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The Chemistry of the Isomeric Complexes Obtained from the Reaction of Copper(II) Perchlorate with Substituted Tri-(2-pyridyl)amines

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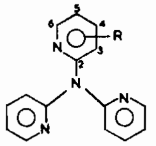
Isomeric complexes of copper(II) perchlorate with 4— and 6-methyl-2-pyridyldi-(2-pyridyl)amine (4- and 6-mpdpa), similar to those previously reported for tri-(2-pyridyl)amine (tripyam), are described viz. $[Cu(4\text{- or }6\text{-mpdpa})_2(ClO_4)_2]$ *(bidentate ligands) and* $[Cu(4\text{- or }6\text{-mpdpa})_2](ClO_4)_2$ *(terdentate ligands). The tetragonal distortion in* $[Cu(6mpdpa)_2](ClO_4)_2$ *is static but that in* $[Cu(tripyam)_2](ClO_4)_2$ *and in* $[Cu(4\text{-mpdpa})_2](ClO_4)_2$ *may be dynamic or static. The perchlorato-complexes are considered tetragonal with* trans-*acido groups. It is considered that the 4-methyl-2-pyridyl group is co-ordinated in* $[Cu(4mpdpa)(ClO_4)_2]$ *but that, for steric reasons, the 6-methyl-2-pyridyl group is free in* $[Cu(6mpdpa)_2(ClO_4)_2]$*. Four complexes of 5-nitro-2-pyridyldi-(2-pyridyl)amine (5npdpa) are reported viz.* $[Cu(5npdpa)_2(ClO_4)_2]$, $[Cu(5npdpa)_2(H_2O)_2](ClO_4)_2$*, and* $[Cu(5npdpa)_2(acetone)_2](ClO_4)_2$ *(two forms). In no case is the ligand terdentate. All four complexes are considered to be tetragonal with* trans *uni-dentate ligands but the nature of the difference between the two modifications of the diacetone complex remains obscure.*

Introduction

Tri—(2—pyridyl)amine is almost unique among vicinal terdentate ligands in that, when co-ordinated to an ion comparable in size to iron(II) ($^1A_{1g}$), it causes no spectroscopically observable distortion of the octahedral angles subtended by the metal.[1] Furthermore the base is often found to function as a bidentate ligand and several pairs of isomers of the type [M(terdentate base)$_2$]X$_2$ and [(bidentate base)$_2$-X$_2$] have been characterised, including the pair for which MX$_2$ is copper(II) perchlorate.[2] The terdentate isomer is now known to be tetragonal, possibly the result of the operation of the dynamic Jahn-Teller effect;[3] but the isotopic e.s.r. spectrum may be due to a random orientation of tetragonal axes of statically distorted ions within the crystal.[4] This paper describes some new compounds of copper(II) perchlorate with recently synthesised mono-substituted tri—(2—pyridyl)amines,[5] the work being undertaken to study further the nature of the above isomerism and of the distortion in the terdentate base complexes. The new ligands considered are shown in Figure 1 together with abrevibations used in this paper.



R=6-methyl—,	6 mpdpa
R=4-methyl—,	4 mpdpa
R=5-nitro—,	5 npdpa

Figure 1. Abbreviations for substituted tri-(2-pyridyl)amine.

Experimental Section

Diperchloratobis(6-methyl-2-pyridyldi(2-pyridyl)-aminecopper(II). Copper perchlorate hexahydrate (0.33 g) in ethanol (10 ml) was added to 6-methyl-2-pyridyldi-(2-pyridyl)amine[5] (0.5 g) in ethanol (10 ml). A dark green precipitate formed immediately, which spontaneously changed to a paler yellow green *complex*. On filtering, the precipitate was washed with ethanol and ether (yield 0.45 g).

