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Synthesis, crystal structure and *in vitro* anticancer studies of bis(dibenzyldithiocarbamato)Zn(II)

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ABSTRACT

Bis(dibenzyldithiocarbamato)Zn(II), [Zn(dbzdtc)$_2$], was synthesized and characterized by spectroscopic techniques, elemental analysis and single crystal X-ray crystallography. The compound is crystallized in a monoclinic space group $P2_1/n$ with Zn(II) located on crystallographic twofold symmetry and coordinated to two molecules of dibenzyl dithiocarbamato anions to form a rare four-coordinate mononuclear Zn(II) complex in a see-saw geometry. The cytotoxicity of the complex was evaluated by MTT assay against breast cancer cells (MCF-7) and human embryonic kidney cells (HEK293). The results showed that the complex is active against MCF-7 breast cancer cells with IC_{50} value of 6.41 and 4.423 μM against HEK293 cell line.

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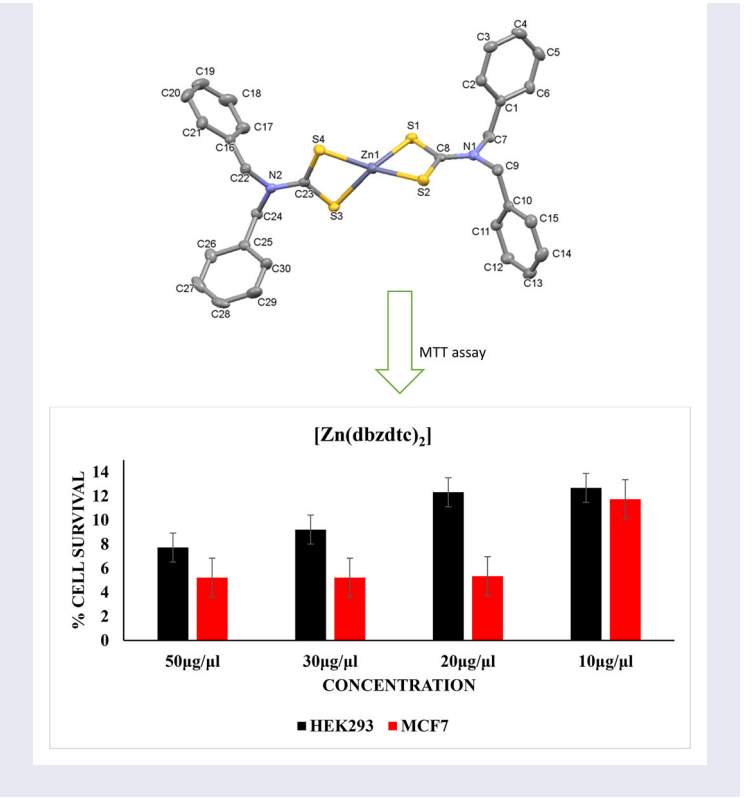

1. Introduction

There is an urgent need to develop metal complexes as novel chemotherapeutic agents as alternative to cisplatin and its derivatives due to their toxic side effects and inherent resistance [1–3]. The evolution of therapeutic drugs using metals such as zinc, iron, copper, palladium or ruthenium [4] is the main objective of bio-inorganic medicinal chemistry research. Metal complexes of chelating ligands such as N,S-amino-thioether [5], N-N-diamines [6], dicarboxylic acids [7], sulfonamide [8] and dithiocarbamate [9] are explored as potential anticancer agents. Among these compounds, sulfur containing compounds are receiving attention due to their resemblance to biomolecules such as vitamins and amino acids, which enhances the transportation of the drugs to the target cells [10]. Organosulfur ligands such as dithiocarbamate have received attention due to the ability of the dithiocarbamates to coordinate metal ions in different oxidation states [11]. Dithiocarbamate transition metal complexes of copper(II), zinc(II), manganese(II), cobalt(II) and ruthenium(II) have been studied as potential anticancer agents [12–16]. Zinc is one of the trace elements required for DNA stabilization, cell proliferation, enzyme and immune system function due to its low toxicity and excellent biocompatibility [17]. Thus, research on zinc(II) dithiocarbamate biological activity is of importance.

