Binuclear metal(II) (M = Co, Cu) complexes of 3,5-bis{*N*,*N*-bis[2-(diethylamino)ethyl]aminomethyl}pyrazole

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Abstract

A new binucleating pyrazole ligand, 3,5-bis{*N*,*N*-bis[2-(diethylamino)ethyl]aminomethyl}pyrazole (HL), has been synthesized. It forms cobalt(II) and copper(II) complexes of the general formula $[M_2(L)(X)](BPh_4)_2 \cdot n$(acetone) (M = Co, Cu; X = CH_3COO^-, N_3^-; $n = 0$–3), where two metal ions are bridged by the endogenous pyrazolate group and the exogenous X group. Electronic spectra of the cobalt(II) and copper(II) complexes suggest a trigonal-bipyramidal configuration around each metal ion. Magnetic properties have been examined over the temperature range 75–300 K. The cobalt(II) complexes $[Co_2(L)(CH_3COO)](BPh_4)_2 \cdot$acetone and $[Co_2(L)(N_3)](BPh_4)_2 \cdot 2$acetone both show a slight increase of magnetic moment with lowering of temperature (from 4.03 and 3.94 μ_B, respectively, at 300 K to 4.16 and 4.08 μ_B, respectively, at 85 K). $[Cu_2(L)(CH_3COO)](BPh_4)_2$ shows a weak antiferromagnetic spin-coupling ($J = -7.02$ cm^{-1} based on spin Hamiltonian $\mathcal{H} = -2J\hat{S}_1 \cdot \hat{S}_2$). $[Cu(L)(N_3)](BPh_4)_2 \cdot$acetone exhibits a much lowered magnetic moment (1.10 μ_B at 300 K) owing to a strong antiferromagnetic spin coupling but its cryomagnetic property could not be simulated based on the Heisenberg model.

Introduction

The bridging function of the pyrazolate group through its two nitrogens is well known [1, 2] and many binuclear copper(II) complexes bridged by a pyrazolate group and another anionic group have been obtained so far [3–10]. Interests in such complexes are to find an appropriate model for the active site of the met-form of type III copper proteins and to gain an insight into the spin-exchange mechanism between copper(II) ions. In line with these interests we have developed two types of binucleating pyrazole ligands possessing two chelating arms attached to the 3 and 5 positions of the pyrazole ring (type A and B in Fig. 1) [3, 11]. Type A ligands with a nitrogenous pendant group at each amidic articular nitrogen (generally abbreviated as H_3(L-A)) form binuclear copper(II) complexes of the formula $[Cu_2(L\text{-}A)(X)]$ (X = CH_3COO^-, N_3^-) where the acetate or azide group functions as the exogenous bridge [3]. Type B ligands with a nitrogenous pendant group at each aminic articular nitrogen (abbreviated as H(L-B)) form dicopper(II) complexes of the formula $[Cu_2(L\text{-}B)_2](BPh_4)_2$ [11]. Single crystal X-ray analysis for a complex with a type B ligand has revealed that two copper(II) ions are doubly bridged by the pyrazolate groups. In spite of our many efforts no binuclear copper(II) complex with a mixed bridging system has been obtained with type B ligands.

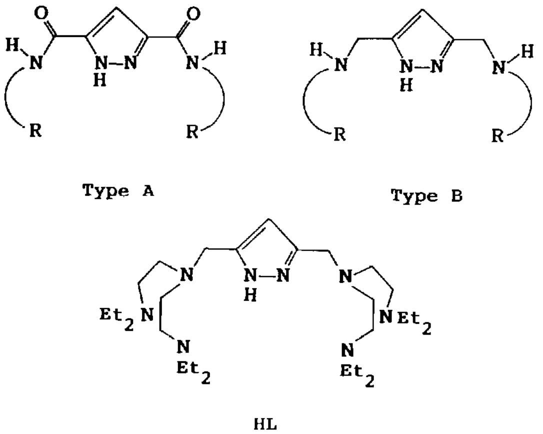

Fig. 1. Chemical structures of binucleating pyrazole ligands.

