# **Inorganic Chemistry**

# Fluorescent Chemosensors for Selective and Sensitive Detection of Phosmet/Chlorpyrifos with Octahedral Ni<sup>2+</sup> Complexes

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**S** Supporting Information

ABSTRACT: The hexadentate ligands H<sub>2</sub>L1-L3 with mixed S, N, O donor sites and possessing substituents having either "no" or electronreleasing/withdrawing nature at terminal ends are synthesized. The ligands H<sub>2</sub>L1-L3 were tested for binding with library of metal ions, wherein maximum efficiency was observed with Ni<sup>2+</sup>, and it motivated us to prepare the Ni<sup>2+</sup> complexes. The ligand H<sub>2</sub>L1 underwent deprotonation and formed binuclear complex when interacted with Ni<sup>2+</sup> as evident from its crystal structure. The H<sub>2</sub>L2 and H<sub>2</sub>L3 having electron-withdrawing/electron releasing groups, respectively, were also deprotonated; however, they afforded mononuclear complexes with Ni<sup>2+</sup> ion. This signifies the importance of steric parameters instead of electronic factors in these particular cases. Impressed by differential



behavior of complexes of  $H_2L1$  and  $H_2L2/H_2L3$  with Ni<sup>2+</sup> and their photophysical and electrochemical properties, all the metal complexes were studied for their chemosensing ability. Nowadays with increased use of organophosphate, there is alarming increase of these agents in the environment, and thus we require efficient technique to estimate the level of these agents with high sensitivity and selectivity in aqueous medium. The Ni<sup>2+</sup> complexes with hydrophobic nature were suspended into aqueous medium for testing them as sensor for organophosphate. The  $(L1)_2$ .  $(Ni^{2+})_2$  could sense phosmet with detection limit of 44 nM, whereas  $L2.Ni^{2+}$  and  $L3.Ni^{2+}$  exhibited the detection limits of 62 and 71 nM, respectively, for chlorpyrifos.

## INTRODUCTION

The metal complexes of imine-linked receptors have been extensively reported because of their pronounced application in research arena of catalysis, biology, mimicking, sensing, and materials science.<sup>1-4</sup> These metal complexes have gained the real impulse in last two decades, when materials were explored comprehensively for modulation of surface area, porous nature, and labile metal-ligand interactions.<sup>5-7</sup> In this context, multinuclear metal complexes are reported, which mimics the metalloenzyme for their catalytic function such as urease, phosphotase, hemerythrin, catechol oxidase, arginase, ribonuclease reductase.<sup>8-10</sup> Similarly, nowadays these metal complexes are intensively being used for sensing of anions, biomolecules, and organophosphate with better optical and electrochemical properties.<sup>11-13</sup> The sensing in aqueous medium is a challenging task due to competition between the solvent and guest for receptor binding sites, and the issue is very severe, if the binding is realized with hydrogen bonding.<sup>14–16</sup> To address this problem of sensing in aqueous medium, the transition metal complexes have gained good reputation through utilizing electrostatic interaction, vacant dorbital to form covalent bond or sometimes replacement of

labile ligand.<sup>17,18</sup> The strategy is explored reasonably; however, many reports are limited to anion sensing only. Contrarily, these activities are applied hardly to warfare chemicals, poisonous materials such as nerve agents, and organophosphates. The sensing of organophosphates is among the most focused areas with respect to environment, as they are the neurotoxins and are poisonous substances to be known as pesticides for agriculture.<sup>19-21</sup> The inherent toxicity of organophosphates lies with their affinity to bind irreversibly with acetylcholinesterase, and this leads to prevent their biological activities; consequently, the accumulation of acetylcholine in the nervous system causes organ failure and eventually death.<sup>22,23</sup> In spite of severe toxicity of organophosphate, they are the far-most choice of farmers as a pesticide, herbicide, and rodenticide.<sup>24</sup> However, the surplus amounts of organophosphate released to environment has alarming consequences, as they have become a part of food chain and ultimately cause great risk to human health, ecosystem, and homeland security. Further to protect our

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natural resources, flora, and fauna, the scientific community has shown seriousness through developing the assay for qualitative and quantitative analysis of organophosphates in soil, water, and foodstuff.<sup>25</sup> The chromatography and mass and NMR spectroscopies<sup>26,27</sup> have been used with good success; however, there is always room for improvement.<sup>28</sup> These techniques are time-consuming, require expensive sample preparation, and need experts to handle the instrument. The other set of assay including chemosensors involving enzymatic assays, colorimetric method, metal-organic frameworks, electrochemical sensors, fluorescence organic molecules, and interferometry is mostly operative in organic solvents.  $^{29-33}$  To overcome this limitation of operation in organic solvents, we developed novel strategies for detection of organophosphate in aqueous medium. Under present manuscript, we developed novel metal complexes and suspended them in aqueous medium. The skeleton of organic receptors is designed in such a way that it is easy to engineer the sensor system, offer modulation in fluorescence emission, and fabricate with multiple binding sites that can afford flexible coordination sphere. Our strategy for metal center glares the open shell, which should reversibly "switch off" the fluorescence intensity, and the interaction of metal complex with analyte must regain the original fluorescence signature of receptor. We compared our result with literature-reported sensor for organophosphate and found that present sensor has multiple advantages as shown in Table S5.