Bis(6-methyl-2-pyridyldi-(2-pyridyl)amine)copper(II) perchlorate. The yellow green complex prepared above was dissolved in aqueous ethanol (50/50 v/v) and the solvent volume reduced by evaporation until a pale blue grey *precipitate* of diaquobis(6-methyl-2-pyridyldi-(2-pyridyl)amine)copper(II) perchlorate was formed. The grey complex was heated in a silicone oil bath forming a yellow green complex below 100 °C. On further heating between 120-180° a mauve blue *complex* was formed. It was noted that heating $[Cu(6mpdpa)_2(ClO_4)_2]$ directly did not cause isomerism to occur prior to evplosive decomposition at 260°.

Diperchloratobis(4-methyl-2-pyridyldi-2-pyridyl)-aminecopper(II). Ethanolic solutions of copper perchlorate hexahydrate (0.35 g) and 4-methyl-2-pyridyl-di-(2-pyridyl)amine[5] (0.54 g) were mixed and refluxed for a short time (15 min). On putting aside, a small

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[1] W.R. McWhinnie, R.C. Poller, and M. Thevarasa, *J. Chem. Soc.* (*A*), 1671 (1967).
[2] W.R. McWhinnie, G.C. Kulasingam, and J.C. Draper, *J. Chem. Soc.* (*A*), 1199 (1966).
[3] G.C. Kulasingam, J.C. Lancaster, W.R. McWhinnie, and J.B. Watts, *Spectrochimica Acta*, *26A*, 835 (1970).
[4] G.C. Kulasingam, Ph.D. Thesis, University of London, 1967.
[5] J.C. Lancaster and W.R. McWhinnie, *J. Chem. Soc.* (*C*), 2435 (1970).

quantity of yellow green *crystals* were formed. The filtered solid was washed with ether (yield 0.12 g).

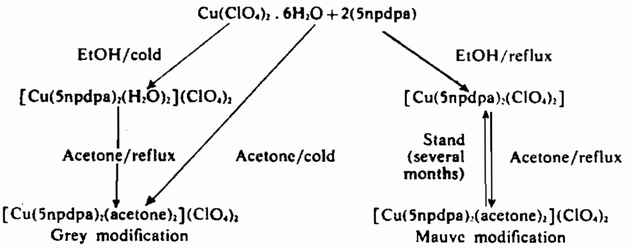
Bis(4-methyl-2-pyridyldi-(2-pyridyl)amine)copper(II) perchlorate. Copper perchlorate hexahydrate 0.4 g in acetone (10 ml) was added to 4-methyl-2-pyridyldi-(2-pyridyl)amine (0.6 g) in acetone (10 ml) and heated for a minute when a pale blue precipitate of a diaquo complex was formed. This was filtered and the remainder of the solution refluxed for several minutes followed by reduction of solvent volume. A green/blue *complex* was formed which on heating in an oven to 100°C for 30 mins formed a mauve blue complex. Yield (0.25 g).

Diaquo bis(5-nitro-2-pyridyldi-(2-pyridyl)amine copper(II) perchlorate. Copper perchlorate hexahydrate (0.82 g) in ethanol 10 ml was added to 5-nitro-2-pyridyldi-(2-pyridyl)amine[5] (1.2 g) in ethanol (10 ml) forming a pale blue green *complex.* The filtered solid immediately absorbed atmospheric moisture to afford dark green $Cu(5mpdpa)_2(H_2O)_2(ClO_4)_2$. Yield 1.03 g.

Diperchloratobis(5-nitro-2-pyridyldi-(2-pyridyl)amine copper(II). Ethanolic solutions (10 ml) of copper perchlorate hexahydrate (0.9 g) and 5 npdpa (1.3 g) were mixed and a pale blue precipitate formed. On refluxing the mixture for five minutes a blue grey precipitate was formed which, on filtering, was not hygroscopic. The solid was washed with ether. (Yield 1.6 g).

Diacetonebis(5-nitro-2-pyridyldi-(2-pyridyl)amine)-copper(II) perchlorate (Mauve modification). Hot ethanolic solutions (10 ml) of 5-nitro-2-pyridyldi-(2-pyridyl)amine (0.45 g) and copper perchlorate hexahydrate (0.31 g) were mixed forming a turquoise blue solution, which turned cloudy. A grey complex appeared which on treatment with acetone under reflux formed a blue solution. On cooling a mauve blue *complex* was obtained (0.2 g).

