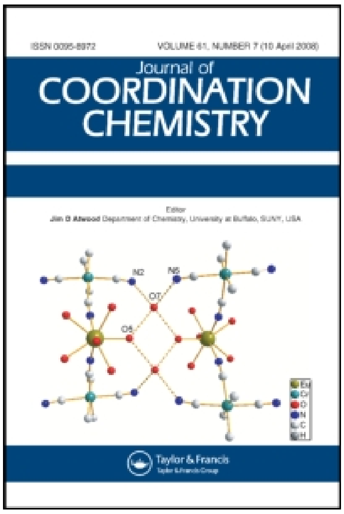

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Synthesis and characterization of a series of bis(L-tartrate)-bridged dinuclear transition metal complexes with 2,2'-bipyridine

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Synthesis and characterization of a series of bis(L-tartrate)-bridged dinuclear transition metal complexes with 2,2′-bipyridine

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Seven bis(L-tartrato)-bridged dinuclear metal complexes with 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen), $[M^{III}_2(\text{L-tartH})_2(\text{bpy or phen})_2]\cdot 4H_2O$ (M = Fe, Mn) or $[M^{II}_2(\text{L-tartH}_2)_2(\text{bpy or phen})_2]\cdot nH_2O$ (M = Ni, Co, Cu), where L-tart^{4-} is $C_4H_2O_6^{4-}$, were synthesized and characterized by the elemental analysis and ESI-mass spectra or powder X-ray patterns. These are the first examples of discrete dinuclear complexes with bpy or phen except for Cr(III) complexes. The protonation of the hydroxyls of the coordinated tartrate systematically changes with the variation of the metal ionic radii, the smaller ionic radii of the central metal, the smaller number of the protons in the hydroxyl groups of the bridging tartrates. The magnetic properties are discussed in connection to analogous Cr(III), Cu(II), and V(IV)O complexes.

Keywords: Dinuclear complexes; Tartrate complexes; Magnetic properties; Ionic radii; Protonation

1. Introduction

A number of tetradentate tartrate-bridged dinuclear metal complexes have been isolated to study their structures and physical properties [1]. Among them are octahedral six-coordinate (OC-6) mixed ligand Cr(III) complexes with 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) [2, 3] or acetylacetonate (acac) [4] and the Mn(III) complex with bpy [5]. There have been several reports on X-ray analysis of L-tartrate complexes with aqua ligands $[M^{II}(\text{L-tartH}_2)_2(H_2O)_2]$ (L-tart$^{4-} = C_4H_2O_6^{4-}$) of Mn(II) [6], Co(II) [7], Ni(II) [8], and Cu(II) [9] and a series of $[M(\text{L-tartH}_2)]$ (M^{II} = Mn, Fe, Co, Ni) with the *catena*-poly(μ-carboxylate)-coordinated structures [10]. These complexes demonstrated the stereospecific formation with the Λ–Λ absolute configuration around two metal ions. For the protonation of the hydroxyl groups of the bridging tartrates, four cases were found among the reported tartrate complexes: fully deprotonated for the DL-tart Cu(II) complex [11, 12] and DL- and L-tart V(IV)O

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complexes [13], one protonated for the L- and meso-tart Cr(III) bpy or phen complexes [2–4], two protonated for the L-tart bpy Mn(III) complex [5], and fully protonated L-tart M(II) complexes [6–10]. The DL-tart-bridged Cu(II) [11, 12] and L-tart V(IV)O dinuclear complexes [14] were reported to demonstrate large magnetic interactions. There has been no report on the magnetic properties of $[M^{II}(\text{L-tartH}_2)_2(H_2O)_2]$. For polymeric $[M(\text{L-tartH}_2)]$ without capping ligands the intramolecular magnetic interactions were claimed to be very small as compared with the intermolecular magnetic interactions, although there has been no direct experimental evidence [10].

In this article, the synthesis and characterization of bis(L-tartrato)-bridged dinuclear metal complexes of Mn(III), Fe(III), Ni(II), Co(II), and Cu(II) with capping bpy or phen are reported with their magnetic properties, which are discussed in comparison with those of the analogous Cr(III), Cu(II), and V(IV)O complexes.

2. Experimental

2.1. *Preparation of complexes*

The starting complexes $[Fe^{III}(bpy)(dmf)Cl_3]$, $[Co^{II}(\text{bpy or phen})Cl_2]$, and $[Cu^{II}(\text{bpy or phen})Cl_2]$ were prepared by a method similar to that of Broomhead and Dwyer [15].

2.1.1. $[Ni^{II}(bpy)(H_2O)_4]SO_4$. To a solution of 10 mmol of $NiSO_4 \cdot 6H_2O$ in 30 mL of H_2O, 10 mmol of bpy was added with stirring at room temperature. After 20 min of stirring, the color of the solution changed to blue. The solution was evaporated under reduced pressure. When crude crystals began to deposit, the evaporation was stopped. After the crude crystals were dissolved again by warming, the solution was allowed to stand at room temperature for 2 days, and blue crystals were obtained.