#### RESULTS AND DISCUSSION

Syntheses and Characterization of Ligands and Metal **Complexes.** The ligand  $H_2L1$  was synthesized through condensation reaction between 2,2'-disulfanediyldianiline and salicylaldehyde in methanol, whereas 2,2'-disulfanediyldianiline was synthesized through the aerial oxidation of 2-aminothiophenol. The ligands  $H_2L2-L3$  were synthesized using the similar condensation procedure as was used for the synthesis of H<sub>2</sub>L1. All the ligands H<sub>2</sub>L1-L3 were fully characterized with spectroscopic methods, and the purity of samples was established with elemental analysis. The formation of imine linkages in H<sub>2</sub>L1–L3 were established from signals at 8.6, 9.1, and 8.5 ppm in <sup>1</sup>H NMR, and <sup>13</sup>C NMR depicted these signals at 163.28, 165.40, and 163.28 ppm; similarly, the imine linkages were characterized with a band between 1600 and 1630 cm<sup>-1</sup> in IR spectra. To prepare the required metal complexes, the reactions of ligand H2L1/H2L2/H2L3 were performed with nickel nitrate, and upon completion of reaction, the metal complexes were separated from reaction mixture. All the complexes were characterized with spectroscopic methods; photophysical properties were measured with absorption and emission spectroscopy, and structure of two complexes  $[(L1)_2$ .  $(Ni^{2+})_2$  and L2.Ni<sup>2+</sup>] was established with crystallography. The IR spectra of all the complexes have shown the bands at 1500-1640 cm<sup>-1</sup> due to CH=N stretching vibration.



Photophysical Properties of Ligands and Metal Complexes. All the three ligands  $H_2L1-L3$  were soluble in dimethyl sulfoxide (DMSO), and their photophysical proper-

ties were evaluated using absorption and emission spectroscopy. The UV-vis absorption spectrum of ligand H<sub>2</sub>L1 has shown a broad absorption band ( $\lambda_{abs}$ ) at 350 nm ( $\varepsilon_o = 35\ 000\ L$ mol<sup>-1</sup> cm<sup>-1</sup>) due to  $\Pi - \Pi^*$  transition. However, the ligands  $H_2L2$  and  $H_2L3$  have shown broad absorption band at 420 ( $\varepsilon_0$ = 55 000 L mol<sup>-1</sup> cm<sup>-1</sup>) and 400 nm ( $\epsilon_0$  = 40 000 L mol<sup>-1</sup> cm<sup>-1</sup>), respectively, again due to  $\prod -\prod^*$  transition. The interaction of ligands **H**<sub>2</sub>**L**1–**L**3 with a library of metal ions (such as Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup>, Sr<sup>2+</sup>, Cr<sup>3+</sup>, Mn<sup>2+</sup>, Fe<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup>, Ag<sup>+</sup>, Pb<sup>2+</sup>, and Al<sup>3+</sup>) exhibited the most significant changes upon binding with Ni<sup>2+</sup>, as interpreted from the modulation in the absorption spectrum of  $H_2L1$ . The absorption band for  $H_2L1$  (10  $\mu$ M) in DMSO (originally at 350 nm) was shifted to 410 nm on addition of 50  $\mu$ M of Ni<sup>2+</sup> ion, clearly showing the binding of Ni<sup>2+</sup>in the coordination sphere of ligand  $H_2L1$  (Figure S13). To investigate the effect of  $[Ni^{2+}]$ on the modulation of absorption profile of ligand H<sub>2</sub>L1, a titration was performed through the addition of 0–50  $\mu$ M of Ni<sup>2+</sup> to the fixed concentration of H<sub>2</sub>L1 (10  $\mu$ M). The successive addition of  $Ni^{2+}$  to the solution of ligand  $H_2L1$  led to the increase in absorbance at 410 nm and decrease in absorption at 350 nm with isosbestic points at 325 and 380 nm (Figure 1A). In the competitive binding experiment, the 50  $\mu$ M of each selected metal ion was added to Ni<sup>2+</sup> solution of H<sub>2</sub>L1, and absorbance was measured. The absorbance measurements showed no interference in the binding of nickel with any of tested ions (Figure S14). Similarly, the L2 (10  $\mu$ M) was tested with the same set of metal ions, and the significant change was observed only with Ni<sup>2+</sup> (Figure S15). The titration of  $H_2L2$  with Ni<sup>2+</sup> (0–50  $\mu$ M) leads to enhance the absorbance at 370 nm and decrease the absorbance at 405 nm with isosbestic point at 390 nm (Figure1B). Further, the competitive binding studies were performed to confirm the selective binding of Ni<sup>2+</sup>, and the experiment revealed that H<sub>2</sub>L2 selectively binds with the nickel ion (Figure S16). The H<sub>2</sub>L3 was then treated with similar library of metal ions; the only change in absorbance was noticed upon the addition of nickel ion. Finally, the titration of H<sub>2</sub>L3 with Ni<sup>2+</sup> (0-50  $\mu$ M) has pronounced hyperchromic shift at 305 nm and hypochromic shift at 400 nm with isosbestic points at 375 and 425 nm (Figure1C). The interference experiment was performed to confirm the selectivity of nickel with the H<sub>2</sub>L3. It was observed from the studies that the nickel ion selectively binds with the  $H_2L3$  (Figure S17). Thus, these significant changes in absorption profiles of ligands H<sub>2</sub>L1-L3 on reacting with Ni<sup>2+</sup> in solution state highlights the pivotal role of mixed S/N/O donor sites in the hexadentate framework of H<sub>2</sub>L1-L3 and also inspired us to synthesize and investigate the metal complexes.

The freshly prepared and purified metal complexes were dissolved in DMSO, and the electronic absorption spectrum of  $(L1)_2$ . $(Ni^{2+})_2$  complex showed a broad absorption band  $(\lambda_{abs})$ , with maxima at 24 390 cm<sup>-1</sup> ( $\varepsilon_o = 14\,000$  L mol<sup>-1</sup> cm<sup>-1</sup>; see Table 1), which is assigned to the spin-allowed transition  ${}^{3}A_{2g}$  (F)  $\rightarrow {}^{3}T_{1g}$  (P), and this supports the distorted octahedral geometry. The electronic absorption spectra of L2.Ni<sup>2+</sup> and L3.Ni<sup>2+</sup> showed broad band ( $\lambda_{abs}$ ) with maxima at 27 027 cm<sup>-1</sup> ( $\varepsilon_o = 11\,000$  L mol<sup>-1</sup> cm<sup>-1</sup>) and 25 000 cm<sup>-1</sup> ( $\varepsilon_o = 8000$  L mol<sup>-1</sup> cm<sup>-1</sup>), respectively, and are assigned spin-allowed transition  ${}^{3}A_{2g}$  (F)  $\rightarrow {}^{3}T_{1g}$  (P) in both the complexes and again highlight the distorted octahedral geometry.<sup>34</sup> The luminescence properties of all the three lignads H2L1–L3 were measured in DMSO, and subsequently the effect of Ni<sup>2+</sup> coordination was evaluated on the fluorescence signature of