In this study we have synthesized another type of binucleating pyrazole ligand, 3,5-bis{*N*,*N*-bis[2-(diethylamino)ethyl]aminomethyl}pyrazole (abbreviated as HL, see Fig. 1), which has two nitrogenous pendant groups at each articular nitrogen. This ligand

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offers two 'tripodal-like' sites for coordination and may incorporate two metal ions bridged by the endogenous pyrazolate group and an exogenous group, providing a five-coordinate surrounding about each metal ion. The present paper reports the synthesis and properties of binuclear cobalt(II) and copper(II) complexes of this ligand.

Experimental

Preparations

Pyrazole-3,5-dicarboxylic acid was purchased from Aldrich Chem. Co. and *N*,*N*-bis[2-(diethylamino)ethyl]amine from Fairfield Chem. Co. Other chemicals were of reagent grade and used as commercially obtained.

3,5-Bis{N,N-bis[2-(diethylamino)ethyl]aminomethyl}pyrazole (HL)

Pyrazole-3,5-dicarboxylic acid was converted into 3,5-bis(chloroformyl)pyrazole by the usual reaction with $SOCl_2$. To a stirred suspension of 3,5-bis(chloroformyl)pyrazole (3.96 g, 0.03 mol) in dry dioxane (150 cm^3) was added dropwise a solution of triethylamine (6.2 g, 0.061 mol) and bis[2-(diethylamino)ethyl]amine (15.7 g, 0.061 mol) in dry dioxane (50 cm^3), and the mixture was allowed to stand at ambient temperature for two days. Triethylamine hydrochloride which precipitated was separated by filtration and the filtrate was evaporated to dryness to give crude 3,5-bis{*N*,*N*-bis[2-(diethylamino)ethyl]carbamoyl}pyrazole as a colourless oily substance. It was dissolved in dry dioxane (50 cm^3) and the solution was dropwise added to a slurry of $LiAlH_4$ (10 g) in dry dioxane (500 cm^3) with vigorous stirring. After the addition was completed the mixture was refluxed for 20 h with stirring. The reaction mixture was decomposed with the minimum amount of water, and the resulting inorganic materials were separated by filter suction and washed with two 50 cm^3 portions of hot dioxane. The filtrate and washings were combined and the solvent was evaporated to dryness to give crude HL as a colourless liquid. It was identified by ^1H NMR spectra and used for the synthesis of metal complexes without further purification.

^1H NMR (60 MHz, $CDCl_3$): 5.93 (s, 1H; ring); 3.67 (s, 4H; N–CH_2–pz); 2.75–2.25 (m, 32H; $-CH_2CH_2N(CH_2CH_3)_2$); 1.01 (t, 24H; $-N(CH_2CH_3)_2$) ppm.

$[Co_2(L)(CH_3COO)](BPh_4)_2\cdot$acetone (1)

Cobalt(II) acetate tetrahydrate (250 mg, 1 mmol) and HL (261 mg, 0.5 mmol) were mixed in methanol (10 cm^3) to form a bluish purple solution. The addition of a methanolic solution of sodium tetraphenylborate (343 mg, 1 mmol) to this solution resulted in the precipitation of pale violet microcrystals. They were recrystallized from acetone as violet crystals. The yield was 880 mg (63%).

Anal. Found: C, 70.40; H, 7.91; N, 7.87; Co, 8.41. Calc. for $C_{82}H_{110}B_2Co_2N_8O_3$: C, 70.58; H, 7.84; N, 8.03; Co, 8.45%.

$[Co_2(L)(N_3)](BPh_4)_2\cdot$2acetone (2)

Cobalt(II) chloride hexahydrate (234 mg, 1 mmol), HL (261 mg, 0.5 mmol), and sodium azide (98 mg, 1.5 mmol) were dissolved in methanol (10 cm^3). To the resulting green solution was added a methanolic solution of sodium tetraphenylborate (343 mg, 1 mmol) to give pale violet microcrystals. They were recrystallized from acetone. The yield was 730 mg (55%).

Anal. Found: C, 69.57; H, 7.86; N, 10.46; Co, 8.37. Calc. for $C_{83}H_{113}B_2Co_2N_{11}O_2$: C, 69.41; H, 7.93; N, 10.73; Co, 8.22%.

