

Supporting Information

Study of paraCEST response on six-coordinated Co(II) and Ni(II) complexes of a pyridine-tetraamide-based ligand

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21. **Fig. S21.** Metal displacement reaction of the $[\text{Co}(\text{PATA})]^{2+}$ complex with competing Cu(II) ions, monitored for 8 hours at 260 nm. Samples containing 50 μM $[\text{Co}(\text{PATA})]^{2+}$ with 1, 2, and 5 equivalent ratios of CuCl_2 salt in aqueous solutions containing 20 mM HEPES and 100 mM NaCl buffered at pH 7.4. A 50 μM $[\text{Cu}(\text{PATA})]^{2+}$ sample is present to determine the absorbance of a 100% dissociation.
22. **Fig. S22.** UV-Vis kinetic study of the complex $[\text{Co}(\text{PATA})]^{2+}$ at 260 nm in acidic conditions, pH 4, and in the presence of competing anions, 25 mM K_2CO_3 and 0.4 mM K_2HPO_4 .
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24. **Table S1.** Selected bond length and bond angles of the PATA-Co complex.

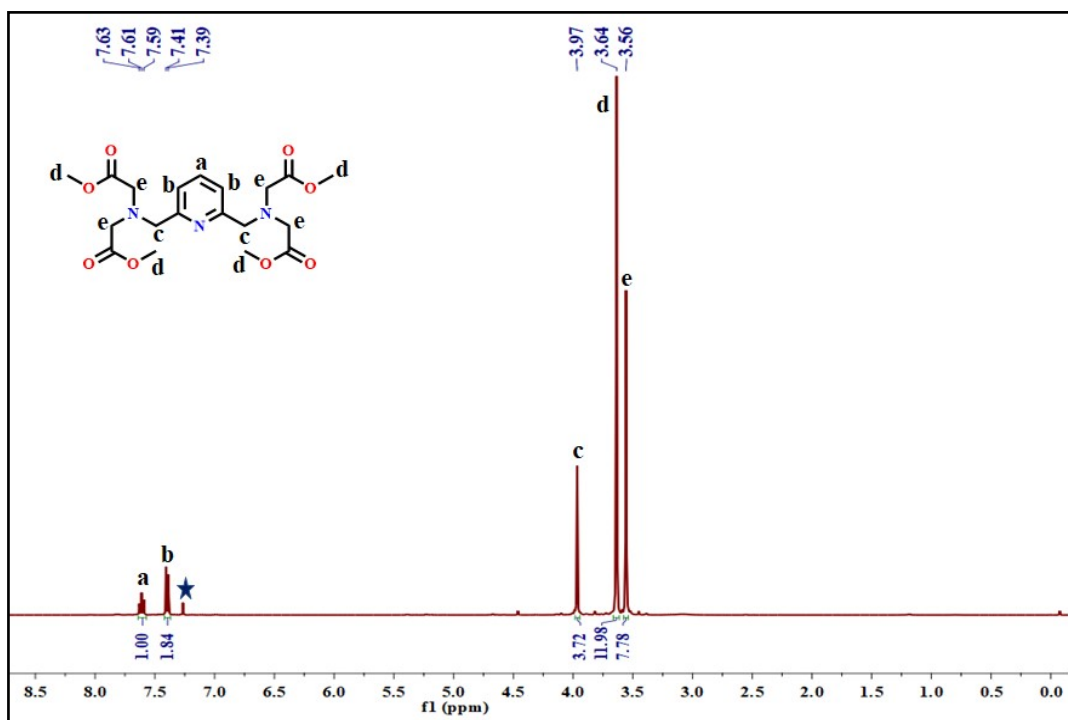


Fig. S1. ¹H NMR (400 MHz) of compound **7** in CDCl₃ (* mark indicates the residual peak of the solvent).

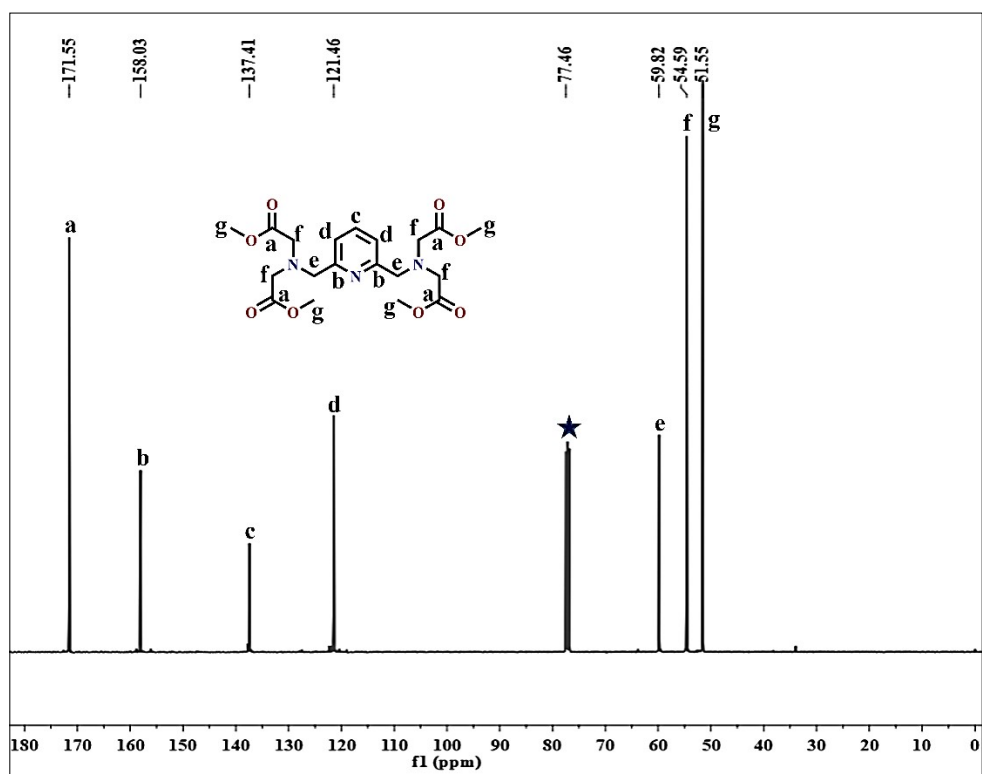


Fig. S2. ^{13}C NMR (100 MHz) of compound 7 in CDCl_3 (* mark indicates the residual peak of the solvent).

