(N-Benzoyl-DL-alaninate)copper(II) Complexes: Effect of Amines on the Amino-acid Co-ordination

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Reaction of amines with the complex $[Cu(Bz\text{-}AlaO)_2]\cdot H_2O$ (Bz-AlaO = N-benzoyl-DL-alaninato) gives adducts of the type $[Cu(Bz\text{-}AlaO)_2]\cdot B_n$ [n = 1, B = piperazine(ppz), 3-methylpyridine(3Me-py), 4Me-py, 2,2′-bipyridine (2,2′-bipy), 4,4′-bipy, and 1,10-phenanthroline (phen); n = 2, B = Meppz, piperidine (pip), morpholine (morp), py, and 4Me-py] and $[Cu(en)_2(Bz\text{-}AlaO)_2]$. Each complex has been characterized by elemental analysis, solid and solution spectroscopy, and magnetic moment. The complexes may be divided into three types from the point of view of their stereochemistry. Type (1) contains complexes having a copper(II) acetate monohydrate type co-ordination such as $[\{Cu(Bz\text{-}AlaO)_2B\}_2]$ [B = H_2O, 3Me-py, 4Me-py, and py (only in solution)], type (2) contains complexes having a square-planar or strongly distorted tetragonal environment with a CuN_2O_2 chromophore such as $[Cu(Bz\text{-}AlaO)_2]\cdot B_n$ (B = Meppz, pip, py, 4Me-py, 2,2′-bipy, and 4,4′-bipy) or a CuN_4 chromophore such as $[Cu(en)_2(Bz\text{-}AlaO)_2]$ (the solution complexes of the Meppz, pip, mor, and 4Me-py adducts, which show a concentration-dependent colour change, are also discussed), and type (3) contains medium tetragonally distorted complexes, as the presence of two d–d bands supports, in the solid $[Cu(mor)_2(Bz\text{-}AlaO)_2]$, solid and solution $[Cu(Bz\text{-}AlaO)_2]\cdot$phen, and in the presence of excess of amine, $[CuB_2(Bz\text{-}\alpha\text{-}AlaO)_2]$ (B = Meppz, pip, mor, 3-Me-py, and 4-Me-py). For the phen adduct a *cis*-octahedral co-ordination with a CuN_2O_4 chromophore is proposed, while for the solution complexes in the presence of an excess of amine the CuN_4O_2 chromophore is suggested.

THIS work is an extension of our previous studies on the interactions of small amino-acids, such as N-acetyl- and N-benzoyl-glycine, with some metal ions, such as Co^{II}, Ni^{II},[1] Cu^{II},[2,3] Zn^{II}, Cd^{II}, and Hg^{II}.[4,5] Copper(II) complexes of amino-acids have been studied in considerable detail, and if there are no complicating donor side chains the acids co-ordinate solely through the amino- and carboxylato-groups, forming stable five-membered chelate rings with the metal ion, as found for each of the twenty or so naturally occurring L-α-amino-acids.[6–8] In these complexes the five-co-ordination could be favoured since the strong ligand field of the four in-plane donor atoms weakens the axial interactions.[8]

The introduction of a substituent, such as the benzoyl group, directly on the amino-group, could reduce the ligand field of the in-plane donor, diminishing the affinity of the amino-group for the metal ion, and could permit a variety of co-ordination types. In this work we have studied the copper complexes of N-benzoyl-DL-alanine (Bz-Ala) and their amine adducts.

EXPERIMENTAL

Preparation of the Complexes.—*Di*(N-*benzoylalaninato*)-*copper*(II) *hydrate*, $[Cu(Bz\text{-}AlaO)_2]\cdot H_2O$. A methanolic solution of the N-benzoyl-DL-alanine was neutralized with methanolic potassium hydroxide and a stoicheiometric amount of copper(II) perchlorate hexahydrate in ethanol was added. The solution was cooled at 4—5 °C overnight and the potassium perchlorate precipitated was filtered off. After evaporation, addition of methanol, and filtration of the potassium perchlorate still present, water was added until precipitation commenced. On cooling a blue-green complex separated.