$[Cu_2(L)(CH_3COO)](BPh_4)_2$ (3)

Copper(II) acetate monohydrate (200 mg, 1 mmol) and HL (261 mg, 0.5 mmol) were dissolved in methanol (10 cm^3), and the pH of the solution was adjusted to 9.5 by adding a sodium methoxide solution. The addition of sodium acetate (205 mg, 2.5 mmol) followed by a methanolic solution of sodium tetraphenylborate (343 mg, 1 mmol) resulted in the precipitation of green microcrystals. They were recrystallized from acetone. The yield was 970 mg (72%).

Anal. Found: C, 69.90; H, 7.66; N, 8.30; Cu, 9.32. Calc. for $C_{79}H_{104}B_2Cu_2N_8O_2$: C, 70.47; H, 7.78; N, 8.32; Cu, 9.44%.

$[Cu_2(L)(N_3)](BPh_4)_2\cdot$acetone (4)

Copper(II) chloride dihydrate (170 mg, 1 mmol) and HL (261 mg, 0.5 mmol) were dissolved in methanol (10 cm^3) and the pH of the solution was adjusted to 9.5 with a sodium methoxide solution. To this mixture were added successively a methanolic solution of NaN_3 (98 mg, 1.5 mmol) and a methanolic solution of sodium tetraphenylborate (343 mg, 1 mmol) to give green microcrystals. They were recrystallized from acetone. The yield was 1.19 g (86%).

Anal. Found: C, 69.38; H, 7.84; N, 11.16; Cu, 9.32. Calc. for $C_{80}H_{107}B_2Cu_2N_{11}O$: C, 69.25; H, 7.77; N, 11.10; Cu, 9.16%.

Physical measurements

Elemental analyses for C, H, and N were obtained at The Service Center of Elemental Analysis, Kyushu

University. Metal analyses were made with a Shimadzu AA-680 atomic absorption/flame emission spectrometer. Electronic spectra were recorded on a Shimadzu multipurpose spectrometer model MPS-2000 in the range 450–900 nm and on a Shimadzu multipurpose spectrometer model MPS-5000 in the range 900–2000 nm. Magnetic susceptibilities were measured with a Faraday balance in the temperature range from liquid nitrogen temperature to room temperature. The apparatus was calibrated with $[Ni(en)_3]S_2O_3$ [12] and diamagnetic corrections were made using Pascal's constants [13].

Results and discussion

General characterization

The complexes obtained in this study have a general formula $[M_2(L)(X)](BPh_4)_2 \cdot n(\text{acetone})$ ($M = Co, Cu$; $X = CH_3COO^-$, N_3^-; $n = 0–3$). It is presumed that the two metal ions are bridged by the endogenous pyrazolate group and the exogenous acetate or azide group. Our attempts to obtain binuclear complexes of the type $[M_2(L)_2]^{2+}$ were unsuccessful. Thus, HL markedly differs from type B ligands in the complexation behavior, but rather resembles type A ligands which form binuclear copper(II) complexes $[Cu_2(L\text{-}A)(X)]$ ($X = CH_3COO$, N_3). However, no binuclear cobalt(II) complex with type A ligands has been obtained. It appears that the ligand HL is flexible enough to fulfil the geometrical requirements of metal ions in a fairly wide range.

Selected IR bands for **1**–**4** are given in Table 1. The complexes except for **3** show a sharp, intense band at 1710–1705 cm^{-1} which can be assigned to the C=O stretching of the acetone molecule captured in the crystal lattice. The antisymmetric and symmetric vibrations of the acetate group, $\nu_a(COO)$ and $\nu_s(COO)$, are found at 1570 and 1440 cm^{-1}, respectively, for both **1** and **3**. The separation between $\nu_a(COO)$ and $\nu_s(COO)$ is less than 200 cm^{-1} and adds support to the bridging structure of the acetate group [14–16]. The azide vibration for **2** and **4** appears in the region 2070–2065 cm^{-1}. The azide group may adopt an end-to-end bridging mode because the Cu--Cu separation in such pyrazolate-bridged binuclear complexes is considerably long (>3.9 Å) [10, 17]. The presence of the BPh_4^- ion is inferred by the very strong bands at 735 and 705 cm^{-1} attributable to δ(C–H) of the phenyl group.

