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Structure, photochemistry and magnetic properties of tetrahydrogenated Schiff base chromium(III) complexes

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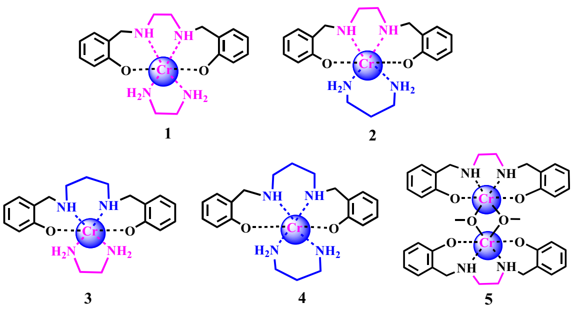
HIGHLIGHTS

- Five tetrahydrogenated Schiff base Cr(III) complexes were composed.
- The stability relates to the chelate effect of rings.
- The photochemistry reaction was studied.
- Complex **5** exhibits a strong antiferromagnetic coupling.

GRAPHICAL ABSTRACT



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ABSTRACT

Four mononuclear chromium(III) complexes $[Cr(L^{(1)})(en)]Br_{0.3}Cl_{0.7}$ (**1**), $[Cr(L^{(1)})(pr)]Cl$ (**2**), $[Cr(L^{(2)})(en)]ClO_4$ (**3**), $[Cr(L^{(2)})(pr)]Cl$ (**4**) along with one dinuclear μ-methoxo $[Cr(\mu\text{-}OMe)(L_1)]_2$ (**5**) were synthesized (en = 1,2-ethanediamine, pr = 1,3-diaminopropane $H_2L^{(1)}$ = Tetrahydrosalen = $H_2[H_4]$salen = N,N′-bis (2-hydroxybenzyl)-1,2-ethanediamine, $H_2L^{(2)}$ = Tetrahydrosalpr = $H_2[H_4]$salpr = N,N′-bis(2-hydroxybenzyl)-1,3-diaminopropane). The competitive reactions in the presence of EDTA were carried out and the first-order rate constants $k(\mathbf{1}) = (5.2 \pm 0.2) \times 10^{-3}\ h^{-1} < k(\mathbf{2}) = (6.7 \pm 0.3) \times 10^{-3}\ h^{-1} < k(\mathbf{3}) = (8.0 \pm 0.1) \times 10^{-3} h^{-1} < k(\mathbf{4}) = (9.5 \pm 0.2) \times 10^{-3}\ h^{-1}$ were obtained by spectroscopic measurements. In addition, photo-induced decomposition was monitored under irradiation of xenon lamp. The sequence of first-order rate constants is $k'(\mathbf{1}) = (4 \pm 0.1) \times 10^{-4}\ s^{-1} < k'(\mathbf{2}) = (6 \pm 0.3) \times 10^{-4}\ s^{-1} < k'(\mathbf{3}) = (1.1 \pm 0.2) \times 10^{-3}\ s^{-1} < k'(\mathbf{4}) = (1.4 \pm 0.2) \times 10^{-3}\ s^{-1}$, which is in accordance with that of kinetics studies with EDTA. Dinuclear complex **5** exhibits a strong antiferromagnetic coupling with the $J = -10.8\ cm^{-1}$.

Introduction

Transition metal complexes with oxygen and nitrogen donor Schiff bases are of particular interest because of their unusual con-figurations, structural lability and sensitivity to molecular environments as functional materials [1]. Although the tetradentate Schiff-base ligands containing N_2O_2 donors are easy to coordinate to transition- and non-transition-metal ions, the coordination geometries afforded to metal centers by these multidentate species has sustained their widespread interest over the past 150 years. It should be noted that hydrogenation of tetradentate Schiff bases will not only increase the donor strength of the internal nitrogen donors, but also increase the ligand flexibility [2]. Taylor and Reglinski have studied the effect of donor groups and geometry on the redox potential of tetrahydrogenated Schiff base complexes by systematically increasing the size of the polymethylene chain between the internal nitrogen donors [1,3]. Although the transition metal complexes of tetrahydrogenated ligand $H_2[H_4]$salen [4] and $H_2[H_4]$Salpr [3] ($H_2[H_4]$salen = N,N′-bis(2-hydroxybenzyl)-1,2-eth-

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anediamine, $H_2[H_4]$salpr = N,N′-bis(2-hydroxybenzyl)-1,3-diaminopropane) have been fully studied, few Cr(III) complexes with salen^{2-}, $[H_4]$salen^{2-}, salpr^{2-} or $[H_4]$Salpr^{2-} have been reported [5–7]. It is well known that Cr(III) complexes with Schiff bases and theirs derivatives play an important role in catalytic reactions, photochemistry, artificial nucleases, carbohydrate metabolism.

