

Binuclear Copper(II) Complexes of New Dinucleating Ligands with a Pyrazolate Group as an Endogenous Bridge. Effects of Exogenous Azide and Acetate Bridges on Magnetic Properties †

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New dinucleating ligands containing pyrazole as an endogenous bridging group, 3,5-bis- $[N-(2\text{-pyridylmethyl})\text{carbamoyl}]$ pyrazole (H_3L^1), 3,5-bis $\{N-[2-(\text{diethylamino})\text{ethyl}]\text{carbamoyl}\}$ pyrazole (H_3L^2), and 3,5-bis $\{N-[3-(\text{dimethylamino})\text{propyl}]\text{carbamoyl}\}$ pyrazole (H_3L^3), and their binuclear copper(II) complexes with azide or acetate ion as an exogenous bridge, $[Cu_2L(N_3)(H_2O)_2]\cdot H_2O$ ($L = L^1-L^3$) and $[Cu_2L^1(O_2CMe)]\cdot 2MeOH$, have been obtained. Cryomagnetic investigations (5–300 K) reveal a significant antiferromagnetic spin exchange for the azide-bridged complexes ($-J = 371\text{--}297\text{ cm}^{-1}$), but a ferromagnetic spin exchange ($J > +8.9\text{ cm}^{-1}$) for the acetate-bridged complex. The azide-bridged complexes are e.s.r. silent. The acetate-bridged complex is unstable in dimethylformamide (dmf) but a quickly prepared dmf frozen solution of the sample gives X-band signals characteristic of a spin-triplet ($S = 1$) state, together with signals due to a spin doublet ($S = \frac{1}{2}$) attributable to monomeric copper(II). Signals at 812, 1 292, and 4 380 G show a seven-line hyperfine structure ($A_{zz} = 0.0103\text{ cm}^{-1}$); the first and third signals are assigned to $\Delta M_s = 1$ transitions and the second to the $\Delta M_s = 2$ transition of the parallel resonance of the spin-triplet state. E.s.r. simulation based on the spin Hamiltonian for the spin triplet of a dicopper(II) system gives $g_{zz} = 2.533$, $D = 0.210\text{ cm}^{-1}$, and $E = 0.020\text{ cm}^{-1}$. Only two components of the perpendicular resonances are recognizable at 2 113 and 3 812 G which give $g_x = 2.055$.

The occurrence of a pair of copper ions at the active site of haemocyanin in many species of arthropods and molluscs¹ has stimulated much interest in mimicking the active site structure, physicochemical properties, and functions of this protein by the use of simple model complexes. Extended X-ray absorption fine structure (EXAFS) investigations for deoxy-, oxy-, and meto-haemocyanins² suggested intermetal distances of 3.43–3.66 Å. The recent X-ray structure analysis for the deoxy form of the spiny lobster haemocyanin³ has revealed that the two copper(I) ions are each co-ordinated by three imidazole nitrogens and that the Cu–Cu separation is 3.8 Å. The presence of an endogenous bridge has been suggested,⁴ though not definitely identified. The realistic candidates are hydroxide, alkoxide from serine or threonine, or phenoxide from tyrosine.⁵ All the three bridges act as good mediators of antiferromagnetic spin-exchange interaction between a pair of copper(II) ions and can reproduce the magnetic properties characteristic of oxyhaemocyanin⁶ and azido-metohaemocyanin.⁷ In view of these facts much effort has been directed to the exploitation of dinucleating ligands which possess an alcoholic or phenolic group as an endogenous bridge in order to achieve Cu–Cu separations of 3.4–4.0 Å.^{8–14}

In this study we have synthesized another type of dinucleating ligand comprised of pyrazole as an endogenous bridge and two chelating arms attached to the 3 and 5 positions of the pyrazole ring: 3,5-bis $[N-(2\text{-pyridylmethyl})\text{carbamoyl}]$ pyrazole (H_3L^1), 3,5-bis $\{N-[2-(\text{diethylamino})\text{ethyl}]\text{carbamoyl}\}$ pyrazole (H_3L^2), and 3,5-bis $\{N-[3-(\text{dimethylamino})\text{propyl}]\text{carbamoyl}\}$ pyrazole (H_3L^3). These ligands are expected to allow incorporation of two metal ions in a close proximity, where three co-ordination positions of each ion are occupied by three nitrogens (one from the pyrazolate group and two from the chelating arm) and the fourth positions of the ions are available for the binding of

