Synthesis and magnetic properties of trinuclear chromium(III)–palladium(II)–chromium(III) complexes bridged by extended dioximato groups

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Summary
Heterotrinuclear CrIII–PdII–CrIII complexes of formulae [Cr(salen)–Pd(dmg)2–Cr(salen)]·H2O (1), [Cr(salen)–Pd(–BD)2–Cr(salen)]·H2O (2) and [Cr(salen)–Pd(–FD)2–Cr(salen)]·2H2O (3) have been prepared and characterized by elemental analysis, i.r. and electronic spectroscopies, and molar conductances. These complexes are thought to contain extended dioximate bridges. The magnetic properties of complexes (1) have been investigated over the 80–300 K range and corresponds to what is expected for an antiferromagnetic CrIII–CrIII pair with $S_{Cr} = 3/2$ and $S_{Pd} = 0$ (PdII is a diamagnetic in a square-planar environment) local spins. The exchange integral ($J$) was evaluated as $-3.38 \text{ cm}^{-1}$ using the spin Hamiltonians $\hat{H} = -2J\hat{S}_A \cdot \hat{S}_B (S_A = S_B = 3/2)$.

Introduction
During the last decade, polynuclear complexes containing multi-atom bridges have received much attention\(^1,2\), mainly because of the need to gain insight into the electron transfer pathway in biological systems and to obtain useful information concerning the design of molecule-based magnets\(^3\). Recently, many groups\(^3,15\) have studied the oximato or dioximato multi-atom bridge system and have shown, by temperature dependent magnetic susceptibility measurements, that long-range magnetic coupling occurs between the two paramagnetic centres. However, to the best of our knowledge, so far no chromium(III)–palladium(II)–chromium(III) complexes with extended dioximato bridges have been reported. In this paper, we describe the synthesis and magnetic characterization of three chromium(III)–palladium(II)–chromium(III) heterotrinuclear complexes: [Cr(salen)–Pd(dmg)2–Cr(salen)]·H2O (1), [Cr(salen)–Pd(–BD)2–Cr(salen)]·H2O (2) and [Cr(salen)–Pd(–FD)2–Cr(salen)]·2H2O (3) (see Figure 1). The temperature-dependent magnetic susceptibility for (1) has been measured in the 80–300 K range.

Experimental

Materials

Starting materials (reagent grade) were purchased from the Peking Chemical Co. The [Cr(salen)(H2O)2]NO3, H2[Pd(dmg)2], H2[Pd(–BD)2] and H2[Pd(–FD)2] complexes were prepared according to literature methods\(^9,16\).

[Cr(salen)–Pd(–BD)2–Cr(salen)]·H2O (1)
To a hot absolute EtOH solution (20 cm3) of H2[Pd(dmg)2] (67.4 mg, 0.2 mmol) and Et3N (2 cm3) was added a hot absolute EtOH solution (20 cm3) containing [Cr(salen)(H2O)2]NO3 (166.1 mg, 0.4 mmol) and HC(O)Et$_3$ (3 cm3). The mixture was boiled under reflux with stirring. After a few minutes pale yellow 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 absolute EtOH and Et2O and dried in vacuo. Yield 74%.[Cr(salen)–Pd(–FD)2–Cr(salen)]·2H2O (3)
This complex was obtained as red–brown microcrystals by the same procedure as above, using H2[Pd(–BD)2] (96.2 mg, 0.2 mmol) instead of H2[Pd(dmg)2]. Yield 62%.[Cr(salen)–Pd(–FD)2–Cr(salen)] (117.0 mg, 0.2 mmol) instead of H2[Pd(dmg)2]. Yield 62%.

Table 1. Relevant physical data are listed in Table 2.

Analysitical data for the complexes are collected in Table 1. Relevant physical data are listed in Table 2.

Measurements

C, H and N elemental analyses were made with a Perkin-Elmer Model 240 elemental analyser. Metal contents were determined by EDTA titration. I.r. spectra were recorded on a Shimadzu Model 480 i.r. spectrophotometer, using KBr pellets. Electronic spectra (DMF) were measured on a Hitachi-240 spectrophotometer. The molar conductance was measured with a DDS-11A conductometer. Variable temperature (80–300 K) magnetic susceptibilities were measured on a Cahn-2000 magnetometer. Diamagnetic corrections were made with Pascal’s constants for all the constituent atoms and the magnetic moment was calculated using the equation $\mu = 2.828(\chi_M T)^{1/2}$.

