Synthesis, Structure, and Magnetism of Binuclear Copper(II) Complexes of Pyrazole Ligands with Nitrogen-containing Chelating Arms. First Example of Di-μ-pyrazolato-dicopper(II,II) Complexes†

Toshiro Kamiusuki, Hisashi Ōkawa,* Naohide Matsumoto, and Sigeo Kida
Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashiku, Fukuoka 812, Japan

The preparation of new dinucleating pyrazole ligands, 3,5-bis[(2-diethylamino)ethylaminomethyl]pyrazole (HL^1) and 3,5-bis[(3-dimethylamino)propylaminomethyl]pyrazole (HL^2), has been accomplished. They afford binuclear copper(II) complexes of the formula $[Cu_2L_2][BPh_4]_2$ ($L = L^1$ or L^2). The structure of $[Cu_2L^1_2][BPh_4]_2$ was determined by single-crystal *X*-ray analysis. It crystallizes in the triclinic space group $P\bar{1}$ with a = 13.437(4), b = 15.192(5), c = 12.364(4) Å, α = 116.38(3), β = 113.71(3), γ = 60.48(2)°, and Z = 1. The complex has a binuclear structure doubly bridged by the pyrazolate groups with the Cu $\cdots$ Cu separation 3.903(2) Å. The configuration geometry of each copper is a square pyramid, whose basal plane is formed by the two pyrazolate nitrogens and the 'articular' nitrogens [Cu–N 1.906(3)—2.028(3) Å] and the apical site by one of the 'terminal' nitrogens [Cu–N 2.496(5) Å]. The other terminal nitrogen is free from co-ordination. Cryomagnetic investigations over the temperature range 100—300 K revealed a strong antiferromagnetic spin exchange in both complexes. The exchange integral (J) based on the Heisenberg model, was evaluated as -214 cm^{-1} for $[Cu_2L^1_2][BPh_4]_2$ and -181 cm^{-1} for $[Cu_2L^2_2][BPh_4]_2$.

It is known that the pyrazolate group functions as a bridge through its two nitrogens to afford bi- and poly-nuclear metal complexes,[1,2] but well characterized binuclear copper(II) complexes with pyrazolate bridges are still rare. Binuclear copper(II) complexes triply bridged by two pyrazolate groups and one halide ion (Cl^- or Br^-) were reported recently,[3] but to the best of our knowledge discrete binuclear copper(II) complexes doubly bridged by pyrazolate groups are not known. The pyrazolate bridge in binuclear copper(II) complexes generally appears in combination with another bridging group such as alcoholate, phenolate, thiolate, acetate, or azide.[4–10] The alcoholate/pyrazolate or phenolate/pyrazolate bridging combination has been obtained by the use of dinucleating ligands that possess an alcoholic or phenolic group capable of acting as an endogenous bridge.[5–10] Such ligands have been designed for model studies on the active site of type III copper proteins and binuclear copper(II) complexes with an endogenous O-bridge and various kinds of exogenous groups were magnetically investigated in the hope of gaining insight into this active site (met form).

In the previous study[4] we reported the synthesis of dinucleating pyrazole ligands with an amidic chelating arm attached to the 3 and 5 positions [see Figure 1(*a*)]. Those ligands incorporate two copper(II) ions with the endogenous pyrazolate bridge. Three co-ordination sites of each copper are occupied by one of the pyrazolate nitrogens and two nitrogens in an arm and the remaining fourth positions of the two metal ions are available for the binding of simple molecules such as the exogenous bridge. Thus, binuclear copper(II) complexes of the pyrazolate/acetate and the pyrazolate/azide combination of bridging groups have been obtained with these ligands. The complexes with an exogenous azide group show a significant antiferromagnetic spin-exchange interaction relevant to azidomethaemocyanin.[11]

In this study we have synthesized new pyrazole-based dinucleating ligands that possess fully reduced nitrogen-containing arms at the 3 and 5 positions; 3,5-bis[(2-diethylamino)ethylaminomethyl]pyrazole (HL^1) and 3,5-bis[(3-dimethylamino)propylaminomethyl]pyrazole (HL^2) [Figure 1(*b*)]. At this stage we have not yet obtained dicopper(II) complexes of mixed bridging systems with these ligands. Instead we have obtained complexes of composition $[Cu_2L_2][BPh_4]_2$ ($L = L^1$ or L^2) in which copper ions are doubly bridged by pyrazolate groups. This paper deals with the synthesis, structure, and magnetic properties of the complexes.

