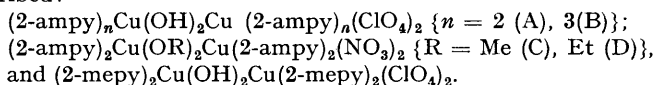


### 570. Complexes of 2-Amino- and 2-Methyl-pyridine with Copper(II) Salts.

By WILLIAM R. MCWHINNIE.

The preparations of the following dimeric copper(II) complexes are described:



Reaction of (A) and (D) with 2,2'-bipyridyl gives (bipy)Cu(OH)<sub>2</sub>Cu(bipy)X<sub>2</sub> (X = ClO<sub>4</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup>, respectively). (2-Ampy)<sub>4</sub>CuCl<sub>2</sub>, (2-mepy)<sub>2</sub>CuCl<sub>2</sub>, and (2-mepy)Cu(NO<sub>3</sub>)<sub>2</sub> are reported; the last two are considered to be monomeric distorted tetrahedral compounds. In dilute ethanolic solution, 1:1 and 2:1 complexes of 2-ampy with copper(II) chloride and copper(II) nitrate, respectively, are shown to exist.

Spectroscopic data for all compounds prepared are presented and discussed.

THIS Paper reports compounds isolated from the reactions of copper(II) perchlorate, nitrate, and chloride, under various conditions, with 2-aminopyridine (2-ampy) and, for comparison, 2-methylpyridine (2-mepy).

Angyal and Angyal<sup>1</sup> have summarised and assessed the structural data available for 2-aminopyridine, and conclude that it exists in the amino- rather than in the tautomeric imino-form ( $K = [\text{amino-form}]/[\text{imino-form}] \simeq 2 \times 10^5$ ).  $pK_a$  values are available for 2-methylpyridine (6.20 at 25°)<sup>2</sup> and for 2-aminopyridine (6.71,<sup>3</sup> 6.86<sup>4</sup>); these may be compared with the value of 5.45 at 25° for pyridine itself.<sup>2</sup> Consideration of the nature of 2-aminopyridine suggests that it can combine with metal ions in three ways: through one nitrogen; as a chelating agent; or, in view of the fact that calculation indicates the nitrogen-nitrogen distance to be *ca.* 2.6 Å, in a "copper acetate" type of structure with ions such as Cr<sup>2+</sup> or Cu<sup>2+</sup>. Some compounds with platinum(II) are known, but in these cases 2-aminopyridine appears to be monobasic, giving compounds of the type (amine)<sub>2</sub>(2-ampy)<sub>2</sub>PtX<sub>2</sub> (X = halogen)<sup>5,6</sup> or (2-ampy)<sub>4</sub>PtCl<sub>2</sub>;<sup>7</sup> only one platinum(II) compound in which the ligand might possibly be bidentate has been isolated, namely, [(NH<sub>2</sub>OH)<sub>2</sub>(2-ampy)Pt]PtCl<sub>4</sub>.<sup>8</sup> [Fe(2-ampy)<sub>3</sub>][Fe<sub>2</sub>(CO)<sub>8</sub>] has been prepared by Hieber and Kahlen,<sup>9</sup> but there appear to be no other compounds known in which the base is other than monodentate.

Complexes of 2-methylpyridine are better known; of particular interest are the study of the solution spectra of copper(II) perchlorate and nitrate in the anhydrous base by Royer,<sup>10</sup> and the amine complexes of nickel(II) halides reported by Quagliano and his co-workers.<sup>11</sup> Very recently, Graddon *et al.*<sup>12</sup> have given details of (2-mepy)<sub>2</sub>CuCl<sub>2</sub>, which is also considered in the present work. The steric effects of the 2-methyl group appear to be important in determining the stability<sup>13</sup> and the stereochemistry<sup>11,12</sup> of the complexes formed; *e.g.*, nickel(II), cobalt(II), and copper(II) chlorides give four-co-ordinate

<sup>1</sup> Angyal and Angyal, *J.*, 1952, 1461.

<sup>2</sup> Bruehlman and Verhoek, *J. Amer. Chem. Soc.*, 1948, **70**, 1401.

<sup>3</sup> Jonassen and Rolland, "Stability Constants" part I, *Chem. Soc. Special Publ.* No. 6, p. 29.

<sup>4</sup> Albert, Goldacre, and Phillips, *J.*, 1948, 2240.

<sup>5</sup> Goremykin and Gladyshevskaya, *J. Gen. Chem. (U.S.S.R.)*, 1943, **13**, 762.

<sup>6</sup> Goremykin, *Bull. Acad. Sci. U.S.S.R., Classe sci. Khim.*, 1943, 401.

<sup>7</sup> Rubinshtiiin, *Bull. Acad. Sci. U.S.S.R., Classe sci. Khim.*, 1944, 42.

<sup>8</sup> Goremykin, *Bull. Acad. Sci. U.S.S.R., Classe sci. Khim.*, 1947, 241.

<sup>9</sup> Hieber and Kahlen, *Chem. Ber.*, 1953, **91**, 2223.

<sup>10</sup> Royer, *J. Inorg. Nuclear Chem.*, 1959, **11**, 151.

<sup>11</sup> Glonek, Curran, and Quagliano, *J. Amer. Chem. Soc.*, 1962, **84**, 2014.

<sup>12</sup> Graddon, Schultz, Watton, and Weedon, *Nature*, 1963, **198**, 1299.

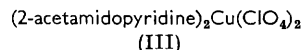
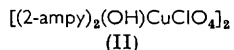
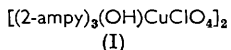
<sup>13</sup> Sacconi, Lombardo, and Paoletti, *J.*, 1958, 848.

complexes with 2-methylpyridine, but six-co-ordinate complexes with pyridine and 4-methylpyridine.<sup>12</sup>

## RESULTS AND DISCUSSION

The reaction of copper(II) chloride and nitrate with a ten-fold excess of 2-amino- or 2-methyl-pyridine in water or aqueous ethanol results in the hydrolysis of the copper salts to the hydroxide. Use of ethanol or methanol as solvent gives  $[(2\text{-ampy})_2(\text{OC}_2\text{H}_5)\text{Cu}(\text{NO}_3)]_2$ ,  $[(2\text{-ampy})_2(\text{OCH}_3)\text{Cu}(\text{NO}_3)]_2$ ,  $(2\text{-ampy})_4\text{CuCl}_2$ , and  $(2\text{-mepy})_2\text{Cu}(\text{NO}_3)_2$ . 2-Methylpyridine gives a mixture of green and deep blue solids with copper chloride; the blue substance,  $(2\text{-mepy})_2\text{CuCl}_2$ , was isolated by using acetone as solvent, and the green solid,  $(2\text{-mepy})\text{CuCl}_2$  (Cu content, 28.4%, Calc., 28.0%), was purified by recrystallisation of the mixed product from ethanol. Equimolar quantities of  $[(2\text{-ampy})_2(\text{OC}_2\text{H}_5)\text{Cu}(\text{NO}_3)]_2$  and 2,2'-bipyridyl reacted in 96% ethanol to give  $[(\text{bipy})(\text{OH})\text{Cu}(\text{NO}_3)]_2$ .

