Ligand Arrangement in Tetragonally Distorted CuO_4N and CuO_4N_2 Chromophores formed from Copper(II) α-Nitroketonates and Sterically Hindered *N*-Bases

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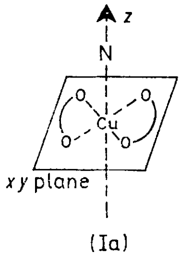
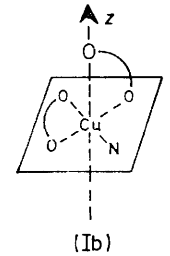
The 1 : 1 and 1 : 2 adducts of copper(II)-α-nitroketonates (CuL_2) with sterically hindered nitrogen bases (B) (L = α-nitroketonato-anion from nitroacetone, 2-nitroacetophenone, 3,3-dimethyl-1-nitrobutan-2-one, or 3-nitrocamphor; B = 2-methyl- or 2,6-dimethyl-pyridine or quinuclidine) have been studied as solids and in solution. An investigation has been carried out on the symmetry and ligand arrangement about Cu^{II} of complexes of formula CuL_2B (CuO_4N chromophore), including those with B = pyridine or 4-methylpyridine. On the basis of room temperature electronic spectra and low temperature (110 K) e.s.r. spectra, all complexes are assigned an approximately square pyramidal structure in solution, most with the nitrogen atom co-ordinated in the basal plane of the pyramid (along the $d_{x^2-y^2}$ or d_{xy} orbitals) and one oxygen atom of an α-nitroketonato-group occupying the apical position. In many cases the position of the nitrogen atom in the corresponding solid complexes, whether basal or apical, could not be established with certainty owing to the lack of pertinent e.s.r. data. For complexes of formula CuL_2B_2 (B = 2-methyl- or 2,6-dimethyl-pyridine) electronic and e.s.r. spectral data indicate tetragonally elongated structures with both nitrogen atoms co-ordinated in the equatorial plane (along the $d_{x^2-y^2}$ or d_{xy} orbitals).

PREVIOUSLY a series of six-co-ordinate [CuL_2B_2] complexes with the chromophore CuO_4N_2, formed from bidentate chelates (L), mainly α-nitroketonato-groups (bite 2·5—3·0 Å), and monodentate nitrogen bases (B), were described.[1] In most cases the nitrogen base co-ordinates in the *xy* plane, *i.e.*, the plane containing the four shortest bonds, forcing the bidentate oxygen donors to assume mixed in-plane–out-of-plane chelation, which, owing to the limited flexibility of these donors, gives rise to tetragonal elongated structures with ' restricted ' distortion. The present paper discusses a series of five-co-ordinate [CuL_2B] complexes with the chromophore CuO_4N, formed by the same [CuL_2] species as before[1] with the monodentate bases 2-methyl- or 2,6-dimethyl-pyridine, quinuclidine, pyridine, or 4-methylpyridine.† Available data concerning [CuL_2B_2] species (B = 2-methyl- or 2,6-dimethyl-pyridine) are also discussed.



(Ia)



(Ib)

Two different types of approximately square pyramidal structure may arise from a CuO_4N chromophore containing two bidentate oxygen donors and one monodentate nitrogen base: (Ia) with an apical nitrogen atom and the four oxygen atoms in the basal plane, *i.e.* with the Cu–N distance slightly longer than the, approximately equal, Cu–O ones and (Ib) having the nitrogen atom and three oxygen atoms in the basal plane and the fourth oxygen atom displaced to the apical position, with $Cu–O_{apical}$ longer than $Cu–O_{basal}$. Structure (Ia) has been found in 4-methylpyridinebis(*o*-hydroxyacetophenonato)-[2] and quinolinebis(acetylacetonato)-copper(II).[3] Structure (Ib) has been found in 4-aminopyridinebis(acetylacetonato)-[4] and 2-methylpyridinebis(2-nitroacetophenonato)-copper(II).[5] E.s.r. spectra indicated that the 1 : 1 adduct formed by bisacetylacetonatocopper(II) with pyridine should be assigned structure (Ia), and the 1 : 1 adducts of bishexafluoroacetylaceto-

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† Abbreviations used for anions L obtained from nitroacetone, 2-nitroacetophenone, 3,3-dimethyl-1-nitrobutan-2-one, 3-nitrocamphor, and hexafluoroacetylacetone are na, nap, nta, nca, and hfa, respectively. The nitrogen bases are abbreviated as follows: 2-methylpyridine = 2-Mepy, 2,6-dimethylpyridine = 2,6-Me_2py, quinuclidine = quin, pyridine = py, and 4-methylpyridine = 4-Mepy.

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[2] V. F. Duckworth and N. C. Stephenson, *Acta Cryst.*, 1969, **B25**, 2245.

[3] S. Ooi and Q. Fernando, *Chem. Comm.*, **1967**, 532.

[4] G. W. Bushnell, *Canad. J. Chem.*, 1971, **49**, 555.

[5] M. Bonamico, G. Dessy, V. Fares, and L. Scaramuzza, *J.C.S. Dalton*, 1972, 2477.

natocopper(II) with pyridine and quinuclidine structure (Ib) in frozen CH_2Cl_2 solution.[6] Structure (Ia or b) has also been assigned to a wider series of nitrogen base adducts of copper(II) β-diketonates on the basis of low temperature e.s.r. spectra in frozen glasses.[7] We report here further spectroscopic studies on these complexes in an attempt to clarify the factors leading to either structure (Ia or b). Of course, trigonal bipyramidal structures should also be taken into consideration. However, there are no data indicating that this type of structure occurs in the complexes.

EXPERIMENTAL

α-Nitroketones and their Cu^{II} and Zn^{II} complexes used as starting materials for the preparation of $[CuL_2B]$ were prepared as before.[8] Nitrogen bases were provided by B.D.H. or K and K; quin was obtained from commercial quin,HCl by treatment with strong base. It can be anticipated that only two base adducts of $[ZnL_2]$ can be prepared, one of which is a bisadduct, *i.e.*, $[Zn(nap)_2(2\text{-Mepy})_2]$. $[Zn(nap)_2(quin)]$ has been obtained but it has not been definitely characterized. The preparations of all the other adducts of $[ZnL_2]$ were attempted without success.