Shiri *et al.* [18] prepared 5-dithiocarbamato-1,3,4-thiadiazole-2-thiol and its Zn(II) complex, which was screened for anticancer activity against MCF-7 cells. The results

showed that the ligand had no noticeable cytotoxic effects when compared to the complex, which suggests that cytotoxic effects are enhanced upon complexation with the metal ion [19]. Singh *et al*. [19] screened a series of Zn(II) binuclear dithiocarbamate complexes against the hepatoma (HepG2) cell line. The screened compounds had better activity compared to cisplatin and shrinkage of the cells was observed due to apoptosis inducing ability of the compounds [19]. Maurya *et al*. [20] reported functionalized dithiocarbamate Zn(II) complexes activity as antibacterial, antibiofilm and antitumor agents; the compounds showed better antibacterial activity. Zn(II) complexes have been reported to have antiproliferative effects on various cancer cells [16, 18] and tumorigenesis effect due to dosage concentration [19]. Also, Zn(II) complexes have been used as photodynamic therapeutic agents [20] and carrier conjugates to target cells [21]. Another interesting attribute of Zn(II) dithiocarbamate is the ability to exist in diverse structural geometries [22]. Zinc(II) bis(dithiocarbamate) complexes are mostly dimeric with distorted octahedral, tetrahedral, trigonal–bipyramidal or square–-pyramidal geometry [10, 14, 19, 23–31]. Monomeric configuration is possible in rare cases that are most often reported as distorted tetrahedral geometry [22, 32–34]. In this study, we report the synthesis, spectroscopic characterization and crystal structure of a mononuclear bis(dibenzyldithiocarbamato)Zn(II) complex in a see-saw geometry and its cytotoxic evaluation against human cancer cell (MCF-7) line and human embryonic kidney cells (HEK293) using cisplatin as a standard.

2. Experimental

2.1. Materials and physical measurements

All chemicals and reagents were used as received. Dibenzylamine, sodium hydroxide, ethanol, CS_2, methanol and DMSO were obtained from Sigma-Aldrich (St. Louis, MO, USA) and Merck (Darmstadt, Germany). ^{1}H and ^{13}C NMR spectra were recorded on 400 and 100 MHz Bruker NMR spectrometers, respectively. Elemental analysis (C, H, N and S) was carried out using a Thermoscientific Flash 2000. Infrared spectra were obtained with an Agilent Technologies Cary 630 FTIR spectrophotometer from 4000 to 600 cm^{-1} using the KBr disk method. Mass spectra were recorded on a LC Premier micro-mass spectrometer and UV–Vis spectra were recorded on a Perkin-Elmer Lambda 25 UV–Vis spectrophotometer.

2.2. Synthesis of ligand and complex

2.2.1. Synthesis of dibenzyldithiocarbamato sodium salt, Na(dbzdtc)

Dibenzyldithiocarbamato sodium salt Na(dbzdtc) was prepared based on a literature [14] procedure with slight modification. Sodium hydroxide (0.05 mol) was dispersed in 10 mL of ethanol and kept at 0 °C. Dibenzylamine (0.05 mol) was added to the ice-cold mixture at 0 °C and stirred for 30 min before adding 3 mL of cold CS_2 (0.5 mol) slowly. The reaction was left to stir for 3 h while maintaining the temperature. The product was filtered and dried. Yield: 8.1189 g, (54%), m.p.t (°C) 123.3–124.8. Selected IR, (cm^{-1}): υ(C-N) 1443, υ(C_2-N) 1346, υ(C-S)$_{Asym}$ 1144, υ(C-S)$_{Sym}$ 969. ^{1}H NMR (D_2O) δ/ppm = 7.33–7.49 (m, C_6H_5), 5.42 (s, CH_2), ^{13}C NMR (D_2O) $\delta = 212.58$ (CS_2),

126.96–128.83 ppm, 136.79 ppm (C), 59.63 ppm (CH_2). MS: *m/z* [M^+] 272.1446. UV–Vis $\pi \rightarrow \pi^*$ (NCS) 261 nm, $\pi \rightarrow \pi^*$ (SCS) 287 nm.

