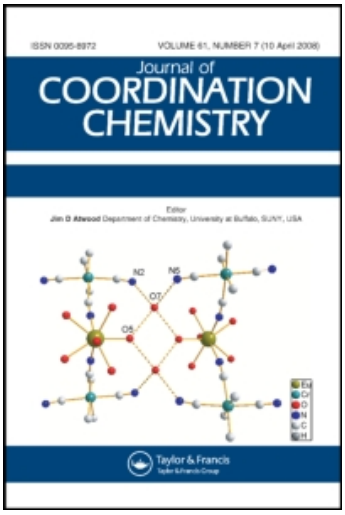

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Synthesis and structure of mononuclear copper(II) complexes with acyclic Schiff-base ligands containing organotellurium substituents: a comparative study with selenium analogs

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Synthesis and structure of mononuclear copper(II) complexes with acyclic Schiff-base ligands containing organotellurium substituents: a comparative study with selenium analogs

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Tellurium-bearing acyclic Schiff bases, 2,6-*bis*({N-[2-(phenyltellurato)ethyl]}benzimidoyl)-4-methylphenol (**HL^3**) and 2,6-*bis*({N-[3-(phenyltellurato)propyl]}benzimidoyl)-4-methylphenol (**HL^4**) of the Te_2N_2O type have been prepared by condensation of 4-methyl-2,6-dibenzoylphenol (mdbpH) with the appropriate phenyltellurato(alkyl)amine. **HL^3** and **HL^4** have been characterized by mass spectrometry, IR, electronic and ^{1}H-NMR spectroscopies and cyclic voltammetry. Their reactions with Cu(II) acetate monohydrate in a 2:1 molar ratio in methanol yield $[(C_6H_2(O)(Me)\{(C_6H_5)C{=}N(CH_2)_nTe(C_6H_5)\}\{(C_6H_5)C{=}O\})_2Cu]$ (**3** ($n=2$), **4** ($n=3$)) as suggested by analytical and spectroscopic data and single crystal X-ray crystallography of **3**. In both complexes, one arm of the ligand undergoes hydrolysis at the C=N position and two molecules of the partially hydrolyzed ligand coordinate to Cu(II) through imido nitrogen and the phenolic oxygen. The telluriums do not form part of the copper(II) distorted square planar coordination sphere which has a *trans*-CuN_2O_2 core. Electrochemical studies of **3** and **4** indicate quasi-reversible reductions ($E^{\circ\prime} = -1.113$ V (**3**) and -1.149 V (**4**)) corresponding to the reduction of copper(II) to copper(I). The interactions of **3** and **4** with calf thymus DNA, investigated by spectrophotometry and cyclic voltammetry, indicate that **3** and **4** bind to DNA *via* intercalation, and the binding affinity of **3** is lower than that of its selenium analog.

Keywords: Hybrid ligands; Copper(II) complexes; X-ray structure; Cyclic voltammetry; DNA binding

1. Introduction

Organochalcogen chemistry has developed rapidly over the past few decades [1–3], and is attributed to potential applications of organochalcogen compounds in transition metal catalyzed organic synthesis [4–12], as single source precursors in metalorganic chemical vapor deposition (MOCVD) processes for developing materials [13–19],

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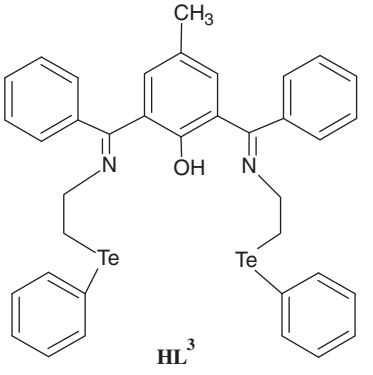
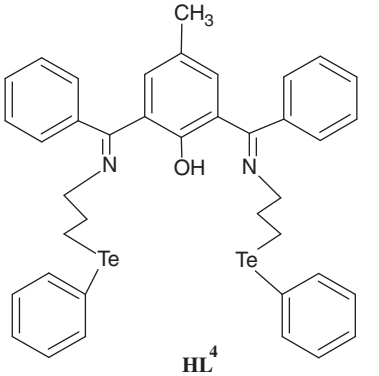
in ligand chemistry [3, 20–23] and biochemistry [24–29]. Applications of organochalcogen compounds have, however, been restricted by difficulties in synthetic methodologies, purification and instabilities of certain derivatives. To overcome these difficulties, sterically bulky substituents and chelating groups in close proximity to selenium and tellurium have been used. Internal chelation has been extended to design and synthesize heterofunctionalized chalcogen-bearing ligands containing both ''hard'' and ''soft'' donors [30, 31]. Such a ligand framework is anticipated to exhibit selective coordination leading to coordinatively unsaturated metal centers and may exhibit new chemistry from their heterofunctionalized nature [32–38]. A number of acyclic hybrid ligands with (O, N, Se/Te), (N_2Se/Te), and (N_3Se_2/Te_2) have been recently reported [39–46].

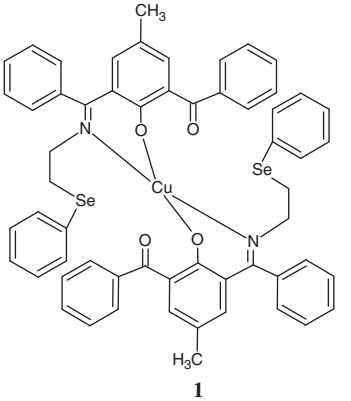
We have very recently reported [47] synthesis of phenol-based Schiff bases, $[PhSe(CH_2)_nN{=}CPh\}_2C_6H_2(4\text{-}Me)(OH)]$ ($n=2$, **HL**^{1}; $n=3$, **HL**^{2}) and their reactions with Cu(II) which yielded $[Cu\{(PhSe(CH_2)_nN{=}CPh\}C_6H_2(4\text{-}Me)C(O)Ph\}_2)]$ ($n=2$, **1**; $n=3$, **2**). The present investigation deals with the synthesis and characterization of potentially pentadentate Te_2N_2O-type acyclic Schiff bases, 2,6-*bis*({N[2-phenyltellurato)alkyl]}benzimidoyl)-4-methylphenol, $[\{PhTe(CH_2)_nN{=}CPh\}_2C_6H_2(4\text{-}Me)(OH)]$ ($n=2$, **HL**^{3}; $n=3$, **HL**^{4}) and their reactions with Cu(II). A comparative study of Cu(II) complexes (**3**, **4**), thus formed, with those of their selenium analogs (**1**, **2**) is reported herein. The structure of ligands **HL**^{3} and **HL**^{4} and those of complexes **1** and **3** are shown below.