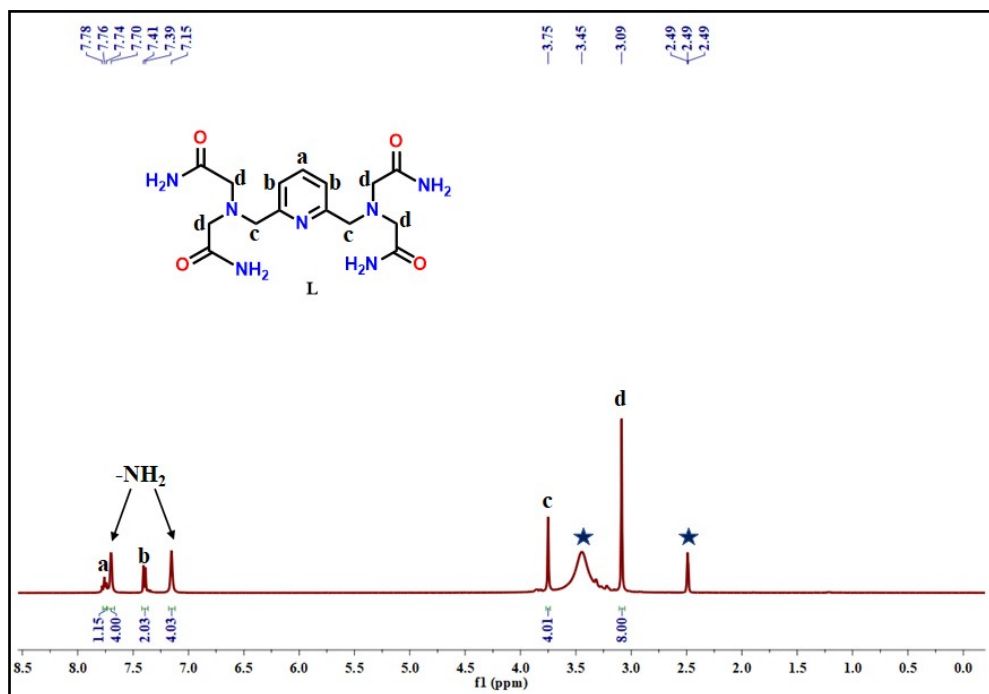


Fig. S3. ^1H NMR (400 MHz) of PATA in DMSO-d_6 (* mark indicates the residual peak of the solvent).

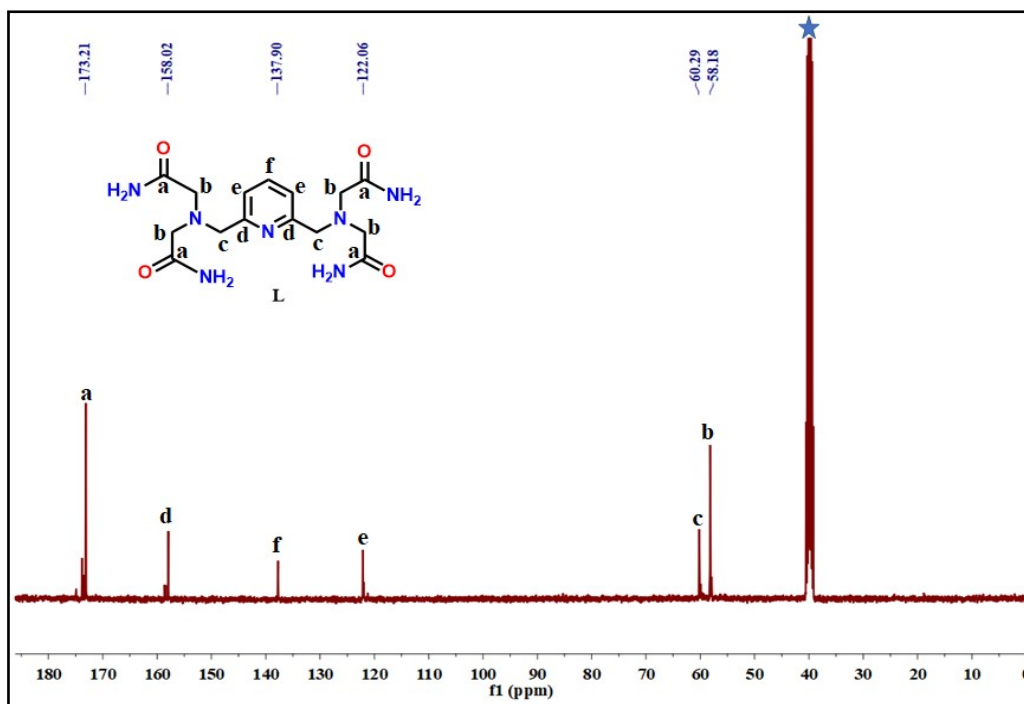


Fig. S4. ^{13}C NMR (100 MHz) of PATA in DMSO-d_6 (* mark indicates the residual peak of the solvent).

