DNA Binding Test, X-Ray Crystal Structure, Spectral Studies, TG-DTA, and Electrochemistry of \([\text{CoX}_2(\text{dmdphphen})]\) (Dmdphphen Is 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline, X = Cl, and NCS) Complexes

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Two new neutral mixed-ligand cobalt(II) complexes, \([\text{CoCl}_2(\text{dmdphphen})]\) 1 and \([\text{Co(NCS)}_2(\text{dmdphphen})]\) 2, where dmdphphen is 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, were synthesized and characterized by an elemental analysis, UV-Vis, IR, TG/DTA, cyclic voltammetry CV, and single X-ray diffraction. Complex 2 crystallized as monoclinic with a space group P2₁/c. Co(II) ions are located in a distorted tetrahedral environment. TG/DTA result shows that these complexes are very stable and decomposed through one-step reaction. The two complexes exhibit a quasireversible one-electron response at \(-550\) and \(580\) mV versus \(\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+\), which has been assigned to Co(I)/Co(II) and Co(II)/Co(III) couples. Absorption spectral studies reveal that such complexes exhibit hypochromicity during their interaction with CT-DNA.

1. Introduction

1,10-Phenanthroline ligands and their derivatives are very attractive in metal complexes [1–3]. In addition, their metal complexes are frequently used as catalyst for the enantioselective hydrolysis of \(\text{N}\)-protected amino acid esters, allylic substitutions, reduction of acetophenone [3–6], and oxidation of olefins [7]. Also, cobalt(II) complexes with a reversible Co(II)/Co(III) are a good oxygen carrier and can oxidize the double bond of the olefins [8–10].

The ability of the cobalt phenanthroline complexes to bind and to cleave DNA under physiological conditions is of current interest because of their potential applications in nucleic acids chemistry [11]. Also, these complexes are useful in footprinting studies [12–17]. The cleavage of DNA usually occurs through the heterocyclic bases, deoxyribose sugar moieties, or phosphodiester linkage [18–20]. For the mixed-ligand complexes to interact efficiently with DNA, the ligands need to be flat, have large surface area, and have a spatial geometry to interact with the base pairs in DNA [15–23].
By changing the ligands or the metal ions, it is possible to modify the interaction with nucleic acids [23–26].

Previously, a series of several mixed-ligand mononuclear [27, 28] and dinuclear [29, 30] metal complexes have a general formula MX$_2$(dmdphphen) (2,9-dimethyl-1,10-phenanthroline, X = Cl, NCS) prepared in our lab. These complexes were found to be suitable precursors for spherical shape metal oxide nanoparticles [31]. Herein, two new neutral mixed-ligand cobalt(II) complexes, [CoCl$_2$(dmdphphen)] and [Co(NCS)$_2$(dmdphphen)] were synthesized and characterized by different spectroscopic methods. Also, the DNA binding and the catalytic oxidation of styrene in the presence of H$_2$O$_2$ for the complexes were investigated.

2. Experimental Section

2.1. Materials and Instrumentation. 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline ligand, CoCl$_2$·6H$_2$O, and Co(NCS)$_2$ were purchased from Acros Organics. Elemental analyses were carried out on an Elementar vario EL analyzer. The IR spectra for samples were recorded using PerkinElmer Spectrum 1000 FT-IR Spectrometer. The UV-Vis spectra were measured by using a TU-1901 double-beam UV-Vis spectrophotometer. TG/DTA spectra were measured by using a TGA-7 PerkinElmer thermogravimetric analyzer. The cyclic voltammograms for the complexes were measured in CH$_3$CN and 0.1 M tetrabutylammonium hexafluorophosphate (TBAHF) using BAS 100 B/W electrochemical workstation (Bioanalytical Systems, West Lafayette, IN, USA) and controlled by a standard 80486 personal computer (BAS control program version 2.0). All electrochemical experiments were carried out at room temperature under argon with a three-electrode cell. Voltalab 80 potentiostat PGZ402 with Pt-disk electrode (Metrohm, A = 0.0064 cm$^2$) was used as working electrode. Platinum wire (ξ 1 mm) spiral with diameter 7 mm was used as a counter electrode. Haber-Luggin double reference electrode was used as a reference one. All potentials in this paper are reported to an external Cp$_2$Fe$^{0/1+}$ standard [32].