HL^{3}



HL^{4}



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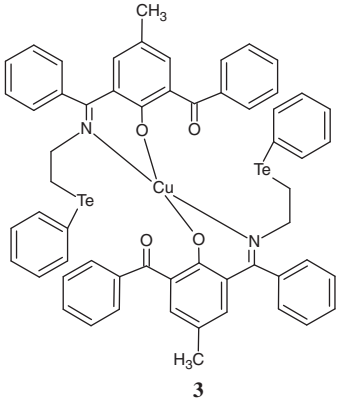


3

2. Experimental

All chemicals were of reagent grade. Solvents were purified by standard methods [48] and freshly distilled prior to use. The precursors, 4-methyl-2,6-dibenzoylphenol (mdbpH) [49] and phenyltellurato(alkyl)amines [50], were synthesized following reported methods. Calf thymus (CT) DNA was obtained from Sigma and used as received. The sodium salt of CT-DNA was stored at 4°C.

2.1. *Physical measurements*

Elemental analyses were carried out on a Carlo Erba Model DP 200 analyzer. Melting points of compounds in capillaries are uncorrected. Molar conductances in 10^{-3} mol L^{-1} CH_3CN solution were measured using a Global DCM-900 digital conductivity meter. The electrospray ion mass spectra (ESIMS) were recorded on a MICROMASS QUATTRO II triple quadrupole mass spectrometer. Infrared spectra were recorded on a Nicolet Magna 750 FT-IR spectrophotometer with KBr pellets (400–4000 cm^{-1}). Electronic spectra in 10^{-4} mol L^{-1} CH_3CN were obtained using a Perkin Elmer Lambda 35 UV-Vis spectrometer. ^{1}H-NMR spectra were recorded on a Brucker AMX 400 FT-NMR spectrometer in $CDCl_3$ with chemical shifts relative to $SiMe_4$.

2.1.1. 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 platinum/glassy carbon as a working electrode, Pt wire as auxiliary electrode and a non-aqueous Ag/Ag^+ reference electrode with 0.1 mol L^{-1} $AgNO_3$ in acetonitrile as filling solution. Tetrabutylammonium perchlorate (0.1 mol L^{-1} solution in CH_3CN) was used as supporting electrolyte. Cyclic voltammograms with scan speeds of 50–400 mV s^{-1} were run in 10^{-4} mol L^{-1} CH_3CN under nitrogen.

2.2. *Synthesis of HL^3 and HL^4*

A solution of 4-methyl-2,6-dibenzoylphenol (1.26 g, 4.00 mmol L^{-1}) in acetonitrile (150 mL) was added dropwise to a solution of the appropriate phenyltellurato(ethyl)amine (1.98 g, 8.00 mmol L^{-1})/phenyltellurato(propyl)amine (2.10 g, 8.00 mmol L^{-1}) in acetonitrile (200 mL) in a 1 : 2 molar ratio with stirring for 7–8 h. Progress of the reaction was monitored by thin layer chromatograpy (TLC). It took about 45 h for completion of the reaction. The organic solvent was removed under reduced pressure and the viscous, oily product, thus obtained, was purified by column chromatography (silica–gel, 60–120 mesh, second fraction) using a solvent mixture of hexane : ethylacetate in 80 : 20 or 70 : 30 ratio. The characteristics of these compounds are given below.

2.2.1. 2,6-*Bis*({N-[2-(phenyltellurato)ethyl]}benzimidoyl)-4-methylphenol (HL^3), [2,6-{$PhTe(CH_2)_2N{=}CPh$}$_2C_6H_2$(4-CH_3)(OH)]. Yellow viscous liquid; Yield: 2.68 g (86%). Positive ES–MS: m/z 779 [MH^+]. FT-IR (cm^{-1}): ν(OH) 3441, ν(C=N) 1598,

ν(C–O) 1252. UV-Vis λ_{max} (nm) (CH_3CN): 423 ($PhO^- \rightarrow Ph$). ^{1}H-NMR ($CDCl_3$, δ ppm): 16.01 (s, 1H, OH), 7.10–7.90 (m, 22H, C_6H_5 and C_6H_2), 3.64 (t, 4H, N–CH_2), 2.99 (t, 4H, Te–CH_2), and 2.27 (s, 3H, CH_3).

2.2.2. 2,6-*Bis*({N-[3-(phenyltellurato)propyl]}benzimidoyl)-4-methylphenol (HL^4), [2,6-{$PhTe(CH_2)_3N{=}CPh\}_2C_6H_2(4\text{-}CH_3)(OH)$]. Yellow viscous liquid; Yield: 2.93 g (91%). Positive ES–MS: m/z 807 [MH^+]. FT-IR (cm^{-1}): ν(OH) 3416, ν(C=N) 1577, ν(C–O) 1253. UV-Vis λ_{max} (nm) (CH_3CN): 429 ($PhO^- \rightarrow Ph$). ^{1}H-NMR ($CDCl_3$, δ ppm): 16.26 (s, 1H, OH), 7.06–7.93 (m, 22H, C_6H_5 and C_6H_2), 3.31 (t, 4H, N–CH_2), 2.82 (t, 4H, Te–CH_2), 2.05 (q, 4-H, mid-CH_2 (CH_2 between N–CH_2 and Te–CH_2)), 2.13 (s, 3H, CH_3).

