Complexing Properties of α-Nitroketones. Part III.[1] A Stereochemical Investigation of Some New Copper(II) α-Nitroketonate Complexes and Their Base Adducts with *O*- and *N*-Donors

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Complexes $[CuL_2]$, $[CuL_2B_2]$, and $[CuL_2B']$ (L = an α-nitroketonato-anion obtained from nitroacetone, 3,3-dimethyl-1-nitrobutan-2-one, and 3-nitrocamphor; B = water or acetone; B′ = 2,2′-bipyridine or 1,10-phenanthroline) have been prepared and investigated by electronic and e.s.r. spectroscopy, and magnetic and *X*-ray measurements. An elongated tetragonal symmetry is assigned to all the solid complexes studied, essentially square planar for the $[CuL_2]$ species (CuO_4 chromophore), six-co-ordinate and pseudo-octahedral for $[CuL_2B_2]$ (CuO_4O_2 chromophore). For the $[CuL_2B']$ species (CuO_4N_2 chromophore), which are also six-co-ordinate and pseudo-octahedral, with restricted tetragonal distortion, e.s.r. spectra indicate that both nitrogen atoms of the *N*-base are equatorially bound to Cu^{II}, with consequent in-plane co-ordination of only two of the oxygen atoms of the α-nitroketonic groups, while the other two oxygen atoms are displaced to the axial positions.

EQUATORIAL, rather than the more usual axial, co-ordination of heterocyclic and other *N*-bases in adducts of the complex bis(2-nitroacetophenonato)copper(II), $[Cu(nap)_2]$, of chromophores CuO_4N and CuO_4N_2 has previously been suggested, mainly on the basis of electronic spectra.[2] Equatorial co-ordination of the *N*-base has been established by *X*-rays in the 1 : 1 adduct of the complex $[Cu(nap)_2]$ with α-picoline, $[Cu(nap)_2(\alpha\text{-pic})]$,[3] and, more recently,[4] in the 1 : 2 adduct of $[Cu(nap)_2]$ with γ-picoline, $[Cu(nap)_2(\gamma\text{-pic})_2]$. Both structures and that of $[Cu(nap)_2]$ [5] have the following salient features which concern the co-ordination about Cu^{II}.

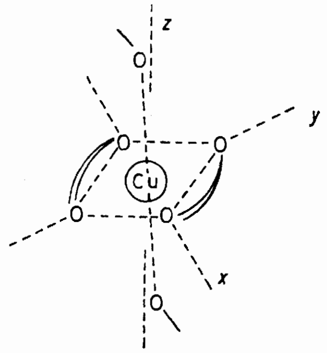
(i) In the complex $[Cu(nap)_2]$ there is *trans-planar* co-ordination (A) with equal in-plane Cu–O bonds (1·93 Å) and longer intermolecular Cu–O contacts (2·59 Å), giving a CuO_4O_2 chromophore.

(ii) The complex $[Cu(nap)_2(\alpha\text{-pic})]$ has an approximately *square-pyramidal* structure (B) with the nitrogen atom co-ordinated in-plane and one oxygen atom of a α-nitroketonic group displaced to the axial position with Cu–O(axial) = 2·16 Å, slightly longer than the other Cu–O in-plane distances (1·95, 1·92, and 1·96 Å).

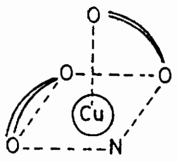
(iii) The complex $[Cu(nap)_2(\gamma\text{-pic})_2]$ is *six-co-ordinate* with *trans* in-plane nitrogen atoms and mixed axial and in-plane co-ordination of both α-nitroketonic groups having Cu–O(axial) = 2·25 Å and Cu–O(in-plane) = 1·99 Å (C).

Apart from this specific class of complexes, (4-aminopyridine)bis(acetylacetonato)copper(II) [6] and (2,2′-bipyridine)bis(hexafluoroacetylacetonato)copper(II) [7] can also be cited as examples of complexes of CuO_4N and CuO_4N_2 chromophores respectively, where equatorial co-ordination of the *N*-base and mixed axial–equatorial co-ordination of the bidentate *O*-donors has been crystallographically proved to occur.

This paper presents the preparation and characterization of a series of complexes $[CuL_2]$, $[CuL_2B_2]$, and $[CuL_2B']$ [LH = nitroacetone (I), 3,3-dimethyl-1-nitrobutan-2-one (II), and 3-nitrocamphor (III) (abbreviations in parentheses in the text indicate the corresponding anions); B = H_2O or MeCOMe; B′ = 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen)]. *X*-Ray powder data and spectroscopic and magnetic measurements are reported. More importantly, direct information on the structure of the $[CuL_2B']$ complexes, including those of $[Cu(nap)_2]$, has been obtained from e.s.r. spectra. The latter technique has proved very useful in investigating the symmetry around the metal ion and in-plane or out-of-plane co-ordination of the



(A)



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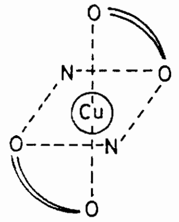

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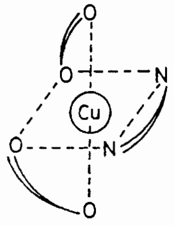

(D)

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

[3] M. Bonamico and G. Dessy, *Chem. Comm.*, 1970, 1218.