$[CuB_2(Bz\text{-}AlaO)_2]$ [B=N-*Methylpiperazine* (Meppz), *piperidine* (pip), *morpholine* (mor), *pyridine* (py), *and* 4-*methylpyridine* (4Me-py)].—These complexes were prepared by dissolving the $[Cu(Bz\text{-}AlaO)_2]\cdot H_2O$ salt directly in the amine. The solid complexes were precipitated on cooling or addition of diethyl ether.

The complex $[Cu(Bz\text{-}AlaO)_2]\cdot$3Me-py was prepared as described above by using as precipitant diethyl ether–acetone (1 : 2). The complex $[Cu(Bz\text{-}AlaO)_2]\cdot$4Me-py was prepared by suspending the $[Cu(4Me\text{-}py)_2(Bz\text{-}AlaO)_2]$ complex in diethyl ether. The complex $[Cu(Bz\text{-}AlaO)_2]\cdot$ppz was obtained by adding an excess of piperazine to an ethanolic solution of the copper salt. The adduct was precipitated on adding diethyl ether and cooling to 4—5 °C.

$[Cu(bipy)(Bz\text{-}AlaO)_2]$ *Adducts*.—The solid 4,4′-bipyridine (4,4′-bipy) adduct was precipitated on adding chloroform to a methanolic solution (10 cm^3) containing the copper salt (10^{-3} mol dm^{-3}) and the amine (2×10^{-3} mol dm^{-3}). The solid 2,2′-bipy adduct was obtained by adding diethyl ether to a chloroform solution (10 cm^3) of the copper salt (10^{-3} mol dm^{-3}) and the amine (10^{-3} mol dm^{-3}). The same complexes were also obtained in the presence of an excess of the amine.

$[Cu(Bz\text{-}AlaO)_2]\cdot$phen.—An ethanolic solution (15 cm^3) of the copper salt (10^{-3} mol dm^{-3}) and of 1,10-phenanthroline (phen) (1.5×10^{-3} mol dm^{-3}, or in excess) was evaporated until an oil was obtained. The oil was dissolved in acetone and the solid complex was precipitated with diethyl ether.

$[Cu(en)_2(Bz\text{-}AlaO)_2]$.—This complex was separated by dissolving the copper salt in an excess of ethylenediamine (en), diluting with acetone, and precipitating with diethyl ether.

Physical Measurements.—The electronic spectra of the complexes were recorded on a Beckman DK 1A spectrophotometer. Solid samples were prepared by grinding the

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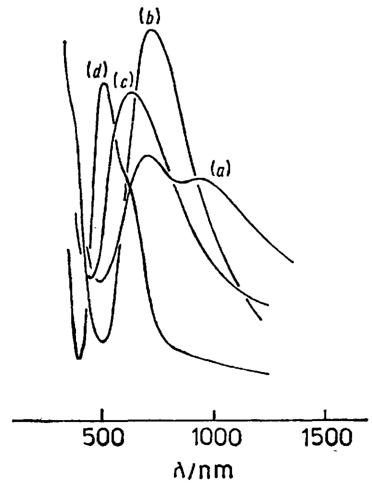
complexes on a filter paper as support. The i.r. spectra of KBr pellets, Nujol mulls, and chloroform solutions were recorded on a Perkin-Elmer 521 spectrophotometer. Room-temperature magnetic moments were measured by the Gouy method using $Hg[Co(SCN)_4]$ or $[Ni(en)_3][S_2O_3]$ as calibrants and correcting for diamagnetism with the appropriate Pascal constants.

Analyses.—Nitrogen, carbon, and hydrogen were analysed by Mr. Giuseppe Pistoni using a Perkin-Elmer 240 Elemental Analyser.