2.2. General Procedure for the Preparation of the Desired Complexes. A mixture of CoX$_2$ salt (2 mmol) in distilled ethanol (15 mL) and free ligand (2.1 mmol) in methanol (10 mL) is stirred for around 0.5 h at room temperature until the precipitation appeared which was filtered, washed with ethanol, and dried. Suitable crystals for X-ray diffraction analysis were growing up by slow diffusion of ethanol into a solution of the complex in CH$_2$Cl$_2$ after two days (yield 88%).

2.2.1. Complex 1. Yield: 0.76 g (90%). Anal. Calc. for C$_{26}$H$_{35}$Cl$_2$CoN$_2$: C, 63.69; H, 4.11; N, 5.71. Found. C, 63.43; H, 4.21; N, 5.48. UV-Vis (nm) bands in dichloromethane: 655, 572, 360, 240, 280 and 304. M.p 320°C. Conductivity in CH$_3$CN: 10.28 (µS/cm).

2.2.2. Complex 2. Yield: 0.94 g (88%). C$_{28}$H$_{36}$CoN$_4$S$_2$: Cal. C, 62.80; H, 3.76; N, 10.46; S, 11.97. Found. C, 62.92; H, 3.85; N, 10.33; S, 11.86. UV-Vis (nm) bands in dichloromethane: 645, 566, 358, 242, 282 and 305. M.p 290°C. Conductivity in CH$_3$CN: 9.52 (µS/cm).

2.3. Crystallography. A suitable single-crystal complex 2 with dimensions of 0.23 × 0.22 × 0.21 mm was chosen for an X-ray diffraction measurement. X-ray intensity data were collected at 296 K on a Bruker CCD diffractometer equipped with Cu K$_{α}$ radiation (λ = 1.54178 Å). Data were collected with the ϕ and ω scan method. The final unit cell parameters were based on all reflections. Data reduction of all the collected reflections and absorption correction were carried out using the APEX 2 [33] package. The structure was solved by direct methods using SHELXS [34]. The structure was then refined by a full-matrix least-squares method with anisotropic temperature factors for nonhydrogen atoms using SHELXL [34]. All the nonhydrogen atoms were revealed in the first Fourier map itself. After several cycles of refinement, the final difference Fourier map showed peaks of no chemical significance and the residual saturated to 0.0671. Details of data collection and refinement are given in Table 1. The geometrical calculations were carried out using the program PLATON [35]. The molecular and packing diagrams were generated using the software MERCURY [36].

3. Results and Discussion

3.1. Synthesis of the Desired Complexes. The mononuclear CoCl$_2$(dmdphphen) complex 1 and Co(NCS)$_2$(dmdphphen) complex 2 were isolated in a good yield without side product as seen in Scheme 1.

The structures of the desired complexes were confirmed by using elemental analysis, IR, UV-Vis, TG/DTA, and X-ray single-crystal measurement for complex 2. The analytical data of the complexes show the formation of [1:1:2] [M : dmdphphen : 2X] ratio in a good agreement with the suggested formula [CoX$_2$(dmdphphen)] of the isolated complexes. The isolated solid complexes are insoluble in water, ethanol, n-hexane, and ethers but soluble in chlorinated solvents as CHCl$_3$ and CH$_2$Cl$_2$. The solubility and molar conductivity showed that the two complexes are nonelectrolytic in their nature.
Table 1: Crystal data and structure refinement for ligand and complex 2.

