Synthesis, characterization and magnetism of μ-chloranilato binuclear chromium(III) complexes

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Five new chloranilato-bridged binuclear chromium(III) complexes have been synthesized and identified as [Cr$_2$(CA)L$_4$]-(ClO$_4$)$_4$ [L denotes 5-methyl-1,10-phenanthroline (Me-phen); 2,9-dimethyl-1,10-phenanthroline (Me$_2$-phen); 5-chloro-1,10-phenanthroline(Cl-phen); diaminoethane (en) or 1,3-diaminopropane (pn)], where CA represents the dianion of chloranilic acid. Based on elemental analyses, molar conductivity and magnetic moment of room-temperature measurements, and IR and electronic spectral studies, it is proposed that these complexes have CA-bridged structures and consist of two chromium(III) ions, each in an octahedral environment. The complexes [Cr$_2$(CA)(Me-phen)$_4$](ClO$_4$)$_4$(1) and [Cr$_2$(CA)(Me$_2$-phen)$_4$](ClO$_4$)$_4$(2) were further characterized by variable temperature (4.2—300 K) magnetic susceptibility 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 parameter $J = -7.8$ cm^{-1} for (1) and $J = -6.5$ cm^{-1} for (2). This result indicates that there is weak antiferromagnetic spin-exchange interaction between the two chromium(III) ions within each molecule.

Keywords   Chloranilato-bridge, binuclear chromium(III) complexes, magnetism

Introduction

Interest in bridged transition-metal polynuclear complexes is fundamental requirement not only for elucidation of the structural and electronic factors governing magnetic interaction between paramagnetic centers, but also for gaining some insight into the electron transfer pathway, mimicking the structural and functional properties in biological systems, and for obtaining useful information concerning the design and synthesis of molecule-based magnets.[1-6]

In view of the effective bridging function of the chloranilate dianions (abbreviated as CA), much work was published on binuclear complexes containing the μ-chloranilato ligand and their magnetic properties studied.[7-9] The effective bridging function of μ-chloranilato and the long-distance magnetic exchange interactions of these complexes have been revealed by single-crystal X-ray and magnetic analyses.[7-9] Thus, inspired by above facts, quite recently, we utilized CA as bridging ligand to prepare the binuclear oxovanadium(IV) complexes and to study their magnetic properties.[10] In order to provide more examples of CA-bridged binuclear complexes and to understand better the magnetic properties of this important group of complexes, and as an extension of that investigation, this paper deals with the synthesis, characterization and magnetism of five new chromium-(III) binuclear complexes using the dianion of chloranilic acid as bridging ligand: [Cr$_2$(CA)L$_4$](ClO$_4$)$_4$ [where CA = dianion of chloranilic acid; L = 5-methyl-1,10-phenanthroline (Me-phen); 2,9-dimethyl-1,10-phenanthroline (Me$_2$-phen); 5-chloro-1,10-phenanthroline (Cl-phen); diaminoethane (en) or 1,3-diaminopropane (pn)].

Experimental

Materials

All the reagents used in the synthesis were of analytical grade. The hydrated chromium(III) perchlorate was prepared by a general method. Chloranilic acid (H_2CA); 5-methyl-1,10-phenanthroline (Me-phen); 2,9-dimethyl-1,10-phenanthroline (Me$_2$-phen); 5-chloro-1,10-phenanthroline (Cl-phen); diaminoethane (en) and 1,3-diaminopropane (pn) were used as commercially obtained.