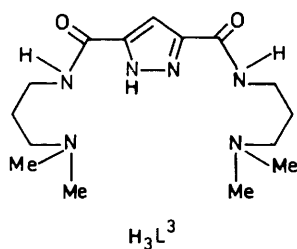
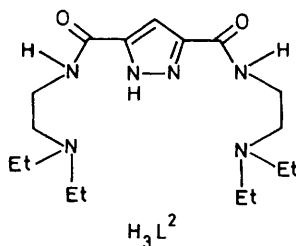
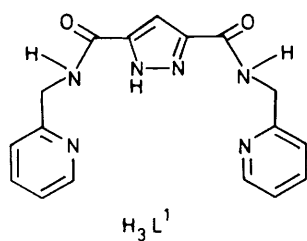
diatomic or simple polyatomic molecules to form exogenous bridges. In this paper we describe the synthesis and properties of dicopper(II) complexes with azide or acetate ion as the exogenous bridge. The dicopper(II) complex of 3,5-bis $\{N-[2-(\text{dimethylamino})\text{ethyl}]\text{carbamoyl}\}$ pyrazole (with hydroxide as the exogenous bridge) was obtained¹⁵ but its detailed physicochemical properties have not been reported.

Experimental

Preparations.—3,5-Bis $[N-(2\text{-pyridylmethyl})\text{carbamoyl}]$ pyrazole (H_3L^1). Pyrazole-3,5-dicarboxylic acid (Aldrich Chem. Co.) was converted into 3,5-bis(chloroformyl)pyrazole by the usual reaction with $SOCl_2$. To a suspension of the acid chloride (1.0 g) in absolute dioxane (60 cm³) was added dropwise a solution of 2-aminomethylpyridine (1.2 g) and triethylamine (1.1 g) in dioxane with stirring. The reaction mixture was allowed to stand overnight, and the crude product was collected by filter suction, washed thoroughly with water to eliminate triethylamine hydrochloride, and crystallized from dichloromethane-methanol (1:1) as colourless needles melting at 234–235 °C. The yield after recrystallization was 69% (Found: C, 60.70; H, 4.70; N, 24.95. Calc. for $C_{17}H_{16}N_6O_2$: C, 60.70; H, 4.80; N, 25.00%).

3,5-Bis $\{N-[2-(\text{diethylamino})\text{ethyl}]\text{carbamoyl}\}$ pyrazole (H_3L^2). This was obtained by the reaction of the acid chloride (1.0 g) and *N,N*-diethylethylenediamine (1.2 g) in dioxane in the presence of triethylamine. Triethylamine hydrochloride was separated by filter suction and the filtrate was condensed to a small portion to give the crude product, which was recrystallized from benzene as colourless prisms melting at 170 °C. Yield

† Non-S.I. unit employed: $G = 10^{-4}\text{ T}$.



53% (Found: C, 57.65; H, 9.15; N, 23.60. Calc. for $C_{17}H_{32}N_6O_2$: C, 57.90; H, 9.15; N, 23.85%).

3,5-Bis{N-[3-(dimethylamino)propyl]carbamoyl}pyrazole (H_3L^3). This was prepared similarly to H_3L^2 . The crude product was recrystallized from dimethyl sulphoxide as colourless prisms melting at 181 °C. Yield 29% (Found: C, 55.45; H, 8.65; N, 25.85. Calc. for $C_{15}H_{28}N_6O_2$: C, 55.55; H, 8.70; N, 25.90%).

