

Synthesis, characterization and magnetism of binuclear cobalt(II) complexes bridged by tetracarboxylato groups

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Three new binuclear cobalt(II) complexes with extended tetracarboxylato-bridge have been synthesized and characterized, namely $[\text{Co}_2(\text{PMTA})(\text{bpy})_4]$ (1), $[\text{Co}_2(\text{PMTA})(\text{phen})_4]$ (2) and $[\text{Co}_2(\text{PMTA})(\text{NO}_2\text{phen})_4]$ (3), where PMTA represents the tetraanion of pyromellitic acid, and bpy, phen, $\text{NO}_2\text{-phen}$ denote 2,2'-bipyridine, 1,10-phenanthroline; 5-nitro-1,10-phenanthroline, respectively. Based on elemental analyses, molar conductivity measurements, IR and electronic spectra studies, it is proposed that these complexes have PMTA-bridged structures and consist of two cobalt(II) ions, each in a distorted octahedral environment. These complexes were further characterized by variable temperature magnetic susceptibility measurements (4–300 K) and the observed data were successfully simulated by the equation based on the spin Hamiltonian operator, $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$, giving the exchange integral $J = -1.02 \text{ cm}^{-1}$ for 1, $J = -1.21 \text{ cm}^{-1}$ for 2 and $J = -1.18 \text{ cm}^{-1}$ for 3, respectively. These results revealed the operation of antiferromagnetic spin-exchange interaction between the two Co(II) ions within each molecule.

Keywords Tetracarboxylato-bridge, binuclear cobalt(II) complex, magnetism

Introduction

The study of syntheses and long-range magnetic exchange interactions of binuclear transition-metal complexes propagated by multiatom bridges has been an active field of research in recent years, not only for gaining some insight into the pathways of electron transfers in bi-

nuclear systems,¹ but also for obtaining information about designing and synthesizing molecule-based magnets,^{2,3} and for investigating the spin-exchange mechanism between paramagnetic metal ions.⁴ So far, much effort has been devoted to the development of multiatom bridging ligands that can afford long-distance magnetic interactions.⁵⁻¹⁴ The tetraanion of pyromellitic acid (abbreviated as PMTA), due to their peculiar structure, could be good candidates in supporting long-distance magnetic exchange interactions. Chaudhuri *et al.*⁸ first utilized the PMTA as a multiatom bridge to synthesize the binuclear copper(II) complex $[\text{LCu}(\mu\text{-tetracarboxylato})\text{CuL}] \cdot 4\text{H}_2\text{O}$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane). It has been revealed by the single crystal X-ray and magnetic analyses⁸ that the long-range antiferromagnetic coupling could occur between the copper(II) ions bridged by the PMTA ligand although the $\text{Cu} \cdots \text{Cu}$ separation is 0.78 nm. In order to provide more examples of PMTA-bridged binuclear complexes and to understand better the factors affecting the superexchange interactions propagated by PMTA, it is necessary to synthesize a series of binuclear complexes of essentially the same structure except for the metal ion. In this paper, we describe the synthesis and magnetic characterization of three new cobalt(II) binuclear complexes using the PMTA as a bridging ligand: $[\text{Co}_2(\text{PMTA})(\text{bpy})_4]$ (1), $[\text{Co}_2(\text{PMTA})(\text{phen})_4]$ (2) and $[\text{Co}_2(\text{PMTA})(\text{NO}_2\text{-phen})_4]$ (3), where PMTA represents the tetraanion of pyromellitic acid, and bpy, phen and $\text{NO}_2\text{-phen}$ denote

Received August 17, 1999; accepted February 29, 2000.

Project supported by the Natural Science Foundation of Shandong Province(No. Q99B12) and the National Natural Science Foundation of China (No. 29873031).

2, 2'-bipyridine, 1, 10-phenanthroline, 5-nitro-1, 10-phenanthroline, respectively. The magnetic properties of the complexes have been studied.

Experimental

Materials

The hydrated cobalt(II) perchlorate was prepared and purified by the literature method.¹⁵ Pyromellitic acid (H_4 PMTA), $LiOH \cdot H_2O$ and the terminal ligands 2, 2'-bipyridine (bpy); 1, 10-phenanthroline (phen); 5-nitro-1, 10-phenanthroline (NO_2 -phen) (analytical grade) were purchased from the Beijing Chemical Company.