The use of copper(II) perchlorate gave rather different complexes with both ligands. No pure compound was isolated when water or aqueous ethanol was used as solvent for reactions involving 2-methylpyridine; however,  $[(2\text{-mepy})_2(\text{OH})\text{CuClO}_4]_2$  crystallised on dilution with benzene of an ethanolic solution of the reactants. Addition of an aqueous solution of 2-aminopyridine to an aqueous solution of copper(II) perchlorate (molar ratio 10 : 1) produced the bright green compound (I); reversal of the order of mixing produced the blue-grey compound (II).



Compound (I) was obtained, with benzene of solvation, from ethanolic benzene, and pure (II) was prepared by using aqueous ethanol. It was possible to convert (I) quantitatively into (II) by treatment with diethyl ether at room temperature for 36 hours; the calculated quantity of 2-aminopyridine was isolated from the ethereal solution (m. p. 57—58°, lit., 58°). Compound (II) was identified by means of analysis and infrared and reflectance spectroscopy. Use of benzene or light petroleum failed to bring about the conversion. Compound (II) could be obtained from acetone, with acetone of solvation (1—2 mol.); this was not removed by drying in a high vacuum, but treatment with ether eliminated the intense infrared band at 1704  $\text{cm}^{-1}$ . Reaction of equimolar quantities of (II) and 2,2'-bipyridyl gave  $[(\text{bipy})(\text{OH})\text{CuClO}_4]_2$ , which was also prepared by the reaction of copper(II) perchlorate and 2,2'-bipyridyl (equimolar amounts) in water buffered at pH 9.27.

An attempt to prepare a mixed acetato-2-amino-pyridine complex, using acetic anhydride as solvent, led to the isolation of (III). Acetylation of the ligand had apparently occurred rapidly, and without the need for application of external heat; because the reactivity of the amino-group in 2-aminopyridine might have been thought to be of the same order as that in *o*-nitroaniline, the ease of acetylation was considered surprising. It is believed that perchloric acid, formed when hydrated copper(II) perchlorate dissolves in acetic anhydride, acts as a catalyst (by producing acylium cations). In support of this, the addition of a few drops of 60% perchloric acid to a solution of 2-aminopyridine in acetic anhydride caused the temperature to rise to 60°; on cooling some 2-acetamidopyridinium perchlorate was isolated. Reaction of this with copper(II) perchlorate gave a pale blue complex, identical with (III).

*Infrared Spectra.*—Details are presented in Table 1, which includes  $(2\text{-ampy})_2\text{AgClO}_4$  and  $2\text{-ampy.HClO}_4$  for comparison. Small but definite shifts of most bands of 2-aminopyridine occur on co-ordination; similar effects have been observed for 2,2'-bipyridyl.<sup>14</sup> Perhaps the most notable change in the case of 2-aminopyridine is the appearance of a single band between 1330 and 1410  $\text{cm}^{-1}$  in place of a split band (1339, 1326  $\text{cm}^{-1}$ ) in the free base. The general features of the spectra of the complexed and the free base are so similar that it seems clear that the ligand co-ordinates in the amino-form.

<sup>14</sup> Schilt and Taylor, *J. Inorg. Nuclear Chem.*, 1959, **9**, 211.

TABLE I.

Infrared spectra (cm.<sup>-1</sup>) for copper(II) complexes.

Complex	OH	NH <sub>2</sub> (stretch)	NH <sub>2</sub> (deform.)	700—800 cm. <sup>-1</sup> region
2-Aminopyridine .....	—	3497, 3322	1637	775, 741
2-Methylpyridine .....	—	—	—	758, 732
[(2-Ampy) <sub>3</sub> (OH)CuClO <sub>4</sub> ] <sub>2</sub> .....	3661	3523, 3324	1642	775, 743
[(2-Ampy) <sub>2</sub> (OH)CuClO <sub>4</sub> ] <sub>2</sub> .....	3656	3488, 3378	1642	772, 743
[(Bipy)(OH)CuClO <sub>4</sub> ] <sub>2</sub> .....	3690	—	—	775, 733
[(2-Ampy) <sub>2</sub> (OC <sub>2</sub> H <sub>5</sub> )CuNO <sub>3</sub> ] <sub>2</sub> .....	—	3430, 3350	1632	780sh, 772, 741
[(2-Ampy) <sub>2</sub> (OCH <sub>3</sub> )CuNO <sub>3</sub> ] <sub>2</sub> .....	—	3400, 3350	1648—1630	776, 772, 742
[(Bipy)Cu(OH)(NO <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> .....	3500	—	—	778, 735
[(2-Ampy) <sub>4</sub> CuCl <sub>2</sub> ] <sub>2</sub> .....	—	3413, 3322	1637	771, 749
[(2-Mepy) <sub>2</sub> (OH)CuClO <sub>4</sub> ] <sub>2</sub> .....	3636	—	—	778, 775, 727
(2-Mepy) <sub>2</sub> Cu(NO <sub>3</sub> ) <sub>2</sub> .....	—	—	—	780, 774, 728, 709
(2-Mepy) <sub>2</sub> CuCl <sub>2</sub> .....	—	—	—	786, 772, 728
(2-Ampy) <sub>2</sub> AgClO <sub>4</sub> .....	—	3484, 3390	1637	769, 738
2-Ampy.HClO <sub>4</sub> .....	—	3497, 3401	1667	770, 722

OH region. The sharp band observed between 3690 and 3500 cm.<sup>-1</sup> (see Table I and Fig. 1) is assigned to the hydroxo-group. Bands due to -OH have been observed between 3700<sup>15</sup> and 3300 cm.<sup>-1</sup><sup>16</sup> for various metal hydroxides. Potassium di-μ-hydroxo-bis[dioxalatocobaltate(III)] trihydrate was prepared,<sup>17</sup> and showed bands at 3676

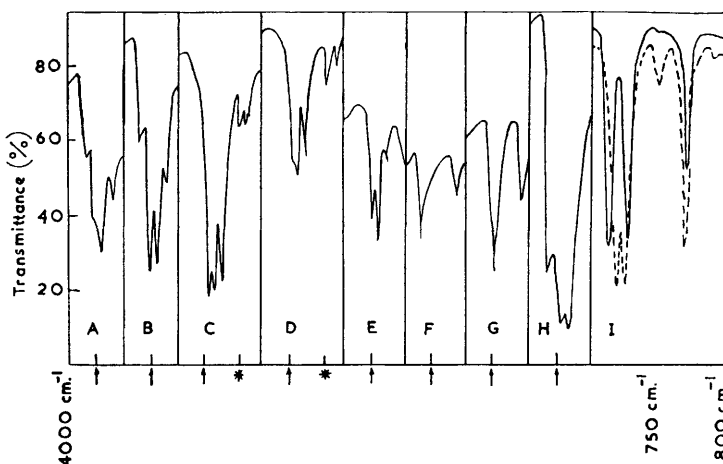


FIG. 1. Infrared spectra for various complexes.