$[Cu_2L^1(O_2CMe)] \cdot 2MeOH$. To a suspension of H_3L^1 (336 mg) in dichloromethane-methanol (1:1, v/v, 20 cm³) were added a methanolic solution of copper(II) acetate monohydrate (399 mg), powdered sodium acetate (140 mg), and sodium hydroxide pellets (120 mg), and the mixture was stirred at ambient temperature to give purple microcrystals. These were collected by filter suction, washed thoroughly with methanol, and dried *in vacuo* (Found: C, 43.45; H, 3.85; Cu, 21.4; N, 14.10. Calc. for $C_{21}H_{24}Cu_2N_6O_6$: C, 43.20; H, 4.15; Cu, 21.8; N, 14.40%).

$[Cu_2L^1(N_3)(H_2O)_2] \cdot H_2O$. A methanolic solution (2 cm³) of copper(II) chloride dihydrate (341 mg) was added to a suspension of H_3L^1 (336 mg) in methanol (20 cm³), and the solution was adjusted to pH 9 by adding a sodium methoxide solution. The addition of powdered sodium azide (excess) resulted in the precipitation of a green crystalline powder. It was collected by filter suction, washed with water, and crystallized from pyridine-methanol (1:1, v/v) as deep green prisms (Found: C, 36.55; H, 3.45; Cu, 22.30; N, 22.90. Calc. for $C_{17}H_{19}Cu_2N_9O_5$: C, 36.70; H, 3.45; Cu, 22.80; N, 22.65%).

$[Cu_2L^2(N_3)(H_2O)_2] \cdot H_2O$. This complex was obtained similarly to the L^1 complex as a deep green crystals. Recrystallization was from methanol (Found: C, 35.60; H, 6.10; Cu, 22.10; N, 22.00. Calc. for $C_{17}H_{35}Cu_2N_9O_5$: C, 35.65; H, 6.15; Cu, 22.20; N, 22.00%).

$[Cu_2L^3(N_3)(H_2O)_2] \cdot H_2O$. This complex was obtained similarly to the L^1 complex as a green crystalline precipitate. It was crystallized from ethanol (Found: C, 32.75; H, 5.70; Cu, 23.70; N, 22.85. Calc. for $C_{15}H_{31}Cu_2N_9O_5$: C, 33.10; H, 5.75; Cu, 24.40; N, 23.15%).

Physical Measurements.—Elemental, C, H, and N, were obtained at The Service Center of Elemental Analysis, Kyushu University. Copper analyses were obtained with a Shimadzu AA-680 atomic absorption/flame emission spectrometer. Infra-red spectra were recorded on a JASCO IR-810 spectrometer on KBr discs or Nujol mulls, e.s.r. spectra on a JES-FE3X spectrometer on powder samples or frozen dimethylformamide (dmf) solutions. Magnetic susceptibilities were determined with a Hokusan SQUID susceptometer in the temperature range 5–80 K and by a Faraday balance, designed in our laboratory, in the range 80–300 K. Diamagnetic corrections were made using Pascal's constants.

Results and Discussion

General Characterization.—Dicopper(II) complexes of general formula $Cu_2L(N_3)(H_2O)_3$ were obtained from all the ligands H_3L^1 – H_3L^3 , deprotonation of both the pyrazole and amide protons on complexation being evidenced by the disappearance of characteristic $\nu(N-H)$ vibrations of the pyrazole ring and amide group (sharp multiplet in the region 3 050–3 400 cm⁻¹). It is presumed that both the pyrazolate and azide groups function as bridges to two copper ions. Each complex shows two i.r. bands at 3 400 and 3 200 cm⁻¹ (Nujol mull), suggesting the presence of two types of water, lattice water and weakly co-ordinated water. The reflectance spectrum of each complex shows a $d-d$ band maximum at 16 500 and a shoulder at 13 500 cm⁻¹, suggesting a distorted five-co-ordination of the metal, presumably with co-ordination of a water molecule. Thus, the complexes may be formulated as $[Cu_2L(N_3)(H_2O)_2] \cdot H_2O$. The azide vibration appears in the region 2 050–2 074 cm⁻¹.

