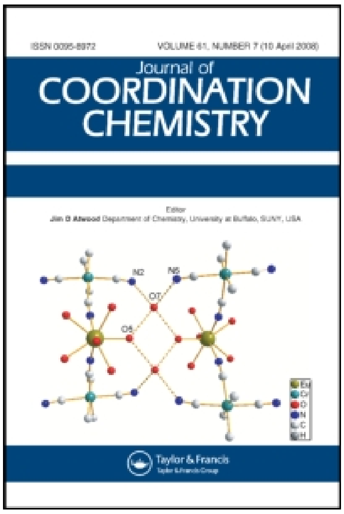

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Synthesis, Structure, and Magnetic Properties of Di-μ-Pyrazolatodicopper(II) Complexes of 3,5-Bis(Aminomethyl)Pyrazole

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SYNTHESIS, STRUCTURE, AND MAGNETIC PROPERTIES OF DI-μ-PYRAZOLATODICOPPER(II) COMPLEXES OF 3,5-BIS(AMINOMETHYL)PYRAZOLE

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3,5-Bis(aminomethyl)pyrazole (Hbampz) forms binuclear copper(II) complexes of the formula $[Cu_2(bampz)_2X_2]$ (X = Cl, Br). The crystal structure of $[Cu_2(bampz)_2Br_2]$ has been determined by the X-ray method: formula = $CuBrN_4C_5H_9$, monoclinic, space group $P2_1/n$, $a = 9.214(1)$, $b = 10.078(1)$, $c = 8.775(1)$ Å, $\beta = 97.33(1)°$, $V = 808.1$ Å^3. Two bampz$^-$ molecules combine with two copper(II) ions *via* the pyrazolate nitrogen and aminonitrogen atoms in the side chains affording an essentially planar N_4 environment for each metal ion. The Cu-Cu separation is 3.947(5)Å. The axial site of each copper is weakly coordinated by a bromide ion with a Cu–Br distance of 2.895(4) Å. Cryomagnetic investigations over the temperature range 80–300 K revealed a significant antiferromagnetic interaction through the pyrazolate bridges. The exchange integrals (J) based on the Heisenberg model ($H = -2J\hat{S}_1.\hat{S}_2$) was estimated at −200.8 and −192.0 cm^{-1} for $[Cu_2(bampz)_2Cl_2]$ and $[Cu_2(bampz)_2Br_2]$, respectively.

Keywords: Binuclear copper(II), pyrazolate bridge, X-ray structure, magnetism, spin coupling

INTRODUCTION

Magnetism of polynuclear complexes containing paramagnetic metal ions has been the subject of many studies over the past two decades, and some empirical rules and theoretical bases have been established for the correlation of magnetic properties and structural features of polynuclear complexes.[1-5] In particular, spin coupling in binuclear copper(II) complexes was extensively investigated in view of stereochemical factors and the nature of bridging groups.[6]

Pyrazoles,[7-12] 1,2,4-triazoles,[10,13,14] pyridazines,[9,15-17] and phthalazines[9,16-18] form a family of bridging ligands which can combine two metal ions with diazine (=N–N=) group, but binuclear complexes containing only diazine bridges are very rare.[8,10,11,13d,14] Pyridazine and phthalazine bridges often appear in combination with another anionic group such as hydroxide.[9,15-18] Similarly, the pyrazolate bridge in binuclear copper(II) complexes generally appears in combination with another group such as an alcoholate, phenolate, thiolate, acetate, or azide ion,[19-25] and discrete binuclear copper(II) complexes, doubly bridged by pyrazolate groups, are still very limited. Drew *et al.* obtained a di-μ-pyrazolatodicopper(II) complex encapsulated with an N_4 macrocycle.[10] A binuclear copper(II) complex triply bridged by two pyrazolate ions and one chloride ion was reported by Ajò *et al.*[12] In a

