Jurnal Akta Kimia Indonesia

INDONESIA CHIMICA ACTA

PAPER

View Article Online
View Journal View Issue

Theoretical Study of Metal Ion Impact on Geometry and Bond Vibrational Properties of Salophen Compound

Cite this: *Indo. Chim. Acta.*, 2024, **17**, **1**.

Received Date:
15th November, 2023
Accepted Date:
20th June, 2024

Keywords:
Salophene;
Semiempirical;
Metal ion.

DOI:
http://dx.doi.org/10.20956/ica.v17i1.31808

Tety Wahyuningsih Manurung[1], Muhammad Hilmi Afthoni[2], Yehezkiel Steven Kur[3], Marvin Horale Pasaribu[1], Mokhamat Ariefin[1], and Rokiy Alfanaar[1*]

Abstract. Coordination compounds are compounds consisting of a metal atom as a center surrounded by ligands, which are important in applications such as catalysts and pharmacological sensors. Salophen, as one of the organic ligands, is capable of forming complexes with various metal ions. This study uses a computational chemistry approach to model the geometry, electronic properties, and bond vibrations of compound complexes between salophen and Zn(II), Cd(II), and Hg(II) metal ions using the PM6 semiempirical method. Modeling results show that the metal ion radius affects the dihedral angle of salophen, with the largest angle occurring in the complex with Hg(II) ions, while the complex with Cd(II) ions tends to be close to planar. FTIR analysis shows that the vibrational pattern is influenced by the bond length of salophen with metal ions. In addition, the HOMO-LUMO gap energy of the three complexes is also slightly different, with the Zn-salophen complex having the smallest Egap of 0.25709 eV.

Introduction

Coordination compounds are compounds consisting of a central metal ion surrounded by ligands. These compounds have a wide range of applications, such as in the fields of catalysis (Bhat & Darensbourg., 2023), sensors (Gul et al., 2023), and medicine (Yunus et al., 2023). One type of research that is currently developing is theoretical modeling research (Liu et al., 2017a; Streitwieser et al., 2010). This research uses computational chemistry methods to predict the properties of coordination compounds, such as structure, energy, and spectroscopic properties.

Salophen is an organic compound that can form coordination compounds with various metal ions (Groysman et al., 2005; Meijboom et al., 2009; Mota et al., 2012; Wu et al., 2008). This compound has four lone pair electron donor atoms that can form coordination bonds with metal ions. Theoretical modeling with computational chemistry can be used to study the properties of salophen coordination compounds. One method that can be used is the PM6 semiempirical method. This method is faster in calculation than the ab initio method but can still provide accurate results. The PM6 semiempirical method can be used to study salophene coordination compounds more quickly and efficiently (Hostaš et al., 2013; Praveen et al., 2015; Řezáč et al., 2009; Thiel, 2014). This research can provide evidence that this method can be used to provide accurate results.This research will be conducted using the PM6 semiempirical method. This method will be used to predict the structure, energy, and spectroscopic properties of salophen coordination compounds with Zinc, Cadmium, and Mercury metal ions.

Salophen is a compound that has a wide range of potential applications. Metal-salophene compounds show diverse potential in various applications, especially as

---

[1] *Departement of Chemistry, Faculty of Mathematic and Sciences, Palangka Raya University, H Timang Street, Palangka Raya, 74111, Indonesia;* ***Email: rokiy.alfanaar@mipa.upr.ac.id***

[2] *Departement of Pharmacy, Faculty of Pharmacy, Jember University, Jl. Kalimantan I No. 2, Sumbersari Jember, Indonesia*

[3] *Departement of Chemistry, Faculty of Mathematic and Sciences, Gadjah Mada University, Sekip Utara, Bulaksumur, Yogyakarta, 55281, Indonesia*

catalysts in redox reactions of organic compounds such as Fe(III)-salophene or Mn(III)-salophene (Ansari et al., 2009). In addition, in complex with metal lanthanides, metal-salophene can bind to neutral molecules such as sugars and lipids, which can act as biomarkers for some cancers such as ovarian cancer (alpturk et al., 2006). In addition to non-redox metal ions, metal ions such as Zn(II) can also be used as fluorescence probes in biological applications (Hai et al., 2011). Different metal ions can have different effects on the structure and spectroscopic properties of salophen coordination compounds (Guino-o et al., 2008; Liu et al., 2017b). Based on that, its better understanding of the properties of these compounds with different ions that have different radius but similar electronic structure in *d* orbital like Zn, Cd, and Hg to help in the development of new applications.

