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Unusual Recognition and Separation of Hydrated Metal Sulfates $[M_2(\mu-SO_4)_2(H_2O)_n, M = Zn^{II}, Cd^{II}, Co^{II}, Mn^{II}]$ by a Ditopic Receptor

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Supporting Information

ABSTRACT: A ditopic receptor L1, having metal binding bis(2picolyl) donor and anion binding urea group, is synthesized and explored toward metal sulfate recognition via formation of dinuclear assembly, $(L1)_2M_2(SO_4)_2$. Mass spectrometric analysis, ¹H-DOSY NMR, and crystal structure analysis reveal the existence of a dinuclear assembly of MSO₄ with two units of L1. ¹H NMR study reveals significant downfield chemical shift of -NH protons of urea moiety of L1 selectively with metal sulfates (e.g., ZnSO₄, CdSO₄) due to second-sphere interactions of sulfate with the urea moiety. Variable-temperature ¹H NMR studies suggest the presence of intramolecular hydrogen bonding interaction toward metal sulfate recognition in solution state,



whereas intermolecular H-bonding interactions are observed in solid state. In contrast, anions in their tetrabutylammonium salts fail to interact with the urea –NH probably due to poor acidity of the tertiary butyl urea group of L1. Metal sulfate binding selectivity in solution is further supported by isothermal titration calorimetric studies of L1 with different Zn salts in dimethyl sulfoxide (DMSO), where a binding affinity is observed for ZnSO₄ ($K_a = 1.23 \times 10^6$), which is 30- to 50-fold higher than other Zn salts having other counteranions in DMSO. Sulfate salts of Cd^{II}/Co^{II} also exhibit binding constants in the order of ~1 × 10⁶ as in the case of ZnSO₄. Positive role of the urea unit in the selectivity is confirmed by studying a model ligand L2, which is devoid of anion recognition urea unit. Structural characterization of four MSO₄ [M = Zn^{II}, Cd^{II}, Co^{II}, Mn^{II}] complexes of L1 that is, complex 1, [(L1)₂(Zn)₂(μ -SO₄)₂]; complex 2, [(L1)₂(H₂O)₂(Cd)₂(μ -SO₄)₂]; complex 3, [(L1)₂(H₂O)₂(Co)₂(μ -SO₄)₂]; and complex 4, [(L1)₂(H₂O)₂(Mn)₂(μ -SO₄)₂], reveal the formation of sulfate-bridged eight-membered crownlike binuclear complexes, similar to one of the concentration-dependent dimeric forms of MSO₄ as observed in solid state. Finally, L1 is found to be highly efficient in removing ZnSO₄ from both aqueous and semiaqueous medium as complex 1 in the presence of other competing Zn^{II} salts via precipitation through crystallization. Powder X-ray diffraction analysis has also confirmed bulk purity of complex 1 obtained from the above competitive crystallization experiment.

INTRODUCTION

Uncontrolled release of heavy metal salts, particularly in the form of metal sulfates, into the environment due to industrialization and urbanization has posed a great concern worldwide.¹ Unlike organic pollutants, heavy metal salts do not degrade into harmless end products.² The presence of heavy metal ions is problematic to many life forms due to their toxicity.³ According to the World Health Organization, among the 10 heavy metals that have been assigned as major public concern, cadmium(II) is ranked almost at the top position of the table,⁴ and the sulfate form of this metal is extremely carcinogenic and very toxic for lungs.⁵ Zinc(II) sulfate, the lighter congener of cadmium(II), is also considered a toxic heavy metal.^{5,6} Intake of MnSO₄ results in many health problems, and hydrated CoSO₄ is considered as a carcinogenic compound. Many industrial wastewaters, in particular, those associated with mining, contain high concentrations of transition metal sulfates that exceed the secondary drinking water standard of 250 mg/L and are in the range from 250 to

2000 mg/L.⁷ During wastewater and nuclear waste treatment, removal of metal sulfates is also very problematic as well as a challenging task due to high solvation energy associated with these metal sulfates.^{8–10}

During the past decade or so liquid–liquid extraction, precipitation, and crystallization techniques have been utilized for the extraction of ion pairs of alkali metal salts from solution using suitable ditopic and dual-host receptors.^{11–16} However, Custelcean et al. had first introduced the concept of selective crystallization for sulfate separation by metal–organic frameworks.^{17–19} Later, several other groups,^{20–30} including ours,^{31–33} have utilized such metal ion-assisted self-assembly processes for selective separation of sulfate via second-sphere coordination. In this strategy, metal ion and sulfate sit in their separate and individual binding pockets by disrupting the contact ion-pair structural features of metal sulfates, which is

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one of the concentration-dependent forms of metal sulfate. In fact, single-crystal X-ray structures of $MSO_4 \cdot xH_2O$ [M = Zn^{II} and Mn^{II}] show the existence of ion-pair bridged dimers $[M_2(\mu - SO_4)_2(H_2O)_n]$ in solid state.^{34,35} Thus, an alternative strategy for metal sulfate recognition and separation would be to trap such dimeric species of metal sulfates, which might be advantageous in terms of overcoming high hydration energy problem associated with the recognition and separation of such metal salts in aqueous environment. Herein, we show selective recognition and separation of hydrated metal sulfates as SO_4^{2-} bridged dimeric form $[(M)_2(\mu - SO_4)_2][M = Zn^{II}/Cd^{II}/Co^{II}/Mn^{II}]$ by a simple ditopic receptor, L1. To the best of our knowledge this represents the first report on the recognition of metal sulfates as bridged dimer in solution.

RESULT AND DISCUSSION

Designing Aspects of Ligands. Recognition of anion generally occurs via interaction of guest anions with the acidic hydrogen of receptors. Binding of metal ion in suitable part of the ligand can also alter the electronic and geometrical parameters of the ligand, which introduces selectivity among the investigated anions.^{36–38} Dimeric form of metal sulfates, that is, $M_2(SO_4)_2(H_2O)_{xy}$ are found to be stabilized by tridentate metal chelating unit along with some assistance from anion binding unit. Keeping these aspects in mind, we prepared ligand L1 having bis(2-picolyl) amine as metal binding unit and pendant tertiary-butyl urea group as anion recognizing unit (Chart 1). Thus, binding of metal could

Chart 1. Synthesis of L1 and Numbering Scheme Used for ¹H NMR Spectral Assignment



influence the binding of the anion counterpart in such a way that selectivity among the investigated anions can be introduced through dissimilar binding with the pendant urea moiety. To investigate the positive role of urea group toward anion selectivity in L1, modified ligand L2 is synthesized (Chart 2), which lacks the anion binding urea moiety having the same metal binding motif.

Mass Spectrometric Analysis. First evidence on the trapping of dinuclear sulfate salts of Zn^{II} and Co^{II} are obtained from electrospray ionization mass spectrometry (ESI-MS) study. When solution of equimolar mixture of L1 and

Chart 2. Synthetic Route Towards Preparation of L2



ZnSO₄·7H₂O and CoSO₄·6H₂O are subjected to ESI(-ve) mass spectrometric analysis, characteristic molecular ion peaks at m/z = 1002.20 and m/z = 992.21 are observed, which correnpond to binuclear $[Zn_2(L1)_2(SO_4)_2]^-$ and $[Co_2(L1)_2(SO_4)_2]^-$ complexes, respectively (Figure 1). The experimental isotope distribution patterns of both the complexes match well with those calculated on the basis of natural abundances. Thus, in all these cases, probably two L1 trap the preformed sulfate-bridged dimeric unit in solution and that even exists in the gas phase. However, other monomeric nonbridged Zn^{II} salts such as Zn(ClO₄)₂·6H₂O, Zn(CF₃SO₃)₂, and ZnCl₂·4H₂O show characteristic peaks that correspond to the mononuclear complexes of Zn^{II} (Figure 2). This suggests different structural motif for complexes of Zn^{II} salts.