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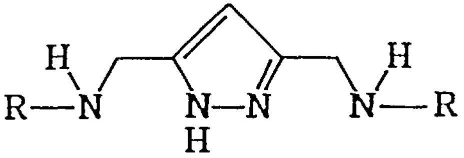
previous study we have reported dicopper(II) complexes of 3,5-bis{*N*-[2-(*N*,*N*-diethylamino)ethyl]aminomethyl}pyrazole (HL^1) and 3,5-bis{*N*-[3-(*N*,*N*-dimethylamino)propyl]aminomethyl}pyrazole (HL^2) (see Figure 1).[8] In those complexes of formula $[Cu_2L_2](BPh_4)_2$, two metal ions are doubly bridged by pyrazolate groups and each copper adopts a square-pyramidal structure with a terminal nitrogen at the axial site. Reedijk *et al.*[13d,14] reported dicopper(II) complexes doubly bridged by 1,2,4-triazole or 1,2,4-triazolato groups, which were derived from 4-amino-3,5-bis(aminomethyl)-1,2,4-triazole (Figure 2 (a)) and 3,5-bis(2-pyridyl)-1,2,4-triazole (Figure 2 (b)), respectively. All these complexes show considerably strong antiferromagnetic interactions, and so far as judged from magnetic data, pyrazolate bridges seem to be a better conductor of antiferromagnetic interactions than 1,2,4-triazole and 1,2,4-triazolate bridges.

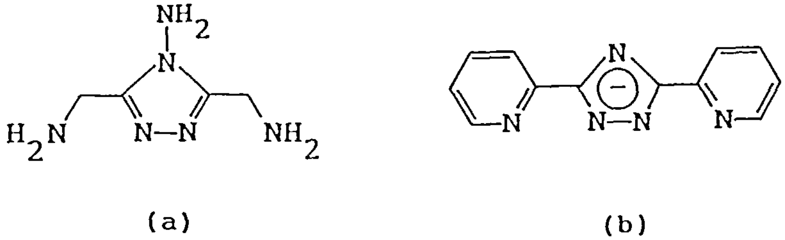


R= $-CH_2CH_2N(C_2H_5)_2$: HL^1

$-CH_2CH_2CH_2N(CH_3)_2$: HL^2

$-H$: Hbampz

FIGURE 1 Chemical structures of pyrazole ligands.



(a) (b)

FIGURE 2 Chemical structures of 4-amino-3,5-bis(aminomethyl)-1,2,4-triazole (a), and 3,5-bis(2-pyridyl)-1,2,4-triazolate (b).

The object of this study is to make an explicit comparison between the effects of pyrazolate and 1,2,4-triazolate (or 1,2,4-triazole) bridges upon the spin coupling between two copper(II) ions in a doubly bridged system based on structurally related complexes. Thus we aimed to prepare 3,5-bis(aminomethyl)pyrazole (abbreviated as Hbampz, see Figure 1) which bears a marked structural resemblance to 4-amino-3,5-bis(aminomethyl)-1,2,4-triazole (Figure 2 (a)). This paper reports the synthesis, structure, and magnetic properties (80–300 K) of binuclear copper(II) complexes of formula $[Cu_2(bampz)_2X_2]$ (X = Cl, Br).

EXPERIMENTAL

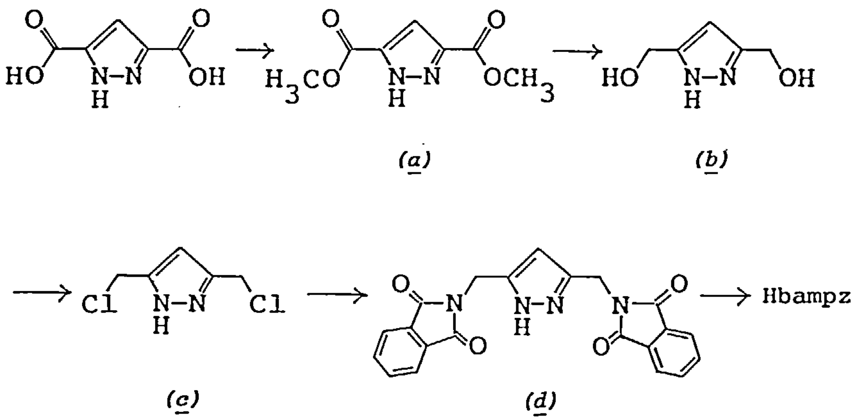
Materials

All chemicals were of reagent grade and were used as commercially purchased.

