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Crystal and molecular structure of *bis*(*N*-(diethylcarbamothioyl)cyclohexane carboxamido)copper(II) complex

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ABSTRACT

Herein, we describe the synthesis and characterization of *bis*(*N*-(diethylcarbamothioyl)cyclohexane carboxamido)copper(II) complex, *cis*-[Cu(L-κ^2S,O)$_2$], has been prepared by the reaction of *N*-(diethyl carbamothioyl)cyclohexanecarboxamide ligand with copper(II) acetate. The green colored crystals of the complex were obtained by slow evaporation of their dichloromethane:ethanol solution (2:1, *v*:*v*). The crystal structure of *cis*-[Cu(L-κ^2S,O)$_2$] was obtained by single-crystal X-ray diffraction. The crystal structure reveals an monoclinic *C*2 (no. 5) space group with cell parameters a = 14.848(3) Å, b = 10.543(2) Å, c = 10.511(2) Å, β = 123.84(3)°, V = 1366.7(7) Å^3, Z = 2, T = 153(2) K, μ(MoKα) = 0.979 mm^{-1}, *Dcalc* = 1.327 g/cm^3, 4979 reflections measured (6.6° ≤ 2Θ ≤ 50.68°), 2243 unique (R_{int} = 0.0223, R_{sigma} = 0.0444) which were used in all calculations. The final R_1 was 0.0225 (>2sigma(I)) and wR_2 was 0.0490 (all data). The angular structural index parameter, τ_4, is equal to 0.40, which confirms the distorted square planar geometry for the title compound. The puckering parameters (q_2 = 0.015(3) Å, q_3 = 0.576(3) Å, Q_T = 0.577(3) Å, θ = 1.6(3)° and φ = 20(11)°) of the title complex show that the cyclohexane ring adopts a chair conformation. The two ethyl groups of the diethyl amine group have *anti-orientation* with respect to one another. The crystal packing shows the molecules stacked in parallel sheets along [010], accompanied by C3-H3A···O1^i (^{i} -*x*, +*y*, 1-*z*) intermolecular contact.

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1. Introduction

Thiourea derivative compounds have a long history as ligands in coordination chemistry due to their ease of synthesis, variability in structural design, and wide range of applications. The nitrogen, oxygen, and sulfur donor atoms of thiourea derivatives provide a multitude of bonding possibilities [1-6]. The thiourea derivatives are able to coordinate to a range of metal centers as neutral ligands, monoanions, or dianions. Both the ligands and their metal complexes display a wide range of biological activity including antibacterial [7-12], antifungal [13-19], antitumor [20-24], antiviral [25] antithyroid [26, 27], anthelmintic [28], rodenticidal [29], insecticidal [30], herbicidal [31], anti-parasitic [32], antileishmanial [24], antioxidant [33] and plant-growth regulator [34] properties. Additionally, especially benzoyl thiourea derivatives possess wide applications in several areas of life sciences as catalysts [35-39], fluorescent sensor [40,41], anion selective sensors [42-46] liquid-liquid extraction [47,48], preconcentration [49-51] and highly efficient chromatographic separation [52,53].

Our research group is interested in the synthesis, characterization, crystal structure, biological applications, and coordination chemistry of novel thiourea derivative compounds [7,8,54-62]. As a part of our ongoing studies into the structure and utility of oxygen and sulfur containing thiourea derivatives, we report the crystal structure of *bis*(*N*-(diethylcarbamothioyl) cyclohexane carboxamido)copper(II) complex.

2. Experimental

2.1. Instrumentation

^{1}H NMR spectrum of the ligand was recorded on a Bruker DPX-400 spectrometer at 400 MHz using CDCl$_3$ as the solvent, with tetramethylsilane as an internal standard. Room temperature attenuated total reflection Fourier transform infrared (FT-IR ATR) spectra of all synthesized compounds were recorded using a Varian FTS1000 FT-IR spectrometer with Diamond/ZnSe prism (4000-525 cm^{-1}; number of scans: 250; resolution: 1 cm^{-1}). The X-ray diffraction data were recorded on a Bruker APEX-II CCD diffractometer. A suitable crystal was selected and coated with Paratone oil and mounted on a Nylon loop on a Bruker APEX-II CCD diffractometer. The crystal was kept at T = 153(2) K during data collection. The data were collected with MoKα (λ = 0.71073 Å) radiation at a crystal-to-detector distance of 40 mm.