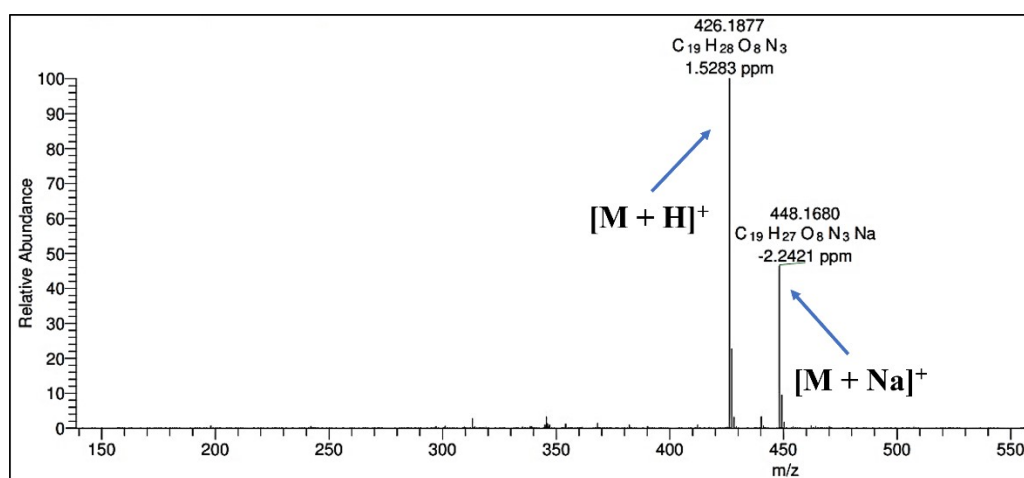


Fig. S5. HRMS spectrum of the compound 7.

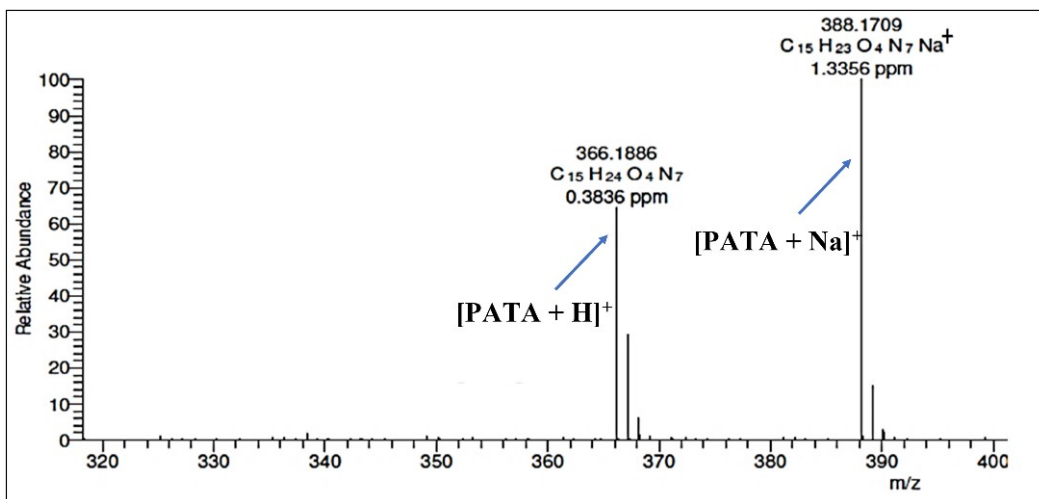


Fig. S6. HRMS spectrum of the ligand PATA.

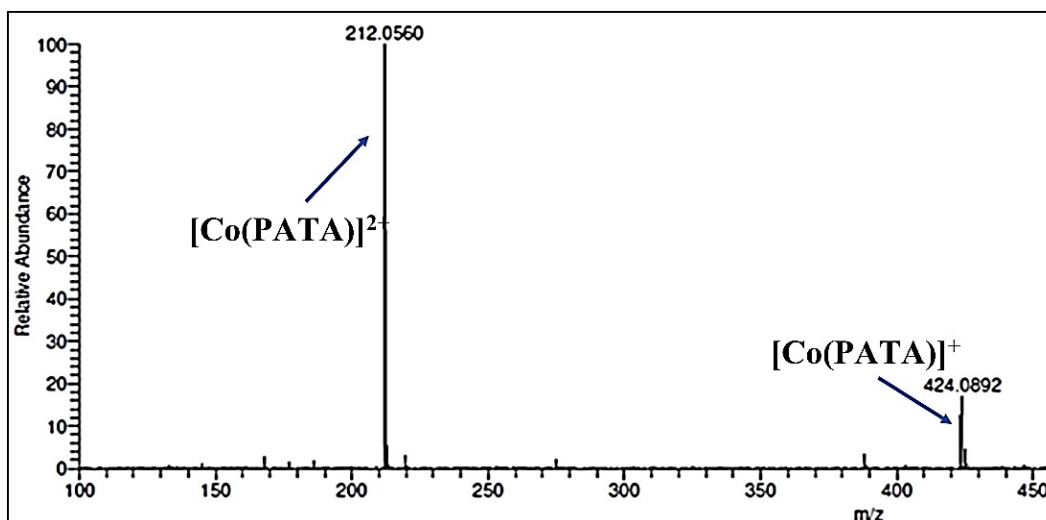


Fig. S7. HRMS spectrum of $[Co(PATA)]^{2+}$.