¹H Nuclear Magnetic Resonance Experiments. As L1 possesses anion binding urea moiety, hence to gain insight into the mode of interaction between the ditopic receptor L1 and various anions, we performed ¹H NMR titrations with different anions having tetrabutylammonium (TBA) countercation in deuterated dimethyl sulfoxide (DMSO- d_6) at 298 K. L1 does not interact with any of the anions irrespective of their basicity (Figure S10). ¹H NMR of a mixture of L1 (5.69 mM) and TBAHSO₄ (61.28 mM) in DMSO- d_6 showed negligible change in chemical shifts of the NH protons of urea moiety. Furthermore, addition of (TBA)₂SO₄ (64.23 mM) into L1 (6.28 mM) also did not alter the peak positions of the urea moiety. This silent behavior of the receptor L1 toward anions can be can be attributed toward combination of (i) intermolecular H bonding between the urea moieties of adjacent L1 units and (ii) weak acidity of NH protons, which make L1 reluctant toward H bonding interaction with anions. This indicates L1 as a poor anion receptor.

However, ¹H NMR analysis of L1 in the presence of equivalent amount of ZnSO₄ (Figure 3j) shows significant downfield shifts of NH protons ($\Delta \delta = 0.65$ ppm for NH_b and $\Delta \delta = 0.52$ ppm for NH_a) of urea unit along with usual shifts of pyridyl protons due to binding of Zn^{II} with bis(2-picolyl) unit (Figure 3). This indicates the binding of SO_4^{2-} with NH protons of L1. Also, NH protons of L1 bind with SO_4^{2-} unit of CdSO₄ as evident from considerably large downfield shift ($\Delta\delta$ = 0.75 ppm for NH_b and $\Delta \delta$ = 0.60 ppm for NH_a) of NH protons of urea unit along with usual shifts of pyridyl ring protons due to binding of Cd^{II} with bis(2-picolyl) unit (Figure 3k). Interestingly, ¹H NMR analysis of L1 in the presence of 1 equiv of other Zn^{II} salts having various counter-anions such as Cl^{-} , Br⁻, NO₃⁻ CH₃CO₂⁻, ClO_4^{-} , CO₃²⁻, or H₂PO₄⁻ (Figure 3) show practically no change in resonance positions of NH protons at 298 K in DMSO- d_6 . Careful analysis of ¹H NMR spectra suggest that most of the Zn^{II} salts react with L1 without any observable chemical shift change of the -NH protons of the urea moiety except in the cases of $Zn(CF_3SO_3)_2$, $Zn(ClO_4)_2$, and $Zn(NO_3)_2$. Slight and same extent of downfield shift (exactly 0.18 and 0.1 ppm for NH_b and NH_a, respectivly, in all the cases) of N-H protons for these three metal salts (Figure 3g-i) can be attributed to the polarization of electron density from -NH protons induced by metal coordination of -C=0group³⁹ adjacent to N-H protons without having any secondsphere interaction between the anionic counterpart of metal salts and -NH protons, which is later confirmed by singlecrystal X-ray diffraction studies (Figure S18). All these data confirmed that among all the salts, SO42- salts are only recognized by L1 through second-sphere interaction.



Figure 1. Experimental (upper) and simulated (lower) ESI-MS(-ve) spectra of (a) complex 1 and (b) complex 3.



Figure 2. ESI-MS(+ve) spectra of monomeric complexes of (a) $Zn(OTf)_2$ complex of L1, (b) $ZnCl_2$ complex of L1, and (c) $Zn(ClO_4)_2$ complex of L1.

Inspired by the above results ¹H NMR titration experiments are performed between L1 with ZnSO₄ to evaluate the binding stoichiometry. During the course of titration NH_b and NH_a protons of free L1 at 5.76 and 5.63 ppm gradually diminish with concomitant increase in intensity of new set of -NH peaks at 6.32 and 6.04 ppm, respectively (Figure 4a). After the addition of nearly 1 equiv of ZnSO₄, complete disappearance of NH_b and NH_a protons are found along with generation of new set of NH peaks, which suggest, for example, that 1:1 could be 2:2 binding stoichiometry between L1 and ZnSO₄ in solution. The actual stoichiometry in solution is determined later by ¹H-DOSY experiment (Figure 8 and Table 2). Also, identical binding stoichiometry between L1 and ZnSO₄ is found by monitoring C5–H1 peak in Figure 4a as the intensity of peak at δ = 8.47 ppm gradually decreases along with concomitant increase in intensity of a peak at δ = 8.98 ppm, which saturates after addition of nearly 1 equiv of ZnSO₄ solution (Figure 4a). To further corroborate the binding stoichiometry of L1 with other SO₄²⁻ salts, we performed ¹H NMR titration experiment of L1 with CdSO₄·8/3 H₂O in DMSO- d_6 (Figure 4b). Similar

¹H NMR spectral pattern is observed in case of CdSO₄ like that of ZnSO₄. In the course of titration with CdSO₄ in DMSO- d_{6i} NH_a and NH_b protons of free L1 at 5.63 and 5.75 ppm diminish gradually, and a new set of N-H peaks originate at 6.20 and 6.44 ppm, respectively. After the addition of nearly 1 equiv of CdSO₄ solution, saturation is attained, which confirmed that 1:1 could be 2:2 binding stoichiometry between L1 and $CdSO_4$ in solution similar to the case of $ZnSO_4$. The actual stoichiometry in solution is later confirmed by ¹H-DOSY experiment (Figure 8 and Table 2). To elaborate the importance of preorganization of MSO₄ through dimerization during its recognition process, binding affinity of complex 5, $[(L1)Zn(CF_3SO_3)_2]$, toward anions having TBA countercation is monitored by ¹H NMR experiments (Figure S15). Addition of DMSO-d₆ solution of anions into a DMSO-d₆ solution of complex 5 resulted in upfield shift of the NH protons, and after saturation the -NH proton peak positions match exactly with the NH peak positions of free L1. This indicates that none of the anion binds with the urea moiety. Instead, some of the anions (e.g., Cl^- , $H_2PO_4^-$, OAc^- , etc.) bind with the metal



Figure 3. ¹H NMR of (a) free L1 (5.81 mM) and changes in resonance position after mixing 1 equiv of each (b) $ZnCO_3$, (c) $Zn(CH_3CO_2)_2 \cdot 4H_2O_3$, (d) $ZnCl_2 \cdot xH_2O_3$, (e) $ZnBr_2$, (f) $Zn(H_2PO_4)_{22}$, (g) $Zn(CF_3SO_3)_{22}$, (h) $Zn(ClO_4)_2 \cdot 6H_2O_3$, (i) $Zn(NO_3)_2 \cdot 6H_2O_3$, (j) $ZnSO_4 \cdot 7H_2O_3$, (k) $3CdSO_4 \cdot 8H_2O_3$ in DMSO- d_6 at 298 K.



