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SYNTHESIS, SPECTRAL AND CHEMICAL TERMITE CONTROL STUDIES OF NITROKETENE DITHIOACETAL-METAL COMPLEXES

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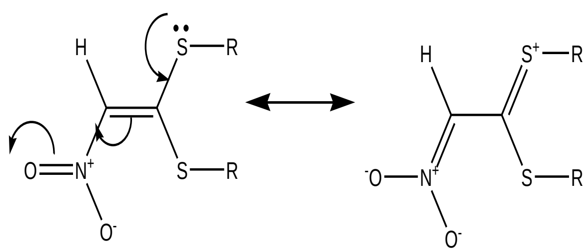
ABSTRACT

In synthetic organic chemistry, the nitroketene dithioacetal motif (NKDA) based organo sulfur compounds are well known intermediates as a two carbon push–pull system. The nitro group acts as a powerful electron-withdrawing group and the two alkylated sulfur atoms readily donate their lone-pair of electrons to make the entire NKDA motif frame work as highly polarized system. Thorough literature search in the field of Nitroketene dithioacetal chemistry showed the importance of this class of compounds in synthetic organo sulfur chemistry. We have reported for the first time that the transition metal complexes with NKDA motif are showing good termicidal activity studies. With this basic knowledge and research experience, we have started to extend our synthesis of NKDA-Metal complexes and to characterize the structure of the complexes using UV-VIS, IR, , FAB- mass studies, EDX analysis and C,H,N elemental analytical studies. The extension of the synthesis of this class of metal complexes with nitroketene dithioacetal motif may result in the formation of library of complexes to study the termicidal activity of complexes.

KEY WORDS: NKDA-Metal complexes, Organo Sulphur compounds, Termicidal activity, *Odontotermes horni.*

INTRODUCTION

In synthetic organic chemistry, the nitroketene dithioacetal motif (NKDA) based organo sulfur compounds are well known intermediates as a two carbon push-pull system (Sakthikumar *et al.,* 2002 and 2003) . The nitro group acts as a powerful electron-withdrawing group and the two alkylated sulfur atoms readily donate their lone-pair of electrons to make the entire NKDA motif frame work as highly polarized system. The push and pull polarization of E-and Z- sulfur lone pair of electrons with respect to the nitro group of the NKDA motif is possibly conjugated which is represented as below



Nitroketene dithioacetals occupy an important role in organo-sulfur chemistry as a two carbon synthon (Bhawal *et al.*,1993; Hsu *et al*., 1997; Fun *et al*., 2000; Rao and Sivakumar, 2005 and 2006; Alan Aitken,2005; Howell and Richardson, 2007; Prakash Rao and Sivakumar, 2007; Rao and Vasantham 2009 and 2011) It acts as good Michael acceptors in the synthesis of variety of sulfur heterocycles Anjukam *et al.,* 2008; Surya Prakash Rao, 2008; Li *et al*., 2011; Bai *et al*.,2012; Bi *et al.,* 2013; Kuthati Bhaskar and Poshala Ramesh, 2013 and Ravi Sankar Reddy and Risy Namratha , 2013), The synthesis of different bis S-alkylated derivatives of nitroketene dithioacetals by a two step process (Bhawal *et al.*,1993 Fun *et al.,* 2000; Sakthikumar *et al.,* 2002 and 2003) From the patent literature it is found that sulfoxide derivatives of nitroketene dithioacetals show impressive insecticidal activity (Hsu *et al.,* 1997). Recently we have reported that the alkyl and aryl group substituted derivatives of nitoketene dithio acetals showed central nervous system depressant activity in albino mice screening animal model experiments (Anjukam *et al.,*2008). Termites are global problem all around the world and especially in tropical areas where relative humidity was higher. Biodegradation of wood caused by termites is recognized as one of the most serious problems for wood utilization. It is also known that termites damage a variety of materials ranging from paper fabrics to even non-cellulosic materials such as asbestos, asphalt bitumen, lead, and metal foils. For nondurable woods, it may be necessary to use inorganic compounds or synthetic pesticides to preserve the woods and prolong their application life. As regards the habitats, there are mainly two kinds of termite,viz ., the wood dwellers and the ground dwellers . Further, the wood dwellers are categorized as damp wood and dry wood dwellers whereas the ground dwellers are classified as subterranean , mound and carton-nest builders. Odontotermes horni is a species of termites of the genus odontotermes. It is native to India and Srilanka. It attacks many dead, decaying trees and fertilized soil. Though nest on ground, they do not construct a termitaria. It is pest of tea , coconut and sugar cane. Many types of termites are in the world. In view of these interesting biological aspects, we became interested to synthesise different NKDA-Metal complexes and to study the termicidal activity (Ananthanarayan and Paniker, 2000), against *Odontotermes horni*.