The azide group can adopt two distinct bridging modes, end-on or end-to-end (side-on). The former affords a rather short Cu–Cu separation (3.05–3.19 Å),^{16–20} whereas the latter longer values (3.6–5.2 Å).^{8a,21–26}

A dicopper(II) complex comprised of a pyrazole-2,5-dicarboxylate ion and a macrocycle has been obtained and X-ray analysis revealed a large Cu–Cu separation (4.45 Å).²⁷ Judging from a similar geometrical requirement for co-ordination of pyrazole-2,5-dicarboxylate and the 2,5-di(carbamoyl)pyrazolate moiety of H_3L^1 – H_3L^3 , the Cu–Cu separation in the present complexes is estimated to be longer than 4.0 Å. This is unfavourable for end-on bridging of azide ion. Thus, end-to-end bridging is most plausible in the present complexes.

It is suggested that the two bridging modes of the azide group can be diagnosed from the $\nu(N_3)$ vibration: end-on bridging generally shows $\nu(N_3)$ at 2 060–2 070 cm⁻¹, whereas end-to-end bridging shows this vibration at 2 020–2 040 cm⁻¹.²¹ Evidently, this is not the case for the present complexes.

The corresponding complex with an acetate group was obtained only with H_3L^1 , $[Cu_2L^1(O_2CMe)] \cdot 2MeOH$. Non-co-ordination of the methanol molecules is suggested by the i.r. band at 3 400 cm⁻¹ in Nujol mull. From a comparison of the i.r. spectrum of this complex and that of the corresponding azide complex, we can assign the antisymmetric and symmetric vibrations of the acetate group for the former as $\nu_{asym}(CO_2)$ 1 577 and $\nu_{sym}(CO_2)$ 1 420 cm⁻¹. The separation between $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ has often been used to diagnose the binding modes of carboxylate groups.²⁸ That is, bridging carboxylate groups show a separation smaller than 200 cm⁻¹ whereas unidentate carboxylate groups show a separation larger than 200 cm⁻¹. Thus, the separation for the present complex (157 cm⁻¹) indicates bridging by the acetate group. The diffuse reflectance spectrum of this complex shows one $d-d$ band at 17 100 cm⁻¹, suggesting a planar configuration around the metal ion.

The preparation of single crystals of the complexes were

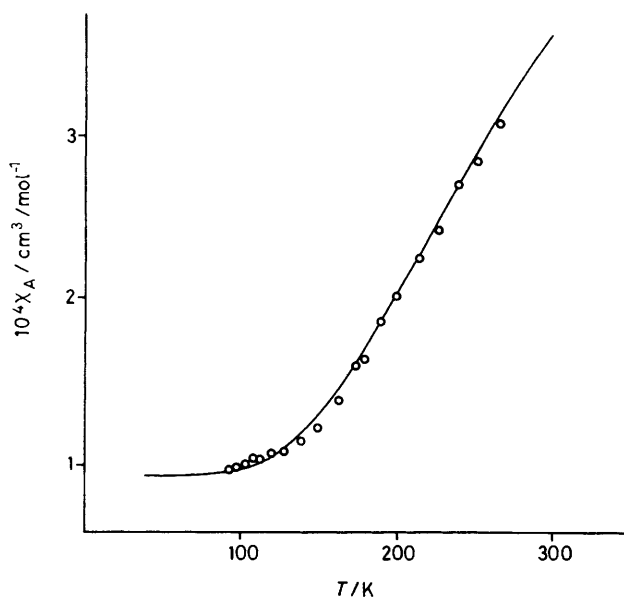


Figure 1. Plot of χ_A vs. T for $[\text{Cu}_2\text{L}^3(\text{N}_3)(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$. The trace is drawn on the basis of equation (1) with the parameters $g = 2.07$, $J = -297 \text{ cm}^{-1}$, and $N\alpha = 95 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$