Diacetonebis(5-nitro-2-pyridyldi-(2-pyridyl)amine)-copper(II) perchlorate (grey modification). Acetone solutions (10 ml) of 5-nitro-2-pyridyldi-(2-pyridyl)amine (0.5 g) and of copper(II) perchlorate hexahydrate (0.32 g) were mixed to afford a dark grey *precipitate* (0.41 g). Alternatively, the same *complex* was prepared by heating diaquobis (5-nitro-2-pyridyldi-(2-pyridyl)-amine copper(II) perchlorate in refluxing acetone for 15 min. The relationship between the various complexes of 5 npdpa is shown in the scheme.



Scheme. The relationship between the complexes of copper(II) perchlorate and 5-nitro-2-pyridyldi-(2-pyridyl)amine.

Diperchloratobis(tri-(2-pyridyl)amine)copper(II) and bis(tri-(2-pyridyl)amine)copper(II) perchlorate were prepared by the method of reference 2. All analytical data are presented in Table I.

Physical Measurements. I.r. spectra were recorded for nujol or fluorochemical mulls using Perkin Elmer 457 and 237 instruments. Electron spin resonance spectra were obtained for microcrystalline samples at room and liquid nitrogen temperatures with a Hilger-Watts microspin spectrometer. g-Factors were determined relative to DPPH using Fremy's salt as calibrant. Some indication of the accuracy of the quoted g factors is obtained from our determination of values from the broad line spectrum of microcrystalline $CuSO_4 . 5H_2O$ viz. $g_1 = 2.08$ (lit. 2.083) and $g_2 = 2.27$ (lit. 2.267). A typical spectrum is illustrated in the Figure 2.

Electronic spectra were recorded with a Unicam SP700 instrument incorporating the SP735 diffuse reflectance attachment. It was noted that spectra of compounds which were previously hand plotted with a SP500 instrument[2] were much better resolved, in particular the earlier instrument tended to «flatten» the spectrum to low wave number. We have been alarmed to discover the extent to which information derivable from the spectrum is a function of the spectrophotometer. Fortunately the conclusions of reference 2 are in no way affected by this finding since no atempt was made at detailed discussion of the spectra.

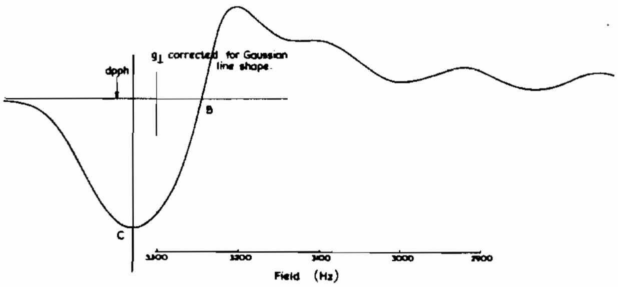


Figure 2. e.s.r. spectrum of microcrystalline $[Cu(6mpdpa)_2ClO_4]_2$.

Results and Discussion

Infra-red Spectra. Clear splittings of the major perchlorate vibration ν_3, (F_2 in T_d) in the case of complexes 1,3 and 6 (Table II) suggests semi-co-ordinated perchlorato-groups[6] to be present in these compounds. The fact that ν_1 (forbidden in T_d symmetry) close to 930 cm^{-1} is of no more than weak to medium intensity confirms the weak nature of the copper(II)-perchlorate interaction. The infra-red data do not indicate the presence of both co-ordinated and ionic perchlorate groups in 1,3 and 6.

Compounds 1 and 3 also exist in mauve isomeric forms (2 and 4 respectively) in which the perchlorate groups are ionic, thus both 4- and 6-methyl-2-pyridyldi-(2-pyridyl)amine follow the parent ligand tri-(2-pyridyl)amine[2] in forming yellow-green and mauve iso-

(6) D.S. Brown, J.D. Lee, B.G.A. Melson, B.J. Hathaway, I.M. Procter and A.A.G. Tomlinson, *Chem. Comun.*, 369 (1967).