RESULTS AND DISCUSSION

The prepared complexes and their analyses are given in Table 1. All the complexes are stable in air and soluble in chloroform or methanol, except the 4,4'-bipy and ppz adducts which are insoluble. The colours, magnetisms, and electronic spectra of the complexes are such as to divide the complexes into three types. Type (1) contains the green complexes with 'anomalous' magnetic moments and intense absorption bands at *ca.* 13 500 cm^{-1} ($\varepsilon > 120$ dm^3 mol^{-1} cm^{-1}), type (2) contains the blue complexes with 'normal' magnetic moments and absorption bands at wavelengths greater than 15 000 cm^{-1} ($\varepsilon < 100$ dm^3 mol^{-1} cm^{-1}), and type (3) contains the blue complexes having 'normal' magnetic moments, and two absorption bands at *ca.* 10 000 and 13 000—15 000 cm^{-1}. Typical electronic spectra are in the Figure.

The ν(NH), ν(CO) (ketonic), antisymmetric and symmetric carboxyl stretching, and bending NH vibrations, which are utilized in the assignment of amino-acid co-ordination, were assigned by comparing the i.r. spectrum of the amino-acid with those of its potassium salt and their deuteriated analogues and of the spectra of other similar amino-acids and peptides.[9-14] These bands, which are straightforward (although the vibrational bands of the aromatic ring also appear,[15] at *ca.* 1 600, *ca.* 1 490, and *ca.* 1 430 cm^{-1}), occurred at 3 350s, 1 612vs, 1 713vs, 1 205vs, and 1 535vs cm^{-1}, respectively, in the amino-acid and at 3 235m, 1 615vs, 1 575vs, 1 390vs, and 1 535vs, respectively, in its potassium salt. The separation (185 cm^{-1}) of the observed carboxyl group frequencies of the potassium salt, which are of primary concern for the co-ordination, is assumed to typify spectra of ionic *N*-benzoyl-DL-alaninate. In general we may exclude co-ordination at the amido group in all the complexes, as ν(NH) (3 400—3 280 cm^{-1}) and ν(CO) (ketonic) (1 635—1 645 cm^{-1}) were shifted to higher energies and δ(NH) (1 521—1 500 cm^{-1}) to lower energies, respectively, with respect to the ligand and the potassium salt.



Typical spectra of type (1) complexes with a binuclear copper(II) acetate monohydrate type arrangement {[{Cu(Bz-AlaO)$_2$·H$_2$O}$_2$], (*b*)}, of type (2) complexes with truly square-planar co-ordination {[Cu(pip)$_2$(Bz-AlaO)$_2$], (*d*)} or strongly distorted tetragonal co-ordination {[Cu(py)$_2$(Bz-AlaO)$_2$], (*c*)}, and of type (3) complexes with medium tetragonally distorted environment {[Cu(Bz-AlaO)$_2$]·phen, (*a*)}

TABLE 1

Analytical data

Complex	Colour	Analysis (%) * C	H	N
[Cu(Bz-AlaO)$_2$]·H$_2$O	Green	51.55 (51.55)	4.85 (4.75)	6.0 (6.0)
[Cu(Bz-AlaO)$_2$]·ppz	Light blue	53.05 (53.95)	6.65 (5.65)	10.3 (10.5)
[Cu(Meppz)$_2$(Bz-AlaO)$_2$]	Light blue	55.75 (55.55)	6.55 (6.85)	12.6 (12.95)
[Cu(pip)$_2$(Bz-AlaO)$_2$]	Violet	58.45 (58.25)	6.95 (6.85)	8.90 (9.05)
[Cu(mor)$_2$(Bz-AlaO)$_2$]	Light blue	54.1 (54.05)	6.85 (6.15)	9.70 (9.00)
[Cu(py)$_2$(Bz-AlaO)$_2$]	Blue	59.25 (59.4)	5.00 (5.00)	8.70 (9.25)
[Cu(Bz-AlaO)$_2$]·(3Me-py)	Green	57.8 (57.7)	5.50 (5.05)	7.65 (7.75)
[Cu(Bz-AlaO)$_2$]·(4Me-py)	Green	57.7 (57.7)	5.20 (5.05)	7.75 (7.75)
[Cu(4Me-py)$_2$(Bz-AlaO)$_2$]	Blue	61.1 (60.6)	6.20 (5.40)	9.40 (8.85)
[Cu(2,2'-bipy)(Bz-AlaO)$_2$]·4H$_2$O	Light blue	52.75 (53.25)	5.45 (5.35)	7.85 (8.30)
[Cu(4,4'-bipy)(Bz-AlaO)$_2$]	Light blue	58.9 (59.6)	4.95 (4.70)	9.20 (9.30)
[Cu(Bz-AlaO)$_2$]·phen	Light blue	61.0 (61.15)	4.35 (4.50)	9.40 (8.95)
[Cu(en)$_2$(Bz-AlaO)$_2$]·4H$_2$O	Violet	45.45 (45.0)	6.95 (6.95)	13.2 (13.15)