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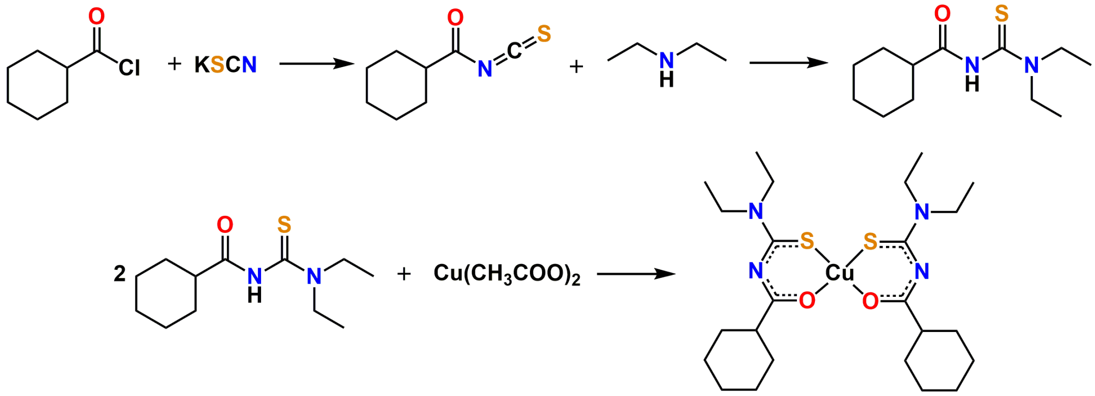

Scheme 1. Synthesis of ligand and its copper complex.

Using Olex2 [63], the structure was solved with the Superflip [64] structure solution program, using the Charge Flipping solution method and refined by full-matrix least-squares technique on F^2 using ShelXL [65] with a refinement of F^2 against all reflections. Hydrogen atoms were constrained by difference maps and were refined isotropically, and all non-hydrogen atoms were refined anisotropically. All geometrical data were calculated using PLATON [66]. Molecular structure and packing diagrams were generated using OLEX2 and MERCURY, respectively [63,67].

2.2. Reagents

All chemicals used for the preparation of the compounds were of reagent grade quality. Acetone was distilled before use. Potassium thiocyanate and cyclohexanecarbonyl chloride were purchased from Merck and used as received. All other chemicals and solvents were obtained from commercial suppliers and used without further purification.

2.3. Synthesis

2.3.1. Synthesis of N-(diethylcarbamothioyl)cyclohexane carboxamide, HL

N-(Diethylcarbamothioyl)cyclohexanecarboxamide (HL) was prepared according to previously published methods [54-62,68]. A solution of cyclohexanecarbonyl chloride (5.00 mmoles, 0.683 mL) in acetone (30 mL) was added dropwise to a suspension of potassium thiocyanate (5.00 mmoles, 0.4908 g) in acetone (30 mL). The reaction mixture was heated (50 °C) under reflux for 30 min and then cooled to room temperature. A solution of diethyl amine (5.00 mmoles, 0.520 mL) in acetone (30 mL) was added and the resulting mixture was stirred for 2 h. Hydrochloric acid (0.1 N, 100 mL) was added and the solution filtered. The solid product was washed with water and purified by recrystallization from an ethanol:dichloromethane mixture (1:2, *v*:*v*) (Scheme 1). Yield: 76% (0.9211 g). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.00 (s, 1H, NH), 3.93 (t, 2H, NCH_2), 3.43 (t, 2H, NCH_2), 2.24 (tt, 1H, CH, Ch), 1.89 (d, 1H, CH, Ch), 1.84 (d, 1H, CH, Ch), 1.78 (m, 1H, CH, Ch), 1.74 (m, 1H, CH, Ch), 1.67 (m, 1H, CH, Ch), 1.64 (m, 1H, CH, Ch), 1.41 (m, 4H, CH, Ch), 1.32 (t, 3H, CH_3), 1.23 (t, 3H, CH_3). FT-IR (cm^{-1}): 3240 ν(NH), 2976, 2926, 2853 ν(CH), 1661 ν(C=O), 1312 ν(C=S) [62].

