Asian Journal of Chemistry; Vol. 32, No. 5 (2020), 1059-1063

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2020.22518

Spectral Studies and Antibacterial Activity of Vanadium(III) Complexes of Heterocyclic Hydrazones

D. KASIMBI[1], K. HUSSAIN REDDY[1,*] and N. DEVANNA[2]

[1]Department of Chemistry, Sri Krishnadevaraya University, Anantapuramu-515003, India
[2]Department of Chemistry, Jawaharlal Nehru Technological University, Anantapuramu-515002, India

*Corresponding author: E-mail: khussainreddy@yahoo.co.in

Received: 1 November 2019; *Accepted*: 16 December 2019; *Published online*: 29 April 2020; AJC-19834

Vanadium(III) complexes having the composition $VLCl_3$ [where L = 2-acetylpyridine acetoylhydrazone (APAH), 2-acetylpyridine benzoylhydrazone (APBH), 2-acetylthiophene acetoylhydrazone (ATAH) and 2-acetylthiophene benzoylhydrazone (ATBH)] have been investigated using physico-chemical and analytical techniques. Molar conductivity data suggested that the complexes are neutral. Structures of all the vanadium(III) complexes are determined based on infrared and UV-visible spectral data. Electronic spectra of vanadium(III) complexes show three peaks suggesting octahedral structure. Comparison of vibrational spectra of hydrazones and complexes suggest that the hydrazones act as neutral tridentate ligands. The ligands and their vanadium derivatives are screened for their bacteria destroying activity against pathogenic bacterial strains *viz.* Gram-negative *E. coli*, Gram-positive *Bacillus*, Gram-positive *Staphylococcus aureus* and Gram-negative *P. aureoginosa*. Bacteria destroying activities of present complexes are comparable to the activity of the streptomycin. Complexes show more activity than their respective ligands in the case of Gram-positive *Bacillus* and Gram-negative *P. aureoginosa*.

Keywords: Synthesis, Characterization, Vanadium(III) complexes, Heterocyclic hydrazones, Antibacterial activity.

INTRODUCTION

Vanadium exits in variable oxidation numbers. In normally existing compounds vanadium is in +3, +4 and +5 oxidation states. Vanadium compounds generally embrace 5-coordinate square pyramidal or 6-coordinate distorted octahedral structures. The combination of same ratio of tridentate ligand with metal salt gives related oxovanadium(IV) derivative [1]. Several enzymes depend on the presence of vanadium; examples are haloperoxidase, nitrogenase, α-olefin polymerase, *etc*. These findings inspired to investigate coordination compounds of vanadium [2]. Vanadium is an essential trace element in biology. It plays essential role in many metabolic and mutagenic processes. Studies on simple coordination compounds of vanadium are useful to predict its biological role. Vanadium complexes of amino acids and peptides are better examples for bioinorganic studies. The ligand field chemistry of vanadium is of great current interest because of its affinity for a variety of organic compounds and structural diversities. The potential applications of vanadium complexes in the fields of biology, medicine and industry have attracted the thoughts of inorganic chemists [3-9]. Vandaium complexes of acylhydrazones are investigated to derive models for enzymes. Vanadium complexes with ONS donor ligands are known to exhibit insulin mimetic activity [10]. Vanadium complexes show tumour growth retardation, prophylaxis against carcinogenesis to in-act enzymes. Certain oxovanadium complexes of thiosemicarbazones show more antituberculosis activity than the free ligands [11].

Vanadium(III) compounds have been studied less frequently than the related vanadium(IV or V) derivatives. However, the vanadium(III) compounds are known to participate in biological redox reactions. For example, in ascidians the principal oxidation state of the metal is +3. Free metal ion has two disadvantages: (1) toxicity and (2) low biological activity. However, the metal on binding with organic ligands show less toxicity and more activity and thus adverse effects of free metal ion are minimized. The vanadium compounds show insulin-mimetic, antihypertension, antihyperlipidemia, antiobesity activities. The finding that certain ascidians contain vanadium(III) complexes in their blood cells, inspired inorganic chemists to cultivate complexes of vanadium [12]. The complexes of vanadium(III) with Schiff base ligands show remarkable biological [13,14] and catalytic [15] activities.

