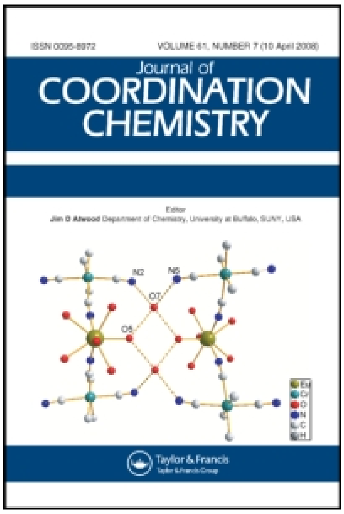

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Reactions of *Bis*(*β*-Alaninato) Metal(II) Complexes with Formaldehyde and Benzamide: The Crystal Structure of *Bis*[*N*-Methyl-*N*-(*N'*-Methyl-Benzamido)-*β*-Alaninato]Copper(II) Monohydrate and Characterization of *Bis*[*N*,*N*-DI(*N'*-Methylbenzamido)-*β*-Alaninato]Metal(II) Complexes

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REACTIONS OF *BIS*(*β*-ALANINATO) METAL(II) COMPLEXES WITH FORMALDEHYDE AND BENZAMIDE: THE CRYSTAL STRUCTURE OF *BIS*[*N*-METHYL-*N*-(*N*′-METHYL-BENZAMIDO)-*β*-ALANINATO]COPPER(II) MONOHYDRATE AND CHARACTERIZATION OF *BIS*[*N*,*N*-DI(*N*′-METHYLBENZAMIDO)-*β*-ALANINATO]METAL(II) COMPLEXES

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The *bis*[*N*-methyl-*N*-(*N*′-methylbenzamido)-*β*-alaninato]copper(II), Cu(II)[Me-MeBA]$_2$, is synthesized by reacting *bis*(*β*-alaninato)copper(II) with formaldehyde and benzamide in the presence of a base (NaOH) over the pH range 5.5–8.5. However, the *bis*[*N,N*-di(*N*′-methylbenzamido)-*β*-alaninato]metal(II) complexes, M(II)[DMeBA]$_2$ (M = Zn, Ni, Co), are obtained when the respective *bis*(*β*-alaninato)metal(II) reacts with formaldehyde and benzamide in the presence of the base in similar pH ranges. Nevertheless, Cu(II)[DMeBA]$_2$ can be synthesized if the reaction is carried out in the absence of base. The M(II)[DMeBA]$_2$ complexes are characterized by elemental analysis, IR and UV-Visible spectroscopy and magnetic susceptibility measurements. X-ray crystal structure analysis of Cu(II)[Me-MeBA]$_2$ suggests that the *N*′-methylbenzamido substituent of the *β*-alanine moiety is formed through Mannich aminomethylation, and that the other *N*-methyl substituent is formed via a Canizzaro-type methylation.

Keywords: *Bis*(*β*-alaninato)metal(II); *β*-alanine; Mannich; Methylation; Benzamide; Formaldehyde

INTRODUCTION

Mannich aminomethylation reactions of chelated *α*-amino acids have received considerable attention [1–3]. So far, there are only two reported instances of such reactions involving *β*-aminoacidato metal(II) complexes [4,5]. The first case is the synthesis of *cis*-[3*N*,7*N*-(1,3,5,7-tetraazabicyclo[3.3.1]nonyl)-di-3-propionato]-copper(II) which was

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formed from the reaction of the trans-*bis*(β-alaninato)copper(II) with formaldehyde and ammonia [4]. Balla later synthesized an *N,N′*-propylene bridged copper(II) complex of 6-methyl-6-nitro-4,8-diazaundecanedioate ligand by reacting *bis*(β-alaninato)copper(II) with formaldehyde and nitroethane [5].

In this study, we report two types of complexes formed from the reaction of *bis*(β-alaninato)metal(II), M(II)[β-ala]$_2$ (M = Cu, Zn, Ni, Co), with formaldehyde and benzamide in the absence and presence of a base. X-ray structural analysis of the Cu(II)[Me-MeBA]$_2$ and the characterization data of the M(II)[Me-MeBA]$_2$ complexes are presented herewith.