A, [(2-ampy)<sub>3</sub>(OH)CuClO<sub>4</sub>]<sub>2</sub>. B, [(2-ampy)<sub>2</sub>(OH)CuClO<sub>4</sub>]<sub>2</sub>. C, [(2-ampy)<sub>2</sub>(OEt)CuNO<sub>3</sub>]<sub>2</sub>. D, [(2-ampy)<sub>2</sub>(OMe)CuNO<sub>3</sub>]<sub>2</sub>. E, (2-ampy)<sub>2</sub>AgClO<sub>4</sub>. F, [(bipy)(OH)CuClO<sub>4</sub>]<sub>2</sub>. G, [(bipy)(OH)CuNO<sub>3</sub>]<sub>2</sub>. H, [(Oxalate)<sub>2</sub>(OH)CoK<sub>2</sub>]<sub>2</sub>. 3H<sub>2</sub>O. I, (2-mepy)<sub>2</sub>CuCl<sub>2</sub>; . . . ., (2-mepy)<sub>2</sub>Cu(NO<sub>3</sub>)<sub>2</sub>. The arrow denotes 3500 cm.<sup>-1</sup>, and the asterisk 3000 cm.<sup>-1</sup>.

(sharp), 3436s, and 3300s cm.<sup>-1</sup> (Fig. 1); the last two bands are assigned to the water, and the first to the bridging hydroxo-groups. The bands between 3636 and 3690 cm.<sup>-1</sup> observed in the present work would not be inconsistent with a bridging group.

NH<sub>2</sub> region. The absence of large, systematic shifts of the -NH<sub>2</sub> stretching frequencies on co-ordination implies that the interaction of the amino-group with copper(II) may be slight, although the intensities are greatly increased, relative to other bands, in the case of

<sup>15</sup> Cabannes Ort, *Compt. rend.*, 1956, **242**, 355.

<sup>16</sup> Glemser, *Nature*, 1959, **183**, 1476.

<sup>17</sup> Palmer, "Experimental Inorganic Chemistry," Cambridge University Press, 1959, p. 551.

$[(2\text{-ampy})_3(\text{OH})\text{CuClO}_4]_2$  and  $[(2\text{-ampy})_2(\text{OH})\text{CuClO}_4]_2$  (Fig. 1). It is known that co-ordination of an amino-group is often accompanied by an increase in intensity of the stretching frequencies, owing to the greater dipole moment of the N-H bond;<sup>18</sup> the phenomenon could, in this case, be explained either in terms of a co-ordinated amino-group or of the increased electron-withdrawing power of the hetero-atom due to co-ordination to copper.

**700—800  $\text{cm}^{-1}$  region.** The intense out-of-plane CH deformation mode of 2-substituted pyridines occurs in this region.<sup>19</sup> Absorptions in this region have also been found to be sensitive to the stereochemistry of some bisbipyridyl<sup>20</sup> and some bispyridine complexes;<sup>11,21</sup> the spectra of  $(2\text{-mepy})_2\text{CuCl}_2$  and  $(2\text{-mepy})_2\text{Cu}(\text{NO}_3)_2$ , in particular, are rich in structure (Fig. 1), and comparison with the observations of Quagliano and his co-workers<sup>11</sup> for bispyridinedi-iodonickel(II) suggests the possibility of a monomeric structure distorted towards a tetrahedral arrangement, cf.  $\text{CuCl}_4^{2-}$ .<sup>22</sup> (Another possible mechanism which could lead to relief of the steric strain in a square-planar arrangement is the rotation of the aromatic ligands about the Cu-N bond out of the molecular plane).

**Anion Bands.**—These are included in Table 2. The perchlorate is clearly ionic in all cases considered.<sup>23</sup> Comparison of nitrate frequencies with the results of Gatehouse, Livingstone, and Nyholm<sup>24</sup> indicates that the group is co-ordinated to copper only in the case of  $(2\text{-mepy})_2\text{Cu}(\text{NO}_3)_2$  (thus supporting this compound's formulation as a monomer).

TABLE 2.

Infrared (anion bands) and diffuse-reflectance spectra for copper(II) complexes.

Complex	Colour	Diffuse-reflectance spectra ( $m\mu$ )	Infrared spectra; anion bands ( $\text{cm}^{-1}$ )
$(2\text{-Ampy})_3\text{Cu}(\text{OH})_2\text{Cu}(2\text{-ampy})_3(\text{ClO}_4)_2$ *	Green	625, 350 (infl.)	1098s, b, 933w
$(2\text{-Ampy})_2\text{Cu}(\text{OH})_2\text{Cu}(2\text{-ampy})_2(\text{ClO}_4)_2$ †	Grey-blue	565, 365 (infl.)	1096s, b, 933w
$(\text{Bipy})\text{Cu}(\text{OH})_2\text{Cu}(\text{bipy})(\text{ClO}_4)_2$	Saxe-blue	565, 360 (infl.)	1087s, b, 933w
$(2\text{-Ampy})_2\text{Cu}(\text{OC}_2\text{H}_5)_2\text{Cu}(2\text{-ampy})_2(\text{NO}_3)_2$	Olive-green	580, 385	1380s, 1322s, 1055m, 832m
$(2\text{-Ampy})_2\text{Cu}(\text{OCH}_3)_2\text{Cu}(2\text{-ampy})_2(\text{NO}_3)_2$	Deep green	595, 415	1380s, 1320s, 1050m, 828m
$(\text{Bipy})\text{Cu}(\text{OH})_2\text{Cu}(\text{bipy})(\text{NO}_3)_2$	Deep blue	595, 380	1400s, 1330s, 945s, 828m
$(2\text{-Ampy})_4\text{CuCl}_2$	Blue black	—	—
$(2\text{-Mepy})_2\text{Cu}(\text{OH})_2\text{Cu}(2\text{-mepy})_2(\text{ClO}_4)_2$	Olive-green	605, 360	1087s, b, 933w
$(2\text{-Mepy})_2\text{Cu}(\text{NO}_3)_2$	Deep blue	595	1490s, 1390s, sh, 1015s, 809m
$(2\text{-Mepy})_2\text{CuCl}_2$	Deep blue	595, 360	—
$(2\text{-Acetamidopyridine})_2\text{Cu}(\text{ClO}_4)_2$	Pale blue	605, 390 (infl.)	1090s, b, 933w

\* Also isolated with benzene of crystallisation,  $\lambda_{\text{max.}} = 625 m\mu$ . † Also isolated with acetone of crystallisation,  $\lambda_{\text{max.}} = 565 m\mu$ .

**Ultraviolet and Visible Spectra.**—These are summarised in Tables 3 and 4; diffuse-reflectance spectra are included in Table 2 and are shown in Fig. 2 [(a) and (b)]. The ultraviolet spectrum is comparatively insensitive to complex-formation and protonation. Complex-formation has been shown to cause a bathochromic shift of the 280  $m\mu$  maximum of bipyridyl,<sup>25</sup> the magnitude of which can be correlated with the formal positive charge on the cation. Albert<sup>26</sup> has observed a bathochromic shift of the 290  $m\mu$  maximum on formation of the 3-aminopyridinium cation, followed by a hypsochromic shift on the addition of a second proton; 2-aminopyridine does not parallel this behaviour. The

<sup>18</sup> Svatos, Curran, and Quagliano, *J. Amer. Chem. Soc.*, 1955, **77**, 6159.

