



Trade Science Inc.

ISSN : 0974 - 746X

Volume 6 Issue 1

Inorganic CHEMISTRY

An Indian Journal

Short Communication

ICAIJ, 6(1), 2011 [12-14]

Synthesis and characterization of new tetrazole ligands with their corresponding silver and mercury complexes

Alireza Dadrass*, Nader Noroozi Pesyan, Fatemeh Sarikhani
Chemistry Department, Urmia University, Urmia 57159-165, (IRAN)

E-mail : dadrassi@yahoo.com

Received: 21st November, 2010 ; Accepted: 1st December, 2010

ABSTRACT

In this article, the ligands of 5-aryloxytetrazoles (aryl = phenoxy, 4-nitro phenoxy, 3,4-dimethylphenoxy, 2,6-dimethoxyphenoxy) were synthesized by the reaction of phenol and its derivatives with cyanogen bromide in the presence of triethyl amine, followed by the sodium azide and then acidified to get final products. The reaction of tetrazole derivatives with silver and mercury salts (1:1) in methanol solvent were stirred for 24h. The products obtained were characterized by IR, ¹H and ¹³C NMR spectroscopy and microanalysis. © 2011 Trade Science Inc. - INDIA

KEYWORDS

Tetrazole ligands;
Tetrazole complexes;
Tetrazole reactions;
Silver complexes;
Mercury complexes.

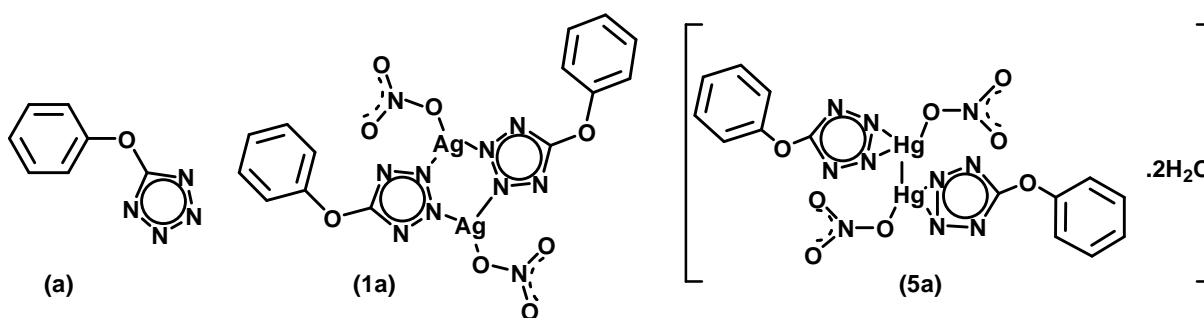
INTRODUCTION

Tetrazoles are an important functionality^[1] with wide ranging applications in photography and information recording systems^[2,3] in material sciences and appealing ligands in coordination chemistry^[4-8]. Tetrazols exhibit a strong networking ability usually acting as mono or bidentate ligands in most of the reported complexes. They are used as *cis*-peptide bond mimics, drugs in pharmaceuticals and bioisosteres for carboxylic acids^[9]. Since the acidity of tetrazole group corresponds closely with that of carboxylic acid, replacement of C-terminal amino acid residue with a tetrazole analogue often preserves or improves the biological activity of parent peptides. Alzheimer's β -secretase (BACE1) inhibitor^[2] KMI-420 and its α -isomer are potent drug molecules that possess tetrazole sub-units. They are also employed as catalysts in asymmetric synthesis, peptide chelating agents and metalloprotein stabilizers. Proline-derived

tetrazole is a powerful enantioselective catalyst used in conjugate addition reactions, asymmetric aldol, mannich reactions and multicomponent reactions. Tetrazoles exist as 1H and 2H tautomers of which the latter is found to be more stable. A difficulty that has to be taken into account in a study of this type is the low stability of these compounds in which isomerization processes (Dimroth rearrangement) may take place on heating, possibly catalysed by acidic or basic pH.