EXPERIMENTAL

Material and Instruments

β-alanine and benzamide were supplied by B.D.H. Chemical Company while the 37% aqueous formaldehyde solution supplied by Merck contains formic acid (max. 0.03%). M(II)[β-ala]$_2$ (Cu, Zn, Ni, Co) were prepared as described previously [6]. Elemental analyses were carried out on a Control Equipment Model 240 XA Analyser, and infrared spectra were measured in KBr pellets from 4000–300 cm^{-1} using a Perkin Elmer 2000 FT-IR Spectrophotometer. Magnetic moments were determined at 293 K using a Newport Variable-Temperature Gouy Balance System and magnetic susceptibilities were corrected for diamagnetic contributions. Solid diffuse reflectance spectra were measured in MgO discs on a Hitachi 330 Spectrophotometer.

Synthesis of Complexes

Cu(II)[Me-MeBA]$_2$

A reaction mixture consisting of Cu(II)[β-ala]$_2 \cdot 4H_2O$(1.0 g, 0.003 mol), formaldehyde (10 mL, 0.12 mol), benzamide (1.2 g, 0.008 mol) and 95% ethanol (1.7 mL) was stirred thoroughly and its pH adjusted to 6.6 by slow addition of aqueous NaOH solution. On standing at room temperature for 24 days, the resultant solution yielded dark blue cuboidal crystals which were filtered, washed with ethanol and finally dried *in vacuo* for 4 h. Yield: 0.6 g, 36%. Anal. Calcd. for $C_{24}H_{30}N_4O_6Cu \cdot H_2O$(%): C, 52.21; H, 5.84; N, 10.15. Found: C, 52.34; H, 5.67; N, 10.15. This complex could be synthesized in the pH range 5.5–8.5.

M(II)[DMeBA]$_2$ (M = Zn, Ni, Co, Cu)

The M(II)[DMeBA]$_2$ complexes (M = Zn, Ni, Co) were prepared in a similar manner to the Cu(II)[Me-MeBA]$_2$. The pH ranges for the syntheses of the Zn(II), Ni(II) and Co(II) complexes were 5.5–8.0, 5.5–8.5 and 5.5–7.5, respectively. Above the upper limits of the pH ranges, decomposition occurs and no M(II)[DMeBA]$_2$ products are obtained. However, Cu(II)[DMeBA]$_2$ was prepared by reacting Cu(II)[β-ala]$_2$ with formaldehyde and benzamide in the absence of base. All complexes were formed within 1–7 days.

Zn(II)[DMeBA]$_2$. Yield: 9%. Anal. Calcd. for $C_{38}H_{40}N_6O_8Zn \cdot 3\frac{1}{2}H_2O$(%): C, 54.52; H, 5.66; N, 10.04. Found: C, 54.54; H, 5.53; N, 10.15. *Ni(II)[DMeBA]$_2$*.

Yield: 24%. Anal. Calcd. for $C_{38}H_{40}N_6O_8Ni \cdot 3H_2O$(%): C, 55.56; H, 5.64; N, 10.23. Found: C, 55.78; H, 5.32; N, 9.98. *Co(II)[DMeBA]*$_2$. Yield: 20%. Anal. Calcd. for $C_{38}H_{40}N_6O_8Co \cdot 5H_2O$(%): C, 53.20; H, 5.87; N, 9.80. Found: C, 53.18; H, 5.61; N, 9.80. *Cu(II)[DMeBA]*$_2$. Yield: 80%. Anal. Calcd. for $C_{38}H_{40}N_6O_8Cu \cdot 2H_2O$(%): C, 56.46; H, 5.49; N, 10.40. Found: C, 56.19; H, 5.36; N, 10.15.

X-ray Crystal Structure Analysis

Intensity data on a single blue needle crystal of dimension 0.8 × 0.6 × 0.6 mm was measured at room temperature (298 K) on a Huber diffractometer using Mo-K_α radiation (graphite monochromator), $\lambda = 0.71073$. The θ–2θ scan technique was employed to measure reflections to $\theta_{\max} \leq 30°$. The data were corrected for Lorentz and polarization effects but not for absorption. Reflections which satisfied the $F > 4.0\ \sigma(F)$ criterion were used in the subsequent analysis. A summary of crystal data and data collection is listed in Table I.

The structure was solved using direct methods [7] and was refined by the full matrix least squares technique [8]. All non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were included in their idealized positions (C–H = 0.96 Å). A weighting scheme of the form $w = [\sigma^2(F) + g(F)^2]^{-1}$, where $g = 0.0018$, was introduced and the refinement continued until convergence. The analysis of variance showed no special features indicating appropriate choice of weighting scheme. The scattering factors for all the atoms were used as incorporated in SHELX76 [8]. Position parameters of non-hydrogen atoms are given in Table II. Table III lists the interatomic bond distances and angles.