<sup>19</sup> Katritzky, *Quart. Rev.*, 1959, **13**, 353.

<sup>20</sup> McWhinnie, *J. Inorg. Nuclear Chem.*, 1964, **26**, 15.

<sup>21</sup> Rao, *Z. anorg. Chem.*, 1960, **304**, 77.

<sup>22</sup> Morosin and Lingafelter, *J. Phys. Chem.*, 1961, **65**, 50.

<sup>23</sup> Hathaway and Underhill, *J.*, 1961, 3091.

<sup>24</sup> Gatehouse, Livingstone, and Nyholm, *J.*, 1957, 4222.

<sup>25</sup> Martin, McWhinnie, and Waing, *J. Inorg. Nuclear Chem.*, 1961, **23**, 207.

<sup>26</sup> Albert, *J.*, 1960, 1020.

TABLE 3.

Ultraviolet spectra for copper(II) complexes in solution.

	[Cu <sup>II</sup> ] or [2-ampy] (10 <sup>5</sup> moles l. <sup>-1</sup> )	[Cu <sup>II</sup> ] : [2-ampy]	$\lambda_1$		$\lambda_2$		$\lambda_3$		Solvent
			(in m $\mu$ )	(10 <sup>3</sup> $\epsilon$ )	(in m $\mu$ )	(10 <sup>3</sup> $\epsilon$ )	(in m $\mu$ )	(10 <sup>3</sup> $\epsilon$ )	
2-Aminopyridine	5	—	201	(2.5)	234	(11.8)	294	(4.2)	Ethanol
"	5	—	—	—	228	(9.1)	295	(5.4)	Water
"	5	—	—	—	229	(8.9)	298	(6.0)	HCl (pH 6-16)
"	5	—	—	—	229	(8.9)	298	(6.3)	HCl (pH 2-35)
"	5	—	—	—	226	(12.8)	296	(9.6)	60% HClO <sub>4</sub>
Cu(ClO <sub>4</sub> ) <sub>2</sub>	1	1 : 3	201	(9.9)	233	(34.0)	296	(15.5)	Ethanol
"	1	1 : 2	201	(11.6)	232	(23.2)	297	(11.3)	"
"	1	1 : 1	202	(5.5)	232	(13.3)	298	(6.1)	"
Cu(NO <sub>3</sub> ) <sub>2</sub>	1	1 : 3	204	(28.7)	232	(36.7)	298	(15.5)	"
"	1	1 : 2	203	(26.0)	232	(26.6)	277	(22.2)	"
"	1	1 : 1	203	(25.0)	232	(15.5)	277	(21.0)	"

TABLE 4.

Visible spectra for copper(II) complexes in ethanol solution.

	[Cu <sup>II</sup> ] : [ligand]			Stoichiometry of complex in solution
	1 : 10 $\lambda_{\max}$ . (in m $\mu$ ) ( $\epsilon$ )	1 : 4 $\lambda_{\max}$ . (in m $\mu$ ) ( $\epsilon$ )	1 : 2 $\lambda_{\max}$ . (in m $\mu$ ) ( $\epsilon$ )	
Cu(ClO <sub>4</sub> ) <sub>2</sub> -2-ampy	571 (88.4)	575 (80.6)	587 (62.6)	
Cu(ClO <sub>4</sub> ) <sub>2</sub> -2-mepy	627 (62.5)		669 (50.6)	
Cu(NO <sub>3</sub> ) <sub>2</sub> -2-ampy	601 (85.5)	615 (57.6)	676 (45.1)	1 : 2
Cu(NO <sub>3</sub> ) <sub>2</sub> -2-mepy	685 (45.5)	690 (41.4)		
CuCl <sub>2</sub> -2-ampy	704 (85.1)	714 (118)	781 (180)	1 : 1
CuCl <sub>2</sub> -2-mepy *	746 (116)	807 (124)		

\* CuCl<sub>2</sub> : 2-mepy ratio of 1 : 90 gives  $\lambda_{\max}$ . = 694 m $\mu$ .

major change occurring in the presence of copper(II) cations is the great increase in intensity of the 201 m $\mu$  band relative to the 234 m $\mu$  peak in the case of copper nitrate; the great similarity of the overall features of the spectra, both in the presence and absence of copper(II) ions, confirms that the ligand co-ordinates in the amino-form. The initial hypsochromic shift of the 294 m $\mu$  maximum in the presence of copper nitrate finds no ready explanation in terms of the data available for the spectrum in acid solution and in the presence of copper(II) perchlorate.

*Solution spectra in the "visible" region.* There was no obvious correlation between the spectra of ethanolic solutions of copper salts containing 2-amino- or 2-methyl-pyridine and the solid-state spectra listed in Table 2; however, it does not follow that the environment of the copper(II) cation would be identical in the solid complex and in dilute ethanolic solution. It was noted that the intense green ethanolic solution used for the preparation of [(2-ampy)<sub>3</sub>(OH)CuClO<sub>4</sub>]<sub>2</sub>C<sub>6</sub>H<sub>6</sub> (*i.e.*, prior to dilution with benzene—see Experimental section), in which the copper concentration was *ca.*  $2 \times 10^{-1}$ M, had a maximum at 625 m $\mu$ ; this is identical with the reflectance minimum of the solid isolated.

Job's method of continuous variation was applied to the three 2-aminopyridine systems in ethanol (Fig. 3); the total concentration of metal and ligand employed, *i.e.*, [Cu<sup>II</sup>] + [2-ampy], was  $2 \times 10^{-2}$ M. The results confirmed the stoichiometry of the copper(II) nitrate system, but were inconclusive for the copper(II) perchlorate system. This was not surprising in view of the isolation of two complexes during the preparative work. A 1 : 1 complex was formed between copper(II) chloride and 2-aminopyridine in ethanolic solution; however, when the reaction was carried out on a preparative scale, green solids of indeterminate composition were precipitated.

Royer<sup>10</sup> has reported the spectra of copper(II) nitrate and perchlorate in anhydrous

2-methylpyridine; the nature of the species in solution was not established but was assumed to be  $(2\text{-mepy})_4\text{Cu}^{2+}$ , and changes of  $\lambda_{\text{max}}$  with concentration of copper were interpreted in terms of the association of the tetra-amine species with solvent molecules

