

Synthesis, Structure and Spectroscopic Properties of Oxovanadium Tris(3,5-dimethylpyrazolyl)borate Aroylthiourea Complexes

(Sintesis, Struktur dan Sifat Spektroskopi Kompleks Oksovanadium Tris(3,5-dwimetilpirazolil)borat Aroiltiourea)

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ABSTRACT

Aroylthiourea ligands, 1-aroil-3-cyclohexyl-3-methylthiourea (HL_1), 1-(2-chloroaroil)-3-cyclohexyl-3-methylthiourea (HL_2), 1-(3-chloroaroil)-3-cyclohexyl-3-methylthiourea (HL_3) and 1-(4-chloroaroil)-3-cyclohexyl-3-methylthiourea (HL_4) were synthesized through a condensation reaction of methylcyclohexylamine and aroylisothiocyanate with a general formula $(X-Ph)(CO)NH(CS)N(C_6H_5)(CH_3)$ where $X = H, o-Cl, m-Cl$ and $p-Cl$, fully characterized by CHNS micro elemental analysis, infrared spectroscopy, UV-visible, nuclear magnetic resonance ($^1H, ^{13}C$) and X-ray crystallography. 1-(3-chloroaroil)-3-cyclohexyl-3-methylthiourea (HL_3) crystallized in the monoclinic system, $a=14.504(3)$, $b=4.9599(11)$, $c=22.325(5)$ Å, $\beta=98.461(7)^\circ$, $Z=4$ and $V=1588.5(6)$ Å³ with space group $P2_1/c$. The IR spectra of the ligands exhibits the characteristic $\nu(CO)$ and $\nu(N-H)$ at range 1701-1640 cm^{-1} and 3317-3144 cm^{-1} , respectively. Whereas the 1H and ^{13}C NMR spectra shows the resonances for N-H and -CO groups at range 8.3-8.5 and 160-163 ppm, respectively. A one-pot reaction involving the aroylthiourea ligand, oxovanadium(IV) ion and potassium hydrotris(3,5-dimethylpyrazolyl)borate (KTp^*) complex gave the desired [oxovanadium(IV)(tris(pyrazolyl)borate)(aroylthiourea)] complexes namely Tp^*VOL_1 , Tp^*VOL_2 , Tp^*VOL_3 and Tp^*VOL_4 and all complexes were characterized accordingly. X-ray study showed that Tp^*VOL_1 adopted a monoclinic crystal, $a=3.415(2)$, $b=19.463(3)$, $c=14.22(3)$ Å, $\beta=107.411(4)^\circ$, $Z=4$ and $V=3542.7(11)$ Å³ with $P2_1/c$ space group. The VO^{2+} center adopted a pseudo-octahedral geometry $O2N3S$, with the oxovanadium(IV) coordinated to the bidentate ligand $(X-Ph)(CO)NH(CS)N(C_6H_5)(CH_3)$ and tridentate Tp^* ligands. The results showed that aroylthiourea ligands behave as bidentate chelate through O and S atom and the $Tp^* C_{3v}$ symmetry adds stabilization to the VO^{2+} through its protective tripodal geometry.

Keywords: Aroylthiourea; chelate; oxovanadium(IV); tris(pyrazolyl)borate; vanadyl

ABSTRAK

Ligan aroiltiourea, 1-aroil-3-sikloheksil-3-metiltiourea (HL_1), 1-(2-kloroaroil)-3-sikloheksil-3-metiltiourea (HL_2), 1-(3-kloroaroil)-3-sikloheksil-3-metiltiourea (HL_3) dan 1-(4-kloroaroil)-3-sikloheksil-3-metiltiourea (HL_4) telah disintesis melalui tindak balas kondensasi antara metilsikloheksilamina dan aroilisotiosianat dengan formula asas, $(X-Ph)(CO)NH(CS)N(C_6H_5)(CH_3)$ dengan $X=H, o-Cl, m-Cl$ dan $p-Cl$. Pencirian penuh telah dilakukan dengan mikroanalisis unsur CHNS, spektroskopi inframerah, ultralembayung boleh nampak, resonans magnet nukleus ($^1H, ^{13}C$) serta kristalografi sinar-X. Ligan, 1-(3-kloroaroil)-3-sikloheksil-3-metiltiourea (HL_3) menghablur dalam sistem monoklinik, $a=14.504(3)$, $b=4.9599(11)$, $c=22.325(5)$ Å, $\beta=98.461(7)^\circ$, $Z=4$ dan $V=1588.5(6)$ dengan kumpulan ruang $P2_1/c$. Spektrum IR bagi kesemua ligan mempamerkan sifat $\nu(CO)$ dan $\nu(N-H)$ masing-masing dalam lingkungan 1701-1640 cm^{-1} dan 3317-3144 cm^{-1} . RMN 1H dan ^{13}C menunjukkan resonans bagi kumpulan (N-H) dan -CO masing-masing dalam lingkungan 8.3-8.5 dan 160-163 ppm. Tindak balas serentak melibatkan ligan aroiltiourea, ion oksovanadium(IV) dan kompleks kalium hidrotris(3,5-dimetilpirazolil)borat (KTp^*) untuk membentuk kompleks yang diinginkan [oksovanadium(IV)(tris(pirazolil)borat)(aroylthiourea)] dinamakan Tp^*VOL_1 , Tp^*VOL_2 , Tp^*VOL_3 dan Tp^*VOL_4 telah berjaya disintesis dan dicirikan. Kristalografi sinar-X menunjukkan Tp^*VOL_1 mempunyai sistem hablur monoklinik, $a=3.415(2)$, $b=19.463(3)$, $c=14.22(3)$ Å, $\beta=107.411(4)^\circ$, $Z=4$ dan $V=3542.7(11)$ Å³ dengan kumpulan ruang $P2_1/c$. Pusat VO^{2+} menyarankan geometri kompleks yang terbentuk adalah pseudo-oktahedral $O2N3S$ dengan pusat oksovanadium(IV) berkoordinat dengan ligan bidentat $(X-Ph)(CO)NH(CS)N(C_6H_5)(CH_3)$ dan ligan tridentat Tp^* . Ligan aroiltiourea bertindak sebagai pengkelat bidentat melalui atom O dan S dan ligan Tp^* yang bersimetri C_{3v} memberikan kestabilan kepada pusat VO^{2+} dengan geometri tripodal.

