



Synthesis and properties of new tetrachlorocobaltate (II) and tetrachloromanganate (II) anion salts with dicationic counterions

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ABSTRACT

New tetrachlorocobaltate (II) and tetrachloromanganate (II) ionic compounds containing various counterions were synthesized and characterized. These salts are soluble in polar solvents such as methanol and water. Physical properties such as thermal stability, melting point, and magnetic susceptibility of these salts depend on the cation or anion structure. The thermal stability of the phosphonium or imidazolium based salts is higher than that of the pyridinium or triethylaminonium analogues. The melting point of these compounds is following the order of triphenylphosphonium > pyridinium > imidazolium dications, and symmetrical dicationic salts > unsymmetrical ones. The magnetic susceptibility (χ_{MT} values) of tetrachloromanganate (II) anions-based salts is higher than that of tetrachlorocobaltate (II) anions-based salts. These dicationic salts exhibit weak antiferromagnetic interactions and have higher magnetic susceptibility than that of the previously reported tetrachloromanganate (II) and tetrachlorocobaltate(II) salts with monocationic counterion.

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1. Introduction

Ionic compounds formed with organic cations often show much lower melting point than the inorganic analogous. Salts are usually defined as ionic liquids (ILs) when they are liquids at temperature lower than 100 °C. Most of the common ILs studied so far are made from the popular mono-cations, such as imidazolium or pyridinium, with inorganic anions, such as Cl^- , PF_6^- , or NTf_2^- (bis(trifluoromethanesulfonyl)amide). The physical and chemical properties of ILs can be readily manipulated by controlling the nature and functionality of the cations and anions to allow a myriad of applications [1–3], including organic synthesis [4], electrochemistry [5], electrolytes for capacitors [6], dye-sensitized solar cells (DSSC) [7], and stationary phases in gas chromatography [8], thermal stability of the ILs also become more important.

For certain applications such as gas chromatography, the thermal stability of the aforementioned ILs is often not satisfactory. To improve the thermal stability, a series of ionic salts, in which two mono-cations are linked together to form a dication that is charge balanced by two separate monoanions, has been developed and the salts are termed dicationic ILs [9–12]. By doing so the thermal stability of the resulted salts is significantly improved. Although many of the dicationic salts exhibit melting points higher

than 100 °C, they are still called “ionic liquids” for convenience [9,10] since they are liquid at the temperatures they are employed. Dicationic ILs have been classified as geminal (the two mono-cations that form the dication are the same, for example, imidazolium-R-imidazolium where R is the alkyl linker) or unsymmetrical (the mono-cations are different, for example, imidazolium-R-pyridinium). While dicationic ILs in which each dication is associated with two monoanions such as PF_6^- and/or NTf_2^- have been intensively reported, dicationic ILs in which each dication is associated with a transition metal complex dianion have not been studied.

Compounds of tetrahalometallate (II) dianion have been studied for their magnetic behavior in recent years. Preparation, crystal structure, and spectra characterization of $[\text{EMIM}]_2[\text{CoCl}_4]$ (EMIM = 1-ethyl-3-methylimidazolium), was reported in 1993 [13]. Turnbull et al. studied the crystal configuration and magnetic behavior of $\text{A}_2[\text{MX}_4]$ salts (A = N-methylmorpholinium; M = Co, Cu, Mn; X = Cl, Br) [14]. Del Sesto et al. discussed the magnetic behavior of ionic liquids containing trihexyl(tetradecyl)phosphonium $[\text{PR}_4]$, 1-decyl-3-methylimidazolium $[\text{C}_{10}\text{mim}]$, and 1-butyl-3-methylimidazolium $[\text{C}_4\text{mim}]$ cations with transition metal complex anions such as $[\text{FeCl}_4]^-$, $[\text{MnBr}_4]^{2-}$, and $[\text{MnCl}_4]^{2-}$ [15]. Hanusa et al. reported the composition, viscosity, and thermal behavior of ILs incorporating tetrachloronickelate $[\text{NiCl}_4]^{2-}$ anions [16]. In the compounds reported in the early literatures, each tetrahalometallate (II) dianion is almost unexceptionally combined with two separate mono-cations as counterions. In view of the fact

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that no tetrahalometallate (II) salts in which each tetrahalometallate (II) dianion is combined with a counterdication rather than two countermonocations, this paper for the first time presents a new series tetrachlorocobaltate (II) or tetrachloromanganate (II) salts in which each tetrahalometallate (II) dianion is associated with a dication formed from 1-methylimidazolium, pyridinium, triethylammonium, and triphenylphosphonium. Due to the structure difference between the mono-cations and dications, the dicationic ILs are expected to exhibit different physical properties from their corresponding monocationic ILs. The thermal properties, solubility in organic solvents, and magnetic susceptibility of these dicationic ILs are discussed.