Table I. Analytical data for new complexes.

No.	Complex	Found C	Found H	Found N	Calculated C	Calculated H	Calculated N
1	$[Cu(6mpdpa)_2(ClO_4)_2]$	48.8	3.6	14.1	48.8	3.6	14.2
2	$[Cu(6mpdpa)_2](ClO_4)_2$	48.9	3.6	14.2	48.8	3.6	14.2
3	$[Cu(4mpdpa)_2(ClO_4)_2]$	48.8	4.0	13.9	48.8	3.6	14.2
4	$[Cu(4mpdpa)_2](ClO_4)_2$	48.0	3.5	14.3	48.8	3.6	14.2
5	$[Cu(6mpdpa)_2(H_2O)_2](ClO_4)_2$	46.2	4.1	13.4	46.6	3.9	13.6
6	$[Cu(5npdpa)_2(ClO_4)_2]$	42.3	2.6	16.4	42.4	2.6	16.5
7	$[Cu(5npdpa)_2(acetone)_2](ClO_4)_2$ [a]	44.8	3.3	14.5	44.8	3.5	14.5
8	$[Cu(5npdpa)_2(acetone)_2](ClO_4)_2$ [b]	44.7	3.5	14.8	44.8	3.5	14.5
9	$[Cu(5npdpa)_2(H_2O)_2](ClO_4)_2$	41.1	3.0	15.6	40.7	2.9	16.0

[a] mauve modification; [b] grey modification

Table II.

No.	Colour	$\nu_3(ClO_4^-)cm^{-1}$	$\nu_1(ClO_4^-)cm^{-1}$	$g_\perp$ [a]	$g_\parallel$	g_{av} [b]	Electronic spectrum (kK) [c]
1	Yellow-green	1108s,1066s	932m	2.03(0)	2.21 [d]		18.95, 15.8 sh*
2	Mauve to blue	1075s				2.06(2)	17.35, 12.1 sh
3	Yellow-green	1102s,1063s	930w-m			2.05(3)	18.9 (assym. to low* cm^{-1})
4	Mauve to blue	1090s				2.06(4)	17.30, 12.0 sh
5	Grey	1104s				2.05(5)	16.15, 14.4 sh
6	Grey	1102s,1068s		2.02(5)	2.22 [e]		17.9 (asym. to low cm^{-1})
7	Mauve	1090s				2.06(2)	17.65
8	Grey	1091s				2.06(2)	17.7
9	Green	1085s		2.05(1)			16.8, 15.8 sh, 10.3 sh
10 [f]	Yellow-green	1119s,1060s	938m-s			2.06(0)	k*
11 [g]	Mauve to blue	1096s				2.07(3)	17.54, 11.90

[a] corrected for Gaussian line shape after ref. 8; [b] estimated from broad isotropic spectra; [c] diffuse reflectance spectra *vs.* MgO; [d] $A_\parallel$ = 171 Hz; [e] $A_\parallel$ = 176 Hz; [f] $[Cu(tripyam)_2(ClO_4)_2]^2$; [g] $[Cu(tripyam)_2](ClO_4)_2^2$; [k] virtually impossible to detect maximum; * we were unable to identify any definite maximum below 10.0 kK for these complexes.

meric pairs of compounds in which the heterocyclic ligands are bi- and terdentate respectively. The great simplification noted for the i.r. spectrum of terdentate tri-(2-pyridyl)amine (C_{3v} local symmetry)[2] is not seen when the new ligands are terdentate since even in this mode of co-ordination the symmetry of the base will be no more than C_s.