Hydrazones, particularly tridentate functionalized ligands have recently attracted considerable interest [15,16]. However, NNO and NOS donor ligands have received little attention [17,18]. Investigations on metal complexes with heterocylic hydrazones having assorted donor atoms exhibit broad spectrum of biological and pharmaceutical (anticancer, antitumour, antimicrobial and antiproliferative) activities [19-24]. The tautomerism of these ligands permits various structural features [25] for the corresponding metal derivatives. The diverse uses of metal complexes with hydrazones in the area of biological [26-28] and industrial processes [29,30] guided us to synthesize the tridentate NNO and NOS functionalized hydrazone ligands and their vanadium(III) compounds. Jang *et al*. [31] have studied bivalent transition metal complexes with 2-acetylpyridine benzoylhydrazone (APBH) and structures of Mn(II) and Zn(II) derivatives with APBH were elucidated. However, there is no report on the structure determination of V(III) complex with ATBH and other selected ligands.

Looking into the importance of V(III) complexes, based on the lacuna identified and to continue our interests [32-36], herein, we report synthesis, spectral characterization and antibacterial activity of new hydrazone ligands and their vanadium(III) derivatives.

EXPERIMENTAL

The organic precursors (2-acetylthiophene, acetichydrazide and benzhydrazide) and VCl_3 were bought from Sigma-Aldrich Chemical companies. Only pure solvents prepared by distillation were used in the making of ligands and their vanadium complexes.

Synthesis of ligands: Recently we have described [33] synthesis of ligands *viz.* 2-acetylpyridine acetoylhydrozone (APAH), 2-acetylpyridine benzoylhydrozone (APBH), 2-acetylthiophene acetoylhydrozone (ATAH) and 2-acetylthiophene benzoylhydrazone (ATBH) ligands.

General procedure for synthesis of complexes: The complexes were synthesized by adding VCl_3 (0.88 g dissolved in 20 mL of methanol; 0.55 mmol) to hot methanolic (20 mL, 0.55 mmol) solution of ligand (APAH/APBH/ATAH/and ATBH) in a clean 100 mL round bottom flask and heating under reflux on water bath for 3 h. Finally, reaction mixture was allowed to stand at room temperature for 1 h. After slow evaporation, yellow coloured compound was separated out. It was collected by filtration, washed with methanol followed by hexane and dried in air. Percentage yields of $V(APAH)Cl_3$; $V(APBH)Cl_3$, $V(ATAH)Cl_3$ and $V(ATBH)Cl_3$ complexes are 65, 62, 60 and 70, respectively. The details of instruments used in the present work were given in published research articles [32-36].

Antibacterial activity: Preparation of sample solution, details of bacterial strains and procedures in the determination activities of compounds are described in previously articles [33,34]. *E. coli* (MTCC 443), *Bacillus cereus* (MTCC 1305), *Staphylococcus aureus* (MTCC 3160) and *Pseudomonas aureoginosa* (MTCC 2453) were targeted in the light of their clinical and pharmacological importance. The cultures were incubated for 1 day at 37 °C on nutrient agar. The microorganisms were cultivated on Mueller-Hinton agar plates at 37 °C. The stock cultures were kept at 4 °C to grow.

Preparation of discs: In a clean and dry petri plates, Whatman No. 1 filter paper discs of 5 mm diameter were autoclaved,. The discs were wetted in solutions of compounds for 5 h and these were taken as test material. The discs were dried in shade after 5 h. The concentrations of compound solutions per disc are calculated for 0.1 g per 1 mL. Later they were carefully transferred to spread on cultured petri plates. Filter paper discs immersed in ethanol are prepared and used as positive control and streptomycin as negative control.