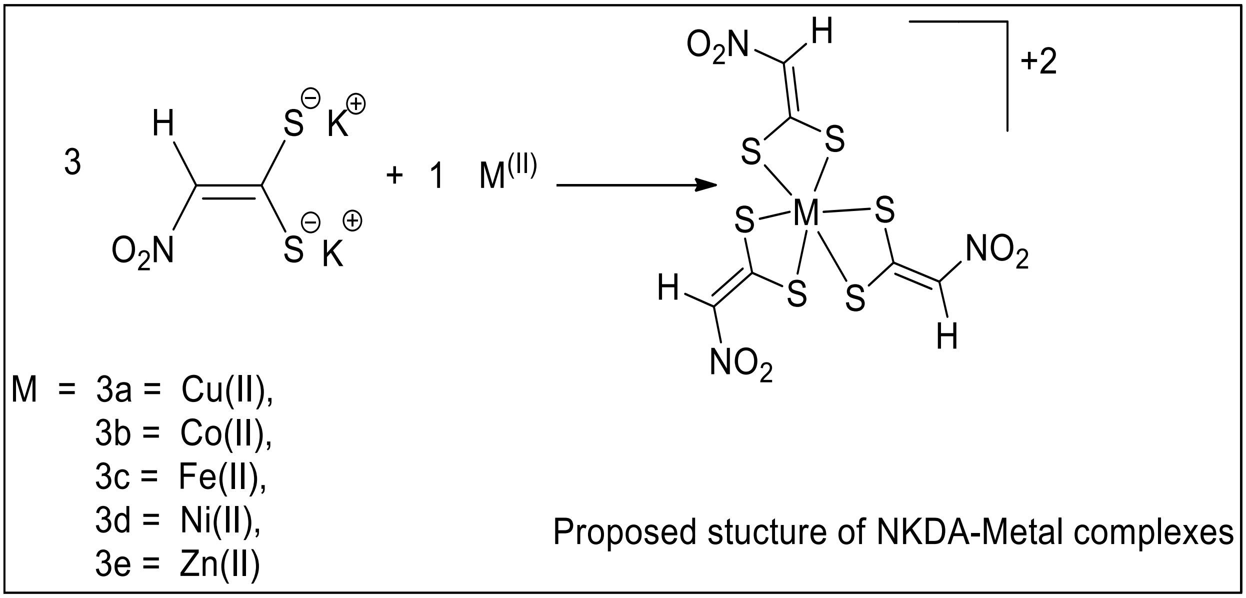
MATERIALS AND METHODS

Analar grade chemicals and reagents were used in all the synthetic steps. The progress of product formation was monitored by TLC using hexane and ethyl acetate solvent system. Purification of all compounds carried out by column chromatography using silica gel 100-200 mesh. IR spectra were recorded in Shimadzu instrument as neat and KBr pellet. ^{1}H & ^{13}C NMR were recorded in Bruker-300 MHz NMR using $CDCl_3$ as solvent.

General procedure for the synthesis of NKDA - Metal Complexes

10 mmol (3.372g) of Nitroketene dithioacetal (NKDA) was dissolved in 20 ml of distilled water. 10 mL of aqueous solution of the metal salt M (3 mmol, where M = $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $ZnCl_2.4H_2O$, $FeCl_3$ and $CuCl_2$) were added to the NKDA solution. The mixture was refluxed for overnight and left to stand. The precipitates formed were filtered, washed with distilled water and methanol. The precipitates formed were

stored in well-labeled containers and dried over $CaCl_2$ in a dessicator.