2.1.2. Synthesis of $[Fe_2^{III}(\text{L-tartH})_2(bpy)_2] \cdot 4H_2O$ and $[M_2^{II}(\text{L-tartH}_2)_2(bpy)_2] \cdot nH_2O$ ($M^{II} = Co^{II}, Ni^{II}, Cu^{II}$). To each solution of $[Fe^{III}(bpy)(dmf)Cl_3]$, $[Co^{II}(bpy)Cl_2]$, $[Ni^{II}(bpy)(H_2O)_4]SO_4$, or $[Cu^{II}(bpy)Cl_2]$ (10 mmol) an equimolar amount of sodium L-(+)-tartrate solution was added and stirred at room temperature. Each resultant precipitate was filtered off, washed with water, methanol, acetone, and ether and dried under vacuum.

2.1.3. $[Mn_2^{III}(\text{L-tartH})_2(phen)_2] \cdot 4H_2O$ and $[M_2^{II}(\text{L-tartH}_2)_2(phen)_2] \cdot nH_2O$ ($M = Co^{II}, Cu^{II}$). These complexes were prepared from $[Mn^{III}(phen)Cl_3(H_2O)]$, $[Co^{II}(phen)Cl_2]$, and $[Cu^{II}(phen)Cl_2]$ by a similar method to that for the bpy complexes [15].

$[Mn_2^{III}(\text{L-tartH})_2(phen)_2] \cdot 4H_2O$ (**1**) (pale brown). Anal. Calcd for $C_{32}H_{30}O_{16}N_4Mn_2$ (%): C, 45.95; H, 3.61; N, 6.70. Found (%): C, 43.61; H, 3.64; N, 6.51.

$[Fe_2^{III}(\text{L-tartH})_2(bpy)_2] \cdot 4H_2O$ (**2**) (orange powder). Anal. Calcd for $C_{28}H_{28}O_{16}N_4Fe_2$ (%): C, 42.65; H, 3.58; N, 7.11. Found (%): C, 42.29; H, 3.66; N, 7.10.

$[Co_2^{II}(\text{L-tartH}_2)_2(bpy)_2] \cdot 10H_2O$ (**3**) (pink powder). Anal. Calcd for $C_{28}H_{42}O_{22}N_4Co_2$ (%): C, 37.18; H, 4.68; N, 6.19. Found (%): C, 36.98; H, 4.78; N, 6.26.

$[Co_2^{II}$ (L-tart$H_2)_2$(phen$)_2] \cdot 12H_2O$ (**3′**) (pink powder). Anal. Calcd for $C_{32}H_{48}O_{24}N_4Co_2$ (%): C, 38.80; H, 4.88; N, 5.66. Found (%): C, 38.35; H, 4.73; N, 5.68.

$[Ni_2^{II}$ (L-tart$H_2)_2$(bpy$)_2] \cdot 6H_2O$ (**4**) (blue-white powder). Anal. Calcd for $C_{28}H_{30}O_{18}N_4Ni_2$ (%): C, 39.46; H, 4.46; N, 6.58. Found (%): C, 39.14; H, 4.36; N, 6.58.

$[Cu_2^{II}$ (L-tart$H_2)_2$(bpy$)_2] \cdot 10H_2O$ (**5**) (light-blue powder). Anal. Calcd for $C_{28}H_{40}O_{22}$ N_4Cu_2 (%): C, 36.72; H, 4.84; N, 6.12. Found (%): C, 36.44; H, 4.68; N, 6.17.

$[Cu_2^{II}$ (L-tart$H_2)_2$(phen$)_2] \cdot 12H_2O$ (**5′**) (light-blue powder). Anal. Calcd for $C_{32}H_{48}O_{24}$ N_4Cu_2 (%): C, 38.44; H, 4.84; N, 5.60. Found (%): C, 38.28; H, 4.58; N, 5.70.

2.1.4. Na[Cr_2(L-tart$_2$H)(phen$)_2$] · 6.5H_2O. This was prepared by the literature method [3] and was characterized as the hemitridecahydrate [2b].

2.2. *Physical measurements*

The negative ion ESI-MS spectra were measured using a Perkin-Elmer API-III Plus Electro Spray Mass spectrometer. Absorption spectra were measured using a Perkin Elmer Lambda-19 spectrophotometer at room temperature. Infrared spectra were recorded on a Perkin-Elmer Spectrum 2000 FT-IR spectrophotometer using KBr disk. Magnetic susceptibility data of the powdery samples were obtained at 2000 Oe between 2 and 300 K using a SQUID susceptometer (MPMS-5S, Quantum Design). Pascal's constants were used for diamagnetic corrections to determine the constituent atom diamagnetism. X-ray powder diffraction data were collected on a Rigaku Multi Flex diffractometer using Cu-Kα radiation.

