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# A combined computational and experimental study on the hydrogen bonding with chloride ion in a crab-claw like site of a new chromium Schiff base complex

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ABSTRACT

A combined experimental and computational study to understand the nature of the hydrogen bonding in a crab-claw site of a new synthesized chromium Schiff base complex is reported. The fully optimized equilibrium structures of the Cr(III) complex in the presence and absence of chloride ion are obtained at the B3LYP functional in conjunction with LanL2DZ basis set. The crystal structure of the chromium Schiff base complex consists of $[CrL_2]^+$ cation, in which L is a tridentate Schiff base ligand with full name of N-(2-(2-hydroxyethylamino)ethyl)5-methoxysalicylideneimine, and a chloride anion, in the asymmetric unit. The chromium(III) cation possesses a distorted octahedral geometry, coordinated with four nitrogen and two phenoxo oxygen atoms derived from two chelate Schiff base ligands. The harmonic vibrational frequencies, infrared intensities and Raman scattering activities of the complexes are also reported. The scaled computational geometry and vibrational wavenumbers are in very good agreement with the experimental values of single crystal X-ray diffraction and FT-IR, respectively. The electronic properties calculations of the complexes are also performed at the TD-B3LYP/LanL2DZ level of theory. The spectroscopic excitation parameters obtained for frontier molecular orbitals of the complexes are reported as well. These findings are in good agreement with the experimental UV–Vis diffuse-reflectance spectroscopy. Parabolic diagrams are derived for the chloride insertion and hydrogen bonding in the crab-claw site with the average optimized H···H distances of the effective hydrogen atoms in the crab-claw site as reaction coordinate.



## 1. Introduction

Hydrogen bonding plays a key role in chemical, catalytic and biochemical processes, as well as in supramolecular chemistry and crystal engineering [1,2]. In the last few decades, considerable attention has been drawn to Schiff bases and their complexes in the fields of coordination and biological chemistry [3,4]. Aromatic Schiff bases and the corresponding metal complexes have recently attracted researchers' attention due to some interesting properties such as catalyzing reactions on oxygenation [5], hydrolysis [6], electro-reduction [7], and decomposition [8], biological activities like antimicrobial [9], antifungal [10], antiviral [11], synergistic action on insecticides [12], plant growth regulator [13], anti-tumor and cytotoxic activities [14].

Chromium is an earth-abundant metal, and surrounding Cr(III) ions with appropriate ligands can produce powerful photooxidants [15]. The excited state properties of Cr(III) tris-diimine (e.g., bpy, phen) complexes are well-known, and the observed long lifetimes (μs) make these compounds potentially useful for dye-sensitized hole-injection photovoltaic devices and/or photooxidative catalytic schemes [15–17].

Enhanced solution stability may be addressed by increasing the density of the ligand(s) chelating the chromium center [18]. Photochemical studies on a few ligated complexes by multidentate amine ligands [19,20] or tethered bipyridines [21] have uncovered long-lived $^2E$ excited states. It is worth noting that all of these