The fact that only one ring carries a methyl substituent introduces a variety of stereochemical possibilities. Thus, in complexes 2 and 4, the rings carrying the methyl-groups may either be located in the same plane, or in separate planes with a dihedral angle of 120°. The available data are insufficiently sensitive to differentiate the possibilities. In the case of complexes 1 and 3, and also for 6-9, the ring carrying the substituent may either be co-ordinated or unco-ordinated. The stereochemical possibilities for the complexes of the bi- and terdentate bases are illustrated in Figure 3. No previous evidence has been obtained for basic character associated with the amine nitrogen atom. Careful study of scale molecular models enables us to eliminate from consideration any structure in which these tri-(2-pyridyl)amines function as terdentate ligands via two ring nitrogen atoms together with the amine nitrogen atom, and any structure involving tetradentate co-ordination. Since 4- and 6-methyl substituents increase the basicity of the ring in which they are substituted, it would be anticipated that these rings will remain co-ordinated. However, in the 6-methyl case steric factors oppose the electronic factors and it is to be anticipated that inerligand repulsions would become dominant if the 6-methyl ring remained co-ordinated. Although it is difficult to obtain a clear experimental distinction between the possibilities, careful analysis of the ligand absorption bands suggests that vibrations at 1625 and 1621 cm^{-1} may be attributed to ν(C: : : N) for the 4-methyl-2-pyridyl ring (Complex 4). Since these bands should undergo a shift to lower wavenumber if the ring becomes unco-ordinated and since in fact the bands occur at 1624 and 1620 cm^{-1} in the i.r. spectrum of 3, we argue that the 4-methyy-2-pyridyl ring remains co-ordinated in compound 3.

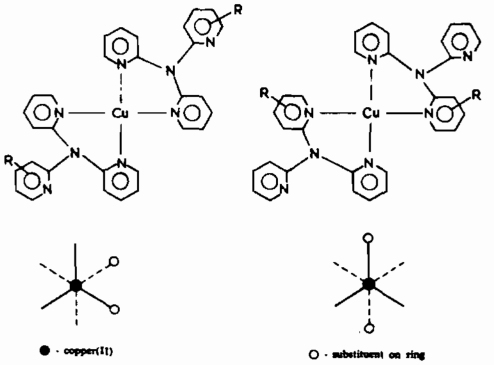


Figure 3. Two possible planar arrangements of a bidentate substituted tri-(2-pyridyl)amine around copper(II).
View down the C_3 axis of the two possible isomers of a bis(terdentate) substituted tri-(2-pyridyl)amine copper(II) cation.

This analysis is not possible for the complexes of 6-methyl-2-pyridyldi-(2-pyridyl)amine since clear separation of ν(C:::N) for the substituted and unsubstituted rings is not seen in the spectra of 1 and 2. This observation is initially surprizing in the case of complex 2, however we anticipate that in this complex there will be strong non bonded repulsive forces between the 6-methyl-group and the metal atom of the type noted for the corresponding nickel(II) complex,[7] which will weaken the interaction between the substituted ring and the metal and thus decrease the magnatude of the shift to high frequency of ν(C:::N). Once this is appreciated it is not difficult to understand how a composite region of absorption corresponding to ν(C:::N) for all three pyridyl groups can result.

It is of interest to note that whereas the green-yellow isomers [Cu(tripyam)$_2$(ClO$_4$)$_2$] and [Cu(4mpdpa)$_2$(ClO$_4$)$_2$] may be isomerised to the mauve isomeric forms by heating, this is not possible for [Cu(6mpdpa)$_2$(ClO$_4$)$_2$] which decomposes before isomerisation occurs. To prepare [Cu(6mpdpa)$_2$](ClO$_4$)$_2$ it is necessary to go through the di-aquo complex (No. 5) as an intermediate. The implication is that a major disruption of the lattice is required, such as that produced by thermal decomposition of the di-aquo complex, before the bidentate 6 mpdpa can invert about the amine nitrogen atom to become terdentate. This is understandable if the ring unco-ordinated in 1 and 5 carries the 6-methyl-group.