Research with the title "Theoretical Study of Metal Ion Impact on Geometry and Bond Vibrational Properties of Salophen Compound" needs to be done to study the effect of metal ions on the structure and spectroscopic properties of salophen coordination compounds. This research is expected to provide a better understanding of the interaction between metal ions and salophen ligands. The results of this research can also be used to develop salophen coordination compounds with desirable properties.

Experimental

Material and Methods

Calculation and optimation was conducted using personal computer with spesification processor Intel® core™ i5-7200 2.5 GHz, harddisk 1000Gb, RAM 8 Gb, and display VGA 2 Gb. Computational calculation was performed using Gausssian 16 and Gaussian View 6. The computational method used in this study is semi-empirical Parameterized Method 6 (PM6) method for geometry optimization and calculation of molecular vibrational frequencies.

Procedures

The test compounds were drawn using ChemDraw software and safe file using mol extention. The compound test were salophen ligands, Zn-salophen complexes, Cd-salophen, and Hg-salophen. After that, the initial structure was optimized and used Gaussian 16 with the semiempirical method PM6. The optimization results are then calculated to obtain bond vibration data. Visualization of compounds is done with gaussian view 6 software. The data results of vibration bond are represented using Excel to get IR spectra of compounds.

Result and Discussion

Optimized Ligand and Complex Structures

The results of salophen ligand structure optimization are available in Figure 2. In the free state, the salophen ligand has a planar structure. Each benzene ring in salophen has a dihedral angle of 0° with respect to the imine bond in the salophen structure. The dimensional parameters for salophen ligands are presented in Table 1.

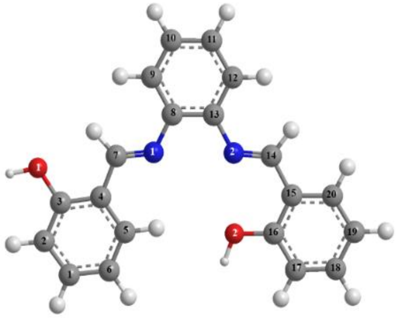

Figure 2. Optimization structure of salophen.

Salophen which acts as a ligand has an active side to form complex compounds with metal ions (Zn^{2+}, $Cd^{2+,}$ and Hg^{2+}). The active side as a chelator on salophen is in the imine group (N = C) and hydroxy group (-OH). Hydroxy groups can act as chelators because they are slightly acidic so that they can interact with metal ions through their anion structure. Furthermore, the mildly basic imine group can act as a Schiff base that donates free electrons pair on the N atom to the metal ion. In metal complex of Zn, Cd, and Hg salophen, each metal form four coordination bonding with salophen through oxygen and nitrogen atom. The complex structures of $[Zn(salophen)]^{2+}$, $[Cd(salophen)]^{2+}$, and $[Hg(salophen)]^{2+}$ is available in Figure 3.

Table 1. Dimensional Parameter of Optimized Ligand Geometry.

Optimized Geometry Parameter					
Bond Angle		**Bond Length**		**Dihedral Angle**	
Atom	Value	Atom	Value	Atom	Value
C_7-N_1-C_8	123.6	N_1-C_8	1.424	O_1,C_3-C_4,C_7	0°
C_{14}-N_2-C_{13}	122°	N_1-C_7	1.298	C_3,C_4-$C_7$$N_1$	0°
H_3-O_1-C_3	112°	N_2-C_{13}	1.428		
O_1-C_3-C_4	115.8°	N_2-C_{14}	1.298		
C_3-C_4-C_7	120.2°	O_1-C_3	1.377		
C_4-C_7-N_1	118.1°	O_2-C_{16}	1.362		

continue from Table 1

Optimized Geometry Parameter					
Bond Angle		**Bond Length**		**Dihedral Angle**	
Atom	Value	Atom	Value	Atom	Value
H_{16}-O_2-C_{16}	111.7°				
O_2-C_{16}-C_{15}	117.9°				
C_{16}-C_{15}-C_{14}	120.7°				
C_{15}-C_{14}-N_2	118.1°				