Adducts $[CuL_2(2\text{-Mepy})]$, $[Zn(nap)_2(2\text{-Mepy})_2]$, *and* $[Zn(nca)_2(2\text{-Mepy})]$.—These adducts were prepared by crystallization of *ca.* 0·1 mmol quantities of the anhydrous or hydrated complex $[ML_2]$ from hexane (50—100 cm^3) containing 2-Mepy (1—10 cm^3).

$[Cu(na)_2(2\text{-Mepy})]$ is the only 1 : 1 adduct of Cu^{II} with 2-mepy which could not be isolated. Under the experimental conditions used (excess of nitrogen base), $[Cu(na)_2]$ forms a very unstable, poorly characterized, 1 : 2 adduct.

Adducts $[CuL_2(2,6\text{-Me}_2py)]$.—$[Cu(na)_2(2,6\text{-Me}_2py)]$. $[Cu(na)_2]$ (300 mg, 1·1 mmol) was crystallized from a mixture of acetone (50 cm^3), heptane (50 cm^3), and 2,6-Me_2py (1 cm^3).

$[Cu(nta)_2(2,6\text{-Me}_2py)]$. $[Cu(nta)_2]$ (185 mg, 0·5 mmol) was dissolved in 1 : 1 acetone–2,6-Me_2py (6 cm^3). After filtration, heptane (*ca.* 100 cm^3) was added and two complexes, both green, separated out. One, bright green and stable, was identified as $[Cu(nta)_2(2,6\text{-Me}_2py)]$. The other, olive green and unstable, was not further investigated.

$[Cu(nca)_2(2,6\text{-Me}_2py)]$. $[Cu(nca)_2(H_2O)_2]$ (300 mg, 0·6 mmol) was crystallized from heptane (30 cm^3) and 2,6-Me_2py (9 cm^3).

$[Cu(nap)_2(2,6\text{-Me}_2py)]$. $[Cu(nap)_2]$ (200 mg, 0·5 mmol) was crystallized from 2,6-Me_2py (8 cm^3).

Adducts $[CuL_2(quin)]$.—$[Cu(na)_2(quin)]$. $[Cu(na)_2]$ (200 mg, 0·75 mmol) was suspended in CH_2Cl_2 (8 cm^3) containing the stoicheiometric amount of quin. The solution was filtered and hexane (25 cm^3) added to precipitate the complex.

$[Cu(nta)_2(quin)]$. $[Cu(nta)_2]$ (250 mg, 0·7 mmol) was crystallized from a hot solution of hexane (20 cm^3) and acetone (3 cm^3) containing the stoicheiometric amount of quin.

$[Cu(nca)_2(quin)]$. $[Cu(nca)_2(H_2O)_2]$ (400 mg, 0·81 mmol) was suspended in hexane (30 cm^3) and quin (180 mg, 1·6 mmol) was added. The adduct precipitated immediately. It was separated by filtration and recrystallized from 1 : 3 methylene chloride–heptane.

$[Cu(nap)_2(quin)]$. $[Cu(nap)_2]$ (200 mg, 0·5 mmol) was crystallized from acetone (5 cm^3), ether (20 cm^3), heptane (30 cm^3), and the stoicheiometric amount of quin.

$[Cu(nta)_2(4\text{-Mepy})]$.—Equimolar amounts of $[Cu(nta)_2]$ (200 mg, 0·6 mmol) and 4-Mepy (0·06 cm^3) were dissolved in hot hexane (20 cm^3) and acetone (4 cm^3). After filtration and cooling of the solution the complex precipitates as green crystals. Although $[Cu(nta)_2(4\text{-Mepy})]$ was obtained from stoicheiometric amounts of $[Cu(nta)_2]$ and 4-Mepy, it is also formed, together with the corresponding 1 : 2 adduct, in the presence of an excess of the nitrogen base.[1] In the presence of 4-Mepy the other copper(II)-α-nitroketonates form only 1 : 2 adducts [1] and the preparation of 1 : 1 adducts by using equimolar amounts of $[CuL_2]$ species and base was not attempted.

Physical Measurements.—*X*-Ray powder spectra and room temperature magnetic measurements were carried out as described elsewhere.[8a] Diffuse reflectance and solution electronic spectra in the near i.r.–visible region were taken with a Beckmann DK 2 spectrophotometer.

Low temperature (110 K) e.s.r. spectra were obtained in 1 : 1 $CHCl_3$ (ethanol free)–CH_2Cl_2 as described previously.[8b] The samples were prepared by using the ^{63}Cu isotope. $[^{63}Cu(nap)_2]$, $[^{63}Cu(na)_2]$, and $[^{63}Cu(nta)_2]$ were used as starting materials. In the case of nca, $[^{63}Cu(nca)_2(H_2O)_2]$ was used owing to the difficulty of preparing anhydrous $[^{63}Cu(nca)_2]$.[8b]

RESULTS AND DISCUSSION

1 : 1 *Adducts* $[CuL_2(2\text{-Mepy})]$.—Since α-nitroketonato-groups (L) act as bidentate ligands,[1,8–11] the complexes $[CuL_2(2\text{-Mepy})]$, as well as all the other $[CuL_2B]$ species in Table 1, may be assumed to have five-co-ordinate $[CuO_4N]$ chromophores. The experimental data (Tables 1—3) indicate mononuclear structures for all the complexes examined, both in the solid state and in solution.