As part of our current studies on the synthesis of new series of heterocyclic tetrazoles, we have reported a facile synthesis of highly functionalized 5-aryloxytetrazoles derivatives such as (aryl = phenoxy (**a**), 4-nitro phenoxy (**b**), 3,4-dimethylphenoxy (**c**), 2,6-dimethoxyphenoxy (**d**)) compounds by published procedures^[10-13].

Silver (I), mercury (I) and mercury (II) are cations that have shown a higher number of different structural motifs when reacting with 5-aryloxytetrazoles^[4-7] and



Scheme 1

this is why we have chosen them for their ease of reactivity with tetrazoles. A dinuclear complexes probably have been obtained and their structures being described here. The reaction of 5- aryloxytetrazoles derivatives as suitable ligands with silver (I), mercury (I) and mercury (II) salts (1:1) in methanol solvent were stirred for 24h. The precipitate of products were separated and purified in chloroform and diethyl ether. The IR spectra of these ligands showed suitable bands at range of 2400-3100 cm^{-1} , which confirms the presence of tetrazoles. In the IR spectra of tetrazole complexes due to coordination via nitrogen atoms these bands were removed. Therefore in this respect we have synthesized five complexes of 5- aryloxytetrazoles with silver (I) nitrate, mercury (II) chloride, and mercury (I) nitrate. The ligand (a) and its complexes (1a), (5a) with silver and mercury salts were given in (Scheme 1).

RESULTS AND DISCUSSION

The $\nu(\text{CO})$ band which is sensitive to complexation occurs at range of 2400-3100 cm^{-1} for the highly functionalized 5- aryloxytetrazoles derivatives as ligand (aryl = phenoxy, 4-nitro phenoxy, 3,4-dimethylphenoxy, 2,6-dimethoxyphenoxy). The structures of compounds (a), (b), (c) and (d) were deduced from melting points, IR spectral data, ^1H , ^{13}C NMR and elemental analyses^[8-11]. The structures of metal complexes also were deduced from IR spectral data, ^1H , ^{13}C NMR and elemental analyses The IR spectra of tetrazole- complexes of (1a), (2b), (3c), (4d) and (5a) show that due to coordination of tetrazoles as ligand via nitrogen atoms these bands of tetrazoles were removed. ^1H and ^{13}C NMR spectroscopy of these complexes did not show much chemical shifts, may be due to remoteness of protons and carbons of 5- aryloxytetrazoles in complexes^[14-18].

EXPERIMENTAL

Starting materials and solvents were obtained from Merck and Aldrich and used without further purification. Melting points were measured on a SMPI apparatus. Elemental analysis for C, H and N were performed using a PE 2400 series II analyzer. IR and NMR spectra were determined in the region 4000- 400 cm^{-1} on a NEXUS 670 spectrometer by preparing KBr pellets. The ^1H and ^{13}C NMR spectra were recorded on Bruker 300 FT-NMR at 300 and 75 MHz, respectively (Urmia University, Urmia, Iran). ^1H and ^{13}C NMR spectra were obtained on solution in $\text{DMSO}-d_6$ as solvents using TMS as internal standard.

Synthesis of metal complexes of 5- aryloxytetrazoles derivatives

Typical synthetic procedure of 5-(phenoxy)1H-tetrazole silver(I) nitrate(1a)

To a magnetically stirred solution of 5-(phenoxy)1H- tetrazole (2.43g, 15 mmol) in pure methanol (20 ml) silver (I) nitrate (2.54, 15 mmol) was added. The mixture of reaction was refluxed for about 24 h. The white precipitate of the silver complex after filtration was obtained. The final product was washed with diethyl ether. Yield: 2.131g, 83%, m.p. 180.0-182.0 $^{\circ}\text{C}$. IR (KBr) (ν_{max} , cm^{-1}): 3421.61(s), 1591.73 (m), 1472.51(s), 1384.40 (m), 1224.42 (m), 1164 (w), 491.13 (w). ^1H NMR (300 MHz , $\text{DMSO}-d_6$, 25 $^{\circ}\text{C}$) δ_{H} : 7.41-7.47 (m, 2H), 7.23-7.29 (m, 2H). ^{13}C NMR (300 MHz , $\text{DMSO}-d_6$, 25 $^{\circ}\text{C}$) δ_{C} : 166.9, 154.8, 130.5, 125.80, 119.2 (5C of ph). Anal.Calc. for $\text{C}_{14}\text{H}_{10}\text{Ag}_2\text{N}_4\text{O}_8$ (659.88): C, 25.39; H, 1.51; N, 21.16. Found: C, 28.07; H, 1.60; 20.89; N, 20.89%.

