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# Antiferromagnetically Coupled Binuclear Chromium(III) Complexes Through $\mu$-Isophthalato-Bridge

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Three new $\mu$-isophthalato-bridged binuclear chromium(III) complexes were synthesized and characterized, namely $[Cr_2(IPHTA)(Me_2bpy)_4](NO_3)_4$ **(1)**, $[Cr_2(IPHTA)(Me_2phen)_4](NO_3)_4$ **(2)** and $[Cr_2(IPHTA)(Cl\text{-}phen)_4](NO_3)_4$ **(3)**, where IPHTA represents the isophthalate dianions; $Me_2bpy$, $Me_2phen$ and Cl-phen stand for 4,4′-dimethyl-2,2′-bipyridine; 2,9-dimethyl-1,10-phenanthroline and 5-chloro-1,10-phenanthroline, respectively. The three complexes have not yet been isolated in crystalline form suitable for X-ray structure analysis, but based on elemental analyses, molar conductance and magnetic moments of room-temperature measurements, and spectroscopic studies, extended IPHTA-bridged structures consisting of two chromium(III) ions, each in an octahedral environment are proposed for these complexes. The complexes $[Cr_2(IPHTA)(Me_2bpy)_4](NO_3)_4$ **(1)** and $[Cr_2(IPHTA)(Me_2phen)_4](NO_3)_4$ **(2)** were further characterized by variable temperature magnetic susceptibility (4~300 K) measurements 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 integrals $J = -1.27$ $cm^{-1}$ for **(1)** and $J = -2.19$ $cm^{-1}$ for **(2)**. This result indicates the presence of weak antiferromagnetic spin-exchange interaction between the metal ions within each molecule.

**Key words:** $\mu$-isophthalato-bridge, binuclear chromium(III) complexes, antiferromagnetism, synthesis

The synthesis and long-range magnetic investigations of exchange-coupled transition metal complexes, in which spin coupling between paramagnetic metals is propagated by multiatom bridges, have been an active field of research with the aim of understanding fundamental factors governing the magnetic properties of transition-metal complexes and to obtain some useful information about designing molecule-based magnets and to mimic the active sites and function of biological substances [1–8].

So far, much effort has been devoted to the development of multiatom bridging that can afford long-distance magnetic interactions. Among other more elaborate ligands employed in the study of magnetic interactions, the benzene dicarboxylate dianions, due to both their versatile bonding mode with metal ions and their peculiar structure –

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*Author to whom all correspondence should be addressed. E-mail: yantuanli@163.com involving carboxylato groups that are non-coplanar relative to each other and with the benzene ring – could be good candidates in supporting long-distance magnetic exchange interactions. Many binuclear transition-metal complexes containing the bridging phenyl dicarboxylate ligands have been synthesized and their magnetic properties have been studied [8–16]. It has been revealed by X-ray diffraction analyses and variable-temperature magnetic susceptibility investigations that the long-range magnetic coupling can occur between the two transition-metal ions centers bridged by the phenyl dicarboxylate groups [8–12]. However, to the best of our knowledge, no isophthalato-bridged binuclear chromium(III) complexes have so far been reported. Taking into account the above facts, it is of considerable interest to synthesize and study binuclear chromium(III) complexes with bridging isophthalato in order to gain some insight into the molecular magnetism of this kind of complexes.

In this work detailed here three new binuclear chromium(III) complexes bridged by isophthalato dianions (IPHTA) and end-capped with 4,4′-dimethyl-2,2′-bipyridine ($Me_2$bpy); 2,9-dimethyl-1,10-phenanthroline ($Me_2$phen) or 5-chloro-1,10-phenanthroline (Cl-phen), respectively, namely $[Cr_2(IPHTA)(Me_2bpy)_4](NO_3)_4$ **(1)**, $[Cr_2(IPHTA)(Me_2phen)_4](NO_3)_4$ **(2)** and $[Cr_2(IPHTA)(Cl\text{-}phen)_4](NO_3)_4$ **(3)**, have been synthesized and characterized. The cryomagnetic properties of the complexes **(1)** and **(2)** were measured and studied between 4.2~300 K.

## EXPERIMENTAL

**Materials:** All the reagents used in the synthesis were of analytical grade. Piperidinium isophthalate was synthesized by the literature method [9]. $Cr(NO_3)_3 \cdot 9H_2O$ and the terminal ligands 4,4′-dimethyl-2,2′-bipyridine ($Me_2$bpy); 2,9-dimethyl-1,10-phenanthroline ($Me_2$phen) and 5-chloro-1,10-phenanthroline (Cl-phen) were used as commercially obtained.