Synthesis of $[Co_2(PMTA)(bpy)_4]$ (1)

To a solution of 254.3 mg (1 mmol) of pyromellitic acid in methanol (20 mL) was added dropwise a methanol solution (20 mL) of 167.8 mg (4 mmol) of $LiOH \cdot H_2O$ under stirring at room temperature. The stirring was continued until the mixture became clear. To this solution was then added a methanol solution (15 mL) of 731.8 mg (2 mmol) of $Co(ClO_4)_2 \cdot 6H_2O$ and 624.7 mg (4 mmol) of bpy in 20 mL methanol solution under N_2 . The color of the solution changed immediately from orange to reddish and a small amount of precipitate formed. Stirring was continued for 3 h, the precipitate formed was filtered, washed with methanol, water and diethyl ether for several times and dried with P_2O_5 under reduced pressure. Recrystallization was carried out from a hot acetonitrile solution. Anal. $C_{50}H_{34}N_8O_8Co_2$. Calcd: C, 60.49; H, 3.45; N, 11.29; Co, 11.87. Found: C, 60.40; H, 3.41; N, 11.02; Co, 11.74.

Synthesis of $[Co_2(PMTA)(phen)_4]$ (2)

This complex was obtained as orange microcrystals by the same procedure using phen instead of bpy. It was recrystallized from 1:2 MeCN/MeOH. Anal. $C_{58}H_{34}N_8O_8Co_2$. Calcd: C, 63.98; H, 3.15; N, 10.29; Co, 10.82. Found: C, 63.88; H, 3.09; N, 10.15; Co, 10.70.

Synthesis of $[Co_2(PMTA)(NO_2-phen)_4]$ (3)

This complex was obtained as dark-yellow micro-

crystals by the same procedure as above, using NO_2 -phen instead of bpy. It was recrystallized from 1:1 DMF/EtOH. Anal. $C_{58}H_{30}N_{12}O_{16}Co_2$. Calcd: C, 54.90; H, 2.38; N, 13.25; Co, 9.29. Found: C, 54.86; H, 2.32; N, 13.08; Co, 9.12.

Physical measurements

C, H and N analyses were performed with a Perkin-Elmer elemental analyzer Model 240. The metal contents were determined by EDTA titration. The IR spectra were measured on a Shimadzu infrared spectrometer Model 810 in KBr pellets. Reflectance spectra were measured on a Hitachi-340 spectrophotometer. The melting points of the complexes were determined by a Model XT 7-1 micro-melting point meter. Molar conductances were measured (DMF solution) with a Shanghai DDS-11A conductometer. Variable temperature magnetic susceptibilities (4–300 K) were measured at the Institute of Physics, Chinese Academy of Sciences, using a Model CF-1 vibrating sample magnetometer (sensitivity $m = 10^{-4}$ emu) made by Neel Laboratory de CNRS, France. Diamagnetic corrections were made with Pascal's constants¹⁶ for all the constituent atoms and the effective magnetic moments were calculated by the equation $\mu_{eff} = 2.828(\chi_M T)^{1/2}$, where χ_M is the magnetic susceptibility per molecule corrected for diamagnetism of the constituting atoms.

Results and discussion

Preparation and composition of the binuclear complexes

The PMTA-bridged binuclear complexes were obtained by the reaction of H_2 PMTA with $Co(ClO_4)_2 \cdot 6H_2O$ and L (L = bpy, phen, NO_2 -phen) in methanol solution in the presence of a base. The use of $LiOH \cdot H_2O$ as the base gave good results because it and its salt ($LiClO_4$) formed in the reaction are fairly soluble in methanol and the products are little contaminated with these inorganic materials. Indeed, elemental analytic data for the newly prepared complexes indicate that the reaction of PMTA with $Co(ClO_4)_2 \cdot 6H_2O$ and L (L = bpy, phen, NO_2 -phen) yielded the binuclear complexes of the general formula $[Co_2(PMTA)L_4]$. Based on the conductivity measurements, spectroscopic characterization and magnetic studies (*vide infra*) these complexes

are presumed to have the coordination environment as shown in Fig. 1.