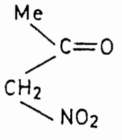
[4] M. Bonamico, G. Dessy, V. Fares, and L. Scaramuzza, *J.C.S. Dalton*, 1972, 2477.

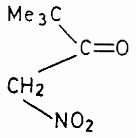
[5] M. Bonamico, I. Collamati, C. Ercolani, G. Dessy, and D. J. Machin, *Chem. Comm.*, 1967, 654.

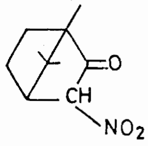
[6] G. W. Bushnell, *Canad. J. Chem.*, 1971, **49**, 555.

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

nitrogen and oxygen atoms in similar chromophores present in several mono- and bis-adducts of copper(II) β-diketonate complexes.[8,9] Determination of *g* values and detection of ^{14}N hyperfine splitting (about $g_{\parallel}$), in conjunction with electronic spectra and the 'model' structures given above, have allowed structural assignments to be made for the $[CuL_2B']$ species studied.


I (na)


II (nta)


III (nca)

EXPERIMENTAL

Previously described procedures were used for the preparation of α-nitroketones (I)—(III)[10] and of the adducts of the complex $[Cu(nap)_2]$.[2]

Preparation of Cu^{II} *and* Zn^{II} *Complexes* $[ML_2]$ *and* $[ML_2B_2]$ (B = *Water or Acetone*).—*Bis(nitroacetonato)copper*(II), $[Cu(na)_2]$. Nitroacetone (4·0 g, 39·0 mmol) was added to $CuAc_2,H_2O$ (3·50 g, 17·5 mmol) suspended in hot 95% ethanol (250 cm³). Yield 75% after cooling. Recrystallization was from 95% ethanol in the presence of a small quantity of (I).

Bis(3,3-*dimethyl*-1-*nitrobutan*-2-*onato*)*copper*(II), $[Cu(nta)_2]$. Solutions of $CuAc_2,H_2O$ (1·25 g, 6·25 mmol; water, 20 cm³) and 3,3-dimethyl-1-nitrobutan-2-one (1·82 g, 12·5 mmol; acetone, 15 cm³) were mixed. Yield 70%. Recrystallization was from acetone–hexane.

Diaquobis(3-*nitrocamphorato*)*copper*(II), $[Cu(nca)_2(H_2O)_2]$. Water solutions of 3-nitrocamphor (Na salt; 2·0 g, 9·1 mmol in 10 cm³ of water) and of $CuAc_2,H_2O$ (0·91 g, 4·55 mmol in 10 cm³ of water) were mixed. Yield 65%. This complex was used without further purification.

Bisacetonebis(3-*nitrocamphorato*)*copper*(II), $[Cu(nca)_2(MeCOMe)_2]$. This complex was obtained on recrystallizing the corresponding dihydrate from acetone. Yield *ca.* 50%.

Diaquobis(*nitroacetonato*)*zinc*(II), $[Zn(na)_2(H_2O)_2]$. $ZnAc_2,2H_2O$ (930 mg, 4·2 mmol) was added to a solution of nitroacetone (1·73 g, 16·8 mmol; twice the stoicheiometric amount) in absolute ethanol (15 cm³) under mild heating. Addition of hexane (60 cm³) yielded, after a few days, 95% of $[Zn(na)_2(H_2O)_2]$. Recrystallization was from absolute ethanol–hexane in the presence of a small quantity of ligand.

Diaquobis(3-*nitrocamphorato*)*zinc*(II), $[Zn(nca)_2(H_2O_2)]$. This complex was prepared as for the corresponding Cu^{II} complex. Recrystallization was from acetone–hexane.

Preparation of Cu^{II} *and* Zn^{II} *Adducts* $[ML_2B']$ (B' = 2,2'-*Bipyridine* or 1,10-*Phenanthroline*).—These adducts were generally prepared by using the above $[ML_2]$ or $[ML_2B_2]$ complexes, as starting materials. Zn^{II} adducts from (II) are exceptions because of the difficulty in obtaining the complex $[Zn(nta)_2]$. Recrystallizations were all carried out in the presence of a small quantity of ligand and base.