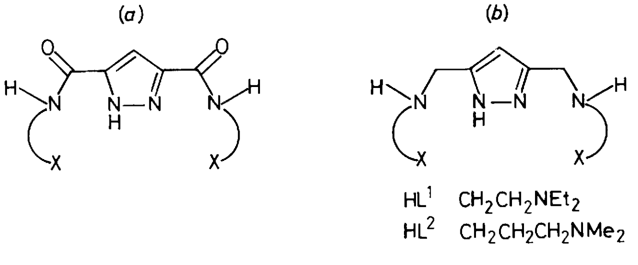

Figure 1. Chemical structures of pyrazole ligands.

Experimental

Preparations.—HL^1. To a slurry of $LiAlH_4$ (3 g) in absolute dioxane (100 cm^3) was added 3,5-bis[(2-diethylamino)ethylcarbamoyl]pyrazole[4] (3 g), and the mixture was stirred under gentle reflux for 12 h. The reaction mixture was decomposed with water (12 cm^3) and the resulting inorganic materials were separated by suction filtration and washed with hot dioxane. The filtrate and washings were combined and evaporated to dryness to give crude HL^1 as a colourless oily substance. The yield was 86%. It was characterized by ^1H N.m.r. spectroscopy δ (60 MHz, CD_3OD): δ 6.21 (1 H, s ring proton), 3.78 (4 H, s, CH_2NH), 2.71—2.37 (16 H, CH_2CH_2 and CH_2CH_3), and 1.02 (12 H, t, CH_2CH_3).

HL^2. This was obtained as a colourless oily substance by reducing 3,5-bis[(3-dimethylamino)propylcarbamoyl]pyrazole[4]

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1. pp. xix—xxii.