**Figure 1.** Changes in UV–vis absorption spectra upon addition of Ni<sup>2+</sup> (0–50  $\mu$ M) to the DMSO solution (10  $\mu$ M) of (A) ligand H<sub>2</sub>L1, (B) ligand H<sub>2</sub>L2, and (C) ligand H<sub>2</sub>L3. (D) A comparison of luminescence spectra recorded with 10  $\mu$ M solution of ligands H2L1–L3 and corresponding metal complexes (L1)<sub>2</sub>.(Ni<sup>2+</sup>)<sub>2</sub>, L2.Ni<sup>2+</sup> and L3.Ni<sup>2+</sup>.

Table 1. Photophysical Parameters of Ligand	l and	l Meta	l Comp	lexes
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sample	ligand/metal complexes	$\lambda_{ m abs}$	$\varepsilon_0 ~(\mathrm{L}~\mathrm{mol}^{-1}~\mathrm{cm}^{-1})$	absorption transition	$\lambda_{\rm em}~({\rm nm})$	quantum yield $(\Phi_{\rm s})$
1.	H <sub>2</sub> L1	350 nm	35 000	$\Pi \to \Pi^*$	407	0.84
2.	$H_2L2$	405 nm	55 000	$\Pi \to \Pi^*$	398	0.82
3.	H <sub>2</sub> L3	400 nm	40 000	$\Pi \to \Pi^*$	398	0.82
4.	$[(L1)_2.(Ni^{2+})_2]$	24 390 cm <sup>-1</sup>	14 000	${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P)$	470	0.54
5.	L2.Ni <sup>2+</sup>	$27\ 027\ cm^{-1}$	11 000	${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P)$	469	0.53
6.	L3.Ni <sup>2+</sup>	$25\ 000\ cm^{-1}$	8000	${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P)$	470	0.55

each ligand (Figure 1D). The excitation of nickel complex  $(L1)_2$   $(Ni^{2+})_2$  at 350 nm exhibited photoluminescence at 470 nm, whereas the L2.Ni<sup>2+</sup> and L3.Ni<sup> $\overline{2}+$ </sup> complexes exhibited the emission at 469 and 470 nm, respectively. All the three ligands  $(H_2L1-3)$ , when excited with same excitation wavelength as that used to excite the metal complexes at same physical conditions, the ligand H<sub>2</sub>L1 emitted at 407 nm; ligands H<sub>2</sub>L2 and H<sub>2</sub>L3 exhibited emission at 398 nm. A comparison of emission profile of a metal complex with respective ligand revealed that the intensity of metal complexes gets quenched as evident from quantum yields. This shows the importance of open shell of metal ion, which causes the quenching of fluorescence intensity. This metal ion mediated modulation of fluorescence intensity may make the sensor system ideal for the recognition of organophosphates. In other words, when these analytes will bind with the metal ions, then these binding events

will be realized through the change in fluorescence intensity as usually happen in "Cation Displacement Assay"/"Anion Displacement Assay".<sup>35-41</sup>

**Crystal Structure of Metal Complexes.** X-ray structure determination revealed that complex  $(L1)_2 \cdot (Ni^{2+})_2$  crystallizes in triclinic crystal system with space group  $P\overline{1}$  and that the unit cell consists of two  $(L1)_2 \cdot (Ni^{2+})_2$  neutral complexes and 6.4 cocrystallized water molecules. The ORTEP view of complex  $(L1)_2 \cdot (Ni^{2+})_2$  along with atom numbering is shown in Figure 2A (for clarity only one complex is shown). In dinuclear complex, the Ni<sup>2+</sup> is surrounded by one sulfur, two nitrogen, and three oxygen atoms, of which one oxygen atom is bridged between two Ni<sup>2+</sup> ions. These ligands are arranged in octahedral coordination fashion (Figure 2B) with average Ni–O, Ni–N, and Ni–S bond distances of 2.058(4), 2.066(5), and 2.489(2) Å. The maximum angular deviation from



Figure 2. (A) ORTEP diagram along with atom numbering scheme of complex  $(L1)_2$ . $(Ni^{2+})_2$  with 40% probability thermal ellipsoids (for clarity only one diatomic complex is shown). (B) Geometry of dinuclear nickel complex  $(L1)_2$ . $(Ni^{2+})_2$ . (C) ORTEP diagram along with atom numbering scheme of complex L2. $Ni^{2+}$  with 40% probability thermal ellipsoids (for clarity only complex is shown, and water molecules are removed). (D) Geometry of mononuclear nickel complex L2. $Ni^{2+}$ .

expected octahedral geometry is 78.27(14) and 158.83(17) in case of angle N(7)–Ni(4)–S(7) and N(6)–Ni(3)–O(8), respectively. The different complex moieties are held in threedimensional crystal lattice with the help of number of hydrogen bonding interactions of type O–H···O, C–H···O, and C–H··· N. The hydrogen bonding parameters are shown in Table S2. Additional crystallographic parameters are given in Table 2.

The complex  $L2.Ni^{2+}$  crystallizes in monoclinic crystal system with space group  $P2_1/c$ . It consists of two neutral mononuclear Ni<sup>2+</sup> complexes and two water molecules of crystallization. The central metal ion, Ni<sup>2+</sup>, adopted the octahedral geometry (Figure 2D), which is satisfied by the two nitrogen, one sulfur, and two oxygen atoms originating from the ligand and one from water molecule. The ORTEP diagram along with atom numbering scheme of complex is shown in Figure 2C (for clarity only one complex is shown). The two water molecules of crystallization are involved in hydrogen bonding with coordinated water molecules, and oxygen atoms of the nitro groups of the ligand to provide robustness to the crystal lattice (hydrogen bonding parameters are shown in Table S4).