3. Results and discussion

3.1. *Preparation and characterization of tartrate-bridged dinuclear complexes*

The chemical constitutions are confirmed to have M : tartH : bpy or phen = 1 : 1 : 1 for the Fe(III), Mn(III) complexes and M : tartH_2 : bpy or phen for the Co(II), Ni(II), and Cu(II) complexes by the elemental analysis. For the iron(III) and Mn(III) complexes, one of two hydorxyl protons of each L-tartrate is deprotonated while two hydroxyl protons of each L-tartrate remain in the M(II) complexes.

3.2. *FT-IR spectra*

The FT-IR spectra for all the complexes have the C–O stretching vibration of the carboxyl group near 1600 cm^{-1} (figure S1), confirming the coordination of the carboxylate of tartrate.

3.3. *ESI-mass spectra*

ESI-mass spectra in the positive mode were measured after adding CsCl to the binuclear Fe(III) (**2**), Co(II) (**3**), and Ni(II) (**4**) neutral complexes in solution (water : methanol = 1 : 1). For the ESI-MS of the binuclear complexes the peaks

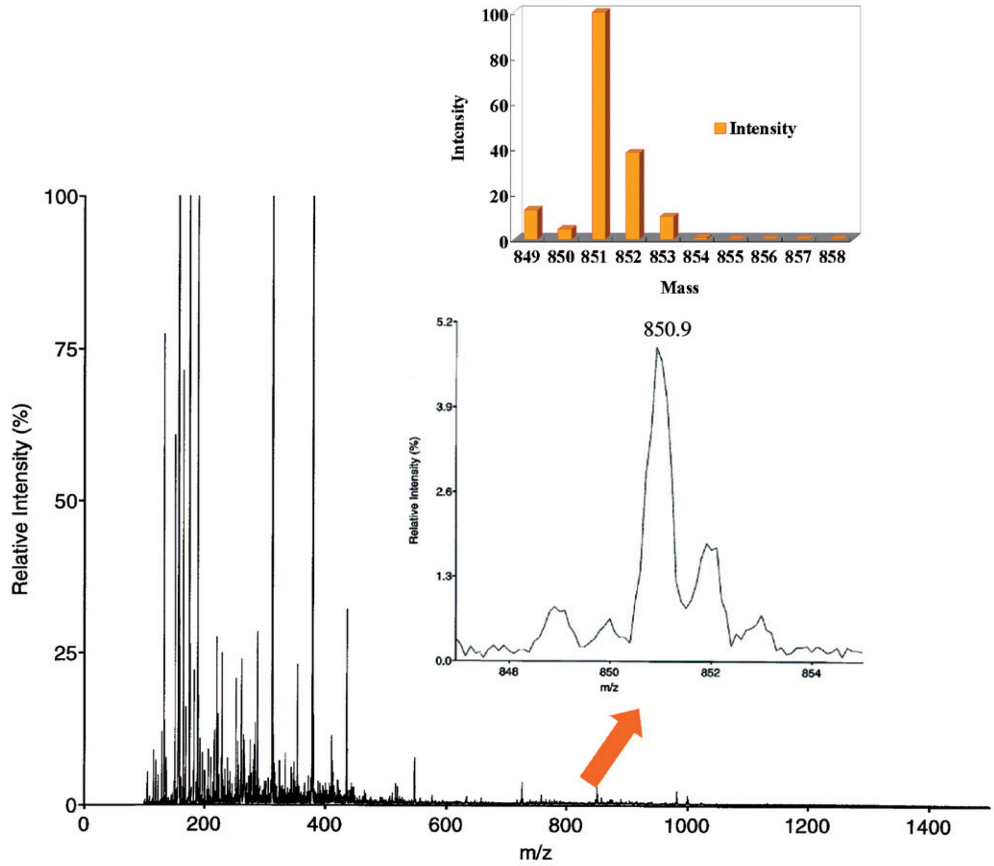

Figure 1. ESI-MS of [Fe$_2^{III}$ (L-tartH)$_2$(bpy)$_2$] · 4H$_2$O in water : methanol = 1 : 1 with CsCl.

of Cs$^+$ + [Fe$_2$(L-tartH)$_2$(bpy)$_2$] ($m/z = 850$), Cs$^+$ + [Co$_2$(L-tartH$_2$)$_2$(bpy)$_2$] ($m/z = 857$), Cs$^+$ + [Ni$_2$(L-tartH$_2$)$_2$(bpy)$_2$] ($m/z = 859$) were observed, respectively, as shown in figures 1–3. The intensity ratios of the observed peaks around $m/z = 850$, 857, and 859, respectively, are consistent with the calculated isotopic distributions for all the binuclear complexes as in figures 1–3. These results substantiate the formation of the L-tartrate-bridged dinuclear **2**, **3**, **4** with the chemical formula as suggested from the elemental analysis; the corresponding Cu(II) (**5**) complex failed to detect any peak for the bis(L-tartrate) dinuclear composition.