Table 1. Atomic co-ordinates (× 10^4) of $[Cu_2L^1{}_2][BPh_4]_2$

Atom	*x*	*y*	*z*
Cu	4 257(1)	1 499(0)	890(1)
N(1)	4 084(3)	2 310(3)	−579(3)
N(2)	2 533(4)	2 481(3)	691(4)
N(3)	3 611(3)	472(3)	−388(4)
N(4)	4 145(3)	−524(3)	−1 110(4)
N(5)	5 005(4)	−2 462(3)	−2 543(4)
N(6)	7 019(5)	−2 340(5)	−3 194(4)
C(1)	2 817(4)	2 962(4)	−789(5)
C(2)	2 361(5)	3 379(4)	348(5)
C(3)	1 738(4)	1 902(4)	−217(5)
C(4)	2 461(4)	804(4)	−884(5)
C(5)	2 213(5)	5(4)	−1 967(5)
C(6)	3 317(5)	−814(4)	−2 063(5)
C(7)	3 760(5)	−1 886(5)	−2 995(6)
C(8)	5 671(6)	−3 119(5)	−3 590(5)
C(9)	5 977(5)	−2 529(5)	−3 955(5)
C(10)	4 767(5)	2 991(4)	−65(5)
C(11)	6 075(5)	2 386(5)	143(6)
C(12)	4 378(5)	1 449(4)	−1 733(5)
C(13)	4 168(6)	1 823(6)	−2 799(5)
C(14)	6 826(9)	−1 258(8)	3 213(7)
C(15)	7 526(8)	−754(6)	−2 315(7)
C(16)	8 066(6)	−3 229(8)	−3 469(8)
C(17)	8 294(8)	−3 554(11)	−4 705(10)
B	7 758(5)	2 966(4)	7 628(5)
C(18)	8 274(4)	2 898(4)	9 054(4)
C(19)	8 148(4)	3 823(4)	10 084(5)
C(20)	8 533(5)	3 805(5)	11 300(5)
C(21)	9 047(5)	2 844(6)	11 520(6)
C(22)	9 185(5)	1 919(5)	10 545(6)
C(23)	8 810(4)	1 946(4)	9 333(5)
C(24)	6 400(4)	3 849(3)	7 494(4)
C(25)	5 642(4)	4 002(4)	8 128(5)
C(26)	4 470(5)	4 682(4)	7 966(5)
C(27)	3 984(4)	5 248(4)	7 128(5)
C(28)	4 704(5)	5 139(4)	6 511(4)
C(29)	5 884(4)	4 463(4)	6 690(4)
C(30)	7 769(4)	1 796(4)	6 657(4)
C(31)	6 794(4)	1 520(4)	6 168(4)
C(32)	6 851(5)	500(4)	5 391(5)
C(33)	7 883(6)	−275(4)	5 070(5)
C(34)	8 861(6)	−35(5)	5 530(6)
C(35)	8 801(5)	978(5)	6 303(6)
C(36)	8 556(4)	3 313(4)	7 291(4)
C(37)	9 193(4)	3 931(4)	8 161(4)
C(38)	9 798(5)	4 276(4)	7 854(5)
C(39)	9 801(6)	3 994(5)	6 643(6)
C(40)	9 182(7)	3 383(6)	5 729(6)
C(41)	8 567(6)	3 054(5)	6 056(5)

with $LiAlH_4$ in nearly the same way as that for HL^1. The yield was 49%. N.m.r. (60 MHz, CD_3OD):δ 6.21 (1 H, s, ring proton), 3.75 (4 H, s, CH_2NH), 2.73—2.38 (8 H, CH_2CH_2), 2.25 (12 H, s, CH_3), and 1.90—1.53 (4 H, $CH_2CH_2CH_2$).

$[Cu_2L^1{}_2][BPh_4]_2$. A methanolic solution (10 cm^3) of HL^1 (320 mg) and copper(II) chloride dihydrate (170 mg) was heated with stirring. To the resulting green solution were added a methanolic solution of NaOH (40 mg) and then a methanolic solution of $NaBPh_4$ (700 mg) to result in the precipitation of pale blue microcrystals. They were recrystallized from acetone as dark blue crystals, yield 94%, M.p. *ca.* 157 °C with decomposition. (Found: C, 69.75; H, 7.90; Cu, 8.80; N, 11.85, Calc. for $C_{82}H_{110}B_2Cu_2N_{12}$: C, 69.70; H, 7.85; Cu, 9.00; N, 11.90%).

$[Cu_2L^2{}_2][BPh_4]_2$. This complex was obtained in a similar way to that for the L^1 complex. Recrystallization was carried out from acetone to give green crystals. The yield was 78%, m.p. *ca.* 155 °C with decomposition. (Found: C, 68.80; H, 7.50; Cu, 9.05; N, 12.30. Calc. for $C_{78}H_{102}B_2Cu_2N_{12}$: C, 69.05; H, 7.60; Cu, 9.35; N, 12.40%.

X-Ray Structure Analysis.—Single crystals of $[Cu_2L^1{}_2][BPh_4]_2$ suitable for *X*-ray analysis were grown by slow crystallization from an acetone solution, and a crystal of dimensions 0.4 × 0.5 × 0.3 mm was used. The unit-cell parameters and intensities were measured on a Rigaku Denki AFC-5 four-circle diffractometer, using graphite-monochromatized Mo-K_α radiation (λ = 0.710 69 Å) at room temperature. The data were corrected for Lorentz and polarization effects but not for absorption.