**Synthesis of $[Cr_2(IPHTA)(Me_2bpy)_4](NO_3)_4$ (1):** To a solution of piperidinium isophthalate (336 mg, 1 mmol) stirred in absolute ethanol solution (20 $cm^3$) was successively added a solution of $Cr(NO_3)_3 \cdot 9H_2O$ (880 mg, 2.2 mmol) in absolute ethanol (10 $cm^3$), followed by a solution of ethyl orthoformate (9 $cm^3$). The stirring was continued at room temperature until the mixture became limpid. Then, to the resulting solution was added an absolute ethanol solution (20 $cm^3$) of $Me_2$bpy (737 mg, 4 mmol). The color of the solution turned from pale-violet to violet-red immediately and a small amount of precipitate formed. The mixture was further refluxed for *ca.* 5 h, the violet-red microcrystals thus obtained were filtered, washed with ethanol and diethyl ether for several times, and dried over $P_2O_5$ under reduced pressure. Recrystallization was carried out from a DMF/ethanol (1:3) mixture. Yield, 751.9 mg (60%), m.p. 267.1 °C. Anal. Calc. for $Cr_2C_{56}H_{52}N_{12}O_{16}$ (m.w. 1253.10): C, 53.68; H, 4.18; N, 13.41; Cr, 8.30%. Found: C, 53.50; H, 4.11; N, 13.17; Cr, 8.16%.

**Synthesis of $[Cr_2(IPHTA)(Me_2phen)_4](NO_3)_4$ (2):** This complex was obtained as brown microcrystals by the same procedure as above but by using $Me_2$phen (833 mg, 4 mmol) instead of $Me_2$bpy. It was crystallized from a hot acetonitrile solution. Yield, 1052 mg (78%), m.p. 304.4℃. Anal. Calc. for $Cr_2C_{64}H_{52}N_{12}O_{16}$ (m.w. 1349.18): C, 56.98; H, 3.88; N, 12.46; Cr, 7.71%. Found: C, 56.71; H, 3.72; N, 12.25; Cr, 7.48%.

**Synthesis of $[Cr_2(IPHTA)(Cl\text{-}phen)_4](NO_3)_4$ (3):** This compound was prepared as described for complex **(1)**, except that Cl-phen (858.6 mg, 4 mmol) was used instead of $Me_2$bpy. Yield, 893.6 mg (65%); m.p. 327.1°C. The pale-brown microcrystals obtained were recrystallized from a hot DMF solution. Anal. Calc. for $Cr_2C_{56}H_{32}N_{12}O_{16}Cl_4$ (m.w. 1374.74): C, 48.93; H, 2.35; N, 12.23; Cr, 7.57%. Found: C, 48.76; H, 2.12; N, 12.01; Cr, 7.32%.

**Physical measurements:** Carbon, hydrogen and nitrogen elemental analyses were performed with a Perkin-Elmer elemental analyzer Model 240. The melting points of the complexes were determined by a Model XT 7-1 micromelting point meter. The metal contents were determined by EDTA titration. IR spectra were recorded with a NICOLET FT-IR 5DX spectrometer using KBr pellets. The electronic spectra (DMF solution) were measured on a Perkin-Elmer Hitachi-240 spectrophotometer. Molar conductances were measured with a DDS-11A conductometer. Magnetic susceptibility measurements at room temperature were carried out by Gouy's method using $Hg[Co(SCN)_4]$ as the calibrant. Variable temperature magnetic susceptibilities were measured using a Quantum Design MPMS SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants [17] for all the constituent atoms and effective magnetic moments were calculated by $\mu_{eff} = 2.828(\chi_M T)^{1/2}$, where $\chi_M$ isthe molar magnetic susceptibility corrected for diamagnetisms of the constituting atoms.

## RESULTS AND DISCUSSION

**Composition and general properties of the binuclear complexes:** On the basis of elemental analyses and physical data, shown in Tables 1 and 2, respectively, it is reasonable to assume that the reaction of IPHTA with $Cr(NO_3)_3 \cdot 9H_2O$ and the terminal ligand L (L = $Me_2$bpy, $Me_2$phen, Cl-phen) in *ca.*1:2:4 mole ratio yielded binuclear complexes of general formula $[Cr_2(IPHTA)L_4](NO_3)_4$, as expected. For the three binuclear complexes, the molar conductance values in DMF solution (see Table 1) fall in the expected range for 1:4 electrolytes [18], indicating that the four nitrate anions lie outside the coordination sphere. This is consistent with the IR data and presumed structure of the complexes shown in Figure 1. All the solid complexes are fairly stable in air and are soluble in some organic solvents, such as DMF, DMSO, acetonitrile and acetone, but attempts to obtain single crystals suitable for X-ray structure determination have so far been unsuccessful. However, the binuclear complexes were further characterized on the basis of the following results.