$[Cu(nap)_2(2\text{-Mepy})]$ is the only example of a $[CuL_2B]$ species previously reported as the solid.[5,9] This 1 : 1 adduct is also formed in $CHCl_3$ solution [10] *via* equilibrium (1; L = nap; B = 2-Mepy) at low concentrations of base. Increasing concentrations of 2-Mepy cause the

$$[CuL_2] + B \rightleftharpoons [CuL_2B] \qquad (1)$$

progressive conversion of the 1 : 1 into the 1 : 2 adduct *via* equilibrium (2). The e.s.r. spectrum of a frozen

$$[CuL_2B] + B \rightleftharpoons [CuL_2B_2] \qquad (2)$$

solution (110 K) of $[^{63}Cu(nap)_2]$ in 1 : 1 $CHCl_3$–CH_2Cl_2 in the presence of an equimolar amount of 2-Mepy (R = [Base]/[Cu] = 1) is given in Figure 1a which clearly indicates the presence of a single species, *i.e.*, the 1 : 1 adduct $[^{63}Cu(nap)_2(2\text{-Mepy})]$. Since room temperature electronic spectra in $CHCl_3$ showed that the formation of the 1 : 1 adduct is complete at R 20,[10] it is deduced that a decrease in temperature favours formation of the adduct,

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[8] D. Attanasio, I. Collamati, and C. Ercolani, (*a*) *J.C.S. Dalton*, 1972, 772; (*b*) *ibid.*, 1973, 2272.

[9] D. Attanasio, I. Collamati, and C. Ercolani, *J. Chem. Soc.* (*A*), 1971, 2516.

[10] I. Collamati and C. Ercolani, *J. Chem. Soc.* (*A*), 1971, 2522.

[11] B. R. McGarvey, 'Transition Metal Chemistry,' ed. R. L. Carlin, Marcel Dekker, New York, 1966, vol. 3, pp. 153—154.

TABLE 1

Elemental analyses and some properties of the Cu^{II} and Zn^{II} complexes

				Analyses					
				Calc. (%)			Found (%)		
Complex	Colour	M.p. (t/°C)	μ_{eff}/B.M. [a]	C	H	N	C	H	N
[Cu(nta)$_2$(2-Mepy)]	Green	105	1·97	48·6	6·1	9·45	49·0	6·0	9·8
[Cu(nca)$_2$(2-Mepy)]	Brown	145	1·95	56·85	6·4	7·65	56·6	6·3	7·6
[Cu(nap)$_2$(2,6-Me$_2$py)]	Deep green	115	1·89	55·35	4·2	8·4	55·2	4·4	8·4
[Cu(na)$_2$(2,6-Me$_2$py)]	Green	120	1·97	41·65	4·6	11·2	41·55	4·6	11·0
[Cu(nta)$_2$(2,6-Me$_2$py)]	Green	127		49·8	6·3	9·2	49·45	5·7	8·7
[Cu(nca)$_2$(2,6-Me$_2$py)]	Dark violet	150	1·91	57·6	6·6	7·5	58·2	6·75	7·8
[Cu(nap)$_2$(quin)]	Deep green	130	1·90	54·9	5·0	8·35	54·9	4·8	8·45
[Cu(na)$_2$(quin)]	Deep green	95	1·85	41·2	5·6	11·1	40·5	5·4	10·8
[Cu(nta)$_2$(quin)]	Deep green	127	1·88	49·3	7·2	9·1	49·25	7·2	9·0
[Cu(nca)$_2$(quin)]	Green	173	1·88	57·2	7·3	7·4	57·1	7·1	7·3
[Cu(nta)$_2$(4-Mepy)]	Green	130	1·96	48·6	6·1	9·45	48·5	6·4	9·9
[Zn(nap)$_2$(2-Mepy)$_2$]	Light yellow		diam.	58·0	4·5	9·65	57·85	4·4	9·65
[Zn(nca)$_2$(2-Mepy)]	White	110	diam.	56·8	6·4	7·65	56·6	6·3	7·6

[a] Room temperature magnetic moments calculated from $\mu_{\mathrm{eff}} = 2·84\ (\chi_{\mathrm{A}}T)^{\frac{1}{2}}$; diamagnetic corrections were calculated from Pascal's constants.

TABLE 2

Reflectance and solution (CH_2Cl_2) electronic spectra of nitrogen base adducts of copper(II)-α-nitroketonates

Complex [a]	Medium [b]	$10^{-3}\nu$/cm^{-1} (ε or D) [c]
[Cu(na)$_2$]	0·2 (%)	13·35 (750, 92)
	0·5 (%)	13·35 (750, 99)
	20 (%)	13·6 (735, 92)
	50 (%)	13·8 (725, 76)
	2-Mepy	13·9 (720, 70)
[Cu(nta)$_2$(2-Mepy)]	Solid	12·9 (775, 0·75); 15·1 (660, 0·65)
	CH_2Cl_2	14·6 (685, 67)
	10 (%)	14·4 (695, 96·5)
	50 (%)	14·1 (710, 76)
	2-Mepy	14·0 (715, 70)
[Cu(nca)$_2$(2-Mepy)]	Solid	8·7 (1150, 0·35); 13·6 (735, 0·66)
	CH_2Cl_2	13·8 (725, 70·5)
	5 (%)	13·35 (750, 89·5)
	50 (%)	13·35 (750, 78)
	2-Mepy	13·35 (750, 71)
[Cu(nap)$_2$(2,6-Me$_2$py)]	Solid	12·7 (790, 0·73); 14·2 (705, 0·74)
	1 (%)	13·25 (755, 180)
	10 (%)	13·25 (755, 168)
	40 (%)	13·35 (750, 146)
	2,6-Me$_2$py	13·5 (740, 121)
[Cu(na)$_2$(2,6-Me$_2$py)]	Solid	12·75 (785, 0·95); 14·3 (700, 0·92)
	1 (%)	13·1 (760, 146)
	10 (%)	13·1 (760, 144)
	40 (%)	13·1 (760, 137)
	92 (%)	13·5 (740, 123)
[Cu(nta)$_2$(2,6-Me$_2$py)]	Solid	12·1 (825, 0·7); 14·3 (700, 0·68)
	CH_2Cl_2	14·3 (700, 82)
	1 (%)	13·25 (755, 153)
	10 (%)	13·35 (750, 153)
	40 (%)	13·35 (750, 140)
	2,6-Me$_2$py	13·5 (740, 120)
[Cu(nca)$_2$(2,6-Me$_2$py)]	Solid	11·6 (860, 0·85); 13·7 (730, 0·78)
	CH_2Cl_2	11·4 (875, 40); 13·8 (725, 56·5)
	2 (%)	11·5 (870, 117); 13·1 (765, 118)
	20 (%)	11·75 (850, 107); 13·1 (765, 109)
	2,6-Me$_2$py	11·75 (850, 96); 13·25 (755, 99·5)
[Cu(nap)$_2$(quin)]	Solid	12·75 (785, 0·77)
	CH_2Cl_2	13·8 (725, 138)
	2 (R)	13·35 (750, 146)
	10 (R)	13·5 (740, 150)
[Cu(na)$_2$(quin)]	Solid	12·3 (815, 0·97); 14·95 (670, 0·93)
	CH_2Cl_2	13·2 (760, 126)
[Cu(nta)$_2$(quin)]	Solid	12·2 (820, 0·79; 14·4 (695, 0·77)
	CH_2Cl_2	13·8 (725, 128)
[Cu(nca)$_2$(quin)]	Solid	11·1 (910, 0·5); 14·3 (700, 0·47)
	CH_2Cl_2	12·5 (800, 102); 14·1 (710, 105)
[Cu(nta)$_2$(4-Mepy)]	Solid	12·6 (795, 0·88); 13·8 (725, 0·89)
	CH_2Cl_2	13·5 (740, 89)
	2 (R)	13·4 (745, 95)
	10 (R)	13·8 (725, 70)
	100 (R)	9·1 (1100, 20); 14·0 (715, 53)
	4-Mepy	9·1 (1100, 20); 14·0 (715, 53)