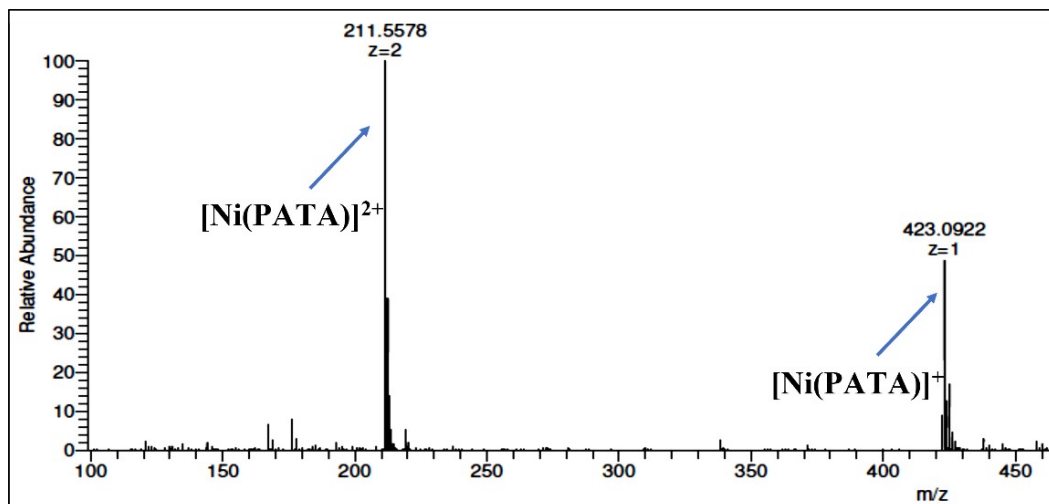


Fig. S8. HRMS spectrum of $[\text{Ni}(\text{PATA})]^{2+}$.

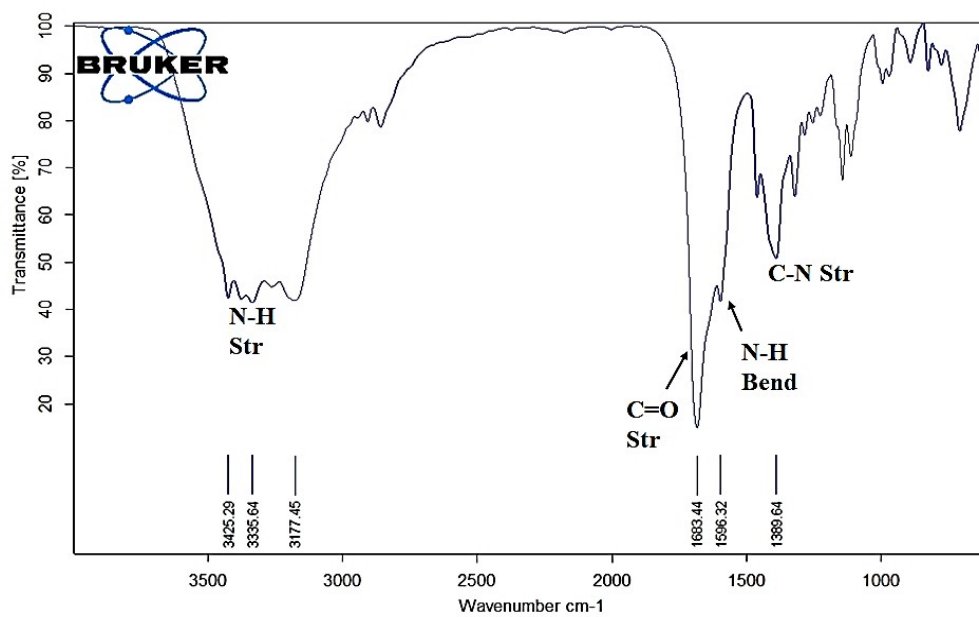


Fig. S9. FT-IR spectrum of PATA at ambient temperature in KBr pellet.

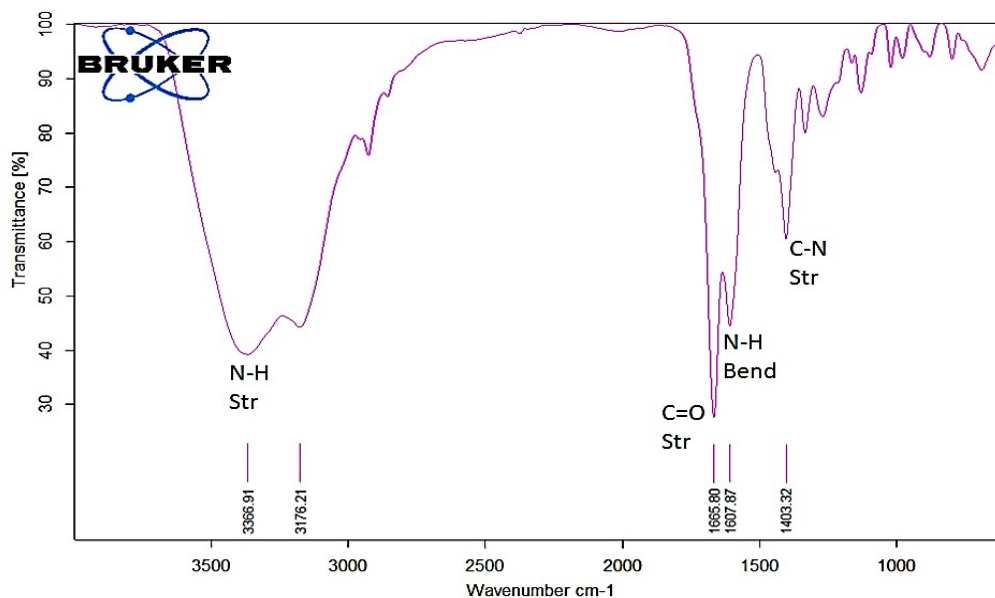


Fig. S10. FT-IR spectrum of $[\text{Co}(\text{PATA})]^{2+}$ at ambient temperature in KBr pellet.