Figure 4. (a) ¹H NMR titration profile of L1 (3.2 mM) upon gradual addition of 0.15 equiv of $ZnSO_4$ (31.25 mM) solution in DMSO- d_6 at 298 K in 300 MHz. Even after addition of 0.9 equiv of $ZnSO_4$, parent peaks could be observed in the baseline, which diminishes after addition of nearly 1.05 equiv of $ZnSO_4$ solution. (b) ¹H NMR titration profile of L1 (2.8 mM) upon gradual addition of 0.12 equiv of $CdSO_4$ (35.6 mM) solution in DMSO- d_6 at 298 K in 300 MHz. Saturation is observed after addition of 0.96 equiv of $CdSO_4$ solution.

center, and hence the metal-bound -C=0 unit gets expelled and becomes pendant urea unit as in free L1. Hence, complex 5 does not show any binding with any anions having TBA countercation as in case of free L1. As after formation of complex 5 preorganization is not possible, hence any of the anions including SO_4^{2-} is not being recognized by urea unit in complex 5. Recognition of SO_4^{2-} via urea -NH protons only with ion-pair of metal sulfates indicates cooperative binding of metal sulfates by L1.

Isothermal Titration Calorimetric Studies. The solutionstate binding affinity of L1 with various anions is performed by isothermal titration calorimetric (ITC) experiments. In a typical ITC experiment, solution of respective anion as its TBA salt in HPLC-grade DMSO is titrated with a solution of receptor L1 in the same solvent at 298 K. ITC studies reveal that L1 does not bind with any of the anions as observed from the ¹H NMR studies (Figure S12a). Interestingly, when L1 is titrated with ZnSO₄·7H₂O in DMSO at 298 K a smooth and clear exothermic titration profile is obtained, and subsequent fitting to a one-site binding profile provided access to the association constant (K_a), enthalpy change (ΔH), entropy change (ΔS), and free energy change (ΔG) of the binding process. The thermodynamic parameters obtained from the above experimental data showed $K_a = 1.23 \times 10^6 \text{ M}^{-1}$, $\Delta S = -25.7 \text{ J mol}^{-1}$ deg⁻¹, and $\Delta H = -42.6 \text{ kJ mol}^{-1}$. However, it should be mentioned that the thermodynamic parameters obtained have contributions from both first- (binding of Zn²⁺ with bis(2picolyl) amine moiety of L1) and second-sphere (binding of



Figure 5. ITC plot in DMSO at 298 K for the addition of a solution of (a) $ZnSO_4$ ·7H₂O (0.685 mM) to a solution of L1 (0.099 mM) and (b) $Zn(ClO_4)_2$ (1.285 mM) to a solution of L1 (0.1087 mM). (upper) The heat pulses experimentally observed in each titration. (lower) The respective time integrals translating as the heat evolved for each aliquot and its coherence to the one-site binding model.



Figure 6. ITC plot in DMSO at 298 K for the addition of a solution of (a) $ZnSO_4$ (0.931 mM) to a solution of L2 (0.124 mM), (b) $Zn(CF_3SO_3)_2$ (0.792 mM) to a solution of L1 (0.099 mM), and (c) $Zn(NO_3)_2$ (0.9208 mM) to a solution of L1 (0.099 mM). (upper) The heat pulses experimentally observed in each titration. (lower) The respective time integrals translating as the heat evolved for each aliquot and its coherence to the one-site binding model.

 SO_4^{2-} with urea moiety of L1) coordination of $ZnSO_4$ with L1. To get insight into the anion recognition via urea moiety or to get an estimate of the second-sphere binding constant (binding of SO_4^{2-} with urea moiety of L1), we must eliminate the firstsphere binding constant. To get the value of only the firstsphere binding constant, L1 is titrated with Zn²⁺ salts having noninteracting counteranions (e.g., $Zn(ClO_4)_2$, $Zn(CF_3SO_3)_2$). In both cases we obtained similar binding constants ($K_a = 5.34$ $\times 10^4$ and $K_a = 7.18 \times 10^4$ for $Zn(CF_3SO_3)_2$ and $Zn(ClO_4)_2$ respectively; Figures 5b and 6 and Table 1), which is significantly smaller than that of ZnSO₄. Similarly, other Zn^{II} salts, for example, $ZnCl_2$ and $Zn(NO_3)_2$, show binding constants K_a in the order of $\sim 1 \times 10^4$ M⁻¹, which is similar to that of $Zn(ClO_4)_2$ and $Zn(CF_3SO_3)_2$ but much smaller as compared to that of ZnSO₄ (Table 1 and Figures 5, 6, and S12). Binding constant values obtained in these cases are mainly a manifestation of primary-sphere binding only. From the binding constant values obatained from the ITC measure-

Table 1. Thermodynamic Parameters Obtained from Isothermal Titration Calorimetric Experiments in Dimethyl Sulfoxide at 298 K

| host | guest | $K_{\rm a} \ ({\rm mol}^{-1})$ | $\Delta H \left(\text{kJ/mol} \right)$ | $\Delta S (kJ/mol/deg)$ | | |
|--|--------------------------------------|--------------------------------|---|-------------------------|--|--|
| L1 | TBAHSO ₄ | n.d. ^{<i>a</i>} | n.d. | n.d. | | |
| L1 | $Zn(ClO_4)_2 \cdot 6H_2O$ | 7.18×10^4 | -20.6 | 24.3 | | |
| L1 | $Zn(CF_3SO_3)_2$ | 5.34×10^{4} | -20.4 | 22.6 | | |
| L1 | $Zn(NO_3)_2 \cdot 6H_2O$ | 6.96×10^{4} | -23.7 | 13.6 | | |
| L1 | $ZnCl_2 \cdot xH_2O$ | 5.27×10^{4} | -20.6 | 21.7 | | |
| L1 | $ZnSO_4 \cdot 7H_2O$ | 1.23×10^{6} | -42.6 | -25.7 | | |
| L1 | CoSO ₄ ·6H ₂ O | 1.58×10^{6} | -58.9 | -78.54 | | |
| L1 | CdSO ₄ ·6H ₂ O | 7.49×10^{6} | -39.4 | -0.1 | | |
| L2 | $ZnSO_4 \cdot 7H_2O$ | 2.4×10^{4} | -33.9 | -29.1 | | |
| ^a None detected indicated by n.d. | | | | | | |

ments, the order of binding affinity of metal salts toward L1 is as follows: $CdSO_4 > CoSO_4 > ZnSO_4 > Zn(ClO_4)_2 >$



Figure 7. ITC plot in DMSO at 298 K for the addition of a solution of (a) $CoSO_4$ · $6H_2O$ (0.7425 mM) to a solution of L1 (0.099 mM) and (b) $CdSO_4$ · $6H_2O$ (0.8695 mM) to a solution of L1 (0.1087 mM). (upper) The heat pulses experimentally observed in each titration. (lower) The respective time integrals translating as the heat evolved for each aliquot and its coherence to one-binding model.



Figure 8. ¹H DOSY NMR of (a) complex 1 and (b) complex 2 in DMSO- d_6 at 298 K.

 $Zn(NO_3)_2 > Zn(CF_3SO_3)_2 > ZnCl_2$. Thus, the enhanced binding constant ($K_{ZnSO4}/K_{ZnX2} \approx 30-50$, where $X = ClO_4^{-/}$ $CF_3SO_3^{-/}NO_3^{-/}Cl^{-}$) in cases of $ZnSO_4$ with L1 indicates participation of different mode of binding for sulfate salts with L1 through preorganization as well as the role of urea group in stabilizing the dimeric unit through second-sphere H-bonding interaction.