[a] The solution spectra were taken by dissolving in CH_2Cl_2 the complexes listed ($c_{\mathrm{Cu}} = 10^{-2}$M). Both reflectance and solution spectra in all cases show a shoulder at 20 000—22 000 cm^{-1}, believed to be non-d–d in origin.[1, 8b, 9, 11] This band is found at 18 000 cm^{-1} in the spectrum of solid [Cu(nca)$_2$(2,6-Me$_2$py)] (Figure 2n). [b] % = the percentage by volume of base in CH_2Cl_2; R = the [base]/[Cu] ratio. [c] ε, molar extinction coefficient; D, arbitrary optical density.

TABLE 3

Low temperature (110 K) e.s.r. spectra of [CuL$_2$B] and [CuL$_2$B$_2$] species in 1 : 1 CHCl$_3$ (ethanol free)–CH$_2$Cl$_2$

Complex	Medium [a]	R [b]	$g_{\parallel}$ ($\pm$0·002)	$g_{\perp}$ ($\pm$0·005)	$10^4(A_{\parallel}{}^{63}\text{Cu} \pm 1)$ /cm^{-1}	$10^4(A^{\text{N}} \pm 0{\cdot}5)$ /cm^{-1}	Nitrogen atoms [c]
[^{63}Cu(nap)$_2$(2-Mepy)]	F.s.	1	2·299	2·061	164	9·0	B
[^{63}Cu(na)$_2$(2-Mepy)]	F.s.	1	2·307	2·061	169	9·2	B
[^{63}Cu(nta)$_2$(2-Mepy)]	F.s.	1	2·306	2·068	170	9·2	B
[^{63}Cu(nca)$_2$(2-Mepy)]	F.s.	1	2·299	2·066	162		A
[Cu–Zn(nca)$_2$(2-Mepy)]	D.s.		2·330	2·086	134		A
[^{63}Cu(nap)$_2$(quin)]	F.s.	15	2·293	2·063	169	9·2	B
[^{63}Cu(na)$_2$(quin)]	F.s.	5	2·298	2·073	174	9·2	B
[^{63}Cu(nta)$_2$(quin)]	F.s.	15	2·297	2·057	172	9·2	B
[^{63}Cu(nca)$_2$(quin)]	F.s.	25	2·291	2·073	163		B
[^{63}Cu(nta)$_2$(2,6-Me$_2$py)]	F.s.	1	2·316	2·070	161	8·6	B
[^{63}Cu(nca)$_2$(2,6-Me$_2$py)]	F.s.	5	2·307	2·083	147		
[^{63}Cu(nap)$_2$(py)]	F.s.	1	2·297	2·068	168	10·0	B
[^{63}Cu(na)$_2$(py)]	F.s.	1	2·303	2·068	174	10·7	B
[^{63}Cu(nta)$_2$(py)]	F.s.	1	2·305	2·067	169	8·6	B
[^{63}Cu(nca)$_2$(py)]	F.s.	1	2·311	2·069	151	9·2	B
[^{63}Cu(nap)$_2$(4-Mepy)]	F.s.	1	2·297	2·067	170	10·0	B
[^{63}Cu(na)$_2$(4-Mepy)]	F.s.	1	2·306	2·069	172	10·7	B
[^{63}Cu(nta)$_2$(4-Mepy)]	F.s.	1	2·306	2·065	171	10·6	B
[^{63}Cu(nca)$_2$(4-Mepy)]	F.s.	1	2·306	2·070	167	9·2	B
[^{63}Cu(nap)$_2$(2-Mepy)$_2$]	F.s.	2	2·307	2·065	160	9·7	2E
[^{63}Cu(na)$_2$(2-Mepy)$_2$]	F.s.	6 (%)	2·312	2·068	165	10·3	2E
[^{63}Cu(nta)$_2$(2-Mepy)$_2$]	F.s.	6 (%)	2·315	2·067	162	10·7	2E
[^{63}Cu(nca)$_2$(2-Mepy)$_2$]	F.s.	15 (%)	2·302	2·067	162	10·7	2E
[^{63}Cu(nap)$_2$(2,6-Me$_2$py)$_2$]	F.s.	6 (%)	2·309	2·070	162	10·5	2E
[^{63}Cu(na)$_2$(2,6-Me$_2$py)$_2$]	F.s.	6 (%)	2·304	2·066	165·5	10·0	2E
[^{63}Cu(nta)$_2$(2,6-Me$_2$py)$_2$]	F.s.	6 (%)	2·312	2·010	160	10·0	2E
[^{63}Cu(nca)$_2$(2,6-Me$_2$py)$_2$]	F.s.	15 (%)	2·310	2·072	162	10·7	2E
[^{63}Cu–Zn(nap)$_2$(2-Mepy)$_2$]	D.s.		2·330	2·074	146	9·8	2E