Preparations

The synthetic method for Hbampz is given in the Scheme.

Scheme



3,5-Bis(methoxycarbonyl) pyrazole (a)

3,5-Dicarboxypyrazole was converted into 3,5-bis(chloroformyl)pyrazole by the usual reaction with thionyl chloride. 3,5-Bis(chloroformyl)pyrazole (19.3 g) was added to absolute methanol (500 cm^3) and the mixture was refluxed for 15 hours with stirring. The excess methanol was evaporated, and the resultant residue was dissolved in hot benzene (500 cm^3) and dried with Na_2SO_4. The benzene solution was slowly diffused with *n*-hexane (200 cm^3) to give the dimethyl ester as white needles. The yield was 17.3 g (94%).

3,5-Bis(hydroxymethyl)pyrazole Hydrochloride (b)

A slurry of $LiAlH_4$ (15 g) in dry ether (100 cm^3) was prepared in a 1 dm^3, three-necked flask which was equipped with a Soxhlet apparatus connected to a reflux condenser. In the paper thimble of the Soxhlet apparatus finely ground 3,5-bis(methoxycarbonyl)pyrazole (18.4 g) was placed, and the mixture was refluxed for 24 hours. During this operation the diester, which is sparingly soluble in ether, was reduced. The reaction mixture in the flask was decomposed with water (50 cm^3). The solvent was evaporated to dryness. The resultant white cake was suspended in methanol (800 cm^3) and neutralized with carbon dioxide. The mixture was stirred under gentle reflux and filtered while hot. The filtrate was evaporated to dryness to give an oily substance. It was dissolved in ethanol (50 cm^3) and the solution was filtered to separate any insoluble materials. The filtrate was evaporated to dryness. The resulting oily substance was dissolved in dry ethanol (20 cm^3), to which was introduced dry hydrogen chloride gas for 30 minutes. Addition of dry ether (15 cm^3) to the ethanolic solution resulted in the precipitation of 3,5-bis(hydroxymethyl)-pyrazole hydrochloride as colourless needles. The yield was 12 g (73%). ^{1}H NMR (d^6-dmso): δ-4.53 (s, 4H, $-CH_2-$), 6.40 (s, 1H, ring proton), 9.6 (br., 4H). *Anal.*: Calcd. for $C_5H_9ClN_2O_2$: C, 36.35; H, 5.51; N, 17.02%. Found: C, 36.35; H, 5.53; N, 16.79%.

3,5-Bis(chloromethyl)pyrazole Hydrochloride (c)

A mixture of 3,5-bis(hydroxymethyl)pyrazole hydrochloride (13.2 g) and $SOCl_2$ (100 cm^3) was heated under gentle reflux for 30 minutes. Excess $SOCl_2$ was removed by distillation under reduced pressure and the residue was dissolved in ethanol (150 cm^3). The solution was filtered and addition of ether (50 cm^3) to the filtrate resulted in the precipitation of colourless plates. The yield was 14.8 g (92%). *Anal.*: Calcd. for $C_5H_7Cl_3N_2$: C, 29.81; H, 3.50; N, 13.90%. Found: C, 29.84; H, 3.52; N, 13.75%.

3,5-Bis(phthalimidomethyl)pyrazole (d)

3,5-Bis(chloromethyl)pyrazole hydrochloride (7.2 g) and potassium phthalimide (20 g) were added to dry *N,N*-dimethylformamide (100 cm^3), and the mixture was heated at 120°C for 3 hours. Chloroform (150 cm^3) was added to the reaction mixture, the whole was poured into water (200 cm^3), and the chloroform layer was separated. The aqueous layer was extracted with two 150 cm^3 portions of chloroform. The combined chloroform extract was washed with a 0.1 M sodium hydroxide solution and then with water, and dried with Na_2SO_4. The solution was concentrated to dryness and the residue thus obtained was used for the next reaction without further purification.