**Electrochemical Properties.** The electrochemical behavior of mononuclear and dinuclear complexes was studied with cyclic voltammetry in DMSO containing 0.1 M tetrabutyl ammonium perchlorate. The redox behavior of dinuclear complex of nickel  $(L1)_2.(Ni^{2+})_2$  showed quasi-reversible reduction<sup>42</sup> wave at  $E_{\rm pc} = -0.40$  V corresponding to Ni<sup>II</sup>Ni<sup>II</sup>. Ni<sup>II</sup>. However, the second reduction peak corresponding to

#### Table 2. Crystal Refinement Data

compound	$(L1)_2 \cdot (Ni^{2+})_2$	L2.Ni <sup>2+</sup>
empirical formula	$C_{104}H_{84}N_8Ni_4O_{14}S_8$	$C_{26}H_{20}N_4O_8S_2Ni$
$M_{ m w}$	2161.11	639.29
temperature, [K]	293(2) K	293(2) K
crystal system	triclinic	monoclinic
space group	$P\overline{1}$	$P2_{1}/c$
a, [Å]	14.0785(8)	13.7815(17)
b, [Å]	14.2423(8)	13.8543(18)
c, [Å]	27.2243(13)	27.356(4)
α, [deg]	76.500(2)	90
β, [deg]	88.452(2)	97.566(4)
γ, [deg]	74.831(2)	90
$V_{,} [Å^{3}]$	5119.6(5)	5177.7(11)
Ζ	2	8
$D_{cr}$ [Mg m <sup>-3</sup> ]	1.402	1.640
$\mu$ , [mm <sup>-1</sup> ]	0.953	0.971
reflections collected	40354	90381
data/restraints/parameters	14 333/1/1292	8896/0/748
unique reflections, $[R_{int}]$	14 333 [ 0.0929]	8896 [0.1256]
$GOF = S_{all}$	0.965	1.025
final R indices		
$R_1, wR_2 [I > 2\sigma I]$	0.0579, 0.1088	0.0772, 0.1411
$R_1$ , $wR_2$ (all data)	0.1436, 0.1258	0.1461, 0.1572
$\Delta ho$ max/ $\Delta ho$ min, [Å <sup>3</sup> ]	0.553 /-0.345	1.695/-0.558



Figure 3. (A) Cyclic voltammogram (scan rate = 100 mV/s) of  $(L1)_2 \cdot (Ni^{2+})_2$ , L2.Ni<sup>2+</sup> and L3.Ni<sup>2+</sup> in DMSO with supporting electrolyte [<sup>*n*</sup>Bu<sub>4</sub>N][ClO<sub>4</sub>]. (B) TGA graph of  $(L1)_2 \cdot (Ni^{2+})_2$ , L2.Ni<sup>2+</sup> and L3.Ni<sup>2+</sup> in the range from 20 to 700 °C at heating rate of 10 °C per minute.

Ni<sup>II</sup>Ni<sup>I</sup>/Ni<sup>I</sup> was not observed possibly due to fast reduction process. The coulometric experiment with potentiostatic exhaustive electrolysis was performed at -0.30 V (lower than 100 mV as compared to cathodic peak), and the reduction peak consumed one electron (n = 0.91) for redox reaction.<sup>43</sup> This peak was attributed to quasi-reversible signal of Ni<sup>II</sup>Ni<sup>II</sup>/Ni<sup>II</sup>Ni<sup>II</sup> redox couple.<sup>44</sup> The effect of scan rate on the redox behavior of  $(L1)_2$   $(Ni^{2+})_2$  was measured in the scan range of 50–300 mV s<sup>-1</sup> (Figure S27). The  $\Delta E$  value (200 mV) is greater than the 59/n mV and increase with the increase in scan rate. The ratio of cathodic to anodic peak current is greater than one  $(i_{pc}/i_{pa} >$ 1). The redox behavior of both mononuclear complexes (L2.Ni<sup>2+</sup> and L3.Ni<sup>2+</sup>) showed irreversible reduction at  $E_{pc}$  = -0.70 and -0.60 V corresponding to Ni<sup>II</sup>/Ni<sup>I</sup> as shown in Figure 3A. The reduction potential ( $E_{pc} = -0.70$  V) of L2.Ni<sup>2+</sup> is higher than the reduction potential of  $(L1)_2 \cdot (Ni^{2+})_2$  and L3.Ni<sup>2+</sup>, which is most likely due to the less distorted octahedral geometry<sup>45-47</sup> in the L2.Ni<sup>2+</sup> as compared to  $(L1)_2$ ,  $(Ni^{2+})_2$  and  $L3.Ni^{2+}$ . In general the electronic density on metal ion and geometry distortion are the governing factors for the reduction process. The electron-withdrawing group attached to metal complexes reduces at lower negative potential than the electron-releasing group bonded metal complexes. However, in our work it was observed that the geometry of complexes is the dominant factor to modulate the reduction potential then the electronic factors. This was also earlier observed with photoluminescence studies, which have shown that the electron-releasing and electron-withdrawing group has not affected the emission profile of Ni<sup>2+</sup> complexes.

**Thermal Studies.** The thermal stability of the complexes  $(L1)_2$ . $(Ni^{2+})_2$ ,  $L2.Ni^{2+}$ , and  $L3.Ni^{2+}$  were analyzed through TGA in the range from 20 to 700 °C at heating rate of 10 °C/min. TGA results showed that the complexes  $(L1)_2.(Ni^{2+})_2$  and  $L2.Ni^{2+}$  were stable and showed adequate crystallinity at room temperature. It was analyzed that the organic ligand in both the complexes decomposed at 450 °C with the loss of 65% mass of the complex, and 35% residue was found to be NiO. In the complex  $L3.Ni^{2+}$ , it was observed that the organic ligand ecomposed up to 350 °C with loss of 54% mass of complex, and remaining NiO residue was observed (Figure 3B).