(2,2'-*Bipyridine*)*bis*(*nitroacetonato*)*copper*(II), $[Cu(na)_2(bipy)]$. The complex $[Cu(na)_2]$ (268 mg, 1·0 mmol) and 2,2'-bipyridine (160 mg, 1·0 mmol) were dissolved in hot absolute ethanol (20 cm³). Yield 95%. Recrystallization was from dichloromethane–hexane.

Bis(*nitroacetonato*)(1,10-*phenanthroline*)*copper*(II), $[Cu(na)_2(phen)]$. The complex $[Cu(na)_2]$ (268 mg, 1·0 mmol) and 1,10-phenanthroline (180 mg, 1·0 mmol) were dissolved in hot absolute ethanol (10 cm³). Precipitation was induced by addition of hexane (10 cm³). Yield 90%. Recrystallization was from dichloromethane–hexane.

(2,2'-*Bipyridine*)*bis*(3,3-*dimethyl*-1-*nitrobutan*-2-*onato*)-*copper*(II), $[Cu(nta)_2(bipy)]$. The complex $[Cu(nta)_2]$ (200 mg, 0·85 mmol) and 2,2'-bipyridine (140 mg, 0·9 mmol) were dissolved in hot absolute ethanol (25 cm³). Precipitation was induced by addition of hexane (20 cm³). Yield 60%. Recrystallization was from absolute ethanol–hexane.

Bis(3,3-*dimethyl*-1-*nitrobutan*-2-*onato*)(1,10-*phenanthroline*)*copper*(II), $[Cu(nta)_2(phen)]$. Hot acetone solutions of the complex $[Cu(nta)_2]$ (200 mg, 0·57 mmol; 100 cm³) and 1,10-phenanthroline (105 mg, 0·58 mmol; 100 cm³) were mixed. Yield 60%. Owing to its low solubility this adduct was used without further purification.

(2,2'-*Bipyridine*)*bis*(3-*nitrocamphorato*)*copper*(II), $[Cu(nca)_2(bipy)]$. A green precipitate of this complex was obtained by dissolving at room temperature $[Cu(nca)_2(H_2O)_2]$ (300 mg, 0·1 mmol) and 2,2'-bipyridine (95 mg, 0·61 mmol) in absolute EtOH and heptane. If the green precipitate was not quickly separated from the mother liquor, it transformed into a purple isomer, which is still under investigation.

Bis(3-*nitrocamphorato*)(1,10-*phenanthroline*)*copper*(II), $[Cu(nca)_2(phen)]$. The complex $[Cu(nca)_2(H_2O)_2]$ (300 mg, 0·61 mmol) and 1,10-phenanthroline (110 mg, 0·61 mmol) were dissolved in absolute ethanol (15 cm³). Precipitation of the complex was determined by addition of hexane (40 cm³). Yield 60%. Recrystallization was from absolute ethanol–hexane.

(2,2'-*Bipyridine*)*bis*(*nitroacetonato*)*zinc*(II), $[Zn(na)_2(bipy)]$ *and bis*(*nitroacetonato*)(1,10-*phenanthroline*)*zinc*(II), $[Zn(na)_2(phen)]$. These complexes were prepared with a procedure similar to that used for the parent Cu^{II} complexes.

(2,2'-*Bipyridine*)*bis*(3,3-*dimethyl*-1-*nitrobutan*-2-*onato*)-*zinc*(II), $[Zn(nta)_2(bipy)]$. $ZnAc_2,2H_2O$ (220 mg, 1·0 mmol) and (II) (350 mg, 2·4 mmol) were dissolved in absolute ethanol (5 cm³) containing 2,2'-bipyridine (160 mg, 1·0 mmol). Precipitation of the complex occurred on addition of hexane (10 cm³). Yield 75%. Recrystallization was from absolute ethanol–hexane.

Bis(3,3-*dimethyl*-1-*nitrobutan*-2-*onato*)(1,10-*phenanthroline*)*zinc*(II), $[Zn(nta)_2(phen)]$. This was prepared similarly to the $[Zn(nta)_2(bipy)]$ adduct. Recrystallization was from absolute ethanol.

(2,2'-*Bipyridine*)*bis*(3-*nitrocamphorato*)*zinc*(II), $[Zn(nca)_2(bipy)]$. $[Zn(nca)_2(H_2O)_2]$ (495 mg, 1·0 mmol) and 2,2'-bipyridine (156 mg, 1·0 mmol) was dissolved in acetone (30 cm³), and heptane (60 cm³) was added to precipitate the complex. Yield 95%. Recrystallization was from

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[8] B. B. Wayland and M. D. Wisniewski, *Chem. Comm.*, 1971, 1205.

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

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

acetone–hexane followed by prolonged drying *in vacuo* to completely eliminate traces of trapped acetone.