Short Communication

Synthesis of 5-(4-nitrophenoxy)-1H-tetrazole silver(I) nitrate complex (2b)

White solid, Yield: 4.327 g, 76%, m.p. 198.0-200.0°C. IR (KBr) (ν_{\max} , cm^{-1}): 3421.93 (s), 3118.61 (m), 1613.40 (m), 1508.18 (s), 1462.93 (s), 1350.36 (s), 747.12 (m). ^1H NMR (300 MHz, DMSO- d_6 , 25°C) δ_{H} : 8.22 (d, $J = 9$ Hz, 2H), 7.30 (d, $J = 9$ Hz, 2H). ^{13}C NMR (300 MHz DMSO- d_6 , 25°C) δ_{C} : 160.79, 160.0 (2C), 143.59, 126.29, 118.4 (5C). Anal. Calcd. for $\text{C}_{14}\text{H}_8\text{Ag}_2\text{N}_{12}\text{O}_{12}$ (749.85): C, 22.36; H, 1.07; N, 22.35. Found: C, 21.90; H, 1.10; N, 22.16%.

Synthesis of 5-(4-nitrophenoxy)1H-tetrazole silver (I) nitrate complex (3c)

White solid, Yield: 3.570g, 71%, m.p. 148.0-150.0°C. IR (KBr)(ν_{\max} , cm^{-1}): 3431.71 (s), 2923.82 (m), 1613.86 (m), 1474.82 (s), 1384.12 (m), 1375.86 (m), 1247.68 (m), 1157.69 (w). ^1H NMR (300 MHz, DMSO- d_6 , 25°C) δ_{H} : 7.41-7.47 (m, 2H), 7.23-7.29 (m, 1H), 2.35 (s, 2CH₃). ^{13}C NMR (75 MHz DMSO- d_6 , 25°C) δ_{C} : 134.3, 139.4, 151.0 (3C), 118.1, 121.7, 13.1 (3C of ph), 14.4, 14.7 (2C of CH₃). Anal. Calc. for $\text{C}_{18}\text{H}_{18}\text{Ag}_2\text{N}_{10}\text{O}_8$ (715.94): C, 30.10; H, 2.53; N, 19.50. Found: C, 29.25; H, 2.41; 20.89; N, 19.34%.

Synthesis of 5-(2,6-dimethoxyphenoxy)1H-tetrazole mercury (II) chloride complex (4d)

Red solid, Yield: 6.159 g, 84%, m.p. 150.0-152.0°C. IR (KBr) (ν_{\max} , cm^{-1}): 3682.99 (s), 3352.52 (s), 1612.15 (s), 1483.62 (m), 1440.47 (w), 1305.26 (w), 1262.43 (m), 1110.68 (m), 760.66(w). ^1H NMR (300 MHz, DMSO- d_6 , 25°C) δ_{H} : 7.2 (d, $^3J_{\text{HH}} = 8.4$ Hz, 1H), 6.75 (d, $^3J_{\text{HH}} = 8.4$ Hz, 2H), 3.7 (s, 6H). ^{13}C NMR (75 MHz DMSO- d_6 , 25°C) δ_{C} : 166.9, 152.6, 138.6, 133.9, 131.0, 120.3, 116.5, 19.9, 19.1. Anal. Calc. for $\text{C}_{18}\text{H}_{18}\text{Cl}_4\text{Hg}_2\text{N}_8\text{O}_6$ (985.95): C, 21.94; H, 1.84; N, 11.37. Found: C, 22.08; H, 1.92; N, 11.44%.