3.4. *X-ray powder diffraction*

The dinuclear structure of the Cu(II) (**5**) and (**5′**) complexes was compared with the Co(II) (**3**) and (**3′**) complexes by using powder X-ray diffractometer (XRD). The L-tart Co(II) and Cu(II) complexes with the same ligands (bpy or phen) having the same number of crystallization water give the same peak pattern (Supplementary material). Thus, they are isostructural with the same configuration as observed previously [16].

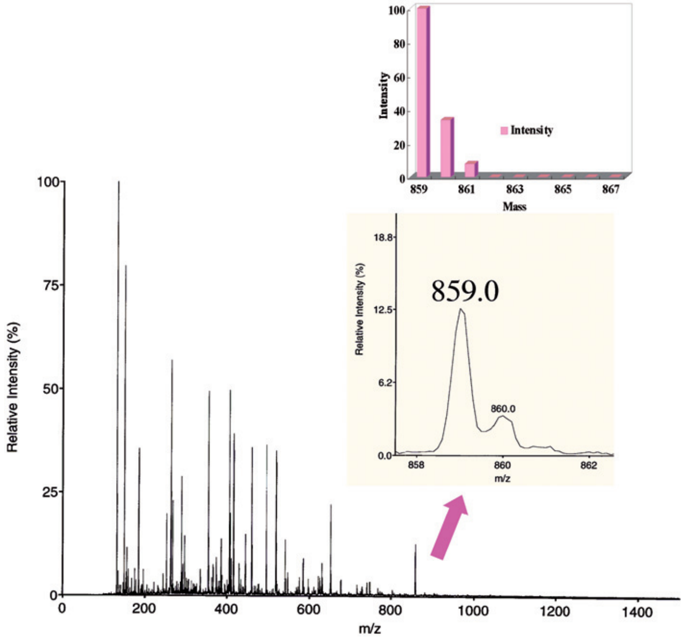

Figure 2. ESI-MS of $[Co^{II}_2\ (L\text{-tartH}_2)_2(bpy)_2]\cdot 4H_2O$ in water : methano = 1 : 1 with CsCl.

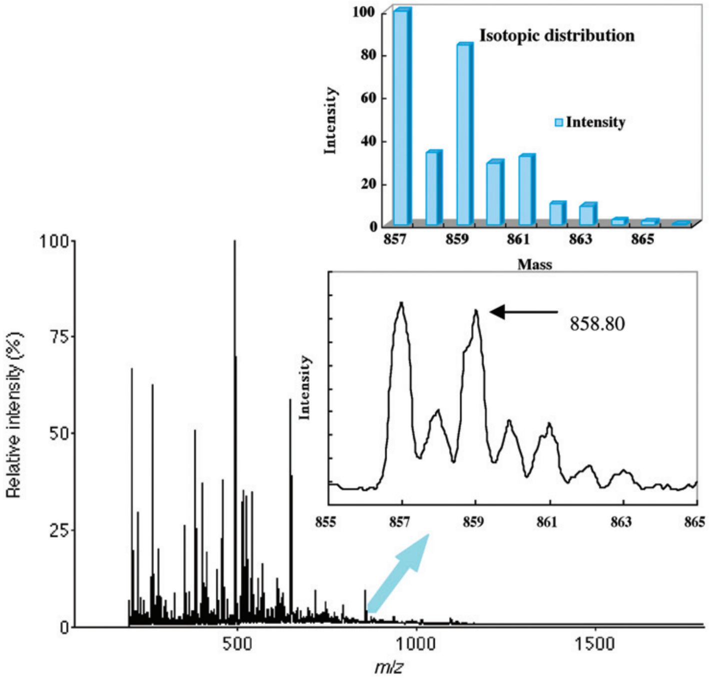

Figure 3. ESI-MS of $[Ni^{II}_2\ (L\text{-tartH}_2)_2(bpy)_2]\cdot 4H_2O$ in water : methanol = 1 : 1 with CsCl.

Thus, **5** and **5′** with bpy and phen take the same tartrate-bridged dinuclear structure as **3** and **3′** for which the dinuclear structure is confirmed by the ESI-MS spectra. However, **4** shows different peaks from that of **3** and **5**, probably owing to the different number of crystallization water (figure S2).

