Ligand Arrangement and Tetragonal Distortion in CuO_4N_2 Chromophores Studied by Electronic and Electron Spin Resonance Spectroscopy

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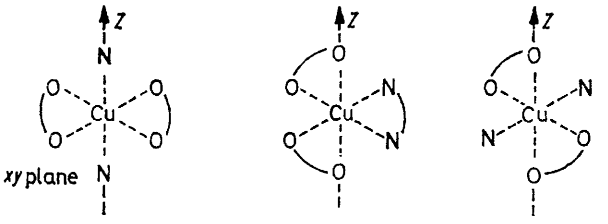
A series of nitrogen-base adducts of copper(II) α-nitroketonates of general formula $[CuL_2B_2]$ (L = α-nitroketonato anion, B = pyridine or 4-methylpyridine; chromophore CuO_4N_2) have been prepared and their structures investigated by magnetic, spectroscopic, and *X*-ray measurements. Room-temperature solid state and solution electronic spectra and low temperature (110 K) e.s.r. spectra, on both polycrystalline samples diluted in their isomorphous or non-isomorphous zinc(II) matrices and frozen solutions in $CHCl_3$–CH_2Cl_2 (1 : 1), indicate that the Cu^{II} ion is in a site of elongated tetragonal symmetry with ' restricted ' distortion caused by in-plane co-ordination of the nitrogen atoms and in-plane–out-of-plane co-ordination of the bidentate *O*-donors. The analogous bis-adducts with pyridine and 4-methylpyridine of bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)copper(II) have also been examined and structures assigned both in the solid state and in solution. For some of the above species the polycrystalline samples give e.s.r. spectra indicative of the presence of additional magnetic centres with compressed tetragonal symmetry.

SIX-CO-ORDINATE copper(II) complexes may have different local symmetry, depending upon the nature and arrangement of the ligands. CuO_4N_2 Chromophores, formed by bidentate *O*-donors, capable of occupying true co-ordination sites (since the bite is 2·5—3·0 Å) and monodentate or bidentate *N*-bases, may take up either compressed or elongated tetragonal structures. With both types of structure, configurations of type (Ia) (Scheme; '*trans*-axial,' referred to the position of the N atoms; all Cu–O distances in plane and approximately equal), (Ib), and (Ic) (*cis*-in-plane and *trans*-in-plane, respectively; $Cu–O_{axial} \neq Cu–O_{in\text{-}plane}$) might be predicted.

Compressed tetragonal structures are unknown for CuO_4N_2 chromophores of the above type, although some, formed with other sets of ligands, have been established *via* *X*-rays [1] or e.s.r.[2] However, at least one example of each of the elongated configurations (Ia—c) has been found by *X*-ray analysis. The adduct $[Cu(hfa)_2(dabco)]$ †[3] is *trans*-axial. *cis*-In-plane and *trans*-in-plane structures have been found in $[Cu(hfa)_2(bipy)]$ [4] and in $[Cu(nap)_2(4\text{-}mepy)_2]$,[5] respectively. For the latter two complexes, in-plane *N*-co-ordination causes mixed in-plane–out-of-plane co-ordination of the bidentate *O*-donor, and $Cu–O_{axial}$ bond distances greater than $Cu–O_{in\text{-}plane}$ are found, due to the different electronic population of the d_{z^2} and $d_{x^2-y^2}$ (or d_{xy}) orbitals.

On the basis of electronic spectra, elongated tetragonal structures have been suggested for many *N*-base adducts of β-diketone- or β-diketone-like copper(II) complexes having chromophore CuO_4N_2.[6] The position of the *N*-base in these complexes was either not discussed or more or less explicitly assumed to be axial. Recent *X*-ray work has shown that this is not always the case.[4] In addition, e.s.r. measurements have shown that co-ordination of pyridine and 4-methylpyridine is axial for $[Cu(acac)_2]$, but in-plane for $[Cu(salal)_2]$ and $[Cu(etacac)_2]$ in frozen solution in the presence of an excess of *N*-base.[7] In-plane *N*-co-ordination was suggested for some solid *N*-base adducts of $[Cu(nap)_2]$ on the basis of electronic spectral evidence, and the need for reconsideration of the structure of the *N*-base adducts of copper(II)–β-diketonates in terms of the configurations (Ia), (Ib), and (Ic) was pointed out.[8] Very recently, a number of these adducts has been assigned structure (Ia) or (Ib) from low temperature e.s.r. spectra in frozen toluene solutions.[9] In-plane *N*-co-ordination has been established by electronic and e.s.r. spectra in a series of copper(II)–α-nitroketonates of formula $[CuL_2B']$ (B′ = bipy or phen),[10] and by *X*-rays in $[Cu(nap)_2(4\text{-}mepy)_2]$.[5]



trans–axial (Ia) *cis*–in–plane (Ib) *trans*–in–plane (Ic)

The number of cases examined has now been extended

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† Abbreviations used in this work are: dabco = 1,4-diazabicyclo[2.2.2]octane; py = pyridine, 4-mepy = 4-methylpyridine, bipy = 2,2′-bipyridyl, phen = *o*-phenanthroline; na, nap, nta, nca = anions from nitroacetone, 2-nitroacetophenone, 3,3-dimethyl-1-nitrobutan-2-one, and 3-nitrocamphor, respectively; hfa, acac, etacac, salal = anions from 1,1,1,5,5,5-hexafluoropentane-2,4-dione, pentane-2,4-dione, ethyl acetoacetate, salicylaldehyde, respectively.