Synthesis of 5-(phenoxy)1H-tetrazole mercury (I) nitrate complex (5a)

White solid, Yield: 6.359 g, 81%, m.p. 165.0-167.0°C. IR (KBr) (ν_{\max} , cm^{-1}): 3448.44 (s), 1618.57 (m), 1476.81 (m), 1384.28 (s), 1201.95 (w). ^1H NMR (300 MHz, DMSO- d_6 , 25°C) δ_{H} : 7.41 (m, 2H), 7.11 (m, 3H), 3.37 (s, 4H). ^{13}C NMR (75 MHz DMSO- d_6 , 25°C) δ_{C} : 169.2, 155.2, 130.3, 125.4, 119.0 (5C of ph). Anal. Calc. for $\text{C}_{14}\text{H}_{14}\text{Hg}_2\text{N}_{10}\text{O}_{10}$ (886.03): C, 19.03; H, 1.60; N, 15.85. Found: C, 20.07; H, 1.60; 20.89; N, 15.89%.

ACKNOWLEDGEMENT

We are highly grateful to the university of Urmia for a grant and Mr. Mehdi Ghavidel for recording the NMR spectra.

REFERENCES

- [1] J.A.Bladin; Ber., **18**, 1544 (1885).
- [2] G.I.Koldobskii, V.A.Ostrovskii; Usp.Khim., **63**, 847-865 (1994).
- [3] V.A.Ostrovskii, M.S.Pevzner, T.P.Kofman, M.B.Sheherbinin, I.V.Tselinskii; Targets Heterocycl.Syst., **3**, 467-526 (1999).
- [4] M.Hisky, D.E.Chavez, D.L.Naud, S.F.Son, H.L.Berghout, C.Bome; Proc.Int.Pyrotech.Semin., **27**, 3 (2000).
- [5] R.N.Butler, A.R.Katritzky, A.J.Boulton (Eds.); Adv.Heterocycl.Chem.Academic Press, New York, **21**, 323-435 (1977).
- [6] C.Matthias-Grunert, P.Weinberger, J.Schweifer, C.Hamper, A.F.Stassen, K.Mereiter, W.Linert; J.Mol.Struc., **733**, 41-52 (2005).
- [7] (a) Y.S.Gyoung, J.G.Shim, Y.Yamamoto; Tetrahedron Lett., **41**, 4193-4196 (2002); (b) A.F.Stassen, E.Dova, J.Ensling, H.Schenk, P.Gutlich, J.G.Haasnoot, J.Reedijk; Inorg.Chim.Acta, **335**, 61-68 (2002).
- [8] H.Singh, A.S.Chawla, U.K.Kapoor, D.Paul, R.K.Malhotra; Prog.Med.Chem., **17**, 151-183 (1980).
- [9] H.A.Dabbagh, W.J.Lwowski; J.Org.Chem., **65**, 7284-7290 (2000).
- [10] H.A.Dabbagh, W.J.Lwowski; J.Org.Chem., **54**, 3952-3957 (1989).
- [11] H.A.Dabbagh, A.R.Modarresi-Alam; J.Of Chem. Res.(S), **44** (2000).
- [12] H.A.Dabbagh, Y.Mansoori; Russian J.Org.Chem., **37**, 1771 (2001).
- [13] L.Carlucci, G.Ciani, D.M.Proserpio; Angew.Chem. Int.Ed., **38**, 3488 (1999).
- [14] T.Wu, R.Zhou, D.Li; Inorg.Chem.Comm., **9**, 341 (2006).
- [15] X.M.Zhang, Y.F.Zhao, H.S.Wu, S.R.Batten, S.W.Ng; Dalton Trans, **3**, 170 (2006).
- [16] Y.Chen, Z.G.Ren, H.X.Li, X.Y.Tang, W.H.Zhang, Y.Zhang, J.P.Lang; J.Mol.Struc., **875**, 339 (2008).
- [17] X.S.Wang, Y.Z.Tang, R.G.Xiong; Chin.J.Inorg. Chem., **21**, 1025 (2005).
- [18] Z.Li, M.Li, X.P.Zhou, T.Wu, D.Li, S.W.Ng; Cryst. Growth Des., **7**, 1992 (2007).