The agar medium was sterilized at 121 °C for 30 min. to test the antibacterial activity. The agar plates were prepared by pouring about 10 mL of the medium into 10 cm petri dishes under autoclave condition and kept undisturbed for 2 h to solidify the culture medium. A 1 mL of inoculums (containing suspension) of *E. coli*, *Bacillus cereus*, *Staphylococcus aureus* and *Pseudomonas aureoginosa* was poured on to the plates separately with solid agar media. The prepared sterile filter paper discs were dipped into the solutions of compounds and shaken well. The test plates were incubated for a period of 2 days in BOD at 37 °C for the growth of inhibitory zones, The average of two independent readings for each organism in each compound solutions were computed. After one day at 37 °C, the retarding zones were determined for bacteria. With the aid of plastic ruler, the diameter of the inhibition zone was measured and computed.

RESULTS AND DISCUSSION

Vanadium compounds are rigid at room temperature and non-hygroscopic. The complexes are partially soluble in water, less soluble in CH_3OH and C_2H_5OH and readily soluble in CH_3CN, DMF and DMSO.

The colours, melting point data & molar conductivity data of complexes are given in Table-1. Millimolar solutions were made in 25 mL volumetric flasks by dissolving the vanadium

TABLE-1
PHYSICO-CHEMICAL AND ANALYTICAL DATA OF LIGANDS AND THEIR VANADIUM COMPOUNDS

Ligand/ compound	f.w.	Colour	m.p. (°C)	Elemental analysis (%): Found (calcd.)				Molar conductivity (Ω^{-1} cm^{-2} mol^{-1})
				C	H	N	V	
APAH	177	Colour less	162-164	61.49 (61.01)	6.21 (6.25)	23.65 (23.71)	–	–
$V(APAH)Cl_3$	334	Pale brown	> 280	(32.33)	(3.29)	(12.57)	(15.25)	1.5
APBH	239	Pale white	145-147	69. 60 (70.27)	5.63 (5.47)	17.72 (17.56)	–	–
$V(APBH)Cl_3$	396	Pale brown	> 280	(42.42)	(3.28)	(10.60)	(12.86)	6.1
ATAH	182	Colourless	176-178	53.25 (52.74)	5.52 (5.49)	15.30 (15.38)	–	–
$V(ATAH)Cl_3$	339	Pale yellow	> 280	(28.31)	(2.94)	(8.25)	(15.02)	2.1
ATBH	244	Pale white	198-200	64.50 (63.93)	4.85 (4.91)	11.60 (11.47)	–	–
$V(ATBH)Cl_3$	401	Brown	> 280	(38.90)	(2.99)	(6.98)	(12.70)	3.9

complexes in DMF and the solution is poured in to a clean 100 mL measuring beaker and conductivity value was measured at room temperature. Molar conductivity values of vanadium complexes are included in Table-1. The values suggest non-electrolytic nature [37] of the complexes.

UV-visible spectroscopy: Spectra of vanadium(III) compounds are scanned in dimethylformamde. Typical UV-visible spectra of $V(APBH)Cl_3$ complex are shown in Fig. 1.

The low energy term for the d^2 free ion is ^3F. It splits in a weak octahedral field to give $^3T_{1g}$ (F), $^3T_{2g}$ and $^3A_{2g}$ spectroscopic states. The next high energy term for the d^2 free ion is ^3P. It does not split, but it is transformed into spectroscopic state *viz.* $^3T_{1g}$ (P). But $^3T_{1g}$ (F) is considered as ground spectroscopic state. UV-visible spectral values of vanadium compounds are given Table-2.