**Infrared spectra:** The IR spectrum taken in the region 4000–400 $cm^{-1}$ provides some information regarding the mode of coordination in the complexes and was analysed in comparison with that of the free ligand. The most relevant IR absorption bands for the complexes, along with their assignments are shown in Table 1 and we will discuss selected bands. It is noteworthy that the spectrum of isophthalato acid ($H_2$IPHTA) shows a broad band near 1700 $cm^{-1}$, which may be attributed to $\upsilon$(C=O) of the carboxylic groups. However, in the IR spectra of all complexes, this band had disappeared, and is accompanied by the appearance of two characteristic strong and broad bands at *ca.* 1580 $cm^{-1}$ and 1400 $cm^{-1}$, attributed to $\upsilon_{as}$(COO) (1570~1580 $cm^{-1}$) and $\upsilon_s$(COO) (1430~1438 $cm^{-1}$) stretching vibrations of the coordinated carboxylate groups. The absence of any splitting of the $\upsilon_{as}$(COO) and $\upsilon_s$(COO) bands strongly suggests end-to-end linking of the isophthalato ligand in an equivalent way at both sites [10]. According to the literature [19], the coordination modes of carboxylate groups have been determined by a separation between $\upsilon_{as}(CO_2)$ and $\upsilon_s(CO_2)$, *i.e.*, bidentate carboxylate groups show a separation smaller than 200 $cm^{-1}$, whereas unidentate carboxylate groups show a larger separation. Thus, for the present complexes, these two bands were separated by *ca.* 140 $cm^{-1}$ (see Table 1), suggesting a bidentate coordination mode for both carboxylate groups of the IPHTA ligand. The bidentate coordination modes of the carboxylates in bridging ligand (IPHTA) have been revealed by X-ray diffraction analysis of the $\mu$-terephthalato nickel(II) binuclear complex [12] $[Ni_2(IPHTA)(bpy)_4](ClO_4)_2$. The appearance of a new band at 560~580 $cm^{-1}$ (see Table 1), due to $\upsilon$(Cr–O), further confirms the coordinated nature of the carboxylate groups in these complexes. On the other hand, the –N=C– stretching vibrations for the terminal ligands ($Me_2$bpy, $Me_2$phen, Cl-phen) are shifted to higher frequencies (1500~1520 $cm^{-1}$) in their binuclear complexes, suggesting that the N atoms of the terminal ligands are coordinated with the chromium(III) ion. The additional band observed at around 480~490 $cm^{-1}$, due to $\upsilon$(Cr–N) (Table 1), further supports this view. In addition, a strong sharp band centered at *ca.* 1380 $cm^{-1}$, typical for a non-coordinated nitrate group [20], was observed for all the binuclear complexes. This is consistent with the conductance data of the binuclear complexes.

**Table 1.** Physical data of the IPHTA-bridged binuclear chromium(III) complexes.

| Complex | $\Lambda_M$ ($s\cdot cm^2\cdot mol^{-1}$) | $\mu_{eff}$ (B.M.) at room temp. | IR ($cm^{-1}$) $\upsilon_{as}(CO_2)$ | $\upsilon_s(CO_2)$ | $\upsilon$(Cr–O) | $\upsilon$(C=N) | $\upsilon$(Cr–N) | $\upsilon(NO_3^-)$ |
|---|---|---|---|---|---|---|---|---|
| **(1)** | 315 | 5.32 | 1576 | 1435 | 580 | 1510 | 480 | 1382 |
| **(2)** | 308 | 5.34 | 1570 | 1430 | 560 | 1512 | 490 | 1380 |
| **(3)** | 305 | 5.28 | 1580 | 1438 | 572 | 1520 | 486 | 1385 |