**Chemosensor Development Using Metal Complexes.** The development of chemosensors becomes passionate in recent years due to the potential applications in the field of chemistry, material science, biological imaging, and diagnostics.<sup>48</sup> The numbers of approaches are reported in literature; however, the most successful approach involves the control over sensitivity, selectivity, solubility, stability, and application at the target. Among all the reported methods, the fluorescence is one of straightforward, least time-consuming, and highly reproducible methods.<sup>49</sup> In present manuscript, we prepared the weakly fluorescent nickel complexes and further suspended them in aqueous medium. The nickel complexes  $(L1)_2 \cdot (Ni^{2+})_2$ were dissolved into DMSO, and the solution was injected to doubly deionized water with sonication at 25  $\pm$  1 °C. After injection, the sonication was continued for 30 min at constant rate to establish the stable sensor system of the nickel complex  $(L1)_{2}$ . (Ni<sup>2+</sup>)<sub>2</sub>. The same procedure was used for the development of sensors system of nickel complexes L2.Ni<sup>2+</sup> and L3.Ni<sup>2+</sup>. The UV-vis absorption spectra of  $(L1)_2$ .(Ni<sup>2+</sup>)<sub>2</sub>, L2.Ni<sup>2+</sup>, and L3.Ni<sup>2+</sup> in DMSO showed broad absorption band at 410, 370, and 400 nm, respectively, which was assigned to spin-allowed transition  ${}^{3}A_{2g}$  (F)  $\rightarrow {}^{3}T_{1g}$  (P). However, the absorption band of (L1)<sub>2</sub>.(Ni<sup>2+</sup>)<sub>2</sub>, L2.Ni<sup>2+</sup>, and L3.Ni<sup>2+</sup> in aqueous medium was shifted drastically due to the change in band gap between highest occupied molecular orbitals and lowest unoccupied orbitals (Figure S26). The chemosensory activities of  $(L1)_2$ . $(Ni^{2+})_2$ , L2. $Ni^{2+}$ , and L3. $Ni^{2+}$  toward various organophosphates were evaluated using emission spectroscopy. The emission spectra of  $(L1)_2 \cdot (Ni^{2+})_2$  recorded with 10  $\mu M$ concentration in 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) buffer at pH 7.4 showed a peak at 470 nm. On addition of tested species (such as ATP, AMP, NADP, NADH, azamethiphos, parathion-methyl, parathion, fenitrothion, chlorpyrifos, and azinphos-methyl) to the solution of  $(L1)_2$ .  $(Ni^{2+})_2$ , no significant change in fluorescence emission profile was shown except for phosmet. The emission profile of  $(L1)_2$ .  $(Ni^{2+})_2$  showed fourfold enhancement in the fluorescence intensity upon binding with phosmet; thus concluded the selective binding of phosmet with  $(L1)_2 \cdot (Ni^{2+})_2$  (Figure 4A). Upon progressive addition of phosmet  $(0-50 \ \mu M)$  into  $(L1)_2$ .  $(Ni^{2+})_2$  solution, the gradual enhancement takes place in the emission profile of metal complex (Figure 4B). The species distribution of metal complex-phosmet was evaluated using hyperspec software,<sup>50</sup> and the nonlinear regression plot is



**Figure 4.** Changes in fluorescence spectra of (A)  $(L1)_2$ . $(Ni^{2+})_2$ ; (C)  $L2.Ni^{2+}$ ; (E)  $L3.Ni^{2+}$  upon addition of various organophosphate (50  $\mu$ M) in HEPES buffered aqueous medium (pH = 7.4). Fluorescence titration of (B)  $(L1)_2.(Ni^{2+})_2$  with phosmet  $(0-50 \ \mu$ M); (D)  $L2.Ni^{2+}$  with chlorpyrifos  $(0-50 \ \mu$ M); (F)  $L3.Ni^{2+}$  with chlorpyrifos  $(0-50 \ \mu$ M) in HEPES buffered aqueous medium (pH = 7.4). The nonlinear plot between fluorescence intensity vs concentration of organophosphate and their species distribution are depicted as inset of respective titration figure.

shown as inset of Figure 4B. It was found that 1:1 species of phosmet and  $(L1)_2$ . $(Ni^{2+})_2$  dominate in the solution at higher concentration. Similarly, the L2. $Ni^{2+}$  and L3. $Ni^{2+}$  showed enhancement in the emission profile upon interaction of chlorpyrifos rather than any other tested organophosphate (Figure 4C,E). The enhancement in emission peak occurred

due to selective binding of chlorpyrifos with corresponding metal complexes. It was further confirmed with titration experiment: on adding an aliquot of chlorpyrifos  $(0-50 \ \mu M)$  to metal complexes the regular enhancement in the fluorescence intensity takes place (Figure 4D,F). A nonlinear plot was drawn between fluorescence intensity versus





Figure 5. Possible mechanism of interaction of (A) phosmet with dinuclear nickel complex and (B) chlorpyrifos with mononuclear nickel complex.

concentration of chlorpyrifos; species formed in the solution at different concentration were checked with hyperspec software, and 1:1 species dominate in the solution at higher concentration. The limit of detection (LOD) of (L1)<sub>2</sub>.  $(Ni^{2+})_2$  toward phosmet was determined by  $3\sigma$  method, using LOD =  $3 \times SD/m$ , and it was found to be 44 nM, where SD is the standard deviation of blanks signal and *m* is the slope of the curve. Similarly, the LOD for L2.Ni<sup>2+</sup> and L3.Ni<sup>2+</sup> toward chlorpyrifos was calculated to be 62 and 71 nM, respectively. The binding events of metal complexes for organophosphates were also evaluated with UV–vis absorption spectroscopy, and the results are shown in Figures S28 and S29.