3,5-Bis(aminomethyl)pyrazole Dihydrochloride (Hbampz.2HCl)

The di-phthalimide derivative obtained above and hydrazine hydrate (4.3 g) were dissolved in ethanol (200 cm^3) and the mixture was refluxed for 3 hours. The reaction mixture was diluted with water (150 cm^3). The volume of the solution was reduced to 150 cm^3. To this was added conc. hydrochloric acid (200 cm^3). The mixture was refluxed for 2 hours and then allowed to cool in ice-water. Phthalic acid which precipitated was removed by filtration. The filtrate was concentrated to dryness and the residue was dissolved in water (100 cm^3). The solution was again cooled to 0°C to precipitate remaining phthalic acid, which was separated by filtration. The filtrate was concentrated to very small volume to yield crude 3,5-bis(aminomethyl)pyrazole dihydrochloride which was recrystallized from a water-methanol mixture as colourless needles. The yield was 5.65 g (80%). *Anal.*: Calcd. for $C_5H_{12}N_4Cl_2.0.5H_2O$: C, 28.86; H, 6.30; N, 26.92%. Found: C, 28.96; H, 6.26; N, 26.73%.

[$Cu_2(bampz)_2Cl_2$] (1)

Hbampz.2HCl (202 mg) was dissolved in methanol (10 cm^3) and neutralized by adding sodium hydroxide (120 mg). To this solution was added a solution of copper(II) chloride dihydrate (170 mg) in methanol (10 cm^3) to result in the precipitation of a pale purple precipitate. It was crystallized from water as red crystals. The yield was 39%. *Anal.*: Calcd. for $C_{10}H_{18}N_8Cl_2Cu_2$: C, 26.79; H, 4.05; N, 24.99; Cu, 28.35%. Found: C, 27.02; H, 3.97; N, 25.10; Cu, 28.60%.

[$Cu_2(bampz)_2Br_2$] (2)

Hbampz.2HCl (200 mg) was dissolved in water (5 cm^3) and neutralized with sodium hydroxide (120 mg). To this solution was added an aqueous solution of silver nitrate (340 mg). The mixture was stirred and allowed to stand for one hour. The resultant silver chloride was removed by filtration. To the filtrate was added dropwise an aqueous solution (5 cm^3) of copper(II) bromide (230 mg) with stirring to give a purple crystalline powder, which was crystallized from water as reddish crystals. The yield was 65%. Anal.: Calcd. for $C_{10}H_{18}N_8Br_2Cu_2$: C, 22.36; H, 3.38; N, 20.86; Cu, 23.66%. Found: C, 22.60; H, 3.41; N, 20.90; Cu, 23.68%.

X-Ray Structure Analysis

Single crystals of 2 were grown from a water solution by slow evaporation. The unit cell parameters and intensities were measured on a Rigaku AFC-5 automated four-circle diffractometer, using graphite-monochromatized MoKα radiation (λ = 0.71069 Å) at room temperature. The data were corrected for Lorentz and polarization effects but not for absorption. Crystal data and details of data collection are given in Table I.

TABLE I
Crystal data and details of data collection

mol. wt.	268.60	Dc, g cm^{-3}	2.208
formula	$CuBrN_4C_5H_9$	cryst. size	0.2 × 0.2 × 0.1
cryst. syst.	monoclinic	scan type	θ–2θ
space group	$P2_1/n$	scan speed, deg min^{-1}	6
cell constants		scan width ≥deg	(1.2 + 0.35tanθ)°
a, Å	9.214(1)	2θ range	2.5–45°
b, Å	10.078(1)	octant measured	+h, +k, ±l
c, Å	8.775(1)	No. of unique data	1146
β, deg	97.33(1)	R	0.095
V, $Å^3$	808.1	R_W	0.112
Z	4		

The structure was solved by direct methods and refined by block-diagonal least-squares methods, where the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with equal weight, $w = 1$, for all reflections. The hydrogen atoms were inserted in their calculated positions and included in the structure factor calculations, but their parameters were not refined. Atomic scattering factors were taken from Ref. 26. All the calculations were carried out on a FACOM M-780 computer in the Computer Centre of Kyushu University using local version[27] of the UNICS-III[28] and ORTEP[29] programs. The final positional parameters for the non-hydrogen atoms are given in Table II.

TABLE II
Final positional parameters (× 10^4) for non-hydrogen atoms of $[Cu_2(bampz)_2Br_2]$.