RESULTS AND DISCUSSION

Cu(II)[Me-MeBA]$_2$

The crystal structure of Cu(II)[Me-MeBA]$_2$ established its formation from the reaction of Cu(II)[β-ala]$_2$ with formaldehyde and benzamide in the presence of NaOH. The molecular structure of Cu(II)[Me-MeBa]$_2$ (Fig. 1) shows that both the amino protons of each β-alanine moiety of Cu(II)[β-ala]$_2$ are deprotonated and are substituted with a methyl and a *N*′-methylbenzamido pendants. This is the first documented case of a chelated amino acid where the same amino nitrogen is both aminomethylated and methylated as contrasted with (i) *N*,*N*-diaminomethylation of *bis*(glycinato)metal(II)

TABLE I Crystal data and refinement details for Cu(II)[Me-MeBA]$_2$

Formula	$C_{24}H_{32}N_4O_7Cu$	λ/Å	0.71073
M	552.1	μ/ mm^{-1}	0.763
Crystal system	Rhombohedral	Scan Type	2θ–θ
Space group	$R\bar{3}$	2 range/°	3–55
a/Å	14.069(7)	Data collcd.	5423
/°	107.69(7)	Unique data	3498
V/Å^3	2274.1(11)	Data with	
F(000)	867	$F > 4.0\ \sigma(F)$	2512
Z	3	*R*	0.084
D_x/M g cm^{-3}	1.209	R_w	0.090

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{Å}^2 \times 10^3$) for Cu(II) [Me-MeBA]$_2$

Atom	*x/a*	*y/b*	*z/c*	U_{eq}[a]
Cu1	0	5000	0	44(1)
O1	1151(3)	4471(3)	158(3)	54(2)
O2	2088(4)	3752(4)	− 600(4)	70(3)
C7	1654(4)	4404(5)	− 451(5)	52(3)
C8	1801(6)	5200(5)	− 983(6)	64(3)
C9	1985(5)	6349(5)	− 211(6)	63(3)
N1	931(4)	6346(4)	− 162(4)	51(2)
C10	185(8)	6396(7)	− 1209(7)	103(5)
C11	1213(5)	7394(5)	790(5)	57(3)
N2	2006(4)	7587(4)	1826(4)	52(2)
C12	1778(5)	6984(5)	2377(5)	51(3)
C1	2614(5)	7322(5)	3502(5)	52(3)
C2	3451(6)	8416(6)	4166(5)	68(3)
C3	4179(7)	8699(7)	5257(6)	94(4)
C4	4086(7)	7950(8)	5648(7)	88(5)
C5	3312(7)	6879(8)	4998(7)	86(5)
C6	2523(6)	6533(6)	3909(5)	69(4)
O3	861(3)	6149(3)	1948(3)	57(2)
O4	2489(12)	571(13)	1859(13)	56(4)
O5	9803(12)	975(13)	268(13)	82(9)
O6	− 2262(54)	6298(53)	− 2848(52)	45(17)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor; O4, O5, O6 have site occupancy factors 0.25, 0.15 and 0.10 respectively; these refer to 3 lattice water molecules with different site occupancy factors which all add up to one water molecule.

with formaldehyde and acetamide [3,9] and (ii) the *N*,*N*-dimethylation of Cu(II)[β-ala]$_2$ with formaldehyde in the absence of base [10]. Both the formation of *N*′-methylbenzamido pendant and the methyl group in the Cu(II)[Me-MeBA]$_2$ presumably involves an intermediate species with a coordinated imine or an uncoordinated iminium. Addition of benzamide to the intermediate species yield the *N*-(*N*′-methylbenzamido) pendant while reduction of the intermediate species results in the *N*-methyl substituent. The reduction process involves both OH^- (from the NaOH base) and formaldehyde which is a type of Canizzaro reaction [11]. This methylation is named Canizzaro methylation to differentiate it from the Eschweiler-Clarke methylation of Cu(II)[β-ala]$_2$ in which the source of hydride ion for reduction is formic acid found in the formaldehyde used [10].