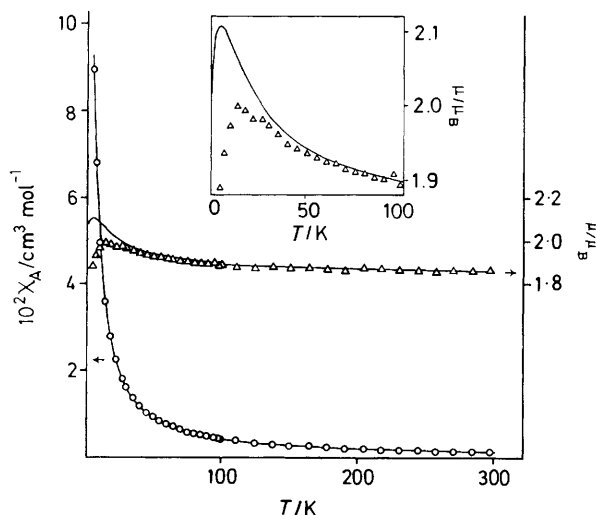


Figure 2. Temperature variations of the magnetic susceptibility and magnetic moment of $[\text{Cu}_2\text{L}^1(\text{O}_2\text{CMe})_2]\cdot 2\text{MeOH}$. The traces are drawn on the basis of equation (2) with magnetic parameters $g = 2.13$, $J = +8.9 \text{ cm}^{-1}$, $D = 0.210 \text{ cm}^{-1}$, and $N\alpha = 0$. The insert shows an expansion in the low-temperature range

Table. Magnetic parameters

| L | Exogenous bridge | J/cm^{-1} | g | $10^6 N\alpha/\text{cm}^3 \text{ mol}^{-1}$ |
|----------------|--------------------------------|--------------------|------|---|
| L ¹ | N ₃ ⁻ | -371 | 2.16 | 40 |
| L ² | N ₃ ⁻ | -335 | 2.12 | 60 |
| L ³ | N ₃ ⁻ | -297 | 2.07 | 95 |
| L ¹ | MeCO ₂ ⁻ | > +8.9* | | |

* Estimated value, see text.

attempted, but all the crystals obtained so far were not suitable for X-ray analysis.

Magnetic Properties.—All the azide-bridged complexes show a subnormal magnetic moment (0.71–0.81 μ_B) at room tem-

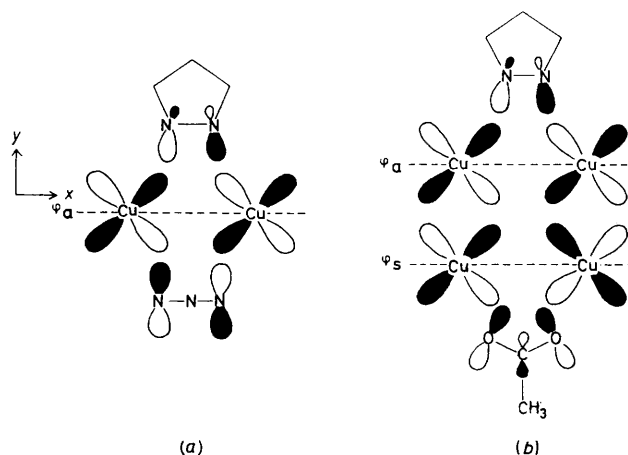


Figure 3. Orbital mechanisms of interaction of ϕ_a and ϕ_s with h.o.m.o.s of bridging groups: (a) complementary interaction in a pyrazolate/azide bridging system and (b) counter-complementary interaction in a pyrazolate/acetate bridging system

perature and are essentially diamagnetic near liquid-nitrogen temperature. This is probably due to the operation of an anti-ferromagnetic spin exchange within each molecule. A plot of χ_A vs. T for the L³ complex is given in Figure 1. The susceptibility decreases gradually with decreasing temperature and reaches a plateau (temperature-independent paramagnetism) below 100 K. Magnetic analyses were carried out using the Bleaney–Bowers equation²⁹ based on the Heisenberg model ($= -2JS_1S_2$), equation (1), where each symbol has its usual

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

meaning. As shown by the trace in Figure 1, a fairly good simulation could be attained with a large negative exchange integral $J = -297 \text{ cm}^{-1}$ for the L³ complex. The cryomagnetic properties of the other azide-bridged complexes could also be explained by this equation with a large negative J value (see Table).