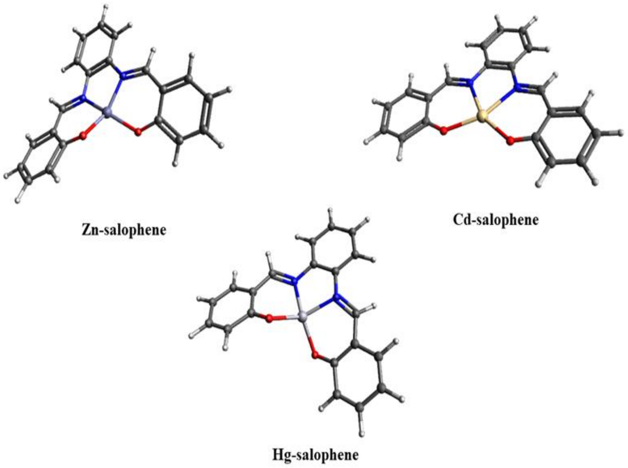

Figure 3. Geometry optimized result for $[M(salophen)]^{2+}$ complex.

The physical parameters of the metal ion complex salophen are provided in Table 2 and the ID number is available in Figure 3. The structures of the Zn, Cd, and Hg ion complexes have bond lengths that vary between M-O and M-N (M = metal). The longest bond length is found in the Cd-salophen complex which is 2.138 for M-O and 2.296 for M-N. This is possible because Cd ions have the longest ionic radius compared to Zn and Hg.

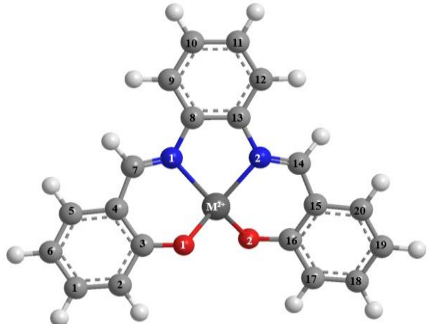

Figure 4. Complex metal-ligand ID number.

The presence of metal ions in salophen changes some characteristics of the ligand. In the salophen ligand, the C=N double bond in the imine group has a length of 1.298. Furthermore, with the presence of metal ions, the length of the C=N bond increases to 1.329, 1.331, and 1.315 in the Zn, Cd, and Hg complexes, respectively. This phenomenon can occur because to maximize the metal chelation process, the bond length on the C=N side will experience stretching.

Not only the length of the C=N bond but changes also occur in the dihedral angle between benzene rings on salophen. In salophen, each benzene ring is in a planar position (dihedral angle 0). The presence of Zn and Hg metals in salophen causes salophen to lose its planar structure. The dihedral angles of the Zn and Hg complexes are available in Table 2. The existence of dihedral angles in the Zn and Hg complex structure is due to the repulsion between electron clouds on the ligand and metal, therefore, an optimum position is needed to obtain a stable structure (lowest energy). However, unlike the Zn and Hg complexes, salophen can maintain its planar shape when it binds to Cd^{2+} ions. This is evidenced by its dihedral angle value of 0°. This is possible because the bond distance between the chelating atoms and the metal is quite large in the Cd-salophen ion complex, so that the bonds in the benzene ring do not need to undergo twisting to get the optimum geometry shape.

Table 2. Dimensional parameter for complex $[M(salophen)]^{2+}$.

Parameter	Atom	Complex $[M(salophen)]^{2+}$		
		Zn	Cd	Hg
Bond length (Å)	N_1-C_8	1.437	1.448	1.436
	N_1-C_7	1.329	1.331	1.315
	N_2-C_{13}	1.437	1.448	1.436
	N_2-C_{14}	1.329	1.331	1.315
	O_1-C_3	1.280	1.278	1.296
	O_2-C_{16}	1.280	1.278	1.296
	M-O_1	1.947	2.138	2.011
	M-O_2	1.947	2.138	2.011
	M-N_1	1.989	2.296	2.067
	M-N_2	1.989	2.296	2.067
Bond Angle (°)	C_7-N_1-C_8	122.4	118.8	124.5
	C_7-N_1-M	124.7	127.0	117.3
	C_8-N_1-M	111.5	114.2	112.1
	C_{14}-N_2-C_{13}	122.4	118.8	124.5
	C_{14}-N_2-M	124.7	127.0	117.3