2.3. *Reactions of HL^3 and HL^4 with Cu(II)*

A degassed solution of $Cu(OCOCH_3)_2{\cdot}H_2O$ (0.10 g, 0.5 mmol L^{-1}) in freshly distilled methanol (5 mL) added to degassed solution of **HL^3** (0.68 g, 1.0 mmol L^{-1})/**HL^4** (0.71 g, 1.0 mmol L^{-1}) in methanol (15 mL) at room temperature gave a dark blue solid almost immediately. The reaction mixture was stirred for 12 h and the precipitate thus obtained was filtered, washed with cold methanol and diethylether, and dried under vacuum. The characteristics of these complexes are given below.

2.3.1. *Bis*(2-[N-{2-(phenyltellurato)ethyl}benzimidoyl]-6-benzoyl-4-methylphenolato)-copper(II) (3); [$(C_6H_2(O)(4\text{-}CH_3)\{PhC{=}N(CH_2)_2TePh\}PhCO)_2{\cdot}Cu$]. Dark blue crystalline solid; Yield: 0.39 g (71%); m.p. 250°C. Anal. Calcd for $C_{58}H_{48}N_2O_4Te_2Cu$: C, 60.27; H, 4.19; N, 2.42. Found: C, 60.18; H, 4.30; N, 2.48%. Positive ES–MS: m/z 1157 [MH^+]. FT-IR (selected, cm^{-1}): ν(C=O) 1654, ν(C=N) 1533, ν(C–O) 1246, ν(Cu–N) 570, ν(Cu–O) 437. UV-Vis λ_{max} (nm) (CH_3CN): 639. Λ_M (10^{-3} mol L^{-1}, CH_3CN, 298 K): 6 $S\,cm^2\,mol\,L^{-1}$.

2.3.2. *Bis*(2-[N-{3-(phenyltellurato)propyl}benzimidoyl]-6-benzoyl-4-methylphenolato)-copper(II) (4); [$(C_6H_2(O)(4\text{-}CH_3)\{PhC{=}N(CH_2)_3TePh\}PhCO)_2{\cdot}Cu$]. Light blue crystalline solid; Yield: 0.36 g (67%); m.p. 180°C. Anal. Calcd for $C_{60}H_{52}N_2O_4Te_2Cu$: C, 60.87; H, 4.43; N, 2.37. Found: C, 60.89; H, 4.41; N, 2.42%. Positive ES–MS: m/z 1185 [MH^+]. FT-IR (selected, cm^{-1}): ν(C=O) 1664, ν(C=N) 1533, ν(C–O) 1244, ν(Cu–N) 570, ν(Cu–O) 440. UV-Vis λ_{max} (nm) (CH_3CN): 613. Λ_M (10^{-3} mol L^{-1}, CH_3CN, 298 K): 8 $S\,cm^2\,mol\,L^{-1}$

2.4. *Crystal structure determination*

Crystals of **3** were grown by slow evaporation of a solution in chloroform. Data were collected with an Oxford Diffraction Gemini R CCD area detector using *CrysAlisPro* software and graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 200(2) K. The structure solution and refinements were made by SHELXS 97 [51]. Hydrogens were placed in their calculated positions and included in the refinement using the riding mode. An absorption correction was performed using *CrysAlis RED* and all

calculations were performed using SHELXTL 2000 [52]. ORTEP-3 [53] was used to prepare the molecular drawings.

2.5. *DNA binding studies*

Experiments involving interaction of the complex with CT-DNA were carried out in doubly distilled water buffer containing 5.0 mmol L^{-1} *tris* [*tris*(hydroxymethyl)-aminomethane] and 50 mmol L^{-1} NaCl and adjusted to pH 7.2 with hydrochloric acid. Solution of CT-DNA gave ratios of absorbance at 260 and 280 nm of about 1.8–1.9, indicating that the DNA was free of protein contamination [54]. The DNA concentration per nucleotide was determined spectrophotometrically by employing a molar absorption coefficient of 6600 $(\text{mol L}^{-1})^{-1}\,\text{cm}^{-1}$ at 260 nm after 1 : 100 dilution [55]. The complex was dissolved in 1% DMSO and 99% *tris*-HCl buffer (5.0 mmol L^{-1} *tris*-HCl, 50 mmol L^{-1} NaCl, pH 7.2) at 3.0×10^{-5} mol L^{-1}. An absorption titration was performed on 30 μmol L^{-1} compound by varying the concentration of nucleic acid. While measuring the absorption spectra, an equal amount of CT-DNA was added to both the compound solution and the reference solution to eliminate absorbance of CT-DNA itself. Titration curves were constructed from the fractional change in the absorption intensity as a function of DNA concentration. The intrinsic binding constant, K_b of complex with CT-DNA was determined according to the following equation [56] through a plot of [DNA]/($\varepsilon_a - \varepsilon_f$) *versus* [DNA].

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

where [DNA] is the concentration of DNA in base pairs, the apparent absorption coefficients ε_a, ε_f, and ε_b correspond to A_{observed}/[Cu], the extinction coefficient for the free copper complex and the extinction coefficient for the bound copper complex, respectively. In plots of [DNA]/($\varepsilon_b - \varepsilon_f$) *versus* [DNA], K_b is given by the ratio of the slope to intercept.

For cyclic voltammetry, the supporting electrolyte was 50 mmol L^{-1} NaCl, 5 mmol L^{-1} *tris*, pH 7.2. The aqueous Ag/AgCl reference electrode was filled with filling solution containing 3 mol L^{-1} NaCl and saturated AgCl.

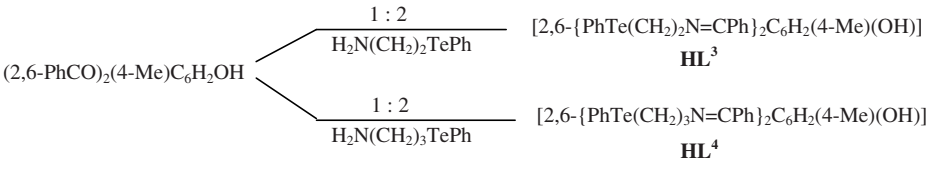
3. Results and discussion

3.1. *Synthesis and properties of the Schiff bases*

The monoprotic hybrid acyclic ligands **HL^3** and **HL^4** were synthesized *via* one-step dipodal condensation of 4-methyl-2,6-dibenzoylphenol with appropriate phenyltellurato(alkyl)amine in 1 : 2 molar ratio in acetonitrile and isolated as yellow viscous liquids (scheme 1).