* Calculated values are given in parentheses.

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Type (1) *Complexes*.—This group of complexes contains green $[Cu(Bz\text{-}AlaO)_2]\cdot H_2O$ and $[Cu(Bz\text{-}AlaO)_2]\cdot B$ (B = 3Me-py and 4Me-py) in the solid and solution state, and $[Cu(py)_2(Bz\text{-}AlaO)_2]$ in $CHCl_3$ solution. As these complexes display similar magnetic and spectral characteristics (Table 2) to those of copper(II) acetate monohydrate and similar binuclear compounds,[16-26] the a range which is characteristic of dimeric carboxylates and their adducts.[22,25]

The room-temperature magnetic moments of these complexes (1.44 and 1.54 B.M.) * are also consistent with the stereochemistry proposed.[19,22,26] Although the interpretation of the anomalous magnetic properties of these and similar complexes remain open, it would seem

TABLE 2

Solid and solution electronic and infrared spectra (cm^{-1}) of the type (1) complexes *

Complex	State	Colour	$\mu_{eff.}$/B.M.	Electronic spectra		I.r. spectra ν(NH)	$\nu(COO)_{asym}$	$\nu(COO)_{sym}$	$\Delta\nu$	δ(NH)
$[Cu(Bz\text{-}AlaO)_2]\cdot H_2O$	Solid	Green	1.44	14 090	27 030 (sh)	3 400, 3 370ms	1 618vs	1 415vs	203	1 505vs
	MeOH	Green		13 330 (121)						
$[Cu(Bz\text{-}AlaO)_2]\cdot(3Me\text{-}py)$	Solid	Green	1.53	13 700	25 640 (sh)	3 310ms	1 625vs	1 406s	219	1 521vs
	$CHCl_3$	Green		13 700 (142)	25 640 (sh) (*ca.* 70)	3 410s	1 629vs	1 409s	220	1 501s
$[Cu(Bz\text{-}AlaO)_2]\cdot(4Me\text{-}py)$	Solid	Green	1.54	13 700	25 640sh	3 280s	1 620vs	1 403vs	217	1 518vs
	$CHCl_3$	Green		13 790 (300)	25 640sh (*ca.* 115)		1 630vs	1 410vs	220	1 500vs
$[Cu(py)_2(Bz\text{-}AlaO)_2]$	$CHCl_3$	Green		13 700 (140)		3 398s, 3 325 (sh)	1 630vs	1 398vs	232	1 502vs

* Absorption coefficients ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) are given in parentheses.