Bis(3-*nitrocamphorato*)(1,10-*phenanthroline*)*zinc*(II), [Zn(nca)$_2$(phen)]. The complex [Zn(nca)$_2$(H$_2$O)$_2$] (300 mg, 0·61 mg) and 1,10-phenanthroline (110 mg, 0·61 mmol) were dissolved in acetone (15 cm^3). The complex was precipitated on adding hexane. Yield 95%. Recrystallization was from dichloromethane–hexane.

(2,2′-*Bipyridine*)*bis*(2-*nitroacetophenonato*)*zinc*(II), [Zn(nap)$_2$(bipy)] *and bis*(2-*nitroacetophenonato*)(1,10-*phenanthroline*)*zinc*(II), [Zn(nap)$_2$(phen)]. The precipitation of these two adducts was obtained by dissolving equivalent amounts of the complex [Zn(nap)$_2$(EtOH)$_2$][11] and of the appropriate base in acetone, followed by addition of hexane. Recrystallization was from acetone–hexane for the 2,2′-bipyridine adduct and from dichloromethane for the 1,10-phenanthroline derivative.

Some properties and elemental analyses of the complexes are summarized in Table 1.

TABLE 1

Some properties and elemental analyses (%) of [ML$_2$], [ML$_2$B$_2$], and [ML$_2$B′] complexes

Complex	Colour	M.p.(t/°C)	μ_{eff}*/B.M.	Calc.			Found		
				C	H	N	C	H	N
[Cu(na)$_2$]	Deep green	169	1·93	26·9	3·0	10·5	26·9	3·0	9·9
[Cu(na)$_2$(bipy)]	Green	136	2·01	45·35	3·8	13·2	45·65	3·9	13·0
[Cu(na)$_2$(phen)]	Green	119	1·95	48·3	3·6	12·5	48·5	3·9	13·1
[Zn(na)$_2$(H$_2$O)$_2$]	White	106		23·6	3·9	9·2	24·0	4·1	9·15
[Zn(na)$_2$(bipy)]	White	185		45·1	3·8	13·2	45·1	3·9	13·05
[Zn(na)$_2$(phen)]	White	150		48·1	3·6	12·5	48·0	3·8	12·3
[Cu(nta)$_2$]	Grey-green	179	1·92	41·0	5·7	8·0	40·2	5·5	8·3
[Cu(nta)$_2$(bipy)]	Pale green	165	1·97	52·0	5·6	11·0	52·2	5·5	10·85
[Cu(nta)$_2$(phen)]	Pale green	195	1·92	54·3	5·3	10·5	54·7	5·3	10·5
[Zn(nta)$_2$(bipy)]	White	203		51·8	5·5	11·0	51·95	5·7	10·5
[Zn(nta)$_2$(phen)]	White	251		54·0	5·3	10·5	54·35	5·4	10·6
[Cu(nca)$_2$(H$_2$O)$_2$]	Pale green	155	2·01	48·8	6·6	5·7	48·7	6·7	5·0
[Cu(nca)$_2$(MeCOMe)$_2$]	Light brown	140	1·93	54·2	7·0	4·9	54·2	6·9	5·2
[Cu(nca)$_2$(bipy)]	Green	188	1·92	58·85	5·95	9·15	60·3	6·2	9·2
[Cu(nca)$_2$(phen)]	Yellow green	180	1·98	60·45	5·7	8·8	60·7	6·0	8·4
[Zn(nca)$_2$(H$_2$O)$_2$]	White	135		48·65	6·5	5·7	48·15	6·5	6·2
[Zn(nca)$_2$(bipy)]	White	210		58·7	5·9	9·1	58·5	6·2	9·2
[Zn(nca)$_2$(phen)]	White	260		60·2	5·7	8·8	60·2	5·8	8·8
[Zn(nap)$_2$(bipy)]	Pale yellow	210		56·8	3·7	10·2	56·7	4·1	10·3
[Zn(nap)$_2$(phen)]	Pale yellow	180		58·6	3·5	9·8	57·8	3·4	10·2

na = Nitroacetonato, bipy = 2,2′-bipyridine, phen = 1,10-phenanthroline, nta = 3,3-dimethyl-1-nitrobutan-2-onato, nca = 3-nitrocamphorato, and nap = 2-nitroacetophenonato.

* Calculated from $\mu_{\text{eff}} = 2{\cdot}84\,(\chi_A T)^{\frac{1}{2}}$; diamagnetic corrections were calculated from Pascal's constants.