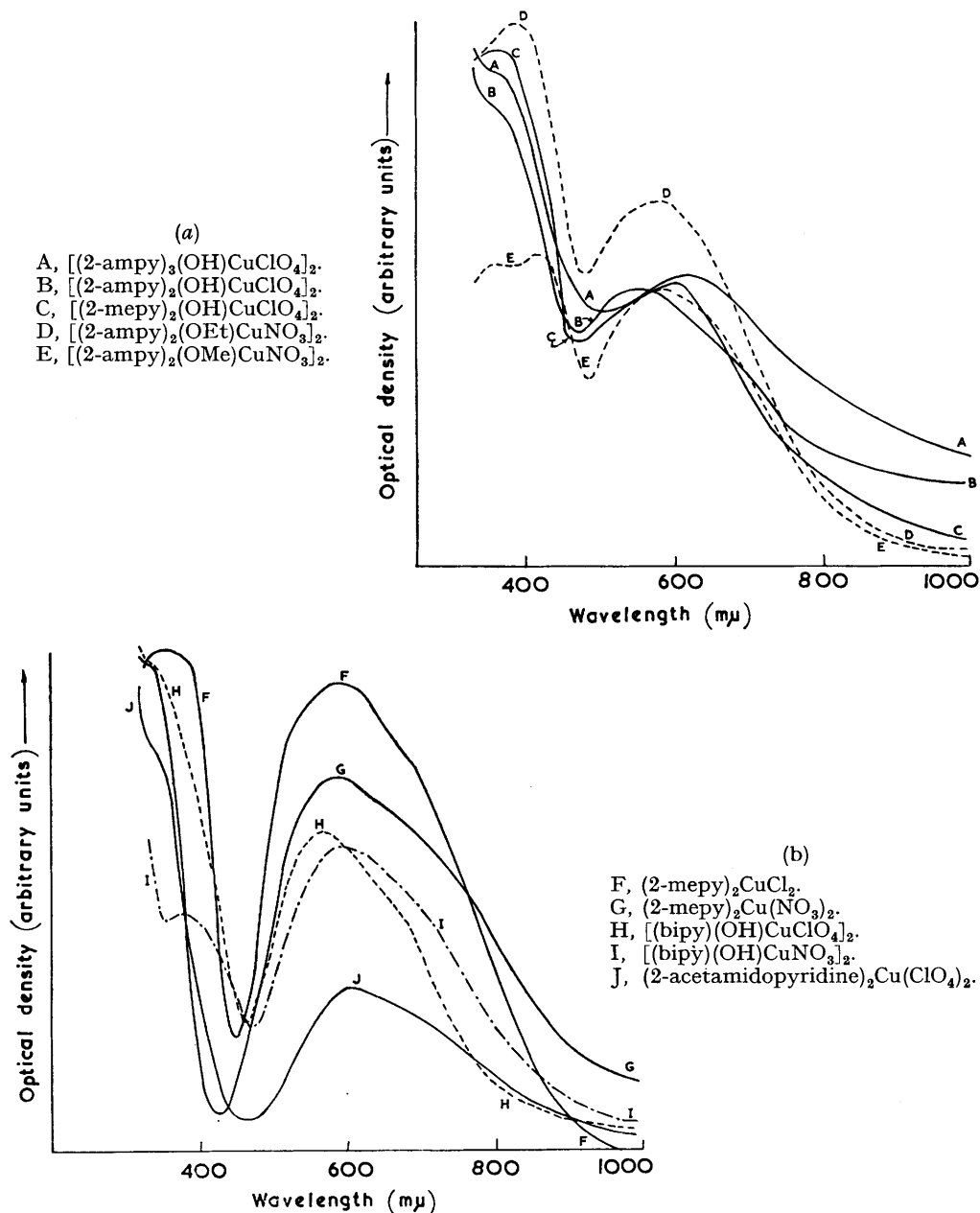


FIG. 2. Diffuse-reflectance spectra for some copper(II) complexes.

(dilute solution) and with anions (concentrated solution). Owing to our failure in the present work to prepare a tetrakis-2-methylpyridine derivative of copper(II) nitrate, the spectrum of  $(2\text{-mepy})_2\text{Cu}(\text{NO}_3)_2$ , prepared in ethanol (or methanol), was measured in

2-methylpyridine. The results appear to be in agreement with Royer's observations<sup>10</sup> on solutions prepared in a different manner, *e.g.*, the maximum is sensitive to concentration—for  $[(2\text{-mepy})_2\text{Cu}(\text{NO}_3)_2] = 1.01 \times 10^{-2}\text{M}$ ,  $\lambda_{\text{max.}} = 621 \text{ m}\mu$  ( $\epsilon$  72); for  $[(2\text{-mepy})_2\text{Cu}(\text{NO}_3)_2] = 7.31 \times 10^{-3}\text{M}$ ,  $\lambda_{\text{max.}} = 615 \text{ m}\mu$  ( $\epsilon$  69). Addition of sodium nitrate shifted the maximum to longer wavelength. Analyses and infrared spectra confirmed that bis-(2-methylpyridine)dinitratocopper(II) was recovered from the solutions, both by precipitation with light petroleum and by removal of solvent under reduced

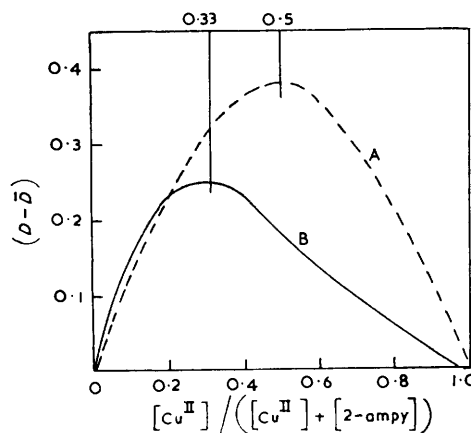


FIG. 3. Application of Job's method of continuous variation to the systems: A, 2-ampy-CuCl<sub>2</sub>; and B, 2-ampy-Cu(NO<sub>3</sub>)<sub>2</sub>, in ethanol.  $[\text{Cu}^{\text{II}}] + [2\text{-ampy}] = 2 \times 10^{-2}\text{M}$ .

pressure. It would therefore appear that the blue solid isolated by Royer<sup>10</sup> from 2-methylpyridine solution after dissolving copper(II) nitrate trihydrate, followed by removal of water by azeotropic distillation with benzene, is identical with that considered here (no analytical data were given<sup>10</sup>) rather than with the supposed tetra-amine; the species in solution are also, in the case of copper(II) nitrate, probably other than those suggested by Royer.

**Diffuse-reflectance spectra.** The spectra of  $[(2\text{-ampy})_3(\text{OH})\text{CuClO}_4]_2$ ,  $[(2\text{-ampy})_2(\text{OH})\text{CuClO}_4]_2$ , and  $[(2\text{-ampy})_2(\text{OR})\text{CuNO}_3]_2$  all show a broad band between 625 and 580  $\text{m}\mu$  which is certainly composite and suggests a rather asymmetric planar or tetragonal arrangement of ligands, *cf.* the results of James, Parris, and Williams<sup>27</sup> for bispyridinebisalicylaldehydecopper(II). The bipyridyl and 2-acetamidopyridine complexes, together with  $[(2\text{-mepy})_2(\text{OH})\text{CuClO}_4]_2$ , give curves typical of a tetragonal or planar copper(II) complex.<sup>27</sup> Most of the compounds show either a maximum or an inflexion between 350 and 415  $\text{m}\mu$ . If the broad band at longer wavelength encloses the envelopes of the  $d_{x^2-y^2} \rightarrow d_{xy}$  and  $d_{x^2-y^2} \rightarrow d_{z^2}$  transitions of the positron, then possibly the above band could be assigned to  $d_{x^2-y^2} \rightarrow (d_{xz}, d_{yz})$ ;<sup>28</sup> however, Williams and his co-workers have pointed out<sup>27</sup> that it would be difficult to distinguish between a genuine  $d-d$  transition and a charge-transfer transition in that region when the intensity is considerable. In this case, no quantitative intensity data are available and any assignment must be highly tentative. The compounds prepared in the present work have been formulated as shown in Table 2; in all but two cases the copper is thought to be in an essentially square-planar environment, and the reflectance spectra do not conflict with this view. The recent work of Hatfield, Piper, and Klabunde,<sup>29</sup> on some di- $\mu$ -hydroxocopper(II) complexes of *N*-substituted ethylenediamines, indicates that the general features of the reflectance spectra of these compounds are similar to those observed here. The spectra of  $(2\text{-mepy})_2\text{CuCl}_2$  and  $(2\text{-mepy})_2\text{Cu}(\text{NO}_3)_2$  resemble more closely those expected

<sup>27</sup> James, Parris, and Williams, *J.*, 1961, 4630.