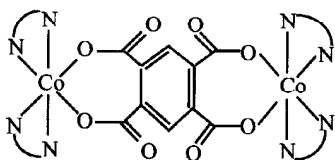


Fig. 1 Coordination environment of the complexes ($\widehat{N-N}$ = bpy, phen, NO_2 -phen).

Solubility and molar conductance

All the binuclear complexes are sparingly soluble in water, ethanol, carbon tetrachloride, chloroform and benzene, but soluble in acetone, acetonitrile, DMF and DMSO to give stable solution at room temperature. For the three complexes, the molar conductance values in DMF solution (see Table 1) show that all the complexes are non-electrolytes.¹⁷ This is consistent with the measured IR data.

Table 1 Physical data for the binuclear complexes

| Complex | M. p (°C) | Δ_M ($\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$) | IR (cm^{-1}) | | | | CT |
|---------|--------------|--|----------------------------------|---------------------------------|--------------------------|--------------------------|----------------|
| | | | $\nu_{\text{as}}(\text{CO}_2^-)$ | $\nu_{\text{s}}(\text{CO}_2^-)$ | $\nu(\text{N}=\text{C})$ | $\nu(\text{N}-\text{M})$ | |
| 1 | 289 | 5.5 | 1620 | 1375 | 1545 | 520 | 37500 39000 |
| 2 | 296 | 5.0 | 1620 | 1380 | 1530 | 520 | 37000 38100 |
| 3 | 312 | 6.5 | 1610 | 1370 | 1540 | 515 | 39800 42000 |

Infrared spectra

The IR spectra taken in the region of 4000—400 cm^{-1} provide some information regarding the mode of coordination in the complexes and were analysed in comparison with that of the free ligand (H_2PMTA). The most relevant IR absorption bands due to the complexes together with their assignments are shown in Table 1. The IR spectrum of pyromellitic acid shows a broad band at near 1700 cm^{-1} which is attributed to $\nu(\text{C}=\text{O})$ of the carboxylic group. However, in the IR spectra of all complexes, this band disappeared, accompanied by the appearance of two characteristic strong and broad bands at *ca.* 1600 cm^{-1} and 1370 cm^{-1} attributed to $\nu_{\text{as}}(\text{CO}_2^-)$ (1620—1610 cm^{-1}) and $\nu_{\text{s}}(\text{CO}_2^-)$ (1380—1370 cm^{-1}) stretching vibrations of the coordinated carboxylate groups. The absence of any splitting of the $\nu_{\text{as}}(\text{CO}_2^-)$ and $\nu_{\text{s}}(\text{CO}_2^-)$ bands strongly suggests the end-to-end linking of the PMTA ligand in an equivalent way at both sites.⁵ Moreover, the coordination modes of carboxylate groups have often been diagnosed by the separation between $\nu_{\text{as}}(\text{CO}_2^-)$ and $\nu_{\text{s}}(\text{CO}_2^-)$. That is, bidentate carboxylate groups show a separation smaller than 200 cm^{-1} , whereas unidentate carboxylate groups show a sep-

aration larger than 200 cm^{-1} . Thus, for the present complexes, these two bands were separated by *ca.* 240 cm^{-1} (see Table 1), suggesting an unidentate coordination mode for the four carboxylate groups of the PMTA ligand.¹⁸ The unidentate coordination modes of the carboxylates in PMTA were supported by the crystal structure of the analogous complex $[\text{LCu}(\mu\text{-tetracarboxylato})\text{CuL}]\cdot 4\text{H}_2\text{O}$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane).⁸ In addition, the $-\text{N}=\text{C}-$ vibrations for the terminal ligands (bpy, phen, NO_2 -phen) are shifted to higher frequencies in corresponding binuclear complexes (see Table 1), suggesting that the N atoms of the terminal ligands coordinated with the metal ion. This view is further supported by the appearance of the band corresponding to the metal-nitrogen stretching vibration at 510—520 cm^{-1} in the complexes. Furthermore, the band centered at 1100 cm^{-1} , typical for the $\nu(\text{Cl}-\text{O})$ stretching of the perchlorate group,¹⁹ was not found for the complexes. This is consistent with the conductance measurements and elemental analyses of the complexes.