[1] K. Knox, *J. Chem. Phys.*, 1959, **30**, 991; F. Hanic and I. A. Cakajdova, *Acta Cryst.*, 1958, **11**, 610; J. G. Forrest, C. K. Prout, and F. J. C. Rossotti, *Chem. Comm.*, 1966, 658; C. K. Prout, R. A. Armstrong, I. R. Carruthers, J. C. Forrest, P. Murray-Rust, and F. J. C. Rossotti, *J. Chem. Soc.* (*A*), 1968, 2791; H. C. von Schnering, *Z. anorg. Chem.*, 1967, **353**, 13.

[2] B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 135.

[3] R. C. E. Belford, D. E. Fenton, and M. R. Truter, *J.C.S. Dalton*, 1972, 2208.

[4] M. V. Veidis, G. H. Schreiber, T. E. Gough, and G. J. Palenik, *J. Amer. Chem. Soc.*, 1969, **91**, 1859.

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

[6] (*a*) D. P. Graddon, *Co-ordination Chem. Rev.*, 1969, **4**, 1, and references therein; (*b*) L. L. Funck and T. R. Ortolano, *Inorg. Chem.*, 1968, **7**, 567, and references therein.

[7] H. Yokoi, M. Sai, and T. Isobe, *Bull. Chem. Soc. Japan*, 1970, **43**, 1078.

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

[9] A. A. Skljaev, V. F. Anufrienko, E. I. Berus, and Yu. N. Molin, *Doklady Akad. Nauk S.S.S.R.*, 1972, **207**, 138.

[10] D. Attanasio, I. Collamati, and C. Ercolani, *J.C.S. Dalton*, 1973, 2242

with the synthesis and investigation by electronic and e.s.r. spectra of a new series of *N*-base adducts of copper(II)-α-nitroketonates of formula [CuL$_2$B$_2$] (B = py, 4-mepy). The intention is to clarify conditions necessary for formation of the tetragonal forms above. The *N*-base adducts of [Cu(hfa)$_2$] and [Cu(salal)$_2$] formed with pyridine or 4-methylpyridine are also included in the present study.

EXPERIMENTAL

Preparation of Ligands.—Nitroacetone was prepared by the method of Hurd and Nilson.[11] 2-Nitroacetophenone was prepared following the procedure reported by Long and Troutman,[12] as modified.[13] The preparation of 3,3-dimethyl-1-nitrobutan-2-one was described previously.[14] 3-Nitrocamphor was used as the sodium salt (K & K) or as prepared from isonitrocamphor,[15] oxidized according to Lowry and Steele [16] and then converted into the sodium salt.

Preparation of Complexes.—[Cu(na)$_2$], [Cu(nta)$_2$], [Cu(nca)$_2$(H$_2$O)$_2$], [Zn(nap)$_2$(EtOH)$_2$], prepared as before,[9,16] and [Zn(na)$_2$(H$_2$O)$_2$] and [Zn(nca)$_2$(H$_2$O)$_x$] were used as starting materials for the preparations of the [ML$_2$B$_2$] species described below.

The preparations described below have the following in common. (a) Recrystallizations of complexes were always performed in the presence of small quantities of both the α-nitroketone and the base. Yields were between 70 and 80%.

(b) Bases were used as supplied (B.D.H. or K & K).

[Cu(na)$_2$(py)$_2$]. Pyridine (1 ml) was added to a solution of [Cu(na)$_2$] (300 mg, 1·1 mmol) in cold acetone (5 ml). Recrystallization was from acetone–hexane.

[Zn(na)$_2$(py)$_2$]. By crystallization of the analogous hydrate from acetone–hexane in the presence of base.

[Cu(nta)$_2$(py)$_2$]. [Cu(nta)$_2$] (300 mg, 0·85 mmol) was dissolved with heating in acetone–hexane containing pyridine.

[Cu(nca)$_2$(py)$_2$]. [Cu(nca)$_2$(H$_2$O)$_2$] (200 mg, 0·4 mmol) was dissolved with heating in a mixture of heptane (80 ml), pyridine (1 ml), and butanol (5 ml). Heptane (60 ml) was added to the filtered solution.

[Cu(na)$_2$(4-mepy)$_2$]. [Cu(na)$_2$] (300 mg, 1·1 mmol) was crystallized from acetone (5 ml) containing the base (1 ml).

[Zn(na)$_2$(4-mepy)$_2$]. [Zn(na)$_2$(H$_2$O)$_2$] (300 mg, 1·1 mmol) crystallized from a mixture of 20 ml of CH$_2$Cl$_2$ (20 ml), hexane (70 ml), and 4-mepy (0·6 ml).

[Cu(nta)$_2$(4-mepy)$_2$]. [Cu(nta)$_2$] (300 mg, 0·85 mmol) was crystallized from acetone (4 ml), hexane (25 ml), and 4-mepy (2 ml).