The electronic spectra of the binuclear cobalt(II) complexes **1** and **2** in acetonitrile are similar to each other and show four d–d bands from the visible to the near IR region (see Fig. 2). The spectral feature is characteristic of cobalt(II) in trigonal-bipyramidal coordination [18–20]. Based on Dreiding model considerations such a trigonal-bipyramidal structure is feasible, with a pyrazolate nitrogen and two pendant nitrogens at the equatorial sites and the articular nitrogen and a donor atom of the bridging acetate or azide group at the axial sites.

The electronic spectra of the binuclear copper(II) complexes **3** and **4** in acetonitrile resemble each other, showing a dominant peak at 12 500 cm^{-1} and a shoulder near 15 500 cm^{-1} (Fig. 3). Such a spectral feature is also characteristic of copper(II) of trigonal-bipyramidal coordination [21–24].

Magnetic property

Magnetic moments of **1** and **2** (per cobalt atom) are 4.03 and 3.94 μ_B, respectively, at room temperature, which are close to the spin-only value for $S = 3/2$ (3.87 μ_B) and considerably smaller than the moments for high-spin octahedral cobalt(II) (4.7–5.2 μ_B [25]) and the moments of tetrahedral cobalt(II) (4.3–4.8 μ_B [25]). Comparable magnetic moments to those of tetrahedral cobalt(II) are reported for some high-spin five-coordinate cobalt(II) complexes [20, 26]. Some five-coordinate cobalt(II) complexes show a subnormal magnetic moment at room temperature because of a spin-crossover between high-spin ($S = 3/2$) and low-spin ($S = 1/2$) forms [27–30]. In all spin-crossover cobalt(II) complexes so far characterized, the $S_T = 1/2$ state is low-lying relative to the $S_T = 3/2$ state so that the complexes go toward low spin as temperature is lowered. Magnetic measurements down to liquid nitrogen temperature have revealed that the magnetic moments of **1** and **2** gradually increase with lowering of temperature to 4.16 and 4.08 μ_B, respectively, at 75 K. The magnetic behavior observed suggests the operation of a ferromagnetic spin exchange between two cobalt(II)

TABLE 1. Selected IR bands of the complexes (ν (cm^{-1}))

	$\nu(N_3^-)$	$\nu(CO)$	$\nu_a(COO)$	$\nu_s(COO)$	δ(CH, ring)
$[Co_2(L)(CH_3COO)](BPh_4)_2 \cdot$acetone (**1**)		1710	1570	1420	735 705
$[Co_2(L)(N_3)](BPh_4)_2 \cdot$2acetone (**2**)	2070	1715			735 705
$[Cu_2(L)(CH_3COO)](BPh_4)_2$ (**3**)			1570	1420	735 705
$[Cu_2(L)(N_3)](BPh_4)_2 \cdot$acetone (**4**)	2065	1710			735 705

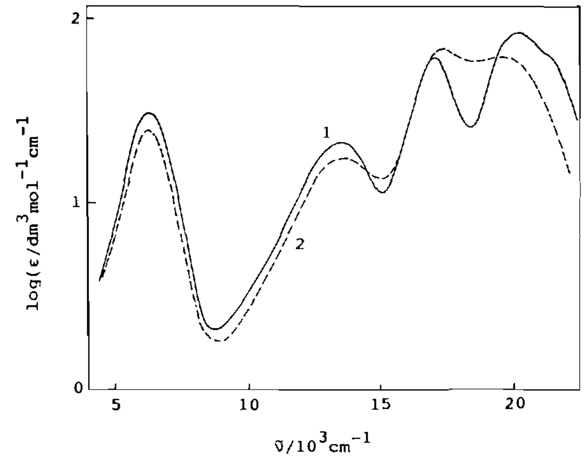

Fig. 2. Electronic spectra of **1** (1) and **2** (2) in acetonitrile.