Mechanism of Sensing of Organophosphate. To study the binding mechanism of interaction of phosmet/chlorpyrifos with metal complexes, the NMR titrations were conducted in DMSO- $d_6$ . NMR spectra were recorded by equimolar addition of respective analytes to the host solution. The <sup>1</sup>H NMR titration revealed (a) significant shift in proton signal in  $(L1)_2$ .  $(Ni^{2+})_2$  upon addition of phosmet and (b) considerable shift in the aromatic proton of phosmet on interacting with  $(L1)_2$ .  $(Ni^{2+})_2$ . The <sup>1</sup>H NMR titration concluded that the metal center binds with the carbonyl group of phosmet, and the other metal center underwent interaction with the sulfur moiety of the thiophosphate group prevailing in phosmet (Figure S30). This was further confirmed through <sup>31</sup>P NMR spectrum that the phosphorus signal of phosmet originally at  $\delta$  = 94.90 ppm was split into  $\delta = 94.53-94.71$  ppm on interaction with (L1)<sub>2</sub>.  $(Ni^{2+})_2$  (Figure S33). On the basis of <sup>1</sup>H NMR and <sup>31</sup>P NMR titrations, the possible mechanism<sup>51-53</sup> of binding of phosmet with nickel complex are shown as follows (see Figure 5).

The  $L2.Ni^{2+}$  and  $L3.Ni^{2+}$  have shown binding affinity with chlorpyrifos because both have same orientation of ligand and

geometry. In <sup>1</sup>H NMR spectrum both complexes show the change in chemical shift value of respective proton with addition of chlorpyrifos. This attribute to change the symmetry of metal complexes when bind with the chlorpyrifos. The possible binding site of chlorpyrifos with metal complex L2.Ni<sup>2+</sup> is the replacement of water molecule by sulphur atom of thiophosphate (P=S) group and simultaneously electrostatic interaction with the pyridine nitrogen to the nickel center (Figure S31). In the <sup>31</sup>P NMR of chlorpyrifos the  $\delta$  value at 61.08 ppm was shifted to  $\delta$  value 60.90 ppm when chlorpyrifos interacted with metal complexes (Figure S34). The binding behavior of chlorpyrifos with L3.Ni<sup>2+</sup> was same as that of chlorpyrifos with L2.Ni<sup>2+</sup> (Figure S32). This was also confirmed from <sup>31</sup>P NMR spectrum, which revealed that the phosphorus signal of chlorpyrifos shifted from ( $\delta$ ) 61.08 to 60.74 ppm, when interacting with L3.Ni<sup>2+</sup> (Figure S35). From the <sup>1</sup>H NMR and <sup>31</sup>P NMR study the possible mechanism<sup>51,54</sup> of interaction of L2.Ni<sup>2+</sup>/L3.Ni<sup>2+</sup> with chlorpyrifos are given below.

#### EXPERIMENTAL SECTION

**General Information.** The analytical-grade chemicals were purchased from Sigma-Aldrich, and bulk chemicals were supplied by SD Fine India. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on JEOL instrument operated at 400 MHz (for <sup>1</sup>H NMR) and 100 MHz (for <sup>13</sup>C NMR). Fourier transform infrared (FT-IR) spectra of dried samples were measured on a Bruker Tensor 27 spectrophotometer using solid cell technique. Elemental analyses were measured through a Fisons instrument (Model EA 1108 CHN). Electrospray ionization mass spectra (ESI-MS) were analyzed on ES-MS Q-TOF mass spectrometer. TGA was performed on a TGA/DSC 1 STAR SYSTEM from Mettler Toledo with temperature increments of 10 °C/min under N<sub>2</sub> stream. The photophysical properties were evaluated with UV-vis absorption spectrophotometer (Shimadzu UV-2400) and fluorescence spectrophotometer (Perkin L55). The analysis range was fixed as 200–900 nm, and measurements were performed at room temperature using a 1 cm path length quartz cuvette. The electrochemical properties were recorded using a potentiostat galvanostat BASI EPSILON using a platinum disc as working electrode, Ag/AgCl as reference electrode (3 M KCl), and platinum wire as counter electrode.

Synthesis and Characterization of  $H_2L1$ . The ligand  $H_2L1$  was synthesized via condensation reaction between 2,2'-disulfanediyldianiline (496 mg, 2 mmol) with salicylaldehyde (488 mg, 4 mmol) in methanol. A yellow colored solid separated out after stirring for 6 h. The precipitates were washed and recrystallized with methanol to give pure product in 91% yield. mp  $\geq$  270 °C; IR (cm<sup>-1</sup>) 3373 (O–H<sub>sym</sub>), 1611 (CH=N<sub>sym</sub>);<sup>1</sup>H NMR (400 MHz in CDCl<sub>3</sub>)  $\delta$  (ppm) = 8.62 (s, CH=N, 1H), 7.65 (d, Ar–H, 1H), 7.4 (m, Ar–H, 2H), 7.23 (d, Ar–H, 1H), 7.18 (t, Ar–H, 1H), 7.14 (d, Ar–H, 1H), 7.05 (d, Ar–H, 1H), 6.95 (t, Ar–H, 1H); <sup>13</sup>C NMR (100 MHz in CDCl<sub>3</sub>)  $\delta$  (ppm): 162.9, 161.2, 146.4, 133.9, 132.8, 131.6, 127.8, 127.7, 127.5, 127.3, 119.3, 117.7, 117.5. Anal. Calcd for C<sub>26</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: C, 68.40; H, 4.42; N, 6.14; found: C, 68.46; H, 4.39; N, 6.18%; ESI-MS (*m*/*z*): 457 (M +1)<sup>+</sup>.

Synthesis and Characterization of  $H_2L2$ . Ligand  $H_2L2$  was synthesized via condensation reaction between 2,2'-disulfanediyldianiline (496 mg, 2 mmol) with 5-nitro-salicylaldehyde (668 mg, 4 mmol) in methanol. A light yellow colored solid was separated out after 6 h. The precipitate was washed and recrystallized with methanol to form the pure product having 89% yield. mp  $\geq 277$  °C; IR (cm<sup>-1</sup>) 3377 (O–H<sub>sym</sub>), 2973 (Ar–H<sub>sym</sub>), 1615 (CH=N<sub>sym</sub>); <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  (ppm) = 9.11 (s, CH=N, 1H), 8.69 (d, Ar–H, 1H), 8.3 (dd, Ar–H, 1H), 7.6 (d, Ar–H, 1H), 7.45 (d, Ar–H, 1H), 7.3 (m, Ar–H, 2H), 7.1(d, Ar–H, 1H); <sup>13</sup>C NMR (100 MHz, DMSO- $d_6$ )  $\delta$  (ppm) = 165.9, 161.9, 146.3, 140.2, 135.9, 131.2, 129.0, 128.3, 127.9, 124.9, 118.5, 116.5, 115.3; Anal. Calcd for C<sub>26</sub>H<sub>18</sub>N<sub>4</sub>O<sub>6</sub>S<sub>2</sub>: C, 57.13; H, 3.32; N, 10.25; found: C, 57.20; H, 3.25; N, 10.28%; ESI-MS (*m*/*z*): 547 (M+1)<sup>+</sup>.