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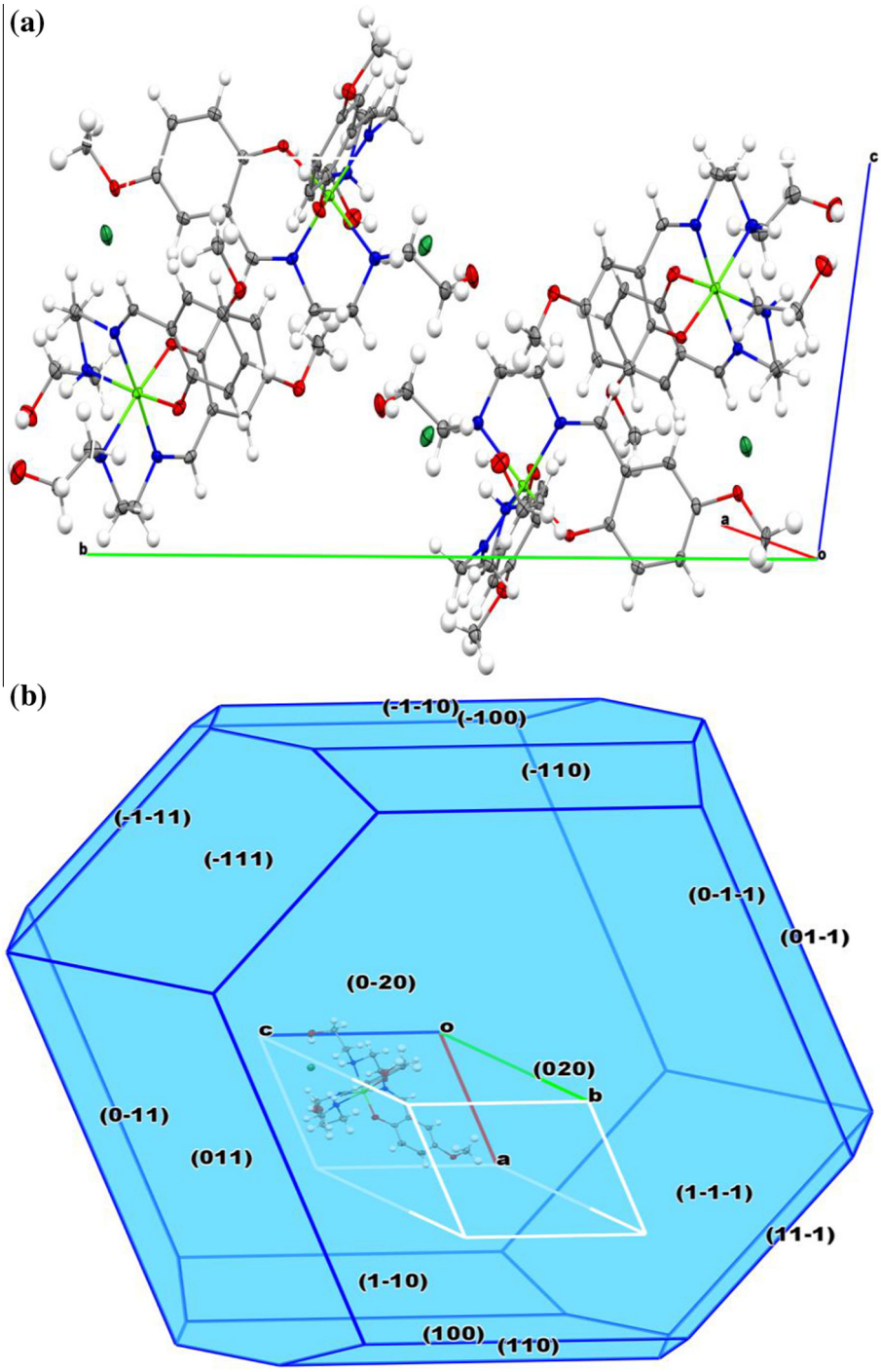


**Fig. 1.** (a) The unit cell packing of the complex. (b) Monoclinic crystal morphology of CSBC with indication of miller indexes.

species are yellow and do not absorb strongly in the visible spectrum. However, a structural study for $[Cr(tren(impy)_3)](ClO_4)_3$ elucidates a "wine-red" color for crystals from the hexadentate ligand-containing Cr(III) complex salt, which contrasts with the typical bright yellow coloration of the hetero- and homo-leptictris (bidentate) polypyridyl complexes [22]. Thus, complexes featuring tripodal ligands could enhance the absorption in visible coupled wavelengths simultaneous to the increased stability against ligand exchange in photoreduced species.

Moreover, Schiff base compounds have been regarded as excellent fluorescent materials due to their ability to achieve high thermal stability as well as high photoluminescent efficiently [23].

**Table 1**
Hydrogen-bond geometry evaluated from X-ray single crystal information file (Å, °).

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N2—H2A···Cl1 | 0.849 (18) | 2.47 (2) | 3.317 (3) | 173 (4) |
| O3—H3A···Cl1 | 0.805 (18) | 2.36 (2) | 3.157 (3) | 170 (4) |
| N4—H4A···Cl1 | 0.85 (4) | 2.36 (4) | 3.213 (3) | 177 (3) |
| O6—H6A···Cl1 | 0.74 (4) | 2.46 (4) | 3.195 (3) | 174 (5) |
| C6—H6···O1$^{i}$ | 0.95 | 2.52 | 3.367 (4) | 149 |
| C11—H11B···N3 | 0.99 | 2.61 | 3.218 (5) | 120 |
| C14—H14···O5$^{i}$ | 0.95 | 2.42 | 3.344 (5) | 164 |
| C17—H17A···Cl1$^{ii}$ | 0.98 | 2.75 | 3.642 (4) | 152 |
| C20—H20···O3$^{ii}$ | 0.95 | 2.33 | 3.272 (5) | 171 |

Symmetry codes: (i) $x, -y+1/2, z+1/2$; (ii) $-x+1, -y, -z+1$.