[a] F.s. = frozen solution; D.s. = diluted solid. [b] % In parentheses indicates the percentage by volume of base. [c] Position of atoms: B basal, A apical, E equatorial, 2E two equatorial.

assuming negligible influence of the solvent. The measured g values (Table 3) are consistent ($g_{\parallel} > g_{\perp}$) with elongated tetragonal symmetry ($d_{x^2-y^2}$ or d_{xy} ground state), thus indicating an approximately square pyramidal structure about Cu$^{\text{II}}$. ^{14}N Hyperfine splitting is also detected on the bands of $g_{\parallel}$ (three peaks of almost equal intensity). Since this hyperfine splitting is largely of the isotropic Fermi contact type,[11] it can be used[1,6,7,12] to locate the nitrogen atom in the basal plane of the square pyramid (along the $d_{x^2-y^2}$ or d_{xy} orbital). Thus structure (Ib), similar to that found by X-ray investigation[5] of the pure solid, may also be assigned to [Cu(nap)$_2$(2-Mepy)] in solution.

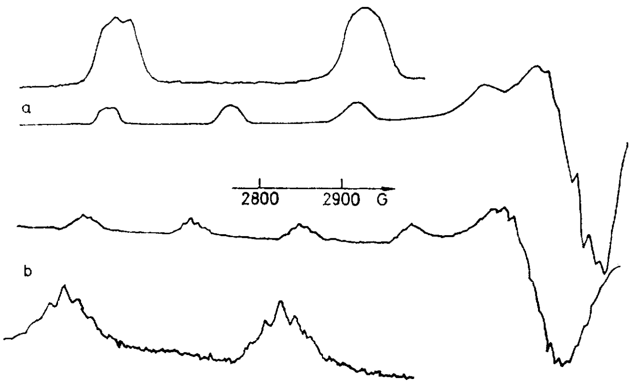

FIGURE 1 E.s.r. spectra of a frozen solution in 1 : 1 CHCl$_3$–CH$_2$Cl$_2$: of a, [^{63}Cu(nap)$_2$(2-Mepy)] and b, of a polycrystalline sample of [^{63}Cu–Zn(nap)$_2$(2-Mepy)$_2$]

The electronic spectral variations observed for [Cu(na)$_2$], [Cu(nta)$_2$], and [Cu(nca)$_2$(H$_2$O)$_2$] in CH$_2$Cl$_2$ in the presence of increasing amounts of 2-Mepy are very similar (Table 2) to those observed previously for the system [Cu(nap)$_2$]–2-Mepy[10] and agree with the occurrence of stepwise equilibria (1) and (2). The fact that [Cu(nca)$_2$(H$_2$O)$_2$] behaves as a [CuL$_2$] species is in keeping with the previous observation that this complex loses the water molecules in CH$_2$Cl$_2$ to yield [Cu(nca)$_2$].[8b] The latter can then interact with 2-Mepy in a way similar to that of the other [CuL$_2$] species.

The spectra in CH$_2$Cl$_2$ of the 1 : 1 adducts [CuL$_2$(2-Mepy)] are characterized by the presence of a d–d envelope with a maximum at 13 000—14 000 cm^{-1}, more intense (ε 90—100 l mol^{-1} cm^{-1}) than the d–d envelope present in the solution spectra of the related [CuL$_2$] (ε *ca.* 50)[8b-10,13] and [CuL$_2$B$_2$] species (ε *ca.* 60—70) (refs. 8*b*, 10, 1 and Table 2). The concentration of 2-Mepy corresponding to complete formation of the 1 : 1 adducts was not exactly determined. Nevertheless, there are sufficient data indicating that it occurs at R values above, although close to, 1. The similarity of the solution spectra of the [CuL$_2$(2-Mepy)] species with those of the similar adducts of [Cu(nap)$_2$] with the same N-base and with 4-Mepy[10] suggests an approximately square pyramidal structure for these complexes too.

The low temperature e.s.r. spectra of frozen solutions of [Cu(na)$_2$] or [Cu(nta)$_2$] in CHCl$_3$–CH$_2$Cl$_2$ (1 : 1) in the presence of 2-Mepy at R 1 also indicate the presence of the 1 : 1 adduct only, as for [Cu(nap)$_2$]. g Values and ^{14}N hyperfine splitting are similar to those observed for the analogous 1 : 1 adduct of [Cu(nap)$_2$], measured

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[13] I. Collamati and C. Ercolani, *J. Chem. Soc.* (*A*), 1969, **1541**.

under the same experimental conditions (Table 3). It is therefore concluded that a structure of type (Ib) is assumed by the two 1 : 1 adducts under discussion, and that the same structure is present for these complexes in solution at room temperature. The frozen solution e.s.r. spectrum of the complex [Cu(nca)$_2$(2-Mepy)] gives g values close to those observed for the other adducts of 2-Mepy, whereas ^{14}N hyperfine splitting on the bands of $g_{\parallel}$ is apparently absent. This suggests a structure of type (Ia), with the N atom in the apical position. It may be pointed out, however, that a structure of type (Ib) cannot be definitely ruled out, since ^{14}N hyperfine splitting could be present but undetected.