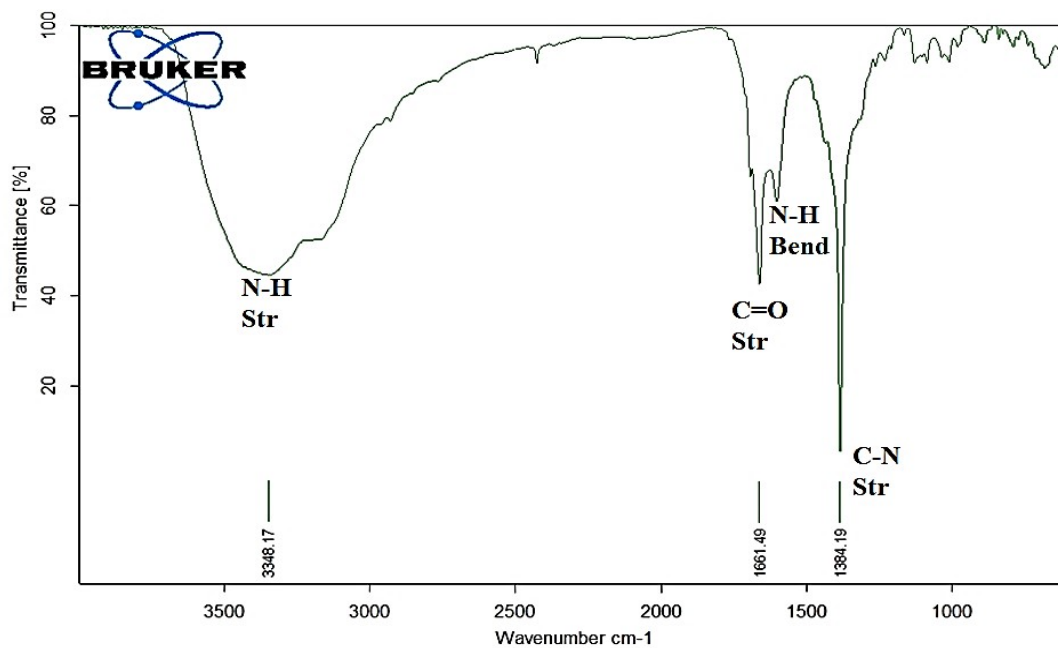


Fig. S11. FT-IR spectrum of $[\text{Ni}(\text{PATA})]^{2+}$ at ambient temperature in KBr pellet.

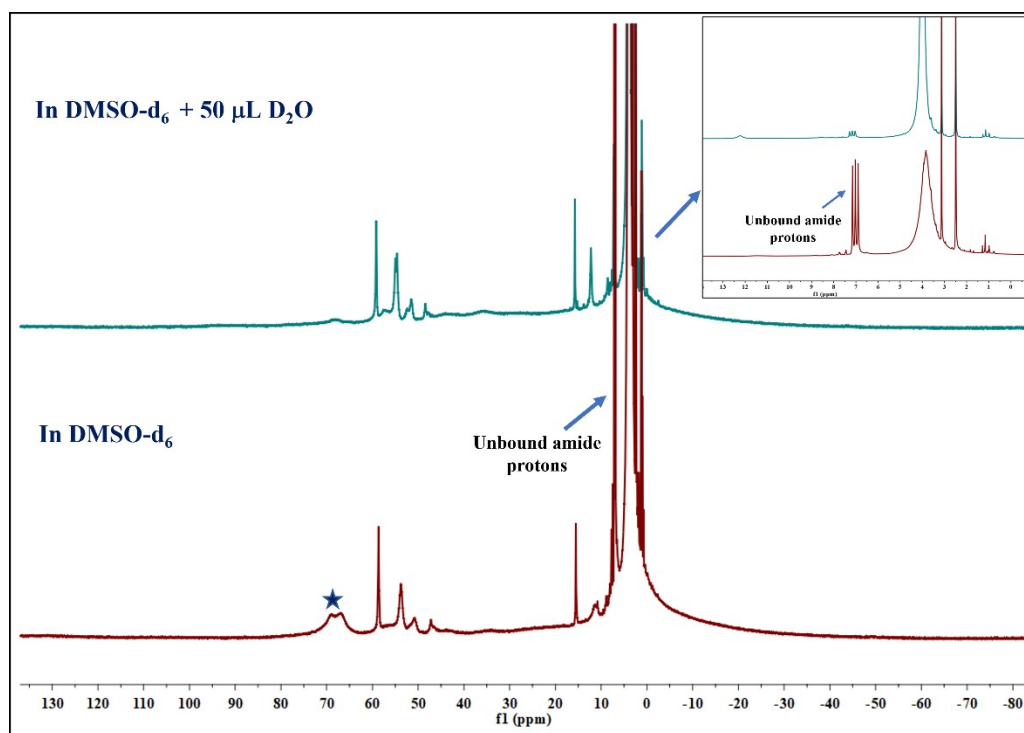


Fig. S12. Detection of exchangeable protons bound to the Co(II) ion in the $[\text{Co}(\text{PATA})]^{2+}$ complex using 400 MHz ^1H NMR (inset represents the aliphatic region and * mark indicates the bound amide protons).