Electronic spectra

In order to obtain further information on the mode

of bonding of the Co(II) ion to the free ligand, the reflectance spectra of the three complexes are measured at room temperature. For all three binuclear complexes, two strong absorptions in the UV range were observed (see Table 1), which may be assigned to the charge-transfer absorption bands,²⁰ and three weaker bands (see Table 2) appearing in the 9020—9400, 19000—19700 and 21120—21300 cm⁻¹ regions which may reasonably correspond to the ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1), ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν_2) and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) transitions, respectively, consistent with the presence of an octahedral coordination geometry²¹ around the cobalt(II) ion. According to Lever's method,^{21,22} some coordination field parameters of the complexes can be obtained by using the two observed bands (ν_1 and ν_3) and the calculated results are summarized in Table 2. Thus, it can be seen that the observed ν_2 values are in agreement with the calculated ones (see Table 2). This shows that the

assignments are reasonable and are additional evidence for the octahedral structure. In addition, the values of $\beta < 1$ show strongly covalent bonding for cobalt(II) in these complexes.²³

All our efforts to grow large crystals of these binuclear cobalt(II) complexes suitable for X-ray structure determination have so far been unsuccessful. However, based on the composition of these complexes, their IR and electronic spectra as well as conductivity measurements, the results of variable-temperature susceptibilities, which we will discuss later, and crystal structure of the analogous complex,⁸ it is reasonable to suppose that these complexes have an extended PMTA-bridged structure, in which each carboxylic group is bound to cobalt(II) ion in a monodentate fashion through only one oxygen atom, yielding two seven-membered rings, each cobalt(II) ion is in a distorted octahedral environment (Fig. 1).

Table 2 Electronic spectral data (cm⁻¹) and some coordination field parameters of the complexes

| Complex | Assignments | | | D_q (cm ⁻¹) | B (cm ⁻¹) | β |
|---------|-------------|----------------------------|---------|------------------------------|--------------------------|---------|
| | ν_1 | ν_2 | ν_3 | | | |
| 1 | 9020 | 19000 (19300) ^a | 21120 | 1022 | 888 | 0.916 |
| 2 | 9300 | 19500 (19800) | 21200 | 1052 | 880 | 0.905 |
| 3 | 9400 | 19700 (20000) | 21300 | 1050 | 885 | 0.912 |

^aValues in parentheses are the calculated values.

Magnetic properties

In order to obtain further information on the structure of the complexes, variable-temperature susceptibility (4—300 K) data were collected for the [Co₂(PMTA)(bpy)₄] (1), [Co₂(PMTA)(phen)₄] (2) and [Co₂(PMTA)(NO₂-phen)₄] (3) complexes and are shown in Fig. 2 in the form of the χ_M , μ_{eff} versus T plot, χ_M being the molar magnetic susceptibility, μ_{eff} the effective moment and T the absolute temperature. The cobalt(II) ion under O_h -symmetry possesses the ${}^4T_{1g}$ ground state whose magnetic moment is temperature-dependent. Therefore, the magnetic susceptibility for a binuclear cobalt(II)-cobalt(II) ($S_1 = S_2 = 3/2$) complex with cobalt(II) under O_h -symmetry is difficult to explain. However, the configuration around the cobalt(II) ion for the present case is somewhat distorted from O_h -symmetry. Therefore, according to Sinn,²⁴ the magnetic susceptibilities for the present cobalt(II)-cobalt(II) com-

plexes can be interpreted by the Heisenberg model, because the symmetry around the metal is lower than for a regular octahedron. From Fig. 2 it is evident that the magnetic behaviors of the three complexes are similar. In the 30—300 K region, the effective magnetic moments (μ_{eff}) are virtually constant, but sharply decrease below 30 K. This behavior is characteristic of weak antiferromagnetic spin-exchange interaction between cobalt(II) ions through the PMTA-bridge within each molecule.