Kata kunci: Aroiltiourea; kelat; oksovanadium(IV); tris(pirazolil)borat; vanadil

INTRODUCTION

Aroylthiourea ligands display a wide range of biological activity such as anticancer (Saeed et al. 2010; Solinas

et al. 2012), anti-photogenic (Limban et al. 2011) and antibacterial (Mohamad Halim et al. 2011). The synthesis of aroylthiourea involves the substitution on

the first and second nitrogen of thiourea functionality ($(>N-C(S)-N<)$) with aroyl group (Saeed et al. 2014). The versatility of the backbone of thiourea brings the development of various new compounds bearing thiourea with significant applications (Khairul et al. 2016; Saeed et al. 2010; Shardin et al. 2017). Derivatives of thiourea are potentially very versatile ligands that able to coordinate to a range of metal center as neutral ligands, monoanion or dianion (Arslan et al. 2009). Oxygen and sulfur donor atom of aroylthiourea derivatives will coordinate to transition metal in monodentate or bidentate manner and has been considered as chelating agent. Metal complexes of aroylthiourea with O, S donor atoms also exhibit a wide application such as antimicrobial (Alfallous & Aburzeza 2015; Arslan et al. 2009), antibacterial (Yang et al. 2012) and catalysts (Gunasekaran & Karvembu 2010; Gunasekaran et al. 2011; Khairul et al. 2014).

Coordination chemistry of oxovanadium(IV), oxovanadium(V) and dioxovanadium(V) has generated interest due to the model of vanadium complexes containing enzymes and serve as good oxidation catalysts as well as exhibit insulin mimetic agent (Mangalam & Kurup 2009). However, oxovanadium complexes(IV) having sulfur donor ligand is not widely studied compare to O and N donor ligands (Parihar et al. 2012; Prasad et al. 2011; Yadava et al. 2012) except a few reports on structural studies and insulin-like activity of ONS ligand (Bai et al. 2010; Mangalam & Kurup 2009). Oxovanadium (IV) complex that have vanadyl moiety VO^{2+} can coordinated to four or five donor atoms to form the VOL_4 and VOL_5 complexes (Mangalam & Kurup 2009). Oxovanadium complexes can also coordinated with sixth donor atoms to form octahedral complex (Cotton & Wilkinson 1966). The VO^{2+} moiety of oxovanadium(IV) complex forms stable coordination complexes with ligands attributed to the strong covalent vanadium-oxygen bonding. Thus, when vanadium ion forms bonding with other ligand, the influence of donor ligand on oxovanadium complex can be studied through reactivity of V-O bond (Mangalam & Kurup 2009). Complexes of oxovanadium(IV) with O,N,S donor atom are studied in the aspect of electronic interaction (Bai et al. 2010; Mangalam & Kurup 2009; Yadava et al. 2012) and application in bioinorganic chemistry (Maia et al. 2009; Maurya et al. 2006; Prasad et al. 2011).

The attempts to isolate oxovanadium(IV) complexes of aroylthiourea (VOL_2) were not successful due to the instability of the product that decompose in the laboratory atmosphere. Therefore, tris(3,5-dimethyl)pyrazoylborate (TP^*) was employed in order to increase and control the stability of the V(IV) complexes.

Hydrotris(3,5-dimethyl-1H-pyrazol-1-yl)borate (TP^*) is a versatile class of anionic nitrogen donor ligands that form tridentate coordination with transition metals (Xing et al. 2007). TP^* that have three pyrazol rings can act as tridentate stabilizing agent by forming steric and electronic effects hence optimizes the reactivity of metal ion center (Pettinari 2004). The tripodal TP^* ligand have

C_{3v} symmetry geometry (Mark et al. 2012a; Wlodarczyk et al. 1996) and the presence of methyl group on position 3 and 5 of pyrazol rings give the stability and high steric effect to the ligand (Mark et al. 2012b). TP^* will coordinate to metal ion center through the three N atom from three pyrazol ring (Mark et al. 2013). Coordination chemistry of oxovanadium(IV) complexes with TP^* ligand has been studied and few reports on the application of the complex in biology process involving organisms (Bai et al. 2010; Collison et al. 1993; Etienne 1996; Xing et al. 2007a).

In this study, oxovanadium complexes with 1-(X-aroil)-3-cyclohexyl-3-methylthiourea ($X=H, o\text{-Cl}, m\text{-Cl}$ and $p\text{-Cl}$) ligands and TP^* ancillary ligand were synthesized. The influence of chlorine (Cl) substituent and its positions (*ortho*, *meta* and *para*) on the aroyl ring of aroylthiourea toward the structural properties of the ligands and consequently, the effects on the physical and chemical properties of the oxovanadium(IV) complexes are presented in this study.

MATERIALS AND METHODS

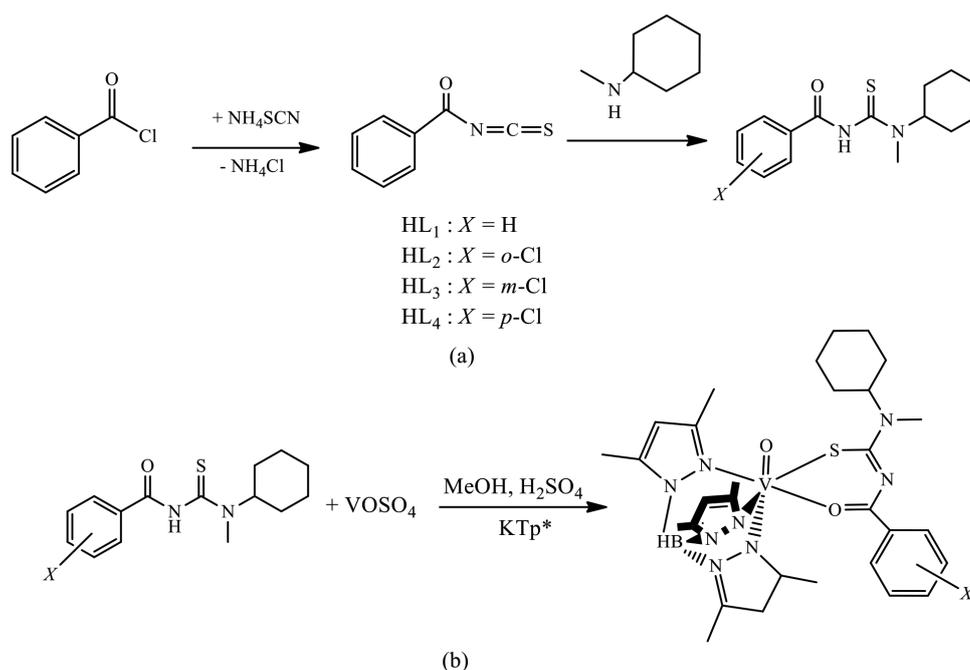
Derivatives of aroyl chloride ($X-C_6H_4COCl$) where ($X = H, o\text{-Cl}, m\text{-Cl}$ and $p\text{-Cl}$), N-methylcyclohexylamine ($C_6H_{11}NHCH_3$), ammonium thiocyanate (NH_4SCN) were purchased from Sigma-Aldrich and used as received. Vanadyl sulphate hydrate ($VOSO_4 \cdot xH_2O$) were purchased from Alfa-Aesar and stored under inert gas. Tris(3,5-dimethyl-1H-pyrazol-1-yl)borate potassium (KTP^*) used in the experiment were synthesized using previously reported method (McCleverty et al. 1976; Wlodarczyk et al. 1996). All solvents were purchased from MERCK (reagent grade) and used without further purification.