3.5. *Proposed structure*

The structures of **2**–**5** are proposed as found for the bpy Cr(III) complex [17] (figure 4). The divalent metal complexes have four protons of the hydroxyl groups which are oriented away from the center of the bridging moiety (figure 4b) as found for the X-ray structures of the corresponding aqua complexes [7–9], whereas two protons are eliminated for the trivalent Mn (**1**) and Fe (**2**) complexes. This is contrasting to the L-tart Cr(III) complex, where one proton of the hydroxyl is hydrogen bonded with the hydroxyl oxygen (*vide infra*) as found in the X-ray structure [17]. Such a tendency of protonation of the hydroxyl groups depends on the ionic radii of the high-spin octahedral six-coordinate (OC-6) metal ions. That is, the larger the ionic radii, the more protons in accordance with increasing M–O bond interaction. The square planar four-coordinate (SP-4) $[Cu_2(\text{L-tart})(\text{D-tart})]$ [11, 12] and square pyramidal five-coordinate (SPY-5) $M_2[(VO)_2(tart)_2]$ [13, 18b,c] are fully deprotonated. The degree of protonation of the coordinated tartrate is classified into four groups according to the ionic radii of the central metal ions as follows: {ionic radii (Å)}(number of protons) [19]; SP-4 Cu^{2+}\{0.540\}(0) and SPY-5 V^{4+}\{0.58\}(0) are smaller than OC-6 Cr^{3+}\{0.615\}(1) $\ll$ OC-6 Mn^{3+}\{0.645\}(2) = Fe^{3+}\{0.645\}(2) $\ll$ OC-6 Ni^{2+}\{0.690\}(4) $\ll$ OC-6 Cu^{2+}\{0.73\}(4) < OC-6 Co^{2+}\{0.745\}(4). Second and third row transition metal complexes accord with this classification: OC-6 $Mo^{VI}O_2^{2+}$ \{0.59\}(0) for $\{NH_4[Mo_2^{VI}O_4Ln^{III}(H_2O)_6(tart)_2]\cdot 4H_2O\}_n$ [20] and Nb^V\{0.64\}(1) for $(gu)_5[Nb^V(O_2)_4(tart)_2H]$ [21]. Fully deprotonated $(gu)_6[Ta^V(O_2)_4(tart)_2]$ seems to be exceptional because of Ta^V\{0.64\}(0) [21]. However, as the average bond length of the Ta–O(hydroxyl groups) is shorter by 0.05 Å than that of the Nb–O [21], the actual ionic radius of Ta^{5+} is likely to be 0.59 Å, the Ta complex would be Ta^V\{0.59\}(0), which is close to V^{4+}\{0.58\}(0), in accord with the above classification. A fully deprotonated Mo complex is formed even in the acidic conditions [20]. For many tartrate

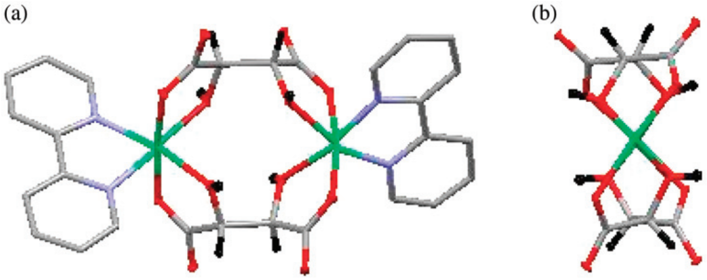

Figure 4. Proposed structure of $[M^{II}(\text{L-tartH}_2)_2(bpy)_2]$ showing the outward disposition of four protons of the hydroxyl groups. Two are deprotonated for the M^{III} complexes. (a) View perpendicular to the M···M direction; (b) view parallel to the M···M direction; bpy ligands are omitted for clarity.

lanthanide(III) complexes with ionic radii of Ln(III) >0.8 Å, the fully protonated tartrates are coordinated, also in accordance with the classification [22].

In summary, the ionic radii criterion is proposed to be $0.59(0) < 0.615(1) < 0.645(2) \ll 0.69(4)$. The degree of protonation of the hydroxyl groups in the tartrate ligand could be gauged by this criterion.

3.6. *Magnetic properties*

The magnetic interaction in the L-tartrate complexes of a series of first row transition metal ions from d^3(Cr(III)), d^4(Mn(III)), d^5(Fe(III)), d^7(Co(II)), d^8(Ni(II)) to d^9(Cu(II)) can be compared with the previously reported tartrate dinuclear complexes. The Cu(II) complex with DL-tartrates, $Na_4[Cu_2(\text{L-tart})(\text{D-tart})] \cdot 10H_2O$ [11, 12] is antiferromagnetic with Cu···Cu distance of 2.98 Å. The vanadyl complexes $(NH_4)_4[(VO)_2(\text{L-tart})_2]$ [13] and $Na_4[(VO)_2(\text{L-tart})(\text{D-tart})]$ [18a] dinuclear complexes with the V···V distance of 4.08–4.35 Å are fairly large ferromagnetic. The recent magnetic and ESR measurements of $M[(VO)_2(\text{L-tart})(\text{D-tart})] \cdot 4H_2O$ (M = Ca, Ba) proposed a weak ferromagnetic interaction with a low lying triplet state [18b,c]. The latter measurements within the 5–300 K range seem to be more reliable than the former one [18a] made above 77 K.