Crystal data. $C_{82}H_{110}B_2N_{12}Cu_2$, M = 1 412.55, triclinic, space group $P\bar{1}$, a = 13.437(4), b = 15.192(5), c = 12.364(4) Å, α = 116.38(3), β = 113.71(3), γ = 60.48(2)°, U = 1 912.61(1.2) $Å^3$, D_c = 1.226 g cm^{-3} (Z = 1), μ(Mo-K_α) = 6.059 cm^{-1}, scan mode 2θ—θ, scan speed 6° min^{-1}, scan width (1.2 + 0.35 tan θ)°, 2θ range 2.5—50°, octand measured $+h$, $\pm k$, $\pm l$, reflections with $|F_o| > 3\sigma(|F_o|)$ 4 933, R = 0.0637, R' = 0.0634.

The structure was solved by the heavy-atom method and Fourier technique and refined by the block-diagonal least-squares method, the function minimized being $\Sigma w(|F_o|-|F_c|)$ with equal weights w = 1 for all reflections. The hydrogen atoms were inserted in their calculated positions, and included in the structure-factor calculation, but their parameters were not refined. Atomic scattering factors were taken from ref. 12. All the calculations were carried out on a FACOM M-780 computer in the Computer Center of Kyushu University by the use of a local version[13] of the UNICS-III[14] and ORTEP programs.[15] The final positional parameters of non-hydrogen atoms are given in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Physical Measurements.—Analytical data (C, H, and N) were obtained at the Elemental Analysis Service Centre, Kyushu University. Copper analyses were made on a Shimadzu AA-680 atomic absorption/flame emission spectrometer. Infrared spectra were recorded on a JASCO spectrometer Model 810 on Nujol mulls, ^1H n.m.r. spectra on a HITACHI R-20B spectrometer in CD_3OD using tetramethylsilane as the internal standard and electronic spectra on a Shimadzu multipurpose spectrometer Model MPS-2000 in acetone. Electric conductivity measurements were carried out on a Denki Kagaku Keiki AOC-10 digital conductometer in acetonitrile (*ca.* 1 × 10^{-3} mol dm^{-3}). Magnetic susceptibilities were measured on powder samples over the temperature range 100—300 K by the Faraday method. The apparatus was calibrated with $[Ni(en)_3]S_2O_3$(en = ethylenediamine),[16] and diamagnetic corrections were made by the use of Pascal constants.

Results and Discussion

Preparations and General Characterization.—In the previous study[4] it was shown that the amide homologues of HL^1 and HL^2 {3,5-bis[(2-diethylamino)ethylcarbamoyl]pyrazole and 3,5-bis[(3-dimethylamino)propylcarbamoyl]pyrazole re-

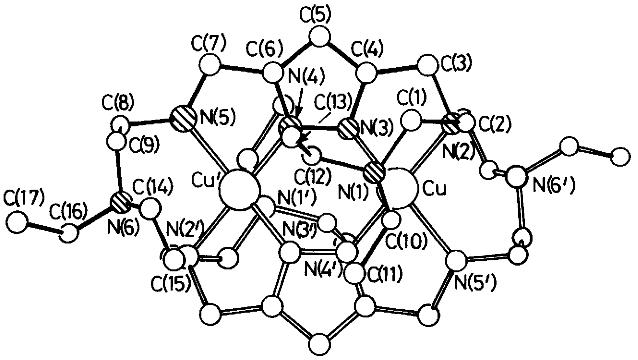

Figure 2. Perspective drawing of the cation $[Cu_2L^1{}_2]^{2+}$ projected on to the copper co-ordination plane, showing the numbering system