Thin layer chromatography (TLC) was performed on silica gel plates from MERCK with dichloromethane/n-hexane as eluent. Column chromatography was conducted using silica gel with pore size 0.06 - 0.20 mm purchased from MERCK. Infrared spectra were recorded using a Nicolet 6700 FTIR spectrophotometer in the range 4000 - 200 cm^{-1} . The 1H and ^{13}C NMR spectra in $CDCl_3$ were acquired from JEOL JNM-ECP 400 MHz and Varian Mercury 300 MHz. Electronic absorption spectra were obtained in dichloromethane on a UV-2450 PC SHIMADZU in the range 235 - 900 nm. Elemental microanalyses for carbon, hydrogen and nitrogen (CHNS) were performed using a CARLO ERBA 1108 elemental analyzer. The mass spectra were recorded on a SHIMADZU QP5050A/ QP2010PLUS and were determined by electron impact (EI) technique. Single crystal structures were determined using X-Ray Diffractometer Bruker D8 Quest SC-XRD.

1-(X-aroil)-3-cyclohexyl-3-methylthiourea ($X = H, o\text{-Cl}, m\text{-Cl}$ and $p\text{-Cl}$) ligands were prepared according to published literature method as shown in Scheme 1(a) (Kavak et al. 2009) with some adjustment. A solution of R-aroil chloride (1.41 g, 0.01 mol) in acetone was added dropwise to a suspension of potassium thiocyanate (0.97 g, 0.01 mol) in acetone and the reaction mixture was stirred for 30 min. A solution of N-methylcyclohexylamine (1.13g,

0.01 mol) in acetone was added and the resulting mixture was stirred for another 2 h. The solution was filtered and poured onto an ice-water mixture to give a white solid precipitate, filtered and washed with water. Then, ligands were purified by recrystallization from an ethanol solution. The structures of HL₁-HL₄ are shown in Figure 1. HL₁ (1-(X-royl)-3-cyclohexyl-3-methylthiourea): Yield 71.1%. Elemental CHNS analysis, % found (% calculated): C 64.93 (65.18); H 9.56 (7.29); N 10.84 (10.14) & S 8.05 (11.60). Infrared spectrum (cm⁻¹): 3317 ν (N-H); 1683 ν (C=O) & 1227 ν (C=S). UV-Vis spectrum λ_{max} /nm ($\epsilon \times 10^4$ M⁻¹cm⁻¹) in dichloromethane solution: 239 nm (22430) & 281 nm (10560). HL₂ (1-(2-chloroaryl)-3-cyclohexyl-3-methylthiourea): Yield 57.9%. Elemental CHNS analysis, % found (% calculated): C 57.93 (57.96); H 8.09 (6.16); N 9.20 (9.01) & S 8.87 (10.32). Infrared spectrum (cm⁻¹): 3132 (N-H); 1688 (C=O) & 1228 (C=S). UV-Vis spectrum λ_{max} /nm ($\epsilon \times 10^4$ M⁻¹cm⁻¹) in dichloromethane solution: 283 nm (5510) & 345 nm (340). HL₃ (1-(3-chloroaryl)-3-cyclohexyl-3-methylthiourea): Yield 46.1% yield. Elemental CHNS analysis, % found (% calculated): C 57.93 (57.96); H 8.09 (6.16); N 9.20 (9.01) & S 8.87 (10.32). Infrared spectrum (cm⁻¹): 3169 (N-H); 1691 (C=O) & 1224 (C=S). UV-Vis spectrum λ_{max} /nm ($\epsilon \times 10^4$ M⁻¹cm⁻¹) in dichloromethane solution: 240 nm (22850) & 284 nm (11650). HL₄ (1-(4-chloroaryl)-3-cyclohexyl-3-methylthiourea): Yield 40.8%. Elemental CHNS analysis, % found (% calculated): C 58.19 (57.96); H 7.98 (6.16); N 9.24 (9.01) & S 8.77 (10.32). Infrared spectrum (cm⁻¹): 3144 (N-H); 1690 (C=O) & 1221 (C=S). UV-Vis spectrum λ_{max} /nm ($\epsilon \times 10^4$ M⁻¹cm⁻¹) in dichloromethane solution: 246 nm (34090).

The oxovanadium(IV) complexes were synthesized as shown in Scheme 1(b). Vanadyl sulphate hydrate (VOSO₄·xH₂O, 0.163, 1 mmol) was dissolved in H₂SO₄ (10%, 1 mL) to form a blue solution. A methanolic solution of 1-(X-royl)-3-cyclohexyl-3-methylthiourea (2 mmol) was added and the pH of resulting green-blue solution was adjusted to pH 2-3 using a solution of sodium bicarbonate, NaHCO₃ (1 M) to give a light blue precipitate immediately. Then, KTp* ligand (0.33 g, 1 mmol) was added and the resulting mixture was filtered to remove the unwanted light-blue precipitate. The solvent was removed under vacuum and a mixture of water/chloroform was used to extract blue violet filtrate, which was the desired complex. The complex was purified by chromatography on silica gel using mixture of dichloromethane to n-hexane ratio of 5:1 as an eluent to obtain a greenish blue product. Tp*VOL₁ (Oxovanadium 1-(H-royl)-3-cyclohexyl-3-methylthiourea hidrottris(3,5-dimethyl-1H-pyrazol-1-yl)): Yield 28.6%. Elemental CHNS analysis, % found (% calculated): C 56.80 (56.25); H 7.05 (6.61); N 18.34 (17.49) & S N/A (4.99). Infrared spectrum (cm⁻¹): 2517 (B-H Tp*); 958 (V=O); 1486 (C=O) & 645 (C-S). UV-Vis spectrum λ_{max} /nm ($\epsilon \times 10^4$ M⁻¹cm⁻¹) in dichloromethane solution: 248 (22830); 582 (35) & 759 (45). MS (m/z): 364 [Tp*VO]; 544 [Tp*VOL₁]⁺ with one pyrazolyl ring lost & 639 [Tp*VOL₁]. Tp*VOL₂ (Oxovanadium 1-(2-chloroaryl)-3-cyclohexyl-3-methylthiourea hidrottris(3,5-dimethyl-1H-pyrazol-1-yl)): Yield 18.4%. Elemental CHNS analysis, % found (% calculated): C 52.94 (53.38); H 7.84 (6.12); N 16.37 (16.60) & S 3.45 (4.75). Infrared spectrum (cm⁻¹): 2522 (B-H Tp*); 959 (V=O); 1484 (C=O) & 645 (C-S). UV-Vis spectrum λ_{max} /nm ($\epsilon \times 10^4$ M⁻¹cm⁻¹) in dichloromethane



SCHEME 1. Schematic reaction for (a) synthesis of aroylthiourea ligand (b) synthesis of oxovanadium(IV) complexes with aroylthiourea and Tp* ligand