TABLE 3

Magnetic moments (B.M.), electronic spectra [cm^{-1}, $\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ (in parentheses)], and infrared spectra (cm^{-1}) of the type (2) complexes

Complex	State	$\mu_{eff.}$	Electronic spectra (*d–d* band)	I.r. spectra ν(NH)	ν(NH) [a]	$\nu(COO)_{asym}$	$\nu(COO)_{sym}$	$\Delta\nu$	δ(NH)
$[Cu(Bz\text{-}AlaO)_2]\cdot ppz$	Solid	1.69	16 260	3 370m, 3 315 (sh)	3 185s	1 590vs	1 389vs	201	1 502s
$[Cu(Meppz)_2(Bz\text{-}AlaO)_2]$	Solid	1.78	16 130	3 305s	3 205s	1 595vs	1 390vs	205	1 523s
$[Cu(pip)_2(Bz\text{-}AlaO)_2]$	Solid	1.84	1 6390 (sh), 19 610	3 360wb	3 192s	1 578vs	1 396vs	182	1 530vs
$[Cu(py)_2(Bz\text{-}AlaO)_2]$	Solid	1.86	16 260	3 310mb, 3 275 (sh)		1 625, 1 610vs	1 389vs		1 515vs
	$CHCl_3$ + py [b]		15 390 (80)	3 382s, 3 270 (sh)		1 618vs	1 389vs	229	1 500vs
$[Cu(4Me\text{-}py)_2(Bz\text{-}AlaO)_2]$	Solid	1.70	16 130	3 400ms, 3 260ms		1 600vs	1 388vs	212	1 535vs
$[Cu(2,2'\text{-}bipy)(Bz\text{-}AlaO)_2]\cdot 4H_2O$	Solid	1.86	15 390	3 389m, 3 265mb		1 614vs	1 395vs	220	1 520ms
	$CHCl_3$		15 390 (74), 25 000 (sh) (*ca.* 33)	3 390ms		1 590vs	1 395vs	195	1 500s
$[Cu(4,4'\text{-}bipy)(Bz\text{-}AlaO)_2]$	Solid	1.98	15 270	3 330m		1 575vs	1 390vs	185	1 520vs
$[Cu(en)_2(Bz\text{-}AlaO)_2]\cdot 4H_2O$	Solid	1.90	18 520	3 335s	3 250s, 3 130s	1 563vs	1 393vs	170	1 532vs
	MeOH		18 180 (68)						
			A [c] → B [c]						
$[Cu(Meppz)_2(Bz\text{-}AlaO)_2]$	$CHCl_3$		14 990 (75) → 15 630 (*ca.* 85)	3 390s, 3 325 (sh)	3 198ms	1 605vs	1 395vs	210	1 502vs
$[Cu(pip)_2(Bz\text{-}AlaO)_2]$	$CHCl_3$		15 310 (85) → 15 870 (95)	3 393ms	3 210w	1 608vs	1 392vs	216	1 502vs
$[Cu(mor)_2(Bz\text{-}AlaO)_2]$	$CHCl_3$		15 630 (70) → 16 390 (75)	3 395m, 3 322s	3 195m	1 600vs	1 390vs	210	1 505vs
$[Cu(4Me\text{-}py)_2(Bz\text{-}AlaO)_2]$	$CHCl_3$		13 790 (80) → 14 710 (65)	3 390m		1 599vs	1 396vs	203	1 499vs

[a] NH Stretching frequency of the heterocyclic amines. [b] Concentration 3.32×10^{-2} mol dm^{-3}. [c] The solutions investigated were in the concentration range 1.60×10^{-3}—6.00×10^{-2} mol dm^{-3}. In the column A are reported the values found at the lowest concentration and in the column B those at the highest concentration. The solution i.r. spectra correspond to the highest concentration.

presence of analogous binuclear entities is indicated. In fact their carboxylate-stretching frequencies and solid and solution electronic spectra are at very similar energies to those reported for copper carboxylates having a dimeric structure.[16-22,25] In particular, the complexes exhibited higher $\nu(COO)_{asym}$ frequencies than those found for the type (2) complexes, confirming the presence of bridging carboxylato-groups,[17] and in the visible region exhibited bands at 25 500—27 000 cm^{-1}, that the Cu · · · Cu separation is not a dominant factor [26] and that this antiferromagnetism seems to result from a magnetic interaction probably operating through the bridging oxygen atoms.