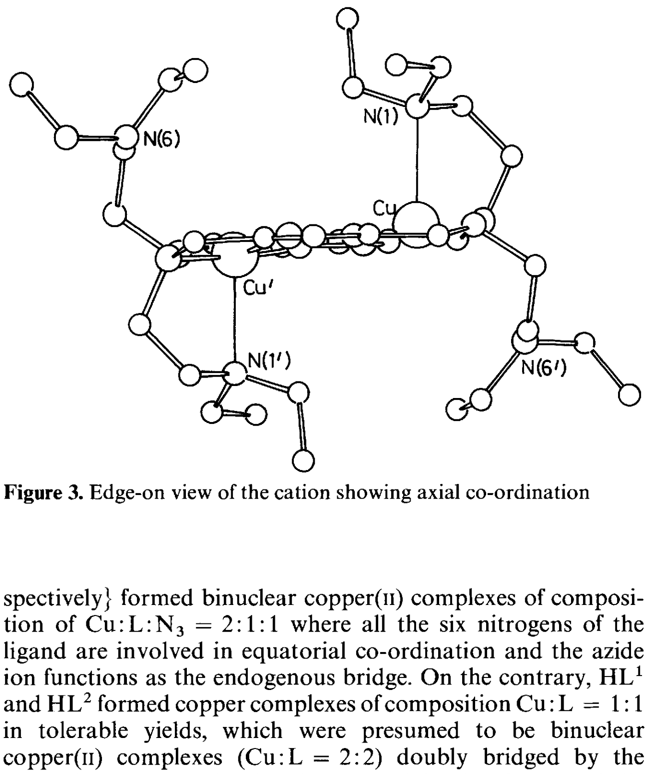

Figure 3. Edge-on view of the cation showing axial co-ordination

Table 2. Selected bond distances (Å) and angles (°) of $[Cu_2L^1{}_2][BPh_4]_2$

Cu...Cu′	3.903(2)	Cu–N(1)	2.496(5)
Cu–N(2)	2.028(3)	Cu–N(3)	1.929(4)
Cu–N(4′)	1.906(3)	Cu–N(5′)	2.108(4)
N(1)–C(1)	1.468(5)	N(1)–C(10)	1.482(8)
N(1)–C(12)	1.479(5)	N(2)–C(2)	1.489(9)
N(2)–C(3)	1.504(7)	N(3)–N(4)	1.358(4)
N(3)–C(4)	1.328(5)	N(4)–C(6)	1.336(6)
N(5)–C(7)	1.455(6)	N(5)–C(8)	1.541(8)
N(6)–C(9)	1.422(8)	N(6)–C(14)	1.542(15)
N(6)–C(16)	1.422(8)	C(1)–C(2)	1.507(9)
C(3)–C(4)	1.493(6)	C(4)–C(5)	1.404(6)
C(5)–C(6)	1.397(6)	C(6)–C(7)	1.504(7)
C(8)–C(9)	1.430(14)	C(10)–C(11)	1.501(7)
C(12)–C(13)	1.349(14)	C(14)–C(15)	1.349(14)
C(16)–C(17)	1.493(16)		
N(1)–Cu–N(2)	79.9(2)	N(1)–Cu–N(3)	94.5(2)
N(1)–Cu–N(4)	103.3(2)	N(1)–Cu–N(5)	97.7(2)
N(2)–Cu–N(3)	82.2(1)	N(2)–Cu–N(5′)	100.0(1)
N(3)–Cu–N(4′)	96.1(1)	N(4)–Cu′–N(5)	80.8(1)
C(1)–N(1)–C(10)	110.1(3)	C(1)–N(1)–C(12)	110.6(3)
C(10)–N(1)–C(12)	112.3(5)	Cu–N(2)–C(2)	108.5(3)
Cu–N(2)–C(3)	109.3(4)	C(2)–N(2)–C(3)	112.7(4)
Cu–N(3)–N(4)	130.6(3)	Cu–N(3)–C(4)	118.6(3)
C(4)–N(3)–N(4)	103.8(3)	Cu′–N(4)–N(3)	131.0(2)
Cu′–N(4)–C(6)	120.5(2)	N(3)–N(4)–C(6)	108.2(3)
Cu′–N(5)–C(7)	110.7(4)	Cu′–N(5)–C(8)	118.1(4)
C(7)–N(5)–C(8)	112.3(4)	C(9)–N(6)–C(14)	106.2(5)
C(9)–N(6)–C(16)	113.2(5)	C(14)–N(6)–C(16)	118.6(9)
C(2)–C(1)–N(1)	111.9(4)	C(1)–C(2)–N(2)	110.3(3)
C(4)–C(3)–N(2)	109.3(4)	C(3)–C(4)–C(5)	134.6(4)
C(3)–C(4)–N(3)	115.9(4)	C(5)–C(4)–N(3)	109.4(3)
C(4)–C(5)–C(6)	103.8(4)	C(5)–C(6)–C(7)	134.8(4)
C(5)–C(6)–N(4)	109.6(4)	C(7)–C(6)–N(4)	115.4(4)
C(6)–C(7)–N(5)	110.7(4)	N(5)–C(8)–C(9)	115.2(5)
C(8)–C(9)–N(6)	115.2(5)	C(11)–C(10)–N(1)	113.9(4)
C(13)–C(12)–N(1)	115.1(4)	C(15)–C(14)–N(6)	117.9(7)
C(17)–C(16)–N(6)	117.6(8)		