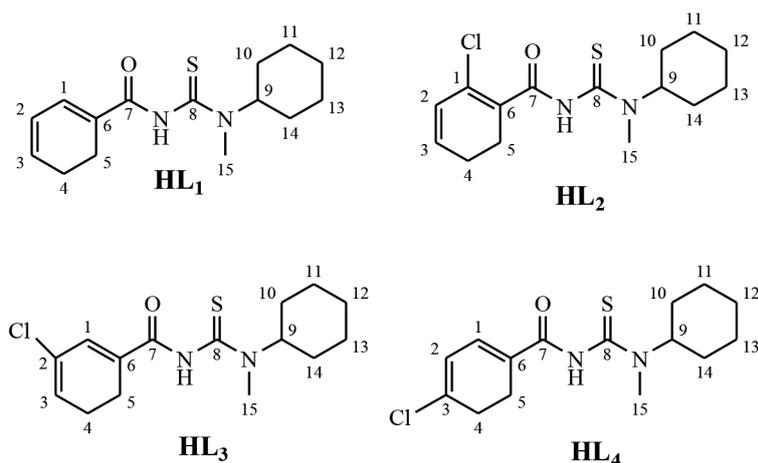


FIGURE 1. The structure of aroylthiourea ligands with the atom numbering for NMR elucidation

solution: 272 (16110); 582 (11) & 754 (16). MS (m/z): 364 [Tp*VO] & 673 [Tp*VOL₂]. Tp*VOL₃ (Oxovanadium 1-(3-chloroaroyl)-3-cyclohexyl-3-methylthiourea hidrotis(3,5-dimethyl-1H-pyrazol-1-yl)): Yield 19.8%. Elemental CHNS analysis, % found (% calculated): C 54.21 (53.38); H 8.61 (6.12); N 16.68 (16.60) & S 3.50 (4.75). Infrared spectrum (cm⁻¹): 2520 (B-H Tp*); 958 (V=O); 1484 (C=O) & 646 (C-S). UV-Vis spectrum λ_{\max} /nm ($\epsilon \times 10^4$ M⁻¹cm⁻¹) in dichloromethane solution: 246 (8920); 581 (17) & 760 (19). MS (m/z): 364 [Tp*VO] & 673 [Tp*VOL₃]. Tp*VOL₄ (Oxovanadium 1-(4-chloroaroyl)-3-cyclohexyl-3-methylthiourea hidrotis(3,5-dimethyl-1H-pyrazol-1-yl)): Yield 23.7%. Elemental CHNS analysis, % found (% calculated): C 51.00 (53.38); H 8.75 (6.12); N 16.40 (16.60) & S 3.21 (4.75). Infrared spectrum (cm⁻¹): 2521 (B-H Tp*); 959 (V=O); 1485 (C=O) & 646 (C-S). UV-Vis spectrum λ_{\max} /nm ($\epsilon \times 10^4$ M⁻¹cm⁻¹) in dichloromethane solution: 257 (15950); 582 (19) & 759 (23). MS (m/z): 364 [Tp*VO] & 673 [Tp*VOL₄].

RESULTS AND DISCUSSION

All ligands were analyzed on the basis of CHNS elemental analysis, mass spectrometer and spectroscopic techniques (IR, UV-Vis and NMR). The spectroscopic properties of HL₁ and its cobalt complex (CoL₁) were already reported (Tan et al. 2014), along with crystal structure of HL₄ (Al-abbasi 2011). The structure of the ligand, 1-(3-chloroaroyl)-3-cyclohexyl-3-methylthiourea (HL₃) and oxovanadium(IV) complex Tp*VOL₁ were determined using single crystal X-ray diffractometer. The X-ray structure of oxovanadium(IV) complex, Tp*VOL₁ confirmed that the amide proton of the aroylthiourea ligand was deprotonated upon complexation. Hence, oxovanadium(IV) metal coordinated with ligands HL₁-HL₄ through a bidentate chelate through (O,S) mode and a tridentate chelate through three N of Tp* to give neutral complexes Tp*VOL_x (x = 1-4).

The micro elemental analysis for C, H and N atoms for both ligands and complexes agree with the empirical

formulae of the expected molecules. The slightly higher percentage of H atom in all compounds might be due to sample were not completely dry during analysis and hence, some water molecule might have contributed to the reading.

The mass of the complexes molecule (Tp*VOL₁ - TP*VOL₄) were determined using electron impact (EI) mass spectroscopy by direct insertion mass spectrometer (DIMS) technique as shown by mass spectra of representative complex, Tp*VOL₃ in Figure 2. Spectra showed the molecular mass for Tp*VOL₃ at m/z 673. Fragmentation pattern of Tp*VOL₃ complexes showed stepwise loss of fragments starting with 3,5-dimethyl-1H-pyrazol-1-yl, followed by the tertiary amine moiety and lastly, the aroylthiourea ligand. The high intensity peak at m/z 364 was also observed correspond to [Tp*VO], after the decomposition of the aroylthiourea ligand. This fragmentation pattern agrees with the X-ray structure of Tp*VOL₁ that shows the aroylthiourea ligand was coordinated to the VO²⁺ centre via a bidentate chelate (O,S).

The IR spectra for all ligands are almost similar. Frequency for ν (N-H) was observed at range 3317-3144 cm⁻¹. The band for ν (C=S) present at range 1230-1220 cm⁻¹. No significant difference for ν (C=S) showed that the different position of Cl substituent group on aroyl moiety have no influence on C=S moiety. All IR spectra of the ligands showed a strong band of ν (C=O) in the range of 1701-1640 cm⁻¹. However, aroylthiourea ligands (HL₂-HL₄) with Cl substituent group on aroyl moiety caused ν (C=O) increase by 5-8 cm⁻¹. Chloro group that act as electron withdrawing group will decrease the electron density on aroyl ring, thus decrease the electron density of C=O by inductive effect through π bond of aroyl ring. This effect increased the double bond characteristic of C=O because the population of π^* C=O orbital on aroylthiourea ligand was decreased. Hence, this would increase the frequency of C=O. Likewise, we can see that the variation in the position of Cl on aroyl ring of the aroylthiourea ligand have no significance effect on ν (C=O), however the presence of Cl on aroyl ring itself gave some effect to the frequency of C=O as discussed above.