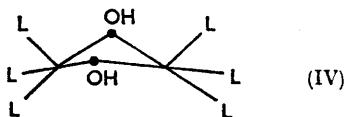
<sup>28</sup> Cotton and Wilkinson, "Advanced Inorganic Chemistry," Interscience, 1962, p. 753.

<sup>29</sup> Hatfield, Piper, and Klabunde, *Inorg. Chem.*, 1963, 2, 629.

for square-planar complexes than for tetrahedral ones. However, Bannister and Cotton<sup>30</sup> have pointed out, in connection with their work on bis(triphenylphosphine oxide)dinitrato-complexes of Co(II), Ni(II), Cu(II), and Zn(II), that no great spectral change would be expected if the structure were a flattened tetrahedron rather than square-planar; the intense colour of these diamine complexes would also be consistent with a non-planar structure.

*General Discussion.*—The compound  $[(2\text{-ampy})_2(\text{OH})\text{CuClO}_4]_n$  could be formulated as a monomer ( $n = 1$ ) with the 2-aminopyridine ligands bidentate and coplanar with copper, and the hydroxo-group bound along the polar axis, to give 5-co-ordinate copper; as a polymer with the above units linked through hydroxo-bridges; or as a dimer. There are two possible types of dimer: a "copper acetate" structure with the hydroxo-groups occupying similar positions to the water molecules in copper acetate monohydrate, or a structure involving two bridging hydroxo-groups; involvement of the amino-groups could, in the latter case, increase the co-ordination number of copper to six. Reaction with bipyridyl gives  $[(\text{bipy})(\text{OH})\text{CuClO}_4]_2$ , which can only be considered as a dihydroxo-bridged dimer in view of the ionic perchlorate; the existence of this species in solution has been established by Gustafson and Martell.<sup>31</sup> This is also the only structure that is satisfactory for  $[(2\text{-mepy})_2(\text{OH})\text{CuClO}_4]$ ; the author favours this structure for  $[(2\text{-ampy})_2\text{Cu}(\text{OH})\text{ClO}_4]_n$ , but, as interpretation of the infrared spectrum in the  $-\text{NH}_2$  region is not unambiguous, a structure of greater molecular complexity for the latter compound is not entirely precluded by the available data. [No suitable solvent was found for molecular-weight or conductance measurements (see Experimental section).] Spectroscopic data do not conflict with these structures; in fact, complexity in the  $700\text{--}800\text{ cm}^{-1}$  region of the spectrum of  $[(2\text{-mepy})_2(\text{OH})\text{CuClO}_4]_2$  would support the *cis*-configuration for the two heterocyclic ligands. The magnetic moment of  $[(2\text{-ampy})_2(\text{OH})\text{CuClO}_4]_2$  is 1.51 B.M. at  $298^\circ\text{K}$ , which, in view of the work of Hatfield *et al.*<sup>29</sup> with  $[(\text{Et}_2\text{NCH}_2\cdot\text{CH}_2\cdot\text{NEt}_2)(\text{OH})\text{CuClO}_4]_2$  and  $[(\text{Et}_2\text{NCH}_2\cdot\text{CH}_2\cdot\text{NHMe})(\text{OH})\text{CuClO}_4]_2$ , for which moments of 1.38 B.M. ( $297^\circ\text{K}$ ) and 1.69 B.M. ( $298^\circ\text{K}$ ), respectively, were found, supports the dimeric structure. Antiferromagnetic behaviour was shown by the *NN'*-disubstituted ethylenediamine compounds.

In view of the apparent readiness with which some of the 2-aminopyridine complexes crystallise with solvent of crystallisation, the true nature of  $[(2\text{-ampy})_3(\text{OH})\text{CuClO}_4]_2$  must be considered. There is no evidence of unco-ordinated ligand from the infrared spectrum, and the reflectance spectrum is considerably different from that of  $[(2\text{-ampy})_2(\text{OH})\text{CuClO}_4]_2$  (whereas the acetone solvate mentioned previously has a reflectance spectrum identical with that of the parent compound). The green tris-2-aminopyridine complex is considered to be a true compound structurally related to the bis-complex (the magnetic moment is 1.49 B.M. at  $298^\circ\text{K}$ ); the extra molecule of 2-aminopyridine per copper atom is believed to be co-ordinated on the polar axis, assuming the diol structure for the bis-complex. There appears to be no reason to suppose that the two copper atoms are coplanar with the



L = 2-aminopyridine

bridging hydroxo-groups; if the structure were similar (IV) to that of  $\mu$ -dichlorobis(dicarbonylrhodium),<sup>1,32</sup> then the failure of more than one extra molecule of 2-aminopyridine to co-ordinate to the bis-complex would be due to steric factors.

<sup>30</sup> Bannister and Cotton, *J.*, 1960, 2276.

<sup>31</sup> Gustafson and Martell, *J. Amer. Chem. Soc.*, 1959, **81**, 525.

<sup>32</sup> Dahl, Martell, and Wampler, *J. Amer. Chem. Soc.*, 1961, **83**, 1762.



The compounds of copper(II) nitrate with 2-aminopyridine are considered to be dimeric with bridging alkoxo-groups; the infrared spectra give no evidence at all of co-ordinate amino-groups, and show the nitrate to be ionic.

The complex [(bipy)(OH)CuNO<sub>3</sub>]<sub>2</sub> is believed to be similar to the corresponding perchlorate. Reflectance spectra for the two compounds are similar, with two bands, but the relative intensities differ, this being responsible for the different colours of the solids. Unfavourable solubility properties precluded conductance measurements. The complex was also obtained by reaction of the perchlorate with sodium nitrate.

Graddon *et al.*<sup>12</sup> have discussed the monomeric nature of (2-mepy)<sub>2</sub>CuCl<sub>2</sub>, and their conclusions are supported by the present work; (2-mepy)<sub>2</sub>Cu(NO<sub>3</sub>)<sub>2</sub> is considered to be similar, and, from infrared data, both compounds are believed to be analogous to Quagliano's and (2-mepy)<sub>2</sub>NiCl<sub>2</sub>,<sup>11</sup> *i.e.*, to possess a distorted (flattened) tetrahedral structure.

Bis-(2-acetamidopyridine)copper(II) perchlorate shows two N-H stretching frequencies (3300, 3210 cm.<sup>-1</sup>); interaction of one -NH group per molecule with the copper atom of another molecule could result in a dimeric structure similar to that established for bis-dimethylglyoximecopper(II),<sup>33</sup> and could also give the observed double -NH band.

