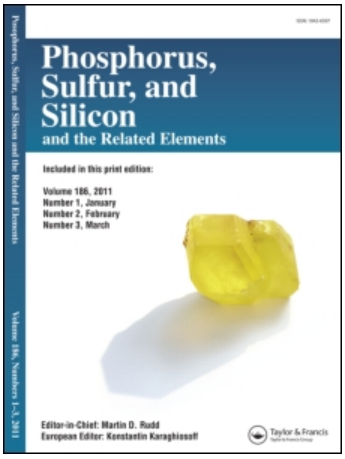

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Synthesis, Characterization, and DNA Binding Studies of S_2N_2 Donor Bis-Mercaptoquinoline Co(II) and Ni(II) Metal Complexes: A New Class of Antimicrobial Agent

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SYNTHESIS, CHARACTERIZATION, AND DNA BINDING STUDIES OF S_2N_2 DONOR BIS-MERCAPTOQUINOLINE Co(II) AND Ni(II) METAL COMPLEXES: A NEW CLASS OF ANTIMICROBIAL AGENT

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This article describes a convenient procedure for the synthesis of metal complexes of the type [ML] [CoMPQT](1), [NiMPQT](2) where M = Co(II), Ni(II) tetradentate (S_2N_2) Schiff-base using 3-{[(2-{[(2-mercaptoquinolin-3-yl)methylene]amino}phenyl)imino]methyl} quinoline-2-thiol ligand (MPQT)L. The synthesized ligand and its metal complexes were characterized by elemental analysis, FT-IR, ^{1}H NMR, mass, and electronic spectra. The mode of bonding and the geometry of the complexes have been confirmed on the basis of IR and UV-vis spectral findings and magnetic measurements. The binding property of the complexes with calf-thymus DNA was studied by absorption spectra, viscosity measurements, and thermal denaturation studies. The intrinsic binding constant (K_b) had the value 2.8×10^4 M^{-1} for 1 and 4.8×10^4 M^{-1} for 2, suggesting that complex 2 binds more strongly to CT-DNA than complex 1. The synthesized metal complexes were screened for antibacterial and antifungal activities.

Supplemental materials are available for this article. Go to the publisher's online edition of* Phosphorus, Sulfur, and Silicon and the Related Elements *to view the free supplemental file.

Keywords Anticancer agent; antimicrobial activities; DNA binding; bis-mercaptoquinoline; metal complexes; viscosity measurements

INTRODUCTION

The high selectivity and strong coordination ability of tetradentate (S_2N_2) type Schiff-base ligands towards transition metal ions have attracted chemists due to their wide range of applications in the areas such as catalysis,[1–3] electron carriers in redox reactions,[4] dioxygen

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carriers,[5,6] ionospheres in a number of biochemical processes,[7–9] separation and extraction of valuable and precious metals from waste materials,[10] and as antitumor drugs.[11] Thus, the transition metal complexes of mixed donor ligands constitute a potentially important class of molecules for molecular electronics and catalytic reductions.[12]