Synthesis of [Cr$_2$(CA)(L)$_4$](ClO$_4$)$_4$ (L = Me-phen, Me$_2$-phen, Cl-phen, en, pn)

The methods used to prepare the complexes are virtually identical and are exemplified by the preparation of

[Cr$_2$(CA)(Me-phen)$_4$](ClO$_4$)$_4$. To a stirred acetonitrile solution (10 mL) of chloranilic acid (0.2 mmol, 41.8 mg) was successively added dropwise an acetonitrile solution (10 mL) of Cr(ClO$_4$)$_3$·6H$_2$O (0.41 mmol, 188.0 mg), a solution of ethyl orthoformate (6 mL) and a solution of Me-phen (0.8 mmol, 155.4 mg) in 10 mL of acetonitrile. After the mixture was refluxed for a few minutes with stirring, a small amount of brown microcrystals deposited. The reflux was continued for *ca*. 2 h. The mixture was then allowed to cool to room temperature and the microcrystals thus obtained were removed by filtration, washed several times with acetonitrile and diethyl ether and dried over P$_2$O$_5$ under reduced pressure. Recrystallization was carried out from DMF/ethanol (1:2) mixture.

All analytical data, colors, yields and melting points of these complexes are collected in Table 1. All of the solid complexes are fairly stable in air, thus allowing physical measurements to be made.

Table 1 Data of elemental analyses, yields, colors and melting points of the complexes

Complex	Empirical formula (Formula weight)	Colour	Yield (%)	mp (℃)	Elemental analysis, Found (Calcd.)			
					C	H	N	Cr
1	Cr$_2$C$_{58}$H$_{40}$N$_8$O$_{20}$Cl$_6$	brown	88	218	46.77	2.65	7.43	6.89
	(1485.70)				(46.80)	(2.71)	(7.54)	(7.00)
2	Cr$_2$C$_{62}$H$_{48}$N$_8$O$_{20}$Cl$_6$	dark-brown	85	297	48.14	3.01	7.05	6.59
	(1541.80)				(48.30)	(3.14)	(7.27)	(6.75)
3	Cr$_2$C$_{54}$H$_{28}$N$_8$O$_{20}$Cl$_{10}$	light-brown	83	306	41.19	1.66	6.97	6.43
	(1567.36)				(41.38)	(1.80)	(7.15)	(6.64)
4	Cr$_2$C$_{14}$H$_{32}$N$_8$O$_{20}$Cl$_6$	reddish	67	312	17.59	3.28	11.63	10.45
	(949.15)				(17.72)	(3.40)	(11.81)	(10.96)
5	Cr$_2$C$_{18}$H$_{40}$N$_8$O$_{20}$Cl$_6$	pale-red	75	199	21.36	3.88	11.03	10.18
	(1005.26)				(21.51)	(4.01)	(11.15)	(10.35)

1 = [Cr$_2$(CA)(Me-phen)$_4$](ClO$_4$)$_4$, 2 = [Cr$_2$(CA)(Me$_2$-phen)$_4$](ClO$_4$)$_4$, 3 = [Cr$_2$(CA)(Cl-phen)$_4$](ClO$_4$)$_4$,
4 = [Cr$_2$(CA)(en)$_4$](ClO$_4$)$_4$, 5 = [Cr$_2$(CA)(pn)$_4$](ClO$_4$)$_4$.

Measurements

Analyses for C, H and N were carried out on a Perkin-Elmer model 240 elemental analyzer. Metal contents were determined by EDTA titration. Infrared spectra were measured on a Shimadzu model 810 infrared spectrometer in KBr pellets. Electronic spectra (DMF solution) were measured on a Perkin-Elmer Hitachi-240 spectrophotometer. Molar conductances were measured (DMF solution) 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 (4—300 K) magnetic susceptibilities were measured at the Institute of Physics, Chinese Academy of Sciences, using a vibrating magnetometer Model CF-1 (sensitivity m = 10^{-4} emu). Diamagnetic corrections were made with Pascal's constants[11] for all the constituent atoms and effective magnetic moments were calculated using the equation $\mu_{eff} = 2.828(\chi_M T)^{1/2}$, where χ_M is the molar magnetic susceptibility corrected for diamagnetism of the constituting atoms.