To assertain the metal sulfate selectivety of L1 we also performed ITC experiments with $CdSO_4 \cdot 8/3 H_2O$ and $CoSO_4 \cdot 6H_2O$ with L1 in DMSO, and the binding constants are found to be 7.49 × 10⁶ and 1.58 × 10⁶ M⁻¹, respectivly (Table 1 and Figure 7), which is quite similar to the value of ZnSO₄ but much larger as compared to the values obtained in case of other Zn^{II} salts.

To confirm the positive role of urea moiety we synthesized a control receptor L2, having similar bis(2-picolyl)amine moiety but lacks any anion binding group (Chart 2). ITC experiment of L2 with ZnSO₄ (Figure 6) under similar experimental condition shows binding constant $K_a = 2.4 \times 10^4$ M⁻¹ (Table 1), which is similar to the cases of L1 and ZnX₂ and much smaller than the case of L1 and ZnSO₄. This confirms the

participation of urea moiety toward selective recognition of MSO_4 in case of L1.

In the course of titration of L1 with $ZnSO_4$, $CdSO_4$, $CoSO_4$, and MnSO₄ the entropy values decrease ($\Delta S = -ve$), whereas entropy values increase ($\Delta S = +ve$) in cases of other Zn salts (Table 1). This clearly suggests more ordering of systems in cases of binding of MSO4 through the formation of sulfatebridged dimer $[M_2(\mu-SO_4)_2(H_2O)_n]$ with L1 when compared with nonbridged mononuclear hydrated form of other Zn^{II} salts. Decrease in values of entropy in solution in cases of MSO_4 and L1 has contrbution of both (i) formation of dimeric unit from monomer and (ii) second-sphere binding between the pendant urea moiety and bridged $\mathrm{SO_4^{2-}}$ unit. The binding process of MSO₄ with L1 is such a highly enthalpy driven (highly exothermic) process that it supersedes the unfavorable negative or nearly zero contribution from entropy to produce high negative value of Gibbs free energy change ($\Delta G = -ve$), which is reflected in high binding constant of MSO₄ with L1. In the course of titration of L2 and ZnSO₄, decrease in entropy value is probably due to the formation of SO₄²⁻ bridged dimer; however, ordering of system due to H bonding is not possible here. All these data support the existence of dimeric unit in solution in case of metal sulfates. In cases of other Zn^{II} salts, the binding process is both moderately entropy and enthalpy driven with lower values of Gibbs free energy change, that is, lower binding constant values.

It is a known fact that adding even a small amount of water to DMSO can significantly weaken the interaction between hydrogen bond donors and anions. So, to find the sustainability of selectivity of L1 toward MSO₄, we performed ITC measurements in 10% H₂O/DMSO binary solvent mixture. ITC results showed highest binding constant for ZnSO₄ ($K_a =$ 4.86 × 10⁶) with L1, which is ~20–30 times higher as compared to other Zn^{II} salts ($K_a \approx 1 \times 10^4$; Figure S24).

To confirm the binding stoichiomentry between MSO₄ (M = Zn^{II}, Cd^{II}) and L1 in solution we performed two-dimensional diffusion-ordered spectroscopy (DOSY), which has become an important technique for studying the self-assembly of supramolecular systems in solution.^{40–42} Figure 8 shows ¹H DOSY NMR of complexes 1 and 2 in DMSO- d_6 . The hydrodynamic radius (r) of the complexes is calculated from the following Stokes–Einstein relation using experimentally obtained diffusion coefficients at 298 K for L1 (Table 2).

hydrodynamic radius
$$r = \frac{KT}{6\pi\eta D}$$

where D = diffusion coefficient; k = Boltzmann constant (1.3807 × 10⁻²³ m² kg S⁻² K⁻¹); T = temperature in kelvin; η = viscosity coefficient of the solution (1.991 × 10⁻² g cm⁻¹ S⁻¹ for DMSO); r = hydrodynamic radius of the molecular sphere.

Assuming spherical shape of the crystal structure we determined molecular diameter of both the complexes by averaging the dimensions of major and minor axes (Figure 9



Figure 9. Space-filling models from single-crystal X-ray structures of (a) complex 1, major axis: $C11-H11\cdots C10-H10 = 13.3$ Å; minor axis: $C14-H14A\cdots C14-H14B = 13.2$ Å and (b) complex 2, major axis: $C19-H19A\cdots C19-H19B = 17.4$ Å, minor axis: $C5-H5\cdots C6-H6 = 10.8$ Å. Blue: nitrogen, Green: hydrogen, Red: oxygen, and Gray: carbon.

| Table 2. Diffusion Coefficient (D) and Hydrodynamic |
|---|
| Diameter $(2r)$ in DMSO- d_6 at 298 K |

| | | 2 <i>r</i> , Å | | |
|--------------------------------|---|--|--|--|
| compound | D, 1×10^{-10} $m^2 s^{-1}$ | calculated (from crystal structure) | experimental (from diffusion coefficient) | |
| L1 | 2.63 | | 8.1 Å | |
| complex 1 | 1.69 | 13.25 Å | 13.18 Å | |
| complex 2 | 1.65 | 14.1 Å | 13.5 Å | |
| 1:1 mixture of L1 and ZnSO4 | 1.72 | | 13.12 Å | |

and Table 2). From Table 2 it is evident that the sizes of both the complexes in solution are significantly larger than that of L1. Interestingly, the molecular diameters of both the complexes in solution match quite well with the calculated diameters from the crystal structures for 2:2 complexes between L1 and ZnSO₄/CdSO₄. This suggests the formation of 2:2 complexes between L1 and $ZnSO_4/CdSO_4$ in solution. All the peaks in the spectra of both the complexes show similar diffusion coefficients, which in turn suggests the formation of a single 2:2 complex in solution. Furthermore, the diffusion coefficient of equivalent amount of L1 and $ZnSO_4$ in DMSO- d_6 solution is found to be 1.72×10^{-10} m²/s, which is similar to that of complex 1 (Figure S25). Thus, we conclude that L1 forms 2:2 complex with MSO₄ in solution as supported by ¹H DOSY experiments. The similar values of molecular diameter also suggest that ZnSO₄/CdSO₄ exists as contact ion pair in solution.