Interested by the thermodynamic, kinetic, and electronic properties of Cr(III) complexes with salicylate and en ligands [8], we initiated an investigation of oligomeric Cr(III) compounds containing the tetrahydrogenated ligand $[H_4]$salen^{2-} or $[H_4]$Salpr^{2-} and ethanediamine (en) or 1,3-diaminopropane (pr). The use of Zn as a reducing agent can turn the inert Cr(III) to reactive Cr(II). The combination of these polydentate ligands can lead to the formation of stable chelates. In this paper five tetrahydrogenated Schiff base Cr(III) complexes were synthesized for the first time. The possible steric effects including the number of chelate rings and the size of chelate ring upon the kinetics stability and photochemistry reaction were investigated by spectroscopic measurements. The magnetic properties of a dinuclear Cr(III) complex were also explored.

Experimental

General procedure

Unless otherwise stated all chemicals were commercially obtained and used without further purification. All manipulations were performed under aerobic conditions. The ligands $H_2L^{(1)}$ and $H_2L^{(2)}$ ($H_2L^{(1)}$ = Tetrahydrosalen, $H_2L^{(2)}$ = Tetrahydrosalpr) were obtained from methods given in the literature (see the ESI) [1c]. All other chemicals were of analytical grade.

^{1}*H NMR* spectra were recorded on Bruker-300 MHz spectrometers, the chemical shifts (δ) were reported as ppm in DMSO. ESI-MS spectra were recorded on an Agilent 6520 Accurate-Mass Q-TOF LC/MS mass spectrometer. UV–visible (UV–Vis) spectra were measured with a Varian 50 BIO spectrophotometer. Elemental analyses were measured on a Vario EL III analyzer. IR spectra were recorded with a Bruker TENSOR 21 FT-IR spectrophotometer.

Synthesis

*$[Cr(L^{(1)})(en)]Br_{0.3}Cl_{0.7}\cdot CH_3OH$ (**1**), $[Cr(L^{(1)})(\mu\text{-}OMe)]_2\cdot 2CH_3OH$ (**5**)*

Complexes **1** and **5** were formed from the same batch. $H_2L^{(1)}$ (136 mg, 0.5 mmol), $CrCl_3\cdot 6H_2O$ (133 mg, 0.5 mmol) and granular (Mesh size 20) zinc (0.10 g, 1.5 mmol) were put in flask, and methanol (20 mL) was added. After an hour's refluxing, ethanediamine (en, 1 mL, 15.0 mmol) was added to the solution; the solution was kept stirring and refluxing for 0.5 h, purple precipitate was obtained. Filtered through the funnel, purple minicrystal and aubergine filtrate were obtained. The purple minicrystal was redissolved by addition of ethanol: H_2O = 1:1, then KBr was added to the solution. The solution was filtered through the funnel, plenty of block purple crystals (complex **1**) were obtained in the filtrate after a few days (yield > 70%). The aubergine filtrate was placed over night, and another aubergine crystal **5** was obtained (yield < 10%). Interestingly, the yield of complex **1** or **5** was affected by the amount of added en solution: the more en was added, the more **1** was produced. Anal. Cacld. for $C_{19}H_{30}Br_{0.3}Cl_{0.7}CrN_4O_3$ (**1**): C, 49.50; H, 6.56; N, 12.15. Find: C, 49.38; H, 6.49; N, 12.19. Anal. Cacld. for $C_{36}H_{52}Cr_2N_4O_9$ (**5**): C, 54.81, H, 6.64, N, 7.10. Find: C, 54.63, H, 6.42, N, 7.22. IR: **1**: 3400, 3113, 1595, 1480, 1275, 1053, 762, 628 cm^{-1}; **5**: 3176, 2925, 1595, 1478, 1290, 1064, 758 cm^{-1}.