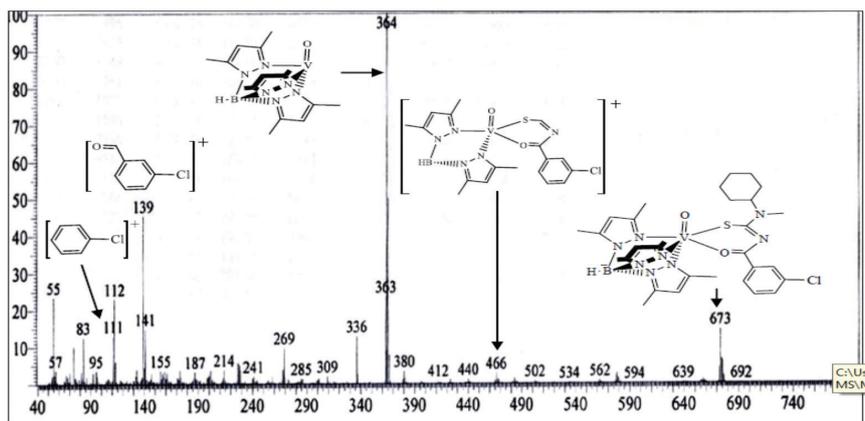


FIGURE 2. Mass Spectra of Tp*VOL3

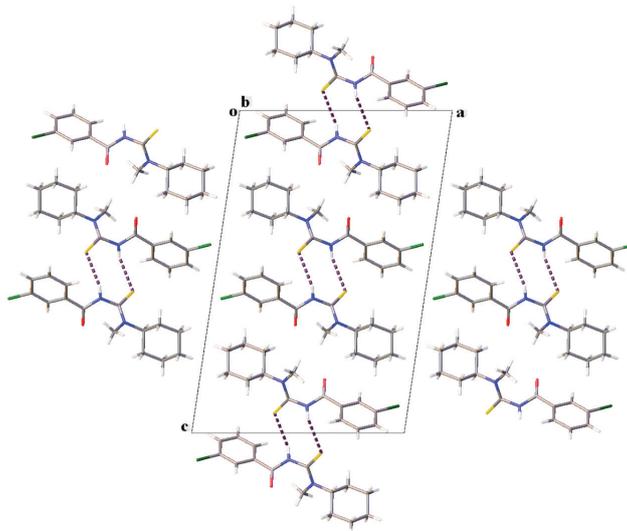
The IR spectra of all complexes were slightly different compared with the IR spectra of the free ligands. The obvious different was the absence of $\nu(\text{N-H})$ ($3320\text{--}3110\text{ cm}^{-1}$) in the spectra of the complexes that confirmed the aroylthiourea ligands were deprotonated in the oxovanadium(IV) complexes. The coordination of VO^{2+} to the carbonyl moiety caused the $\nu(\text{C=O})$ band ($1691\text{--}1672\text{ cm}^{-1}$) in free ligands, shifted to lower values after complexation ($1490\text{--}1480\text{ cm}^{-1}$). The decrease in the $\nu(\text{C=O})$ value was due to the deprotonation that promote electron delocalization in the thioamide fragment (CONCS) (Tan et al. 2014). The disappearance of $\nu(\text{C=S})$ in the range of $1240\text{--}1210\text{ cm}^{-1}$ and the presence of new band with medium intensity at $646\text{--}645\text{ cm}^{-1}$ for $\nu(\text{C-S})$ in the spectra of the complexes, suggested the formation of V-S bond via thiolation process as reported in the previous literature (Hernández et al. 2005; Mangalam & Kurup 2009; Nguyen & Abram 2007; Tan et al. 2014). In addition, the presence of a band at $2521\text{--}2517\text{ cm}^{-1}$ that corresponded to frequency of B-H in all spectra of the complexes suggested the present of the Tp* moiety. The value was comparable with frequency of the B-H (2545 cm^{-1}) reported for similar complex [Tp*VOCl(DMF)(H₂O)] (Kime-hunt et al. 1989). The sharp band observed at 1542 cm^{-1} indicated the presence of aromatic C=C for pyrazol ring of Tp* ligands. Besides, all IR spectra of the complexes displayed a strong band in the range of $959\text{--}958\text{ cm}^{-1}$ corresponding to the frequency of $\nu(\text{V=O})$ which is comparable with $\nu(\text{V=O})$ (959 cm^{-1}) observed for previously reported oxovanadium(IV) trispyrazolylborate complex, $\text{VO}(\text{O}_2)(\text{pzH})(\text{HB}(\text{pz})_3)$ (Xing et al. 2007a). The stretching band for V=O of all complexes are practically similar and suggested that there is no influence from structural variations of aroylthiourea ligand toward the V=O moiety.

The UV-Vis spectra for both ligands and complexes were collected in dichloromethane solution. The ligands showed the absorption bands at around $235\text{--}269\text{ nm}$ and was assigned to the $\pi \rightarrow \pi^*$ transition of the aromatic ring. The absorption bands at around $260\text{--}297\text{ nm}$ and $319\text{--}353\text{ nm}$ were attributed to the $n \rightarrow \pi^*$ transition of

C=O and C=S, respectively. The effect of Cl substituent on different positions were observed on C=O bands for HL₃ and HL₄ at 240 and 246 nm , respectively, but no significant effect was observed for HL₂. The withdrawing effect of Cl group created an inductive effect to the aroyl ring, thus the hypsochromic effect shifted the C=O band to shorter wavelength compared with that of HL₁ (281 nm). Moreover, the transition of $n \rightarrow \pi^*$ were observed in UV-Vis spectra of HL₂ ($283, 345\text{ nm}$) and HL₃ (284 nm) but was absence in spectrum of HL₄. The stronger inductive effect of Cl group at the *ortho* position of aroyl moiety in HL₄ resulted in hypsochromic shift causing the $n \rightarrow \pi^*$ band not to be observed in HL₄.

UV-Vis spectra of complexes show a strong and broad absorption bands around $246\text{--}271\text{ nm}$, which were assigned to $\pi \rightarrow \pi^*$ of aroyl ring of the aroylthiourea ligand, $n \rightarrow \pi^*$ transitions of C=O and the aromatic chromophore of Tp* ligand (Li et al. 2009). UV-Vis spectra of all complexes also showed the present of *d-d* transition in the visible region at 581 and 760 nm . All UV-Vis spectra complexes also showed the present of three absorption bands for the *d-d* transitions in the visible range, $400\text{--}900\text{ nm}$. These low intensity band are indicative of the presence of $d\pi\text{--}d\pi$ transitions which is forbidden according to Laporte rule (Tan et al. 2014). There are two absorption bands at 582 and 755 nm and a shoulder at around 410 nm that corresponded to the transition of $d(z^2) \rightarrow d(xy)$ and $d(z^2) \rightarrow d(yz)$ transitions, respectively. There is no observable difference in the spectra of the complexes with the variation in the position Cl group on the aroyl moiety of aroylthiourea ligands.