2.3.2. Synthesis of copper complex, Cu(L-$\kappa^2S,O)_2$

Paramagnetic copper complex was prepared according to the method described in the literature [62]. A solution of copper(II) acetate (10.0 mmoles, 1.8163 g) in ethanol (30 mL) was added dropwise to a solution of *N*-(diethylcarbamothioyl) cyclohexanecarboxamide (22.0 mmoles, 5.3324 g) in a 1:2 ratio with a small excess of *N*-(diethylcarbamothioyl)cyclohexane carboxamide in ethanol (30 mL) at room temperature and the resulting mixture was stirred for 30 min. The solid complex was filtered and re-crystallized from ethanol: dichloromethane mixture (1:2, *v*:*v*) (Scheme 1). *Bis*(*N*-(diethylcarbamothioyl) cyclohexanecarboxamido)copper(II) [Cu(L-κ^2S,O)$_2$]: Color: Green. M.p.: 71-73 °C. Yield: 81 % (4.4161 g). FT-IR (ATR, cm^{-1}): 2972, 2924, 2854 ν(CH), 1522 ν(CN), 1489 ν(CO) [62].

3. Results and discussion

The block-shaped green colored crystals of the copper complex was obtained by slow evaporation of their dichloromethane:ethanol solution (2:1, *v*:*v*). The molecular structure of the copper complex was determined by single crystal X-ray diffraction. The copper complex crystallized in the monoclinic space group *C*2 (No. 5) and the crystal and structure refinement data are given in Table 1. Selected bond lengths and angles are given in Table 2. The molecular structure of the complex with the atomic numbering scheme is shown in Figure 1.

The reaction between *N*-(diethylcarbamothioyl)cyclohexane carboxamide ligands and copper(II) ion produces a metal complex with the expected metal:ligand ratio of 1:2. The chelating two thiourea ligands are coordinated with a copper(II) ion in a bidentate mode, forming two six-membered chelate rings (Cu1-S1-C5-N1-C6-O1). The six-membered rings are formed via oxygen and sulphur atoms, and the dihedral angle between these chelate rings in the copper complex is 44.96° (Figure 2). The bond angles around the copper ion are S1-Cu1-O1 = 95.97(5)° and S1^i-Cu1-S1 = 92.94(4)° (^{i} -*x*, +*y*, 1-*z*) for *cis*-[CuL_2], so the bite angles of the complex deviate slightly from the ideal angle (90°) [69]. The copper center, surrounded by oxygen and sulphur atoms in the complex form, has a distorted square planar geometry as shown in Figure 1. The sum of the equatorial angles S1-Cu1-O1, S1-Cu1-S1^i, O1-Cu1-O1^i, and O1^i-Cu1-S1^i (^{i} -*x*, +*y*, 1-*z*) are 373.20°, which is consistent with distorted square planar geometry. In addition, it is clear that the τ_4 parameter is essential for four-coordinate transition metal complexes since square planar and tetrahedral geometries are the extremes [70]. The angular structural index parameter, $\tau_4 = (360-(\beta+\alpha))/141$, evaluated from the two largest angles in the four-coordinated geometry, which has ideal values of 1 for a perfect tetrahedral geometry and 0 for a perfect square planar geometry, is equal to 0.40, which confirms the distorted square planar geometry for the title compound.

The distance of copper atom from the best plane through the coordination sphere is 0.000 Å. The deviations from the best plane (O1/S1/Cu/S1^i/O^i; ^{i} -*x*, +*y*, 1-*z*) are 0.548(2) and 0.428(2) Å for O1 and S1 atoms, respectively.

Table 1. Crystal data and structure refinement for [Cu(L-κ^{2}S,O)$_2$].

Empirical formula	$C_{24}H_{42}CuN_4O_2S_2$
Formula weight	546.28
Temperature (K)	153(2)
Crystal system	Monoclinic
Space group	*C*2
a (Å)	14.848(3)
b (Å)	10.543(2)
c (Å)	10.511(2)
β (°)	123.84(3)
Volume (Å^3)	1366.7(7)
Z	2
ρ_{calc} (g/cm^3)	1.327
μ (mm^{-1})	0.979
F(000)	582.0
Crystal size (mm^3)	0.22 × 0.22 × 0.07
Radiation	MoKα (λ = 0.71073 Å)
2Θ range for data collection (°)	6.6 to 50.68
Index ranges	$-17 \le h \le 17, -12 \le k \le 10, -12 \le l \le 12$
Reflections collected	4979
Independent reflections	2243 [R_{int} = 0.0223, R_{sigma} = 0.0444]
Data / restraints / parameters	2243/1/153
Goodness-of-fit on F^2	1.027
Final R indexes [I≥2σ (I)]	R_1 = 0.0225, wR_2 = 0.0476
Final R indexes [all data]	R_1 = 0.0249, wR_2 = 0.0490
Largest diff. peak /hole (e.Å^{-3})	0.29/-0.20
Flack parameter	0.620(11)

Table 2. Bond lengths and angles for [Cu(L-κ^{2}S,O)$_2$].