Single-Crystal X-ray Studies. Finally, we ascertained the existence of the dimeric $[M_2(\mu-SO_4)_2]$ unit in MSO₄ complexes of L1 by single-crystal X-ray diffraction studies. Block-shaped crystals of complex 1, $[Zn_2(L1)_2(\mu-SO_4)_2]$; complex 2, $[Cd_2(L1)_2(\mu-SO_4)_2(H_2O)_2];$ complex 3, $[Co_2(L1)_2(\mu SO_4_{10}(H_2O_2)$; and complex 4, $[Mn_2(L1)_2(\mu - SO_4)_2(H_2O_2)]$ are obtained from the mixture of L1 and ZnSO₄·7H₂O, CdSO₄· 8/3H₂O, CoSO₄·6H₂O, and MnSO₄·6H₂O, respectively, both from DMSO/H₂O (3:1 v/v) binary solvent system and pure water. Crystallographic details of complexes 1-4 are given in Table 3. Interestingly, all the structures reveal that dimeric metal sulfate cluster $M_2(\mu$ -SO₄)₂(H₂O)_m [m = 0 and 2 for M = Zn^{II} and Cd^{II}/Co^{II}/Mn^{II}, respectively] is trapped between two units of L1. In all these complexes ligated water molecules of the dinuclear sulfate-bridged complex $M_2(SO_4)_2(H_2O)_x$ are displaced from the primary coordination sphere in the course of complexation according to the coordination requirement of respective metal ions, keeping the bridged unit intact. Crystals of complex 1 are isolated by the slow evaporation of DMSO/ H₂O (3:1) solution of L1 and ZnSO₄·7H₂O. Crystal structure analysis reveals the presence of two pentacoordinated Zn^{II} having trigonal bipyramidal (TBP) geometry. The five coordination sites of each Zn^{II} are occupied by three nitrogen atoms (N1, N2, and N3) of bis(2-picolyl) unit and two oxygen atoms (O2 and O3) of two bridging SO_4^{2-} . One oxygen atom of the bridging SO_4^{2-} (O2) is coordinated to the Zn^{II} in the equatorial plane along with N1 and N3, whereas the other two axial positions are occupied by one tertiary nitrogen atom (N2) of bis(2-picolyl) unit and one oxygen atom (O3) of SO_4^{2-} group (Figure 10). The index of trigonality (τ) value is measured as 0.61, which falls between the ideal τ value for a perfect square pyramidal geometry ($\tau = 0$) and TBP geometry $(\tau = 1)$. All the bond distances and bond angles are provided in Table S1. Two SO₄²⁻ anions act as bidentate ligand and bridge two Zn^{2+} centers by forming an eight-membered zigzag ring exactly similar to the structure of molecular crownlike structure of S_8 (Figure S13). Coordination environment of SO_4^{2-} shows two oxygens (O2 and O3) of SO_4^{2-} anions are coordinated to Zn^{II} , where the equatorial Zn(1) - O(2) bond has smaller bond length (1.961 Å) as compared to the axial Zn(1)-O(3) bond (2.054 Å) as expected from the TBP geometry. All the bond angles fall in the region between 106° and 130°, which are quite common with distorted TBP coordination environment. The two equatorial bond lengths of Zn(1)-N(1) and Zn(1)-N(3)are 2.048 and 2.089 Å, respectively, which is in agreement with the tridentate ligands containing pyridyl units (2.02–2.09 Å),

Table 3. Crystal Data and Refinement Details of Complexes 1-4

| compound | complex 1 | complex 2 | complex 3 | complex 4 |
|--|-----------------------------------|-----------------------------------|-----------------------------------|--|
| chemical formula | $C_{38}H_{54}N_{10}O_{12}S_2Zn_2$ | $C_{42}H_{78}Cd_2N_{10}O_{18}S_4$ | $C_{42}H_{66}Co_2N_{10}O_{18}S_4$ | $C_{38} \ H_{54} \ Mn_2 N_{10} O_{14} S_2$ |
| formula mass | 1037.77 | 1364.18 | 1245.15 | 1048.91 |
| crystal system | triclinic | monoclinic | monoclinic | monoclinic |
| a/Å | 9.1081(5) | 16.1563(12) | 16.0294(11) | 13.439(2) |
| b/Å | 9.5838(5) | 11.0458(8) | 10.8894(8) | 10.8861(17) |
| c/Å | 14.8352(8) | 16.3922(12) | 16.4207(12) | 19.870(3) |
| α/\deg | 78.6128(12) | 90.00 | 90.00 | 90 |
| $\beta/{ m deg}$ | 73.7441(11) | 104.037(2) | 104.5296(16) | 109.719(4) |
| γ/deg | 66.1009(11) | 90.00 | 90.00 | 90 |
| unit cell volume/Å ³ | 1131.38(11) | 2838.0(4) | 2774.6(3) | 2736.5(8) |
| temperature/K | 150(2) | 150(2) | 150(2) | 150(2) |
| space group | $P\overline{1}$ | P2(1)/n | P2(1)/n | P2(1)/n |
| no. of formula units per unit cell, Z | 1 | 2 | 2 | 2 |
| radiation type | Μο Κα | Μο Κα | Μο Κα | Μο Κα |
| absorption coefficient, μ/mm^{-1} | 1.223 | 0.973 | 0.826 | |
| no. of reflections measured | 10 841 | 32 918 | 32 372 | 23 492 |
| no. of independent reflections | 3945 | 4993 | 4865 | 4417 |
| R _{int} | 0.0234 | 0.0226 | 0.0409 | 0.0581 |
| final R_1 values $(I > 2\sigma(I))$ | 0.0301 | 0.0190 | 0.0356 | 0.1038 |
| final $wR(F^2)$ values $(I > 2\sigma(I))$ | 0.0927 | 0.0510 | 0.1243 | 0.3126 |
| final R_1 values (all data) | 0.0325 | 0.0198 | 0.0438 | 0.1246 |
| final $wR(F^2)$ values (all data) | 0.0950 | 0.0515 | 0.1363 | 0.3233 |
| goodness of fit on F^2 | 1.070 | 1.090 | 1.094 | 1.153 |







Figure 11. Ball and stick representation of crystal structures of (a) Complex 3, $[(L1)_2Co_2(SO_4)_2]$ and (b) Complex 4, $[(L1)_2Mn_2(SO_4)_2(H_2O)_2]$. Hydrogen atoms, except those of the urea group, are omitted for clarity.

Н

and the other axial Zn(1)–N(3) bond length (2.264 Å) is slightly higher as observed with TBP geometry. One of the coordinated oxygen atoms of SO_4^{2-} group having longer Zn^{II}– O (Zn1–O3) bond length (2.054 Å) is involved in strong intermolecular hydrogen bonding interaction with the N–H group (N5–H5) of urea moiety, while other oxygen atom (O2) having stronger interaction with the metal center is reluctant in hydrogen bonding with the urea group (Figure S14).

Similarly, we obtained the crystals of complex 2 $[Cd_2(L1)_2(SO_4)_2(H_2O)_2]$ by slow evaporation of equimolar mixture of L1 and $CdSO_4 \cdot 8/3$ H₂O in DMSO/H₂O (3:1 v/v) binary solvent system and pure water. Crystal structure of 2



Figure 12. Change in chemical shifts of NH_a protons in (a) complex 1 and (b) complex 2 upon change in temperature in DMSO-d₆.

