



Synthesis, crystal structure, DFT and spectroscopic studies of mononuclear chromium(III) complex with bidentate ligand

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ABSTRACT

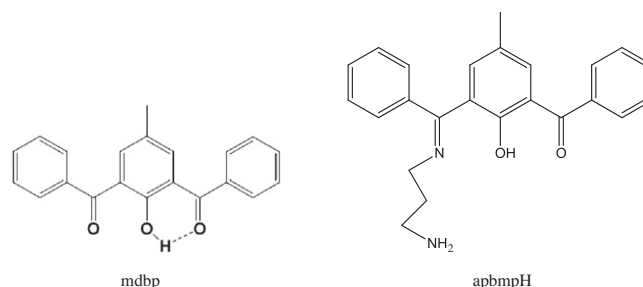
The mononuclear neutral Cr(III) complex, $[\text{Cr}(\text{L})_3]$ (**1**) (where LH = 4-methyl-2,6-dibenzoylphenol (mdbpH)) has been synthesized and characterized by elemental analysis, conductivity measurement, mass spectrometry, IR, electronic and ESR spectroscopy, cyclic voltammetry and X-ray crystallography. Crystal structure determination reveals that **1** comprises three monoanionic bidentate ligands (2,6-PhCO)₂(4-Me)C₆H₂O⁻ coordinating through phenolic O and benzoyl O atoms to give a *mer*-CrO₃O₃ octahedral configuration. The optimized geometry and the electronic transitions of the complex were calculated using methods based on the density functional theory. The ESR spectra indicate a weak tetragonal distortion. The redox behavior was studied by cyclic voltammetry and was compared with that observed for the free ligand.

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1. Introduction

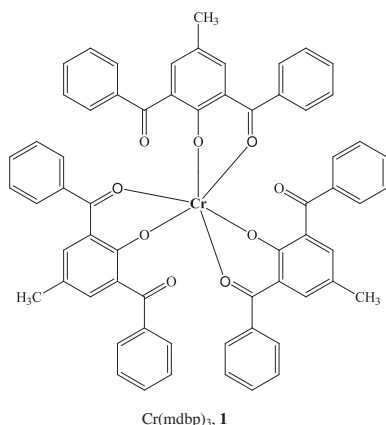
There is much current interest in the synthesis of coordination compounds from phenol-based compartmental Schiff bases [1–7] due to their potent biological applications [8,9]. These are widely used as antitumor drugs and can prove promising substitute for radiotherapy in treatment of hypoxic tumor cells [10]. Chromium with +3 oxidation state, under physiological conditions, is neither an oxidizing agent nor a reducing agent. However Cr(III) due to its d³ electronic configuration forms stable and substantially inert metal complexes. Chromium(III) is a potential therapeutic agent that is involved in the treatment of insulin insensitivity and related conditions [11,12]. Although the molecular mechanisms of chromium(III) are not fully understood [13], it is suggested that biological activities of chromium(III) are dependent upon the ligand to which chromium(III) is bound [14,15]. Previously we have reported several Co^{III} Schiff base complexes with phenol-based Schiff bases [16–18]. As Co^{III} and Cr^{III} are kinetically inert,

we attempted to prepare a similar complex from tridentate ligand, 2-{N-(3-aminopropyl)benzimidoyl}-6-benzoyl-4-methylphenol (apbmpH), but, to our surprise, obtained instead a good yield of neutral Cr^{III} complex, $[\text{Cr}(\text{mdbp})_3]$ (mdbpH = 4-methyl-2,6-dibenzoylphenol). Herein, we report the synthesis, crystal structure, spectroscopic and electrochemical properties of tris(4-methyl-2,6-dibenzoylphenolato)chromium(III). Geometry optimization and calculation of electronic transitions are also reported and compared with those of observed data. The structures of the precursors and complex are shown below.



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2. Experimental

2.1. General

All the chemicals were of reagent grade and were used as received. Solvents were purified by standard methods [19] and freshly distilled prior to use. 4-Methyl-2,6-dibenzoylphenol (mdbpH) and the tridentate ligand, 2-[N-(3-aminopropyl)benzimidoyl]-6-benzoyl-4-methylphenol (apbmpH) were synthesized following the reported methods [16,17].

2.2. Physical measurements

Elemental analyses were carried out on a CARLO ERBA modal DP 200 instrument. The molar conductance of the complex was measured using a Century CC-601 digital conductivity meter in 10^{-3} mol L⁻¹ CH₃CN solution. Melting points of compounds in capillaries are uncorrected. The electrospray ion mass spectra (ESIMS) were recorded on a MICROMASS QUATTRO II triple quadrupole mass spectrometer. Infrared spectra were recorded on a Shimadzu IR prestige-21 FT spectrophotometer with KBr pellets (4000–400 cm⁻¹). Electronic spectra in 10^{-3} mol L⁻¹ CH₃CN solution were obtained on a Perkin-Elmer Lambda 35 UV-Visible spectrophotometer. The X-band EPR spectra of chromium complex were obtained on a Varian E 112 EPR spectrometer. The spectra were recorded both for polycrystalline solid at RT and CHCl₃ solution at LNT (77 K) using tetracyanoethylene (TCNE, $g = 2.00278$) as field marker. Hyperfine splitting for ⁵³Cr nuclei ($I = 3/2$, 9.8% natural abundance) could not be detected due to the broad experimental lines.

