charge transfer bands.[16] Lower energy (i.e., 22,000–24,000 cm^{-1}) charge transfer bands are present in the spectra of most of these complexes due to other charge transfer bands. A band at 20,410 cm^{-1} in the spectrum of Cu$_3$(CH)$_4$Br$_6$ is assigned to a Br→Cu(II) transition. The d-d transitions and e.s.r. parameters are compiled in Table 2 and are included in the discussions of the individual complexes.

[Cu(CH)$_4$](BF$_4$)$_2$

The molar conductivity value (Table 1) indicates a 1:2 electrolyte and the magnetic moment shows that this complex is monomeric. Confirming the non-coordination of the BF$_4^-$ ions is the observance of a broad doublet for ν_3(BF$_4$) at 1053 and 1040 cm^{-1} and a weaker, sharper band at 532 cm^{-1} assignable to ν(BF$_4$).[17] The splitting of the ν_3 band is indicative of the ion's distortion due to crystal structure requirements of a large cation. An energy of 3365 cm^{-1} for ν(NH) suggests that the distortion of BF$_4^-$ may not be caused by its involvement in hydrogen bonding with the amine proton; large polyatomic anions are known to be more likely to hydrogen bond than smaller anions.[18]

Previous work has shown that the energy of the composite ν(dd) band for these CuO$_4$ chromophores is dependent on the size of the alkyl substituent (i.e., [Cu(BH)$_4^{2+}$] > [Cu(PH)$_4^{2+}$] > [Cu(EH)$_4^{2+}$] > [Cu(MH)$_4^{2+}$], where BH, PH, EH and MH are 2-butyl-, 2-propyl-, 2- ethyl- and 2-methylaminopyridine N-oxides, respectively).[4] Also, branching of the alkyl substituent decreases the energy of the ν(dd) band (e.g., [Cu(PH)$_4^{2+}$] > [Cu(IPH)$_4^{2+}$] and [Cu(BH)$_4^{2+}$] > Cu(IBH)$_4^{2+}$] > [Cu(SBH)$_4^{2+}$] > [Cu(TBH)$_4^{2+}$] where IPH, IBH, SBH, and TBH are 2-isopropyl-, 2-isobutyl-, 2-sec-butyl- and 2-tert- butylpyridine N-oxides). The present [Cu(CH)$_4^{+2}$] band maximum at 16,390 cm^{-1} (Table 2) is lower in energy than all but [Cu(MH)$_4^{+2}$] and [Cu(TBH)$_4^{+2}$] among this group of complexes. Therefore, straight-chain hydrocarbon substituents more effectively inhibit axial bonding of potentially bridging N-oxide oxygens attached to adjacent copper centres. The crystal structure[19] of [Cu(MH)$_4$](BF$_4$)$_2$ showed the pyridine N-oxide rings to be twisted from the CuO$_4$ plane in a propellar-like manner with trans

TABLE 2
ELECTRON SPIN RESONANCE PARAMETERS AND d-d BANDS OF THE COPPER(II) COMPLEXES OF 2-CYCLOHEXYLAMINOPYRIDINE N-OXIDE

Compound	Temp (°K)	$g_{\|}/g_1$	g_2	$g_{\|}/g_3$	g_{av}	ν(dd)*
$[Cu(CH)_4](BF_4)_2$	298 77 $CHCl_3$ 298 DMSO 77	2.257 $A_{\|} = 180G$ 2.262 $A_0 = 71G$ 2.246 $A_{\|} = 140G$	2.060 2.077	2.010 2.054 2.046	2.109 2.123 $g_0 = 2.127$ 2.123	16390 15080
$[Cu(CH)_2(NO_3)_2]$	298 77 $CHCl_3$ 298	2.276 2.270 $A_0 = 64G$	2.059 2.063f	2.040 2.051	2.125 2.128 $g_0 = 2.146$	14080 13770
$\{Cu(CH)Cl_2\}_x$	298 77 $CHCl_3$ 298	no signal no signal no signal				18020 13250
$[Cu_3(CH)_4Br_6]$	298 77 $CHCl_3$ 298				$g_{iso} = 2.175$ $g_{iso} = 2.101$	12090 11830
$[Cu(CH–H)_2]$	298 77 $CHCl_3$ 298 77 Py + $CHCl_3$ 298 77	2.181 2.168 $A_0 = 59G$ 2.212 $A_{\|} = 173G$ $A_0 = 58G$ 2.214 $A_{\|} = 157G$	2.073 2.074 2.054	2.047 2.050 2.047 2.044	2.100 2.097 $g_0 = 2.110$ 2.102 $g_0 = 2.116$ 2.104	18180 12530 16890 16950

$*cm^{-1}$

ligands having the methylamino function directed above (or below) the plane so that both axial positions are equally blocked. A consequence of the bulkiness of CH is the resolution of $g_{\parallel}$ in the powder e.s.r. spectrum; three of the butylaminopyridine N-oxide complexes prepared with copper(II) tetrafluoroborate also had resolved $g_{\parallel}$ features[4]