[Zn(nta)$_2$(4-mepy)$_2$]. 3,3-Dimethyl-1-nitrobutan-2-one (300 mg, 2·1 mmol) was added to [Zn(OCOCH$_3$)$_2$(H$_2$O)$_2$] (220 mg, 1 mmol) dissolved in a mixture of 4-mepy (1 ml) and butanol (2·5 ml). The complex precipitates on addition of heptane (20 ml). Crystallization was from CH$_2$Cl$_2$–heptane.

[Cu(nca)$_2$(4-mepy)$_2$]. [Cu(nca)$_2$(H$_2$O)$_2$] (300 mg, 0·6 mmol) was crystallized from hot hexane (40 ml), containing base (2 ml) and a few drops of acetone.

[Zn(nca)$_2$(4-mepy)$_2$]. [Zn(nca)$_2$(H$_2$O)$_x$] (230 mg, 0·5 mmol) was crystallized from a mixture of hexane (30 ml) and 4-mepy (6 ml).

[Zn(nap)$_2$(4-mepy)$_2$]. [Zn(nap)$_2$(EtOH)$_2$] (600 mg, 1·2 mmol) was crystallized from boiling 4-mepy (4 ml).

[Cu(nap)$_2$(py)$_2$] and [Zn(nap)$_2$(py)$_2$] were prepared as before.[8,17] [Cu(hfa)$_2$(py)$_2$], [Cu(hfa)$_2$(4-mepy)$_2$],[18] [Cu(salal)$_2$],[19] and [Zn(hfa)$_2$(H$_2$O)$_2$] [20] were prepared as in the literature. [Zn(hfa)$_2$(py)$_2$]. [Zn(hfa)$_2$(H$_2$O)$_2$] (500 mg, 0·97 mmol) was crystallized from a mixture of benzene, (12 ml), pyridine (1·5 ml), and hexane (25 ml).

[Zn(hfa)$_2$(4-mepy)$_2$]. [Zn(hfa)$_2$(H$_2$O)$_2$] (500 mg, 0·97 mmol) was crystallized from a mixture of benzene (8 ml), 4-mepy (1·5 ml), and hexane (50 ml).

Physical Measurements.—Magnetic, spectroscopic, and *X*-ray measurements were carried out by the usual techniques.[14]

E.s.r. spectra were recorded on CHCl$_3$(ethanol free)–CH$_2$Cl$_2$ (1 : 1) frozen solutions or diluted polycrystalline samples, at 110 K on a Varian V 4502-4 spectrometer (*X*-band). $A_\perp$ Values were usually not resolved; *g* values were obtained directly from the spectra after calibration with DPPH.

Isotopically pure ^{63}Cu was used, and dilution accomplished by simply cocrystallizing the Cu and Zn complexes (*ca.* 1 : 200) from the appropriate solvent. A large excess of base (*ca.* 5%) was used during measurements of solution spectra of the 1 : 2 adducts. Use of stoicheiometric quantities gave identical spectra.

RESULTS AND DISCUSSION

Copper(II)-α-nitroketonates (chromophore CuO$_4$) including [Cu(nap)$_2$],[17] show comparable tendency towards bis-adduct formation with pyridine and 4-methylpyridine (Table 1). The tendency is also comparable towards mono-adduct formation with α,α′-bipyridyl and *o*-phenanthroline [10] and also with 2-methylpyridine, 2,6-dimethylpyridine, and quinuclidine.[21] This behaviour is in keeping with the previously noticed [14] scarce influence exerted by the substituents on the donor properties of the α-nitroketonic group L, which determines almost undifferentiated Lewis acceptor properties for the [CuL$_2$] species. Only in the case of interaction of [Cu(nta)$_2$] with an excess of 4-methylpyridine is there simultaneous formation of both the mono- [21] and the bis-adduct. The latter transforms into the former in air. This behaviour probably arises from the appreciable electron-repulsive effect of the Me$_3$C-group which determines a greater co-ordinative saturation on copper(II) in [Cu(nta)$_2$], thus tending to stabilize the mono-adduct with respect to the bis-adduct.

A discussion of the [CuL$_2$B$_2$] species presented here will necessarily start from the assessment of their co-

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[11] C. D. Hurd and M. E. Nilson, *J. Org. Chem.*, 1955, **20**, 927.

[12] L. M. Long and H. O. Troutman, *J. Amer. Chem. Soc.*, 1949, **71**, 2469.

[13] C. Ercolani, I. Collamati, and G. Sartori, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1966, **40**, 558.

[14] D. Attanasio, I. Collamati, and C. Ercolani, *J.C.S. Dalton*, 1972, 772.

[15] G. Oddo, *Gazzetta*, 1893, **23**, 85.

[16] T. M. Lowry and V. Steele, *J. Chem. Soc.*, 1916, 1038.

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

[18] W. R. Walker and N. C. Li, *J. Inorg. Nuclear Chem.*, 1965, **27**, 2255.

[19] Y. Muto, *Bull. Chem. Soc. Japan*, 1958, **31**, 56.

[20] M. L. Morris, R. W. Moshier, and R. E. Sievers, *Inorg. Chem.*, 1963, **2**, 411; S. C. Chattaraj, A. G. Cupka, and R. E. Sievers, *J. Inorg. Nuclear Chem.*, 1966, **28**, 1937.