Physical Measurements.—Instruments and techniques used for *X*-ray powder patterns, magnetic measurements, diffuse-reflectance, and solution visible spectra have been described previously.[10]

E.s.r. spectra were obtained, at 110 K, with a Varian 4502–4 spectrometer, using 100 kHz modulation within a Varian multipurpose cavity. Microwave frequencies were of the order of 9·15 GHz and were measured on a Hewlett–Packard X532B frequency counter; field measurements were made by the Fieldial magnetic system. The accuracy of g values was repeatedly checked with a polycrystalline sample of diphenylpicrylhydrazyl. Generally perpendicular copper coupling constants were not resolved; g values were obtained directly from the spectra. All the spectra were recorded on CHCl$_3$ (ethanol free) : CH$_2$Cl$_2$ (1 : 1) frozen solutions or diluted polycrystalline samples. The latter were prepared by recrystallization of the appropriate zinc(II) adduct in the presence of a small amount of the corresponding copper(II) adduct. Good results were obtained by recrystallizing the Zn$^{\text{II}}$ and Cu$^{\text{II}}$ adducts in a molar ratio of *ca.* 200 : 1. The final ratio in the diluted solid samples was not determined. Some of the copper complexes were prepared from ^{63}Cu (98%) isotope (purchased as ^{63}CuO from Oak Ridge National Laboratories, U.S.A.).

RESULTS AND DISCUSSION

The room-temperature magnetic moments of the complexes [Cu(na)$_2$] and [Cu(nta)$_2$], and of the bis(aquo) and bis(acetone) derivatives of [Cu(nca)$_2$] are given in Table 1. Data concerning their diffuse-reflectance and solution spectra are given in Table 2. A series of spectra of the complex of [Cu(na)$_2$] are shown in Figure 1. All four complexes have μ_{eff} values within 1·92 and 2·01 B.M., well above the 'spin-only' magnetic moment and scarcely diagnostic of the stereochemistry present. Visible reflectance spectra were very similar to one another and to the corresponding spectra in solution. They all showed a main absorption at *ca.* 15—16 kK and a shoulder at 20—22 kK. The latter absorption is assumed to be non-*d–d* in origin, for the reasons given previously for the complex [Cu(nap)$_2$][11] and its base adducts.[2] For all four complexes the *d–d* spectrum then consists of the envelope at 15—16 kK only, which is indicative of a tetragonally distorted ligand field. This is very probably essentially square planar for [Cu(na)$_2$] and [Cu(nta)$_2$], as it is for the complex [Cu(nap)$_2$], whose visible spectrum also shows a *d–d* absorption envelope at *ca.* 16 kK for the solid and at 15·3 kK in dichloromethane solution. The two bis-adducts of [Cu(nca)$_2$] are tentatively assigned a six-co-ordinate tetragonal structure with axial co-ordination of the solvent molecules.

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

The water and acetone molecules are relatively easily removed from the two adducts of the complex [Cu(nca)$_2$]. In acetone solution the water molecules of [Cu(nca)$_2$(H$_2$O)$_2$] are replaced by acetone molecules. This was indicated by the shift to higher frequency of ν_2 to a position identical with ν_2 in the reflectance and acetone solution spectrum of the complex [Cu(nca)$_2$(MeCOMe)$_2$]. Both the complexes [Cu(nca)$_2$(H$_2$O)$_2$] and [Cu(nca)$_2$(MeCOMe)$_2$] give identical spectra in CH$_2$Cl$_2$ solution and the shift of ν_2 to higher frequency suggests a more tetragonal character. This presumably occurs by elimination of the axial water and acetone molecules. This conclusion is supported by the fact that addition of hexane to a dichloromethane solution of the bis(hydrate) gave a light green precipitate which had an i.r. spectrum identical (apart from the absence of water bands in the 3600—3400 cm^{-1} region) to that of the bis(hydrate). The crystalline precipitate, which was not further investigated, is very hygroscopic, reverting to the complex [Cu(nca)$_2$(H$_2$O)$_2$] in air, and is thus believed to be [Cu(nca)$_2$].

TABLE 2

Diffuse-reflectance and solution spectra * of [CuL$_2$] complexes and their adducts in the region 6·0—25·0 kK