The mass spectra of **HL^3** and **HL^4** exhibit the molecular ion corresponding to [2,6-{$PhTe(CH_2)_2N{=}CPh\}_2C_6H_2$(4-Me)(OH)] and [2,6-{$PhTe(CH_2)_3N{=}CPh\}_2C_6H_2$(4-Me)(OH)], respectively.

The IR spectrum of **HL^3** shows an absorption at 1598 cm^{-1} and that of **HL^4** at 1577 cm^{-1} due to ν(C=N). The vibration at 3441 cm^{-1} is due to ν(OH) and appears almost at the same position as in the precursor 4-methyl-2,6-dibenzoylphenol.



Scheme 1. Preparation of ligands.

Table 1. CV data of a 0.1 mmol L^{-1} solution of HL^3 and HL^4 in CH_3CN/0.1 mol L^{-1} NBu_4ClO_4 at a platinum electrode *vs.* Ag/0.1 mol L^{-1} $AgNO_3$ at different scan rates.

Compounds	Scan rate	E_{pa} (V)	i_{pa} (μA)	E_{pc} (V)	i_{pa} (μA)
HL^3	100	0.176	05.95		
	200	0.188	25.09		
	300	0.194	37.17		
	400	0.200	47.02		
	500	0.194	55.15		
HL^4	100	0.230	8.81	0.825	−44.43
	200	0.225	29.72	0.830	−61.32
	300	0.205	52.04	0.955	−93.85
	400	0.200	73.44	0.995	−116.80

Electronic absorption spectra of ligands consist of an intense band at 423–429 cm^{-1} attributable to charge transfer from phenolate oxygen to phenyl [57]. The π–π^* transitions associated with azomethine chromophore [58] may also be responsible for this band.

^{1}H-NMR spectra exhibit a significant downfield shift of phenolic OH (signals between 16.01 and 16.26 ppm) in comparison to mdbpH (δ 12.2 ppm) due to intramolecular hydrogen bonding between the benzimidoyl nitrogen and the phenolic OH [59, 60]. In fact, the downfield in them is more and so the intramolecular hydrogen bonding is greater, than in the corresponding selenium analogs (δ 15.9 ppm) [47].

The cyclic voltammogram of HL^3 (Supplementary material; table 1) shows one irreversible oxidation at 0.190 V whereas HL^4 exhibits one quasi-reversible oxidation at 0.558 V *versus* Ag/0.1 mol L^{-1} Ag^+ with 100–500 mV s^{-1} scan rates. The peak separation, ΔE_p, in HL^4 varies as a function of scan rate. Also the ratio of peak current ($i_{pa}/i_{pc} = 0.45$) is less than 1.0, which indicates that electron transfer is followed by a slow chemical reaction. Under similar experimental conditions, the observed oxidation potentials in tellurium-bearing ligands are shifted to more negative potentials than selenium analogs (0.778 V (HL^1), 0.567 V (HL^2)). These observations suggest that tellurium bearing ligands are more sterically hindered than selenium analogs, consistent with X-ray observations.

3.2. *Properties of 3 and 4*

The addition of methanolic solution of copper acetate monohydrate to HL^3 and HL^4 in 1 : 2 molar ratio resulted in precipitation of air stable blue **3** and **4** (scheme 2).

$$2[2,6\text{-}\{PhTe(CH_2)_nN{=}CPh\}_2C_6H_2(4\text{-}Me)(OH)] + Cu(OCOCH_3)_2{\cdot}H_2O \xrightarrow{MeOH}$$

$$[(C_6H_2(O)(4\text{-}Me)\{PhC{=}N(CH_2)_nTePh\}PhCO)_2Cu] + 2PhTe(CH_2)_nNH_2 + 2\,CH_3COOH$$

n=2, **3** ; n=3, **4**

Scheme 2. Preparation of the complexes.

The analytical data (sections 2.3.1 and 2.3.2) of the complexes suggest their formulation as $[(C_6H_2(O)(4\text{-Me})\{PhC{=}N(CH_2)_nTePh\}PhCO)_2.Cu]$; $n=2$, **3**; $n=3$, **4**. The formula of the complexes indicates hydrolysis of one arm of the ligands at C=N and release of acetic acid due to combination of an acetate with phenolic proton of the ligands. The complexes are non-electrolytes, as suggested by conductivity data.

Mass spectra of **3** and **4** exhibit a molecular ion peak corresponding to a mass of double the hydrolyzed ligand plus one Cu(II), suggesting complexes of 2 : 1 ligand to metal stoichiometry. Absorptions at 1654 (**3**) and 1664 cm^{-1} (**4**) in IR spectra can be due to ν(C=O) which are almost at the same position as in the precursor 4-methyl-2,6-dibenzoylphenol. Further, a band at 1533 cm^{-1} in both complexes may be due to ν(C=N). The appearance of ν(C=O) as well as ν(C=N) suggests cleavage of one arm of the ligand due to hydrolysis at C=N during complexation. The unchanged position of ν(C=O) in spectra suggest non-involvement of benzoyl oxygen in coordination. However, the ν(C=N) band shows a red shift of 44–66 cm^{-1} which may be attributed to participation of azomethine nitrogen in coordination [61]. Further, the absence of ν(OH) in the spectra indicates deprotonation of phenolic proton and bonding of phenolic oxygen with copper. Appearance of medium intensity bands at 570 cm^{-1} and 440–437 cm^{-1} for both complexes is due to ν(Cu–N) and ν(Cu–O), respectively [61].

Electronic spectra of paramagnetic Cu(II) complexes in CH_3CN show only one band in the 613–639 nm region other than charge transfer at higher frequency. This band is $e_g \rightarrow b_{1g}$ transition characteristic of a distorted square planar geometry [62, 63].

Thus, the spectroscopic data suggest that the two molecules of the partially hydrolyzed ligand coordinate through azomethine N and phenolic O to one Cu(II) to give N_2O_2 coordination with two stable six-membered rings around Cu(II). The structure is confirmed by the spectroscopic data and a single crystal X-ray study.