In the Cu(II)[Me-MeBA]$_2$ complex, the two *N*-methyl-*N*-(*N*′-methylbenzamido)-β-alaninate ligands are tridentate and encapsulate the central copper atom. Both β-alanine residues are coordinated to the copper atom *via* their amino nitrogen and carboxylato oxygen atoms, forming a square-planar coordination plane, and the octahedral coordination is completed by two apical carbonyl oxygen atoms of the *N*-methylbenzamido fragments. Characteristically for copper(II), the two axial bonds are longer than the four equatorial bonds in the coordination square. The methylbenzamido carbonyl O3 is at a distance of 2.386(4) from the copper atom while the amino nitrogen atom N1 and carboxylate O1, are 2.071(6) and 1.959(5), respectively, from the latter. The Cu1, N1, O1, N1a and O1a atoms in the equatorial plane are coplanar with Cu1 as a center of symmetry [N1-Cu1-N1a; symmetry operation a: $-x$, $-y$, $-z$]. The octahedral geometry of the six ligating atoms is only slightly distorted.

TABLE III Selected bond parameters for Cu(II)[Me-MeBA]$_2$

Bond distances (Å)			
Cu1–O1	1.959(5)	Cu1–N1	2.071(6)
Cu1–O3	2.386(4)	Cu1–O1a	1.959(5)
Cu1–N1a	2.071(6)	Cu1–O3a	2.386(4)
O1–C7	1.265(9)	O2–C7	1.248(10)
C7–C8	1.524(12)	C8–C9	1.539(10)
C9–N1	1.503(10)	N1–C10	1.565(12)
N1–C11	1.500(8)	C11–N2	1.425(8)
N2–C12	1.346(10)	C12–C1	1.478(8)
C12–O3	1.258(6)	C1–C2	1.409(7)
C1–C6	1.386(12)	C2–C3	1.410(11)
C3–C4	1.320(16)	C4–C5	1.362(11)
C5–C6	1.414(10)		
Bond angles (°)			
O1–Cu1–N1	91.8(2)	O1–Cu1–O3	90.9(2)
N1–Cu1–O3	87.6(2)	O1–Cu1–O1a	180.0(1)
N1–Cu1–O1a	88.2(2)	O3–Cu1–O1a	89.1(2)
O1–Cu1–N1a	88.2(2)	N1–Cu1–N1a	180.0(1)
O3–Cu1–N1a	92.4(2)	O1a–Cu1–N1a	91.8(2)
O1–Cu1–O3a	89.1(2)	N1–Cu1–O3a	92.4(2)
O3–Cu1–O3a	180.0(1)	O1a–Cu1–O3a	90.9(2)
N1a–Cu1–O3a	87.6(2)	Cu1–O1–C7	124.9(5)
O1–C7–O2	123.6(7)	O1–C7–C8	118.9(7)
O2–C7–C8	117.4(7)	C7–C8–C9	111.3(7)
C8–C9–N1	111.9(5)	Cu1–N1–C9	114.3(5)
Cu1–N1–C10	108.7(4)	C9–N1–C10	110.9(7)
Cu1–N1–C11	109.1(4)	C9–N1–C11	108.9(4)
C10–N1–C11	104.5(6)	N1–C11–N2	114.0(6)
C11–N2–C12	123.1(5)	N2–C12–C1	119.1(5)
N2–C12–O3	120.6(5)	C1–C12–O3	120.3(7)
C12–C1–C2	121.9(7)	C12–C1–C6	117.7(5)
C2–C1–C6	120.4(6)	C1–C2–C3	118.9(8)
C2–C3–C4	120.7(7)	C3–C4–C5	120.9(8)
C4–C5–C6	122.0(10)	C1–C6–C5	116.9(6)
Cu1–O3–C12	119.5(5)		

Formation of Cu(II)[Me-MeBA]$_2$ has not altered the *trans* configuration of the β-alanine residues as found in Cu(II)[β-ala]$_2 \cdot 4H_2O$[6(a)]. The two *N*-methyl groups, which are attached to different β-alanine residues are also *trans* with respect to each other; these groups lie on opposite sides of the O1/N1/Cu1/O1a/N1a plane. The bond lengths of both the β-alanine and methylbenzamido residues are normal [6(a), 12]. Unlike the similar octahedral *bis*[*N*,*N*-di-*N*′-methylacetamido)glycinato]copper(II) dihydrate [3], the absolute configuration of the amino nitrogen N1 in the present complex is *R* whereas that of the former is *S*.