TABLE-2
UV-VISIBLE SPECTRAL DATA (cm^{-1}) OF VANADIUM COMPLEX IN DMF

Complex	Transitions			Structure assignment
	$^3T_{1g}(F) \rightarrow {}^3T_{2g}$	$^3T_{1g}(F) \rightarrow {}^3A_{2g}$	$T_{1g}(F) \rightarrow {}^3T_{1g}(P)$	
$V(APAH)Cl_3$	12,990	26,315	34,100	Octahedral
$V(APBH)Cl_3$	12,900	25,970	33,900	Octahedral
$V(ATAH)Cl_3$	12,560	24,660	32,320	Octahedral
$V(ATBH)Cl_3$	12,200	24,100	31,150	Octahedral

Three peaks are noticed in the electronic spectra of $V(APBH)Cl_3$ compound at 12,903, 25,974 and 33898 cm^{-1}. And these bands are, respectively assigned to $^3T_{1g}(F) \rightarrow {}^3T_{2g}$, $^3T_{1g}(F) \rightarrow {}^3A_{2g}$ and $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ electronic transitions in favour of octahedral structure [38].

Vibrational spectroscopy: FT-IR spectra of compounds in the region 4000-400 cm^{-1} are analyzed in comparison with that of the spectra of metal vanadium free hydrazone ligands. The typical peaks of hydrazone ligands and their palladium(III) complexes are given in Table-3. IR spectra of all the four vanadium complexes are very similar in peak positions and intensities. This observation indicates a close structural similarity among vanadium complexes.

TABLE-3
ASSIGNMENT OF IR DATA (cm^{-1}) OF LIGANDS AND THEIR VANADIUM COMPLEX

Compound	ν(NH)	ν(C=O)	ν(C=N)	ν(V-N)	ν(V-O)
APAH	3185	1678	1620	–	–
$V(APAH)Cl_3$	3195	1650	–	547	458
APBH	3177	1654	1616	–	–
$V(APBH)Cl_3$	3095	1659	–	574	549
ATAH	3174	1666	1606	–	–
$V(ATAH)Cl_3$	3075	1647	1581	590	–
ATBH	3327	1651	1608	–	–
$V(ATBH)Cl_3$	3148	1660	1604	543	498

The IR spectra free ligands show strong peaks in the 1678-1651 cm^{-1} region. These peaks are assigned to ν(>C=O) of amido group. This band is shifted to lower frequencies indicating the involvement of amido oxygen in coordination to vanadium(III). The vibrational peaks in 1620-1606 cm^{-1} region are due to the ν(C=N) of azomethine. These bands are changed to lower energies on complex formation suggesting the participation of azomethine nitrogen in coordination bonding to the vanadium [39]. Vibrational bands in the 3327-3174 cm^{-1} region may be assigned to the ν(N-H) for the metal free ligands. These bands are present in all the complexes indicating that the ligands do not undergo enolization. These observations suggest that the present hydrazones act as neutral tridentate ligands. The pyridine and thiophene ring deformation modes observed in 625-620 and 715-710 cm^{-1} regions, respectively. These peaks are moved to higher wave number indicating coordination of hetrocyclic N/S to