continue from Table 2

Parameter	Atom	Complex $[M(salophen)]^{2+}$		
		Zn	Cd	Hg
	C_{13}-N_2-M	111.5	114.2	112.1
	C_3-O_1-M	124.1	134.3	111.1
	C_{16}-O_2-M	124.1	134.2	111.1
	O_1-M-N_1	92.5	82.3	95.3
	O_1-M-O_2	104.7	120.4	111.7
	N_1-M-N_2	85.1	74.9	82.1
	N_2-M-O_2	92.5	82.3	95.7
Dihedral Angle (°)	M,O_1-C_3C_2	163.4	179.8	143.2
	M,O_1-C_3C_4	18.8	0.1	42.3
	M,O_2-$C_{16}C_{17}$	163.4	179.9	143.2
	M,O_2-$C_{16}C_{15}$	18.8	0.1	42.3
	M,N_2-C_{14},C_{15}	0.3	0.0	18.4
	M,N_2-C_8,C_{13}	4.8	0.0	0.1

Infrared Spectra and Energy Level of Optimized Complex

The predicted infrared (IR) vibrational spectra of the salophen ligand, [Zn(salophen)], [Cd(salophen)], and [Hg(salophen)] ions can be seen in Figure 4. IR prediction using semiempirical PM6 reveal typical vibration for (C-H) stretching, which occurs at 2539 cm^{-1} and its bending vibration showed at 809 cm^{-1}. Spectrum at 1600-1718 cm^{-1} indicated stretching vibration of (C=C) aromatic ring. Imine group (C=N) stretching vibration strong band in 1479 cm^{-1}. In the ion complex $[M(salophene)]^{2+}$, almost all the absorbances of the salophene ligand experience a red shift and an increase in absorbance intensity. The absorption values of salophene ligand and ion complex are available in Table 4. the ν(C=N) of salophen ligand around 1479 cm^{-1} experienced a downshift to 1343-1354 cm^{-1} and ν(C-O) aromatic downshift from 1377-1362 cm^{-1} to 1280-1289 cm^{-1}. This downshift is caused by the increase in the length of the C=N or C-O bond due to the presence of metal in the complex ion (Hasegawa et al., 2002).

The existence of metal ions not only affects the vibration of the bond, but also affects the energy level possessed by the salophen ligand. The energy levels of salophen and ion complex $[M(salophen)]^{2+}$ can be seen in Figure 6. In Figure 6, the salophen ligand has a HOMO value of -0.30595 and LUMO -0.21532. The HOMO value of the $[M(salophen)]^{2+}$ complex slightly increases at levels between -0.30535 to -0.29887. The presence of Zn, Cd, and Hg metal ions does not give significant changes to the HOMO value. In other hand, the LUMO value changes significantly with the presence of metal ions. The LUMO value of the compound increases at the level of -0.04826 to -0.04093. This phenomenon can be explained because the filled *d* orbital of metal ion donates electron density into the empty or partially π^* orbital of the ligand. The interaction stabilizes the metal-ligand bond. The back donation of electron density from the metal ion into the ligand's π^* orbital may raise the energy of ligand's LUMO.

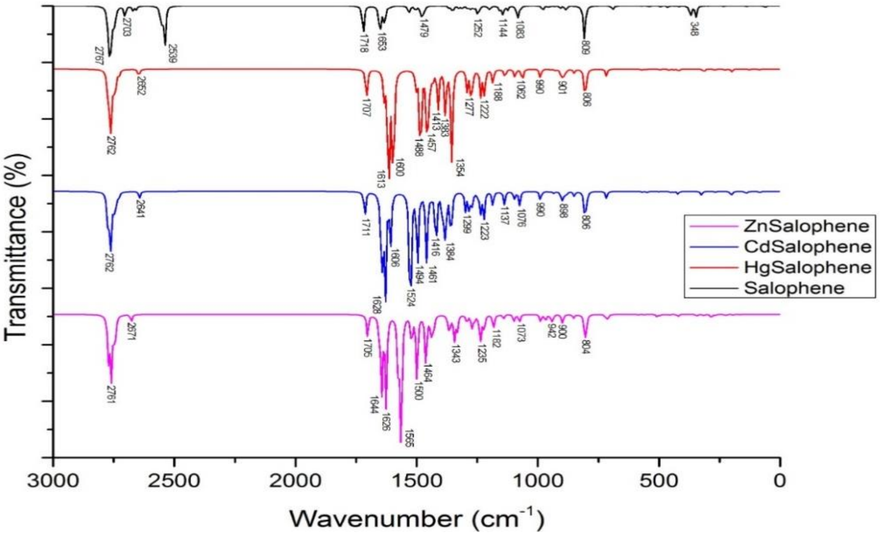

Figure 5. Infrared (IR) spectrum for salophen and ion $[M(salophen)]^{2+}$.