[21] D. Attanasio, I. Collamati, and C. Ercolani, unpublished results.

TABLE 1

Elemental analyses and some properties of the complexes

Compound	Colour	M.p. (t/°C) *	μ_{eff} (B.M.) †	Analyses (%) Calc. C	H	N	Found C	H	N
$[Cu(na)_2(py)_2]$	Light green	104	1·87	45·1	4·25	13·15	44·95	4·3	13·15
$[Cu(na)_2(4\text{-}mepy)_2]$	Bright green	138	1·93	47·6	4·9	12·35	47·65	5·1	12·45
$[Cu(nta)_2(py)_2]$	Emerald green	110	1·88	51·8	5·95	11·0	51·15	6·0	10·55
$[Cu(nta)_2(4\text{-}mepy)_2]$	Emerald green	110	1·92	53·55	5·8	10·35	53·55	6·35	10·4
$[Cu(nca)_2(py)_2]$	Yellow-brown	136	1·94	58·6	6·2	9·1	58·6	6·15	9·3
$[Cu(nca)_2(4\text{-}mepy)_2]$	Light green	140	1·96	59·85	6·55	8·7	59·7	6·85	8·35
$[Zn(na)_2(py)_2]$	White	104	diam.	44·95	4·2	13·1	44·8	4·3	13·1
$[Zn(na)_2(4\text{-}mepy)_2]$	White	140	diam.	47·4	4·85	12·3	47·15	4·9	12·65
$[Zn(nta)_2(4\text{-}mepy)_2]$	Light yellow	162	diam.	53·35	6·3	10·35	53·35	6·35	10·25
$[Zn(nca)_2(4\text{-}mepy)_2]$	White	145	diam.	59·6	6·5	8·7	59·9	6·15	7·8
$[Zn(nap)_2(4\text{-}mepy)_2]$	Light yellow	155	diam.	58·0	4·5	9·65	58·15	4·7	9·5
$[Zn(hfa)_2(py)_2]$	White	150	diam.	37·5	1·9	4·4	38·7	2·1	4·3
$[Zn(hfa)_2(4\text{-}mepy)_2]$	White	147	diam.	39·7	2·4	4·2	40·0	2·45	4·1

* Melting or decomposition point. † Calculated from the formula $\mu_{eff} = 2{\cdot}84\ (\chi_A . T)^{\frac{1}{2}}$; diamagnetic corrections were calculated from Pascal's constants.

ordination number. All these $[CuL_2B_2]$ species may be rather straightforwardly assigned a monomeric six-co-ordinate structure (chromophore CuO_4N_2) on the basis of their stoicheiometry, and the well established bidentate nature of the *O*-donors [14] and monodentate nature of the *N*-bases. Further support to this assignment derives from the following arguments. (i) The room temperature magnetic moments (Table 1) of all solid $[CuL_2B_2]$ species are above the spin-only value, as expected for non-associated species. (ii) $[Cu(na)_2(py)_2]$ and $[Cu(nta)_2(py)_2]$ are isomorphous with their cobalt(II) and nickel(II) analogues [14] known to be six-co-ordinate and pseudo-octahedral from magnetic and spectroscopic data. (iii) The reflectance and solution spectra of all $[CuL_2B_2]$ species in the region 6·0—25·0 kK are very similar to one another in number and intensity of the absorptions present (Figure 1, Table 2), and are also very similar to that [8] of the six-co-ordinate [5] $[Cu(nap)_2(4\text{-}mepy)_2]$ and of other similar species for which a six-co-ordinate structure was suggested.[8,10]

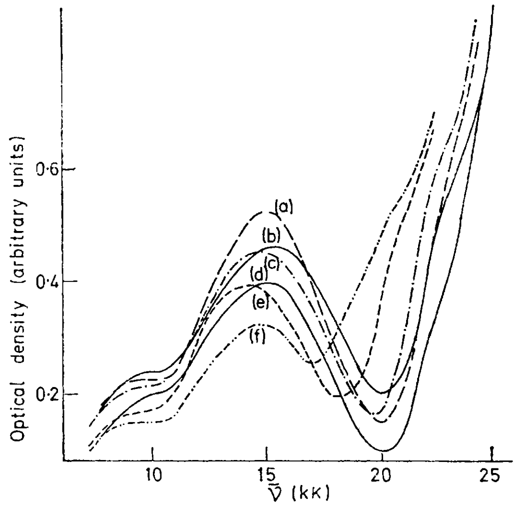

FIGURE 1 Reflectance spectra of (a), $[Cu(na)_2(py)_2]$; (b), $[Cu(na)_2(4\text{-}mepy)_2]$; (c), $[Cu(nta)_2(py)_2]$; (d), $[Cu(nta)_2(4\text{-}mepy)_2]$; (e), $[Cu(nca)_2(4\text{-}mepy)_2]$; (f), $[Cu(nca)_2(py)_2]$

Information as to the symmetry and arrangement of the ligands around copper(II) in the $[CuL_2B_2]$ species can be achieved from the electronic and e.s.r. spectral data summarized in Tables 2 and 3. These data will now be discussed in some detail.