| Property                        | Complex 2                              |
|---------------------------------|----------------------------------------|
| Empirical formula               | C_{28}H_{20}N_{4}S_{2}Co               |
| Formula weight                  | 535.55                                 |
| Temperature                     | 293(2) K                               |
| Wavelength                      | 1.5417 Å                               |
| Crystal system                  | Monoclinic                             |
| Space group                     | P2_1/c                                 |
| Unit cell dimensions            |                                        |
| a                               | 14.8373(12) Å                         |
| a (°)                           | 90°                                    |
| b                               | 21.0942(11) Å                         |
| β (°)                           | 100.191(4)°                           |
| c                               | 8.2470(6) Å                           |
| c (°)                           | 90°                                    |
| Volume                          | 2540.4(3) Å                           |
| Z                               | 4                                      |
| Density (calculated)            | 1.400 Mg/m³                            |
| Absorption coefficient          | 7.017 mm⁻¹                             |
| F(000)                          | 1100                                   |
| Crystal size                    | 0.30 × 0.25 × 0.15 mm³                 |
| Theta range for data collection | 3.0° to 63.9°                          |
| Index ranges                    | −15 ≤ h ≤ 17, −21 ≤ k ≤ 24, −9 ≤ l ≤ 6 |
| Reflections collected           | 8247                                   |
| Independent reflections         | 3934 [R(int) = 0.0671]                 |
| Refinement method               | Full-matrix least-squares on F²        |
| Data/restraints/parameters      | 3934/0/318                             |
| Goodness-of-fit on F²           | 1.047                                  |
| Final R indices [I > 2σ(I)]     | R1 = 0.0671, wR2 = 0.1910             |
| R indices (all data)            | R1 = 0.1715, wR2 = 0.2661             |
| Largest diff. peak and hole     | 0.641 and −0.870 e Å⁻³                |

Table 2: Selected bond distances (Å) and bond angles (°) of the complex 2.

| Bond angles (°) | Bond distances (Å) |
|-----------------|--------------------|
| N2–Co1–N13      | 82.1(18)           |
| Co1–N13         | 2.035(4)           |
| N2–Co1–N30      | 108.7(2)           |
| Co1–N2          | 2.032(4)           |
| N2–Co1–N33      | 122.3(2)           |
| Co1–N30         | 1.923(7)           |
| N13–Co1–N30     | 109.3(2)           |
| Co1–N33         | 1.905(5)           |
| N13–Co1–N33     | 122.8(2)           |
| N30–Co1–N33     | 109.0(2)           |
| Co1–N13         | 2.035(4)           |
| Co1–N2          | 2.032(4)           |
| Co1–N30         | 1.923(7)           |
| Co1–N33         | 1.905(5)           |
| Co1–N13         | 2.035(4)           |
| Co1–N2          | 2.032(4)           |
| Co1–N30         | 1.923(7)           |
| Co1–N33         | 1.905(5)           |
| Co1–N13         | 2.035(4)           |
| Co1–N2          | 2.032(4)           |
| Co1–N30         | 1.923(7)           |
| Co1–N33         | 1.905(5)           |

3.2. X-Ray Crystal Structure. Crystal structure data and selected bonds length for complex 2 are compiled in Tables 1 and 2, respectively. ORTEP drawing of the complex is shown in Figure 1. The central cobalt metal ion is coordinated to the two nitrogen atoms (N2 and N13) of the dmdphphen ligand and to two nitrogen atoms (N30 and N33) of the isothiocyanate ligand in a tetrahedral symmetry. The phenanthroline ring in the dmdphphen moiety is essentially planar with an rms deviation of 0.0752 Å. The phenyl rings (C8–C13 and C24–C29) are twisted out of the plane of the dmdphphen.
moiety as indicated by the dihedral angle values of 43.2(4)° and 47.2(4)°, respectively. All coordination distances and bond angles are similar to those found in similar compounds [37]. No classic hydrogen bonds were observed. In the crystal structure there is a \( \pi-\pi \) stacking interaction between adjacent dmdphphen and distances 3.7109(17) Å and 3.8070(17) Å, which may account for stabilizing the crystal structure (Figure 2). The packing of the molecules when viewed down along the \( a \) axis indicates that the molecules are interlinked by weak hydrogen bonds to form one dimensional chain.