2.2.2. Synthesis of bis(dibenzyldithiocarbamato)Zn(II) complex, [Zn(dbzdtc)$_2$]

[Zn(dbzydtc)$_2$] was prepared using a modified literature method [35]. $ZnCl_2$ (5 mmol) was dissolved in water and added to 10 mmol aqueous solution of the sodium salt of dibenzyldithiocarbamate. A white precipitate immediately formed; the reaction mixture was stirred for 2 h at room temperature. The product was filtered, washed with water–methanol (1:2 ratio) and dried at room temperature. Yield: 2.3173 g (78.5%), m.p.t (°C) 186–193, Anal. Calcd. for $C_{30}H_{28}N_2S_4Zn$ (%): C, 59.05; H, 4.63; N, 4.59; S, 21.02. Found: C, 58.67; H, 4.79; N, 4.54; S, 21.35. Selected IR, (cm^1): υ(C-N) 1482, υ(C-S) 941. ^{1}H NMR (DMSO-d_6) δ/ppm = 5.08 ppm (s, CH_2), 7.33–7.39 ppm (m, C_6H_5) and ^{13}C NMR (DMSO-d_6) δ/ppm = 56.07 ppm (CH_2), 128.39–127.24 ppm (CH), 135.29 ppm (CS_2), 206.82 ppm. Mass spec M^+ 414.0539 *m/z* UV–Vis MLCT-285 nm. Recrystallization of the complex in DCM/hexane gave clear crystals suitable for X-ray analysis.

2.3. Crystal structure determination and structure refinement

Single yellow block-shaped crystals of [Zn(dbzdtc)$_2$] were recrystallized from DCM/hexane solution by slow evaporation. A Bruker SMART APEX2 area detector diffractometer was used to collect the crystal data at $T = 100$ K. ShelXS-2013 [36] was used for space group ($P2_1/c$ (# 14)) identification. The structure was solved and refined by least squares minimization with ShelXL-2016/6 [37]. All non-hydrogen atoms were refined anisotropically. Hydrogen positions were calculated geometrically and refined using the riding model.

2.4. In vitro anticancer activity

Cytotoxicity assay of [Zn(dbzdtc)$_2$] in comparison with cisplatin was analyzed using MTT (3-(4,5-dimethylthiozol-2yl)-2,5-diphenyltetrazolium bromide) assay adapted from the reported protocol [38]. MCF-7 and HEK293 cells were seeded at a density of 2×10^3 cells per well grown in 96-well microtiter plates in growth medium (100 μL) and incubated for 24 h at 37 °C. After which the growth medium was substituted with a fresh medium of the complex prepared in DMSO at different concentrations (50, 30, 20 and 10 μg/mL^{-1}). The cells were then treated with the complex for 48 h at 37 °C in triplicate, followed by addition of the incubation growth medium (100 μL) containing 10 μL MTT salt solution (5 mg/mL in PBS) and cells were incubated for 4 h at 37 °C. DMSO (100 μL) was added after the removal of medium-MTT solution. Cell survival was measured by absorbance of each well at 540 nm. The experiment controls were also screened against human embryonic kidney cancer cell HEK293 and human breast cancer cell MCF-7.