Synthesis and Characterization of  $H_2L3$ . Ligand  $H_2L3$  was synthesized via condensation reaction between 2,2'-disulfanediyldianiline (496 mg, 2 mmol) with 4,4'-diethylamino-2-hydroxybenzaldehyde (772 mg, 4 mmol) in methanol. A deep yellow colored solid was separated out after 6 h. The precipitate was treated and recrystallized in methanol to get pure product having 85% yield. mp  $\geq$  296 °C; IR (cm<sup>-1</sup>) 3373 (O–H<sub>sym</sub>), 1615 (CH=N<sub>sym</sub>);<sup>1</sup>H NMR (400 MHz in CDCl<sub>3</sub>)  $\delta$  (ppm) = 8.48 (s, CH=N, 1H), 7.7 (d, Ar–H, 1H), 7.23 (t, Ar–H, 2H), 7.15 (d, Ar–H, 2H), 6.25 (m, Ar–H, 2H), 3.4 (q, CH<sub>2</sub>, 4H), 1.3 (t, CH<sub>3</sub>, 6H); <sup>13</sup>C NMR (100 MHz in CDCl<sub>3</sub>)  $\delta$  (ppm) = 163.2, 160.4, 152.1, 146.4, 134.1, 131.2, 127.0, 126.3, 126.1, 117.1, 109.2, 103.9, 97.8, 44.7, 12.3; Anal. Calcd for C<sub>34</sub>H<sub>38</sub>N<sub>4</sub>O<sub>2</sub>S<sub>2</sub>: C, 68.19; H, 6.40; N, 9.36; found: C, 68.24; H, 6.29; N, 9.31%; ESI-MS (m/z): S99.1 (M+1)<sup>+</sup>.

Synthesis and Characterization of Ni<sup>2+</sup> Metal Complex of L1. The 912 mg (2 mmol) of ligand L1 dissolved in tetrahydrofuran (THF) and aqueous solution of nickel nitrate 560 mg (2 mmol) was mixed and stirred at 100 °C for 30 min. The green colored solution was obtained, which was filtered and kept for slow evaporation at room temperature to get crystalline material. After 10 d, the formation of green colored crystals occurred, which are suitable for X-ray crystallography, and yield was 59%. Anal. Calcd (%) for  $C_{52}H_{36}N_40_4S_4Ni_2$ : C, 60.84; H, 3.53; N, 5.46; found: C, 60.76; H, 3.50; N, 5.49%; IR (cm<sup>-1</sup>): 1613 ( $\nu_{CH=N}$ ), 1303 ( $\nu_{S-S}$ ); ESI-MS (m/z): 1025.2 (M+1)<sup>+</sup>.

Synthesis and Characterization of Ni<sup>2+</sup> Metal Complex of L2. The 560 mg (2 mmol) of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 1092 mg (2 mmol) of L2 were dissolved in THF, and the mixture was stirred at 110 °C for 2 h. A light green colored solution was formed, which was kept for slow evaporation at room temperature to achieve crystallization. After a few days green colored crystals are formed, which were washed with THF and were suitable for X-ray crystallographic studies. Yield: 49%; Anal. Calcd(%) for C<sub>26</sub>H<sub>18</sub>N<sub>4</sub>O<sub>7</sub>S<sub>2</sub> Ni: C, 50.26; H, 2.92; N, 9.02; found: C,

50.29; H 3.01; N, 9.09%; IR (cm<sup>-1</sup>) 1615 ( $\nu_{\rm CH=N}$ ); ESI-MS (m/z): 620.9 (M+1)<sup>+</sup>.

Synthesis and Characterization of Ni<sup>2+</sup> Metal Complex of L3. The 560 mg (2 mmol) of NiNO<sub>3</sub>·6H<sub>2</sub>O and 1196 mg (2 mmol) of L3 were dissolved in THF, and the reaction mixture was stirred for 8 h at 150 °C. A light greenish-brown colored precipitate was formed, which was washed with THF, filtered, and dried to obtain a greenish-brown powder. Yield: 35%. Anal. Calcd for C<sub>34</sub>H<sub>38</sub>N<sub>4</sub>O<sub>3</sub>S<sub>2</sub>Ni: C, 60.63; H, 5.69; N, 8.32; found C, 60.61; H, 5.67; N, 8.30%; IR (cm<sup>-1</sup>) 1634 ( $\nu_{CH=N}$ ); ESI-MS (m/z): 672 (M+).

X-ray Data Collection and Refinement. After repeated attempts the crystals were obtained, and the data were collected for some of the single crystals. The X-ray diffraction data for (L1)2.(Ni<sup>2+</sup>)2 and L2.Ni<sup>2+</sup> were collected on a Bruker X8 APEX II KAPPA CCD diffractometer and Bruker D8 Venture PHOTON 100 CMOS CCD diffractometer, respectively, at 293 K using graphite/mirrors monochromatized Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The crystals were positioned at 50 mm from the CCD, and the diffraction spots were measured using a counting time of 15s. Data reduction and multiscan absorption were performed using the APEX II program suite (Bruker, 2007). The structures were solved by direct methods with the SIR97 program [S1] and refined using full-matrix least-squares with SHELXL-97[S2]. Anisotropic thermal parameters were used for all non-H atoms. In case of complex  $(L1)_2.(Ni^{2\scriptscriptstyle +})_2$  three water molecules O4W, O5W, and O6W were found disordered. O4W was disordered over two positions, while O5W and O6W were disordered over three positions. In the case of L2.Ni<sup>2+</sup>, two water molecules of crystallization O1W and O2W are disordered over two positions each. The hydrogen atoms of C-H groups were with isotropic parameters equivalent to 1.2 times those of the atom to which they were attached. All other calculations were performed using the programs WinGX [S3] and PARST [S4]. The molecular diagrams were drawn with DIAMOND [S5]. Final R-values together with selected refinement details are given in Table 1. Selected bond lengths and bond angles for complexes (L1)2.(Ni<sup>2+</sup>)2 and L2.Ni<sup>2+</sup> are given in Tables S2 and S4.