The magnetic susceptibilities of the present complexes from 2 to 300 K were measured in the powder state. The plots of the products of the magnetic susceptibility and temperature ($\chi_M T$) values *versus* T are shown in figure 5, where χ_M are the molar magnetic susceptibilities per a dinuclear complex. The magnetic susceptibility measurements for these complexes show that the Mn(III) (**1**), Fe(III) (**2**), and Co(II) (**3**) complexes are high-spin because the $\chi_M T$ ($cm^3\,mol^{-1}\,K$) values at room temperature are close to spin-free values (g values): 6.56(2.09) for **1**, 9.05(2.03) for **2**, and 6.80(2.13) for **3**. The fittings for the plots of $\chi_M T$ *versus* temperature were carried out by two methods. First, the plots were fitted according to the Van Vleck equation

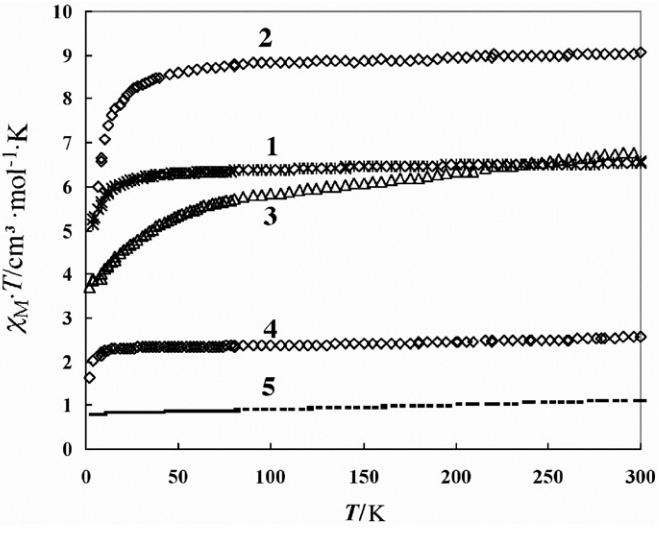

Figure 5. Plots of $\chi_M T$ *vs.* T for **1–5**.

with the Hamiltonian $H = -2JS_1 \cdot S_2$ (figure S3). The data fitting resulted in the following J (cm^{-1}) values (g values): −0.08(2.07) for **1** as compared with −0.15(2.05) for the bpy Mn complex [4]; −0.13(2.03) for **2**; −0.18(2.20) for **4**; poor fitting occurred for **3** and **5**. More detailed fittings with magnetic couplings (J) and TIP were attempted including the zero-field splitting (D) for **1**, **2**, and **4** and spin-orbit coupling (λ), orbital angular momentum reduction factor (k), and crystal field splitting (Δ) for **3**, and those including TIP for **5** (figures S4-1–S4-5). The resultant J (cm^{-1}) values [g, D (cm^{-1}), TIP (cm^3 mol^{-1})] are 0.04[2.05, −2.10, +0.0009] for the Mn(III) (**1**) complex; −0.12[2.01, 1.96, +0.0009] for the Fe(III) (**2**) complex; −0.06[2.15, 1.61, +0.0008] for the Ni(II) (**4**) complex and J (cm^{-1}) [k, Δ (cm^{-1}), λ (cm^{-1}), TIP (cm^3 mol^{-1})] for the Co(II) (**3**) complex is −0.00[0.69, −532, 80.5, +0.0062]; J (cm^{-1}) [TIP (cm$^3 \cdot$ mol^{-1})] for the Cu(II) (**5**) complex is −0.10 cm^{-1} [+0.0010]. A fitting for the temperature-dependent magnetic moments for $\text{Na}[\text{Cr}_2(\text{L-tart}_2)\text{H(phen)}_2] \cdot 6.5\text{H}_2\text{O}$ showed $J = 0.08\,\text{cm}^{-1}$ with $g = 2.05$, $D = 0.112$ cm^{-1}, and TIP = −0.0033 cm^{-1} (figure S4-6). This J value is more reliably determined than the previously reported one for the corresponding bpy L-tart and meso-tart Cr(III) complexes [4] because of the magnetic susceptibility measurements only above 77 K. Although the fitting procedures were carried out excluding Zeeman splitting, the D values for **1**, **2**, and **4** are within an order of magnitude for the reported ones, a few wave number for Mn(III) [23], Fe(III) [24], and Ni(II) [25]. The estimated values for k, Δ, and λ for **3** also range within commonly expected values [26].

For the present complexes, therefore, the magnetic interactions in the dinuclear units are too small to support the dinuclear structures assumed for the polymeric $[\text{M}_2(\text{L-tartH}_2)_2]$ with no capping ligands [10]. This contrasts to the large magnetic interaction ($2J = -12$ to $-18\,\text{cm}^{-1}$) for SP-4 $\text{Na}_4[\text{Cu}_2(\text{L-tart})(\text{D-tart})] \cdot 10\text{H}_2\text{O}$ with all deprotonated hydroxyl groups and the short Cu ··· Cu distance (2.98 Å) [11, 12]. It is likely that the weak magnetic interaction for the L-tart M$^{\text{II}}$ complexes with the fully protonated hydroxyl groups results from the long M ··· M distances (5.2–5.5 Å) as found for the X-ray analysis of the aqua L-tart complexes [6–10]. On the other hand, the V(IV)O complex $\text{M}_2[(\text{VO})_2(\text{L-tart})(\text{D-tart})] \cdot 4\text{H}_2\text{O}$ (M = 2Na, Ca, Ba) [13, 18] with all deprotonated hydroxyl groups and a little shorter V ··· V distance (4.08–4.35 Å), as well as the L-tart Cr(III) complex with one proton of the hydroxyl groups [17], gives weak magnetic interaction. Therefore, the magnetic interactions in the tartrate-bridged dinuclear complexes depend on the M ··· M distance and coordination polyhedron (SP-4 *vs.* OC-6 or SPY-5), but not necessarily on the protonation of the hydroxyl groups.