Scheme 1: Schematic representation of synthesis of NKDA-Metal complexes

Structural characterization of NKDA-Copper complex(3a)

Blue colour solid; Melting point = 244-246 ˚C; Yield: 56.4%; UV (methanol) λ_{max}: 540 and 745 nm; IR(nujol): $\nu_{(C=C)}$1653, $\nu_{(C-NO2)}$1398, $\nu_{(M-S)}$423, $\nu_{(N-CH=C)}$1455, $\nu_{(N-O\ Stret)}$ 1165 cm^{-1}; FAB mass(*m/z*): 465 (M^+); Anal. Calcd: C, 43.2; H, 2.05; N, 3.47; O, 14.78; S, 29.6; Found: C, 47.56; H, 2.93; N, 3.01; O, 14.89; S, 28.98. Molar conductance ($ohm^{-1}cm^2mol^{-1}$) : 18.75

Structural characterization of NKDA-Cobalt complex(3b)

Dark pink solid ; Melting Point: 260-262 ˚C; Yield: 52.0%; UV (methanol) λ_{max}: 282 and 585 nm. IR(nujol): $\nu_{(C=C)}$1652, $\nu_{(C-NO2)}$1395, $\nu_{(M-S)}$465, $\nu_{(N-CH=C)}$1464, $\nu_{(N-O\ Stret)}$1149 cm^{-1}; FAB mass (*m/z*): 463 (M^+); Anal. Calcd for: C, 46.9; H, 2.71; N, 3.17; O, 16.38; S, 32.8; Found: C, 47.56; H, 2.93; N, 3.01, O, 16.89, S, 32.98. Molar conductance ($ohm^{-1}cm^2mol^{-1}$): 19.23

Structural characterization of NKDA-Iron complex(3c)

Green, solid; Melting Point = 260-262 ˚C; Yield: 52.0% ; UV (methanol) λ_{max} 580 nm; IR(nujol): $\nu_{(C=C)}$1644, $\nu_{(C-NO2)}$1404, $\nu_{(M-S)}$427, $\nu_{(N-CH=C)}$1460, $\nu_{(N-O\ Stret)}$1167 cm^{-1}; ^{1}H NMR (300 MHz, d_6-DMSO): δ 6.70 (s, 3H) ppm; ^{13}C NMR (75 MHz, d_6-DMSO): δ113.6 (olefinic-C), 146.1(quaternary=C) ppm. FAB mass (*m/z*): 463(M^+); Anal. Calcd : C, 43.69; H, 2.13; N, 3.55; O, 14.96; S, 29.9; Found: C, 45.76; H, 2.12; N, 3.67; O, 14.89; S, 29.98. Molar conductance ($ohm^{-1}cm^2mol^{-1}$): 15.64

Structural characterization of NKDA-Nickel complex(3d)

Brown solid; Melting Point = 272-274 ˚C; Yield: 45.6%; UV (methanol): λ_{max} 284 and 683 nm; FAB mass (*m/z*): 463(M^+); Anal. Calcd: C, 43.5; H, 2.10; N, 3.52; O, 14.89; S, 29.8. Found: C, 46.72; H, 2.65; N, 3.41; O, 14.78; S, 29.28. Molar conductance ($ohm^{-1}cm^2mol^{-1}$): 15.78.

Structural characterization of NKDA-Zinc complex(3e)

Purple solid; Melting Point = 280-282˚C; Yield: 48.8%;UV (methanol): λ_{max} 277nm;IR(nujol): $\nu_{(C=C)}$1644, $\nu_{(C-NO2)}$1404, $\nu_{(M-S)}$427, $\nu_{(N-CH=C)}$1460, $\nu_{(N-O\ Stret)}$1167 cm^{-1} ^{1}H NMR (300 MHz, d_6-DMSO): δ 6.70 (s, 3H) ppm; ^{13}C NMR (75 MHz, d_6-DMSO): δ113.6 (olefinic-C), 146.1(quaternary =C) ppm. FAB mass (*m/z*): 468(M^+); Anal. Calcd : C, 46.18; H, 2.04; N, 3.45; O, 14.78; S, 29.5;Found: C, 46.71; H, 2.83; N, 3.80; O, 14.18; S, 29.28. Molar conductance ($ohm^{-1}cm^2mol^{-1}$): 15.2. Note: The molar conductance of the complexes was determined in DMSO using HANNA instrument conductivity meter, with a cell constant of 0.83. The lower value observed of molar conductivities in DMSO indicates the non electrolyte behavior of the complexes.