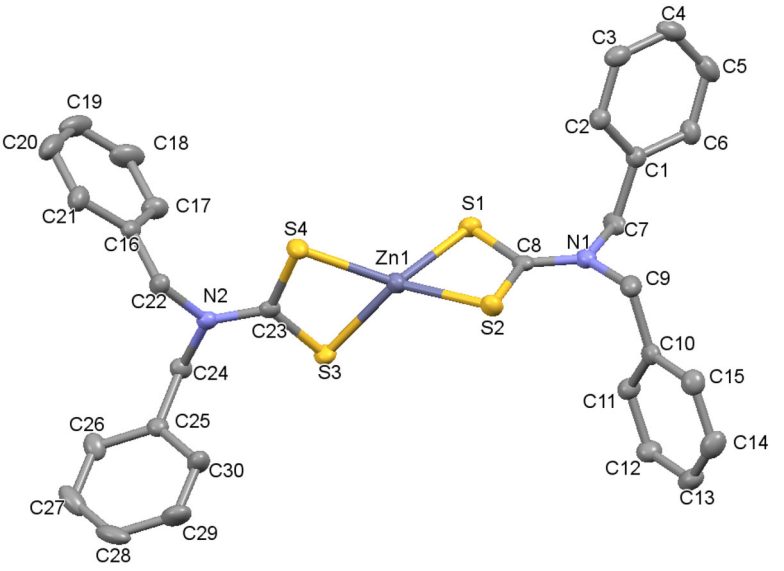

Figure 1. Molecular structure of bis(dibenzyldithiocarbamato)Zn(II) complex.

3. Results and discussion

3.1. Synthesis

In this study, the ligand was synthesized by reaction of dibenzylamine with CS_2 and sodium hydroxide at low temperature. The white solid obtained was stable and soluble in water, ethanol and methanol. Reaction of two molar equivalents of dibenzyl dithiocarbamate ligand with one equivalent of zinc(II) chloride gave the Zn(II) dithiocarbamate complex in high yield. The complex was soluble in dichloromethane and DMSO. Mass spectrometry of the ligand gave M^+ of 272.1446 *m/z* and 414.0539 *m/z* for the complex, indicating a metal to ligand ratio of 1:2.

3.2. Molecular structure of [Zn(dbzdtc)$_2$]

The molecular structure of [Zn(dbzdtc)$_2$] is shown in Figure 1. Crystal data and structure refinement are presented in Table 1, while selected bond lengths and angles are shown in Table 2. [Zn(dbzdtc)$_2$] adopted a four-coordinate mononuclear structure in which the Zn(II) ion is coordinated to two symmetrical dibenzyl dithiocarbamate anions. The compound crystallized in the least common monomeric structure of Zn(II) dithiocarbamate [22, 32–34] due to the steric hinderance imposed on the molecule by the bulky dibenzyl groups.

Most reports on the crystal structures of Zn(II) dithiocarbamate complexes indicate they are dimeric or with zinc in a five-coordinate geometry [25, 39, 40]. Decken *et al.* [41] reported the crystal structure of bis(*N*,*N*-dibenzyldithiocarbamato)zinc(II), [Zn(bzydtc)$_2$] as a *Pbcn* orthorhombic system but the current compound crystallizes in a monoclinic system with a space group $P_{21/C}$. The bond lengths of Zn-S1 (2.3629(3) Å) and Zn-S2 (2.3312(3) Å) [41] were slightly different from this current compound with Zn-S1 (2.3459(4) Å) and Zn-S2 (2.3355(4) Å). The Zn—S bond lengths [2.3573(4),

Table 1. Crystal data and structure refinements of bis(dibenzyldithiocarbamato) Zn(II).

Compound	$[Zn(dbzdtc)_2]$
Formula	$C_{30}H_{28}N_2S_4Zn$
Dcalc./g cm^{-3}	1.433
μ/mm^{-1}	1.187
Formula weight	610.15
Color	Yellow
Shape	Block
Size/mm^3	$0.34 \times 0.18 \times 0.12$
T/K	100
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	13.1994(7)
b/Å	9.2486(5)
c/Å	23.1722(13)
α/°	90
β/°	91.830(2)
γ/°	90
V/Å^3	2827.3(3)
Z	4
Z′	1
Wavelength/Å	0.71073
Radiation type	MoK_a
Θmin/°	1.759
Θmax/°	27.482
Measured refl.	45135
Independent refl.	6442
Reflections with $I > 2(I)$	6089
R_{int}	0.0323
Parameters	334
Restraints	0
Largest peak	0.399
Deepest hole	−0.386
GooF	1.045
wR_2 (all data)	0.0633
wR_2	0.0626
R_1 (all data)	0.0261
R_1	0.0245

Table 2. Selected bond lengths (Å) and angles (°) for bis(dibenzyldithiocarbamato)Zn(II).