Table 3. Vibrational bond and wave number of salophen and $[M(salophen)]^{2+}$ complex ion from semiempirical calculation.

Vibration	Wavenumber (cm^{-1})			
	Salophen	$[Zn(salophen)]^{2+}$	$[Cd(salophen)]^{2+}$	$[Hg(salophen)]^{2+}$
V stretching (C–H)	2539, 2703, 2767	2671, 2761	2641, 2762	2641, 2762
V stretching (C=C) aromatic	1653, 1718	1626, 1644, 1705	1606, 1628, 1711	1600, 1612, 1703
V stretching (C=N)	1479	1343, 1464, 1500, 1565	1384, 1416, 1461, 1494, 1524	1354, 1388, 1457, 1488
V stretching (C-O) aromatic	1083, 1144, 1252	1073, 1182, 1235	1076, 1137 1223, 1299	1062, 1188, 1222, 1277
V bending (C–H)	809	804	806	806
V stretching (O-M-O)	-	900,942	898,990	901,990

M = metal (Zn, Cd, Hg)

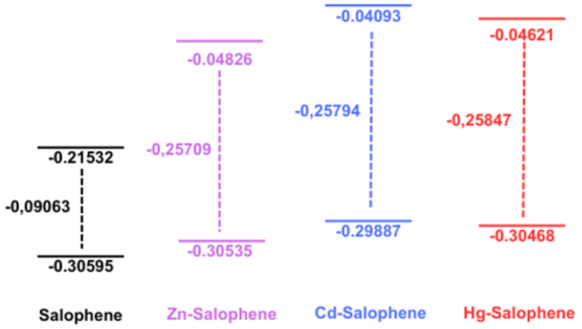

Figure 6. The energy levels of salophen and ion complex $[M(salophen)]^{2+}$.

Conclusion

Modeling of the complex structure of salophen ion and Zn^{2+}, Hg^{2+}, and Cd^{2+} metals has been carried out using a semiempirical method. Through modeling using the PM6 method, it was found that the radius of the metal ion affects the dihedral angle of the salophen ligand. Cd^{2+} metal has a dihedral angle value close to planar (0°) compared to Zn^{2+} and Hg^{2+} which is due to the longer bond of Cd^{2+} salophen compared to Zn^{2+} and Hg^{2+} salophen. the vibrational characteristics of metal-complex bonds are also influenced by the bond length between salophen and metal ions which can be seen from the modeling results of its FTIR spectra. In addition, the presence of metal ions can increase the energy gap of the salophene ligand.

Conflict of Interest

The authors declare that there is no conflict of interest.

References

Alptürk, O., Rusin, O., Fakayode, S. O., Wang, W., Escobedo, J. O., Warner, I. M., Crowe, W. E., Král, V., Pruet, J. M., & Strongin, R. M. (2006). Lanthanide complexes as fluorescent indicators for neutral sugars and cancer biomarkers. *Proceedings of the National Academy of Sciences,* 103(26), 9756–9760. https://doi.org/10.1073/pnas.0603758103

Ansari, K. I., Kasiri, S., Grant, J. D., & Mandal, S. S. (2009). Apoptosis and anti-tumour activities of manganese(iii)-salen and -salphen complexes. *Dalton Transactions*, 40, 8525. https://doi.org/10.1039/b905276c

Bhat, G. A., & Darensbourg, D. J. (2023). Coordination complexes as catalysts for the coupling reactions of oxiranes and carbon dioxide. *Coordination Chemistry Reviews*, 492, 215277.

Groysman, S., Sergeeva, E., Goldberg, I., & Kol, M. (2005). Salophan Complexes of Group IV Metals. *European Journal of Inorganic Chemistry*, 2005(12), 2480–2485. https://doi.org/10.1002/ejic.200500243

Guino-o, M. A., Baker, E., & Ruhlandt-Senge, K. (2008). The metal influence on the structural chemistry of alkynes: synthetic, spectroscopic and structural studies on magnesium acetylides. *Journal of Coordination Chemistry*, 61(1), 125–136. https://doi.org/10.1080/00958970701732790

Gul, Z., Khan, S., Ullah, S., Ullah, H., Khan, M. U., Ullah, M., & Altaf, A. A. (2024). Recent development in coordination compounds as a sensor for cyanide ions in biological and environmental segments. *Critical Reviews in Analytical Chemistry*, 54(3), 508-528.