Bond	Distance (Å)	Bond	Distance (Å)
Cu1-S1^1	2.2341(8)	N2-C5	1.339(3)
Cu1-S1	2.2341(8)	C1-C2	1.510(3)
Cu1-O1	1.9197(16)	C3-C4	1.520(4)
Cu1-O1^1	1.9197(16)	C6-C7	1.522(3)
S1-C5	1.739(2)	C7-C8	1.532(3)
O1-C6	1.276(2)	C7-C12	1.529(3)
N1-C5	1.345(3)	C8-C9	1.523(3)
N1-C6	1.322(3)	C9-C10	1.531(3)
N2-C1	1.477(3)	C10-C11	1.517(4)
N2-C3	1.464(3)	C11-C12	1.523(3)
Bond	**Angles (°)**	**Bond**	**Angles (°)**
S1^1-Cu1-S1	92.94(4)	N1-C5-S1	127.22(18)
O1^1-Cu1-S1^1	95.97(5)	N2-C5-S1	117.53(19)
O1^1-Cu1-S1	152.08(5)	N2-C5-N1	115.05(19)
O1-Cu1-S1	95.97(5)	O1-C6-N1	128.8(2)
O1-Cu1-S1^1	152.08(5)	O1-C6-C7	114.92(19)
O1-Cu1-O1^1	88.39(10)	N1-C6-C7	116.29(18)
C5-S1-Cu1	104.90(9)	C6-C7-C8	111.68(18)
C6-O1-Cu1	129.69(16)	C6-C7-C12	114.17(18)
C6-N1-C5	126.30(19)	C12-C7-C8	109.94(19)
C3-N2-C1	115.54(17)	C9-C8-C7	111.11(19)
C5-N2-C1	120.86(19)	C8-C9-C10	110.84(19)
C5-N2-C3	123.59(19)	C11-C10-C9	111.1(2)
N2-C1-C2	111.62(19)	C10-C11-C12	111.5(2)
N2-C3-C4	112.4(2)	C11-C12-C7	111.12(19)

[1] Symmetry code: -*x*, +*y*, 1-*z*.

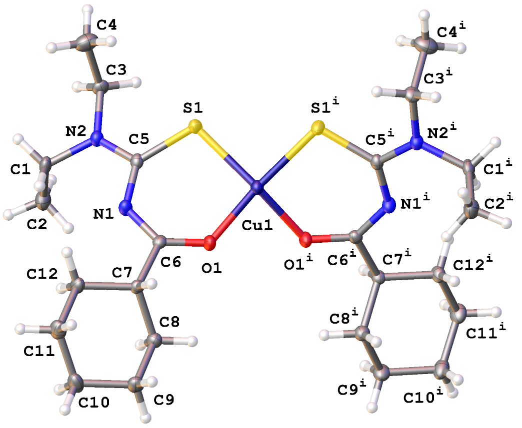

Figure 1. The molecular structure of *bis*(*N*-(diethylcarbamothioyl)cyclohexane carboxamido)copper(II) complex with atom labeling scheme. Displacements of ellipsoids are shown at the 50% probability level, ^{i} -*x*, +*y*, 1-*z*.

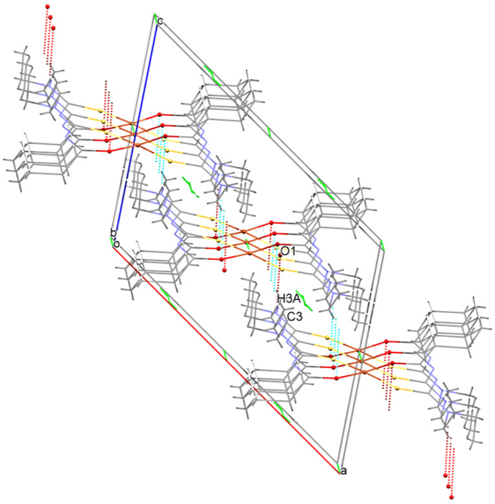

Figure 2. Packing diagram for *bis*(*N*-(diethylcarbamothioyl)cyclohexane carboxamido)copper(II) complex, viewed along [010]. Intermolecular C-H···O contact is indicated by dashed lines.