**Evaluation of Photophysical Properties.** The recognition properties of ligand H<sub>2</sub>L1–L3 were conducted at 25 ± 1 °C, and before recording the experiment, the solution of ligand (10  $\mu$ M) was shaken well to ensure the uniformity. The metal binding behavior of ligand H<sub>2</sub>L1–L3 was checked with a library of different metal ions in DMSO and was investigated through change in absorbance spectrum. The titration was recorded with the standard solution of ligand (10  $\mu$ M) with constant addition of nickel nitrate (0–50  $\mu$ M) solution, and respective changes in absorbance were observed.

**Electrochemical Measurement of Metal Complexes.** All electrochemical properties were recorded on a BASI EPSILION. All studies were performed on a single compartment under nitrogen atmosphere at 100 mV s<sup>-1</sup> scan rate  $(25 \pm 2 \text{ °C})$ , with a platinum disc as working electrode, Ag/AgCl as reference electrode (3 M KCl), and platinum wire as counter electrode. The solution of metal complexes was prepared with concentration of 50  $\mu$ M in DMSO along with tertiary ammonium perchlorate as supporting electrolytes.

Chemosensors Activities of Metal Complexes. The metal complexes were suspended in aqueous solution using re-precipitation methods.<sup>55</sup> In this typical method, the metal complex was dissolved in DMSO (1.0 mL), and solution was injected into 99.0 mL of doubly distilled deionized water with a constant injection rate and under vigorous sonication. All organophosphate binding studies were performed at  $25 \pm 1$  °C, and before recording the experiment enough time was given to ensure the uniformity of the solution. The organophosphate binding behavior was evaluated from the change in the UV-vis absorption and fluorescence spectra of metal complex (10  $\mu$ M) on addition of tested organophosphate (50  $\mu$ M) in aqueous medium. To further confirm the experiment, the reproducibility of the titration was performed. For titration, volumetric flasks were taken for each standard solution of metal complex along with various amounts of organophosphate  $(0-50 \ \mu M)$  in aqueous buffered solution. Fluorescence quantum yield ( $\Phi$ s) was determined by using an optically matching solution as standard (9,10-diphenyl anthracene in

ethanol) at excitation wavelength of 350–370 nm, and quantum yield is calculated by the following equation as  $^{56}$ 

$$\Phi s = \Phi r \times \frac{I}{Ir} \frac{ODr}{OD} \frac{\dot{\eta}}{\dot{\eta}r}$$

Whereas  $\Phi$ s and  $\Phi$ r are the quantum yield of sample and reference, ODr and OD are the optical density of reference and sample, respectively. *I* and Ir are the intensities, and  $\hat{\eta}$  and  $\hat{\eta}$ r are the refractive index of sample and reference solution, respectively. For calculation of LOD a graph was plotted between fluorescence intensity and concentration, and the slope and standard deviation ( $\sigma$ ) were determined from a linear regression graph. The LOD was calculated<sup>57</sup> by using formula  $\sigma = 3 \times \text{SD/slope}$ .

**Safety Consideration.** *Caution!* Organophosphates are very toxic. Full precautions were taken for preparation and handling of these solutions. All the solutions of organophosphates were prepared in separate fumehood and protective clothes; gloves and eyeglasses were used. After complete recognition studies, the organophosphate solution was disposed of carefully by using standard protocol.

### CONCLUSION

In conclusion we have synthesized and characterized nickel complexes of L1–L3, which are composed of two Ni<sup>2+</sup> centers coordinated to mixed S, N, and O sites of the ligand (L1) in  $(L1)_2 (Ni^{2+})_2$  complex, and one Ni<sup>2+</sup>center is coordinated to mixed S, N, and O sites of ligand (L2/L3) in L2.Ni<sup>2+</sup> and L3.Ni<sup>2+</sup> complexes. In complex  $(L1)_2 \cdot (Ni^{2+})_2$  the two Ni<sup>2+</sup>centers coordinated through an oxygen bridge and have Ni(1)-O(2), Ni(1)-O(4), Ni(2)-O(2), and Ni(2)-O(4)distances 2.041, 2.058, 2.064, and 2.041 Å, respectively. All the ligands are arranged in octahedral coordination fashion with average Ni-O, Ni-N, and Ni-S bond distances of 2.058(4), 2.066(5), and 2.489 (2) Å. Further, prepared metal complexes were explored as sensors for organophosphates; these nickel complexes were suspended in aqueous medium using literature reported. The  $(L1)_{2}$  (Ni<sup>2+</sup>)<sub>2</sub> binds selectively with the phosmet, and  $L2.Ni^{2+}/L3.Ni^{2+}$  selectively bind with chlorpyrifos, which was confirmed through absorption and fluorescence spectroscopy. The metal complexes have shown low detection limit in nanomolar range toward phosmet and chlorpyrifos. The binding mechanisms of phosmet with  $(L1)_2 \cdot (Ni^{2+})_2$  and chlorpyrifos with  $L2.Ni^{2+}/L3.Ni^{2+}$  have been studied with <sup>1</sup>H NMR and <sup>31</sup>P NMR spectroscopy.

#### ASSOCIATED CONTENT

#### S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b00332.

Spectroscopic data including NMR, IR, and mass spectra;

graphs for photophysical properties. (PDF)

X-ray crystallographic information. (CIF)

X-ray crystallographic information. (CIF)

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#### Notes

The authors declare no competing financial interest.

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