Weak magnetic interaction for the L-tart Cr(III) complex may be elucidated as follows. The one proton of the hydroxyl groups is hydrogen bonded between the two oxygens of the hydroxyl groups, each coordinated with different Cr(III) ions as found for X-ray analysis of bpy and phen L-tart complexes [17] and the meso-tart complex $\text{Na}[\text{Cr}_2(\text{meso-tart}_2\text{H})(\text{bpy})_2] \cdot 7\text{H}_2\text{O}$ [27]. The O ··· O distance (2.6 Å) and the Cr–O ··· O–Cr torsion angle (~50°) in the hydrogen bonding moiety (CO ··· HOC) and the Cr ··· Cr distance for the L-tart complexes are similar to those (O ··· O = *ca* 2.5 Å; Cr–O ··· O–Cr = 60°; Cr ··· Cr = 5 Å) for the hydroxoaqua (HO ··· HOH)-bridged dinuclear Cr(III) complexes [27, 28]. The latter hydroxoaqua complexes exhibit unexpectedly large antiferromagnetic interactions in view of the long Cr ··· Cr distance, where hydrogen bonds act as an antiferromagnetic exchange path [28]. For the L-tart Cr(III) complex, the almost perpendicular arrangement of the two coordination planes (O–Cr–O for the hydroxyl groups) in the bridging moiety leads to the tetrahedral disposition of the four oxygens of the hydroxyl groups, in contrast to the almost coplanar one for the bis(hydroxoaqua)-bridged complexes. Such a disposition results in the through-space orthogonal magnetic d_π orbital overlap, which brings about ferromagnetic interaction. Both the hydrogen bond path and the orthogonal overlap of the magnetic d_π orbitals may be responsible for weak magnetic coupling for the L-tart complex. However, the magnetic interactions of **1–5** are much different from the L-tart Cr(III) complex because these complexes have no hydrogen bonding proton in the bridging moiety, and also both magnetic d_σ and d_π orbitals.

4. Conclusion

In conclusion, a series of octahedral metal complexes are characterized as L-tartrate-bridged dinuclear complexes with capping bpy or phen. An ionic radii criterion is found such that the protonation of the hydroxyl groups for the L-tartrate increases with the increasing ionic radii of the metal ions or weakening M–O bond interaction by comparing tartrate-bridged dinuclear complexes. This criterion is a useful guide for the synthesis, characterization, and design of tartrate complexes with chiral supramolecular architectures. The very weak magnetic interactions of the present complexes arise from long $M \cdots M$ distance, but not from protonation of the hydroxyl groups as compared with the analogous Cr(III) and V(IV)O or Cu(II) complexes.

Supplementary materials

Supplementary data (figures S1–S4) associated with this article are available free of charge and can be found in the internet version.

References

[1] (a) R.E. Tapscott, R.L. Belford, I.C. Paul. *Coord. Chem. Rev.*, **4**, 323 (1969); (b) R.E. Tapscott. *Trans. Met. Chem.*, **8**, 253 (1982).

[2] (a) S. Kaizaki, J. Hidaka, Y. Shimura. *Bull. Chem. Soc. Jpn*, **42**, 988 (1969); (b) N. Koine, M. Iida, T. Sakai, N. Sakagami, S. Kaizaki. *J. Chem. Soc., Chem. Commun.*, 1714 (1992).

[3] G.L. Robbins, R.E. Tapscott. *Inorg. Chem.*, **15**, 154 (1976).

[4] M. Nakahanada, T. Fujihara, N. Koine, S. Kaizaki. *J. Chem. Soc., Dalton Trans.*, 3423 (1992).

[5] S. Kaizaki, M. Nakahanada, A. Fuyuhiro, M. Ikedo-Urade, Y. Abe. *Inorg. Chim. Acta*, **362**, 5117 (2009).

[6] C. Ruiz-Pérez, M. Hernández-Molina, C. González-Silco, T. López, C. Yanes, X. Solans. *Acta Crystallogr. C*, **C52**, 2473 (1996).

[7] Y. Gu, M. Yang. *Cryst. Res. Technol.*, **43**, 1331 (2008).

[8] (a) S. Scherb, C. Nather, W. Bensch. *Acta Crystallogr. C*, **58**, m135 (2002); (b) Q. Gao, Y.-B. Xie, D. Wang. *J. Chem. Crystallogr.*, **38**, 587 (2008).