3.3. IR Spectrum. The IR spectrum of complex 1 (Figure 3(b)) showed four characteristic absorptions peaks in the range of 3060, 2950, 550, and 350 cm\(^{-1}\) [7–10] which was assigned to H–Ph, H–CH\(_3\), Co–N, and Co–Cl stretching vibrations, respectively. New band at 2150 cm\(^{-1}\) which was assigned to NCS vibrations was observed in IR spectrum of complex 2 (Figure 3(c)). The H–Ph, H of CH\(_3\) in dmdphphen bands appeared in their expected areas (Figure 3(a)).

3.4. Electronic Absorption Spectral Study. The experimental absorption spectra (UV-Vis) of the [CoX\(_2\)(dmpphen)] complexes 1, 2 in dichloromethane solution presented three dominant bands in the regions 200–800 nm (Figure 4). The bands in the UV region centered at around 240, 280, and 300 nm were assigned ligand-centered \( \pi-\pi^* \) transitions (in both complexes). The bands at 360, 572, and 635 nm for complex 1 (above) and at 365, 560, and 645 nm for complex 1 (down) can be assigned to the \( d \rightarrow d \) transition and MLCT, respectively [14–20].

3.5. Thermal Decomposition Analysis of Complexes 1. The thermal analysis of complex 1 (Figure 5) was investigated in the range of 0–600°C and heating rate of 10°C/min. Figure 5 shows that there is no uncoordinated or coordinated water in the range of 0–150°C and 150–180°C, respectively. Also, it shows that there are no decomposition intermediate steps of the coordinated chloride and dmdphphen ligands; both inorganic and organic ligands were destructured away from the Co metal with one-step broad decomposition in 200–330°C with weight loss \( \sim 81\% \) and an exothermic DTA signal at \( \sim 315°C \); the final residue was confirmed by IR to be CoO.

3.6. Electrochemistry. The electron-transfer behavior of the complexes in acetonitrile solution was examined by cyclic voltammetry. As a representative example, the cyclic voltammogram for complex 2 is shown in Figure 6. Complex 2 exhibited two single electron reversible oxidative responses
3.7 DNA-Complex 1 Binding Test. The affinity of Co(II) complexes for double-stranded CT-DNA was explored using UV-Vis titrations in deionised water. The results of representative titrations are shown in Figure 7. Complex 1 showed good DNA binding affinity. Complex 1 has three characteristic absorption peaks at 360 nm, 572 nm, and 655 nm, respectively. There is a decrease in an intensity for all peaks for complex 1 by adding several concentrations of DNA. This suggests that the cobalt complex might be bind to DNA by an intercalative mode [38]. However, by comparing the small shift for complex 1 with 7 nm red-shift values for Os(phen)$_2$(dppz)$_2$$^{2+}$ [39] and 9 nm for [Co(phen)$_2$(pdtp)]$^{3+}$ [40], this demonstrates that the intercalative strength of such complexes into DNA is not very strong.

4. Conclusions

Tetrahedral cobalt(II) complexes [CoCl$_2$(dmdphphen)] 1 and [Co(NCS)$_2$(dmdphphen)] 2 were made available in good yield. Complex 2 was solved by XRD as monoclinic with a space group P2$_1$/c. Co(II) ions are located in a distorted tetrahedral environment. TG/DTA result shows that these complexes are very stable and decomposed through one-step
reaction; the complexes exhibit a quasireversible one-electron response at ∼−550 mV assigned to Co(I)/Co(II) and ∼−580 mV assigned to Co(II)/Co(III) versus Cp₂Fe/Cp₂Fe⁺. Absorption spectral studies reveal that such complexes exhibit good DNA binding.

Additional Material

Crystallographic data for complex 1 has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 1014019. Copies of this information may be obtained free of charge via https://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44-1223-336033; e-mail deposit@ccdc.cam.ac.uk).

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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