$[Cu(CH)_2(NO_3)_2]$

The non-electrolytic behaviour, as well as its magnetic moment, indicate $(Cu(CH)_2(NO_3)_2)$ to be monomeric with nitrato ligands rather than ionic nitrates. Coordination of the nitrato ligands is confirmed by the appearance[14] of a broad $\nu(CuO)$ at 340 cm^{-1} and a strong band at 1013 cm^{-1} due to $\nu_2(NO_3)$. The difference in the $[\nu_2 + \nu_5 (1768\ cm^{-1})$ and $\nu_2 + \nu_6\ (1723\ cm^{-1})$ bands of 45 cm^{-1} is consistent with bidentate coordination of the nitrato ligands.[20] Since copper(II) complexes often form 4 + 2 coordination centers, these bidentate nitrato ligands must coordinate with unequal Cu–O bonds at axial and equatorial positions. The axial bonding of the nitrato ligands lowers ν(dd) and raises the lowest g-value, g_1, consistent with weaker planar bonding compared to $[Cu(CH)_4](BF_4)_2$. The spectral properties of $[Cu(CH)_2(NO_3)_2]$ are remarkedly similar to an analogous complex of 2-amino-4,6- lutidine N-oxide, which was proposed to have the same structure.[21]

$\{Cu(CH)Cl_2\}_x$

Many of the previously studied 2-alkylaminopyridine N-oxides yield orange, dimeric CuL_2Cl_2 complexes.[4] The crystal structure[22] of $\{Cu(M)_2Cl_2\}_2$ (M = 2-methylaminopyridine N-oxide) showed it to be a centrosymmetric bridged dimer with each copper(II) bonded to three terminal atoms (one O and two Cl) and two bridging O atoms. However, many of the 2-aminopicoline N-oxide[6] and the 2- isobutylaminopyridine N-oxide, IB, complex[4] isolated from copper(II) chloride have $CuLCl_2$ stoichiometry. They must be polymeric in order to achieve the “minimum” coordination number of four since the amino group is not involved in coordination. The energy of $\nu(CuCl)$ suggests terminal chlorines[23] so that bridging by the N-oxide oxygens is likely. A dimeric structure with two bridging N-oxide and two chloro ligands making up the planar arrangement about each copper(II) and chloro ligands from adjacent dimers bonding weakly in opposite axial positions gives the same centrosymmetric arrangement as for $\{Cu(M_2Cl_2\}_2$.[22] Also, this is identical to the structure reported for $\{Cu(4PicO)Br_2\}_2$ where 4PicO is 4-picoline N-oxide.[24]

$[Cu_3(CH)_4Br_6]$

Two different preparations yielded complexes having elemental analyses fitting this stoichiometry. A linear trimeric species with two N-oxide ligands bridging the central copper(II) from both sides, the two terminal coper(II) ions completing their planes with two bromo ligands, and the two remaining bromides in axial positions on the two outer copper(II) centers is one possibility. Another would be similar to the 2-picoline N-oxide complex isolated from copper(II) chloride,[25] which consists of dimers (described earlier) bridged by $CuBr_2$ groups through long Cu-Br bonds to form infinite chains. A crystal structure of this complex needs to be obtained prior to discussion of its spectral properties.

[Cu(CH–H)2]

A number of these molecular copper(II) solids involving an anion of a 2-alkylaminopyridine N-oxide[4,9] or 2-alkylaminopicoline N- oxide[7] have been previously reported. Also, the crystal structure of [Cu(E–H)$_2$], where E–H is the anion of 2-ethylaminopyridine N- oxide, showed it to be a rigorously planar, trans 4-coordinate complex with no significant axial interaction.[26] The magnetic moment, molar conductivity, and infrared spectrum of [Cu(CH–H)$_2$] indicate studied molecular copper(II) complexes all had at least two d-d bands in their visible spectrum in both the solid state and $CHCl_3$ solution. A single d-d band in solution for [Cu(CH–H)$_2$] may indicate a distortion towards tetrahedral symmetry. The higher value of $g_{\|}/g_1$ in solution compared to the powder spectrum (Table 2) is supportive of this suggestion. Only [Cu(IP–H)$_2$] and [Cu(SB–H)$_2$] (IP–H = 2-isopropyl-˙ and SB–H = 2-sec- butylaminopyridine N-oxide, respectively) has $g_{\|}/g_1$ as high as 2.215; lower values occur with smaller alkyl substituents. Addition of excess pyridine to the chloroform solution does not significantly change the electronic and e.s.r. spectra of [Cu(CH–H)$_2$).

Meaningful orbital reduction factors $k_{\|}$ and $k_{\perp}$ can't be calculated from the solution spectra, but little variation from 0.60 and 0.70, respectively, was found for this series of complexes.[4,7,9] The covalency parameter, α^2,[27] has a value of 0.76, which is in good agreement with the previous molecular complexes. The results for [Cu(CH–H)$_2$] are supportive of the observation that branching of the alkyl groups has a more significant effect on the spectral values than lengthening the chain.

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