spectively} formed binuclear copper(II) complexes of composition of $Cu:L:N_3 = 2:1:1$ where all the six nitrogens of the ligand are involved in equatorial co-ordination and the azide ion functions as the endogenous bridge. On the contrary, HL^1 and HL^2 formed copper complexes of composition Cu : L = 1 : 1 in tolerable yields, which were presumed to be binuclear copper(II) complexes (Cu : L = 2 : 2) doubly bridged by the pyrazolate groups. The electric conductivity data in acetonitrile [229 S cm^2 mol^{-1} for the complex of L^1 and 220 S cm^2 mol^{-1} for the complex of L^2] indicated that the complexes behave as 2 : 1 electrolytes.[17] Our attempts to synthesize binuclear copper(II) complexes with an exogenous bridging group like azide ion were all in vain. In the case of a type ligands the in-plane co-ordination of the terminal nitrogen takes place readily because the 'articular' nitrogen (amidate–nitrogen) adopts sp^2 hybridization, whereas in the case of b type ligands such an in-plane co-ordination seems difficult for steric reasons because the articular nitrogen adopts sp^3 hybridization. A related ligand with sulphur as the articular donor atom, 3,5-bis[2-(2-pyridylethyl)thiomethyl]pyrazole, was suggested by Urback[18] to form a dicopper(II) complex with in-plane co-ordination for the terminal pyridyl nitrogen, but its detailed structure and physicochemical properties have not been reported.

The ligands HL^1 and HL^2 show some i.r. bands attributable to the N–H vibrations in the region 3 300—3 100 cm^{-1} while their complexes show a sharp i.r. band at 3 275 cm^{-1}. The electronic spectra of the complexes in acetonitrile each shows one *d–d* band in the visible region: $\lambda_{max.}$ 580 nm (ε 110 dm^{3}mol^{-1}cm^{-1} per copper) for $[Cu_2L^1{}_2][BPh_4]_2$ and $\lambda_{max.}$ 592 nm (ε 141 dm^{3}mol^{-1}cm^{-1}) for $[Cu_2L^2{}_2][BPh_4]_2$. The spectral data suggest a tetragonal configuration around each copper ion.

Crystal Structure of $[Cu_2L^1{}_2][BPh_4]_2$.—An ORTEP view of the cation is shown in Figure 2 together with the numbering system. Relevant bond distances and angles with their estimated standard deviations are given in Table 2.