The nature of many of the compounds considered here is doubtless affected by steric factors, *i.e.*, by the difficulty of arranging four molecules such as 2-methyl- or 2-aminopyridine around copper(II). Previous examples of  $\mu$ -dihydroxo-compounds of copper(II) have been restricted to the complexes of bidentate tertiary amines;<sup>29,34</sup> the steric effects of the 2-methyl group in 2-methylpyridine have already been commented upon. However, the existence of (2-ampy)<sub>4</sub>CuCl<sub>2</sub> and [(bipy)(OH)CuClO<sub>4</sub>]<sub>2</sub> suggests that steric factors are not the only ones that should be considered. Jørgensen<sup>35</sup> has pointed out that the strong tendency of copper to form hydroxo-complexes often results in the precipitation of Cu(OH)<sub>2</sub> in the presence of amines; perhaps the hydroxo-complexes are then best considered to arise from partial hydrolysis of the copper(II) perchlorate. The failure of pyridine to give similar complexes under the same experimental conditions could be a reflection of its weaker basic strength and of the more favourable steric factors.

#### EXPERIMENTAL

Infrared spectra were recorded, with a Perkin-Elmer 137 spectrophotometer, as Nujol or hexachlorobutadiene mulls between rock-salt plates. Ultraviolet and visible spectra in solution were measured with a Unicam S.P. 700 recording spectrophotometer, in 1 cm. silica cells, and diffuse-reflectance spectra were obtained by using a Unicam S.P. 500 spectrophotometer with the S.P. 540 diffuse-reflectance attachment; absorbance measurements were made with the latter instrument. Magnetic measurements were by the Gouy method at room temperature.

Absolute ethanol was dried with magnesium and iodine. Copper(II) perchlorate was recrystallised and dried to a composition of Cu(ClO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O. 2-Aminopyridine (B.D.H.) was recrystallised from benzene-light petroleum, and had m. p. 56.5–58°. 2-Methylpyridine (B.D.H.) was redistilled twice before use (40°/5 mm.). All other materials were AnalaR grade. Copper was determined gravimetrically as Cu(py)<sub>2</sub>(SCN)<sub>2</sub> (py = pyridine) after removal of organic matter with concentrated sulphuric acid. The 2-amino- and 2-methyl-pyridine complexes were titrated with standard sodium thiosulphate after reaction with potassium iodide; in all cases the oxidation state of the copper was two.

*Di- $\mu$ -hydroxo-bis[tri-(2-aminopyridine)copper(II)] Diperchlorate*, (2-ampy)<sub>3</sub>Cu(OH)<sub>2</sub>Cu-(2-ampy)<sub>3</sub>(ClO<sub>4</sub>)<sub>2</sub>.—(i) 2-Aminopyridine (2.0 g.) in water (5 ml.) was added to copper(II) perchlorate (0.8 g.) in water (5 ml.) with vigorous stirring. The green precipitated *solid* was dried and washed with light petroleum, and had  $\mu_{\text{eff}}$  1.49 B.M. [Found: C, 39.1; H, 4.0; Cu, 13.5; N, 18.1. (C<sub>15</sub>H<sub>10</sub>ClCuN<sub>6</sub>O<sub>5</sub>)<sub>2</sub> requires C, 39.0; H, 4.1; Cu, 13.7; N, 18.2%].

(ii) As above, using 50% (v.v.) ethanolic benzene (10 ml.) as solvent. Green *crystals*

<sup>33</sup> Frasson, Bardi, and Bezzi, *Acta Cryst.*, 1960, **13**, 893.

<sup>34</sup> Mann and Watson, *J.*, 1958, 2772.

<sup>35</sup> Jørgensen, "Absorption Spectra and Bonding in Complexes," Pergamon, 1962, p. 273.

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appeared on standing; these were washed with benzene and dried [Found: C, 43.4; H, 4.75; Cl, 7.4; Cu, 12.1; N, 16.2.  $(C_{15}H_{19}ClCuN_6O_8)_2 \cdot C_6H_6$  requires C, 43.1; H, 4.2; Cl, 7.1; Cu, 12.7; N, 16.8%].

*Di- $\mu$ -hydroxo-bis[di-(2-aminopyridine)copper(II)] Diperchlorate*,  $(2\text{-Ampy})_2Cu(OH)_2Cu(2\text{-ampy})_2(ClO_4)_2$ .—(i) Copper perchlorate (0.8 g.) in water (5 ml.) was added to 2-aminopyridine (2.0 g.) in water (5 ml.) with stirring. The grey-blue *product* was dried and then washed with light petroleum, and had  $\mu_{\text{eff}}$  1.48 B.M. [Found: C, 32.5; H, 3.4; Cu, 17.3; N, 15.3.  $(C_{10}H_{13}ClCuN_4O_5)_2$  requires C, 32.6; H, 3.6; Cu, 17.3; N, 15.2%].

(ii) As above, using 50% (v/v.) aqueous ethanol (10 ml.) as solvent. The complex crystallised on standing for 30 min., and had  $\mu_{\text{eff}}$  1.53 B.M. [Found: C, 32.8; H, 3.45; Cl, 9.85; Cu, 17.2; N, 14.9.  $(C_{10}H_{13}ClCuN_4O_5)_2$  requires Cl, 9.6%].

(iii) Treatment of the tri-(2-aminopyridine) complex with diethyl ether for 24 hr. at room temperature gave the di-(2-aminopyridine) complex in amorphous form (Found: C, 33.2; H, 3.7; Cu, 17.25%).

(iv) Use of acetone (10 ml.) as solvent gave a *product* containing acetone of solvation [Found: C, 37.6; H, 4.9; Cu, 13.5; N, 12.4.  $(C_{10}H_{13}ClCuN_4O_5)_2 \cdot Me_2CO$  requires C, 37.4; H, 4.3; Cu, 13.7; N, 12.0%] ( $\nu_{C=O}$  1704  $cm^{-1}$ ). The reflectance spectra of the products from the above four methods were identical. It was found that a molar ratio of at least 1 : 6 for Cu : 2-ampy was necessary for the isolation of pure specimens.