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*eqv
Br	3528(2)	4925(2)	3130(3)	3.31(5)
Cu	1496(2)	6363(2)	4778(3)	2.16(5)
N1	3188(18)	7008(14)	6380(17)	2.45(38)
N2	1110(17)	5293(14)	6435(17)	2.39(37)
N3	190(16)	4294(13)	6598(17)	2.10(36)
N4	−1392(17)	2209(15)	6861(17)	2.60(40)
C1	2991(22)	6569(18)	7934(22)	2.82(48)
C2	1887(19)	5449(15)	7868(18)	1.76(39)
C3	1456(22)	4569(19)	8917(21)	2.69(49)
C4	376(21)	3816(16)	8054(19)	2.30(44)
C5	−678(23)	2727(17)	8346(23)	2.92(50)

Physical Measurements

Elemental analyses were obtained at The Service Centre for Elemental Analysis, Kyushu University. Analysis of copper was made with a Shimadzu AA-680 Atomic Absorption/Flame Emission Spectrometer. Infrared spectra were recorded on a JASCO IR-810 spectrometer in KBr disks or nujol mulls. Magnetic susceptibilities were determined with a Faraday balance designed in our laboratory over the temperature range 80–300 K. The apparatus was calibrated with $[Ni(en)_3]S_2O_3$.[30] Diamagnetic corrections were made using Pascal's constants.[31]

RESULTS AND DISCUSSION

Synthesis and Characterization

In our previous study[8] we found *N*,*N*-disubstituted derivatives of Hbampz, HL^1 and HL^2, could be conveniently synthesized by the $LiAlH_4$ reduction of *N*,*N*-disubstituted 3,5-dicarbamoylpyrazoles. In this study we attempted to prepare Hbampz by the reduction of 3,5-dicarbamoylpyrazole with $LiAlH_4$, but this method gave a very poor result because 3,5-dicarbamoylpyrazole is hardly soluble in any solvents suitable for reduction with $LiAlH_4$ (ether, tetrahydrofuan, dioxane, *etc*). Thus, we adopted another synthetic route as shown in the Scheme which involves the esterification of 3,5-dicarboxypyrazole, the reduction of the diester (a) to the dialcohol (b), the conversion to the dihalide (c), and then conversion to Hbampz by the Gabriel amine synthesis. By this method Hbampz was obtained in a total yield of 50.5%.

The reaction of Hbampz.2HCl and copper(II) chloride dihydrate at 1:1 stoichiometry in methanol gave $[Cu_2(bampz)_2Cl_2]$ (**1**) as blue microcrystals. For the synthesis of $[Cu_2(bampz)_2Br_2]$ (**2**) Hbampz.2HCl was treated with silver nitrate to remove the chloride ion and subsequently reacted with copper(II) bromide in methanol.

Molar conductivities of **1** and **2** in water (1×10^{-3} mol dm^{-3}) were 233 and 242 S cm^2 mol^{-1}, respectively, indicating that both complexes behave as 2:1 electrolytes.[32] Thus the halide ions are not coordinated in aqueous solutions whereas the X-ray structural analysis for **2** has demonstrated weak coordination of the bromide ion to copper in the solid state as discussed below. The electronic spectra of **1** and **2** in water are similar and show a d–d band at 528 nm (ε: 95 M^{-1} cm^{-1}), which is higher in energy as compared with the d–d band maximum found for the di-μ-pyrazolatodicopper(II) complexes $[Cu_2(L^1)_2](BPh_4)_2$ and $[Cu_2(L^2)_2](BPh_4)_2$[8] (580 and 592 nm, respectively). As mentioned above the X-ray analytical result for $[Cu_2(L^1)_2](BPh_4)_2$[8] revealed a square-pyramidal configuration about each copper ion with a terminal nitrogen at the axial site. It appears that the five-coordinate structure of $[Cu_2(L^1)_2](BPh_4)_2$ (probably the same in $[Cu_2(L^2)_2](BPh_4)_2$ is maintained when it is dissolved in acetonitrile.

Crystal Structure

An ORTEP view of the complex **2** is shown in Figure 3, together with the numbering system. Relevant bond distances and angles with their estimated standard deviations are given in Table III.