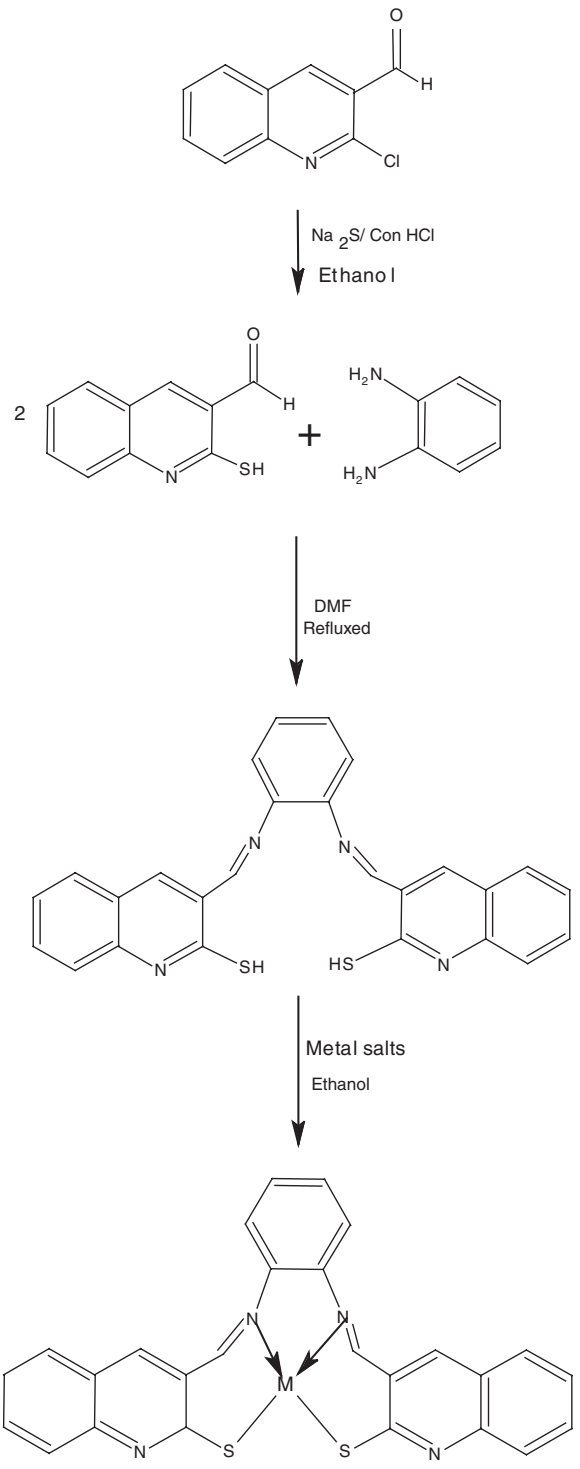
The nickel complexes containing sulfur donors have received considerable attention due to the identification of a sulfur-rich coordination environment in biological metal centers.[13] Several metal thiolate complexes have been proposed as simple model compounds, and considerable advances have been achieved in metal sulfur chemistry.[14–19] The recent crystal structure determination of the hydrogenase from *Desulfovibrio gigas* showed that the metal complex is coordinated by four sulfur donors and has revealed the hetero-bimetallic nature of the active site.[20] This finding has promoted the current investigation towards the synthesis on model compounds of bimetallic complexes.[21] Nevertheless, some important aspects of metal–sulfur chemistry have remained poorly understood, in particular the role of coordinated sulfur donors in the stabilization of unusual oxidation states for metal complexes.

On other hand, the interaction of transition metal complexes with CT-DNA has been extensively studied in the past few years. Among the first row transition metal ions, cobalt, nickel, manganese, and copper offer the choice of biocompatibility in biological systems and have been recognized as having important biological effects. The study of antitumor activity and DNA binding properties of these metals complexes has been well documented in the literature.[22–26]

The purpose of this work was to study the synthesis of metal complex and DNA binding changes induced by sulfur donors in the coordination sphere of Co(II) and Ni(II) metal complexes. In order to assess chemical changes attributable to different bridges, are ideally suited to evaluate the influence of sulfur donors in metal complexes as they form a complete set of coordination spheres in N_2S_2, without any other changes in the ligand skeleton.