Results and discussion

Composition of the complexes

The elemental analytic data for the newly prepared complexes, listed in Table 1, indicate that the reaction of chloranilic acid (H_2CA) with $Cr(ClO_4)_3 \cdot 6H_2O$ and the terminal ligands L (L = Me-phen, Me_2-phen, Cl-phen, en, pn) in 1:2:4 mole ratio yielded the binuclear complexes of the general formula $[Cr_2(CA)L_4]$-$(ClO_4)_4$, as expected. Based on the conductivity, room temperature magnetic moment measurements, spectroscopic characterization and magnetic studies (vide infra) these complexes are presumed to have the structure as shown in Fig. 1.
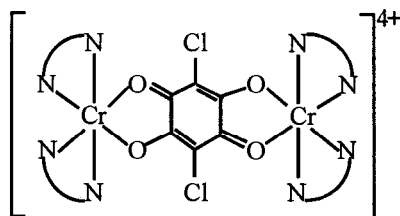

Fig. 1　Proposed structure of the complexes ($\widehat{NN}$ = Me-phen, Me_2-phen, Cl-phen, en, pn).

Solubility and molar conductances of the binuclear complexes

All the complexes are very soluble in DMSO and DMF; moderately soluble in water, acetone and practically insoluble in carbon tetrachloride, chloroform and benzene. For the five complexes, the molar conductances in DMF solution at 25℃ (see Table 2) fall in the expected range for 1:4 electrolytes,[12] indicating that the four perchlorates anions are situated outside the metal coordination sphere. This is in agreement with the results of IR spectra.

Infrared spectra

Since the IR spectra of all complexes are quite similar, the discussion is confined to the most important vibration of the 400—4000 cm^{-1} region in relation to the structure. The most relevant IR absorption bands due to the complexes along with their assignments are shown in Table 2. We will only discuss the selected infrared bands. In the IR spectra of the five complexes, a very

strong peak at 1520—1530 cm^{-1} and a medium peak at 1380—1385 cm^{-1} is observed due to C = O stretching vibrations of the CA ligand. This agrees with D_{2h} symmetry for the CA ligand and suggests a bridging bis-bidentate coordination mode.[7,8] The bis-bidentate coordination modes of the bridging ligand (CA) have been revealed by X-ray diffraction analyses of analogous complexes.[7,8] The appearance of a new band at 560—585 cm^{-1} due to $\nu(Cr - O)$ further confirms the coordinated nature of the CA groups in these complexes. On the other hand, the - N = C - and - NH$_2$ stretching vibrations for the terminal ligands (Me-phen, Me_2-phen, Cl-phen, en, pn) were shifted to higher frequencies (ca. 10—15 cm^{-1}) in corresponding binuclear complexes, suggesting that the N atoms of the terminal ligands be coordinated with the metal ion. The additional band observed at around 430—460 cm^{-1} due to $\nu(Cr - N)$ further supports this view. In addition, a strong and broad band centered at ca. 1100 cm^{-1}, and a strong sharp band at ca. 630 cm^{-1} typical for a non-coordinated perchlorate group,[13,14] were present for all the binuclear complexes. This is consistent with the conductance data of the complexes.

Electronic spectra

In order to clarify the mode of bonding, the electronic spectra of the free ligand (H_2CA) and binuclear chromium(III) complexes were studied and assigned on the basis of a careful comparison of the latter with the free ligand. As shown in Table 3, the electronic spectra of the five complexes in DMF solutions are similar. For all five complexes, three weak intensity bands appearing in the 15950—16300, 23580—24200 and 32750—33650 cm^{-1} region are observed, which may be reasonably assigned to the $^4A_{2g}(F) \rightarrow {}^4T_{2g}(\nu_1)$, $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ (ν_2) and $^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) transitions in the order of increasing energy, consistent with the presence of an octahedral coordination geometry around chromium(III) ion.[15] According to the literature,[16] some ligand field parameters, such as interelectronic repulsion (Racah) parameter (B), crystal field splitting energy (10 D_q), nephelauxetic ratio (β) and the ligand field stabilization energy (LFSE) of the complexes can be evaluated from these observed bands (ν_1, ν_2, ν_3) and the calculated results are summarized in