**Table 2.** Electronic spectral bands ($cm^{-1}$) and some coordination field parameters of the complexes.

| Complex | Assignments $\nu_1$ $^4A_{2g}\rightarrow{}^4T_{2g}$ | $\nu_2$ $^4A_{2g}\rightarrow{}^4T_{1g}(F)$ | $\nu_3$ $^4A_{2g}\rightarrow{}^4T_{1g}(P)$ | CT ($10^3\ cm^{-1}$) | Dq ($cm^{-1}$) | B ($cm^{-1}$) | $\beta$ | LFSE (kJ/mol) |
|---|---|---|---|---|---|---|---|---|
| **(1)** | 16280 | 23450 | 32850 | 37.6 | 1628 | 497 | 0.541 | 232.7 |
| **(2)** | 16210 | 23520 | 32700 | 37.3 | 1621 | 506 | 0.551 | 231.7 |
| **(3)** | 16300 | 23280 | 32870 | 37.9 | 1630 | 483 | 0.526 | 232.9 |

**Electronic spectra:** Since the electronic absorption spectra of the three complexes in DMF solution are quite similar, the discussion is confined to the most important bands to the structure. As shown in Table 2, for all three complexes, a strong absorption at *ca.* $37\times10^3$ $cm^{-1}$ found for all the complexes may be attributed to the charge-transfer absorption band [21]. Further investigation of these and similar systems is still required in order to obtain a detailed assignment for charge transfer. In addition, three weaker bands (Table 2) appearing in the 16210~16300, 23280~23520 and 32700~32870 $cm^{-1}$ regions, which may reasonably assign to $^4A_{2g}(F)\rightarrow{}^4T_{2g}$ ($\upsilon_1$), $^4A_{2g}(F)\rightarrow{}^4T_{1g}(F)$ ($\upsilon_2$) and $^4A_{2g}(F)\rightarrow{}^4T_{1g}(P)$ ($\upsilon_3$) transitions in the order of increasing energy, consistent with the presence of an octahedral coordination geometry [22] around the chromium(III) ion. The ligand field parameters are evaluated from these spectral bands as given below.

The $v_1$, $v_2$, $v_3$, interelectronic repulsion (Racah) parameter (B) and crystal field splitting energy (10 Dq) are related by: $v_2 + v_3 = 15B + 30Dq$, $v_2 + v_3 = 15B + 3v_1$ (10 Dq = $v_1$ for Cr(III) octahedral complex), $B = (v_2 + v_3 - 3v_1)/15$. Putting the values of $v_1$, $v_2$, $v_3$, we can get B for the complexes. The nephelauxetic ratio is defined as $\beta = B/B_0$, where $B_0$ is Racah parameter for the free $Cr^{3+}$ ion (918 $cm^{-1}$). In addition, the ligand field stabilization energy (LFSE) is calculated as: LFSE = $[4.18(n_1t_{2g} \times 4Dq - n_2e_g \times 6Dq)]/351$ (kJ/mol), where $n_1$ and $n_2$ are numbers of the electrons in $t_{2g}$ and $e_g$ orbitals, respectively. As shown in Table 2, the ligand field parameters are commensurate with octahedral geometry for the complexes [22].

Based on the above discussion and the analogous crystal structure study [12] on the complex $[Ni_2(TPHA)(bpy)_4](ClO_4)_2$, we conclude that these complexes have an extended isophthalato-bridged structure and contain two chromium(III) ions, in which the IPHTA ligand bridges in a *bis*-bidentate fashion and each chromium(III) ion is in a six-coordinated octahedral environment, as shown in Fig. 1. The plausible structure is further characterized by magnetic studies.

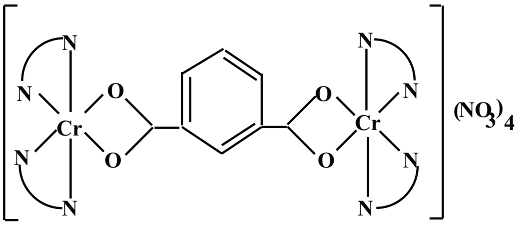
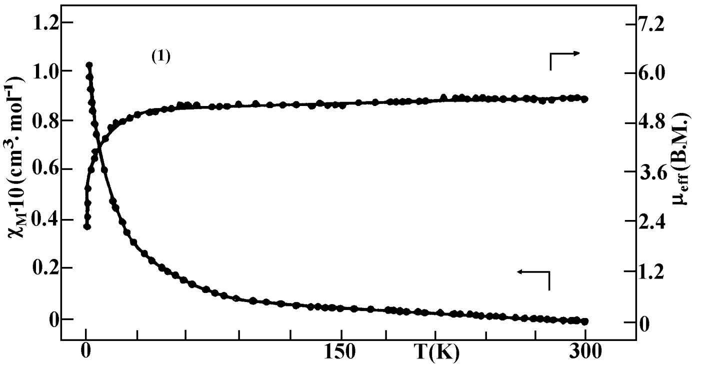


**Figure 1.** Plausible coordination environment of the complexes ($\widehat{\mathrm{N\;N}}$ = $Me_2$bpy, $Me_2$phen, Cl-phen).