The crystal structure of HL₃ obtained from this study will be used to discuss the effect of different position of Cl atom toward structural properties of the ligands. The experimental details for the X-ray data and structure refinement parameters for ligand HL₃ are summarized in Table 1. In the structure of HL₃, the aroyl moiety of adopted an *trans* conformation with respect to thiono CS group across a partially double N1—C8 bond (Figure 3), with the torsion angle, C7-N1-C8-S1 of $126.7(15)$, comparative to that 1-aryol-(3-propyl-3-methyl)thiourea (Tan et al. 2014) and 1-(4-chloroaryl)-3-(cyclohexyl)-3-

FIGURE 4. Packing diagram of HL_3 viewed down the b -axisTABLE 2. Crystal data and refinement parameters for the complex Tp^*VOL_1

Subject	Tp^*VOL_1
Empirical formulae	$C_{30}H_{41}BN_8O_2SV.CH_3CN$
Formula weight	680.6
Temperature/K	298(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
$a/\text{\AA}$	3.415(2)
$b/\text{\AA}$	19.463(3)
$c/\text{\AA}$	14.220(3)
$\alpha/^\circ$	90
$\beta/^\circ$	107.411(4)
$\gamma/^\circ$	90
Volume/ \AA^3	3542.7(11)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.199
μ/mm^{-1}	0.376
F(000)	1348
Crystal size(mm)	0.42 × 0.27 × 0.26
Θ range for data collection	1.83 to 23.29
Goodness-of-fit on F^2	1.155
Independent reflections/Rint	2228 [Rint = 0.0670, Rsigma = N/A]
Data/restraints/parameters	5095/0/419
Final R indexes [$I > 2\sigma(I)$]	$R_1 = 0.0630$ wR2 = 0.1642

reported values of $[Tp^*VO(acac)]$ (1.596(2) Å) (Beddoes et al. 1990), $[TpVO(ph-acac)]$ (1.603(8) Å) (Xing et al. 2007b) and that of $[Tp^*VO(Cl)(DMF)]$ (1.649(5) Å) (Kimehunt et al. 1989). Tp^*VOL_1 crystal structure confirms that the aroylthiourea ligands are deprotonated and coordinated to the vanadium ion through the S and O atoms; generating a planar six-membered chelating ring. The O2–V1–S1 angle (87.76(9) Å) showed that there is a slight distortion from a regular octahedral arrangement of sulphur and oxygen atoms around the vanadium metal center. The

bonding characteristic in the chelate rings is best described with an extended π -system. The corresponding C–O and C–S bonds, in the coordinated ligand for oxovanadium complex Tp^*VOL_1 (Table 3) (1.733(4) Å and 1.2373(5) Å, respectively) are longer than those in the free ligand HL_1 (1.667(4) Å and 1.223(4) Å, respectively). The bond lengths of N1–C7 and N1–C8 (1.300(5) Å and 1.361(5) Å, respectively) were shorter than in the free ligand (1.361(5) Å and 1.408(5) Å, respectively). It is evident that there is an extensive delocalization of electrons inside the

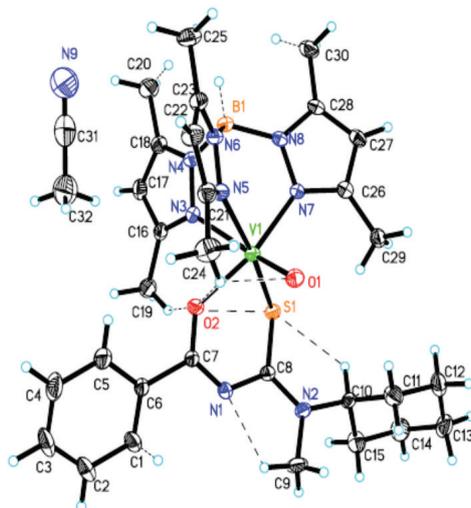


FIGURE 5. The molecular structure of complex Tp^*VOL_1 drawn at 30% probability ellipsoid with the atom numbering scheme. The dotted line indicated intramolecular hydrogen bonds

TABLE 3. Selected bond distances of oxovanadium complex, Tp^*VOL_1 compared to their corresponding free ligand, HL_1

	S1-C-8	O2-C7	N1-C7	N1-C8	N2-C8
Tp^*VOL_1	1.733(4)	1.2373(5)	1.300(5)	1.361(5)	1.331(5)
HL_1	1.667(4)	1.223(4)	1.361(5)	1.408(5)	1.331(5)

six-membered rings in the complex. Thus, considerable π -electron density is transferred to the chelate ring upon complexation. This is due to the coordination effect of the deprotonated aroylthiourea ligand that formed a partial double bond character in the C–N bonds. The elongation of C–S and C–O and the shortening of N–C bond lengths, observed in Tp^*VOL_1 was in agreement with other aroylthiourea metal complexes (Hernández et al. 2005; Nguyen & Abram 2007). The molecular structure of the complex agreed with elemental analysis for CHNS, spectroscopic (IR, UV-vis) and mass spectrometry data showing the vanadium atom in a distorted octahedral coordination geometry.

The ^1H and ^{13}C NMR signals of aroylthiourea ligands were collected in Tables 4 and 5, respectively. The NMR

spectra of HL_1 were not recorded since the data were reported previously by Tan et al. (2014). The numbering atom for NMR elucidation showed in Figure 2.

The ^1H and ^{13}C NMR spectra of the ligands showed almost similar chemical shift for cyclohexyl moiety on amine group in the range of 1.05–2.00 ppm for ^1H and 25–35 ppm for ^{13}C . Proton H9 (4.7–4.9 ppm) shifted to downfield due to the deshielding effect of the N atom where a normal chemical shift for sp^3 CH is 1.4–1.7 ppm in the range of 6.9–8.1 ppm. Splitting patterns of the peak are different according to the position of Cl on the aroyl ring. The chemical shift for C=O (C7/160–163 ppm) and C=S (C8/178–179 ppm) were most downfield positions because of the electronegativity effect of the O and S atoms toward carbon that is attached to it. Besides, the downfield shift

TABLE 4. ^1H NMR data of the aroylthiourea ligands

Compound	Chemical Shift, δ (ppm)											
	H1	H2	H3	H4	H5	H9	H10	H11,H13	H12	H14	H15	NH
HL_2	--	7.37t (1H)	7.60t (1H)	7.30m (1H)	7.37t (1H)	4.83t (1H)	1.95s (2H)	1.41m (4H)	1.18d (2H)	1.81d (2H)	3.09s (3H)	8.37s (1H)
HL_3	7.76s (1H)	--	7.63d (1H)	7.36t (1H)	7.50d (1H)	4.86t (1H)	1.95d (2H)	1.40m (4H)	1.11d (2H)	1.81d (2H)	3.00s (3H)	8.38s (1H)
HL_4	7.78d (1H)	7.46d (1H)	--	7.46d (1H)	7.78d (1H)	4.94p (1H)	2.18m (2H)	1.47m (4H)	1.15d (2H)	1.87d (2H)	3.09s (3H)	8.49s (1H)

TABLE 5. ¹³C NMR data of the aroylthiourea ligands

Compound	Chemical Shift, δ (ppm)											
	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10,C14	C11,C13	C15
HL ₂	132.47	130.61	133.50	127.31	130.36	132.47	161.82	178.04	63.17	29.03	25.46	35.52
HL ₃	128.21	134.31	132.97	130.21	125.83	135.13	160.48	179.39	63.26	29.10	25.54	35.39
HL ₄	129.4	129.4	139.50	129.4	129.4	131.20	162.36	179.26	63.51	29.26	25.57	30.50

was also due to the exchange in electron density between the CO and –NH– groups through resonance (Tan et al. 2014). However, there is not much difference observed on the chemical shift of C=O and C=S for ligands HL₁ – HL₄ with different positions for the Cl atom on the aroyl ring of the aroylthiourea ligand that suggested the positions of the Cl atom has no influence on C=O and C=S groups.