RESULTS AND DISCUSSION

The ligand and complexes were synthesized by standard procedure with slight modification give good yield and are pure (Table I). The prepared ligand and its metal complexes are characterized by IR, ^{1}H NMR, mass, and elemental analyses, and agree with the proposed complex structure. The IR spectra of the ligand show the absence of bands corresponding to the amino groups of *o*-phenylinediamine, and carbonyl groups of aldehydic 2-mercaptoquinoline-3-carbaldehyde suggested the formation of the ligand (**L**) (Scheme 1). The confirmation regarding the formation of the ligand has been obtained from the appearance of intense bands at 3054 cm^{-1} for (Ar—CH), 1619 cm^{-1} for (C=N), and the tautomeric form of (C=S) appears at 747 cm^{-1}[27,28] to the uncoordinated group, respectively. ^{1}H NMR spectra show broad peaks at $\delta = 14.36$ and 13.25 due to s, 2H, SH, and 2H, CH=N, D_2O exchangeable, and 7.24–7.95 (m, 14H, Ar—H,) confirms the proposed structure of the ligand. Further the structure was confirmed by its mass spectra with a molecular ion peak at m/z = 450 [M+H], corresponding to the mass of the ligand. However, the IR spectra of complexes derived from the ligand (**L**) show a slight shift to the frequency in the region of 1694–1676 cm^{-1} for (C=N), 736–753 cm^{-1} for ν(C=S), and 3064–3076 cm^{-1} for (Ar—CH), respectively. The appearance of new medium-intensity band at 627–508 cm^{-1} and 593–502 cm^{-1} are assigned as ν(M-N) and ν(M-S) vibrations, respectively.



Scheme 1 Synthesis of 3-{[(2-{[(2-mercaptoquinolin-3-yl)methylene]amino}phenyl) imino]methyl}quinoline-2-thiol metal complexes, where M = Co(II) and Ni(II).

Table I Analytical and physical properties of the metal complexes 3-{[(2-{[(2-mercaptoquinolin-3-yl)methylene]amino}phenyl)imino]methyl}quinoline-2-thio metal complexes

Complex	Color	Molecular weight	Yield %	Mp °C	$\Delta m\ \Omega^1 cm^2\ mol^{-1}$	μeff (BM)	Elemental analysis Calc. (Found)
[MPQT] L $C_{26}H_{18}N_4S_2$	Greenish red	450.58	78	143–145	—	—-	C: 69.31 (69.27)
							H: 4.03 (4.10)
							N: 12.43 (12.48)
							S: 14.23 (14.18)
[Co(L)](1) $C_{26}H_{16}\ S_2CoN_4$	Dark bluish	509.45	63	226–228	2.7	3.26	C: 70.11 (70.19)
							H: 4.07 (4.00)
							N: 12.58 (12.66)
							S: 12.64 (12.53)
							Co:13.23 (13.26)
[Ni(L)](2) $C_{26}H_{16}\ S_2NiN_4$	Reddish brown	509.15	67	242–243	2.9	1.53	C: 70.15 (70.21)
							H: 4.08 (4.05)
							N: 12.59 (12.62)
							S: 12.64 (12.57)
							Ni:13.19 (13.26)

Electronic Spectra and Magnetic Moment

Electronic spectra of [CoMPQT] and [NiMPQT] complexes were recorded at room temperature in DMF. The electronic spectra of Co(II) complex **1** shows a weak band at 2066–2188 cm^{-1}, $^2B1g \rightarrow {}^2A1g$ attributed due to d–d transitions, which are expected to be square planar geometry.[28,29] The complex **2** has diamagnetic behavior, and its electronic spectrum shows a shoulder at 17,632–18,541 cm^{-1} ascribed to $^2A1g \rightarrow {}^2B1g$ transition supporting tetrahedral geometry around the Ni(II) ion.[22] The observed magnetic moment value is 3.26 BM for Co(II), greater than spin-only value 1.75 BM, and hence paramagnetic in nature, whereas the Ni(II) complex is observed at 1.53 BM. The molar conductivities for both the complexes were in the range of 2.9–2.5 $\Omega^{-1}\ cm^{-2}\ mol^{-1}$, indicating that they are non-electrolytic in nature.