2. Experimental

2.1. General

1,3-Dibromopropane (Alfa Aesar, purity: 99.9%), 1,4-dibromobutane (Alfa Aesar, purity: 99.9%), pyridine (Fluka, purity: 98%), 1-methylimidazole (Fluka, purity: 99.9%), triphenylphosphine (Fluka, purity: 99.9%), triethylamine (Fluka, purity: 99.9%), cobalt dichloride hexahydrate (Showa, purity: 99.9%), manganese dichloride tetrahydrate (Showa, purity: 99.9%), methanol (J.T. Baker, ACS grade, $\leq 0.01\%$ H₂O), and ethanol (J.T. Baker, ACS grade, $\leq 0.01\%$ H₂O) were purchased from a commercial supplier and used without any pre-treatment.

The ¹H spectra of the purified products (for **1**, **2a–2f**) were recorded in D₂O (Cambridge Isotope Laboratories Inc., 99.9% D) on a Bruker Avance 200 spectrometer at 200 MHz at a temperature of 25 °C. The crystal structures, which were dissolved in methanol and crystallized by ethyl ether, were characterized with an X-ray single-crystal diffractometer (model: Siemens Smart CCD, Germany). Elemental analyses were conducted using an Elementar analyzer (model: Vario EL III), thermal decomposition temperatures were measured using a thermogravimetric analyzer (TGA, model: TGA-50, Shimadzu) with a heating rate of 10 °C/min (the T_d was selected at a temperature corresponding to 10% weight loss), melting points were measured using a capillary melting point apparatus (model: Buchi B-540) with a heating rate of 10 °C/min, and direct current magnetic susceptibility (called χ_{MT} value) was measured using a superconducting quantum interference device (SQUID, model: MPMS7, Quantum Design).

2.2. General procedure for the synthesis of **1**

Pyridine (5.0 g, 63.2 mmol) was mixed with 1,3-dibromopropane (19.1 g, 94.8 mmol) and stirred under neat condition at room temperature for 4 days, and then washed using ethyl acetate to obtain the required products (white solids for **1**, 17.6 g).

2.2.1. [1-(3-Bromopropyl)pyridinium] bromide (**1**)

Yield 99%. ¹H NMR (200 MHz, D₂O): δ 2.58 (quin, $J = 6.6$ Hz, 2H), 3.48 (t, $J = 6.6$ Hz, 2H), 4.85 (t, $J = 6.6$ Hz, 2H), 8.08 (t, $J = 6.8$ Hz, 2H), 8.54 (t, $J = 7.2$ Hz, 1H), 8.89 (d, $J = 6.3$ Hz, 2H).

2.3. General procedure for the synthesis of bromide anion salts containing unsymmetrical dications (**2a**)

Compound **1** (5.0 g, 17.8 mmol) was reacted with 1-methylimidazole (2.9 g, 35.6 mmol), and stirred in methanol under reflux for 24 h, and then precipitated from ethyl acetate to obtain the required products (white solids for **2a**, 5.7 g).

2.3.1. [1-(1-Pyridinium-yl-propyl)-3-methylimidazolium] dibromide (**2a**)

Yield 88%. ¹H NMR (200 MHz, D₂O): δ 2.70 (quin, $J = 7.5$ Hz, 2H), 3.92 (s, 3H), 4.43 (t, $J = 7.5$ Hz, 2H), 4.77 (t, $J = 7.5$ Hz, 2H), 7.49 (s, 1H), 7.56 (s, 1H), 8.12 (t, $J = 7.1$ Hz, 2H), 8.61 (t, $J = 7.3$ Hz, 1H), 8.84 (s, 1H), 8.92 (d, $J = 6.5$ Hz, 2H).