The chelate ring systems, Cu1–O1–C6–N1–C5–S1, are nearly planar as well with the largest deviations from the best plane being 0.175(2) Å for C5 atom.

The C6-O1 and C5-S1 bond lengths are 1.276(2) and 1.739(2) Å for copper(II) complex which are slightly longer than the corresponding distance found in free ligand (C=O, 1.228(3) and C=S, 1.664(2) Å) [62]. This indicates the existence of electron delocalization over the six-member chelate rings (Cu1-S1-C5-N1-C6-O1 and Cu1-S1^{i} -C5^{i} -N1^{i} -C6^{i} -O1^{i}; ^{i} -*x*, +*y*, 1-*z*) due to the coordination of the oxygen and sulfur atoms with the copper(II) ion. This result was also confirmed by the short C-N bond distance (N1-C5, 1.345(3) and N1-C6, 1.322(3) Å) which are shorter than the average for C-N single bond distance (1.48 Å) [71,72]. The molecular structure is very close to the related *bis*(*N*-(di-*n*-propylcarbamothioyl)cyclohexanecarboxamido) copper(II) complex, [71] and shows similar short Metal-S, Metal-O, C-O, C-N and C-S bonds indicating the known π-bonding character in the chelate rings. All other bond lengths are within normal ranges (Table 2) [72].

The cyclohexane ring in the title complex exhibits a puckered conformation with puckering parameters q_2 = 0.015(3) Å, q_3 = 0.576(3) Å, Q_T = 0.577(3) Å, θ = 1.6(3)° and φ = 20(11)°. These puckering parameters show that the cyclohexane ring adopts a chair conformation [73].

The torsion angles of the diethyl amine group are C5-N2-C3-C4 = -90.1(3)° and C5-N2-C1-C2 = -88.2(3)°. According to these torsion angles, the ethyl substituents (C5-N2-C3-C4 and C5-N2-C1-C2) are in (-) *anticlinal* (-ac) and (-) *synclinal* (-sc) orientation, respectively [74]. In addition, the two ethyl groups of the diethyl amine group are *anti-orientation* with respect to one another.

The crystal packing shows the molecules stacked in parallel sheets along [010] (Figure 2), accompanied by the following intermolecular contact: C3-H3A···O1^{i}, with C-H = 0.96 Å, H···O 2.70 Å, and C-H···O 134°; symmetry code ^{i} -*x*, +*y*, 1-*z*. Possible intramolecular interactions are C1-H1B···N1, with C-H = 0.96 Å, H···O 2.33 Å, and C-H···O 100° and C3-H3B···S1, with C-H = 0.96 Å, H···S 2.57 Å, and C-H···O 106°.

4. Conclusion

A copper(II) complex, having the general formula *cis*-[Cu(L-κ^2S,O)$_2$], has been prepared with *N*-(diethylcarbamothioyl) cyclohexanecarboxamide ligand and copper(II) acetate, and characterized by a single crystal X-ray diffraction study, where the ligands coordinate to copper(II) ion in a *cis* conformation. The obtained copper complex, *cis*-[Cu(L-κ^2S,O)$_2$], crystallized in the monoclinic space group *C*2. The copper center has a slightly distorted square planar geometry and the puckering parameters of the title complex show that the cyclohexane ring adopts a chair conformation. The crystal packing shows the molecules stacked in parallel sheets along [010], accompanied by C3-H3A···O1^{i} (^{i} -*x*, +*y*, 1-*z*) intermolecular contact.