*$[Cr(L^{(1)})(pr)]Cl$ (**2**)*

$H_2L^{(1)}$ (136 mg, 0.5 mmol), $CrCl_3\cdot 6H_2O$ (133 mg, 0.5 mmol) and granular (Mesh size 20) zinc (0.10 g, 1.5 mmol) were put in flask, and methanol (20 mL) was added. After an hour's refluxing, 1,3-diaminopropane (pr, 2 mL, 24.0 mmol) was added to the solution, the solution was kept stirring and refluxing for 0.5 h, purple precipitate was obtained. Filtered through the funnel, purple minicrystal (complex **2**) was obtained. Anal. Cacld. for $C_{20}H_{32}ClCrN_4O_3$: C, 51.78; H, 6.95; N, 12.08. Find: C, 51.74; H, 6.99; N, 12.11. ESI-MS spectra: m/z = 396.16 (Fig. S4), $[M]^+$; $[M]^+$ calculated: 396.16. IR: 3271, 3113, 2930, 1595, 1480, 1276, 1080, 760 cm^{-1}.

*$[Cr(L^{(2)})(en)]ClO_4$ (**3**)*

$H_2L^{(2)}$ (143 mg, 0.5 mmol), $CrCl_3\cdot 6H_2O$ (133 mg, 0.5 mmol) and granular (Mesh size 20) zinc (0.10 g, 1.5 mmol) were refluxing in methanol (20 mL) for an hour, then en (1 mL, 15.0 mmol) was added to the solution, the solution was kept stirring and refluxing for 0.5 h, purple precipitate was obtained. The solution was filtered through the funnel; purple minicrystal and aubergine filtrate were obtained. Sodium perchlorate (0.12 g, 1.0 mmol, note: perchlorate salts are explosive) was added to the aubergine filtrate carefully in room temperature, purple crystal were obtained (complex **3**) over night. Anal. Cacld. for $C_{19}H_{28}ClCrN_4O_2$: C, 52.96; H, 6.32; N, 13.00. Find: C, 52.98; H, 6.218; N, 13.03. IR: 3303, 3244, 1595, 1479, 1286, 1107, 766 cm^{-1}.

*$[Cr(L^{(2)})(pr)]Cl\cdot CH_3OH$ (**4**)*

$H_2L^{(2)}$ (143 mg, 0.5 mmol), $CrCl_3\cdot 6H_2O$ (133 mg, 0.5 mmol) and granular (Mesh size 20) zinc (0.10 g, 1.5 mmol) were refluxing in methanol (20 mL) for an hour, then pr (2 mL, 24 mmol) was added to the solution, keep refluxing for 0.5 h and purple precipitate was obtained. The result solution was filtered and the aubergine filtrate was placed, purple crystal (complex **4**) was obtained over night. Anal. Cacld. for $C_{21}H_{34}ClCrN_4O_3$: C, 52.77; H, 7.17; N, 11.72. Find: C, 52.79; H, 7.14; N, 11.69. IR: 3107, 2934, 1596, 1482, 1278 cm^{-1}.

X-ray structure determination

For each sample, a single crystal with suitable dimensions for X-ray diffraction analyses was mounted on a glass rod, the crystal data were collected with a Siemens (Bruker) SMART CCD diffractometer using monochromated Mo-Ka radiation (0.71073 Å) at 293 K. In all cases intensity data were measured by thin-slice ω- or ω- and φ-scans. The method used to solve the structure was direct method and the structure was further expanded using Fourier difference techniques with the SHELXTL-97 program package [9]. Absorption corrections were carried out using the SADABS program supplied by Bruker [10]. The anisotropic refinement was applied for all non-hydrogen atoms while hydrogen atoms in all samples were included in idealized positions and their U_{iso} values were set to ride on the U_{eq} values of the parent carbon, nitrogen or oxygen atoms. Details of the crystallographic data collection, structural determination and refinement are summarized in Table 1. Selected bond lengths (Å) and angles (°) of **1**, **3**, **4**, and **5** are shown in Table 2. For crystallographic data in CIF format, see the ESI. CCDC reference numbers: 712642, 913849, 1002820, 1002821.

Photochemical stability

1×10^{-3} M complex **1**–**4** in Tris–HCl buffer (0.01 M, pH = 7.4) was exposed to light of xenon lamp (CEL-S500/350, 50 mW/cm^2, AM 1.5) in methanol, 293 K for hours. This course was monitored by UV–Vis spectra.

Magnetic measurements

Variable-temperature magnetic susceptibility on a crystalline sample was performed on a Quantum Design MPMS-XL SQUID