[9] (a) C.K. Prout, J.R. Carruthers, F.J.C. Rossotti. *J. Chem. Soc. (A)*, 3336 (1971); (b) R.J. Missavage, R.L. Belford, J.C. Paul. *J. Coord. Chem.*, **2**, 145 (1972); (c) F. Han, P. Zhao, Q. Wang. *J. Coord. Chem.*, **58**, 1133 (2005).

[10] E. Coronado, J.R. Galan-Mascaros, C.J. Gomez-Garcia, A. Maurcia-Matinez. *Chem.-Eur. J.*, **12**, 3484 (2006).

[11] R.L. Belford, R.J. Missavage, I.C. Paul. *Chem. Commun.*, 508 (1971).

[12] V.H. Grawford, W. Hatfield. *J. Mol. Struct.*, **37**, 157 (1977).

[13] (a) J.G. Forrest, C.K. Prout. *J. Chem. Soc. (A)*, 1312 (1967); (b) R.E. Tapscott, R.L. Belford, I.C. Paul. *Inorg. Chem.*, **7**, 356 (1968).

[14] M.V. Hanson, C.B. Smith, G.O. Carlisle. *Inorg. Nucl. Chem. Lett.*, **11**, 865 (1975).

[15] J.A. Broomhead, F.P. Dwyer. *Aust. J. Chem.*, **14**, 250 (1961).

[16] (a) S.-M. Peng, Y. Wang, C.-K. Chen, J.-Y. Lee, D.-S. Liaw. *J. Chin. Chem. Soc.*, **33**, 23 (1986); (b) N. Okabe, Y. Muranishi, M. Odoko. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, **C60m**, m345 (2004).

[17] (a) N. Koine, N. Sakagami, S. Kaizaki. X-ray analysis for $H[Cr_2(\textsc{l}\text{-tart}_2H)(bpy)_2]\cdot 3.5H_2O$, The 61st National Meeting of the Chemical Society of Japan, Yokohama, Abstract., Num. 1P07, March (1991); (b) S. Kaizaki, Y. Kato-Igawa. Preliminary X-ray analysis for $Na[Cr_2(\textsc{l}\text{-tart}_2H)(phen)_2]\cdot 6.5H_2O$, unpublished result.

[18] (a) G.O. Carlisle, G.D. Simpson. *J. Mol. Struct.*, **5**, 219 (1975); (b) J. Garcia-Jaca, T. Rojo, J.L. Pizarro, A. Goni, M.I. Arriortua. *J. Coord. Chem.*, **30**, 327 (1993); (c) J. Garcia-Jaca, M. Insausti, R. Cortes, T. Rojo. *Polyhedron*, **13**, 357 (1994).

[19] R.D. Shannon. *Acta Crystallogr.*, **A32**, 751 (1976).

[20] C.-D. Wu, C.-Z. Lu, S.-F. Lu, H.-H. Zhuang, J.-S. Huang. *Dalton Trans.*, 3192 (2003).

[21] D. Bayot, B. Tinant, M. Devillers. *Inorg. Chem.*, **44**, 1554 (2005).

[22] (a) S. Thushari, J.A.K. Cha, H.H.-Y. Sung, S.S.-Y. Chui, A.L.-F. Leung, Y.-F. Yen, I.D. Williams. *Chem. Commun.*, 5515 (2005); (b) P. Yan, J. Xing, G. Li, W. Sun, J. Zhang, G. Hou. *J. Coord. Chem.*, **62**, 2095 (2009).

[23] (a) Q. Scheifele, C. Riplinger, F. Neese, H. Weihe, A.-L. Barra, F. Juranyi, A. Podlesnyak, P.L.W. Tregenna-Piggott. *Inorg. Chem.*, **47**, 439 (2008); (b) B.J. Kennedy, K.S. Murray. *Inorg. Chem.*, **24**, 1552 (1985).

[24] B.J. Kennedy, K.S. Murray. *Inorg. Chim. Acta*, **132**, 153 (1987).

[25] R.L. Carlin. *Magnetochemistry*, Springer-Verlag, Berlin, Heidelberg, New York, Tokyo (1986).

[26] F. Lloret, M. Julve, J. Cano, R. Ruiz-García, E. Pardo. *Inorg. Chim. Acta*, **361**, 3432 (2008).

[27] R.B. Ortega, R.E. Tapscott, C.F. Camana. *Inorg. Chem.*, **21**, 2517 (1982).

[28] (a) M. Ardon, A. Binno, K. Michelsen, E. Pedersen. *J. Am. Chem. Soc.*, **109**, 5855 (1987); (b) P.A. Goodson, J. Glerup, D.J. Hodgson, K. Michelsen, U. Rychlewska. *Inorg. Chem.*, **33**, 359 (1994); (c) M. Ardon, A. Binno, K. Michelsen, E. Pedersen, R.C. Thompson. *Inorg. Chem.*, **36**, 4147 (1997).