Hai, Y., Chen, J.-J., Zhao, P., Lv, H., Yu, Y., Xu, P., & Zhang, J.-L. (2011). Luminescent zinc salen complexes as single and two-photon fluorescence subcellular imaging probes. *Chem. Commun*., 47(8), 2435–2437. https://doi.org/10.1039/C0CC04113K

Hasegawa, K., Ono, T., & Noguchi, T. (2002). Ab Initio Density Functional Theory Calculations and Vibrational Analysis of Zinc-Bound 4-Methylimidazole as a Model of a Histidine Ligand in Metalloenzymes. *The Journal of Physical Chemistry A*, 106(14), 3377–3390. https://doi.org/10.1021/jp012251f

Hostaš, J., Řezáč, J., & Hobza, P. (2013). On the performance of the semiempirical quantum mechanical PM6 and PM7 methods for noncovalent interactions. *Chemical Physics Letters*, 568–569, 161–166. https://doi.org/10.1016/j.cplett.2013.02.069

Liu, P., Qin, R., Fu, G., & Zheng, N. (2017a). Surface Coordination Chemistry of Metal Nanomaterials. *Journal of the American Chemical Society*, 139(6), 2122–2131. https://doi.org/10.1021/jacs.6b10978

Liu, P., Qin, R., Fu, G., & Zheng, N. (2017b). Surface Coordination Chemistry of Metal Nanomaterials. *Journal of the American Chemical Society*, 139(6), 2122–2131. https://doi.org/10.1021/jacs.6b10978

Meijboom, R., Bowen, R. J., & Berners-Price, S. J. (2009). Coordination complexes of silver(I) with tertiary phosphine and related ligands. *Coordination Chemistry Reviews*, 253(3–4), 325–342. https://doi.org/10.1016/j.ccr.2008.03.001

Mota, V. Z., de Carvalho, G. S. G., Corbi, P. P., Bergamini, F. R. G., Formiga, A. L. B., Diniz, R., Freitas, M. C. R., da Silva, A. D., & Cuin, A. (2012). Crystal structure and theoretical studies of the keto-enol isomerism of N,N′-bis(salicylidene)-o-phenylenediamine (salophen). Spectrochimica Acta Part A: *Molecular and Biomolecular Spectroscopy*, 99, 110–115. https://doi.org/10.1016/j.saa.2012.09.002

Praveen, P. A., Babu, R. R., & Ramamurthi, K. (2015). *Validation of PM6 & PM7 semiempirical methods on polarizability calculations*. 090011. https://doi.org/10.1063/1.4917991

Řezáč, J., Fanfrlík, J., Salahub, D., & Hobza, P. (2009). Semiempirical Quantum Chemical PM6 Method Augmented by Dispersion and H-Bonding Correction Terms Reliably Describes Various Types of Noncovalent Complexes. *Journal of Chemical Theory and Computation*, 5(7), 1749–1760. https://doi.org/10.1021/ct9000922

Streitwieser, A., Reyes, J. R., Singhapricha, T., Vu, S., & Shah, K. (2010). Ab Initio Modeling of Organolithium Equilibria. *The Journal of Organic Chemistry*, 75(11), 3821–3830. https://doi.org/10.1021/jo100864y

Thiel, W. (2014). Semiempirical quantum–chemical methods. *WIREs Computational Molecular Science*, 4(2), 145–157. https://doi.org/10.1002/wcms.1161

Wu, J.-C., Liu, S.-X., Keene, T. D., Neels, A., Mereacre, V., Powell, A. K., & Decurtins, S. (2008). Coordination Chemistry of a π-Extended, Rigid and Redox-Active Tetrathiafulvalene-Fused Schiff-Base Ligand. *Inorganic Chemistry*, 47(8), 3452–3459. https://doi.org/10.1021/ic800138x

Yunus, M. A., Indah, R., Nurfiansyah, N., & Mimin , S. (2023). The Synthesis, Characterization Gd(Iii) Complex with Heptilmethyl- Ditiocarbamate and 2,9-Dimethyl Phenanthroline as Anti-Tuberculosis. *Jurnal Akta Kimia Indonesia (Indonesia Chimica Acta)*, 16(1), 9-12. https://doi.org/10.20956/ica.v16i1.26900