Electronic and E.S.R. Spectra.—Both solid state and solution electronic spectra of $[CuL_2B_2]$ species consist of three bands at 9·0—9·75 kK (ν_1), 14—15 kK (ν_2), and 19—22 kK (ν_3). Assuming an elongated tetragonal structure, the lowest energy absorption (ν_1) is associated with the transition $d_{z^2} \longrightarrow d_{x^2-y^2}$ (or d_{xy}), whereas the main visible absorption envelope (ν_2) consists of the other overlapping *d–d* transitions; the near u.v. band is believed to be non-*d–d* in origin.[8,10,17] Taking the energy of ν_1 as indicative of the amount of tetragonality present,[22,10] then 'restricted' tetragonal distortion may be assigned to the $[CuL_2B_2]$ species in both phases, since the ν_1 values are in all cases close to the value (9·5 kK) observed for solid $[Cu(nap)_2(4\text{-}mepy)_2]$,[8] in which 'restricted' tetragonal distortion was unequivocally established by *X*-ray data [10] [(Ic) type structure]. It may be also be noticed that this type of distortion was found in *cis*-$[CuL_2B']$ species [10] [(Ib) type structure], for which ν_1 values of 9—10 kK were observed. Electronic spectra, therefore, clearly indicate 'restricted' tetragonal distortion for the $[CuL_2B_2]$ species. We anticipate that this arises from the in-plane co-ordination of the N atoms and in-plane–out-of-plane co-ordination of the bidentate *O*-donors, as supported by e.s.r. spectra.

Low temperature e.s.r. spectra of $[CuL_2B_2]$ species both as solid samples, diluted in isomorphous or non-isomorphous zinc(II) matrices, and frozen solutions in $CHCl_3$(ethanol free)–CH_2Cl_2 indicate the presence in all cases of a magnetic centre with $g_{\parallel}$ *ca.* 2·30 and $g_{\perp}$ *ca.* 2·07. These g values are indicative of tetragonal elongated structures. More complicated spectra are observed in a few cases for the polycrystalline materials, due to the presence of magnetic centres with tetragonally compressed environments (see below). E.s.r. spectra consistent with elongated symmetries also

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[22] R. J. Dudley and B. J. Hathaway, *J. Chem. Soc.* (*A*), 1970, 2794.

show, except for solid $[\mathrm{Cu(nta)_2(4\text{-}mepy)_2}]$, clearly detectable ^{14}N hyperfine splitting on the bands of $g_{\|}$ (at least on that of $M_I = -3/2$). Such hyperfine splitting is of the type observed previously [10] for similar $\mathrm{CuO_4N_2}$ chromophores (five peaks with 1 : 2 : 3 : 2 : 1 intensity ratio) and consistent with two equivalent N atoms co-ordinated to copper(II) in the *xy* plane (along the $d_{x^2-y^2}$ or d_{xy}) (Table 3, last column). It therefore appears from the above data that, although the e.s.r. data were taken under different experimental conditions than the electronic spectra, nevertheless, both sets of data allow the same conclusions to be drawn about the structure present in these $[\mathrm{CuL_2B_2}]$ species.

TABLE 2

Electronic spectra of copper(II) complexes in the region 6·0—25·0 kK

Compound [a]	Medium [b]	ν_1 [c]	ν_2 [c]	ν_3 [c]	D [d]
$[\mathrm{Cu(na)_2(py)_2}]$	DR	*9·25* (1080, 0·21)	15·05 (665, 0·48)	*23·0* (435)	0·44
$[\mathrm{Cu(na)_2}]$	Pyridine	*9·25* (1080, 23·5)	13·9 (720, 51)		0·46
$[\mathrm{Cu(na)_2(4\text{-}mepy)_2}]$	DR	*9·6* (1040, 0·21)	15·3 (655, 0·43)	*23·3* (430)	0·49
$[\mathrm{Cu(na)_2}]$	$\mathrm{CH_2Cl_2}$–4-mepy	9·75 (1025, 26)	14·1 (710, 59)		0·44
$[\mathrm{Cu(nta)_2(py)_2}]$	DR	*9·1* (1100, 0·19)	14·8 (675, 0·44)	*22·8* (440)	0·45
$[\mathrm{Cu(nta)_2}]$	Pyridine	*9·1* (1100, 24·5)	14·0 (715, 55)		0·45
$[\mathrm{Cu(nta)_2(4\text{-}mepy)_2}]$	DR	*9·1* (1100, 0·18)	15·2 (660, 0·39)	*22·8* (440)	0·46
$[\mathrm{Cu(nta)_2}]$	4-mepy	*9·5* (1025, 25·5)	14·0 (715, 57)		0·45
$[\mathrm{Cu(nca)_2(py)_2}]$	DR	*9·0* (1115, 0·15)	14·8 (675, 0·31)	*20·4* (490)	0·46
$[\mathrm{Cu(nca)_2(Me_2CO)_2}]$	Pyridine	*8·95* (1120, 21)	13·8 (725, 51)		0·41
$[\mathrm{Cu(nca)_2(4\text{-}mepy)_2}]$	DR	*9·0* (1115, 0·16)	14·2 (705, 0·38)	*20·6* (485)	0·42
$[\mathrm{Cu(nca)_2(Me_2CO)_2}]$	4-mepy	*9·05* (1110, 21)	14·1 (710, 52)	*22·5* (445, 94)	0·41
$[\mathrm{Cu(nap)_2(py)_2}]$ ‘a’	DR	7·0 (1425, 0·39)	13·0 (770, 0·54)	*21·3* (470)	0·72
$[\mathrm{Cu(nap)_2(py)_2}]$ ‘b’	DR	9·1 (1100, 0·28)	14·3 (705, 0·32)	*21·5* (465)	0·88
$[\mathrm{Cu(nap)_2(py)_2}]$ ‘b’	Pyridine	9·5 (1050, 23)	14·2 (705, 57)	*21·7* (460, 125)	0·41
$[\mathrm{Cu(nap)_2(4\text{-}mepy)_2}]$	DR	*9·5* (1050, 0·22)	15·4 (650, 0·53)	*21·9* (455)	0·42
$[\mathrm{Cu(nap)_2(4\text{-}mepy)_2}]$	4-mepy	9·9 (1010, 24·5)	14·5 (590, 58·5)	*20·5* (485, 75)	0·42
$[\mathrm{Cu(hfa)_2(py)_2}]$	DR	9·1 (1100, 0·60)	14·4 (695, 0·55)	*22·7* (440), 24·1 (415)	1·10
$[\mathrm{Cu(hfa)_2(H_2O)_2}]$	Pyridine	9·15 (1090, 21·5)	14·3 (700, 44)		0·49
$[\mathrm{Cu(hfa)_2(4\text{-}mepy)_2}]$	DR	*8·9* (1125, 0·16)	13·6 (735, 0·35)	*23·0* (435), 24·4 (410)	0·46
$[\mathrm{Cu(hfa)_2(H_2O)_2}]$	4-mepy	9·4 (1065, 21)	14·4 (695, 46)		0·46