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Supporting information

CCDC-2039559 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

Disclosure statement

Conflict of interest: The authors declare that they have no conflict of interest.
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References

[1]. Beyer, L.; Hoyer, E.; Liebscher, J.; Hartmann, H. *Z. Chem.* **2010**, *21(3)*, 81-91.
[2]. Bourne, S.; Koch, K. R. *J. Chem. Soc., Dalton Trans.* **1993**, *13*, 2071-2072.
[3]. Koch, K. R.; Wang, Y.; Coetzee, A. *J. Chem. Soc., Dalton Trans.* **1999**, *6*, 1013-1016.
[4]. Che, D. J.; Li, G.; Yao, X. L.; Wu, Q. J.; Wang, W. L.; Zhu, Y. *J. Organometal. Chem.* **1999**, *584(1)*, 190-196.
[5]. Kemp, G.; Roodt, A.; Purcell, W.; Koch, K. R. *J. Chem. Soc., Dalton Trans.* **1997**, *23*, 4481-4484.
[6]. Nkabyo, H. A.; Procacci, B.; Duckett, S. B.; Koch, K. R. *Dalton Trans.* **2019**, *48(46)*, 17241-17251
[7]. Arslan, H.; Duran, N.; Borekci, G.; Koray Ozer, C.; Akbay, C. *Molecules* **2009**, *14(1)*, 519-527.
[8]. Arslan, H.; Flörke, U.; Külcü, N. *J. Chem. Crystallog.* **2003**, *33(12)*, 919-924.
[9]. Rauf, M. K.; Imtiaz-ud-Din; Badshah, A.; Gielen, M.; Ebihara, M.; Vos, D. de; Ahmed, S. *J. Inorg. Biochem.* **2009**, *103(8)*, 1135-1144.
[10]. Nordin, N. A.; Chai, T. W.; Tan, B. L.; Choi, C. L.; Abd Halim, A. N.; Hussain, H.; Ngaini, Z. *J. Chem.* **2017**, *2017*, 1-7.
[11]. Saeed, S.; Rashid, N.; Ali, M.; Hussain, R. *Eur. J. Chem.* **2010**, *1(3)*, 200-205.
[12]. Yang, W.; Liu, H.; Li, M.; Wang, F.; Zhou, W.; Fan, J. *J. Inorg. Biochem.* **2012**, *116*, 97-105.
[13]. del Campo, R.; Criado, J. J.; Garcia, E.; Hermosa, M. R.; Jimenez-Sanchez, A.; Manzano, J. L.; Monte, E.; Rodriguez-Fernandez, E.; Sanz, F. *J. Inorg. Biochem.* **2002**, *89(1-2)*, 74-82.
[14]. Ramadas, K.; Suresh, G.; Janarthanan, N.; Masilamani, S. *Pestic. Sci.* **1998**, *52(2)*, 145-151.
[15]. Weiqun, Z.; Wen, Y.; Liqun, X.; Xianchen, C. *J. Inorg. Biochem.* **2005**, *99(6)*, 1314-1319.
[16]. Wu, J.; Shi, Q.; Chen, Z.; He, M.; Jin, L.; Hu, D. *Molecules* **2012**, *17(5)*, 5139-5150.
[17]. Saeed, S.; Rashid, N.; Ali, M.; Hussain, R.; Jones, P. G. *Eur. J. Chem.* **2010**, *1(3)*, 221-227.
[18]. Perez, H.; O'Reilly, B.; Plutin, A. M.; Martinez, R.; Duran, R.; Collado, I. G.; Mascarenhas, Y. P. *J. Coord. Chem.* **2011**, *64(16)*, 2890-2898.
[19]. Kulakov, I. V.; Nurkenov, O. A.; Akhmetova, S. B.; Seidakhmetova, R. B.; Zhambekov, Z. M. *Pharm. Chem. J.* **2011**, *45(1)*, 15-18.
[20]. Hallur, G.; Jimeno, A.; Dalrymple, S.; Zhu, T.; Jung, M. K.; Hidalgo, M.; Isaacs, J. T.; Sukumar, S.; Hamel, E.; Khan, S. R. *J. Med. Chem.* **2006**, *49(7)*, 2357-2360.
[21]. Rao, X. P.; Wu, Y.; Song, Z. Q.; Shang, S. B.; Wang, Z. D. *Med. Chem. Res.* **2010**, *20(3)*, 333-338.