**Magnetic studies:** The observed magnetic moment per binuclear complex at room temperature, shown in Table 1, is slightly less than the spin-only value (5.48 B.M.) for binuclear chromium(III) (S = 3/2) complexes in the absence of an exchange interaction. This result reflects that both chromium(III) ions of the binuclear complexes are in the S = 3/2 ground state and suggests the presence of a weak antiferromagnetic spin-exchange interaction in these complexes [23]. In order to obtain further structural information, magnetic susceptibility data on polycrystalline samples for $[Cr_2(IPHTA)(Me_2bpy)_4](NO_3)_4$ **(1)** and $[Cr_2(IPHTA)(Me_2phen)_4](NO_3)_4$ **(2)** complexes were collected between 4.2~300 K. The results are shown in Fig. 2 in the form of plots of $\chi_M$ *vs.* T and $\mu_{eff}$ *vs.* T, where $\chi_M$, $\mu_{eff}$ and T denote the magnetic susceptibility per molecule, effective magnetic moment per molecule, respectively. From Fig. 2 it can be seen that the magnetic behavior of the two complexes is similar. In the 30~300 K region, the curves of the effective magnetic moments ($\mu_{eff}$) decrease steadily with decreasing temperature, but sharply decrease below *ca.* 30 K. This behavior is characteristic for a weak antiferromagnetic interaction between the two chromium(III)



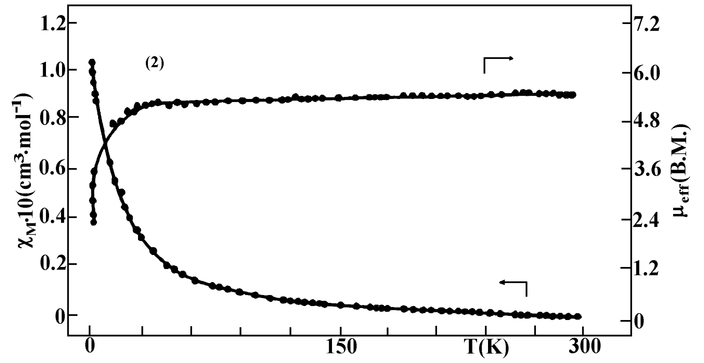


**Figure 2.** Plots of molar magnetic susceptibility ($\chi_M$) and effective magnetic moment ($\mu_{eff}$) *vs*. T for $[Cr_2(IPHTA)(Me_2bpy)_4](NO_3)_4$ **(1)** and $[Cr_2(IPHTA)(Me_2phen)_4](NO_3)_4$ **(2)** complexes. The point denotes the experimental data, the solid line represents the best least-squares fit to the experimental data using the parameters given in the text.

ions through the IPHTA-bridge within each molecule [23]. This is consistent with the room-temperature magnetic moments of the complexes.

In order to understand quantitatively the magnitudes of spin-exchange interaction, the magnetic susceptibility data were analysed by the spin Hamiltonian for isotropic binuclear magnetic exchange interaction, $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$, where the exchange integral J is negative for an antiferromagnetic interaction and positive for a ferromagnetic. For the chromium(III)–chromium(III) ($S_1 = S_2 = 3/2$) system, the molar magnetic susceptibility is given by:

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

where $\chi_M$ is the molecular susceptibility per binuclear complex and the remaining symbols have their usual meaning. As shown in Fig. 2, good least-squares fit to the experimental data were obtained with (1) for complexes **(1)** and **(2)**. The magnetic parameters thus determined and the agreement factor F, defined here as $F = \Sigma[(\chi_M)_{obs.} - (\chi_M)_{calc.}]^2/\Sigma(\chi_M)_{obs.}$ are: $J = -1.27$ cm$^{-1}$, $g = 2.01$, $F = 3.6 \times 10^{-4}$ for **(1)**; and $J = -2.19$ cm$^{-1}$, $g = 2.02$, $F = 2.1 \times 10^{-4}$ for **(2)**. These results indicate that these complexes are essentially binuclear and undergo weak antiferromagnetic spin-exchange interaction between the chromium(III) ions within each molecule. These small J values of complexes **(1)** and **(2)** may be brought out mainly by the geometry structures of the complexes and the properties of the bridged-ligand [21].

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