RESULTS AND DISCUSSION

TERMICIDAL ACTIVITY STUDY OF NITROKETENE DITHIO ACETAL METAL COMPLEXES

The test termite species *Odontotermes horni* was collected from our College campus and were maintained in segment of colonies until used .The colony was incubator at 26°C and 80% RH. Water and paper used as the food sources. The termicidal activity for the complexes (3a,3b,3c,3d)was carried out using *no-choice method.* The termicidal activity studies maintained in dark place incubator for the following termites *Odontotermes horni* was carried out. The effect of the compound on the orientation and survival of the termite odontotermes horni was evaluated for termicidal activity by the no-choice method. The termicidal activity of the complexes (3a,3b,3c,3d) against odontotermes horni by taking deltamethrin as a standard and is reported in Table – 1, Table – 2 , Table -3, Table - 4 and Table - 5. The termite mortality percentage was calculated using the following standard formula.

$$\text{Termite mortality(\%)} = \frac{\text{Number of dead termites}}{\text{Total number of test termites}} \times 100\%$$

TABLE 1 : TERMICIDAL ACTIVITY OF NITROKETENE DITHIOACETAL-COPPER COMPLEX AGAINST <u>ODONTOTERMES HORNI</u>

Concentration of compound	Number of Termite	Death rate (after 1 hour)	Mortality of termites (%)
Control	**30**	**0**	**0**
Deltamethrin (standard)- 0.1mg	**30**	**8**	**26.6**
NKDA-Coppercomplex 1mg	**30**	**16**	**53.3**
Percentage of termicidal activity =			**26.7**

TABLE 2 :TERMICIDAL ACTIVITY OF NITROKETENE DITHIOACETAL-COBALT COMPLEX AGAINST ODONTOTERMES HORNI

Concentration of compound	Number of Termite	Death rate (after 1 hour)	Mortality of termites (%)
Control	30	0	0
Deltamethrin (standard)- 0.1mg	30	12	40.0
NKDA – Cobalt complex1mg	30	23	76.6
Percentage of termicidal activity			36.6

TABLE 3 : TERMICIDAL ACTIVITY OF NITROKETENE DITHIOACETAL-IRON COMPLEX AGAINST ODONTOTERMES HORNI

Concentration of compound	Number of Termite	Death rate (after 1hour)	Mortality of termites (%)
Control	30	0	0
Deltamethrin (standard)- 0.1mg	30	15	50.0
NKDA –Iron complex 1mg	30	27	90.0
Percentage of termicidal activity =			40.0

TABLE 4 : TERMICIDAL ACTIVITY OF NITROKETENE DITHIOACETAL-NICKEL AGAINST ODONTOTERMES HORNI

Concentration of compound	Number of Termite	Death rate (after 1hour)	Mortality of termites (%)
Control	30	0	0
Deltamethrin (standard)- 0.1mg	30	9	30.0
NKDA–Nickel complex1mg	30	18	60.0
Percentage of termicidal activity =			30.0

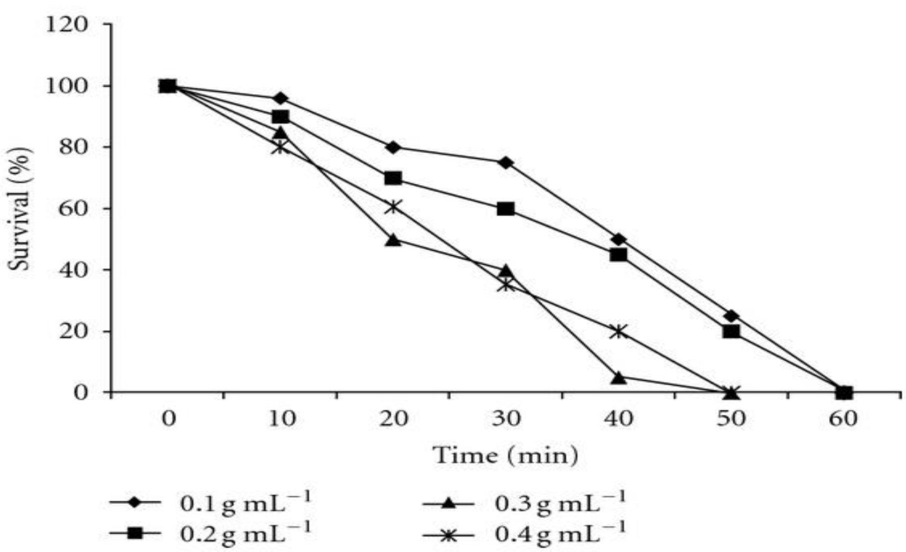
TABLE 5 : TERMICIDAL ACTIVITY OF NITROKETENE DITHIOACETAL-ZINC COMPLEX AGAINST ODONTOTERMES HORNI