2.4. General procedure for the synthesis of bromide anions salt containing geminal dications and propyl linkage chains (**2b**)

1,3-Dibromopropane (5.0 g, 24.8 mmol) was reacted with pyridine (3.9 g, 49.5 mmol), stirred in methanol and refluxed for 24 h, and then precipitated from ethyl acetate to obtain the required products (all white solids for **2b**, 8.5 g).

2.4.1. [1,1'-(Propane-1,3-diyl)-bis(pyridinium)] dibromide (**2b**)

Yield 95%. ¹H NMR (200 MHz, D₂O): δ 2.86 (quin, $J = 7.8$ Hz, 2H), 4.86 (t, $J = 7.8$ Hz, 4H), 8.14 (t, $J = 7.3$ Hz, 4H), 8.62 (t, $J = 7.3$ Hz, 2H), 8.96 (t, $J = 6.5$ Hz, 4H).

2.5. General procedure for the synthesis of bromide anions salt containing geminal dications and butyl linkage chains (**2c**, **2d**, **2e**, and **2f**)

1,4-Dibromopropane (5.0 g, 23.2 mmol) was reacted with 1-methylimidazole (3.8 g), pyridine (3.7 g), triethylamine (4.7 g), and triphenylphosphine (12.1 g), respectively (all using 46.3 mmol), stirred in methanol under reflux for 24 h, and then precipitated from ethyl acetate to obtain the required products (all white solids for **2c** (8.1 g), **2d** (8.3 g), **2e** (9.0 g), and **2f** (15.9 g)).

2.5.1. [1,1'-(Butane-1,4-diyl)-bis(di-pyridinium)] dibromide (**2c**)

Yield 94%. ¹H NMR (200 MHz, D₂O): δ 2.14 (quin, $J = 7.3$ Hz, 4H), 4.70 (t, $J = 7.3$ Hz, 4H), 8.09 (t, $J = 7.1$ Hz, 4H), 8.57 (t, $J = 7.1$ Hz, 2H), 8.87 (t, $J = 7.1$ Hz, 4H).

2.5.2. [1,1'-(Butane-1,4-diyl)-bis(3-methylimidazolium)] dibromide (**2d**)

Yield 94%. ¹H NMR (200 MHz, D₂O): δ 1.94 (quin, $J = 7.3$ Hz, 4H), 3.91 (s, 6H), 4.28 (t, $J = 7.3$ Hz, 4H), 7.47 (s, 2H), 7.50 (s, 2H), 8.58 (s, 2H).

2.5.3. [1,1'-(Butane-1,4-diyl)-bis(triethylaminonium)] dibromide (**2e**)

Yield 93%. ¹H NMR (200 MHz, D₂O): δ 1.27–1.39 (m, 18H), 1.79–1.90 (m, 4H), 3.29–3.43 (m, 16H).

2.5.4. [1,1'-(Butane-1,4-diyl)-bis(triphenylphosphonium)] dibromide (**2f**)

Yield 93%. ¹H NMR (200 MHz, D₂O): δ 1.74–1.78 (m, 4H), 3.24–3.30 (m, 4H), 7.64–7.86 (m, 30H).

2.6. General procedure for the synthesis of [CoCl₄]²⁻ anion salts (**3a1**, **3b1**, **3c1**, **3d1**, **3e1**, and **3f1**)

Compounds **2a** (3.0 g, 8.3 mmol), **2b** (3.0 g, 8.3 mmol), **2c** (3.0 g, 8.0 mmol), **2d** (3.0 g, 7.9 mmol), **2e** (3.0 g, 7.2 mmol), and **2f** (3.0 g, 4.1 mmol), respectively, were reacted with cobalt dichloride hexahydrate (4.9 g, 20.7 mmol reacted with **2a**; 5.0 g, 20.8 mmol with **2b**; 4.8 g, 20.0 mmol with **2c**; 4.7 g, 19.7 mmol with **2d**; 4.3 g, 17.9 mmol with **2e**; 2.4 g, 10.1 mmol with **2f**), and stirred in ethanol at room temperature for 4 days. The required products were then precipitated from ethanol (all blue solids for **3a1** (2.7 g), **3b1** (2.8 g), **3c1** (2.8 g), **3d1** (2.9 g), **3e1** (2.7 g), and **3f1** (2.5 g)). The detailed crystal structure refinements are summarized in supporting information. The element analysis data are described below.

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