The co-ordination of the amines through the nitrogen is suggested by the shift of the bands in the 500—800 cm^{-1} region for the adducts with respect to the free amines.[23,24] The packing of the molecules within the

* 1 B.M. $\approx 9.27 \times 10^{-24}$ A m^2.

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crystal may permit some hydrogen bonding of the NH group of the amino-acid, which is removed in solution as suggested by the shift of ν(NH) and δ(NH) for the adducts.

Type (2) *Complexes*.—These complexes, which are considered to have similar co-ordination sites, are reported in Table 3. They have 'normal' magnetic moments, and room-temperature electronic spectra which show absorption bands in the 15 200—19 700 cm^{-1} range. The position and shape of the *d–d* band of these complexes, when compared with those of other complexes for which structural information is available from *X*-ray analysis and e.s.r. spectra,[27-29] are consistent with in-plane square-planar co-ordination involving probably reported for the binuclear type (1) complexes. Also, as in the type (1) complexes, some hydrogen bonding of the NH group of the amino-acid in the solid state may occur. The co-ordination of the amines through the nitrogen atom is confirmed by the shift to lower frequencies of ν(NH) in the adducts of the heterocyclic amines and by the shift of the bands in the 500—800 cm^{-1} region in the py, 4Me-py, and bipy adducts.[4]

The *d–d* band of the $[Cu(en)_2(Bz\text{-}AlaO)_2]$ complex (Table 3) is in the range found for other $[Cu(en)_2]^{2+}$ complexes and complexes with a square-planar structure with CuN_4 chromophores.[29] The position of the ν(NH) amine bands is consistent with bidentate co-ordination of en,[31] and the positions of the carboxylate bands, which

TABLE 4

Electronic [cm^{-1}, ε/dm^3 mol^{-1} cm^{-1} (in parentheses)] and infrared (cm^{-1}) spectra of the type (3) complexes [a]

Complex	State	Electronic spectra	I.r. spectra ν(NH)	ν(NH) [b]	$\nu(COO)_{asym}$	$\nu(COO)_{sym}$	Δν	δ(NH)
$[Cu(Meppz)_2(Bz\text{-}AlaO)_2]$	$CHCl_3$ + Meppz	10 200 (sh) (*ca.* 51), 14 290 (100)	3 390w		1 600vs	1 390s	210	1 500s
$[Cu(pip)_2(Bz\text{-}AlaO)_2]$	$CHCl_3$ + pip	10 000 (sh) (*ca.* 40), 15 220 (100)	3 380 (sh), 3 312s		1 594vs	1 390s	204	1 500vs
$[Cu(mor)_2(Bz\text{-}AlaO)_2]$ [c]	Solid	11 240, 13 330	3 350s	3 180wb	1 587vs	1 372s	215	1 521vs
	$CHCl_3$ + mor	10 200 (sh) (*ca.* 32), 15 040 (75)	3 400 (sh), 3 320s	3 205m	1 598vs	1 390vs	208	1 503vs
$[Cu(Bz\text{-}AlaO)_2]$·(3Me-py)	$CHCl_3$ + 3Me-py	10 000 (sh) (*ca.* 20), 15 630 (75)	3 370sb		1 615vs	1 408s	207	1 500vs
$[Cu(4Me\text{-}py)_2(Bz\text{-}AlaO)_2]$	$CHCl_3$ + 4Me-py	10 000 (sh) (*ca.* 20), 15 270 (75)	3 360 (sh)		1 594vs	1 406vs	188	1 499s
$[Cu(Bz\text{-}AlaO)_2]$·phen [d]	Solid	10 530, 14 290	3 365sb		1 588vs	1 380vs	208	1 505vs
	$CHCl_3$	10 530 (sh) (*ca.* 23), 14 710 (60)	3 378sb		1 592vs	1 390vs	202	1 500vs
	MeOH	10 530 (38), 14 710 (60)						

[a] The concentration of the solutions were *ca.* 6.0 × 10^{-2} mol dm^{-3}. [b] NH Stretching frequency of the heterocyclic amines.
[c] μ = 1.74 B.M. [d] $\mu_{eff.}$ = 1.64 B.M.

the N_2O_2 donor set or strongly distorted tetragonal co-ordination.