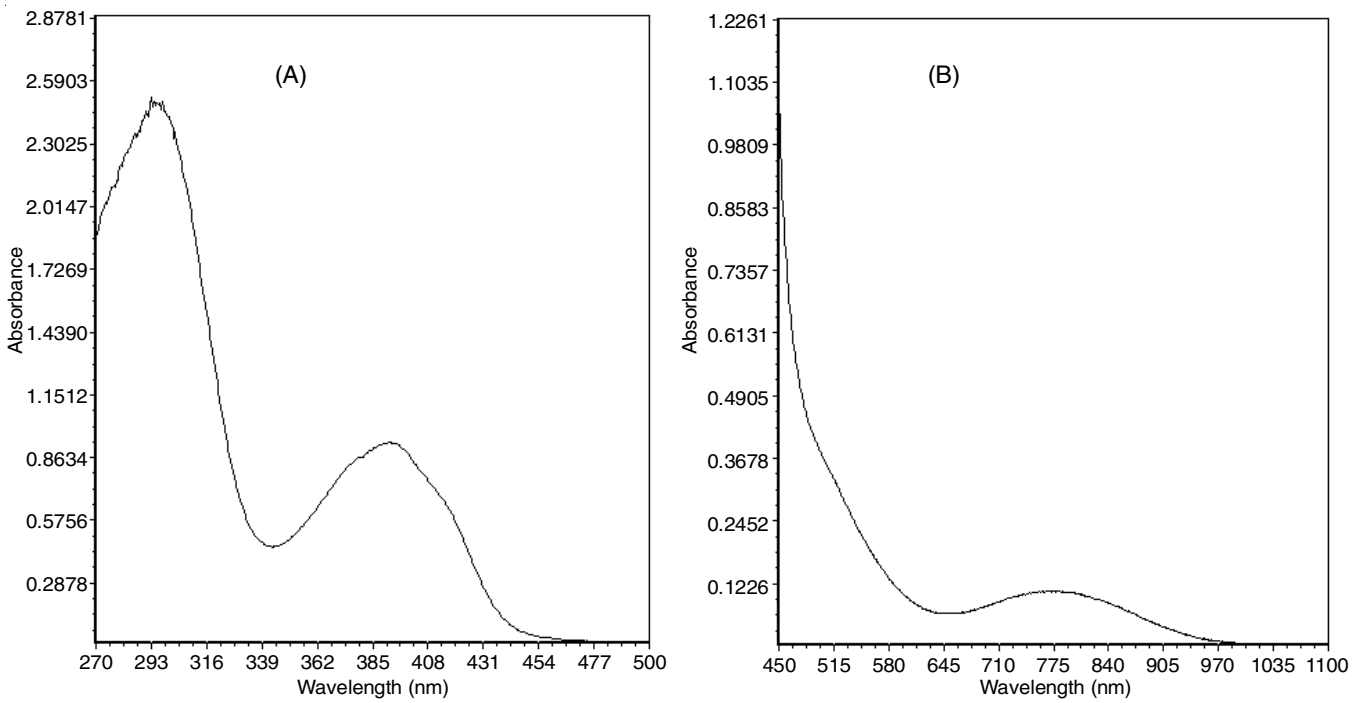

Fig. 1. UV-visible spectra of $V(APBH)Cl_3$ (A) in the UV region and (B) in the visible region. In total three peaks are observed in A and B

TABLE-4
ZONE OF INHIBITION (mm) DATA SHOWING ANTIBACTERIAL ACTIVITY OF LIGANDS* AND THEIR VANADIUM COMPLEXES

Compound	Gram-negative						Gram-positive					
	E. coli			*P. aureoginosa*			*Bacillus*			*Staphylococcus aureus*		
	200 µg	300 µg	500 µg	200 µg	300 µg	500 µg	200 µg	300 µg	500 µg	200 µg	300 µg	500 µg
$V(APAH)Cl_3$	2 (4.2)	2.5 (5.6)	3 (6.6)	2 (7)	2 (8)	3 (8.5)	5 (5)	6 (6)	8.5 (6.5)	4 (7)	5 (8)	6 (9)
$V(APBH)Cl_3$	1 (2)	1.5 (4)	2 (6)	4 (6)	6 (7)	8 (7.5)	6 (5)	6.6 (5.5)	8 (6)	3 (4)	3 (6)	5 (8)
$V(ATAH)Cl_3$	2 (4)	2 (6)	3 (6.5)	6 (5)	7 (5)	8 (6)	4 (5)	5 (6)	6 (7)	5 (6)	5.5 (8)	6 (9)
$V(ATBH)Cl_3$	2 (5.5)	2.2 (4.5)	3.5 (5.5)	8 (5)	8 (5)	9 (6)	5 (4)	6 (5)	7 (6)	4 (4)	5 (6)	7 (7)
Streptomycin	5.5	6.6	7.5	6	8	10	6.6	7.5	9.5	10	12	13

*Inhibition data of ligands are shown in parenthesis

vanadium atom. The new peaks in 590-543 and 498-488 cm^{-1} regions are ascribed, respectively to ν(V-N) and ν(V-O) vibrations. The tridentate behaviour of hydrazone ligands and the stoichiometry of complexes are in similarity with earlier observation [40].