As to the solid complexes [CuL$_2$(2-Mepy)] (Table 1), [Cu(nap)$_2$(2-Mepy)] was shown by X-rays [5] to approximate to a structure of type (Ib). An e.s.r. spectrum consistent with this structure could not be found for the diluted solid, since [Zn(nap)$_2$(2-Mepy)] could not be obtained, and co-crystallization of [^{63}Cu(nap)$_2$] and [Zn(nap)$_2$] in the presence of 2-Mepy leads to the formation of [^{63}Cu–Zn(nap)$_2$(2-Mepy)$_2$] (see below). The e.s.r. spectrum of the undiluted solid confirms a tetragonal elongated structure ($g_{\parallel}$ 2·29, $g_{\perp}$ 2·07).

[Cu(nta)$_2$(2-Mepy)] can only be tentatively assigned structure (Ib) because of the similarity of its reflectance spectrum (double peaked *d–d* envelope centred at 14 000 cm^{-1}) (Figure 2b) to that of [Cu(nap)$_2$(2-Mepy)] (Figure 2a), and the fact that structure (Ib) is assumed by the latter in solution. The e.s.r. spectrum of the undiluted solid confirms a tetragonal structure for this complex ($g_{\parallel}$ 2·31, $g_{\perp}$ 2·09).

[Cu(nca)$_2$(2-Mepy)] has a reflectance spectrum with a sharp peak of relatively low intensity at 13 600 cm^{-1}, accompanied by a less intense shoulder on the low energy side, at *ca.* 8700 cm^{-1} (Figure 2c). Such a *d–d* spectrum approaches that of the six-co-ordinate complexes of chromophore CuO$_4$N$_2$ examined elsewhere,[1,8b] rather than that of the five-co-ordinate complexes reported here. A polycrystalline sample obtained by co-crystallizing [Cu(nca)$_2$(2-Mepy)] and the isomorphous Zn^{II} complex (1 : 100) gives g values close to, although somewhat higher than, those observed for the frozen solution (Table 3). Once again, ^{14}N hyperfine splitting is absent in the $g_{\parallel}$ bands. A square pyramidal structure (Ia) is thus suggested for solid [Cu(nca)$_2$(2-Mepy)], as for the same complex in solution. In an attempt to reconcile the e.s.r. and reflectance spectra of [Cu(nca)$_2$(2-Mepy)], we refer to the crystal structure of [Cu(nap)$_2$(2-Mepy)] [5] [structure (Ib)], where the methyl group of 2-Mepy is found along the sixth (axial) co-ordination position with the carbon atom 3·1 Å from Cu^{II}. It may be suggested that in [Cu(nca)$_2$(2-Mepy)] there is a similar

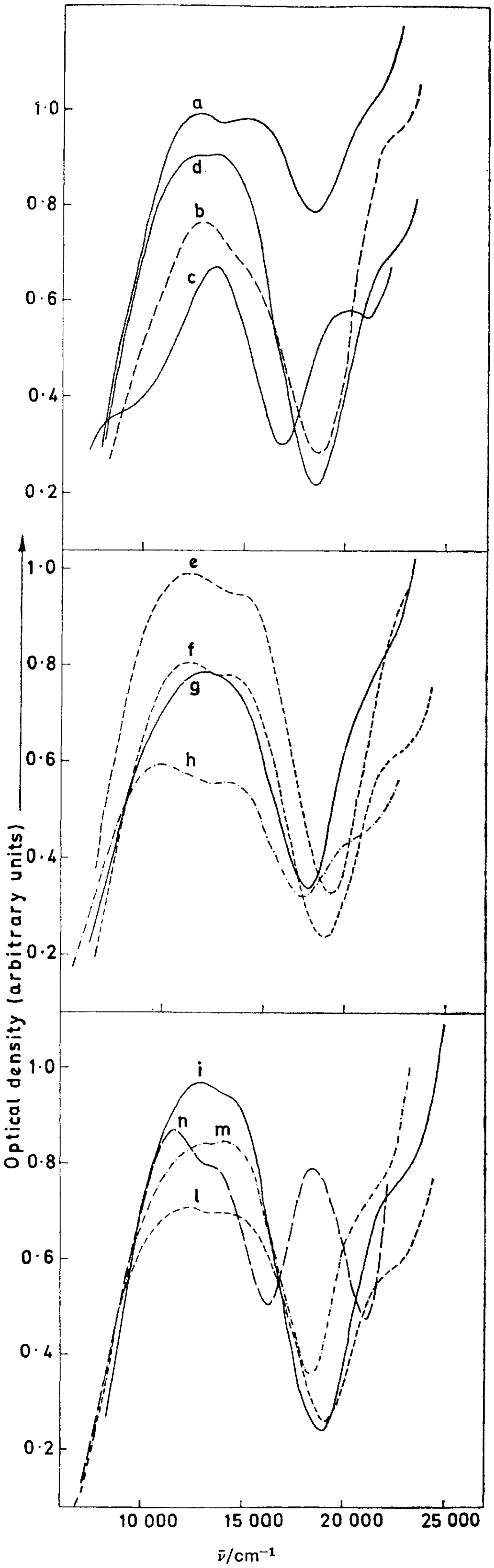

FIGURE 2

Caption for Figure 2:

FIGURE 2 Diffuse reflectance spectra of: a, [Cu(nap)$_2$(2-Mepy)]; b, [Cu(nta)$_2$(2-Mepy)]; c, [Cu(nca)$_2$(2-Mepy)]; d, [Cu(nta)$_2$(4-Mepy)]; e, [Cu(na)$_2$(quin)]; f, [Cu(nta)$_2$(quin)]; g, [Cu(nap)$_2$(quin)]; h, [Cu(nca)$_2$(quin)]; i, [Cu(na)$_2$(2,6-Me$_2$py)]; l, [Cu(nta)$_2$(2,6-Me$_2$py)]; m, [Cu(nap)$_2$(2,6-Me$_2$py)]; n, [Cu(nca)$_2$(2,6-Me$_2$py)] structure, but with the nitrogen atom and the methyl group of 2-Mepy interchanged. In this case the ligand field would be weakened in the xy plane and strengthened along the z direction. This situation might simulate the kind of ligand field, elongated with 'restricted' tetragonal distortion, found in the CuO_4N_2 chromophores previously discussed.[1,8b] The unique behaviour of $[Cu(nca)_2(2\text{-}Mepy)]$ has stimulated an X-ray investigation, now in progress.