DNA Binding Studies (Electronic Absorption Spectroscopy)

Electronic absorption spectroscopy is universally employed to determine the binding of the complex with calf-thymus DNA.[22] The absorption spectrum of complexes **1** and **2** shows well resolved absorbance maxima at 214, 245 nm for complex **1** and 211, 240 nm for complex **2**. The addition of increasing higher concentration of CT-DNA led to hypochromic and bathochromic changes in its visible absorption spectra as a result of the formation of more stable complexes.[30] In the presence of increasing amounts of CT-DNA, complexes **1** and **2** showed a decrease in absorbance accompanied by a shift towards higher wavelengths of hypochromicity (about 7% for **1** 10% for **2**) and bathochromic shifts (maximum: 2 ± 1 nm) for their most red-shift absorption peak maxima (Table II). The change in the absorbance values with increasing amounts of CT-DNA were used to evaluate the intrinsic binding constants (K_b), and the observed binding constant value for complexes **1** and **2** were $2.8 \times 10^4\ M^{-1}$ and $4.8 \times 10^4\ M^{-1}$, respectively, suggesting that the complex **2** binds

Table II Absorption spectral properties mercaptoquinoline complexes of Co(II) and Ni(II) bound to CT-DNA

Complex	λ_{max} (nm)	K_b (M^{-1})	T_m (°C)
Complex (1)	214	2.8×10^4	65
Complex (2)	211	4.8×10^4	68

more strongly to CT-DNA than complex **1**. The obtained data are summarized in Table II[31] and Figure S1 (available online in the Supplemental Materials).

Viscosity Measurements

The binding modes of complexes with CT-DNA was further confirmed by viscosity measurements. Hydrodynamic measurements that are sensitive to length change are regarded as the most critical tests of binding in solution in the absence of crystallographic structure data.[32] A classical intercalative mode causes a significant increase in viscosity of DNA solution, due to an increase in separation of base pairs at intercalation sites and hence an increase in overall DNA length. By contrast, complexes that bind exclusively in the DNA grooves by partial and/or nonclassical intercalation, under the same conditions, typically cause negative or no change in DNA solution viscosity.[33] The effects of the complex on the viscosity of rodlike DNA are shown in Figure S1 (Supplemental Materials). As expected, the viscosity of the complex has obvious effect; the relative viscosity of CT-DNA increases with an increase in concentration of the added complex.

Thermal Denaturaration Studies

Additional information on the DNA binding properties was obtained from melting studies. The stability of the DNA helix increased with melting temperature. The stability of the DNA helix with temperature indicates an interaction between DNA to metal complex in the concentration ratio of 25 and (T_m) values was determined by monitoring the absorbance of DNA at 260 nm as a function of temperature. In the present study, when the complexes solutions are added to the solution of calf-thymus DNA, the melting temperature is increased. This indicates that there is an interaction between DNA and the metal complexes. The melting of DNA in absence of the complex was found to be 60 ± 1°C. Under the same experimental conditions, the presence of complexes **1** and **2** increased the melting temperature by about 5 to 8°C, as shown in Figure S2 (Supplemental Materials). Likewise, there was a similar outcome with the stabilized double strand of calf-thymus DNA.[34–36]

Table III Characteristic IR absorption bands (in cm^{-1}) for ligand and metal complexes

L [MPQT] $C_{26}H_{18}N_4S_2$	3054m	1619s	1559w	1487m	1217s,	1137s,	747s	608m	—
[Co(L)](1) $C_{26}H_{16}CoN_4S_2$	3064m	1694s	1599m	1498m	1262s	1157s	753m	627w	508w
[Ni(L)](2) $C_{26}H_{16}NiN_4S_2$	3076m	1679s	1597m	1495m	1280s	1165s	756m	623w	501w

s = strong, m = medium, w = weak.