3.3. *Crystal structure of 3*

The molecular structure (figure 1) and the crystal data (tables 2 and 3) of **3** show that, like **1**, it has no molecular symmetry. The two monoanionic ligands are bidentate coordinating through imido nitrogen and phenolic oxygen with nitrogen donors and phenolic oxygen donors *trans* to each other. The replacement of Se by the larger Te results in significant changes in the overall shape of the molecule. The phenyl groups attached to Se in **1** stick out on either side whereas in **3** they are folded over in the same direction. The distortions from square planar toward tetrahedral geometry are common with Cu(II)N_2O_2 complexes when there are interactions within or between bulky ligands [64]. The mean Cu–N and Cu–O distances in **3** [1.996(17), 1.878(14) Å] differ significantly from those in **1** [1.973(3), 1.898(2) Å] and the O–Cu–O and N–Cu–N

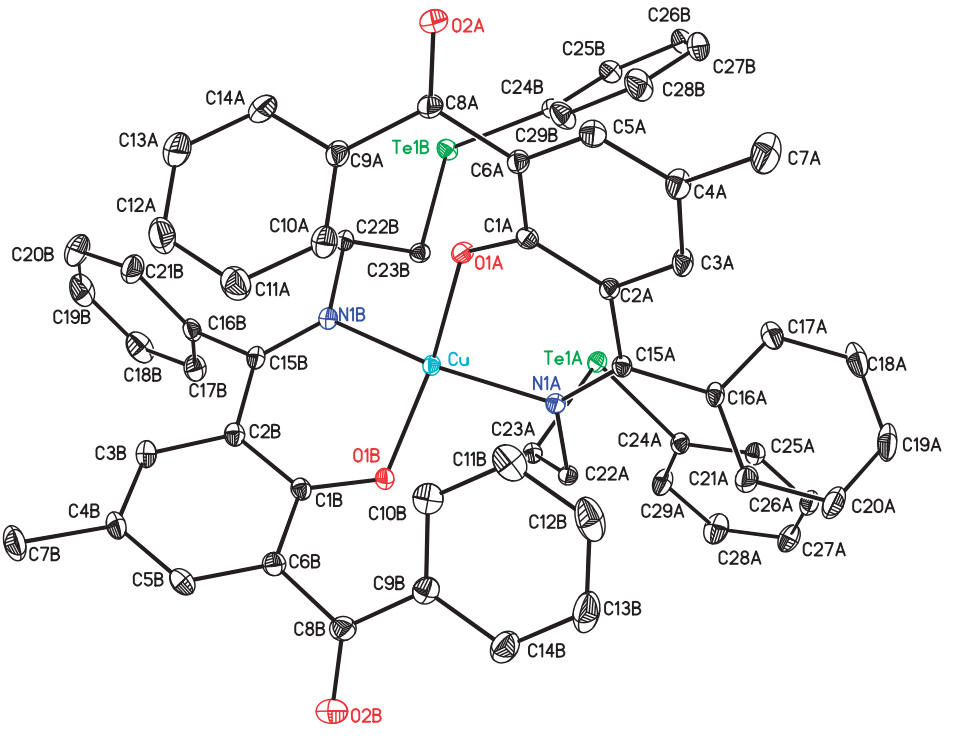


Figure 1. Molecular structure of **3**.

angles in **3** [160.4(6), 152.5(7)] are smaller than those in **1** [167.4(11), 164.5(12)°]. Complex **3** is more distorted from square planar toward tetrahedral geometry than **1**. Pulkkinen *et al*. [65] suggested that ring–ring interactions affect the crystal packing and this in turn affects coordination at copper. The distortion toward tetrahedral geometry is in general associated with longer Cu–N and Cu–O bonds; however, in this case, it is associated with longer Cu–N but smaller Cu–O bonds in a *trans* configuration. Intraligand steric interactions are enhanced by replacement of Se by the larger Te, shown by narrowing of the angle C–Se/Te–C at the chalcogen by the usual inert pair (relativistic) effect [cf C–Se–C 100°, 99°; CTe–C 94°, 97°]. Further, there are significant differences in the C–C–Se–C and C–C–Te–C torsion angles [cf 60°, 61° (**1**); 105°, 84° (**3**)] which suggest that distortions are driven by steric interactions in the ligand system.

3.4. *Electrochemical studies*

Cyclic voltammetric (CV) data (tables 4 and 5) for **3** and **4** have been collected in 0.1 mmol L^{-1} solution of CH_3CN/0.1 mol L^{-1} $[NBu_4][ClO_4]$ under nitrogen with 50–400 mV s^{-1} scan rates; potentials are reported with reference to Ag/0.1 mol L^{-1} Ag^+. In the cyclic voltammograms of **3** and **4** (Supplementary material), quasi-reversible waves at $E_{pc} - 0.857$ V, $E_{pa} - 1.368$ V for **3** and $E_{pc} - 0.826$ V, $E_{pa} - 1.473$ V

Table 2. Crystal data and structure refinement for **3**.

Empirical formula	$C_{58}H_{48}CuN_2O_4Te_2$
Formula weight	1155.72
Temperature (K)	200(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	*C* 2/*c*
Unit cell dimensions (Å, °)	
a	1232(13)
b	13.9603(4)
c	20.0461(6)
α	90
β	105.694(4)
γ	90
Volume (Å^3), *Z*	10001.6(5), 8
Calculated density (Mg m^3)	1.535
Absorption coefficient (mm^{-1})	1.629
F(000)	4600
Crystal size (mm^3)	$0.52 \times 0.47 \times 0.18$
q range for data collection (°)	4.63–34.86
Index ranges	$-59 \le h \le 40$; $-19 \le k \le 22$; $-31 \le l \le 30$
Reflections collected	46999
Independent reflections	20,078 [R(int) = 0.0395]
Completeness to $q = 25.00$ (%)	99.1
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.58997
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	20,078/0/604
Goodness-of-fit on F^2	0.909
Final R indices [$I > 2s(I)$]	$R_1 = 0.0441$, $wR_2 = 0.0837$
R indices (all data)	$R_1 = 0.1000$, $wR_2 = 0.0951$
Largest difference peak and hole (e Å^{-3})	1.814 and −0.651