[a] Spectra in solution are of starting compounds in neat base. [b] DR = diffuse reflectance. [c] Absorptions given in italic numbers indicate shoulders, values in units of kK, numbers in parentheses are absorption frequency in nm, and optical density or molar extinction coefficient. [d] D = intensity ratio ν_1/ν_2.

TABLE 3

Low temperature (110 K) e.s.r. spectra of diluted solid samples and frozen solutions of $^{63}\mathrm{Cu^{II}}$ complexes

Compound	Medium [a]	$g_{\|} \pm 0{\cdot}002$	$g_{\perp} \pm 0{\cdot}005$	$(A_{\|}^{^{63}\mathrm{Cu}} \pm 1{\cdot}0) \,.\, 10^4\ \mathrm{cm^{-1}}$	$(A^{\mathrm{N}} \pm 0{\cdot}5) \,.\, 10^4\ \mathrm{cm^{-1}}$	$A_{\perp}^{^{63}\mathrm{Cu}}\ (\mathrm{cm^{-1}})$	S [b]	N [c]
$^{63}\mathrm{Cu,Zn(nap)_2(4\text{-}mepy)_2}$	DS	2·302	2·073	149	9·6		E	2
$^{63}\mathrm{Cu(nap)_2(4\text{-}mepy)_2}$	FS	2·304	2·066	162	10·2		E	2
$^{63}\mathrm{Cu,Zn(na)_2(4\text{-}mepy)_2}$	DS	2·309	2·068	161	10·8		E	2
$^{63}\mathrm{Cu(na)_2(4\text{-}mepy)_2}$	FS	2·302	2·070	161·5	9·9		E	2
$^{63}\mathrm{Cu,Zn(na)_2(py)_2}$	DS	2·306	2·071	158	10·7		E	2
		2·033	2·247	45		69	C	?
$^{63}\mathrm{Cu(na)_2(py)_2}$	FS	2·305	2·064	161·5	10		E	2
$^{63}\mathrm{Cu,Zn(nap)_2(py)_2}$	DS	2·323	2·080	146			E	?
		2·052	2·228			68	C	?
$^{63}\mathrm{Cu(nap)_2(py)_2}$	FS	2·307	2·069	162	10·2		E	2
$^{63}\mathrm{Cu,Zn(nta)_2(4\text{-}mepy)_2}$	DS	2·335	2·095	133	8·7		E	1
$^{63}\mathrm{Cu(nta)_2(4\text{-}mepy)_2}$	FS	2·311	2·068	165·5	10·7		E	2
$^{63}\mathrm{Cu(nta)_2(py)_2}$	FS	2·314	2·071	163	10·7		E	2
$^{63}\mathrm{Cu(nca)_2(py)_2}$	FS	2·300	2·061	153·5	10·0		E	2
$^{63}\mathrm{Cu(nca)_2(4\text{-}mepy)_2}$	FS	2·293	2·068	160·5	9·6		E	2
$^{63}\mathrm{Cu,Zn(hfa)_2(py)_2}$	DS	2·321	2·070	154	10		E	2
$^{63}\mathrm{Cu(hfa)_2(py)_2}$	FS	2·306	2·074	162	9·7		E	2
$^{63}\mathrm{Cu,Zn(hfa)_2(4\text{-}mepy)_2}$	DS	2·339	2·075	146	9·7		E	2
			2·249		8·5	91	C	?
$^{63}\mathrm{Cu(hfa)_2(4\text{-}mepy)_2}$	FS	2·302	2·071	160	9·7		E	2
$^{63}\mathrm{Cu(salal)_2(py)_2}$	FS	2·324	2·069	163	10		E	2
$^{63}\mathrm{Cu(salal)_2(4\text{-}mepy)_2}$	FS	2·321	2·070	162·5	9·6		E	2

[a] DS = Diluted solid, FS = Frozen solution. [b] S = Tetragonal symmetry, E = elongated, C = compressed. [c] N = Equatorial nitrogen atoms.