As expected the cation has a binuclear structure, comprising two copper(II) ions and two ligands in the anionic form, and has the inversion symmetry at the centre of the cation. The articular nitrogens [N(2), N(2′), N(5), and N(5′)] and the pyrazolate nitrogens [N(3), N(3′), N(4), and N(4′)] co-ordinate to the copper(II) ions to form an essentially planar Cu_2N_8 skeleton, doubly bridged by the pyrazolate groups. The Cu...Cu′ separation is 3.903(2) Å. The copper-pyrazolate nitrogen distances [1.929(4) and 1.906(3) Å] are short compared with those (> 1.94 Å) found for oligonuclear copper(II) complexes having pyrazolate bridges.[19,20] The bond distances with the articular nitrogens, Cu-N(2) and Cu-N(5′), are slightly longer [2.028(3) and 2.108(4) Å, respectively]. One of the terminal nitrogens, N(1), co-ordinates to the axial position of the copper [Cu-N(1) 2.496(5) Å] but the other terminal nitrogen, N(6), is not co-ordinated (see Figure 3). The Cu-N(1) bond is nearly perpendicular to the least-squares equatorial plane so that the configuration around each copper is best described as a square pyramid.

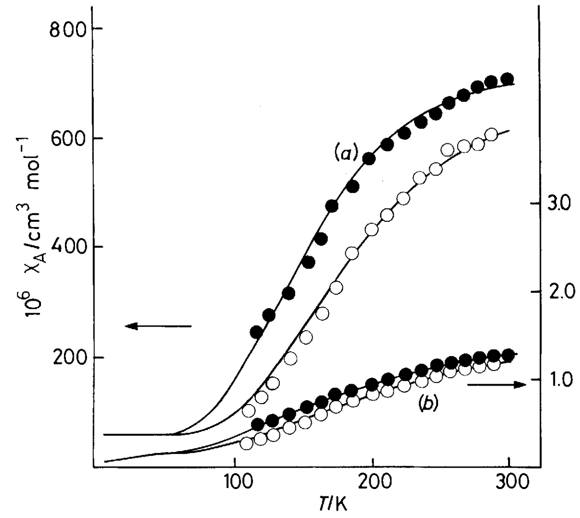

Figure 4. Temperature variations of magnetic susceptibility, (*a*); and magnetic moment (*b*); $[Cu_2L^1{}_2][BPh_4]_2$ (○), $[Cu_2L^2{}_2][BPh_4]_2$ (●)

Magnetic Properties.—Both complexes show a subnormal magnetic moment at room temperature, suggesting the operation of an antiferromagnetic spin exchange within each molecule. Magnetic susceptibilities were determined over the temperature range 100—300 K on powder samples and the results are given in Figure 4. In both cases the magnetic susceptibility decreases with decreasing temperature. Such a magnetic behaviour is characteristic of spin-coupled dicopper-(II,II). Thus, magnetic simulations were performed by use of the Bleaney–Bowers equation (1)[21] based on the spin Hamiltonian $\mathcal{H} = -2JS_1S_2$.

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

In this equation each symbol has its usual meaning. The solid lines in Figure 4 are based on this equation using the magnetic parameters $J = -214$ cm^{-1}, $g = 2.19$, and $N\alpha = 60 \times 10^{-6}$ cm^3 mol^{-1} for $[Cu_2L^1{}_2][BPh_4]_2$, and $J = -181$ cm^{-1}, $g = 2.10$, and $N\alpha = 60 \times 10^{-6}$ cm^3 mol^{-1} for $[Cu_2L^2{}_2][BPh_4]_2$.

The exchange integrals obtained are larger than the values (~ -120 cm^{-1}) found for $PPh_4[Cu_2\{H_2B(pz)_2\}_2(pz)_2X][H_2B(pz)_2$ = dihydrobis(1-pyrazolyl)borate, X = Cl^- or Br^-], triply bridged by two pyrazolate groups and a halide ion.[3] In the case of these complexes both the two CuN_4 co-ordination planes and the planes of the pyrazolate rings are not parallel. Ajō *et al.*[3] carried out extended-Huckel calculations on the model complex $[\{Cu(pz)Cl_2\}_2]^{2-}$ to see the effects of deviations from coplanarity upon the antiferromagnetic spin-exchange interaction and suggested that the deviation from coplanarity of two pyrazolate bridges has the largest effect. In the present complexes the two pyrazolate rings and the co-ordination planes are all coplanar, affording a favourable situation for an efficient antiferromagnetic spin coupling through the pyrazolate bridge.