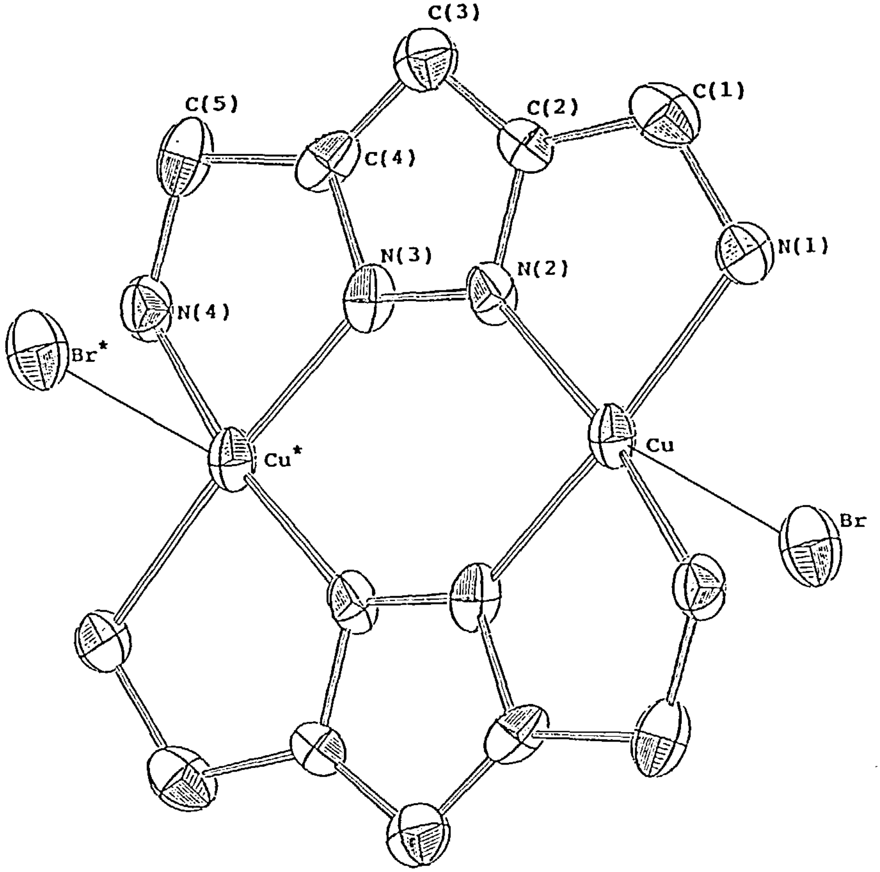


FIGURE 3 ORTEP view of $[Cu_2(bampz)_2Br_2]$ with the numbering system.

TABLE III
Relevant bond distances (Å) and angles (deg) for [$Cu_2(bampz)_2Br_2$].

(a) Bond distances			
Cu-Br	2.895(4)	Cu-N1	2.07(1)
Cu-N2	1.88(2)	Cu*-N3	1.96(1)
Cu*-N4	2.03(2)	N2-N3	1.34(2)
N1-C1	1.47(2)	N2-C2	1.37(2)
N3-C4	1.36(2)	N4-C5	1.49(2)
C1-C2	1.52(3)	C2-C3	1.37(3)
C3-C4	1.40(3)	C4-C5	1.51(3)
(b) Bond angles			
N1-Cu-N2	81.7(6)	N1-Cu-N4*	102.9(6)
N2-Cu-N3*	94.0(6)	N3*-Cu-N4*	80.9(6)
C1-N1-Cu	111(1)	C2-N2-Cu	121(1)
N3-N2-Cu	134(1)	N2-N3-Cu*	131(1)
C4-N3-Cu*	117(1)	C5-N4-Cu*	110(1)
N1-C1-C2	111(1)	C1-C2-N2	113(1)
C1-C2-C3	135(2)	N2-C2-C3	112(1)
N2-N3-C4	111(1)	C2-C3-C4	104(2)
C3-C4-N3	108(2)	C3-C4-C5	137(2)
N3-C4-C5	114(1)	C4-C5-N4	109(2)
C2-N2-N3	105(1)		