Bond length		Bond angle	
Atom	Length/Å	Atom	Angle/°
Zn1-S1	2.3459(4)	S1-Zn1-S2	78.307(13)
Zn1-S2	2.3355(4)	S3-Zn1-S4	78.023(13)
Zn1-S3	2.3573(4)	S1-Zn1-S3	119.466(15)
Zn1-S4	2.3403(4)	S2-Zn1-S4	130.800(14)
S1-C8	1.7323(14)	S1-Zn1-S4	128.978(14)
S2-C8	1.7252(13)	S2-Zn1-S3	128.342(14)
S3-C23	1.7271(13)	S1—C8—S2	117.50(8)
S4-C23	1.7320(13)	S4—C23—S3	117.49(8)
N1-C8	1.3260(18)	C8—S1—Zn1	81.65(5)
N2-C23	1.3323(17)	C8—S2—Zn1	82.10(5)

2.3403(4), 2.3355(4) and 2.3459(4) Å] are almost equal and similar to reported Zn(II) dithiocarbamate monomeric complexes [22, 32–34].

The most significant difference between the reported compound by Decken *et al.* [41] and the current compound is the dithiocarbamato S—Zn—S bite angles. In the

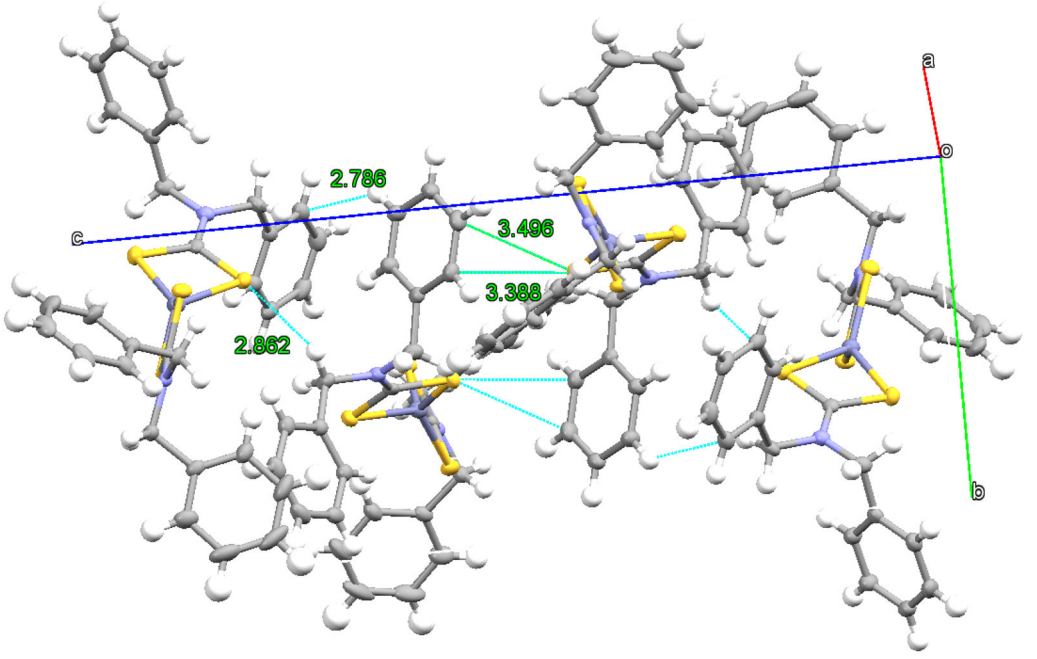

Figure 2. Packing diagram of bis(dibenzyldithiocarbamato)Zn(II).