No example of a complex in which 5-nitro-2-pyridyl-di-(2-pyridyl)amine functions as a terdentate complex is known.[7] Since the 5-nitro-group is expected to lower the basicity of the ring in which it is substituted, and since the i.r. spectra of complexes 6-9 are very similar indeed, with respect to 5npdpa vibrations, to compounds of iron(II) and nickel(II),[7] there is no reason to suppose that the 5-substituted 2-pyridyl ring is co-ordinated to copper(II) in 6-9.

Visible and es.r. spectra (i) *Mauve isomers.* The visible spectra of complexes 2, 4 and 11 are very similar (Table II) with the exception that greater asymmetry is noted in the major absorption band of 2 than for 4 or 11.

Microcrystalline specimens of complexes 4 and 11[3] give isotropic e.s.r. spectra, an observation apparently incompatible with the visible data which imply copper(II) ions in a tetragonal environment.[3,8] These observations are compatible either if there is a dynamic distortion or if there is a static distortion with a random orientation of tetragonal axes within the crystals.[8] A Mössbauer study of [Fe(4mpdpa)$_2$](ClO$_4$)$_2$[7] suggested that the symmetry of the electron density about the metal ion was lowered by the electronic effect of the methyl-groups on two of the six surrounding 2-pyridyl-rings. Thus in the case of compounds 2 and 4 we have a greater probability of a static distortion than for compound 11.

Although $g_\parallel$ is not well resolved for complex 2, the e.s.r. spectrum definitely requires two g factors, thus making a static distortion probable in this case. We would expect this to be so due to the repulsive forces operative between the metal ion and the 6-methyl-group (*vide supra*). X-ray powder photographs of **2**, 4, and 11 are similar, particularly with respect to the stronger reflections, thus it is likely that the spacings of the heavier atoms are similar in all three cases; but little more can be implied. The question as to the exact nature of the distortion in 4 and 11 must remain open.

(ii) *Yellow-green Isomers.* Apart from the detailed mode of co-ordination of the bidentate heterocyclic base discussed above, the major stereochemical problem is to decide whether the ligands are *trans* in a tetragonal complex, or *cis* in a complex of lower symmetry. Unlike the case of 2,2′ bipyridyl,[9] there is no reason why two bidentate tri(2-pyridyl)amine ligands should not be *trans* and indeed the visible spectra of 1,3 and 10 are more compatible with the tetragonal model than with authentic examples of *cis*-distorted octahedral complexes e.g. [Cu(bipy)$_2$(ONO)](NO$_3$)[10] or trigonal bipyramidal complexes e.g. [Cu(bipy)$_2$I]I.[11] Also the spectra are more similar to the spectrum of [Cu(dipyam)$_2$(NO$_3$)$_2$] (dipyam = di(2-pyridyl)amine), which is considered tetragonal, than to the spectra of [Cu(dipyam)$_2$X$_2$] (X = Cl$^-$, NO$_2^-$, NCS$^-$) for which more distorted structures had to be postulated.[12] The e.s.r. spectrum of 1 requires two g factors for interpretation and in addition splitting of the $g_\parallel$ peak by the nuclear spin of the copper(II) ion was noted (Figure 4). The lowest g factor for 1 is perhaps a little low for a pure $d_{x^2-y^2}$ ground state,[8] thus while we believe that the broad description of these compounds as *trans* diperchlorato-complexes is justified, further small distortions may occur within the primary co-ordination sphere and recently other cases have been found where a g factor 2.05 corresponds to a $d_{x^2-y^2}$ ground state.[13] The e.s.r. spectrum of 3 was uninformative but the similar visible spectrum to 1 and 10 implies a similar structural situation. The visible spectrum of [Cu(6mpdpa)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$ also implies a basically tetragonal environment with the shift to lower wave number compared with complex 1 implying a stronger interaction of Cu(6mpdpa)$_2^{2+}$ with water than with perchlorate. The e.s.r. spectrum of 5 gave no useful information.