The complex molecule is composed of two copper(II) ions, two bampz$^-$ anions, and two bromide ions, forming a binuclear copper(II) skeleton doubly bridged by the pyrazolate anions. The molecule has an inversion centre. The binuclear skeleton formed by two copper(II) ions and two bampz$^-$ anions is nearly coplanar. The Cu...Cu separation is 3.947(4) Å, which is slightly longer than that (3.903(2) Å) in [$Cu_2(L^1)_2$]($(BPh_4)_2$).[8] The bromide ion is located at the axial site of the copper ion but the Cu-Br bond distance is significantly elongated (2.895(4) Å). Thus, the configuration around each copper can be regarded as a distorted square pyramid. The copper ion is shifted by 0.156 Å out of the least-squares plane towards the axial bromide ion. The two five-membered chelate rings, Cu-N(1)-C(1)-C(2)-N(2) and Cu*-N(3)-C(4)-C(5)-N(4), are not equivalent. In particular, the Cu-N(2) bond distance (1.88(2) Å) is considerably short as compared with the corresponding Cu*-N(3) distance (1.96(1) Å). Instead, the Cu-N(1) bond (2.07(1) Å) is longer than the Cu*-N(4) bond to release intra-chelate strain. The average of the two Cu-N(pyrazolate) bond distances (1.919 Å) is comparable to the average value (1.918 Å) in [$Cu_2(L^1)_2$]($(BPh_4)_2$).[8] In the related di-μ-(1,2,4-triazolato)dicopper(II) and di-μ-(1,2,4-triazole)copper(II) complexes of 3,5-bis(2-pyridyl)-1,2,4-triazolate anion[13d] and 4-amino-3,5-bis(aminomethyl)-1,2,4-triazole[14] (Figure 2 (a) and (b), respectively), the average Cu-N bond distances (1.946 and 1.944 Å, respectively) are significantly longer than the above values. Binuclear copper(II) complexes doubly bridged by pyridazine or phthalazine groups are not known, but complexes bridged by a pyridazine or phthalazine group and another bridging group like OH^- are.[17,18] The Cu-N bond distances in those binuclear complexes are much more elongated, being nearly 2.0 Å,[17,18] probably because pyridazine and phthalazine are neutral bridges whereas pyrazolate is negatively charged. It appears that pyrazolate bridges for copper(II) ions are significantly stronger than other diazine bridges.