shows two symmetrical Cd^{II} centers in a distorted octahedral environment, coordinated by N₃O₃-type ligand motif in a facial geometrical arrangement (Figure 10). Two Cd^{II} centers are connected to each other via two bridging $\mathrm{SO_4^{2-}}$ anions. In the facial-type geometry one face is formed by the coordination of three nitrogen atoms (N1, N2, and N3) from bis(2-picolyl) unit, and the other face is formed by two oxygen atoms (O5, O2) from two bridging SO_4^{2-} anion and one oxygen atom from coordinated H₂O molecule. The other two noncoordinated oxygen atoms (O3 and O4) of SO_4^{2-} anion are involved in intermolecular hydrogen bonding interaction with the -NH group of urea moiety (N4-H4···O3 and N5-H5···O4). Both of the hydrogen bond lengths (2.095 and 2.119 Å, respectively, for N4-H4...O3 and N5-H5...O4) in complex 2 are much shorter as compared to that of complex 1 (2.185 Å N5-H5... O3; Figure S15). Similarly, we also got the crystal structure of complex 3 via slow evaporation of DMSO/H₂O (3:1) binary solvent mixture and pure H₂O solution of L1 and CoSO₄. 6H2O. Crystal structure reveals the presence of two symmetrical Co^{II} units in a distorted octahedral geometry with N₃O₃-type donor ligands (Figure 11). Two Co^{II} centers are connected to each other via two bridging SO_4^{2-} anions in this facial type of octahedral geometry in which one of the faces is formed by the coordination of three nitrogen atoms (N1, N2, N3) of bis(2-picolyl) unit, while the other face contains two oxygen atoms (O2 and SO_4^{2-}) and one oxygen atom of coordinated H_2O molecule (O3). In the square plane the four bond angles range from 78° to 100°, which is in quite acceptable range for a distorted octahedral geometry. Nearly same bond distance of Co1-N3 and Co1-N1 suggests that the two pyridyl nitrogen along with O2 and O3 are positioned in the square plane and that the other two atoms (N2 and O5) are placed in the axial position. In the course of secondary sphere interaction^{37,38,43} as contradictory with ZnSO₄ here the other two noncoordinated oxygen atom of SO₄²⁻ anion are involved in intermolecular hydrogen bonding interaction with the two N-H (N4-H4...O4 and N5-H5...O6) protons of urea moiety in which the hydrogen bond distances are much shorter as compared to those of complex 1 (Figure S16). Crystals of complex 4 $[Mn_2(L1)_2(SO_4)_2(H_2O)_2]$ are obtained by slow evaporation of equimolar mixture of L1 and MnSO₄·6H₂O in DMF/H_2O (3:1 v/v) binary solvent system and pure water. Crystal structure of 4 shows two symmetrical Mn^{II} centers in a distorted octahedral environment, coordinated by N₃O₃-type ligand motif in a facial geometrical arrangement (Figure 11). Two Mn^{II} centers are connected to each other via two bridging SO_4^{2-} anions. In the facial-type geometry one face is formed by

the coordination of three nitrogen atoms (N4, N5, N3) from bis(2-picolyl) unit, and the other face is formed by two oxygen atoms (O3, O6) from two bridging SO_4^{2-} anion and one oxygen atom from coordinated H₂O molecule. All the bond distances and bond angles are provided in Table S1. The crystal structure of complex 4 also shows intermolecular H-bonding interaction between SO42- unit and urea moiety from another unit (Figure S17). We also obtained the crystals of complex 5 by diffusing a solution of di-isopropyl ether into acetonitrile solution of 1:1 mixture of L1 and Zn(OTf)₂. Crystal structure analysis of complex 5 shows Zn^{II} ion is in a distorted TBP geometry in which the three coordination sites are occupied by the thee nitrogen atoms of bis(2-picolyl) unit (N1, N2, and N3) and the remaining two positions are occupied by the carbonyl oxygen atom (O1) and one water molecule (O8; Figure S18). In the crystal structure N2, N3 from the bis(2picolyl) unit and along with the carbonyl oxygen, O1 coordinates to the central Zn^{II} in the equatorial plane. All the bond angles in the equatorial plane range within 108°-128°, which are relatively close to the ideal TBP geometry, whereas the axial O8–Zn1–N1 bond angle is measured as 167°, which deviates nearly 13° from the ideal structure, and the index of trigonality (τ) value is calculated as 0.68, which falls between the ideal τ value for a perfect square pyramidal geometry (τ = 0) and TBP geometry ($\tau = 1$). All the bond distances and bond angles are provided in Table S1. The CF₃SO₃⁻ counteranions in complex 5 are in weak hydrogen bonding interactions with the urea -NH protons. The lengthening of C15-O1 bond (1.28 Å) in complex 5 as compared to the free ligand L1 (1.23 Å)Å) is in agreement with -C=0 coordination to the central Zn^{II} atom.

Intramolecular Versus Intermolecular Hydrogen Bonding. It is important to mention here that in solid state all the sulfate complexes show intermolecular H-bonding interaction between SO42- unit and pendant -NH group of urea moiety as evident from the crystal structure analysis (Figures S14 and S15). However, variable-temperature ¹H NMR spectra (Figure 12) and dilution experiments (Figures S26 and S27) confirmed the existence of intramolecular H bonding in these complexes in solution. In temperaturedependent studies, in case of complex 1, when changes in chemical shift of the urea protons are plotted against temperature, negative slope value of $-3.6 \times 10^{-3} \ \text{K}^{-1}$ is obtained, which is in acceptable range for intramolecular H bonding in solution in highly polar solvent such as DMSO.⁴⁴ Also, much lower value of negative slope, that is, -1×10^{-3} , is obtained in case of complex 2, which also supports intramolecular H bonding in solution. These results suggest that although in solid state these compounds show intermolecular H bonding, but in solution state they show preference for intramolecular H bonding. This is not surprising at all because in solid state crystal packing is much more important than minor contribution obtained from entropic factors (which favors intramolecular H bonding) and thus we observe different H-bonding mode in solution and solid state.

Selective Trapping and Removal of MSO₄ from Aqueous and Semiaqueous Medium. Inspired by the high degree of affinity of L1 toward MSO4 in solution we proceeded to investigate the ion-pair selectivity and separation properites of L1 in both DMSO/H₂O binary mixture and pure water. L1 quantitaively forms complex with ZnSO₄ in 100% water (Figures S20 and S23) and is capable of removing ZnSO₄ via precipitation through crystallization. We performed a competitive crystallization experiment where equimolar amounts of several competing Zn^{II} salts [e.g., ZnCl₂, ZnBr₂, $Zn(NO_3)_2$, $Zn(ClO_4)_2$, $Zn(OTf)_2$, $Zn(OAc)_2$, $ZnCO_3$, and ZnSO₄] and L1 in 100% water and 3:1 DMSO/H₂O showed that only complex 1 crystallizes from solution that is confirmed by ¹H NMR studies (Figures 13 and S21), crystal structure analysis, and finally by PXRD experiments of the isolated crystals.



Figure 13. Comparison of ¹H NMR spectra of (a) DMSO- d_6 solution of crystals of complex 1 and (b) ¹H NMR in DMSO- d_6 of crystals obtained from mixture of L1 with several Zn^{II} salts from DMSO/H₂O solvent mixture. Both spectra were recorded in 300 MHz at 298 K.

This selectivity pattern in solution is well-understood when mixture of equimolar several Zn^{II} salts and L1 in either DMSO d_6 or D₂O showed a ¹H NMR spectrum similar to the ¹H NMR of complex 1 in either DMSO- d_6 or D₂O, respectively (Figures 14 and S22). This result indicates that L1 selectively binds with ZnSO₄ in solution among all other Zn^{II} salts and crystallizes as complex 1 from both aqueous and semiaqueous solution.

Finally, we performed powder XRD experiments to determine the nature and bulk purity of the isolated complexes (in the form of crystals) from mixture of several Zn salts and L1 in DMSO/H₂O solvent mixture and pure H₂O. PXRD patterns of of the isolated crystals from above two solvent systems show similar diffraction patterns with the simulated pattern obtained from the single-crystal X-ray data of complex 1 (Figure 15). This result also suggests that only complex 1 is selectively separated from mixture with high degree of bulk purity. We also checked elemental analysis of the isolated product from

competitive crystallization experiment in H₂O, which gives values of C 45.19%, H 5.28%, and N 13.18% that matches quite well with the theoretically calculated C, H, and N values of complex 1. The elemental analysis of the crystal obtained from competitive crystallization experiment in DMSO/H₂O mixture did not match well with the calculated one most probably because of presence of residual high-boiling DMSO molecules, which are not easily removable. We calculated the separation efficiency of L1 by weighing the isolated complex obtained from mixture of L1 and equivalent amount of several Zn^{II} salts. L1 (200 mg, 0.6 mmol) is found to selectively precipitate out complex 1 (360 mg, 0.35 mmol) with 58% yield from DMSO/H₂O.