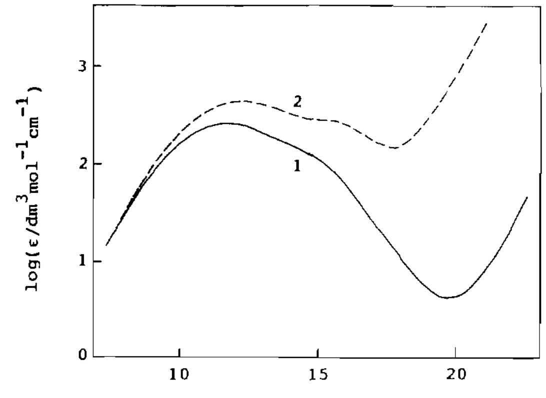

Fig. 3. Electronic spectra of **3** (1) and **4** (2) in acetonitrile.

ions, though we cannot rule out the possibility of a spin-crossover with low-lying $S_T = 3/2$ relative to $S_T = 1/2$.

The cryomagnetic property of **3** is shown in Fig. 4(A) in the forms of χ_A versus T and μ_{eff} versus T curves. This complex has a common magnetic moment at room temperature (1.80 μ_B) but the moment gradually decreases with lowering of temperature to 1.72 μ_B at 84.6 K. This is probably due to the operation of a weak antiferromagnetic spin exchange between the copper(II) ions. Magnetic analysis was carried out using the Bleaney–Bowers eqn. [31]

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

where each symbol has its usual meaning. As indicated by the traces in Fig. 4 a good simulation was attained with this equation using the magnetic parameters, $g = 2.05$, $J = -7.02$ cm^{-1}, and $N\alpha = 60 \times 10^{-6}$ cm^3 mol^{-1}. The discrepancy factor $\sigma = [\Sigma(\chi_{obs} - \chi_{calc})^2/\Sigma\chi_{obs}{}^2]^{1/2}$ was 0.0011. It should be mentioned that a ferromagnetic interaction is operating in the di-

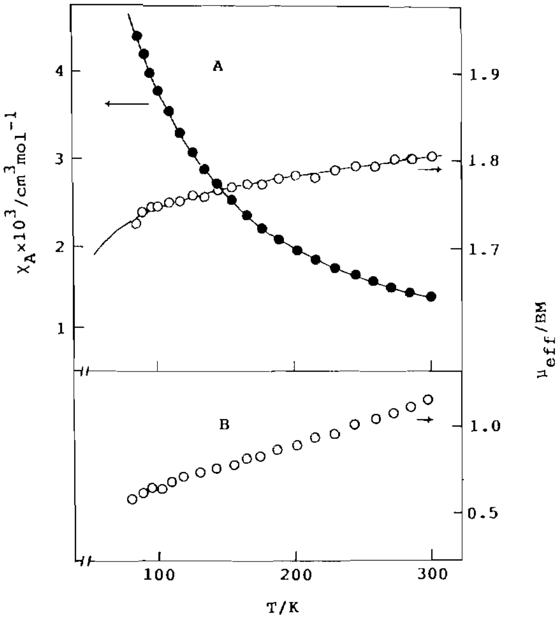

Fig. 4. Temperature variations of magnetic susceptibility and magnetic moment for **3** (A) and temperature variation of magnetic moment for **4** (B).

copper(II) complex of a type A ligand (R = 2-pyridylmethyl, see Fig. 1) and with an acetate group as the exogenous bridge ($J > +8.9$ cm^{-1}) [3].

The magnetic moment of **4** is 1.15 μ_B at room temperature and 0.58 μ_B at 84.6 K (see Fig. 4(B)), suggesting a strong antiferromagnetic spin coupling in this case. The temperature dependence of the magnetic susceptibility, however, could not be simulated by the Bleaney–Bowers equation even if the presence of a paramagnetic impurity was taken into consideration. We have repeated magnetic measurements on newly prepared samples and confirmed that the magnetic results coincide within experimental error. Such an unusual magnetism might be due to a structural change with temperature since temperature-dependence of the exchange integral (J) associated with a structural change has been noticed in some binuclear copper(II) complexes [32–35].

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