*Di- $\mu$ -hydroxo-bis-[2,2'-bipyridylcopper(II)] Diperchlorate*,  $(bipy)Cu(OH)_2Cu(bipy)(ClO_4)_2$ .—2,2'-Bipyridyl (0.16 g.) and copper(II) perchlorate (0.34 g.) in water (10 ml.), buffered at pH 9.27, gave a mauve-grey *solid*, which was washed with water [Found: C, 36.1; H, 2.9; Cu, 18.7; N, 8.0.  $(C_{10}H_9ClCuN_2O_5)_2$  requires C, 35.7; H, 3.3; Cu, 18.9; N, 8.3%]. The same product was obtained from the reaction of 2,2'-bipyridyl (0.16 g.) with copper(II) perchlorate (0.4 g.) in the presence of 2-amino-pyridine (0.1 g.) in aqueous ethanol (10 ml., pH 9.4) (Found: C, 36.6; H, 2.9; N, 8.0%). The infrared and reflectance spectra of the two solids were identical. [At neutral pH, the reaction of copper(II) perchlorate with 2,2'-bipyridyl in 1 : 1 molar ratio, as above, yields bis-2,2'-bipyridylcopper(II) perchlorate.<sup>20</sup>]

*Di- $\mu$ -ethoxo-bis[di-(2-aminopyridine)copper(II)] Dinitrate and Di- $\mu$ -methoxo-bis[di-(2-aminopyridine)copper(II)] Dinitrate*,  $(2\text{-ampy})_2Cu(OR)_2Cu(2\text{-ampy})_2(NO_3)_2$  (R = Et or Me).—Copper(II) nitrate trihydrate (0.48 g.) and 2-aminopyridine (2.0 g.) were dissolved in ethanol (or methanol) (10 ml.). Olive-green *crystals* separated slowly from the ethanolic, and dark green *crystals* from the methanolic, solution. Both solids were washed with light petroleum [Found: C, 40.4; H, 4.8; Cu, 17.4; N, 19.35; OEt, 12.5.  $(C_{12}H_{17}CuN_5O_4)_2$  requires C, 40.15; H, 4.78; Cu, 17.7; N, 19.5; OEt, 12.6%. Found: C, 39.1; H, 4.5; Cu, 18.7; N, 21.4; OMe, 8.8.  $(C_{11}H_{15}CuN_5O_4)_2$  requires C, 38.3; H, 4.5; Cu, 18.4; N, 20.3; OMe, 9.0%].

*Di- $\mu$ -hydroxo-bis-[2,2'-bipyridylcopper(II)] Dinitrate*,  $[(bipy)(OH)Cu(NO_3)_2]_2$ .—2,2'-Bipyridyl (0.2 g.) in 96% ethanol (10 ml.) was added. Di- $\mu$ -hydroxo-bis[di-2-(aminopyridine)copper(II)] dinitrate (0.3 g.) and the mixture warmed. The green solid dissolved on boiling to give a deep blue solution; deep blue crystals deposited on cooling. The *solid* was recrystallised from ethanol containing a few drops of water [Found: C, 39.3; H, 3.0; Cu, 21.8; N, 14.1.  $(C_{10}H_9CuN_3O_4)_2$  requires C, 40.2; H, 3.0; Cu, 21.3; N, 14.1%].

*Tetrakis-(2-aminopyridine)copper(II) Dichloride*,  $(2\text{-ampy})_4CuCl_2$ .—Copper(II) chloride dihydrate (0.7 g.) and 2-aminopyridine (1.0 g.) were dissolved in ethanol (10 ml.). The solvent was evaporated under reduced pressure and the tar-like residue was left overnight; any *crystals* formed were washed many times with light petroleum (the tar did not always crystallise, but no better conditions were found) (Found: C, 47.2; H, 5.15; Cl, 13.7.  $C_{20}H_{24}Cl_2CuN_6$  requires C, 46.9; H, 4.7; Cl, 13.9%).

*Bis-(2-acetamidopyridine)copper(II) Diperchlorate*,  $(2\text{-CH}_3 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_5\text{H}_4\text{N})_2Cu(ClO_4)_2$ .—(i) Copper(II) perchlorate (0.37 g.) and 2-aminopyridine (1.0 g.) were dissolved in acetic anhydride (5 ml.). The deep green solution was diluted with benzene (10 ml.) and the pale blue solid which separated was washed with benzene.

(ii) Addition of a few drops of 60% perchloric acid to the reaction mixture after acetylation of 2-aminopyridine precipitated 2-acetamidopyridinium perchlorate, which was recrystallised from ethanol. 2-Acetamidopyridinium perchlorate (0.17 g.) and copper perchlorate (0.12 g.) were dissolved in boiling ethanol (10 ml.); pale blue *crystals* separated on cooling. The infrared and reflectance spectra of the products from (i) and (ii) were identical (Found: C, 32.2; H, 3.2; Cu, 11.2; N, 10.9.  $C_{14}H_8Cl_2CuN_4O_{10}$  requires C, 31.3; H, 3.0; Cu, 11.8; N, 10.4%).

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*Bis-(2-methylpyridine)dinitratocopper(II)*,  $(2\text{-mepy})_2(\text{NO}_3)_2\text{Cu}$ .—Copper(II) nitrate trihydrate (0.24 g.) and 2-methylpyridine (1.0 g.) were dissolved in methanol (10 ml.). Dilution with light petroleum (10 ml.) gave a deep blue *solid* (Found: C, 39.0; H, 4.1; Cu, 17.0; N, 14.5.  $\text{C}_{12}\text{H}_{14}\text{N}_4\text{O}_6\text{Cu}$  requires C, 38.6; H, 3.8; Cu, 17.0; N, 15.0%).

*Bis-(2-methylpyridine)dichlorocopper(II)*,  $(2\text{-mepy})_2\text{Cl}_2\text{Cu}$ .—Copper(II) chloride dihydrate (0.17 g.) and 2-methylpyridine (1.0 g.) were dissolved in acetone (10 ml.). Deep blue crystals of the *complex* separated on standing (Found: C, 44.9; H, 4.6; Cl, 22.3; Cu, 19.8.  $\text{C}_{12}\text{H}_{14}\text{Cl}_2\text{CuN}_2$  requires C, 44.9; H, 4.4; Cl, 22.1; Cu, 19.8%).

*Di-μ-hydroxo-bis[di-(2-methylpyridine)copper(II)] Diperchlorate*,  $(2\text{-mepy})_2\text{Cu}(\text{OH})_2\text{Cu}(2\text{-mepy})_2(\text{ClO}_4)_2$ .—Copper perchlorate (0.8 g.) and 2-methylpyridine (2.0 g.) were dissolved in 50% (v/v) ethanolic benzene. Olive-green *crystals* appeared on standing and were washed with benzene [Found: C, 40.7; H, 4.1; Cl, 9.7; Cu, 17.2; N, 7.0.  $(\text{C}_{12}\text{H}_{15}\text{ClCuN}_2\text{O}_5)_2$  requires C, 39.3; H, 4.1; Cl, 9.7; Cu, 17.35; N, 7.6%].

*Bis-(2-aminopyridine)silver(I) Perchlorate*,  $(2\text{-ampy})_2\text{AgClO}_4$ .—Silver perchlorate (0.23 g.) and 2-aminopyridine (1.0 g.) were dissolved in water (10 ml.). Pale yellow *crystals* separated on stirring (Found: C, 30.3; H, 3.4; N, 13.8.  $\text{C}_{10}\text{H}_{12}\text{AgClN}_4\text{O}_4$  requires C, 30.35; H, 3.0; N, 14.2%).

The solubility of the 2-amino- and 2-methyl-pyridine complexes in a range of solvents was investigated. Perchlorate and nitrate species were insufficiently soluble in nitrobenzene and nitromethane to allow conductance or molecular-weight determinations to be made. The solids were slowly decomposed by cold ethanol and water in which they were sparingly soluble; in the boiling solvents, the perchlorate species were decomposed to brown solids containing no organic matter, and the nitrate species gave green solids with considerably increased copper content.

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