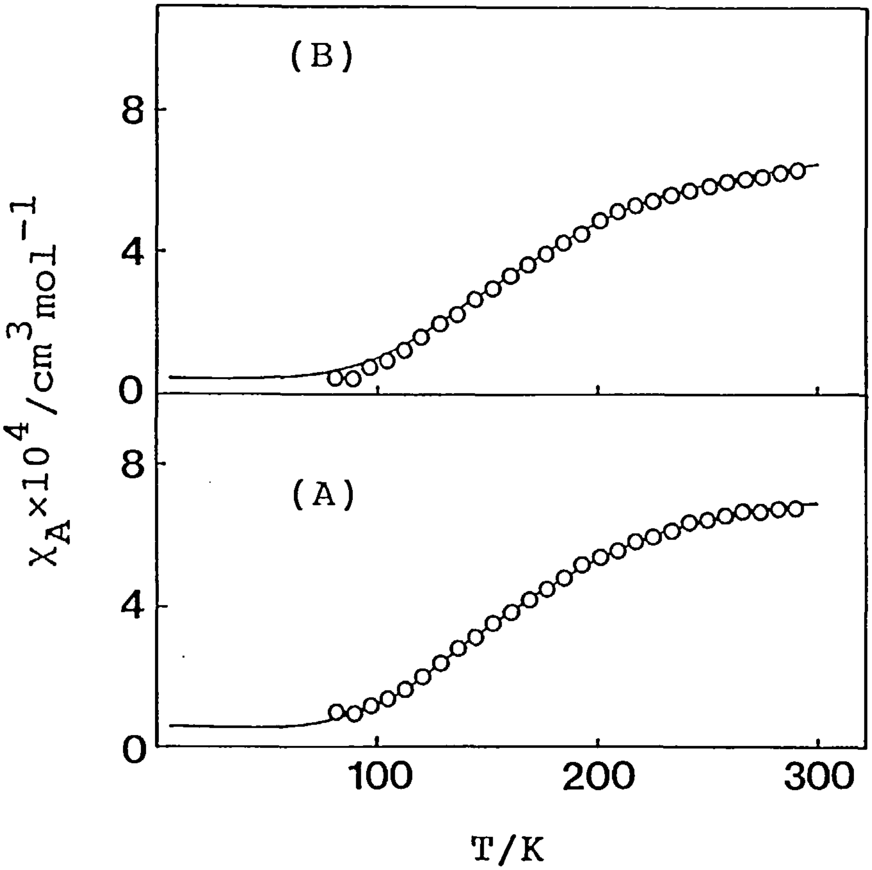


FIGURE 4 Temperature variations of magnetic susceptibilities of (A): $[Cu_2(bampz)_2Cl_2]$, (1) and (B): $[Cu_2(bampz)_2Br_2]$ (2).

Magnetic Properties

Both 1 and 2 show a subnormal magnetic moment at room temperature (1.19 μ_B and 1.25 μ_B per copper atom, respectively). This was presumed to be due to an intramolecular antiferromagnetic spin-coupling through the pyrazolate bridges. The magnetic measurements were carried out to liquid nitrogen temperatures and the results are given in Figure 4. In both complexes the susceptibility decreases with decreasing temperature and reaches a plateau around 80 K. The magnetic analyses were carried out by use of the Bleaney–Bowers equation,[33]

$$\chi_A = (Ng^2\beta^2/kT)[3 + \exp(-2J/kT)]^{-1} + N\alpha$$

where each symbol has its usual meaning. As indicated by the traces in Figure 4, good simulations could be attained with this equation using magnetic parameters as follows: $g = 2.20$, $J = -200.8\,cm^{-1}$, and $N\alpha = 40 \times 10^{-6}\,cm^3\,mol^{-1}$ for 1 and $g = 2.18$, $J = -192.0\,cm^{-1}$, and $N\alpha = 54 \times 10^{-6}\,cm^3\,mol^{-1}$ for 2. The discrepancy factors, $\sigma = [\Sigma(\chi_{obs.} - \chi_{calc.})^2/\Sigma\chi_{obs.}]^{1/2}$, in the least-squares fits were 0.053 and 0.046 for **1** and **2**, respectively. The exchange integrals found for the present complexes are comparable to those of $[Cu_2(L^1)_2](BPh_4)_2$ and $[Cu_2(L^2)_2](BPh_4)_2$ (-214 and -181 cm^{-1}, respectively).[8] A slightly larger exchange integral ($-J = 240$ cm^{-1}) has been reported for a binuclear copper(II) complex triply bridged by two pyrazolate and one chloride ions.[12] The exchange integral found for the di-μ-pyrazolato-dicopper(II) complex encapsulated by an N_4-macrocycle is smaller ($-J = 135$ cm^{-1}).[10] This is probably because of a large distortion in the binuclear skeleton, *i.e.* two copper coordination planes involving pyrazolate nitrogens are tilted with a dihedral angle of 85.1° and two bridging pyrazolate rings are also tilted with a dihedral angle of 34.8°.

For the related di-μ-(1,2,4-triazole)dicopper(II) complexes of 4-amino-3,5-bis-(aminomethyl)pyrazole the exchange integrals were evaluated as $-100 \sim -112$ cm^{-1}.[14] For the di-μ-(1,2,4-triazolato)dicopper(II) complexes of 3,5-bis(2-pyridyl)-1,2,4-triazolate exchange integrals of $-102 \sim -118$ cm^{-1} have been reported.[13d] Thus, antiferromagnetic spin coupling in binuclear copper(II) complex doubly bridged by 1,2,4-triazole groups is little increased even when the bridging group is replaced with the 1,2,4-triazolate group. We may conclude that the pyrazolate bridge is a stronger mediator than 1,2,4-triazole and 1,2,4-triazolate bridges in antiferromagnetic spin-coupling between copper(II) ions because of the short Cu–N (pyrazolate) bond distance as compared with those in Cu–N(triazole or triazolate) cases.

SUPPLEMENTARY DATA

Full lists of bond lengths and angles, hydrogen positions, anisotropic thermal parameters and observed and calculated structure factors are available from the authors.

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