2.3. Electrochemical measurements

Cyclic voltammetric measurements were carried out with an Advanced Electrochemical System, PARSTAT 2253 instrument equipped with a three-electrode system. The micro-cell model KO264 consisted of a platinum working electrode, Pt wire as auxiliary electrode and a non-aqueous Ag/Ag⁺ reference electrode with 0.1 M AgNO₃ in acetonitrile as filling solution. Tetrabutylammonium perchlorate (0.1 M solution in CH₃CN) was used as the supporting electrolyte. Cyclic voltammograms with scan speeds of 100–500 mV s⁻¹ were run in 10^{-3} M CH₃CN solution under a nitrogen atmosphere. Under these conditions the ferrocenium/ferrocene (fc⁺/fc) couple shows a peak separation of 84 mV.

2.4. Synthesis of tris(4-methyl-2,6-dibenzoylphenolato)chromium(III) (1)

To the stirred yellow boiling solution of tridentate ligand, 2-[N-(3-aminopropyl)benzimidoyl]-6-benzoyl-4-methylphenol (apbmpH) (0.819 g, 2.23 mmol) in the mixture of CH₃CN and EtOH, a solution

of CrCl₃(THF)₃ (0.277 g, 0.743 mmol) in CH₃CN was added drop wise under argon with constant stirring. The resulting wine-red solution was heated to reflux. The clear solution so obtained was allowed to cool and dark brown crystals suitable for X-ray diffraction were obtained in 53% yield. M.p. 250 °C.

Compound 1 was also prepared by reacting metal salt (0.187 g, 0.500 mmol) with the precursor mdbpH (0.474 g, 1.50 mmol) in 1:3 molar ratios. Yield 60%, m.p. 255 °C. *Anal. Calc.* for C₆₃H₄₅O₉: C, 75.82; H, 4.54. Found: C, 75.60; H, 4.41%. Positive ES-MS: m/z 999 (100, MH)⁺. FT IR (selected, KBr, cm⁻¹): 1667 [ν (C=O)], 1647 [ν (C=O/bonded)], 1612 [ν (C-C)/ring], 1556 [ν (C-O)]. UV-Vis (λ_{max}/nm) ($\epsilon/M^{-1} cm^{-1}$) (CH₃CN): 349 (29876), 442 (2436), 601 (100). Λ_M (10^{-3} M, CH₃CN, 298 K): 23.0 S cm² mol⁻¹.

2.5. X-ray crystallography

X-ray data for (1) was collected with an Oxford Diffraction Xcalibur Ruby Gemini CCD diffractometer using *CrysAlisPro* software [20] and graphite-monochromated Cu K α ($\lambda = 1.54178$ Å) at 123(2) K. The structure was solved by direct methods using *SHELXS97* [21] and all of the non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 using *SHELXL97* [21]. Hydrogen atoms were placed in their calculated positions and then refined using the riding model with Atom-H lengths of 0.93 Å (CH) or 0.96 Å (CH₃). Isotropic displacement parameters for these atoms were set to 1.20 (CH) or 1.50 (CH₃) times U_{eq} of the parent atom. An analytical absorption correction was applied to the collected reflections with *CrysAlisPro* [20]. Graphics were generated using *SHELXTL* [22]. Crystal data collection and refinement are summarized in Table 1.

Table 1
Crystal data and structure refinement for compound 1.

Empirical formula	C ₆₃ H ₄₅ CrO ₉
Formula weight	997.99
Temperature	123(2) K
Wavelength	1.54178 Å
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
<i>a</i> (Å)	11.2693(5)
<i>b</i> (Å)	17.5595(8)
<i>c</i> (Å)	24.7504(10)
α (°)	90
β (°)	92.898(4)
γ (°)	90
Volume (Å ³)	4891.4(4)
<i>Z</i>	4
Density (calculated) (Mg/m ³)	1.355
Absorption coefficient (mm ⁻¹)	2.431
<i>F</i> (000)	2076
Crystal size (mm ³)	0.66 × 0.16 × 0.11
Theta range for data collection (°)	3.09–75.75
Index ranges	$-6 \leq h \leq 14$, $-21 \leq k \leq 19$, $-30 \leq l \leq 29$
Reflections collected	20321
Independent reflections	9887 [R(int) = 0.0592]
Reflections with $I > 2\sigma(I)$	7568
Completeness to $\theta = 67.50^\circ$	99.9%
Absorption correction	Analytical
Max. and min. transmission	0.809 and 0.454
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	9887/0/661
Goodness-of-fit on F^2	1.000
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0525$, $wR_2 = 0.1315$
<i>R</i> indices (all data)	$R_1 = 0.0691$, $wR_2 = 0.1440$
Largest difference in peak and hole (e Å ⁻³)	0.444 and -0.415

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