Analytical, physico-chemical and spectral data are suggestive of octahedral structure for the V(III) complexes. A general structure is shown in Fig. 2.

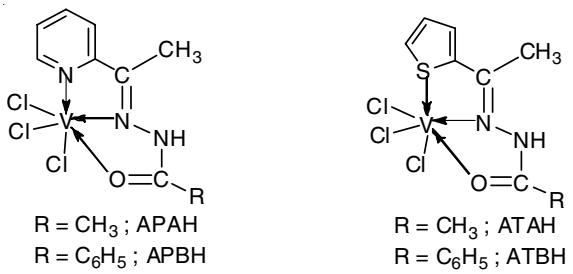

Fig. 2. Structures of V(III) complexes with APAH, APBH, ATAH and ATBH ligands

Antibacterial activity studies: The diameters (mm) of the zones of complete inhibition are given in Table-4. The activities of our compounds are almost similar to the activity of the standard drug (streptomycin).

A comparison (Table-4) of growth inhibition zones of APAH, APBH, ATAH and ATBH ligands and their vanadium complexes suggests that the complexes showed more antibacterial activity than the free ligand, This observation is similar to findings in literature [41-43]. For example, $V(APAH)Cl_3$, $V(APBH)Cl_3$ and $V(ATBH)Cl_3$ show increased activity than the respective ligands against *Bacillus.* In a similar way, $V(ATAH)Cl_3$ and $V(ATBH)Cl_3$ complexes showed superior activity than the constituent ligands. Such increased activity of ligand on complex formation is explained on the basis of chelation. The increased activity of vanadium complexes may be understood with Overtone's concept [43] and Tweedy's chelation theory [44]. The cell membrane is a bi-layer. It is composed of both protein and lipid layers. As per the principles of cell permeability, lipid solubility is the prime factor for showing antibacterial activity. In complexes the polarity metal greatly decreases due to delocalization of π-electrons. The low polarity of metal in the complex enhances its penetration ability into the lipid membrane. On entering into the cells metal derivatives blocks the enzymes of the microorganisms [44,45] leading to death of bacteria.