for **4** *versus* Ag/Ag^+ are observed. These are attributed to Cu^{II} to Cu^{I} reduction [66]. The cathodic peak potential values for **3** and **4** [−0.857 V, −0.826 V] being more positive than those of **1** and **2** [−1.422 V, −1.550 V] suggest that copper in **3** and **4** has greater distortion, consistent with the X-ray structure. The electrochemical behavior of **3** and **4** has also been studied on glassy carbon working electrode (table 5), where observed reduction potentials [−0.778 V; −0.304 V for **3** and **4**] are more positive compared to those with platinum working electrode [−0.857 V; −0.826 V]. This suggests that reduction of Cu(II) to Cu(I) is faster on the glassy carbon electrode surface as compared to that on the platinum electrode.

3.5. *DNA-binding properties of 3 and 4*

3.5.1. Electronic absorption spectra. Complexes binding with DNA through intercalation usually result in hypochromism and bathochromism due to intercalative mode involving a strong stacking intercalation between an aromatic chromophore and the DNA base pairs. The extent of the hypochromism commonly parallels the intercalative strength. Absorption spectra (figure 2) of **3** and **4** have been studied in the absence or

Table 3. Selected bond lengths (Å) and angles (°) for **3**.

Bond lengths	
Te(1A)–C(24A)	2.116(3)
Te(1A)–C(23A)	2.150(2)
Te(1B)–C(24B)	2.113(2)
Te(1B)–C(23B)	2.154(2)
Cu–O(1B)	1.8658(16)
Cu–O(1A)	1.8834(16)
Cu–N(1B)	1.988(2)
Cu–N(1A)	1.995(2)
O(1A)–C(13A)	1.320(3)
O(2A)–C(7A)	1.214(3)
O(1B)–C(13B)	1.307(3)
O(2B)–C(7B)	1.211(3)
N(1A)–C(15A)	1.291(3)
N(1A)–C(22A)	1.482(3)
N(1B)–C(15B)	1.294(3)
N(1B)–C(22B)	1.476(3)
Bond angles	
C(24A)–Te(1A)–C(23A)	97.19(10)
C(24B)–Te(1B)–C(23B)	93.72(9)
O(1B)–Cu–O(1A)	160.43(8)
O(1B)–Cu–N(1B)	91.67(8)
O(1A)–Cu–N(1B)	95.26(8)
O(1B)–Cu–N(1A)	90.97(8)
O(1A)–Cu–N(1A)	91.26(8)
N(1B)–Cu–N(1A)	152.54(8)
C(15A)–N(1A)–Cu	124.41(17)
C(22A)–N(1A)–Cu	114.06(16)
C(15B)–N(1B)–Cu	125.87(16)
C(22B)–N(1B)–Cu	112.48(15)

Table 4. CV data of 0.1 mmol L^{-1} solutions of **3** and **4** in CH_3CN/0.1 mol L^{-1} NBu_4ClO_4 at a platinum electrode *vs.* Ag/0.1 mol L^{-1} $AgNO_3$ at different scan rates.

Complexes	Scan rate	E_{pa}/V (i_{pa})/μA	E_{pc}/V (i_{pc})/μA	ΔE_p (mV)	$E^{\circ\prime}$ (V)
3	50	−1.304 (11.52)	−1.004 (−4.98)	300	−1.154
	100	−1.310 (10.49)	−0.968 (−12.25)	342	−1.139
	200	−1.370 (41.88)	−0.812 (−10.46)	558	−1.091
	300	−1.406 (54.69)	−0.776 (−16.83)	630	−1.091
	400	−1.454 (72.69)	−0.728 (−26.90)	726	−1.091
4	100	−1.480 (16.33)	−0.920 (−2.93)	560	−1.200
	200	−1.428 (27.53)	−0.824 (−11.09)	604	−1.126
	300	−1.496 (36.49)	−0.792 (−17.73)	704	−1.144
	400	−1.488 (43.07)	−0.768 (−24.59)	720	−1.128

$\Delta E_p = (E_{pa} - E_{pc})$; $E^{\circ\prime} = ½\ (E_{pa} + E_{pc})$; Supporting electrolyte, NBu_4ClO_4; Working electrode, Pt; Reference electrode, Ag/Ag^+.

presence of CT-DNA. In the presence of CT-DNA, absorption of **3** at 423 nm exhibits hypochromism of about 45% and bathochromism of about 2 nm (table 6). Complex **4** at 416 nm exhibits hypochromism of about 51% and bathochromism of 4 nm. The binding constants K_b for these complexes are 1.26×10^4 and $1.0 \times 10^4\,(\text{mol L}^{-1})^{-1}$, respectively, quite comparable to other Schiff-base square

Table 5. CV data of 0.1 mmol L^{-1} solutions of **3** and **4** in CH_3CN/0.1 mol L^{-1} NBu_4ClO_4 at a glassy carbon electrode *vs.* Ag/0.1 mol L^{-1} $AgNO_3$ at different scan rates.

Complexs	Scan rate	E_{pa} (V)	i_{pa} (μA)	E_{pc} (V)	i_{pc} (μA)
3	100	−1.664	24.24	−1.034	−1.826
	200	−1.636	32.95	−1.006	−3.809
	300	−1.125	13.10	−0.537	−11.22
	400	−1.104	15.26	−0.536	−10.70
4	100	−1.280	16.14	−0.536	−7.172
	200	−1.4567	26.69	−0.280	−19.28
	300	−1.648	34.27	−0.272	−25.62
	400	−1.712	41.26	−0.128	−24.26

Table 6. Absorption spectroscopic data of **3** and **4** upon addition of CT-DNA.