		(λ/nm, ε/l mol^{-1} cm^{-1})		
Complex	Medium	ν_1	ν_2	ν_3
[Cu(na)$_2$]	Solid, refl.		15·05 (665)	*22·3* (470)
	CHCl$_3$		14·9 (670, 35)	*21·5* (465, 45)
	MeCOMe		14·7 (680, 41)	*21·8* (460, 65)
[Cu(nta)$_2$]	Solid, refl.		15·75 (635)	*20·4* (490)
	CH$_2$Cl$_2$		15·4 (650, 44)	
	MeCOMe		14·8 (675, 47)	*22·0* (455, 77)
[Cu(nca)$_2$(H$_2$O)$_2$]	Solid, refl.		13·9 (720)	*20·2* (495)
	CH$_2$Cl$_2$		15·05 (665, 46)	*20·2* (495, 66)
	MeCOMe		14·4 (695, 47)	*20·4* (490, 61)
[Cu(nca)$_2$(MeCOMe)$_2$]	Solid, refl.		14·3 (700)	*20·4* (490)
	CH$_2$Cl$_2$		15·15 (660, 47)	*20·0* (500, 71)
	MeCOMe$_3$		14·4 (695, 52)	*20·4* (490, 70)
[Cu(na)$_2$(bipy)]	Solid, refl.	9·1 (1 100)	13·8 (725)	*22·5* (445)
	CHCl$_3$: CH$_2$Cl$_2$ (1 : 1)	*9·8* (1 020, 44)	13·8 (725, 66)	
[Cu(nta)$_2$(bipy)]	Solid, refl.	10·0 (1 000)	13·9 (720)	*22·5* (445)
	CHCl$_3$: CH$_2$Cl$_2$ (1 : 1)	*9·5* (1 050, 45)	14·0 (715, 65)	
[Cu(nca)$_2$(bipy)]	Solid, refl.	9·55 (1 045)	14·0 (715)	*20·9* (480)
	CHCl$_3$: CH$_2$Cl$_2$ (1 : 1)	*9·45* (1 060, 49)	13·35 (750, 76)	20·0 (500, 100)
[Cu(nap)$_2$(bipy)]†	Solid, refl.	*10·0* (1 000)	14·2 (705)	*21·5* (465)
	CH$_2$Cl$_2$	10·0 (1 000, 39)	14·2 (705, 63)	21·5 (465, 178)
[Cu(na)$_2$(phen)]	Solid, refl.	*9·6* (1 040)	13·7 (730)	*22·2* (450)
	CHCl$_3$: CH$_2$Cl$_2$ (1 : 1)	*9·65* (1 035, 40)	13·7 (730, 59)	
[Cu(nta) (phen)]	Solid, refl.	9·1 (1 100)	13·8 (725)	*22·5* (445)
	CHCl$_3$: CH$_2$Cl$_2$ (1 : 1)	*9·5* (1 050, 45)	14·0 (715, 65)	
[Cu(nca)$_2$(phen)]	Solid, refl.	8·5 (1 175)	13·8 (725)	*20·6* (485)
	CHCl$_3$: CH$_2$Cl$_2$ (1 : 1)	*9·4* (1 060, 48)	13·5 (740, 70)	*20·0* (500·105)
[Cu(nap)$_2$(phen)]†	Solid, refl.	*10·5* (950)	13·8 (725)	*21·5* (465)
	CH$_2$Cl$_2$	10·0 (1 000, 25)	14·1 (710, 67)	*21·7* (460, 95)

* Italicized figures indicate shoulders. † See ref. 4.

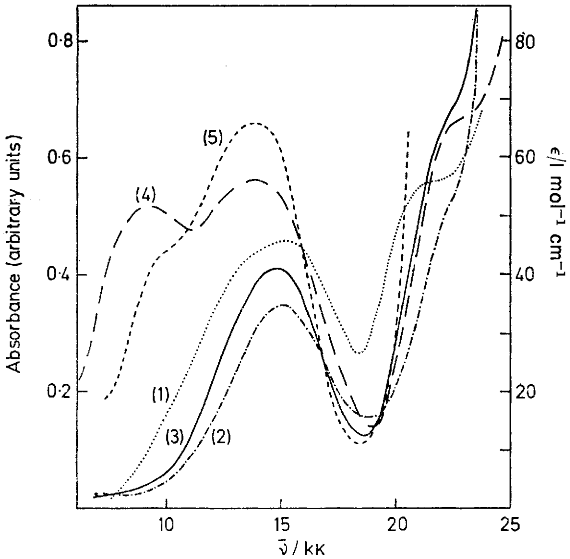

FIGURE 1 Spectra of the complexes [Cu(na)$_2$] (1)—(3) and [Cu(na)(bipy)] (4), (5): (1) and (4), diffuse reflectance; (2), solution in CHCl$_3$ (ethanol-free); (3), solution in acetone; and (5), solution in CHCl$_3$ (ethanol-free) : CH$_2$Cl$_2$ (1 : 1)

The [CuL$_2$B'] complexes are magnetically normal (Table 1) and had reflectance spectra (Table 2) between 6·0 and 25·0 kK, with ligand-field absorptions of comparable intensity at 8·5—10·0 kK (ν_1) and 13·8—14·0 kK (ν_2). The non-*d*-*d* shoulder was also present at 20·0—22·0 kK (ν_3) in all the spectra. These remained substantially unchanged in CHCl$_3$: CH$_2$Cl$_2$ (1 : 1) solution with ν_1, ν_2, and ν_3 having similar energies and relative intensity. Representative spectra are given in Figure 1 for the complex [Cu(na)$_2$(bipy)], both in the solid state and in solution. Spectra practically identical to the above were also exhibited by the parent complexes derived from 2-nitroacetophenone, *i.e.* [Cu(nap)$_2$(phen)] and [Cu(nap)$_2$(bipy)], the latter being isomorphous with the corresponding Ni^{II} complex, found to be six-co-ordinate and pseudo-octahedral from its reflectance spectrum.[2]