ACKNOWLEDGEMENTS

One of the authors (KHR) is thankful to UGC, New Delhi for the sanction of UGC-BSR Faculty Fellowship (No. F. 18-1/2011(BSR) 21/12/2018). The authors also thank UGC and DST for providing equipment facility under SAP and FIST programs, respectively.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. B. Jing, J. Dong, J. Li, T. Xu and L. Li, *J. Coord. Chem.*, **66**, 520 (2013); https://doi.org/10.1080/00958972.2013.763939
2. M. Sutradhar, T.R. Barman, G. Mukherjee, M.G.B. Drew and S. Ghosh, *Polyhedron*, **34**, 92 (2012); https://doi.org/10.1016/j.poly.2011.12.022
3. M. Xie, L. Gao, L. Li, W. Liu and S. Yan, *J. Inorg. Biochem.*, **99**, 546 (2005); https://doi.org/10.1016/j.jinorgbio.2004.10.033
4. A. Sheela and R. Vijayaraghavan, *J. Coord. Chem.*, **64**, 511 (2011); https://doi.org/10.1080/00958972.2010.550916
5. S. Mahajan, B. Singh, H.N. Sheikh and B.L. Kalsotra, *Chem. Sci. Trans.*, **1**, 23 (2012); https://doi.org/10.7598/cst2012.109
6. S. Singh, N. Bharti and P.P. Mohapatra, *Chem. Rev.*, **109**, 1900 (2009); https://doi.org/10.1021/cr068217k
7. A.M. Evangelou, *Crit. Rev. Oncol. Hematol.*, **42**, 249 (2002); https://doi.org/10.1016/S1040-8428(01)00221-9
8. D. Maity, J. Marek, W.S. Sheldrick, H. Mayer-Figge and M. Ali, *J. Mol. Catal. Chem.*, **270**, 153 (2007); https://doi.org/10.1016/j.molcata.2007.01.041
9. M.R. Maurya, S. Agarwal, C. Bader and D. Rehder, *Eur. J. Inorg. Chem.*, **2005**, 147 (2005); https://doi.org/10.1002/ejic.200400211
10. H. Sakurai, Y. Kojima, Y. Yoshikawa, K. Kawabe and H. Yasui, *Coord. Chem. Rev.*, **226**, 187 (2002); https://doi.org/10.1016/S0010-8545(01)00447-7
11. P.I. da S. Maia, F.R. Pavan, C.Q.F. Liete, S.S. Lemos, G.F. de Sousa, A.A. Batista, O.R. Nascimento, J. Ellena, E.E. Castellano, E. Niquet and V.M. Deflon, *Polyhedron*, **28**, 398 (2009); https://doi.org/10.1016/j.poly.2008.11.017
12. K. Kanamori, *Coord. Chem. Rev.*, **237**, 147 (2003); https://doi.org/10.1016/S0010-8545(02)00279-5
13. R.S. Nair, M. Kuriakose, V. Somasundaram, V. Shenoi, M.R.P. Kurup and P. Srinivas, *Life Sci.*, **116**, 90 (2014); https://doi.org/10.1016/j.lfs.2014.09.011
14. A.-M. Li, *J. Coord. Chem.*, **67**, 2076 (2014); https://doi.org/10.1080/00958972.2014.931577
15. A. Rana, R. Dinda, P. Sengupta, S. Ghosh and L.R. Falvello, *Polyhedron*, **21**, 1023 (2002); https://doi.org/10.1016/S0277-5387(02)00913-0
16. A. Rana, R. Dinda, S. Ghosh and A. Blake, *Polyhedron*, **22**, 3075 (2003); https://doi.org/10.1016/j.poly.2003.06.001
17. S.S. Tandon, S. Chander and L.K. Thompson, *Inorg. Chim. Acta*, **300-302**, 683 (2000); https://doi.org/10.1016/S0020-1693(00)00010-4
18. H. Nazir, M. Yildiz, H. Yilmaz, M.N. Tahir and D. Ulku, *J. Mol. Struct.*, **524**, 241 (2000); https://doi.org/10.1016/S0022-2860(00)00393-8