	λ_{max} (nm)				
Complexes	Free	Bound	Δλ	Hypochromism[a] (%)	Binding constant, K_b (M^{-1})
3	423	425	2	45	1.26×10^4
4	416	420	4	51	1.00×10^4

[a]Hypochromism $= [(A_{free} - A_{bound})/A_{free}] \times 100\%$.

planar Cu(II) complexes reported in the literature [67, 68]. These results suggest an association of the compounds with CT-DNA *via* intercalation [69–72]. The observed binding constants for **3** and **4** are lower than that of **1** (1.46×10^4 $(mol\ L^{-1})^{-1}$). These results suggest that **1**, in comparison to **3** and **4**, binds more strongly with DNA. The higher binding affinity of selenium containing complex can be attributed to its more planar structure than the tellurium analogs [73–78] (figure 2).

3.5.2. Cyclic voltammetry. Cyclic voltammetric technique has been employed to study the interaction of the redox active Cu(II) complex with DNA to confirm the DNA binding mode suggested by the spectral studies. Typical CV (figure 3, table 7) behavior of copper complex has been studied in the absence (curve A) and presence (curve B) of CT-DNA. In the absence of CT-DNA, E_{pc} and E_{pa} are 0.180 V and −0.028 V for **3** and 0.193 V and −0.032 V for **4** *versus* Ag/AgCl. The formal potentials, $E^{\circ\prime}$ (or voltammetric $E1/2$), taken as the average of E_{pc} and E_{pa}, are 0.076 and 0.080 V, respectively. The separation of anodic and cathodic peak potentials, ΔE_p, 152 mV for **3** and 160 mV for **4**, indicates a quasi-reversible one-electron redox process [79, 80]. In the presence of 30 μmol L^{-1} DNA, at the same concentration of the complex, the E_{pc} and E_{pa} are 0.200 and −0.023 V for **3** and 0.196 and −0.026 V for **4** *versus* Ag/AgCl. Thus, the peak potentials, E_{pc} and E_{pa} as well as $E^{\circ\prime}$ (0.088 V (**3**) and 0.085 V (**4**)), are shifted to more positive values as compared to a solution without DNA. The values of ΔE_p in the presence of DNA are 177 and 170 mV, showing that reversibility of the electron transfer is maintained under these conditions. The apparent $E^{\circ\prime}$ shifts to more positive potentials by 25 and 10 mV, respectively, in the presence of DNA. In addition to

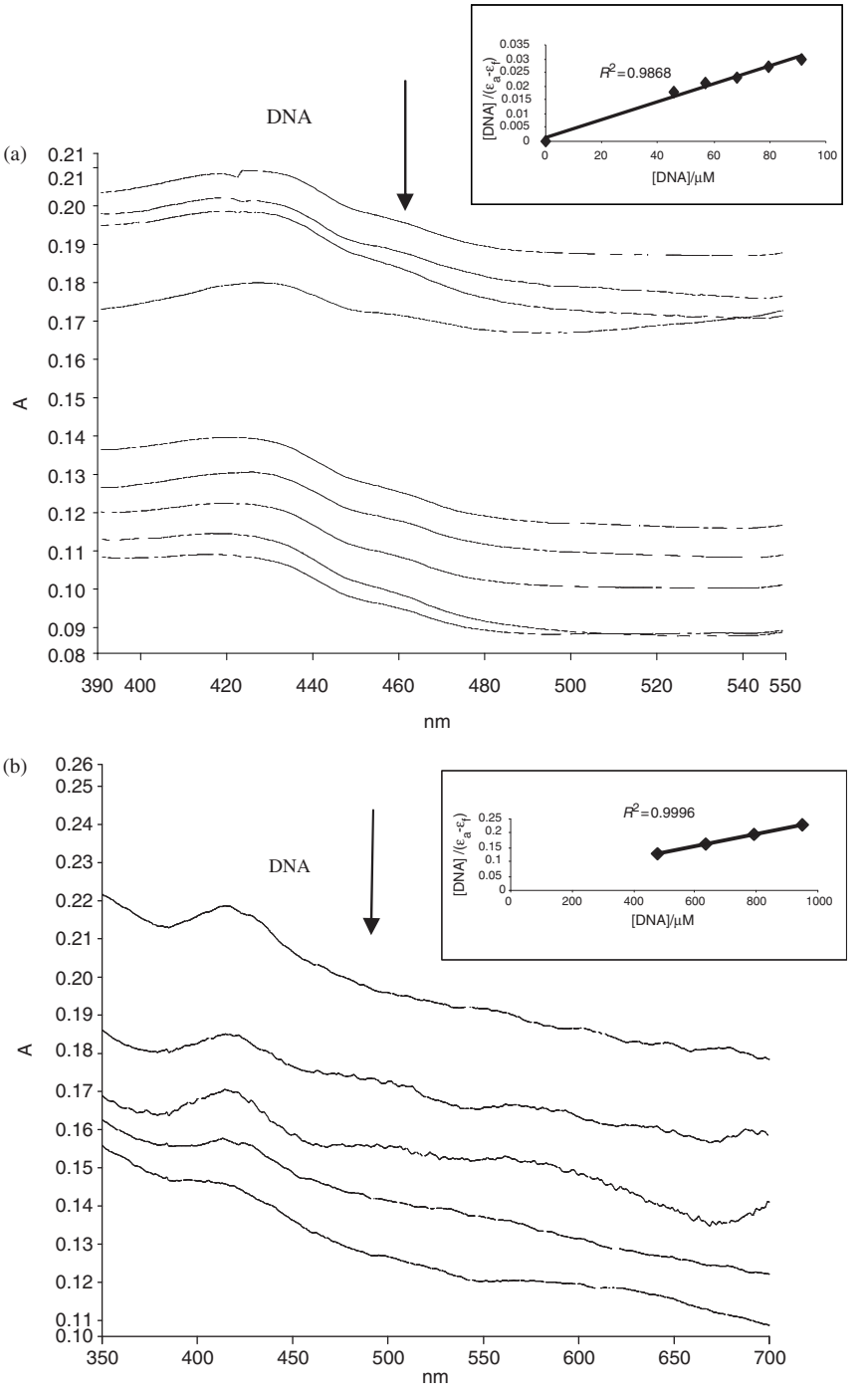


Figure 2. Absorption spectra of **3** (30 μmol L^{-1}) (a) and **4** (139 μmol L^{-1}) (b) at 7.2 pH in the presence of increasing amount of CT–DNA (0–210 μmol L^{-1}). Inset: plot of [DNA]/($\varepsilon_a - \varepsilon_f$) *vs.* [DNA] for the titration of DNA with **3** and **4**.