current compound, the S1—Zn1—S2 and S3—Zn1—S4 bite angles are 78.307(13)° and 78.023(13)°, respectively, which leads to enlargement of other perinuclear angles to 119.466(15)°–130.800(14)°, consequently, deviating from the ideal 109.5° for tetrahedral geometry [25]. Whereas in the reported bis(*N*,*N*-dibenzyldithiocarbamato)zinc(II) described as distorted tetrahedral geometry, the S1–Zn–S2 (78.043(11)) and S1–Zn–S2*i* (123.975(12)) [41] bond angles are not symmetrical with one small bite angle and while the other was greater than 120°. In order to determine whether the molecular structure of the present [Zn(dbzdtc)$_2$] is tetrahedral, see-saw, square planar or trigonal pyramidal, the geometric parameter for four-coordinate compounds, τ_4 proposed by Houser *et al*. [42] which quantitatively evaluates the geometry of four-coordinate complexes was used. The geometric parameter is given by $\tau_4 = \frac{360-(\alpha+\beta)}{141}$, where α and β are the two largest θ angles. The calculated τ_4 value of 0.72 for the [Zn(dbzdtc)$_2$] indicates the molecular structure could best be described as see-saw geometry. The C—S bond ranges from 1.7252(13) to 1.7323(14) Å with a mean value of 1.7291 Å, shorter than the 1.8 Å observed in a typical C—S single bond and longer than a typical C—S double bond. This suggests that all the C—S bonds in the complex have partial double bond character common in dithiocarbamate compounds.

The bond lengths for N1—C8 and N2—C23 are 1.3260(18) and 1.3323(17) Å, respectively, which are between a typical single N—C (1.47 Å) and N—C double bond (1.28 Å) because of its partial double bond attributes, suggest the delocalization of π–electrons in the thioureide moiety [43]. The packing diagram of the complex in a unit cell viewed down the *b*-axis (Figure 2) shows four monomeric complexes within the crystal packing. The molecular packing is stabilized by C-H--S and C-H--π contacts forming a head-to-tail zigzag layer. The C-H--S contacts were 3.388, 3.496 and 2.862 Å

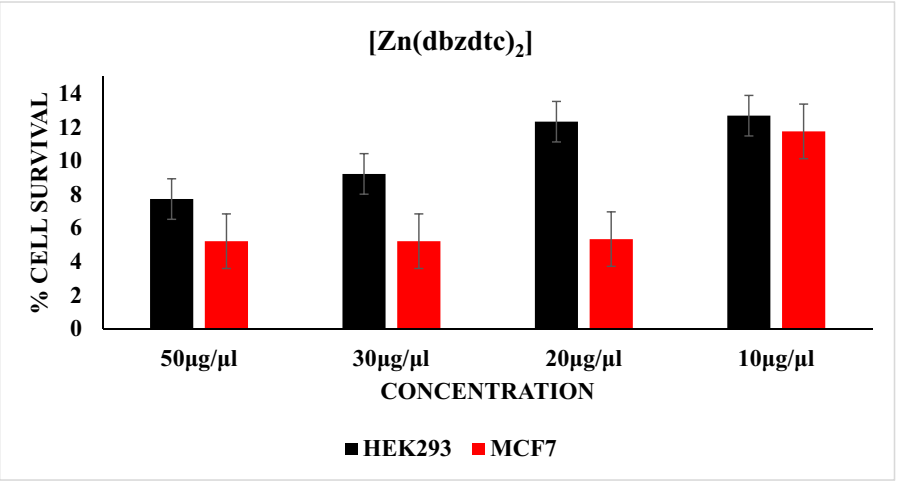

Figure 3. Cytotoxic activity of bis(dibenzyldithiocarbamato)Zn(II) against MCF7 and HEK293 cell lines.

while C-H–-π contacts were 2.786 Å. These contacts are slightly greater than those previously reported [20, 44].