Results and discussion

General characterization
Elemental analyses indicate that the complexes H2[Pd(dmg)2], H2[Pd(–BD)2] and H2[Pd(–FD)2] react with [Cr(salen)(H2O)2]NO3 to yield trinuclear complexes which are presumed to have the coordination...
Table 1. Elemental analyses and relevant physical data for complexes

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Yield (%)</th>
<th>Found (Calcd.) (%)</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>Cr</th>
<th>Pd</th>
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</thead>
<tbody>
<tr>
<td>(1) C₄₀H₄₂N₂O₉Cr₂Pd</td>
<td>74</td>
<td>48.2(48.6)</td>
<td>4.0(4.3)</td>
<td>11.2(11.3)</td>
<td>10.6(10.3)</td>
<td>11.0(10.8)</td>
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</tr>
<tr>
<td>(2) C₆₀H₅₀N₂O₉Cr₂Pd</td>
<td>62</td>
<td>57.8(58.2)</td>
<td>3.8(4.1)</td>
<td>9.0(9.1)</td>
<td>8.5(8.2)</td>
<td>9.0(8.6)</td>
<td></td>
</tr>
<tr>
<td>(3) C₆₂H₄₄N₂O₄Cr₂Pd</td>
<td>56</td>
<td>51.3(51.4)</td>
<td>3.6(3.6)</td>
<td>9.2(9.1)</td>
<td>8.7(8.4)</td>
<td>9.0(8.6)</td>
<td></td>
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</table>

\(a\) (1), \([\text{Cr(salen)-Pd(dmg)}₂-\text{Cr(salen)}\]H₂O; (2), \([\text{Cr(salen)-Pd(α-BD)}₂-\text{Cr(salen)}\]H₂O; (3), \([\text{Cr(salen)-Pd(α-FD)}₂-\text{Cr(salen)}\]₂H₂O.

Table 2. Physical data for the trinuclear complexes

| Compound | Colour | \(\Lambda_{\text{abs}}\) (DMF) \((\Omega \cdot \text{cm}² \cdot \text{mol}⁻¹)\) | \(\text{I.r.}\) \((\text{cm}⁻¹)\) \((\text{C}≡\text{N})\) \((\text{N}–\text{O})\) | \(\text{U.v.-vis.}\) \((\text{cm}⁻¹)\) \((\text{d-d})\) \((\text{CT})\) |
|----------|--------|-----------------|-----------------|-----------------|-----------------|
| (1) | pale yellow | 0.80 | 1535 | 1235 | 20920, 25641, 31250 | 37174 |
| (2) | red-brown | 0.70 | 1525 | 1290 | 20000, 25641, 31446 | 37453 |
| (3) | brown | 0.65 | 1532 | 1295 | 19417, 26178 | 37174 |

\(a\) (1), \([\text{Cr(salen)-Pd(dmg)}₂-\text{Cr(salen)}\]H₂O; (2), \([\text{Cr(salen)-Pd(α-BD)}₂-\text{Cr(salen)}\]H₂O; (3), \([\text{Cr(salen)-Pd(α-FD)}₂-\text{Cr(salen)}\]₂H₂O.

Magnetic properties

The magnetic moment observed for trinuclear complex (1) at room temperature is 5.12 \(\mu_B\), i.e. slightly lower than the spin-only value (5.47 \(\mu_B\)) implying an operation of an antiferromagnetic spin-exchange interaction. The temperature dependence (80–300 K) of the susceptibility and magnetic moment for complex (1) is shown in Figure 2. Considering that a palladium(II) ion with a square-planar environment is diamagnetic, this trinuclear complex can be considered as a homodinuclear chromium(III)-chromium(III) system. The magnetic analysis was carried out using the susceptibility equation based on the Heisenberg environment shown in Figure 1a–c, respectively. For all complexes, the molar conductances (Table 2) fall in the expected range for non-electrolytes and are in accord with the presumed structures. The significant i.r. spectral bands of the complexes are listed in Table 2. The starting complexes \(\text{H}_₂\{\text{Pd(dmg)}₂\}, \text{H}_₂\{\text{Pd(α-BD)}₂\}\) and \(\text{H}_₂\{\text{Pd(α-FD)}₂\}\) exhibit a broad i.r. band at 2300–2700 cm⁻¹, which may be assigned to the \(v(\text{OH})\) vibration of the hydrogen bonded \(\text{N}–\text{OH}...\text{O}–\text{N}\) group; this band is absent from the spectra of complexes (1)–(3), indicating that the dioxime protons have been completely removed. It is noteworthy that the \(\text{NO}_3\) stretching band at 1380 cm⁻¹ in \([\text{Cr(salen)}\{\text{H}_₂\text{O}\}₂\text{NO}_3]\) is missing in the spectra of trinuclear complexes, which is commensurate with their non-electrolytic nature. In addition, two medium intensity bands at 1230–1260 and 1080–1102 cm⁻¹ are assigned to \(\text{N}–\text{O}\) stretches. All complexes are stable in the solid state. The electronic absorption spectral data (DMF solutions) are given in Table 2. A strong absorption in the u.v. range and a weak absorption in the vis. range are observed. The former may be attributed to the charge-transfer transition and is thought to be \(\text{d}–\text{π}^*\) in character. The latter may be attributed to the \(\text{d–d}\) transition of six-coordinate chromium(III).

Figure 1. Proposed chemical structures of: (a) (1); (b) (2); (c) (3).