[22]. Peng, H.; Liang, Y.; Chen, L.; Fu, L.; Wang, H.; He, H. *Bioorg. Med. Chem. Lett.* **2011**, *21(4)*, 1102-1104.
[23]. Saeed, S.; Rashid, N.; Jones, P. G.; Ali, M.; Hussain, R. *Eur. J. Med. Chem.* **2010**, *45(4)*, 1323-1331.
[24]. Yaseen, S.; Rauf, M. K.; Zaib, S.; Badshah, A.; Tahir, M. N.; Ali, M. I.; Imtiaz-ud-Din; Shahid, M.; Iqbal, J. *Inorg. Chim. Acta* **2016**, *443*, 69-77.
[25]. Burgeson, J. R.; Moore, A. L.; Boutilier, J. K.; Cerruti, N. R.; Gharaibeh, D. N.; Lovejoy, C. E.; Amberg, S. M.; Hruby, D. E.; Tyavanagimatt, S. R.; Allen, R. D.; Dai, D. *Bioorg. Med. Chem. Lett.* **2012**, *22(13)*, 4263-4272.
[26]. Williams, R. H.; Frame, E. G. *Bull. Johns Hopkins Hosp.* **1945**, *77*, 314-328.
[27]. Madan, V. K.; Taneja, A. D. *Indian Chem. Soc.* **1991**, *68*, 471-472.
[28]. Dziduch, K.; Kołodziej, P.; Paneth, A.; Bogucka-Kocka, A.; Wujec, M. *Molecules* **2020**, *25(12)*, 2770.
[29]. Schroeder, D. C. Thioureas. *Chem. Rev.* **1955**, *55(1)*, 181-228.
[30]. Zhang, J. F.; Xu, J. Y.; Wang, B. L.; Li, Y. X.; Xiong, L. X.; Li, Y. Q.; Ma, Y.; Li, Z. M. *J. Agric. Food Chem.* **2012**, *60(31)*, 7565-7572.
[31]. Kea, S.Y.; Xue, S. J. *Arkivoc* **2006**, *2006(10)*, 63-68.
[32]. Limban, C.; Vasile, A.; Chirita, I.C.; Caproiu, M. *Rev. De Chim.* **2010**, *61*, 946-950.
[33]. Abosadiya, H. M. *Eur. J. Chem.* **2020**, *11(2)*, 156-159.
[34]. Hu, J. H.; Fan, X. H.; Du, X. L.; Wei, T. B. *Phosph. Sulfur Silicon Relat. Elem.* **2010**, *185(12)*, 2558-2562.
[35]. Gunasekaran, N.; Remya, N.; Radhakrishnan, S.; Karvembu, R. *J. Coord. Chem.* **2011**, *64(3)*, 491-501.
[36]. Gunasekaran, N.; Karvembu, R. *Inorg. Chem. Commun.* **2010**, *13(8)*, 952-955.
[37]. Gunasekaran, N.; Jerome, P.; Ng, S. W.; Tiekink, E. R. T.; Karvembu, R. *J. Mol. Catal. A: Chem.* **2012**, *353-354*, 156-162.
[38]. Gunasekaran, N.; Ramesh, P.; Ponnuswamy, M. N. G.; Karvembu, R. *Dalton Trans.* **2011**, *40(46)*, 12519-12516.
[39]. Tzeng, Z. H.; Chen, H. Y.; Reddy, R. J.; Huang, C. T.; Chen, K. *Tetrahedron* **2009**, *65(15)*, 2879-2888.
[40]. Hasan, S.; Hamedan, N. A.; Razali, A. A. A.; Uyup, N. H.; Zaki, H. M. *IOP Conf. Ser.: Mater. Sci. Eng.* **2017**, *172*, 012050.
[41]. Hamedan, N. A.; Hasan, S.; Zaki, H. M.; Alias, N. Z. *IOP Conf. Ser.: Mater. Sci. Eng.* **2017**, *172*, 012038.
[42]. Chen, H. L.; Guo, Z. F.; Lu, Z. *Org. Lett.* **2012**, *14 (19)*, 5070-5073.
[43]. Gemili, M.; Nural, Y.; Keles, E.; Aydiner, B.; Seferoglu, N.; Sahin, E.; Sari, H.; Seferoglu, Z. *J. Mol. Liquids* **2018**, *269*, 920-932.
[44]. Zhang, Y. M.; Cao, C.; Wei, W.; Xie, T. B. *Chin. J. Chem.* **2007**, *25(5)*, 709-713.
[45]. Zhang, Y.; Qin, J.; Lin, Q.; Wei, T. *J. Fluorine Chem.* **2006**, *127(9)*, 1222-1227.
[46]. Hu, S.; Guo, Y.; Xu, J.; Shao, S. *Spectrochim. Acta A* **2009**, *72(5)*, 1043-1046.