In view of the invariably bidentate nature of both types of ligand present and of the above spectral data, a six-co-ordinate tris(chelate) structure (chromophore

CuO_4N_2) is assumed for all the [CuL_2B'] species. As was also pointed out previously,[2] a visible spectrum quite similar (in fact almost identical) is also shown by the complex (2,2′-bipyridine)bis(hexafluoroacetylacetonato)copper(II). This complex is six-co-ordinate, *cis*-octahedral, with in-plane nitrogen atoms and mixed in-plane–out-of-plane inequivalent co-ordination of the β-diketonato-groups [7] (D). A similar arrangement, implying in-plane co-ordination of the bidentate *N*-base and mixed co-ordination of the chelating *O*-donor groups to give Cu–O(axial) slightly longer than Cu–O(in-plane), was previously suggested for the complexes [$Cu(nap)_2(bipy)$] and [$Cu(nap)_2(phen)$] and is now proposed as a probable configuration for all the [CuL_2B'] complexes presented here.

TABLE 3

E.s.r. spectral data of [CuL_2B'] species

Complex	Medium *	$g_\parallel$ (±0·002)	$g_\perp$ (±0·005)	$10^{-4}A_\parallel(^{63}Cu)/cm^{-1}$ (±1)	$10^{-4}A(N)/cm^{-1}$ (±1)	$10^{-4}A_\parallel(^{65}Cu)/cm^{-1}$ (±1)
[$^{63}Cu(nap)_2(bipy)$]	A(63)	2·281	2·066	167·5	10	
	C(63)	2·314	2·076	151	10	
[$Cu(na)_2(bipy)$]	A	2·301	2·074	163·5	10	179
	B(63)	2·303	2·074	156	10	
[$Cu(nta)_2(bipy)$]	A	2·299	2·076	163·5	10	180
	C	2·311	2·084	144·5	10	161
[$Cu(nca)_2(bipy)$]	A	2·297	2·070	162	10·5	178
[$^{63}Cu(nap)_2(phen)$]	A	2·289	2·069	164	10	
[$Cu(na)_2(phen)$]	A	2·301	2·072	158	10	173
	C(63)	2·310	2·073	154	9·5	
[$Cu(nta)_2(phen)$]	A	2·307	2·078	160	10	177
	B	2·301	2·074	157	9·5	175
[$Cu(nca)_2(phen)$]	A	2·314	2·080	159	10·5	175
	C	2·311	2·072	152	10	166

* Spectra recorded at 100 K: A, solution spectra in $CHCl_3$ (ethanol free): CH_2Cl_2 (1 : 1) (*ca.* $2·0 \times 10^{-3}$M); B, polycrystalline samples diluted in isomorphous matrices; C, polycrystalline samples diluted in non-isomorphous matrices; 63 given in parentheses indicates use of the ^{63}Cu isotope.

For the [CuL_2B'] complexes equatorial co-ordination of both nitrogen atoms is clearly established by the ^{14}N hyperfine structure in the e.s.r. spectra of frozen solutions of $CHCl_3 : CH_2Cl_2$ (1 : 1) and of polycrystalline samples diluted with the analogous Zn^{II} complexes. Data are shown in Table 3, which also includes results for the complexes [$Cu(nap)_2(bipy)$] and [$Cu(nap)_2(phen)$]. All e.s.r. spectra and the measured g values ($g_\parallel > g_\perp$) suggest an axially elongated 'tetragonal' ligand field, there being no evidence for a d_{z^2} ground state. However, on the basis of the experimental data, it is not possible to establish whether the ligand field around Cu^{II} has some rhombic character or not. Spectra of the bipy derivatives are shown in Figure 2 for the bands corresponding to $M_I = -3/2$ and $-1/2$. Similar spectra were observed for the phen complexes. All the spectra showed ^{14}N hyperfine splitting. For the spectra of the complexes prepared from the ^{63}Cu isotope, *i.e.* [$Cu(nap)_2(bipy)$] and [$Cu(na)_2(bipy)$] [(*a*), (*b*), and (*d*) of Figure 2], five components of relative intensity 1 : 2 : 3 : 2 : 1, present on the low-field bands given by $M_I = -3/2$ and $-1/2$, unequivocally establish that both N atoms of the bidentate *N*-base co-ordinate in the equatorial plane. A similar interpretation applies to the phen complexes. Not all the Zn^{II} complexes, used as matrices, were isomorphous with the corresponding Cu^{II} complexes (Table 3). However, from the spectra observed, it seems that equatorial co-ordination of the *N*-base and the overall symmetry around Cu^{II} are not greatly affected by the crystal structure assumed by the Zn^{II} complexes, since the spectra of the Cu^{II} complexes diluted in non-isomorphous matrices did not differ significantly from the others. Since, then, in [CuL_2B'] species both nitrogen atoms are co-ordinated in-plane, it follows that only two oxygen atoms of the α-nitroketonic groups are equatorially co-ordinated and two are occupying axial positions (D).