The acetate-bridged complex shows a normal magnetic moment (1.87 μ_B) at room temperature. When the temperature is lowered, the moment gradually increases to 2.01 μ_B at 10 K and then decreases rapidly (Figure 2). The magnetic behaviour is essentially ferromagnetic, and the decrease in magnetic moment at very low temperature suggests the operation of some other mechanisms such as zero-field splitting of the $S_T = 1$ term or intermolecular antiferromagnetic spin coupling. As discussed later, e.s.r. investigations have revealed a significant zero-field splitting in this complex. Thus, we attempted a magnetic analysis on the basis of the susceptibility equation (2) including

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

the zero-field splitting term D . As shown by the trace in Figure 2, the tendency of the magnetic moment to decrease at very low temperature can partly be explained by taking into consideration the D term (0.210 cm^{-1} determined by e.s.r. spectroscopy is used here), but the magnetic simulation below 30 K is still very poor. It is likely that an intermolecular antiferromagnetic spin exchange is also operating in this complex. In this magnetic analysis the exchange integral was estimated to be +8.9 cm^{-1} . When simulations were carried out at temperatures higher than 50 K on the basis of equation (1) larger J values up to 14 cm^{-1} were estimated depending upon the choice of g value. Despite the uncertainty in J , we may

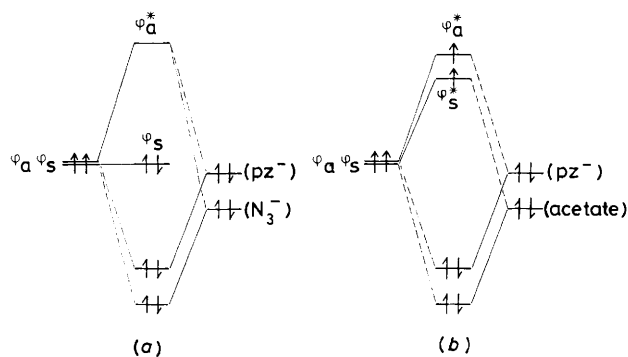


Figure 4. Schematic representations of orbital interactions in (a) an azide-bridged complex and (b) an acetate-bridged complex

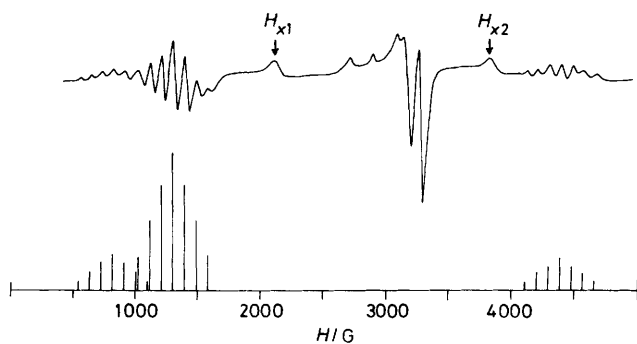


Figure 5. E.s.r. spectrum of the acetate-bridged complex: X-band on frozen dmf-toluene (2:1) solutions at 10 K. Stick spectrum indicates the simulation of parallel resonances based on the spin Hamiltonian given in the text

conclude that a ferromagnetic spin exchange ($J > +8.9 \text{ cm}^{-1}$) is operating in this case.