Concentration of compound	Number of Termite	Death rate (after 1 hour)	Mortality of termites (%)
Control	30	0	0
Deltamethrin (standard)- 0.1mg	30	13	43.3
NKDA–Zinc complex 1mg	30	25	83.3
Percentage of termicidal activity			40.0

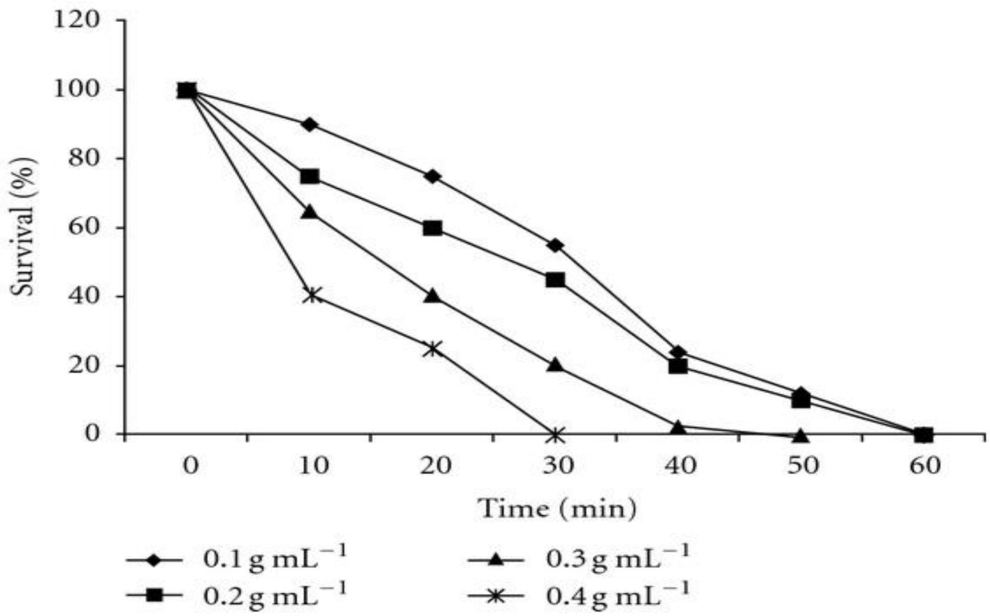
The proximate determination of the synthesized NKDA-Metal complexes showed varying values between the complexes and standard.

The termiticidal action of the NKDA-Metal complexes showed that mortality was achieved faster at higher concentrations than at lower concentration levels.

For standard, at 0.1 mg mL^{-1} treatment, all the termites died within 40 minutes while it took 60 minutes for all the termite workers to die when exposed to the 1m g mL^{-1} treatment with NKDA-Copper complex (Figure 1).



For standard, at 0.1 mg mL^{-1} treatment, all the termites died within 30 minutes while it took 60 minutes for all the termite workers to die when exposed to the 1mg mL^{-1} treatment with NKDA-Coblat complex (Figure 2).



Termicidal activity was not detected in the control experiments. The variations obtained in the values of standard and NKDA-Metal complexes may be due to the effect of heavy metals such as cobalt, nickel, zinc, and copper, which are basic natural components of the earth crust and the presence of these heavy metals in the complexes, in addition to the factor of polar organic compounds arising from the interactions between the mineral constituents and the extracting medium may therefore explain the termiticidal action of these complexes.

In this paper, we have reported the synthesis of NKDA – Metal complexes. The structure of NKDA – Metal complexes was characterized using UV, IR, ^{1}HNMR, ^{13}CNMR, C,H,N elemental analysis, EDX analysis and FAB mass spectral techniques. We have reported the results of termicidal activity against *Odontotermes horni*.

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