19. N. Nawar and N.M. Hosny, *Chem. Pharm. Bull.*, **47**, 944 (1999); https://doi.org/10.1248/cpb.47.944
20. J. Easmon, G. Purstinger, K.S. Thies, G. Heinisch and J. Hofmann, *J. Med. Chem.*, **49**, 6343 (2006); https://doi.org/10.1021/jm060232u
21. P.V. Bernhardt, G.J. Wilson, P.C. Sharpe, D.S. Kalinowski and D.R. Richardson, *J. Biol. Inorg. Chem.*, **13**, 107 (2008); https://doi.org/10.1007/s00775-007-0300-4
22. A.A.R. Despaigne, L.F. Vieira, I.C. Mendes, F.B. Costa, N.L. Speziali and H. Beraldo, *J. Braz. Chem. Soc.*, **21**, 1247 (2010); https://doi.org/10.1590/S0103-50532010000700012
23. A.A.R. Despaigne, G.L. Parrilha, J.B. Izidoro, P.R. da Costa, R.G. dos Santos, O.E. Piro, E.E. Castellano, W.R. Rocha and H. Beraldo, *Eur. J. Med. Chem.*, **50**, 163 (2012); https://doi.org/10.1016/j.ejmech.2012.01.051
24. M. Alagesan, N.S.P. Bhuvanesh and N. Dharmaraj, *Dalton Trans.*, **42**, 7210 (2013); https://doi.org/10.1039/c3dt50371b
25. J.C. Jeffery, P. Thornton and M.D. Ward, *Inorg. Chem.*, **33**, 3612 (1994); https://doi.org/10.1021/ic00094a029
26. S.K. Dutta, E.R.T. Tiekink and M. Chaudhury, *Polyhedron*, **16**, 1863 (1997); https://doi.org/10.1016/S0277-5387(96)00491-3
27. J.P. Scovill, *Phosphorus Sulfur Silicon Rel. Elem.*, **60**, 15 (1991); https://doi.org/10.1080/10426509108233920
28. J.C. Pessoa, I. Tomaz and R.T. Henriques, *Inorg. Chim. Acta*, **356**, 121 (2003); https://doi.org/10.1016/S0020-1693(03)00395-5
29. R. Ando, T. Yagyu and M. Maeda, *Inorg. Chim. Acta*, **357**, 2237 (2004); https://doi.org/10.1016/j.ica.2003.12.031
30. R. Ando, S. Mori, M. Hayashi, T. Yagyu and M. Maeda, *Inorg. Chim. Acta*, **357**, 1177 (2004); https://doi.org/10.1016/j.ica.2003.09.033
31. Y.J. Jang and Y.U.K. Lee, *Bull. Korean Chem. Soc.*, **26**, 925 (2005); https://doi.org/10.5012/bkcs.2005.26.6.925
32. M. Pragathi and K.H. Reddy, *Asian J. Chem.*, **31**, 148 (2019); https://doi.org/10.14233/ajchem.2019.21558
33. D. Kasimbi, K.H. Reddy and N. Devanna, *Orient. J. Chem.*, **35**, 557 (2019); https://doi.org/10.13005/ojc/350208
34. P. Hari Babu and K.H. Reddy, *Indian J. Chem.*, **52A**, 327 (2013).
35. M. Pragahi and K.H. Reddy, *Inorg. Chim. Acta*, **413**, 174 (2014); https://doi.org/10.1016/j.ica.2014.01.010
36. P. Hari Babu, Y.K. Patil, K.H. Reddy and M. Nethaji, *Transition Met. Chem.*, **39**, 167 (2014); https://doi.org/10.1007/s11243-013-9786-5
37. W.J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971); https://doi.org/10.1016/S0010-8545(00)80009-0
38. A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier: Amsterdam (1984).
39. D.N. Kumar and B.S. Garg, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **64**, 141 (2006); https://doi.org/10.1016/j.saa.2005.07.008
40. K. Raja, A. Suseelamma and K.H. Reddy, *J. Chem. Sci.*, **128**, 23 (2016); https://doi.org/10.1007/s12039-015-1003-y
41. R.V. Prasad and N.V. Thakkar, *J. Mol. Catal.*, **92**, 9 (1994); https://doi.org/10.1016/0304-5102(94)00063-8
42. S. Belaid, A. Landreau, S. Djebbar, O. Benali-Baitich, G. Bouet and J.-P. Bouchara, *J. Inorg. Biochem.*, **102**, 63 (2008); https://doi.org/10.1016/j.jinorgbio.2007.07.001
43. N. Dharmaraj, P. Viswanathamurthi and K. Natarajan, *Transition Met. Chem.*, **26**, 105 (2001); https://doi.org/10.1023/A:1007132408648
44. B.G. Tweedy, *Phytopathology*, **55**, 910 (1964).
45. M.A. Neelakantan, M. Esakkiammal, S.S. Mariappan, J. Dharmaraja and T. Jeyakumar, *Indian J. Pharm. Sci.*, **72**, 216 (2010); https://doi.org/10.4103/0250-474X.65015