The shift of the *d–d* band to higher energy in the order bipy < Meppz, 4Me-py, py < pip may involve a change in the co-ordination number and geometry. In fact the pip adduct exhibits the electronic spectrum expected for truly four-co-ordinate Cu^{II} with the four ligand atoms in the molecular plane and no significant ligand field in the axis normal to the plane. Similar spectra are given by some amino-acid complexes of Cu^{II} and by bis-(pentane-2,4-dionato)copper(II) and similar complexes.[30]

Ligands of the type 2,2′-bipyridine must be bidentate, binding to the same copper ion, and those of the type 4,4′-bipyridine cannot be bidentate but have two donor sites and must therefore bind to different copper ions. Clearly, this results in a polymeric structure for the 4,4′-bipy complex, as indicated by its insolubility. This conclusion is supported by the similar behaviour exhibited by the piperazine adduct.[2,5]

The i.r. spectra of the complexes (Table 3) are consistent with unidentate co-ordination of the amino-acid carboxylato-group, as the $\nu(COO)_{asym}$ values are greater than those of the potassium salt and lower than those showed the lowest Δν and $\nu(COO)_{asym}$ values in the present study, are similar to those reported for the potassium salt, suggesting no, or weak, unidentate co-ordination of the amino-acid, occupying axial positions at long bond distances.

The complexes $[CuB_2(Bz\text{-}AlaO)_2]$ (B = Meppz, pip, mor, and 4Me-py) in solution (1.60 × 10^{-3}—6.00 × 10^{-2} mol dm^{-3}) gave a concentration-dependent colour change from green (lower concentration) to blue (higher concentration) with a consequent blue shift of the *d–d* band. This shift is due to a change in the co-ordination geometry from a dimeric copper(II) acetate monohydrate type present in the lower concentration range (green complex) to a tetragonal distorted geometry present in the higher concentration range (blue complex), according to equilibrium (1). With the py adduct complete

$$2[CuB_2(Bz\text{-}AlaO)_2] \rightleftharpoons [\{CuB(Bz\text{-}AlaO)_2\}_2] + 2B \quad (1)$$

dissociation persists in the most concentrated solution and this complex follows the Lambert–Beer law in the concentration range investigated. With the adducts of the heterocyclic amines, progressive dissociation of the

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amines and replacement by solvent molecules, accompanied by a decrease in the molar absorption, is indicative of diminished tetragonal distortion about the copper ion.[32]

Type (3) *Complexes*.—This type contains the solid mor and solid and solution phen adducts and solutions, containing an excess of the amine, of the Meppz, pip, mor, 3Me-py, and 4Me-py adducts. The complexes have 'normal' magnetic moments and exhibited two absorption bands in the near-infrared and visible spectra (Table 4), which indicate the presence of tetragonally distorted octahedral species.[27,28] With the type (2) complexes the distortion is slight and only one band is seen as the energy separation between the split bands will be small, while with type (3) the presence of more than one band indicates medium distortion. Analogously to type (2), the i.r. spectra of complexes of type (3) in solution are consistent with unidentate co-ordination of the amino-acid carboxylato-group and the presence of the CuN_4O_2 chromophore is suggested.

For the solid and solution phen adduct, although the i.r. spectra are not conclusive in the assignment of bidentate co-ordination of the amino-acid carboxylato-group, we propose the presence of a CuN_2O_4 chromophore and *cis*-octahedral stereochemistry because of the great similarity of the electronic spectra of this complex to those exhibited by the bipy adduct of copper(II) nitroketonates and their parent complexes derived from 2-nitroacetophenone[27] which are six-co-ordinate *cis*-octahedral with a CuN_2O_4 chromophore.

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