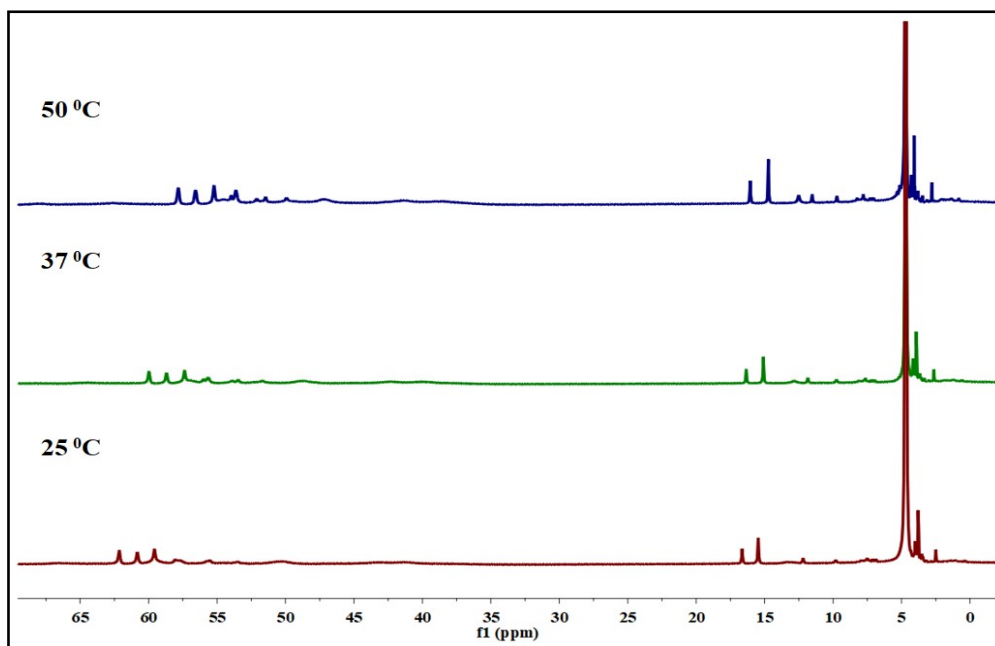


Fig. S13. Temperature variation ^1H NMR spectra of $[\text{Co}(\text{PATA})]^{2+}$ complex in D_2O solvent.

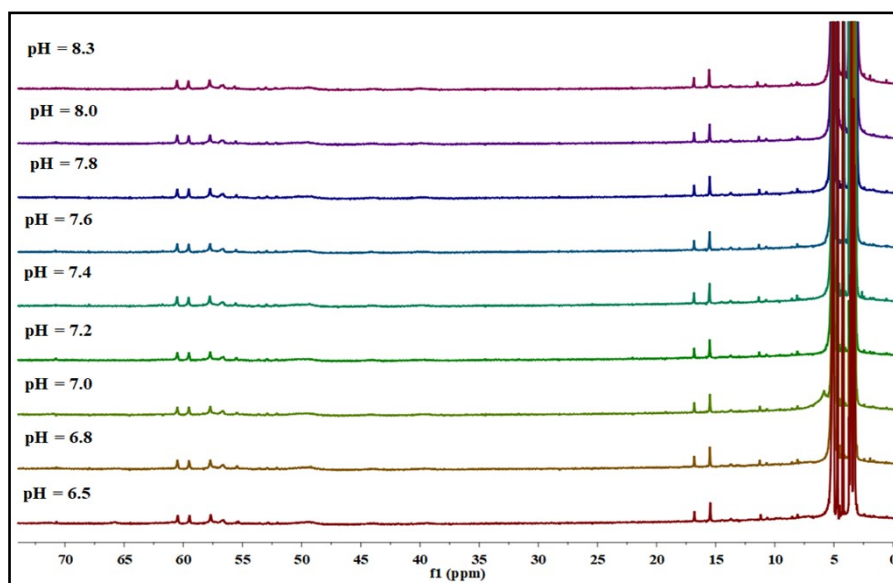


Fig. S14. Variable pH ^1H NMR of complex $[\text{Co}(\text{PATA})]^{2+}$ in water solvent with 20 mM HEPES and 100 mM NaCl. All spectra were recorded at 37 °C and D_2O containing sealed capillary was used for locking purposes.

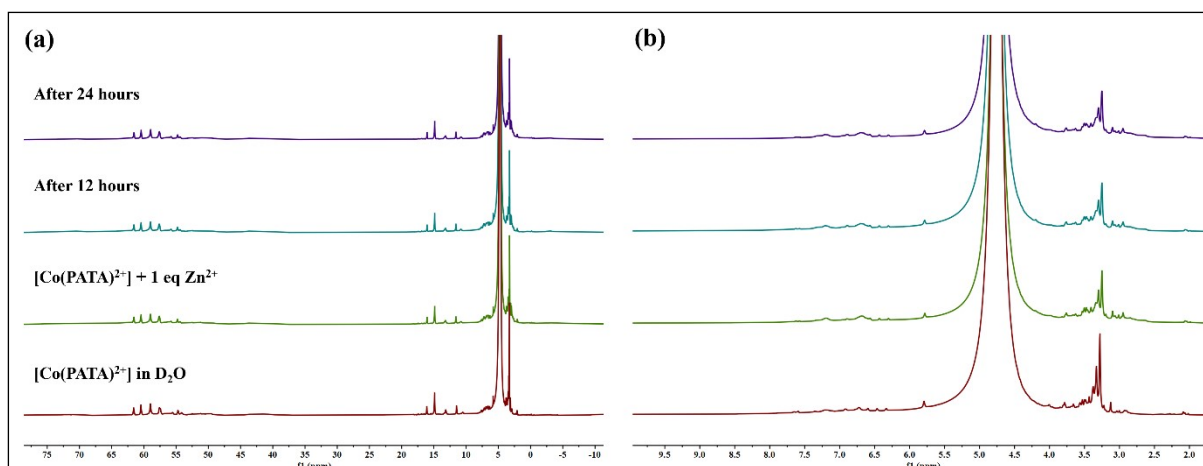


Fig. S15. ^1H NMR metal dissociation studies of the $[\text{Co}(\text{PATA})]^{2+}$ complex in the presence of Zn^{2+} ions (a) full range spectra and (b) aliphatic regions at 0 h, 12 h, and 24 h. The spectra were recorded in D_2O solvent, maintaining a pD of nearly 7.4.