CONCLUSION

In conclusion, a ditopic receptor having tridentate metal chelating site and a pendant urea moiety as anion recognition element shows selective trapping and separation of metal sulfate as sulfate-bridged bimetallic ion-pair from aqueous and semiaqueous solutions. Recognition of metal sulfates in solution is depicted by ¹H NMR and further supported by thermodynamic parameters obtained from ITC studies. 2:2 binding stoichiometry between L1 and ZnSO₄/CdSO₄ in solution is confirmed by ¹H DOSY NMR spectroscopy. Ligand also shows potential ability for removal of metal sulfates from aqueous medium in the presence of several competing salts as dimeric assembly of metal sulfate with L1, which is confirmed by ¹H NMR, powder XRD, and single-crystal X-ray diffraction analysis. The existence of ZnSO₄/CdSO₄ as ion pair in solution is confirmed by comparing the molecular diameters obtained from ¹H DOSY NMR with the diameter of crystal structure, where $ZnSO_4/CdSO_4$ exists as ion pair with two units of L1. This represents unique examples of metal sulfate recognition as dimeric bonded ion-pair structure, which is one of the concentration-dependent forms of metal sulfate in solution. Our approach of recognizing metal sulfates in this unusual form could motivate the development of a new generation of anionbridged metal salt receptors. Presently, we are working on such ditopic systems using the above approach to develop various metal sulfate receptors in aqueous/semiaqueous media.

EXPERIMENTAL SECTION

Materials. All reactions were performed in argon gas atmosphere followed by workup at ambient conditions. Dichloromethane (DCM) and acetonitrile were dried over CaH₂ and collected before use. HPLC-grade DMSO was purchased from Spectrochem Pvt. Ltd., India, and used for complexation, crystallization, and ITC studies. Deuterated solvents, tetrabutylammonium salts of F⁻, Cl⁻, Br⁻, I⁻, AcO⁻, BzO⁻, ClO₄⁻, NO₃⁻, HCO₃⁻, HO⁻, HSO₄⁻, H₂PO₄⁻, and zinc triflate were purchased from Sigma-Aldrich and were used as received. ZnSO₄·7H₂O, CdSO₄·8/3H₂O, and CoSO₄·6H₂O were purchased from Merck India Pvt. Ltd. *Caution!* Although we experienced no difficulties with the perchlorate salts, these should be regarded as potentially explosive and handled with care.

Methods. ESI-MS experiments were performed with a Waters QtoF Model YA 263 mass spectrometer in positive/negative ESI mode. All the samples for mass spectrometry were prepared by dissolving the compounds in methanol having following concentrations (i) 2.1×10^{-6} (M) for L1, (ii) 3.3×10^{-6} (M) for complex 1, (iii) 1.4×10^{-6} (M) for complex 3, (iv) 2.5×10^{-6} (M) for (L1)Zn(ClO₄)₂ complex, (v) 1.8×10^{-6} (M) for (L1)Zn(CF₃SO₃)₂ complex, and (vi) 2.3×10^{-6} (M) for (L1)ZnCl₂ complex. ¹H and ¹³C experiments were performed on FT-NMR Bruker DPX 500/300 MHz NMR spectrometer. Elemental analysis was performed on PerkinElmer 2500 series II elemental analyzer, PerkinElmer, USA. Chemical shifts



Figure 14. Selective formation of Zn^{II} sulfate complex in solution from mixture of several competing Zn(II) salts at 298 K in D_2O . ¹H NMR of (a) L1 in D_2O , (b) 1:1 mixture of L1 and $ZnSO_4$ in D_2O , (c) 1:1 mixture of L1 and various Zn^{II} salts in D_2O , and (d) crystals obtained as precipitate from solution of 1:1 mixture of L1 and various Zn^{II} salts in D_2O .



Figure 15. Comparative of PXRD patterns of (a) crystals obtained from mixture of L1 with several Zn^{II} salts in H_2O (experimental), (b) crystals obtained from mixture of L1 with several Zn^{II} salts from DMSO/ H_2O solvent mixture (experimental), and (c) complex 1 (simulated).

for ¹H and ¹³C NMR were reported in parts per million, calibrated to the residual solvent peak set, with coupling constants reported in hertz. ¹H NMR titration was performed on 300 MHz Bruker DPX NMR spectrometer.

Isothermal Titration Calorimetric Studies. The ITC experiments were performed with a MicroCal VP-ITC instrument. The titrations were performed at 298 K in HPLC-grade DMSO solvent. A solution of host in DMSO was placed in the measuring cell. This solution was then titrated with 30/60 injections of the respective guest solution (5/10 μ L) that was prepared in DMSO. An interval of 220 s was allowed between each injection, and the stirring speed was set at 329 rpm. The obtained data were processed by using Origin 7.0 software that was supplied with the instrument and was fitted to a one-site binding model. A blank titration of plain solvent was also performed and

subtracted from the corresponding titration to remove any effect from the heats of dilution from the titrant.

Diffusion Measurements. All ¹H DOSY experiments were performed on a Bruker AVII 500 MHz spectrometer. Data analyses were performed using tools within TOPSPIN 2.1 software. Sample volumes were 450 μ L, and the concentration of the samples were 5.2 mM for complex 1 and 5.5 mM for complex 2. All the experiments were performed in DMSO- d_6 solvent. Diffusion coefficients and hydrodynamic radii are correlated theoretically by the Stokes–Einstein relation.

X-ray Crystallographic Refinement Details. Crystals suitable for single-crystal X-ray diffraction studies for complexes 1–5 were selected from the mother liquor and immersed in paratone oil and then mounted on the tip of a glass fiber and cemented using epoxy resin. Intensity data for the all the crystals were collected using Mo K α ($\lambda = 0.7107$ Å) radiation on a Bruker SMART APEX II diffractometer equipped with CCD area detector at 150 K. The data integration and reduction were processed with SAINT software⁴⁵ provided with the software package of SMART APEX II. An empirical absorption correction was applied to the collected reflections with SADABS.⁴⁶ The structures were solved by direct methods using SHELXL⁴⁷ and were refined on F^2 by the full-matrix least-squares technique using the SHELXL-97⁴⁸ program package. Graphics were generated using PLATON⁴⁹ and MERCURY 2.3.⁵⁰ Non-hydrogen atoms were refined anisotropically until convergence was reached.