The NMR for oxovanadium complexes was not collected because VO²⁺ ion has *d*¹ system and the electronic configuration in the neutral state is [Ar]3d¹ (Kripal & Shukla 2009). The present of an unpaired electron in the *d* orbital of the VO²⁺ ion give a paramagnetic characteristic to the oxovanadium(IV) complexes and renders the collection of NMR spectrum of the complex not possible with a standard procedure.

CONCLUSION

Octahedral oxovanadium(IV) complexes with 1-(*X*-aroyl)-3-cyclohexyl-3-methylthiourea (*X*=H, *o*-Cl, *m*-Cl and *p*-Cl) ligands were successfully synthesized. The aroylthiourea ligands coordinate to the VO²⁺ ion through a bidentate OS chelate coordination mode. The tripodal ligand hydrotris(3,5-dimethyl-1H-pyrazol-1-yl)borate (Tp*) served as stabilizing agent coordinated to the VO²⁺ ion through the three nitrogen atoms of the pyrazol rings. The positions of the Cl atom on the aroyl ring of aroylthiourea ligand have no significant effects on VO²⁺ metal center.

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REFERENCES

Al-Abbasi, A.A., Yamin, B.M. & Kassim, M.B. 2011. 1-(4-Chlorobenzoyl)-3-cyclohexyl-3-methylthiourea. *Acta Crystallographica Section E Structure Reports Online* 67(8): 1891.

Alfallous, K.A. & Aburzeza, M.M. 2015. Synthesis, characterization, biological activity and use of thiourea derivative (PhTTU) studies of Cd(II) ion complex. *International Journal of Science and Research* 4(6): 350-352.

Arslan, H., Duran, N., Borekci, G., Ozer, C.K. & Kabay, C. 2009. Antimicrobial activity of some thiourea derivatives and their nickel and copper complexes. *Molecules* 14(1): 519-527.

Bai, F.Y., Li, X.T., Zhu, G.S. & Xing, Y.H. 2010. Synthesis and structure of a new scorpionate-dithio carboxyl oxovanadium complex and an organic dithio carboxyl compound. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 75(5): 1388-1393.

Beddoes, R.L., Collison, D., Mabbs, F.E. & Passand, M.A. 1990. Synthesis and characterization of some -diketonate derivatives of hydrotris(3,5-dimethylpyrazolyl)borato oxovanadium(IV). The crystal and molecular structure of hydrotris(3,5-dimethylpyrazolyl)borato pentane-2,4-dionato oxovanadium(IV). *Polyhedron* 9(20): 2483-2489.

Collison, D., Eardley, D.R., Mabbs, F.E., Powell, A.K. & Scott, S. 1993. Synthesis, crystallographic and spectroscopic characterization, and magnetic properties of mixed-ligand oxovanadium(IV) hydrotris(3,5-dimethylpyrazolyl)borate complexes. *Inorganic Chemistry* 32(5): 664-671.

Cotton, F.A. & Wilkinson, G. 1966. *Advanced Inorganic Chemistry*. New York: John Wiley and Sons. pp. 409-412.

Etienne, M. 1996. Hydridotris (pyrazolyl) borato complexes of the group 5 metals: Inorganic and organometallic chemistry. *Coordination Chemistry Reviews* 156: 201-236.

Gunasekaran, N. & Karvembu, R. 2010. Synthesis, characterization, and catalytic applications of Ru(III) complexes containing N-[di(alkyl/aryl)carbamoithioyl]benzamide derivatives and triphenylphosphine/triphenylarsine. *Inorganic Chemistry Communications* 13(8): 952-955.

Gunasekaran, N., Remya, N., Radhakrishnan, S. & Karvembu, R. 2011. Ruthenium(II) carbonyl complexes with N-[di(alkyl/aryl)carbamoithioyl]benzamide derivatives and triphenylphosphine as effective catalysts for oxidation of alcohols. *Journal of Coordination Chemistry* 64(3): 491-501.

Hernández, W., Spodine, E., Beyer, L., Schröder, U., Richter, R., Ferreira, J. & Pavani, M. 2005. Synthesis, characterization and antitumor activity of copper(II) complexes, [CuL₂] [HL¹⁻]³⁻ = N,N-Diethyl-N'-(R-Benzoyl)Thiourea (R=H, *o*-Cl and *p*-NO₂). *Bioinorganic Chemistry and Applications* 3(3-4): 299-316.

Halim, N.I.M., Kassim, K., Fadzil, A.H. & Yamin, B.M. 2011. Synthesis, characterization and antibacterial studies of benzoylthiourea derivatives. *2nd International Conference on Chemistry and Chemical Engineering* 14: 55-59.

Kavak, G., Ozbey, S., Binzet, G. & Nevzat, K. 2009. Synthesis and single crystal structure analysis of three novel benzoylthiourea derivatives. *Turkish Journal of Chemistry* 33: 857-868.

Khairul, W.M., Tukimin, N. & Rahamathullah, R. 2016. Synthesis, characterization and electrical properties of N-([4-(aminophenylethynyl)toluene]-N'-(cinnamoyl)thiourea (AECT) as single molecular conductive film. *Sains Malaysiana* 45(5): 825-831.