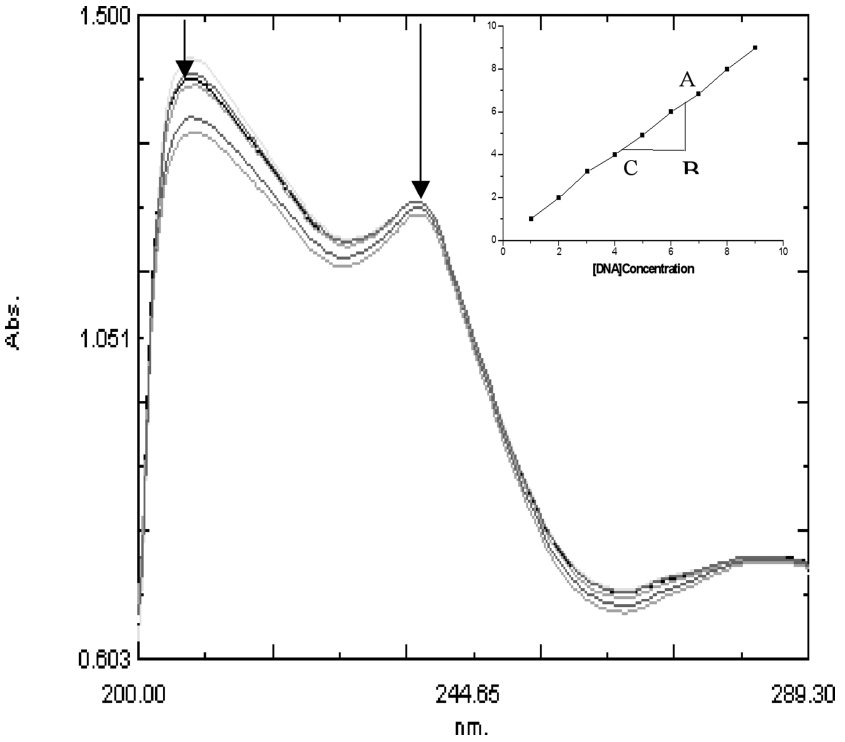


Figure 1 Absorption spectral traces of complex [Ni(L)] (**2**) in Tris HCl buffer (0.01 M, pH 7.2) upon addition of CT-DNA = 0.5 μm, = 10 μm, drug, 20 μm; 30 μm; 40 μm; 50 μm. The arrow shows the absorbance changing upon increase of DNA concentration.

CONCLUSIONS

The synthetic route adopted for synthesis of the ligand and its metal complexes of the type [CoMPQT] and [NiMPQT] was very simple and gave good yield. In DNA binding studies, the absorption spectral results indicate hypochromic and bathochromic shifts of the complex **1** and **2** when they bind with base pairs of CT-DNA. The binding constant values of metal complexes 2.8×10^4 M^{-1} for **1** and 4.8×10^4 M^{-1} for **2** suggested that the complex **2** binds more avidly to CT-DNA than complex **1**. In addition, increasing the viscosity of sonicated rod-like DNA fragments and melting temperature of CT-DNA supports the binding mode. The antimicrobial activity shows that both the ligand and its complex exhibit significant inhibitory activity.

EXPERIMENTAL

All chemicals used for the synthesis were of analytical grade and were purchased from Sigma Chemical Co., USA. or E. Merck Company, India. *o*-Phenylinediamine was purchased from S.D. Fine Chemicals Pvt. Ltd. 2-Mercaptoquinoline-3-carbaldehyde was synthesized according to the procedure in the literature.[37] The TLC was performed on Baker-Flex silica gel 1B-F (1.55) plates in ethyl acetate and petroleum ether (8:2). Melting points were determined on a Mel-Temp apparatus and are uncorrected. IR spectra were

recorded using (KBr) pellets with a Perkin-Elmer 1430 spectrometer.^{1}H NMR spectra were recorded on a Jeol spectrometer (400 MHz), and chemical shifts (δ) are given in ppm using $CDCl_3$ relative to the signal for TMS as internal standard. Mass spectra were recorded on a Jeol JMS-D 300 mass spectrometer operating at 70 eV. C, H, and N analyses were performed at Sophisticated Test & Instrumentation Center, Kochi, Kerala, India. Conductivity measurements were determined in DMF (10^{-3} M) using an ELICO-CM82 Conductivity Bridge. UV-vis absorption spectra were recorded on a Perkin–Elmer model 1654 with Shimazdu UV-Vis recording spectrophotometer using quartz cuvettes of 10 mm light-path.