In the previous paper[4] we have suggested that the antisymmetric highest occupied molecular orbital (h.o.m.o.) of bridging pyrazolate plays a major role in antiferromagnetic superexchange between copper(II) ions. On the other hand, it is also suggested that the symmetric h.o.m.o. of pyrazolate contributes significantly to magnetic spin exchange between copper(II) ions.[3,6] In the present case of di-μ-pyrazolato-dicopper(II,II), however, it is evident that the two h.o.m.o.s of the pyrazolate bridges interact complementarily with the magnetic orbitals of the copper(II) ions, irrespective of the symmetry of the pyrazolate h.o.m.o., to give rise to an effective antiferromagnetic spin-exchange interaction.

References

1 S. Trofimenko, *Chem. Rev.*, 1972, **72**, 497.
2 M. Inoue and M. Kubo, *Coord. Chem. Rev.*, 1976, **21**, 1.
3 D. Ajō, A. Bencini, and F. Mani, *Inorg. Chem.*, 1988, **27**, 2437.
4 T. Kamiusuki, H. Ōkawa, E. Kitaura, M. Koikawa, N. Matsumoto, H. Ohsio, and S. Kida, *J. Chem. Soc., Dalton Trans.*, 1989, 2077.
5 R. Robson, *Aust. J. Chem.*, 1970, **23**, 2217; W. D. McFadyen, R. Robson, and H. Schaap, *Inorg. Chem.*, 1972, **11**, 1777.
6 Y. Nishida and S. Kida, *Inorg. Chem.*, 1988, **27**, 447.
7 H. P. Berends and D. W. Stephan, *Inorg. Chem.*, 1987, **26**, 749.
8 W. Mazurek, A. M. Bond, M. J. O'Connor, and A. G. Wedd, *Inorg. Chem.*, 1986, **25**, 906.
9 M. Louey, P. D. Nichols, and R. Robson, *Inorg. Chim. Acta*, 1980, **47**, 87.
10 P. Iliopoulos, G. D. Fallon, and K. S. Murray, *J. Chem. Soc., Dalton Trans.*, 1988, 1823; P. Iliopoulos, K. S. Murray, R. Robson, J. Wilson, and G. A. Williams, *ibid.*, 1987, 1585.
11 E. I. Solomon, D. M. Dooley, R. Wang, and H. B. Gray, *J. Am. Chem. Soc.*, 1976, **98**, 1029.
12 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
13 S. Kawano, *Rep. Comput. Cent., Univ. Kyushu*, 1980, **13**, 39.
14 T. Sakurai and K. Kobayashi, *Rep. Inst. Phys. Chem. Res.*, 1979, **55**, 69.
15 C. K. Johnson, Rep. No. 3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1965.
16 N. F. Curtis, *J. Chem. Soc.*, 1961, 3147.
17 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.
18 F. L. Urbach, 'Metal Ions in Biological Systems,' ed. H. Sigel, Marcel Dekker, New York, 1981, vol. 13, p. 73.
19 R. W. M. ten Hoedt, F. B. Hulsbergen, G. C. Verschoor, and J. Reedijk, *Inorg. Chem.*, 1982, **21**, 2369.
20 F. B. Hulsbergen, R. W. M. ten Hoedt, G. C. Verschoor, J. Reedijk, and A. L. Spek, *J. Chem. Soc., Dalton Trans.*, 1983, 539.
21 B. Bleaney and K. D. Bowers, *Proc. R. Soc. London, Ser. A*, 1952, **214**, 451.

Received 14*th March* 1989; *Paper* 9/01102A