The intensity ratio $D = \nu_1/\nu_2$ is reported for all the species examined (use has been made of the optical densities for the solid and molar extinction coefficients for the solution) in the last column of Table 2. Confining attention to the complexes of α-nitroketones only, it is observed that, with the exception of the two solid isomers of $[\mathrm{Cu(nap)_2(py)_2}]$ (for these two complexes see further discussion below), D is always within the narrow range 0·42—0·49. A D value of 0·45 has been found for solid *trans*-$[\mathrm{Cu(nap)_2(4\text{-}mepy)_2}]$ [(Ic) type structure]. In contrast, for the series of *cis*-hetero-tris-chelates of formula $[\mathrm{CuL_2B'}]$ [10] [B′ = bipy, phen; (Ib) type structure] the D values, calculated from both the solid state and solution spectra, have been found to lie, with only one exception, between 0·65 and 1·0. Ligand arrangement around copper(II) in these complexes should be very similar to that found by *X*-rays in $[\mathrm{Cu(hfa)_2(bipy)}]$.[4] The electronic spectrum of this complex, which has a D value of 0·90, has been interpreted in terms of D_2 effective symmetry (ground state d_{xy}).[22] More importantly, ν_1 (9·4 kK) was associated with the electronically allowed (z) $d_{z^2} \longrightarrow d_{xy}$ transition. Conversely, in the case of a *trans*-arrangement of the ligands around copper(II) in an elongated tetragonal environment an electronically forbidden transition $d_{z^2} \longrightarrow d_{x^2-y^2}$ (or d_{xy}) would be expected, whatever the effective symmetry around copper(II). This might be expected to result in a lower D value, as indeed occurs for solid *trans*-[Cu(nap)$_2$(4-mepy)$_2$]. The D values observed for the [CuL$_2$B$_2$] species are consistently lower than those found for the *cis*-complexes discussed above and closely approach the value found for solid *trans*-[Cu(nap)$_2$(4-mepy)$_2$]. If diagnostic use is made of the above data, then a *trans*-structure would be suggested for the [CuL$_2$B$_2$] species on the basis of the D values observed. This suggestion appears to be in keeping with the general observation that, when allowance is made for *trans*- or *cis*-structures, the former are found more frequently than the latter.

It has already been pointed out that neutral [CuL$_2$] species formed from β-diketones show Lewis acid properties comparable to those exhibited by the corresponding copper(II) complexes of α-nitroketones only when L carries strongly electron withdrawing groups.[23] This is why hexafluoroacetylacetone has been taken as a representative example for comparison, and it is not surprising that [Cu(hfa)$_2$], like copper(II)–α-nitroketonates, forms solid stable bis-adducts with pyridine and 4-methylpyridine. The electronic and e.s.r. spectra of these two adducts are summarized in Tables 2 and 3. All e.s.r. spectra indicate the presence of a magnetic centre of elongated tetragonal symmetry ($g_\parallel > g_\perp$) and equatorial N atoms. The *cis*-structure (Ib) is strongly suggested by the electronic spectrum of solid [Cu(hfa)$_2$(py)$_2$], which gives a D value of 1·10, the highest observed among all the *cis*-complexes examined.* Instead, a D value of 0·49 is obtained in neat pyridine (*ca.* 0·33 is the value estimated directly from the spectrum taken in CCl$_4$ [6b]) and this suggests the assignment of a *trans*-structure (Ic) to the complex in solution. These assignments are in contrast with those given by Funck and Ortolano,[6b] who assumed axial ligation of the N atoms. Furthermore, they are only in partial agreement with the *cis*-structure suggested by Dudley and Hathaway,[22] who made reference to the energy of ν_1 and ν_2, but not to their relative intensity, and apparently no distinction between solid state and solution. In the case of [Cu(hfa)$_2$(4-mepy)$_2$] a *trans*-arrangement (Ic) can be proposed for both the solid and solution, since in both media a D value of 0·46 is obtained.

If the above and previous [10] results, and those given by H. Yokoi *et al.*[7] confirmed by us on the bis-pyridine and bis-4-methylpyridine derivatives of Cu(salal)$_2$ (Table 3), are combined together, it is concluded that 'restricted' tetragonal distortion, implying in-plane co-ordination of the N atoms and in-plane–out-of-plane co-ordination of the chelating *O*-donors, occurs quite commonly in the type of CuO$_4$N$_2$ chromophores discussed here.