[47]. Habtu, M. M.; Bourne, S. A.; Koch, K. R.; Luckay, R. C. *New J. Chem.* **2006**, *30(8)*, 1155.
[48]. Muhl, P.; Gloe, K.; Dietze, F.; Hoyer, E.; Beyer, L. *Z. Chem.* **2010**, *26(3)*, 81-94.
[49]. Luckay, R. C.; Mebrahtu, F.; Esterhuysen, C.; Koch, K. R. *Inorg. Chem. Commun.* **2010**, *13(4)*, 468-470.
[50]. Luckay, R. C.; Sheng, X.; Strasser, C. E.; Raubenheimer, H. G.; Safin, D. A.; Babashkina, M. G.; Klein, A. *Dalton Trans.* **2009**, *39*, 8227.
[51]. Schuster, M.; Schwarzer, M. *Anal. Chim. Acta* **1996**, *328(1)*, 1-11.
[52]. Mautjana, A. N.; Miller, J. D. S.; Gie, A.; Bourne, S. A.; Koch, K. R. *Dalton Trans.* **2003**, *10*, 1952-1960.
[53]. König, K. H.; Schuster, M.; Schneeweis, G.; Steinbrech, B. *Z. Anal. Chem.* **1984**, *319(1)*, 66-69.
[54]. Bozkurt, S.; Gumus, I.; Arslan, H. *J. Organometal. Chem.* **2019**, *884*, 66-76.
[55]. Gumus, I.; Solmaz, U.; Binzet, G.; Keskin, E.; Arslan, B.; Arslan, H. *Res. Chem. Intermed.* **2018**, *45(2)*, 169-198.
[56]. Binzet, G.; Turunc, E.; Flörke, U.; Külcü, N.; Arslan, H. *J. Chem.* **2018**, *2018*, 1-8.
[57]. Solmaz, U.; Gumus, I.; Binzet, G.; Celik, O.; Balci, G. K.; Dogen, A.; Arslan, H. *J. Coord. Chem.* **2018**, *71(2)*, 200-218.
[58]. Binzet, G.; Gumus, I.; Dogen, A.; Flörke, U.; Kulcu, N.; Arslan, H. *J. Mol. Struc.* **2018**, *1161*, 519-529.
[59]. Gumus, I.; Solmaz, U.; Binzet, G.; Keskin, E.; Arslan, B.; Arslan, H. *J. Mol. Struc.* **2018**, *1157*, 78-88.
[60]. Binzet, G.; Zeybek, B.; Kılıç, E.; Külcü, N.; Arslan, H. *J. Chem.* **2013**, *2013*, 1-7.
[61]. Binzet, G.; Kavak, G.; Külcü, N.; Özbey, S.; Flörke, U.; Arslan, H. *J. Chem.* **2013**, *2013*, 1-9.
[62]. Ozer, C. K.; Arslan, H.; Vanderveer, D.; Binzet, G. *J. Coord. Chem.* **2008**, *62(2)*, 266-276
[63]. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009**, *42(2)*, 339-341.
[64]. Palatinus, L.; Chapuis, G. *J. Appl. Cryst.* **2007**, *40(4)*, 786-790.
[65]. Sheldrick, G. M. *Acta Crystallogr. C* **2015**, *71(1)*, 3-8.
[66]. Spek, A. L. *Acta Crystallogr. C* **2015**, *71(1)*, 9-18.
[67]. Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P. A. *J. Appl. Cryst.* **2008**, *41(2)*, 466-470.
[68]. Arslan, H.; Külcü, N.; Flörke, U. *Trans. Metal Chem.* **2003**, *28(7)*, 816-819.
[69]. Binzet, G.; Flörke, U.; Külcü, N.; Arslan, H. *Eur. J. Chem.* **2012**, *3(2)*, 211-213.
[70]. Yang, L.; Powell, D. R.; Houser, R. P. *Dalton Trans.* **2007**, *9*, 955-964.
[71]. Gumus, I.; Ozer, C. K.; Vanderveer, D.; Arslan, H. *Eur. J. Chem.* **2016**, *7(4)*, 416-420
[72]. Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, *12*, S1.
[73]. Cremer, D.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97(6)*, 1354-1358.
[74]. Anslyn, E. V.; Dougherty, D. A. Modern Physical Organic Chemistry. University Science. p. 95. ISBN 978-1891389313, 2006.