Thus, the spin exchange within a molecule is highly dependent upon the nature of the exogenous bridge; *i.e.* strongly antiferromagnetic for the case of the azide bridge, significantly ferromagnetic for the acetate bridge. According to Hoffmann's concept,³⁰ a strong antiferromagnetic spin exchange occurs in binuclear complexes when the energy separation between the symmetric (ϕ_s) and antisymmetric (ϕ_a) combinations of the two magnetic orbitals becomes large. When we adopt the co-ordination axis as shown in Figure 3, the ϕ_a and ϕ_s orbitals are represented as $\phi_a = d_{xy}^1 + d_{xy}^2$ and $\phi_s = d_{xy}^1 - d_{xy}^2$. The highest-occupied molecular orbital (h.o.m.o.) is antisymmetric for azide ion³¹ but symmetric for acetate ion.³⁰ The h.o.m.o. of pyrazolate ion is antisymmetric,³² though some contribution of the symmetric h.o.m.o. to magnetic exchange is suggested.³³ Hence, in the azide-bridged complexes both the h.o.m.o.s of the pyrazolate and azide bridges interact with ϕ_a but not with ϕ_s [Figure 3(a)]. This leads to a significant energy separation between the ϕ_a and ϕ_s orbitals and gives rise to a strong antiferromagnetic spin-exchange interaction (orbital complementarity) [see Figure 4(a)]. In the case of the acetate-bridged complex the h.o.m.o. of the pyrazolate group interacts only with ϕ_a , while the h.o.m.o. of the acetate group interacts only with ϕ_s [see Figure 3(b)]. This leads to little separation of ϕ_a and ϕ_s and give rise to the spin-triplet ground state (counter-complementarity) [see Figure 4(b)].

E.S.R. Spectra.—Each e.s.r. spectrum of the azide-bridged complexes with a spin-singlet ground state is featureless, only a broad and weak signal being found around 3 200 G both for powder samples and frozen d.m.f. solutions at 10 K. On the

other hand, the acetate-bridged complex with a spin-triplet ground state showed a broad but intense signal centred around 3 200 G (band width of *ca.* 1 500 G) when measured on a powder sample. Except for this, no e.s.r. signal was found at magnetic fields up to 10 000 G.

The acetate-bridged complex was slightly soluble in dmf, though considerably unstable in this solvent at ambient temperature to give an uncharacterized, dmf-insoluble material. Thus, a frozen dmf solution of the sample was quickly prepared and subjected to e.s.r. measurements. The X-band (9.229 GHz) spectrum at 10 K is given in Figure 5. The signal at 2 600–3 400 G is typical of monomeric copper(II) which presumably results from the decomposition of the binuclear complex in dmf. The remaining signals may be attributed to the parallel or perpendicular resonances of the spin-triplet state. Three signals at 812, 1 292, and 4 380 G show a well resolved, seven-line hyperfine structure ($A = 0.0103 \text{ cm}^{-1}$) and are attributed to the parallel resonances; $\Delta M_s = 1$ transitions at 812 and 4 380 G and a $\Delta M_s = 2$ transition at 1 292 G. The latter is a so-called forbidden transition but often appears as a fairly strong signal for compounds of triplet state with a large zero-field splitting.³⁴ E.s.r. analysis was carried out with the usual spin Hamiltonian for a triplet state,²⁹ equation (3). As shown by the stick spectra

$$\mathcal{H} = DS_z^2 + E(S_x^2 - S_y^2) + \beta(g_z H_z S_z + g_x H_x S_x + g_y H_y S_y) \quad (3)$$

in Figure 5, a good simulation could be attained with this Hamiltonian using $g_z = 2.533$, $D = 0.210 \text{ cm}^{-1}$, and $E = 0.020 \text{ cm}^{-1}$.

As for the perpendicular resonances, only two components of the possible transitions were observed as weak signals at 2 113 and 3 812 G. Using the spin Hamiltonian (3) and the zero-field splitting parameters above, these two signals were reasonably assigned to the *x* components (H_{x1} and H_{x2}) (Figure 5). The g_x value evaluated from this simulation is 2.055, which is common for dimeric copper(II) complexes.^{35–39}

Some e.s.r. data are available for the triplet states of anti-ferromagnetically coupled binuclear copper(II) complexes,^{35–39} but little for ferromagnetically coupled binuclear copper(II) systems. The zero-field splitting parameters D and E determined for the acetate-bridged complex are comparable to those found for dicopper(II) complexes with spin-singlet ground states. It is noteworthy that the g_z value found for the acetate complex (2.533) is large compared with those (2.22–2.40) reported for the dicopper(II) complexes with spin-singlet ground states.

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