- Khairul, W.M., Faisol, S.L.M., Jasman, S.M., Che Soh, S.K. & Shamsuddin, M. 2014. Catalytic studies featuring palladium(II) benzoylthiourea derivative as catalyst in sonogashira reaction. *Bulletin of Chemical Reaction Engineering and Catalysis* 9(3): 241-248.
- Kime-Hunt, E., Spartalian, K., DeRusha, M., Nunn, C.M. & Carrano, C.J. 1989. Synthesis, characterization and molecular structures of a series of [(3,5-Dimethylpyrazolyl)borato] vanadium(III) and -(IV) complexes. *Inorganic Chemistry* 28: 4392-4399.
- Kripal, R. & Shukla, S. 2009. 4 symmetry crystal field and ground state wavefunction of the VO^{2+} Ion. *Chinese Physics Letter* 26(8): 26-29.
- Li, Z.P., Xing, Y.H., Cao, Y.Z., Zeng, X.Q., Ge, M.F. & Niu, S.Y. 2009. Synthesis, structure and properties of a series of scorpionate oxovanadium(IV)-carboxylate complexes. *Polyhedron* 28(4): 865-871.
- Limban, C., Marutescu, L. & Chifiriuc, M.C. 2011. Synthesis, spectroscopic properties and antipathogenic activity of new thiourea derivatives. *Molecules (Basel, Switzerland)* 16(9): 7593-7607.
- Mark Lee, W.F., Pui, L.K., Heng, L.Y. & Kassim, M. 2013. Molybdenum complex as potential photosensitizer for direct water splitting. *Materials Science Forum* 756: 231- 237.
- Mark Lee, W.F., Ng, K.H., Lorna, J.M., Umar, A.A. & Kassim, M. 2012a. Penentuan aras jalur tenaga kompleks tungsten nitrosilditiolena. *Sains Malaysiana* 41(4): 439-444.
- Mark Lee, W.F., Lorna, J.M. & Kassim, M. 2012b. Sifat fotokimia kompleks molybdenum ditiolena. *Sains Malaysiana* 41(5): 597-601.
- Maia, P.I.D.S., Pavan, F.R., Leite, C.Q.F., Lemos, S.S., de Sousa, G.F., Batista, A.A., Nascimento, O.R., Ellena, J., Castellano, E.E., Niquet, E. & Deflon V.M. 2009. Vanadium complexes with thiosemicarbazones: Synthesis, characterization, crystal structures and anti-mycobacterium tuberculosis activity. *Polyhedron* 28(2): 398-406.
- Mangalam, N.A. & Kurup, M.R.P. 2009. Synthesis and spectral investigations of vanadium(IV/V) complexes derived from an ONS donor thiosemicarbazone ligand. *Spectrochimica Acta. Part A, Molecular and Biomolecular Spectroscopy* 71(5): 2040- 2044.
- Maurya, M.R., Kumar, A., Abid, M. & Azam, A. 2006. Dioxovanadium(V) and μ -oxo bis[oxovanadium(V)] complexes containing thiosemicarbazone based ONS donor set and their antimicrobial activity. *Inorganica Chimica Acta* 359(8): 2439-2447.
- McCleverty, J.A., Seddon, D., Bailey, N.A. & "Joe" Walker, N.W. 1976. The chemistry of cyclopentadienyl and related nitrosyl complexes of molybdenum. Part V. dihalogenonitrosyl[tris(pyrazolyl)borato]molybdenum complexes, their alcoholysis, and the crystal structure of chloronitrosylisopropoxo[tris(4-chloro-3,5-dimethylpyraz.)]. *Dalton Transactions* 10: 898-908.
- Nguyen, H.H. & Abram, U. 2007. Rhenium and technetium complexes with N,N-dialkyl-N'-benzoylthioureas. *Inorganic Chemistry* 46(13): 5310-5319.
- Parihar, S., Pathan, S., Jadeja, R.N., Patel, A. & Gupta, V.K. 2012. Synthesis and crystal structure of an oxovanadium(IV) complex with a pyrazolone ligand and its use as a heterogeneous catalyst for the oxidation of styrene under mild conditions. *Inorganic Chemistry* 51: 1152-1161.
- Pettinari, C. 2004. Scorpionates: Pinch and Sting the Metal. *La Chimica e l'Industria* 86(10): 94-100.
- Prasad, K.S., Kumar, L.S., Shekar, S.C., Prasad, M. & Revanasiddappa, H.D. 2011. Oxovanadium complexes with bidentate N, O ligands: Synthesis, characterization, DNA binding, nuclease activity and antimicrobial studies. *Chemical Sciences Journal* 12: 1-10.
- Rauf, M.K., Imtiaz-ud-Din, Badshah, A., Gielen, M., Ebihara, M., Vos, D.D. & Ahmed, S. 2009. Synthesis, structural characterization and *in vitro* cytotoxicity and anti-bacterial activity of some Copper(I) complexes with N,N'-disubstituted thioureas. *Journal of Inorganic Biochemistry* 103(8): 1135-1144.
- Saeed, A., Flörke, U. & Erben, M.F. 2014. A review on the chemistry, coordination, structure and biological properties of 1-(acyl/aroyle)-3-(substituted) thioureas. *Journal of Sulfur Chemistry* 35(3): 318-355.
- Saeed, S., Rashid, N., Jones, P.G., Ali, M. & Hussain, R. 2010. Synthesis, characterization and biological evaluation of some thiourea derivatives bearing benzothiazole moiety as potential antimicrobial and anticancer agents. *European Journal of Medicinal Chemistry* 45(4): 1323-1331.
- Shardin, R., Tan, S.S. & Kassim, M.B. 2017. Synthesis and structural characterization of N-bromobenzoyl-N'-(1,10-phenanthroline-5-yl)thiourea derivatives. *Malaysian Journal of Analytical Sciences* 21(1): 60-71.
- Solinas, A., Faure, H., Roudaut, H., Traiffort, E., Schoenfelder, A., Mann, A., Manetti, F., Taddei, M. & Ruat M. 2012. Acylthiourea, acylurea, and acylguanidine derivatives with potent hedgehog inhibiting activity. *Journal of Medicinal Chemistry* 55(4): 1559-1571.
- Tan, S.S., Al-Abbasi, A.A., Tahir, M.I.M. & Kassim, M.B. 2014. Synthesis, structure and spectroscopic properties of cobalt(III) complexes with 1-benzoyl-(3,3-disubstituted) thiourea. *Polyhedron* 68: 287-294.
- Wiberg, K.B. & Wang, Y. 2011. Transition metal-catalyzed formation of C-O and C-S bonds. *Arkivoc* 2011(5): 45-56.
- Wlodarczyk, A., Richardson, R.M., Ward, M.D., McCleverty, J.A., Hursthouse, M.H.B. & Coles, S.J. 1996. Complexes of tris(3,5-Dimethylpyrazolyl)borates alkylated on the 4-position of the pyrazolyl rings. X-ray crystal structure of molybdenum dicarbonyl nitrosyl tris(3,5-dimethyl-4-n-butylpyrazolyl) borate. *Polyhedron* 15(1): 27-35.
- Xing, Y., Zhang, Y., Sun, Z., Ye, L., Xu, Y., Ge, M., Zhang, B. & Niu, S. 2007a. Two new scorpionates vanadium haloperoxidases model complexes: Synthesis and structure of $VO(O_2)(pzH)(HB(pz)_3)$ and $VO(O_2)(pzH)(B(pz)_4)$ (pzH = pyrazole($C_3H_4N_2$)). *Journal of Inorganic Biochemistry* 101(1): 36-43.
- Xing, Y., Bai, F.Y., Aoki, K., Sun, Z. & Ge, M.F. 2007b. Syntheses and structures of oxovanadium (IV) complexes, $HB(pz)_3VO(ph-acac)_2H_2O$ (pz, pyrazole) and $HB(3,5-Me_2pz)_3VO(ph-acac)_2H_2O$ and $V_2O_4[HB(pz)_3]_{22}CH_3CN$. *Synthesis and Reactivity in Inorganic, Metal-Organic and Nano-Metal Chemistry* 37(3): 203-211.
- Yadava, A.K., Yadav, H.S., Yadav, U.S. & Rao, D.P. 2012. Synthesis and structural characterization of novel square pyramidal oxovanadium (IV) complexes with ligands. *Turkish Journal of Chemistry* 36: 624-630.
- Yang, W., Liu, H., Li, M., Wang, F., Zhou, W. & Fan, J. 2012. Synthesis, structures and antibacterial activities of benzoylthiourea derivatives and their complexes with cobalt. *Journal of Inorganic Biochemistry* 116: 97-105.

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