3.3. Spectra studies of the dibenzyldithiocarbamate ligand and bis(dibenzyldithiocarbamato) Zn(II) complex

FTIR spectra of the ligand and complex were compared and assigned. In the FTIR spectrum of the ligand (Figure S1), the peaks at 1443 and 1346 cm^{-1} are assigned to the thiouride ν(C—N) and $\nu(C_2$—N) stretching vibrations, respectively. These vibrations indicate an electron flow from nitrogen to sulfur through a planar delocalized π-orbital system [45]. In the complex (Figure S2), there is only one band observed for ν(C—N) vibration at 1482 cm^{-1} which is shifted to higher frequency compared to the ligand and further confirms the delocalization of the thioureide moiety toward the zinc center. Two bands assigned to $\nu(C—S)_{Sym}$ and $\nu(C—S)_{Asym}$ were observed at 969 and 1144 cm^{-1} in the spectrum of the ligand but in the complex it appeared as a single band at 941 cm^{-1}, which indicates that the ligand coordinates to the metal center through the sulfurs as a bidentate ligand [46].

The ^{1}H NMR spectrum of the ligand (Figure S3) shows two peaks, one singlet at 5.42 ppm assigned to the methylene protons and a multiplet at 7.33–7.49 ppm assigned to the benzene ring protons. These peaks shifted to 5.08 ppm for the methylene protons and 7.35–7.41 ppm for benzene ring protons for the complex (Figure S4). The observed shifts are due to the coordination to Zn(II). The ^{13}C NMR spectrum of the ligand (Figure S5) shows a peak at 56.32 ppm which could be assigned to methylene group carbon bonded to the nitrogen; this peak is observed in Figure S6 at 56.82 ppm in the complex. The peaks assigned to aryl methine carbons are observed between 128.83–126.96 for the ligand and at 127.24–128.39 for the complex. The peak for a quaternary carbon on a benzene ring is observed at 136.65 ppm on the ligand

Table 3. IC_{50} (μM) values of the complex and cisplatin against MCF7 and HEK293 cell lines.

	IC_{50} (μM)	
Compounds	MCF7	HEK293
$[Zn(dbzdtc)_2]$	6.408	4.423
Cisplatin	2.5	3.2

and at 136.03 ppm on the complex. These observed shifts are an indication of complexation. Decken *et al*. [41] synthesized bis(*N*,*N*-dibenzyldithiocarbamate) zinc(II) and found CH_2 hydrogen at 5.08 ppm and carbon at 55.7 ppm, which are not too different from the present compound.

3.4. Anticancer activity studies

The cytotoxic activity of $[Zn(dbzdtc)_2]$ was tested against MCF7 and HEK239 cell lines using MTT assay at different concentrations. Figure 3 shows the cytotoxicity to be concentration-dependent with a concentration of 10 μg/μL smallest activity against MCF7 and HEK293 cells. At other concentrations, $[Zn(bzydtc)_2]$ showed higher cytotoxicity against MCF7 cells, exhibiting considerable selectivity. Cell growth inhibition of 50% (IC_{50}) was determined by non-regression analysis using GraphPad Prism software. Table 3 presents the IC_{50} values. The IC_{50} value of the complex against MCF7 cells was 6.41 μM, showing potent cytotoxicity although it was less active *in vitro* in comparison to cisplatin. The activity of the complex against HEK293 cell line which are non-cancer cells is 4.423 μM; this is slightly less than cisplatin. This lower activity may imply that this compound may not cause severe side effects on normal cells.

4. Conclusion

Bis(dibenzyldithiocarbamato)Zn(II) was synthesized and characterized by spectroscopic techniques and single crystal X-ray crystallography. The molecular structure of the compound revealed Zn(II) bonded to two dibenzyl dithiocarbamate anions to form a four-coordinate see-saw geometry. Cytotoxic activity of the compound was tested against breast adenocarcinoma (MCF-7) cancer cell line and embryonic kidney (HEK293) cells at four different concentrations. The cytotoxicity studies reveal that the complex was less potent than cisplatin, but active against MCF-7 breast cancer cells with IC_{50} value of 6.41 and 4.423 μM against HEK293 cell line.

Disclosure statement

No potential conflict of interest was reported by the authors.

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