The Cu(II)[Me-MeBA]$_2$ is centrosymmetric with the copper atom as its center of inversion. As such, only the atoms of one of the two tridentate ligands are labeled in Fig. 1. Interestingly, hydrogen bonding links the >NH of each benzamido fragment of the complex molecule with the carbonyl oxygen atom of an adjacent molecule such that N2-H2A...O2b angle (symmetry operation b: y, $z+1$, x) is 149° and H2A...O2b bond is 1.959 Å. As a result, each complex molecule has four such strong intermolecular contacts with four other separate adjacent complex molecules, thus yielding a three-dimensional network in the crystal lattice, as shown in Fig. 2.

The above network of interlinking complex molecules merely traps the lattice water molecules without any hydrogen bonding between the former and the latter. As far as

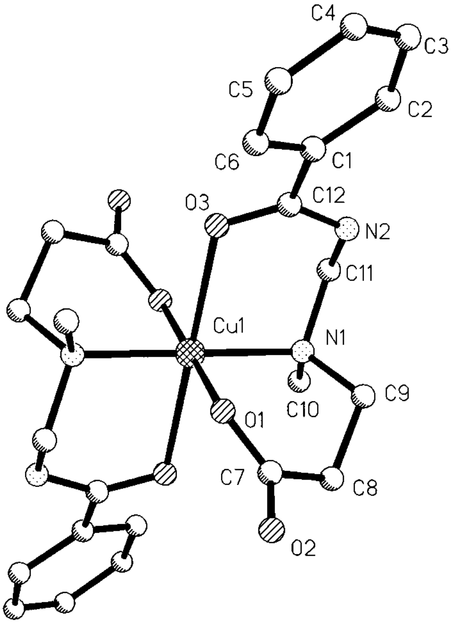

FIGURE 1 Molecular Structure of *bis*([*N*-methyl-*N*-(*N'*-methylbenzamido)-β-alaninato]copper(II) monohydrate.

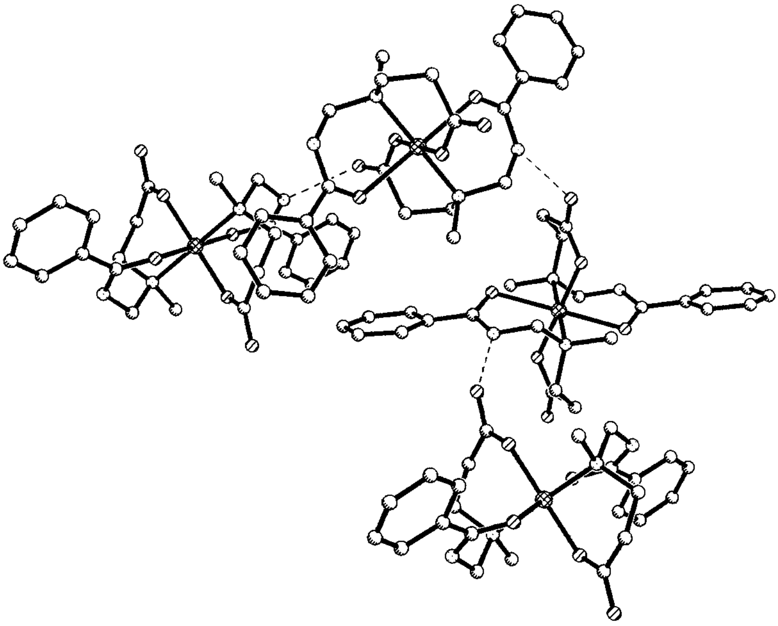

FIGURE 2 Diagram showing hydrogen bonding between Cu(II)[Me-MeBA]$_2$ complex molecules in the solid state; only one of the two 'polymeric' chains per complex molecule is shown.

TABLE IV Hydrogen bonding distances and angles[a]

D–H	*Distance* (Å) *D–H*	*Distance* (Å) *H...A*	*Angle* (°) *D–H...A*	*A*	*Symmetry Operation*
N2–H2A	0.900(12)	1.959(12)	148.94(7)	O2b	$b: y, z+1, x$
O4–H4B	0.960(10)	2.482(10)	115.49(9)	O5c	$c: -x+1, -y, -z$
O5–H5C	0.853(9)	2.202(9)	118.24(8)	O4d	$d: y+1, z, x$
O5–H5C	0.853(10)	2.306(10)	118.13(9)	O4e	$e: z+1, x, y$
O6–H6C	1.043(12)	1.856(12)	158.14(10)	O6f	$f: z, x+1, y-1$

[a] Hydrogen bonds with H...A $< r(A) + 2.000$ and D–H...A angle > 110°.

we know, this is the first case where there is no such intermolecular contacts between lattice water molecules and (i) chelated amino acid molecules or (ii) complexes derived from Aldol-type condensation or Mannich reaction of chelated amino acids. Although the molecular structure shows one water molecule of crystallization per complex molecule, there are actually three lattice water molecules per symmetry unit, and the occupancy factors are 0.25, 0.15 and 0.10 for O4, O5 and O6, respectively. As these water molecules (with a total occupancy factor of 0.5) are centrosymmetrically located, their symmetry operation generates one water molecule per Cu(II)[Me-MeBA]$_2$ complex. Nevertheless, these water molecules do establish close contact with symmetry related water molecules and these are tabulated in Table IV.