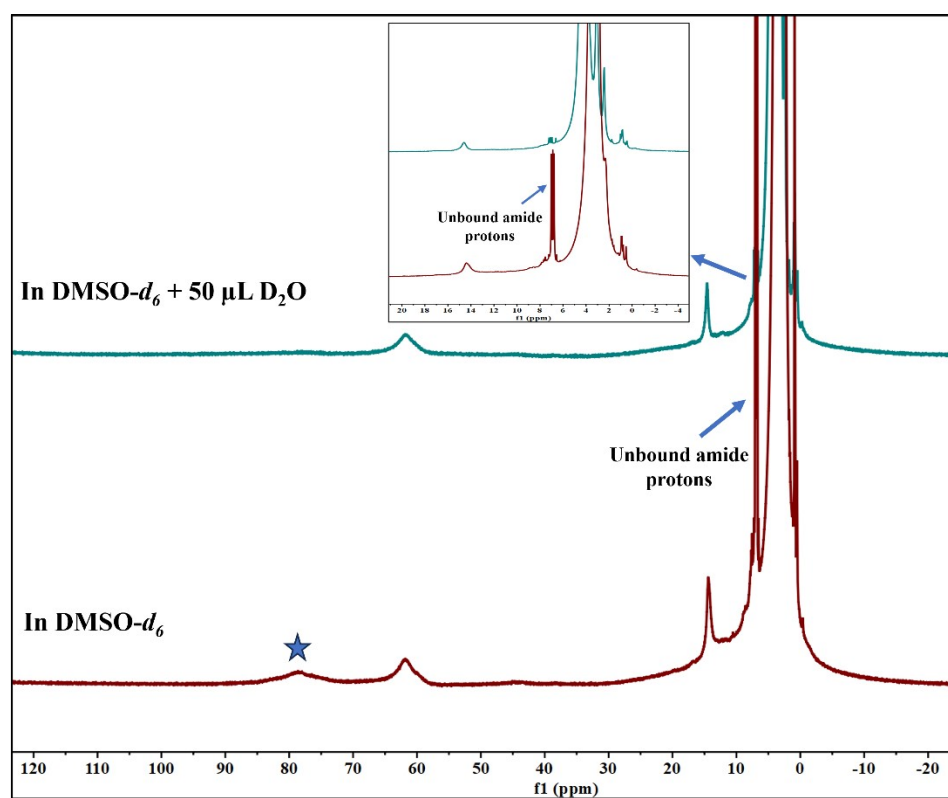


Fig. S16. Detection of exchangeable protons bound to the Ni(II) ion in the $[\text{Ni}(\text{PATA})(\text{OH}_2)]^{2+}$ complex using 400 MHz ^1H NMR (inset represents the aliphatic region and * mark indicates the bound amide protons).

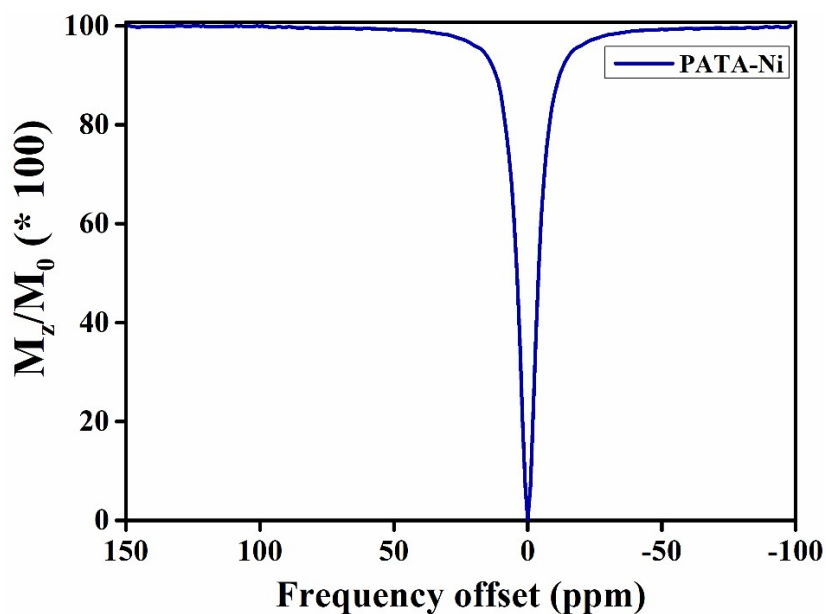


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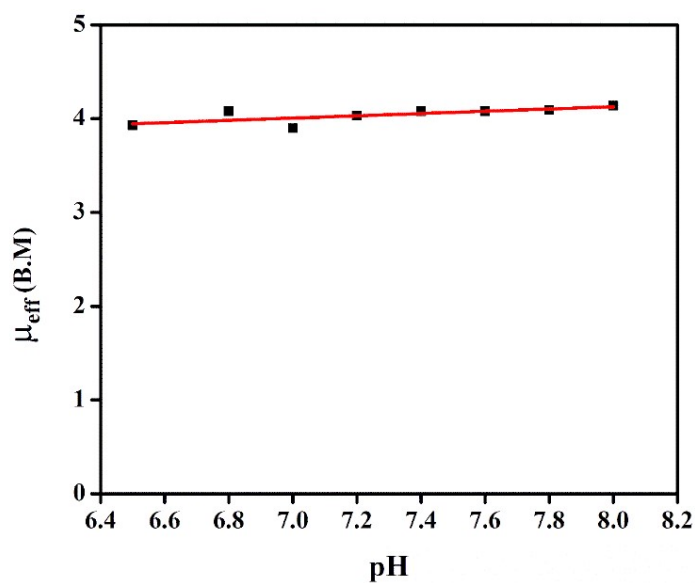