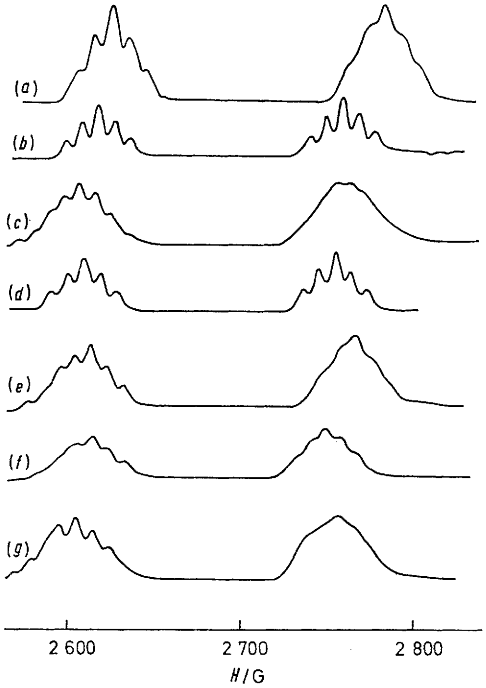

FIGURE 2 E.s.r. spectra of frozen solutions and diluted polycrystalline samples, respectively, of the complexes [$Cu(nap)_2(bipy)$] (*a*) and (*b*), [$Cu(na)_2(bipy)$] (*c*) and (*d*), [$Cu(nta)_2(bipy)$] (*e*) and (*f*), and [$Cu(nca)_2(bipy)$] (*g*) (frozen solution)

Inequivalent co-ordination of the oxygen atoms of the α-nitroketonic groups in the [CuL$_2$B′] species is suggested by the fact that this has been observed to occur in both the complexes [Cu(nap)$_2$(α-pic)] [3] and [Cu(nap)$_2$(γ-pic)$_2$].[4] That such a bonding situation may be ascribed mainly to the different electron-density distribution along the axial and equatorial directions, caused by the different population of the d_{z^2} and $d_{x^2-y^2}$ orbitals of Cu^{II}, is strongly supported by the fact that in the complex [Cu(nap)$_2$],[5] where chelation of the α-nitroketonic groups occurs only in the equatorial plane, Cu–O bond distances are all equal, although the two *O*-donor sites of each α-nitroketonic group are not identical.

Complex	R_S/Å	R_L/Å	$T(=R_S/R_L)$	ν_1/kK	Assignment
[Cu(nap)$_2$(γ-pic)$_2$]	1·99	2·25	0·85	9·5	$d_{z^2} \rightarrow d_{x^2-y^2}$ (or d_{xy})
[Cu(hfa)$_2$(bipy)]	1·97	2·30	0·86	9·4	$d_{z^2} \rightarrow d_{xy}$ (ref. 12)

In an attempt to estimate approximately the extent of inequivalent co-ordination in the [CuL$_2$B′] species the following considerations can be made. For the complexes [Cu(nap)$_2$(γ-pic)$_2$] and [Cu(hfa)$_2$(bipy)] (hfa = hexafluoroacetylacetonato) Cu–O(in-plane) (R_S) and Cu–O(axial) (R_L) bond distances are given below and the tetragonality (T) [12] and the energy of the transition $d_{z^2} \longrightarrow d_{x^2-y^2}$ (or d_{xy}) are also reported. It is observed that both structural (T) and spectroscopic (ν_1) data are very similar for the two complexes. From these data it is concluded that the complexes [Cu(nap)$_2$(γ-pic)$_2$] and [Cu(hfa)$_2$(bipy)] exhibit a substantially identical tetragonal distortion. This is significant because, while having the same chromophore CuO$_4$N$_2$, the two complexes have different *O*- and *N*-donors as well as different arrangements of the in-plane CuO$_2$N$_2$ chromophore (*trans* in one case, *cis* in the other). The high value of T for [Cu(nap)$_2$(γ-pic)$_2$], *i.e.* restricted distortion, is undoubtedly determined, as for the complex [Cu(hfa)$_2$(bipy)],[12] by the limited flexibility of the bidentate *O*-donor. For [CuL$_2$B′] species the reflectance spectra show ν_1 to vary between 8·5 and 10·5 kK (Table 2). The range of variation of ν_1 for the spectra taken in solution is even more restricted (9·4—10·0 kK). This presumably means that the tetragonal distortion varies only slightly for all the [CuL$_2$B′] species, particularly in solution, and T values should not differ very much from 0·85 to 0·86. Thus the inequivalent co-ordination in [CuL$_2$B′] species should be comparable to that observed in the two *X*-ray structures discussed.

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