M(II)[DMeBA]$_2$ (M = Cu, Zn, Ni, Co)

The Cu(II)[DMeBA]$_2$ complex is prepared by reacting Cu(II)[β-ala]$_2$ with formaldehyde and benzamide in the absence of a base; this blue compound is formed within the same day. Impure products are obtained for the reactions of the M(II)[β-ala]$_2$ (M = Zn, Ni, Co) with formaldehyde and benzamide under the same conditions; these cannot be separated and thereby characterized. Addition of a few drops of sodium hydroxide solution to the latter reaction mixtures brings about rapid formation of a series of complexes with infrared spectra closely resembling that of Cu(II)[DMeBA]$_2$. These latter complexes are postulated to be homologous to the Cu(II)[DMeBA]$_2$ and are thus similarly abbreviated as M(II)[DMeBA]$_2$ (M = Zn, Ni, Co).

All the M(II)[DMeBA]$_2$ complexes contain coordinated β-alanine as evidenced by the presence of antisymmetric and symmetric carboxylate stretching frequencies at ~ 1600 and $\sim 1400\,\text{cm}^{-1}$, respectively, in their infrared spectra. Deprotonation of both amino protons is suggested by the absence of amino nitrogen proton peaks in each M(II)[β-ala]$_2$ [13]. The infrared spectrum of each M(II)[DMeBA]$_2$ complex shows an amide > NH peak at $\sim 3060\,\text{cm}^{-1}$, which is similarly observed for *bis*[*N*,*N*-di(*N*′-methylacetamido)glycinato]metal(II) complexes, M(II)[DMeAG]$_2$, which have been established to be formed from the reactions of *bis*(glycinato)metal(II) with formaldehyde and acetamide [3,9]. Thus, *N*,*N*-diaminomethylation occurs and the M(II)[DMeBA]$_2$ complexes are postulated to be *bis*[*N*,*N*-di(*N*′-methylbenzamido)-β-alaninato]metal(II), as shown in Fig. 3. Microanalytical results support the above postulated structure. The above results are in accord with the reactions of the free β-alanine with formaldehyde and benzamide which has yielded the *N*,*N*-di(*N*′-methylbenzamido)-β-alanine [14]. Magnetic and electronic spectral data (Table V) of the M(II)[DMeBA]$_2$ complexes indicate octahedral hexa-coordination [9,15].

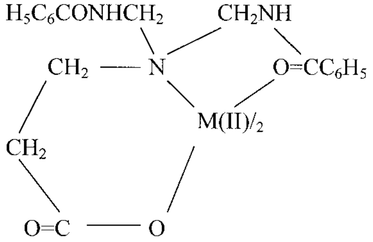

FIGURE 3 Molecular Structure of M(II)[DMeBA]$_2$.

TABLE V Magnetic moment and electronic spectral data of M(II)[DMeBA]$_2$ (M = Cu, Ni, Co)

Compound M(II)[DMeBA]$_2$	*Magnetic moment* μ_{eff}(B.M.)	*Observed band* (cm^{-1})	*Tentative assignment of transition*
Cu(II)	1.85	8200(100)[a]	$^2A_{1g} \leftarrow {}^2B_{1g}$
		13700(100)	$^2E_{1g} \leftarrow {}^2B_{1g}$
Ni(II)	2.91	8200(100)	$^3T_{2g} \leftarrow {}^3A_{2g}$
		16100(100)	$^3T_{1g} \leftarrow {}^3A_{2g}$
		25800(100)	$^3T_{1g}(P) \leftarrow {}^3A_{2g}$
Co(II)	4.92	8100(100)	$^4T_{2g} \leftarrow {}^4T_{1g}$
		20800(100)	$^4T_{1g}(P) \leftarrow {}^4T_{1g}$

[a] Standard deviation is quoted in parenthesis.

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