1 : 1 *Adducts* $[CuL_2(2,6\text{-}Me_2py)]$ *and* $[CuL_2(quin)]$.—As for the adducts with 2-Mepy, there are more data on structures in solution than in the solid state for $[CuL_2B]$ where B is 2,6-Me_2py or quin. Electronic spectra of $[CuL_2]$ in CH_2Cl_2 in the presence of variable amounts of the nitrogen bases show trends similar to those observed for 2-Mepy and compatible with equilibria (1) and (2). The 1 : 1 adducts are clearly established, at the R values reported (Table 3), as the preponderant (2,6-Me_2py), or the only (quin), species present, by the low temperature e.s.r. spectra in $CHCl_3$–CH_2Cl_2. These R values, >1 in several cases, underline the greater difficulty with which the 1 : 1 adducts, particularly those of quin, are formed compared with those of 2-Mepy. The g values of the complexes with 2,6-Me_2py and quin listed in Table 3 indicate tetragonal elongated structures ($g_{\parallel} > g_{\perp}$); the observed ^{14}N hyperfine splitting allows assignment of structure (Ib) to those species. The e.s.r. spectra of the 1 : 1 adducts of $[Cu(na)_2]$ and $[Cu(nap)_2]$ with 2,6-Me_2py are complicated by the fact that uncertainty exists about the assignment of g values, at least partially due to the presence of more than one species, and therefore are not reported in Table 3.

The intensity of the main visible band found in the electronic absorption spectra of the 1 : 1 adducts with 2,6-Me_2py and quin is noticeably higher (Table 2) than that found in the spectra of the adducts with 2-Mepy. The higher intensity may be explained by the lower symmetry of the adducts formed, caused by the greater steric hindrance exerted by 2,6-Me_2py and quin compared with 2-Mepy. Molecular models show that for an approximately square pyramidal structure strain is large in both 2,6-Me_2py and quin adducts, assuming that all Cu–O and Cu–N bonds are short ($\leqslant 2{\cdot}30$ Å). They also indicate that strain would be somewhat released by going from distorted square pyramidal towards trigonal bipyramidal structures, particularly for the adducts with 2,6-Me_2py. Despite this, even for the solid adducts with 2,6-Me_2py and quin, the reflectance spectra (Figure 2e—n), similar to those of the corresponding derivatives of 2-Mepy, suggest an approximately square pyramidal structure. For one of these species, $[Cu(nap)_2(quin)]$, the e.s.r. spectrum of an undiluted sample was examined and the measured g values ($g_{\parallel}$ 2·29, $g_{\perp}$ 2·08) are consistent with the proposed structure. Since Zn^{II} complexes could not be obtained and hence the e.s.r. spectra of diluted solids were not examined, nothing can be said about the position of the nitrogen base in the solid 1 : 1 adducts with 2,6-Me_2py and quin.*

1 : 1 *Adducts* $[CuL_2(py)]$ *and* $[CuL_2(4\text{-}Mepy)]$.—Equilibria (1) and (2) also occur in solution for $[CuL_2]$ in the presence of either py or 4-Mepy. With increasing amounts of base, in CH_2Cl_2, spectral variations are quite similar to those observed for all the $[CuL_2]$ species with 2-Mepy and for $[Cu(nap)_2]$ with 4-Mepy.[10] For the system $[Cu(nta)_2]$–4-Mepy the data in Table 2 indicate that the 1 : 1 adduct undergoes some dissociation by dissolution in pure CH_2Cl_2 and that it is formed completely at $1 < R < 10$, probably at R *ca.* 2, as for the $[Cu(nap)_2]$–4-Mepy system, also in CH_2Cl_2.[10]

The 1 : 1 adducts of $[CuL_2]$, including that derived from $[Cu(nca)_2(H_2O)_2]$, with 4-Mepy and py were examined by low temperature e.s.r. spectra in $CHCl_3$–CH_2Cl_2 for R 1. The g values and ^{14}N hyperfine splitting are in all cases consistent with the formation of structure (Ib), *i.e.* square pyramidal with the nitrogen atom basal (Table 3, last column). Solid $[Cu(nta)_2(4\text{-}Mepy)]$, the only 1 : 1 adduct with 4-Mepy isolated in the solid state with either this base or py, is tentatively assigned structure (Ib), because of the similarity of its reflectance spectrum (Figure 2d) to that of $[Cu(nap)_2(2\text{-}Mepy)]$ and the fact that structure (Ib) is assigned to the latter in solution.

From the structural assignments in the last column of Table 3 it is seen that structure (Ib), implying basal co-ordination of the nitrogen atom, occurs in almost all cases. The observed g values and ^{14}N hyperfine splitting are similar to those found for $Cu(hfa)_2(py)$ and $Cu(hfa)_2(quin)$, for which structure (Ib) was also suggested.[6,7] Once again, similar structural features are encountered between Cu^{II} complexes of α-nitroketones and those of hexafluoroacetylacetone (see below).

1 : 2 *Adducts* $[CuL_2(4\text{-}Mepy)_2]$, $[CuL_2(2\text{-}Mepy)_2]$, *and* $[CuL_2(2,6\text{-}Mepy)_2]$.—As mentioned above, electronic spectra show that formation of 1 : 2 adducts of formula $[CuL_2B_2]$ where B is 4-Mepy, 2-Mepy, or 2,6-Me_2py is possible in CH_2Cl_2 solution. The data given in Table 2 indicate that these 1 : 2 adducts are progressively more difficult to form on going from 4-Mepy to 2-Mepy and 2,6-Me_2py, as expected on steric grounds. $[Cu(nta)_2(4\text{-}Mepy)_2]$ is formed completely at R *ca.* 100, as is $[Cu(nap)_2(4\text{-}Mepy)_2]$.[10] For $[CuL_2(2\text{-}Mepy)_2]$ neat 2-Mepy is required as solvent before complete, or nearly so, formation of the 1 : 2 adducts is accomplished. The formation of the complexes $[CuL_2(2,6\text{-}Me_2py)_2]$ does not go to completion for any of the $[CuL_2]$ species examined, even in neat base. Concentrations of quin higher than those used for the formation of 1 : 1 adducts seem to lead to dissociation of the $[CuL_2]$ species with expulsion of the α-nitroketonato-groups from the co-ordination sphere of the metal ion. Consequently, formation of 1 : 2 adducts of this base could not be observed.