In order to understand quantitatively the magnitudes of the spin-exchange interaction between cobalt(II) and cobalt(II) ions, a magnetic analysis was performed with the susceptibility equation derived from the Heisenberg spin operator $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$, where the exchange integral J is negative for antiferromagnetic interaction and positive for ferromagnetic interaction. For the Co(II)-Co(II) ($S_1 = S_2 = 3/2$) system, the molar magnetic susceptibility is given by the expression²⁵ of Eq. (1):

$$\chi_M = \frac{2N\beta^2 g^2}{KT} \left[\frac{14 + 5\exp(-6J/KT) + \exp(-10J/KT)}{7 + 5\exp(-6J/KT) + 3\exp(-10J/KT) + \exp(-12J/KT)} \right] \quad (1)$$

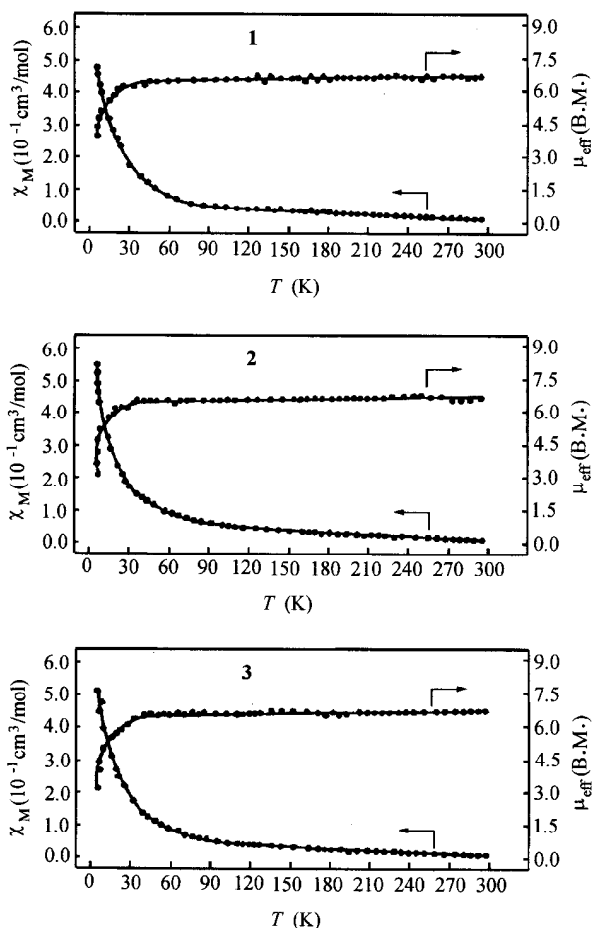


Fig 2. Temperature variation of χ_M (lower curve) and μ_{eff} (upper curve) for the complexes $[\text{Co}_2(\text{PMTA})(\text{bpy})_4]$ (1), $[\text{Co}_2(\text{PMTA})(\text{phen})_4]$ (2) and $[\text{Co}_2(\text{PMTA})(\text{NO}_2\text{-phen})_4]$ (3). The curves are based on Eq. (1) using the magnetic parameters given in the text. (●), experimental data. (-), calculated curves as described in the text.

where χ_M denotes the susceptibility per dinuclear complex and the remaining symbols have their usual meanings. As shown in Fig. 2, good least-squares fitting of the experimental data to Eq. (1) gave $J = -1.02 \text{ cm}^{-1}$, $g = 2.38$ for **1**, $J = -1.21 \text{ cm}^{-1}$, $g = 2.41$ for **2** and $J = -1.18 \text{ cm}^{-1}$, $g = 2.40$ for **3**. The agreement factor F , $F = [\sum(\chi_M)_{\text{obs.}} - \sum(\chi_M)_{\text{calc.}}]^2 / \sum(\chi_M)_{\text{obs.}}$, is then equal to 1.7×10^{-5} for **1**, 1.9×10^{-5} for **2** and 2.3×10^{-5} for **3**. The results (negative and small J val-

ues) indicate that the complexes exhibit weak antiferromagnetic spin-exchange interaction between binuclear cobalt(II) centre in the three complexes. These small J values of these complexes may be brought out²⁰ mainly by the geometry structures of the complexes and the properties of the bridged-ligand.

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(E9908101 SONG, J.P.; DONG, L.J.)