DNA Binding Experiments

The concentration of CT-DNA per nucleotide [C(p)] was measured by using its known extinction coefficient at 260 nm (6600 $M^{-1}cm^{-1}$).[38] The observed data for complexes **1** and **2** were then fit into Equation (1) to obtain the intrinsic binding constant, K_b.[39]

$$[DNA]/(\varepsilon_a - \varepsilon_f) = [DNA]/(\varepsilon_b - \varepsilon_f) + 1/K_b(\varepsilon_b - \varepsilon_f) \quad (1)$$

Where ε_a, ε, and ε_b are the apparent, free, and bound metal complex extinction coefficients at 214 nm, 245 nm for Co(II) and 211nm, 240 nm for Ni(II), respectively. The melting temperature [(T_m) the temperature at which 50% of double-stranded DNA becomes single-stranded] and the curve width [(σT) (the temperature range between which 10% and 90% of the absorption increases occurred] were calculated using the reported procedure.[40,41] Other details are presented in the Supplemental Materials (available online).

Synthesis of Ligand [MPQT]

Synthesis of 3-{[(2-{[(2-Mercaptoquinolin-3-yl)methylene]amino}phenyl)imino]methyl}quinoline-2-thiol [MPQT]. A mixture of 2-mercaptoquinoline-3-carbaldehyde (5.67 g, 0.03 mol) and *o*-phenylinediamine (3.24 g, 0.03 mol) were stirred for 1 h in DMF and then refluxed for 6 h on a water bath. A greenish red solid precipitated upon pouring into ice-cold water. The resulting solid was collected by filtration, dried, and recrystallized in ethanol. Yield, 78%; mp = 143–145°C; Anal. (%) Calcd for $C_{26}H_{18}N_4S_2$ (450) Found: C, 69.27; H, 4.10; N, 12.48, S. 14.18%.Calculated; C, 69.31; H, 4.03; N, 12.43; S. 14.23; IR (KBr) νmax/cm^{-1} 3054 cm^{-1} (Ar—CH), 747 (C=S); 1619 cm^{-1}(C=N) 1559, 1487, 1217, 1137, 1044 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 7.20–7.95 (m, 14H, Ar—H), 14.36 (s, 2H, SH), 13.25 (s, 2H, CH=N, D_2O exchangeable), mass spectra, m/z = 450 [M+H].

Preparation of Complexes

A general method has been adopted for the preparation of the complexes. A hot ethanol solution of the ligand with the corresponding hydrated metal salt in a 1:1 equimolar ratio was refluxed for about 3–4 h, at 80 ± 5°C. The residue was recrystallized from ethanol/dichloromethane. Various attempts to develop the crystals suitable for X-ray diffraction studies such as slow diffusion, crystallization using mixtures of solvents, and low temperature crystallization were unsuccessful.

Synthesis of 3-{[(2-{[(2-Mercaptoquinolin-3-yl)methylene]amino}phenyl) imino]methyl}quinoline-2-thio Metal Complexes. Ligand (**L**) (2.5 g, 0.005 mol) was dissolved in 25 mL ethanol and added to the 25 mL hot ethanolic solution of hydrated metal salt (1.34 g, 0.0056 mol) cobalt(II) chloride in a 1:1 molar ratio under boiling conditions and refluxed for 3–4 h. A dark blue colored precipitate formed, and was collected by filtration and dried with 63% yield. Similarly same procedure was followed for Ni(II) complex with 67% yield. The observed experimental data are summarized in Table I.

Evaluation of Antimicrobial Activity

The *in vitro* antimicrobial activity was carried out against 24-hour-old cultures of two bacteria and two fungi by cup-plate method.[42] The details are summarized in the Supplemental Materials (available online).

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