Syntheses. Synthesis of [tert-Butyl 2-(bis(pyridin-2-ylmethyl)amino)ethylcarbamate] (L1"). The ligand was synthesized following the literature procedure.⁵¹

Synthesis of [1-(2-(Bis(pyridin-2-ylmethyl)amino)ethyl)-3-tert-butylurea] (L1). In a 100 mL round-bottom flux 625 mg (1.82 mmol) of L1" was dissolved in 20 mL of dry DCM and a solution of 2 mL trifluoroacetic acid in 10 mL dry DCM was added dropwise via a dropping funnel into the previously mentioned solution at 0 °C. The resulting solution was allowed to stir at room temperature for 6 h. The solution was evaporated to get an oily product, which was used in the next step without further purification. The oily product (1.8 mmol) was dissolved in dry DCM, and dry triethylamine (2.53 mL, 18.2 mmol) was added into it; the resulting solution was stirred for 10–15 min, and after that 220 μ L (1.9 mmol) of tertiarybutyl isocyanate in dry DCM was added dropwise via a pressure-equalizing funnel into the stirring solution at 0 °C. The reaction mixture was allowed to stir overnight, and then the solvent was evaporated. After addition of water into the crude solution it was extracted with DCM for 2-3 times. The overall DCM was collected and washed with brine solution and then dried with Na₂SO₄. The DCM part was filtered and evaporated to get an oily product, which after washing with hexane for several time vielded solid 398 mg L1 in 65% vield. Anal. Calcd for C10H27N5O (MW 341.4) C, 66.83; H, 7.97; N, 20.51; found: C, 66.73; H, 7.93; N, 20.45%; ESI MS $C_{19}H_{28}N_5O$ calcd, m/z = 342.22; found, m/z =342.15. ESI MS $C_{19}H_{27}N_5ONa$ calcd, m/z = 364.21; found, m/z =364.11. ESI MS $C_{10}H_{27}N_5OK$ calcd, m/z = 380.18; found, m/z =380.09. ¹H NMR (300 MHz, DMSO- d_6): $\delta = 8.476 - 8.462$ (d, 2H, H₁, J = 4.2 Hz, $\delta = 7.777 - 7.720 \text{ (t, 2H, H}_3, J = 8.5 \text{ Hz}$), $\delta = 7.598 - 7.572 \text{ Hz}$ (d, 2H, H₂, J = 7.8 Hz), $\delta = 7.261 - 7.217$ (m, 2H, H₄), $\delta = 5.766$ (s, 1H, H_b), $\delta = 5.649 - 5.612$ (t, 1H, H_a, J = 5.4 Hz), $\delta = 3.739$ (s, 4H, H₅), $\delta = 3.135 - 3.074$ (q, 2H, H₇, J = 6.3 Hz), $\delta = 1.121$ (s, 9H, H₈) ppm, ¹³C NMR (75 MHz, DMSO-*d*₆): 159.81, 157.76, 149.15, 136.90, 123.10, 122.54, 60.15, 54.36 49.40, 37.51, 29.82 ppm.

Synthesis of Complex 1. Into a clear solution of ligand L1 (40 mg, 0.12 mmol) in DMSO, a solution of ZnSO₄:7H₂O (34 mg, 0.118 mmol) in water was added and stirred for 1 h yielding a clear solution. This solution was kept for crystallization, and after 2–3 d crystals suitable for X-ray diffraction were obtained from the solution. Anal. Calcd for C₃₈H₅₄N₁₀O₁₀S₂Zn₂ (M.W: 1005.80) C, 45.38; H, 5.41; N, 13.3. Found: C, 45.05; H, 5.33; N, 12.96%. ESI MS(-ve) C₃₈H₅₄N₁₀O₁₀S₂Zn₂ calcd, *m*/*z* = 1002.2049; found, *m*/*z* = 1002.1024. ¹H NMR (300 MHz, DMSO-*d*₆): δ = 8.99–9.01 (d, 2H, *J* = 6 Hz), δ = 8.06–8.00 (t, 2H, *J* = 9 Hz), δ = 7.54–7.48 (m, 4H), δ = 6.44 (bs, 1H,), δ = 6.20 (bs, 1H), δ = 2.93 (bs, 2H), δ = 2.84 (bs, 2H) ppm.

Synthesis of Complex 2. Into a solution of ligand L1 (40 mg, 0.12 mmol) in DMSO, a solution of CdSO₄·8/3 H₂O (90.24 mg, 0.117 mmol) in water was added and stirred for 1 h yielding a clear solution. This solution was kept for crystallization, and after 1–2 d crystals suitable for X-ray diffraction were obtained from the solution. Anal. Calcd for C₃₈H₅₄Cd₂N₁₀O₁₀S₂ (MW 1099.84) C, 41.50; H, 4.95; N, 12.74. Found: C, 41.25; H, 4.93; N, 12.96%. ESI MS(-ve) C₃₈H₅₂Cd₂N₁₀O₁₀S₂ calcd, *m*/*z* = 1100.1527; found, *m*/*z* = 1099.9821. ¹H NMR (300 MHz, DMSO-*d*₆): δ = 8.83–8.81 (d, 2H, *J* = 6 Hz), δ = 7.96–7.92 (t, 2H, *J* = 8 Hz), δ = 7.47–7.42 (m, 4H), δ = 6.32 (s, 1H), δ = 6.04 (bs, 1H), δ = 2.88 (bs, 2H), δ = 2.75 (bs, 2H) ppm.

Synthesis of Complex 3. Into a solution of ligand L1 (40 mg, 0.12 mmol) in DMSO, a solution of $CoSO_4$ · $6H_2O$ (30.08 mg, 0.114 mmol) in water was added and stirred for 1 h yielding a clear solution. This solution was kept for crystallization, and after 1–2 d crystals suitable for X-ray diffraction were obtained from the solution. Anal. Calcd for $C_{38}H_{54}Co_2N_{10}O_{10}S_2$ (MW 992.89) C, 45.97; H, 5.48; N, 14.11. Found: C, 45.38; H, 5.37; N, 13.82%. HRMS ESI-MS(-ve) $C_{38}H_{55}Co_2N_{10}O_{10}S_2$ calcd, m/z = 993.8928; found, m/z = 993.7819.

Synthesis of Complex 5. To a suspension of L1 (40 mg, 0.1172 mmol) in acetonitrile, 42.6 mg (0.1172 mmol) of $Zn(CF_3SO_3)_2$ was added. The suspension immediately became soluble, and the whole solution was allowed to stir at room temperature for 6 h. Evaporation of solvent and addition of diethyl ether into the dried mass gives complex 1 in 95% yield. Anal. Calcd for $C_{23}H_{31}F_6N_5O_7S_2Zn$ (MW 733.032) C, 37.69; H, 4.26; N, 9.55. Found: C, 37.45; H, 4.19; N, 9.37%. ESI MS (+ve) $C_{22}H_{31}F_3N_5O_4SZn$ calcd, m/z = 582.13; found, m/z = 582.09. ESI MS (+ve) $C_{21}H_{31}N_5OZn$ calcd, m/z = 432.18; found, m/z = 432.09. ¹H NMR (300 MHz, DMSO- d_6): $\delta = 8.662-8.606$ (d, 2H, J = 4.8 Hz), $\delta = 8.107-8.056$ (t, 2H, J = 7.5 Hz), $\delta = 7.620-7.549$ (m, 4H,), $\delta = 5.957$ (s, 1H,), $\delta = 5.904-5.881$ (t, 1H, J = 4.5 Hz), $\delta = 3.739$ (s, 4H), $\delta = 3.135-3.074$ (q, 2H, J = 6.3 Hz), $\delta = 1.121$ (s, 9H) ppm, ¹³C NMR (75 MHz, DMSO- d_6): 158.62, 155.20, 148.20, 141.13, 125.21, 124.91, 58.28, 56.24, 49.95, 39.17, 29.71 ppm.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b00176.

Spectral characterization of each compound, solutionstate ¹H NMR studies, ITC experiments, truncated S_8 view of complexes, hydrogen bonding pattern in complexes 1 and 2, ORTEP views of L1 and other complexes, selected bond distances and angles for complexes 1–5, hydrogen bonding data for complexes 1–4, ¹H NMR of selectivity and separation studies. (PDF) (CIF)

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Notes

The authors declare no competing financial interest.

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