Table 3. As shown in Table 3, the ligand field parameters are commensurate with octahedral geometry for the complexes, the values of $\beta < 1$ show strongly covalent bonding of chromium(III) in these complexes. In addition, a broad band at about 19700—20500 cm^{-1} was ob-

served in the electronic spectra of the complexes. It is attributed to charge-transfer bands arising from CA ligand, as expected for p-benzoquinones,[17] further supporting a bridging bis-bidentate coordination proposed for CA.

Table 2 Physical data for the binuclear complexes

Complex	Λ_M	μ_{eff}	IR (cm^{-1})					
	(S·cm^2·mol^{-1})	(B.M.)	$\nu(C=O)$	$\nu(Cr-O)$	$\nu(Cr-N)$	$\nu(C=N)$	$\nu(NH_2)$	$\nu(ClO_4^-)$
1	300	5.37	1380,1520	580	440	1550	—	1100,630
2	315	5.36	1385,1530	575	430	1565	—	1098,630
3	305	5.40	1380,1528	560	445	1560	—	1105,625
4	320	5.33	1385,1530	585	460	—	3250	1100,628
5	320	5.30	1380,1530	580	450	—	3320	1100,630

Table 3 Electronic spectral bands (cm^{-1}) and some coordination field parameters of the binuclear complexes

Complex	Assignments			CT	D_q	B	β	LFSE
	$^4A_{2g}\xrightarrow{\nu_1}{}^4T_{2g}$	$^4A_{2g}\xrightarrow{\nu_2}{}^4T_{1g}(F)$	$^4A_{2g}\xrightarrow{\nu_3}{}^4T_{1g}(P)$	(10^3 cm^{-1})	(cm^{-1})	(cm^{-1})		(kJ/mol)
1	16300	23580	34000	19.8	1630	578.7	0.6304	232.9
2	16180	24200	32750	20.0	1618	560.7	0.6108	231.2
3	15950	23950	32800	19.7	1595	593.3	0.6463	227.9
4	16250	23870	33650	20.5	1625	584.7	0.6369	232.2
5	15980	23780	32800	19.9	1598P	576.0	0.6275	228.4

In spite of our many efforts, attempts to obtain single crystals suitable for an X-ray structure determination have so far been unsuccessful. However, based on the composition of these complexes, their infrared spectra, electronic spectra, conductivity measurements, magnetic characterization (*vide infra*), and the crystal structure study of the analogous compounds,[7,8] these complexes are proposed to have an extended CA-bridged structure and to contain two Cr(III) ions bridged by the CA ligand in a *bis*-bidentate fashion. Each chromium(III) ion has an octahedral coordinated environment, as shown in Fig. 1. The plausible binuclear structure is further characterized by the following magnetic studies.

Magnetic properties

The observed magnetic moment per binuclear complex at room temperature, shown in Table 2, is slightly lower than the spin-only value (5.48 B.M.) for binuclear chromium(III) ($S = 3/2$) complexes in the ab-