The two bands usually found in the spectra of complexes containing the CuO_4N_2 chromophore having a tetragonal elongated structure with 'restricted' distortion [1,8b,10] are also present in the solution spectrum of

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* An approximately square pyramidal structure has very recently been established by X-ray examination of $[Cu(nap)_2(2,6\text{-}Me_2py)]$ (M. Bonamico, G. Dessy, V. Fares, and L. Scaramuzza, unpublished results).

$[Cu(nta)_2(4\text{-}Mepy)_2]$ at 9100 and 14 000 cm^{-1}. For the series of complexes $[CuL_2(2\text{-}Mepy)_2]$ the lower energy band is less easily located since it is masked by the tail of the higher energy envelope. However, its presence is unequivocally established by the formation, in equilibrium (2), of an isosbestic point at *ca.* 9000 cm^{-1}, as for $[Cu(nap)_2(2\text{-}Mepy)]$.[10] Thus, the spectra of the 1 : 2 adducts with 2-Mepy reported here are also consistent with a six-co-ordinate CuO_4N_2 chromophore. There are no electronic spectral data which can unequivocally support the six-co-ordinate structures of 1 : 2 adducts of 2,6-Mepy. Molecular models show that much strain is produced in the six-co-ordinate $[CuL_2(2,6\text{-}Me_2py)_2]$ species. To our knowledge, there are no examples of solid six-co-ordinate 1 : 2 adducts of this base. Recently, a 1 : 2 adduct of formula $[Ni(nap)_2(2,6\text{-}Me_2py)_2]$, six-co-ordinate from electronic spectra, was isolated in the solid state.[14] Whether a six-co-ordinate or any other kind of tetragonal structure, implying a lower co-ordination number, actually occurs in $[CuL_2(2,6\text{-}Me_2py)_2]$ remains uncertain.

Concentrations of nitrogen base lower than those necessary at room temperature are required at 110 K to cause formation of the 1 : 2 adducts for both 2-Mepy and 2,6-Me_2py, as shown by e.s.r. spectra, thus indicating that decrease in temperature also favours the formation of the 1 : 2 adducts. E.s.r. spectra of all the adducts with 2-Mepy and 2,6-Me_2py give *g* values and ^{14}N hyperfine splitting consistent with tetragonal elongated structures with both nitrogen atoms in-plane, probably in a *trans*-arrangement, as found for similar chromophores.[1]

Co-crystallization of $[^{63}Cu(nap)_2]$ and $[Zn(nap)_2]$ (1 : 100) in the presence of 2-Mepy leads to formation of $[^{63}Cu\text{–}Zn(nap)_2(2\text{-}Mepy)_2]$, isomorphous with both $[Zn(nap)_2(2\text{-}Mepy)_2]$ (Table 1) and the corresponding six-co-ordinate [9] Ni^{II} complex, and thus expected to contain $[^{63}Cu(nap)_2(2\text{-}Mepy)_2]$ (CuO_4N_2 chromophore). The e.s.r. spectrum of a polycrystalline sample of $[^{63}Cu\text{–}Zn(nap)_2(2\text{-}Mepy)_2]$ gives $g_{\parallel}$ 2·330 and $g_{\perp}$ 2·074. ^{14}N Hyperfine splitting is as expected [1,8b] for a six-co-ordinate structure with nitrogen atoms co-ordinated in the equatorial plane (Figure 1b).

The uniform tendency of copper(II)-α-nitroketonates to form solid stable 1 : 2 adducts with py or 4-Mepy has been previously discussed.[1] The negligible effect exerted by substituents on the donor properties of the α-nitroketonato-anion is presumably also the reason why copper(II)-α-nitroketonates all give rise to solid stable 1 : 1 adducts with 2-Mepy, 2,6-Me_2py, and quin. The formation of solid 1 : 1, rather than 1 : 2 adducts, probably depends on the steric features of these bases. Studies in solution, where strain is released, have, in fact, shown that the high Lewis acid strength of copper(II)-α-nitroketonates makes possible the formation of six-co-ordinate 1 : 2 adducts, at least for 2-Mepy.

The stereochemistry and arrangement of the ligands about the metal ion also seem to be practically independent of the α-nitroketonato-anion in the sense that co-ordination of the nitrogen base normally occurs along the $d_{x^2-y^2}$ (or d_{xy}) orbital, with consequent displacement of the bidentate oxygen donor ligand onto the d_{z^2} orbital, for both CuO_4N_2 and CuO_4N (distorted square pyramidal) chromophores. The similar behaviour between $[CuL_2]$ and their β-diketone analogues containing strongly electron-attracting groups, such as $Cu(hfa)_2$, as regards adduct formation with nitrogen bases, is also paralleled by the similar structures of their base adducts. It has been shown that for all the known base adducts of $[Cu(hfa)_2]$, whether CuO_4N_2 [1,7,8b,15] or CuO_4N,[6,7] the base co-ordinates along the $d_{x^2-y^2}$ (or d_{xy}) orbital. This is not an isolated case, since analogous structures have also been found for similar chromophores formed from trifluoroacetylacetone,[7] salicylaldehyde, and ethyl acetoacetate.[12] Only when peripheral substituents on the bidentate oxygen donor are not strongly electron attracting may the ligand arrangement in the corresponding nitrogen base adducts change, thus making it also dependent on the nature of the base itself.[6,7,12]

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