Complexes of 5-nitro-2-pyridyldi-(2-pyridyl)amine. Four complexes, 6-9 have been isolated (see scheme). The grey compound 6 is a diperchlorato-complex comparable with 1,3 and 10. The visible and e.s.r. data are comparable with those of 1 and 10 although the visible absorption maximum occurs at lower wave number which we take to imply a stronger interaction between perchlorate groups and copper(II) in 6. There is some evidence that conjugative effects may be transmitted via the amino-nitrogen atom in the bidentate ligands,[14] thus the 6-methyl group in 1 and the 5-nitro-group in 6 may influence to a small degree the basicity of the unsubstituted 2-pyridyl-groups bond-

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(7) J.C. Lancaster and W.R. McWhinnie, *J. Chem. Soc. (A)*, 2673 (1970).

(8) B.J. Hathaway and D.E. Billing, *Co-ordin. Chem. Rev.*, *5*, 143 (1970).

(9) W.R. McWhinnie and J.D. Miller, *Adv. Inorg. Radiochem.*, *12*, 135 (1969).

(10) I.M. Procter and F.S. Stephens, *J. Chem. Soc. (A)*, 1248 (1969); also B.J. Hathaway, I.M. Procter, R.C. Slade and A.A.G. Tomlinson, *J. Chem. Soc. (A)*, 2219 (1969).

(11) H. Elliot, B.J. Hathaway, and R.C. Slade, *J. Chem. Soc. (A)*, 1443 (1966).

(12) J.C. Lancaster, W.R. McWhinnie, and P.L. Welham, *J. Chem. Soc. (A)*. 1742 (1971).

(13) R.J. Dudley and B.J. Hathaway, *J. Chem. Soc. (A)*, 2799 (1970).

(14) W.R. McWhinnie, *Co-ordin. Chem. Rev.*, *5*, 293 (1970).

ed to copper. The electronic nature of the substituents would leave copper(II) with a higher effective positive charge in 6 than in 1 and hence, by the electroneutrality principle, result in the stronger perchlorate interaction in 6.

We consider that the di-aquo complex 9, is structurally similar to 6. Observed differences in physical data for the two complexes parallel those for 1 and 5 and similar arguments may be advanced in explanation.

Complexes 7 and 8 form a puzzling pair. Apparent identity of visible e.s.r. and i.r. data obviously suggest that the colour difference is a function of crystal size or polymorphism. However the difference in colour persists on prolonged grinding but the X-ray powder photographs are identical. Furthermore the syntheses in the experimental section are reproducible but afford only the indicated modification. The «obvious» explanation is now less obviously correct. Although the nature of the difference between 7 and 8, if any, remains obscure, it is possible to interpret the physical data in terms of tetragonal *trans* di-acetone complexes (ν(CO) = 1690 cm^{-1} cf. ~1720 cm^{-1} for free acetone in solution[15]). As with other complexes of the bidentate bases further perturbations of the tetragonal structure can occur.

The X-ray powder photograph of 6 resembles quite closely those of 1,3 and 10, again with respect to the more intense lines, and differs from those of 2,4 and 11 and from the photograph of the presumably tetrahedral $[Zn(5npdpa)_2](ClO_4)_2$. This statement must be qualified by the observation that the e.s.r. spectra of 1 and 6 showed nuclear hyperfine splitting of the $g_{\parallel}$ peak whereas the spectra of 3 and 10 did not. Thus while the pairs 1 and 6 and 3 and 10 may individually have similar crystal structures it is less likely that both pairs have the *same* overall crystal structure. It is however of interest to note that the two complexes showing resoluion of nuclear hyperfine splittings are those for which we have postulated structures in which the unco-ordinated 2-pyridyl-ring carries the substituent group. These observations support our view that 5 npdpa is bidentate in 6 and that the complex is structurally analogous to those of other bidentate tri-(2-pyridyl)amine.

Acknowledgments. We thank Miss A.E. McCarthy for the X-ray powder photography and the S.R.C. for a studentship (to J.C.L.).

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[15] L.J. Bellamy « The Infra-red Spectra of Complex Molecules », Methuen (1966), p. 135.