sence of an exchange interaction, implying an operation of an antiferromagnetic spin-exchange interaction in these complexes.[18] Being interested in the magnetic behaviour of the complexes, variable-temperature (4—300 K) magnetic susceptibility data for polycrystalline samples for complexes 1 and 2 were further collected in the temperature 4.2—300 K region. The results 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 magnetic moment and T the absolute temperature. From Fig. 2 it can be seen that the magnetic behavior of the two complexes are similar. When the temperature is lowered, the curve of the effective magnetic moment exhibits a continuous decreases. This behavior is characteristic of weak antiferromagnetic spin-exchange interaction between chromium(III) ions through the CA-bridge within each molecule.[19] Thus, as noted above, the observed magnetic behavior both at room-temperature and variable-temperature clearly demonstrates that the chromium (III)-chromium(III) ions coupling is antiferro-magnetic
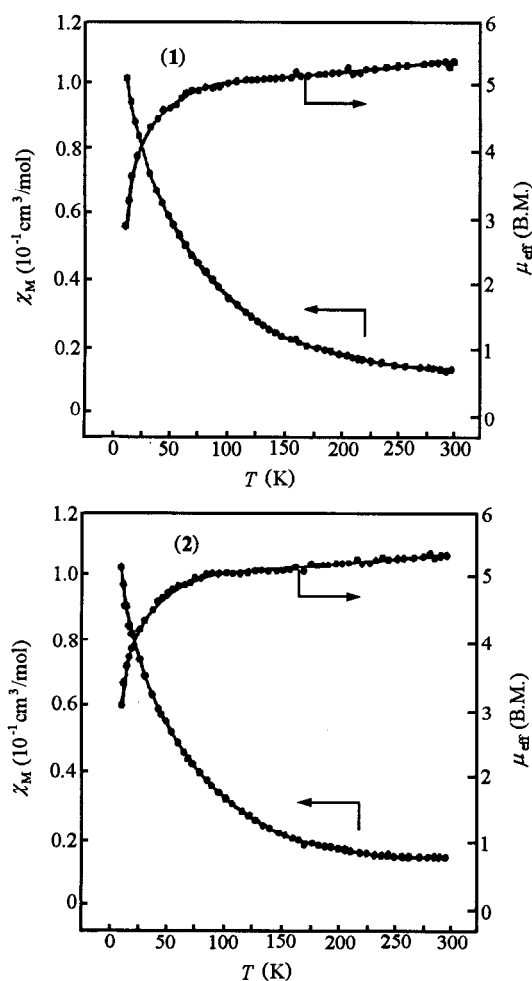
and fairly substantial among these complexes.[20-22]

Fig. 2 Temperature variation of χ_M (lower curve) and μ_{eff} (upper curve) for the complexes $[Cr_2(CA)(Me\text{-phen})_4]$-$(ClO_4)_4$ (1) and $[Cr_2(CA)(Me_2\text{-phen})_4](ClO_4)_4$ (2). The curve is based on Eq. (1) using the magnetic parameters given in the text. (●), experimental data; (—), calculated curve as described in the text.

In order to understand quantitatively the magnitude of the spin-exchange interaction, the magnetic analysis was carried out using the spin Hamiltonian for isotropic binuclear magnetic exchange interaction ($\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$), where the exchange parameter 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 Eq. (1).

$$\chi_M = \frac{2N\beta^2 g^2}{kT}[\frac{A}{B}] \qquad (1)$$

$$A = 14 + 5\exp(-6J/kT) + \exp(-10J/kT)$$

$$B = 7 + 5\exp(-6J/kT) + 3\exp(-10J/kT) + \exp(-12J/kT)$$

where χ_M denotes the molecular susceptibility per binuclear complex, and the remaining symbols have their usual meanings. As shown in Fig. 2, good least-squares fit to the experimental data was obtained with Eq. (1) for complexes 1 and 2. The magnetic parameters thus determined and the agreement factor F, defined here as $F = ([(\chi_M)_{calc} - (\chi_{obs})]^2/\sum(\chi_M)_{obs}$ are: $J = -7.8$ cm^{-1}, $g = 2.00$, $F = 1.1 \times 10^{-5}$ for 1; and $J = -6.5$ cm^{-1}, $g = 2.01$, $F = 5.1 \times 10^{-5}$ for 2. The results (small and negative J value) indicate that the complexes are essentially binuclear and undergo weak antiferromagnetic spin-exchange interaction between the chromium-(III) ions within each molecule. These small J values of the present complexes are very similar with those of related chloranilato-bridged binuclear complexes previously reported.[7-10] The weak antiferromagnetic behavior for these systems may be brought out mainly by the geometry structures of the complexes and the properties of the bridged-ligand.[23]

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