Some of the polycrystalline samples given in Table 3 show anomalies which need to be discussed in some detail. E.s.r. spectra of different samples of [Cu(na)$_2$(py)$_2$], diluted in the isomorphous zinc(II) matrix, are given in Figure 2. These spectra indicate the presence of two magnetic centres, apparently obtained casually, sometimes separately (Figure 2a and 2b), sometimes simultaneously (Figure 2c). The e.s.r. spectrum of Figure 2a shows the copper(II) ion involved in the already discussed elongated tetragonal environment ($g_\parallel > g_\perp$). Instead, that of Figure 2b is indicative of a compressed tetragonal symmetry ($g_\parallel < g_\perp$; d_{z^2} ground state), rather uncommon for copper(II). Since the spectra of Figure 2 were obtained from samples of different preparations, isomorphous among themselves and also with the analogous pure copper(II) and zinc(II) complexes, we presume that the casual formation of only one or both sites is not due to a significant variation in the crystal packing, but, rather, to small distortions at the molecular level.

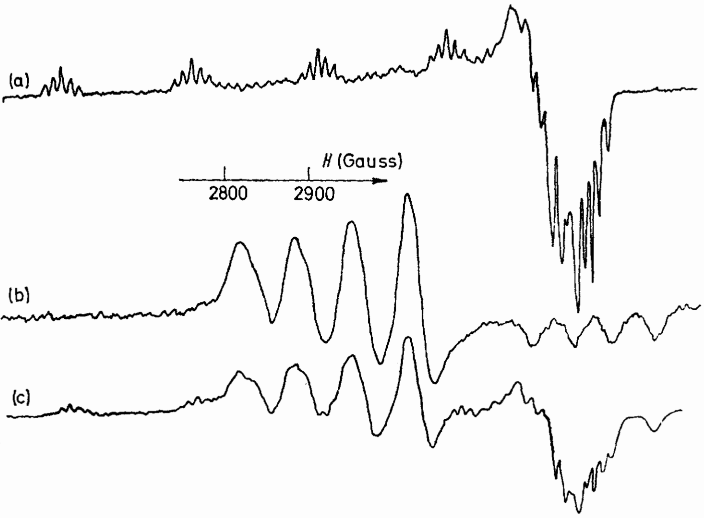

FIGURE 2 E.s.r. spectra of polycrystalline samples of [^{63}Cu(na)$_2$(py)$_2$] diluted in the isomorphous zinc(II) matrix

Two isomers of [Cu(nap)$_2$(py)$_2$] were previously described and their structures investigated mainly on the basis of electronic spectra.[8] The yellow isomer, known to be *trans* and isomorphous with the zinc(II) analogue from *X*-rays,[8] was assigned structure (Ia), with the nitrogen atoms at the axial positions. The much more easily obtainable green isomer was, instead, tentatively assigned a *cis*-structure of type (Ib). Further support to this assignment comes from the similarity of the electronic spectrum with those of all the *cis*-[CuL$_2$B′] species,[10] not only in number and energy of the bands present, but also in the relative intensity of ν_1 and ν_2 ($D = 0{\cdot}88$). Dilution of the

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* Very recently the crystal and molecular structure determination of Cu(hfa)$_2$(py)$_2$ has confirmed the existence of a *cis*-CuO$_4$N$_2$ chromophore (J. Pradilla-Sorzano and J. P. Fackler, jun., *Inorg. Chem.*, 1973, **12**, 1174).

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

green *cis*-isomer into the host lattice of the corresponding zinc(II) complex gives a polycrystalline sample isomorphous with both the yellow isomer and the zinc(II) complex, as expected. The e.s.r. spectrum of the diluted sample indicates the presence of both elongated ($g_{\parallel} > g_{\perp}$) and compressed ($g_{\parallel} < g_{\perp}$) tetragonal sites (Table 3), with no evidence of ^{14}N hyperfine structure for either. If the pure yellow isomer is assigned the elongated tetragonal structure, as it seems more likely, then the presumed absence of ^{14}N hyperfine splitting, would further support the structure (Ia), with axial nitrogen atoms, which was previously suggested for this isomer.

A peculiarity is shown by the e.s.r. spectrum of $[Cu(nta)_2(4\text{-mepy})_2]$ when diluted in the non-isomorphous zinc(II) matrix. Since $g_{\parallel} > g_{\perp}$ the structure is elongated tetragonal; however, the ligand hyperfine splitting (3 peaks about $M_I = -3/2$ of roughly equal intensity) indicates interaction of the unpaired electron with only one nitrogen atom. This may be explained in two ways: (a) $[Cu(nta)_2(4\text{-mepy})_2]$ enters the zinc(II) matrix as such, with the two nitrogen atoms co-ordinated one in-plane and the other out-of-plane; (b) more likely, a mono-adduct is formed (which has, in fact, been isolated in the pure state [21]), and a five-co-ordinate species, approximately square pyramidal with the nitrogen atom in-plane, enters the zinc(II) matrix.

Finally, the e.s.r. spectrum of $[Cu(hfa)_2(4\text{-mepy})_2]$ also shows an additional magnetic centre with compressed tetragonal symmetry ($g_{\parallel} < g_{\perp}$; d_{z^2} ground state). ^{14}N Hyperfine splitting occurs, of the type expected for two equivalent nitrogen atoms. However, this hyperfine does not allow localization of the nitrogen atoms, since the shape of the d_{z^2} orbital implies interaction of the unpaired electron with axial as well as in-plane nitrogen atoms.

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