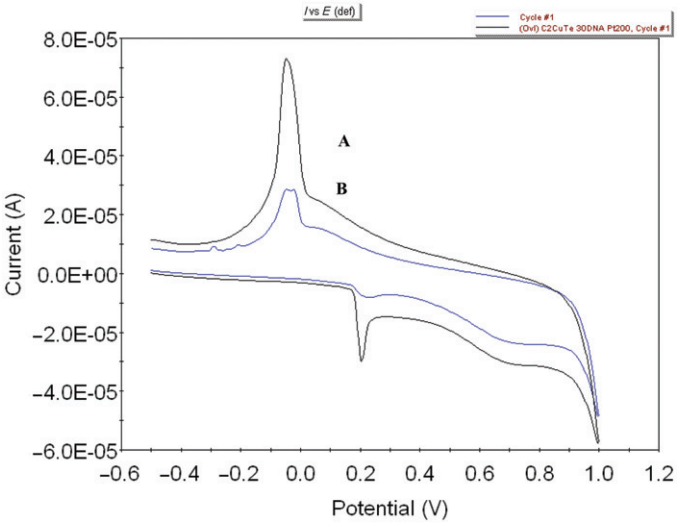


Figure 3. Cyclic voltammograms of **3** (30 μmol L^{-1}) in the absence (A) and the presence (B) of CT–DNA (90 μmol L^{-1}) in 50 mmol L^{-1} NaCl, 5 mM *Tris*, pH 7.2 at scan rate 200 mV s^{-1}.

Table 7. Cyclic voltammetric behavior of **3** and **4** in the presence of CT–DNA.

Complexes	Scan rate mV s^{-1}	R	E_{pa}/V (i_{pa})/μA	E_{pc}/V (i_{pc})/μA	ΔE_p (mV)	$E^{\circ\prime}$ (V)
3	100	0	−0.028 (33.82)	0.180 (−23.95)	152	0.076
		30	−0.023 (38.89)	0.200 (−16.20)	177	0.086
		60	−0.020 (37.11)	0.199 (−15.40)	179	0.089
		90	−0.017 (41.24)	0.199 (−17.90)	182	0.091
	200	0	−0.047 (73.52)	0.205 (−31.16)	158	0.078
		30	−0.044 (73.30)	0.208 (−30.64)	164	0.081
		60	−0.044 (77.00)	0.208 (−31.40)	164	0.082
		90	−0.041 (81.30)	0.208 (−25.50)	167	0.083
4	100	0	−0.032 (36.32)	0.193 (−31.00)	161	0.080
		30	−0.026 (36.04)	0.196 (−30.70)	170	0.084
		60	−0.026 (38.50)	0.196 (−25.10)	170	−0.085
		90	−0.023 (34.04)	0.199 (−25.60)	176	−0.087
	200	0	−0.056 (69.83)	0.199 (−48.73)	143	0.071
		30	−0.050 (71.60)	0.202 (−44.10)	152	0.076
		60	−0.050 (71.90)	0.202 (−48.70)	152	−0.075
		90	−0.050 (74.60)	0.203 (−34.35)	153	−0.076

$\Delta E_p = (E_{pa} - E_{pc})$; $E^{\circ\prime} = ½ (E_{pa} + E_{pc})$; Complex 30 μmol L^{-1}; R = [DNA]/[Complex] supporting electrolyte, 50 mmol L^{-1} NaCl + 5 mmol L^{-1} *Tris*, pH 7.2; Working electrode, Pt; Reference electrode, Ag/AgCl.

changes in formal potential upon addition of DNA, the cathodic peak current, i_{pc}, decreased to 33% for **3** and 13% for **4** compared to that in the absence of DNA for a solution with $R = 30$ (100 mV s^{-1}). Similar observations have recently been reported in the literature [67, 68]. Bard and co-workers [79] suggested that the electrochemical potential of small molecules would shift in a positive direction when intercalated into DNA and it would shift in a negative direction if bound to DNA by electrostatic interaction. Thus, the observed results imply that **3** and **4** bind to DNA by intercalation involving stacking interaction between the aromatic chromophore of the complex and the base pairs of DNA.

4. Conclusion

HL^{3} and **HL**^{4} have been synthesized by single step dipodal condensation of 4-methyl-2,6-dibenzoylphenol with the appropriate phenyltellurato(alkyl)amine in 1 : 2 molar ratio. The reactions of these ligands with copper acetate monohydrate result in partial hydrolysis of ligands and formation of $[(C_6H_2(O)(Me)\{(C_6H_5)C{=}N(CH_2)_n Te(C_6H_5)\}(C_6H_5)C{=}O)_2Cu]$; $n = 2$ (**3**); 3 (**4**). The partially hydrolyzed monoanionic ligands are bidentate coordinating through the imido N and phenolic O to one Cu(II) to give N_2O_2 coordination. The X-ray structure of **3** suggests that it is more distorted from square planar toward tetrahedral than is **1**. In cyclic voltammetry, a quasi-reversible reduction peak from −0.857 to −0.826 V (*vs.* Ag/Ag^+) is assigned to the Cu(II)/Cu(I) couple. The cathodic peak potential value for **3** and **4** being more positive than those of their selenium analogs **1** and **2** suggests that the copper is somewhat more distorted, consistent with the X-ray structures. Binding of the complexes to CT-DNA has been investigated by absorption and cyclic voltammetric measurements, which indicate that the complexes can intercalate into DNA base pairs; the binding affinity of selenium containing complex is higher than for tellurium analogs.

Supplementary material

CCDC 739452 contains the supplementary crystallographic data for **3**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 123-336-033; or E-mail: deposit@ccdc.cam.ac.uk. Figures of cyclic voltammogram of the ligands (**HL**^{3} and **HL**^{4}) and complexes (**3** and **4**) can be found in the online supplementary material at informaworld.com

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