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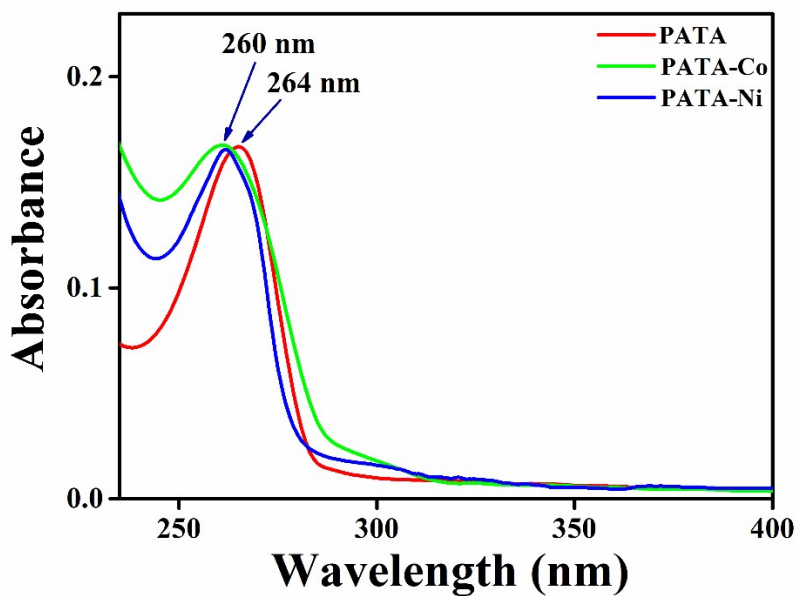


Fig. S19. UV spectra of PATA, $[\text{Co}(\text{PATA})]^{2+}$, and $[\text{Ni}(\text{PATA})]^{2+}$, recorded at $30 \mu\text{M}$ concentration in an aqueous medium containing 20 mM HEPES and 100 mM NaCl at room temperature.

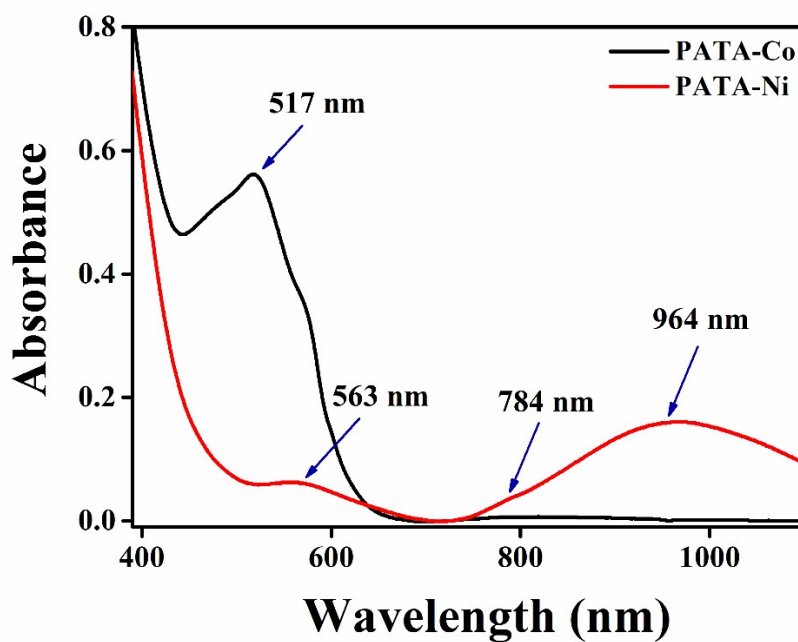


Fig. S20. UV-Vis spectra of $[\text{Co}(\text{PATA})]^{2+}$ and $[\text{Ni}(\text{PATA})]^{2+}$, were recorded at 10 mM concentration in an aqueous medium containing 20 mM HEPES and 100 mM NaCl at room temperature.

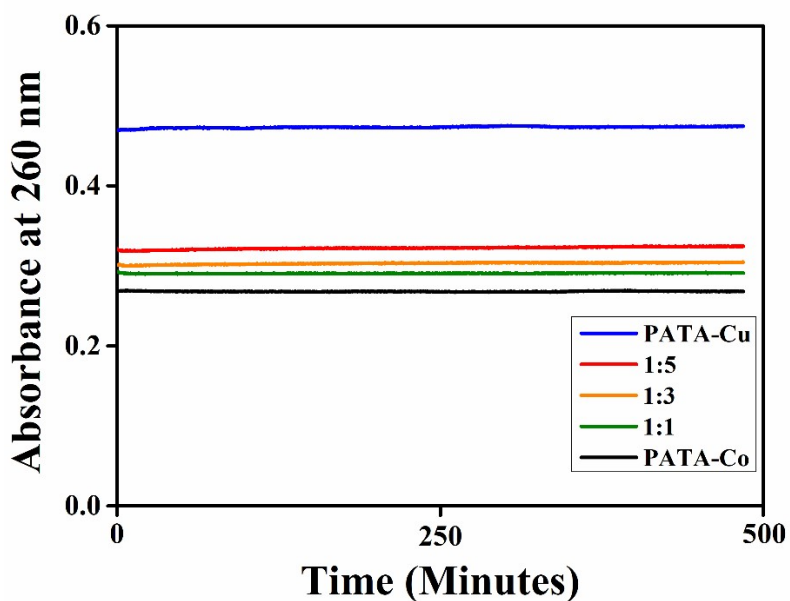


Fig. S21. Metal displacement reaction of the $[\text{Co}(\text{PATA})]^{2+}$ complex with competing $\text{Cu}(\text{II})$ ions, monitored for 8 hours at 260 nm. Samples containing $50 \mu\text{M}$ $[\text{Co}(\text{PATA})]^{2+}$ with 1, 2, and 5 equivalent ratios of CuCl_2 salt in aqueous solutions containing 20 mM HEPES and 100 mM NaCl buffered at pH 7.4. A $50 \mu\text{M}$ $[\text{Cu}(\text{PATA})]^{2+}$ sample is present to determine the absorbance of a 100% dissociation.

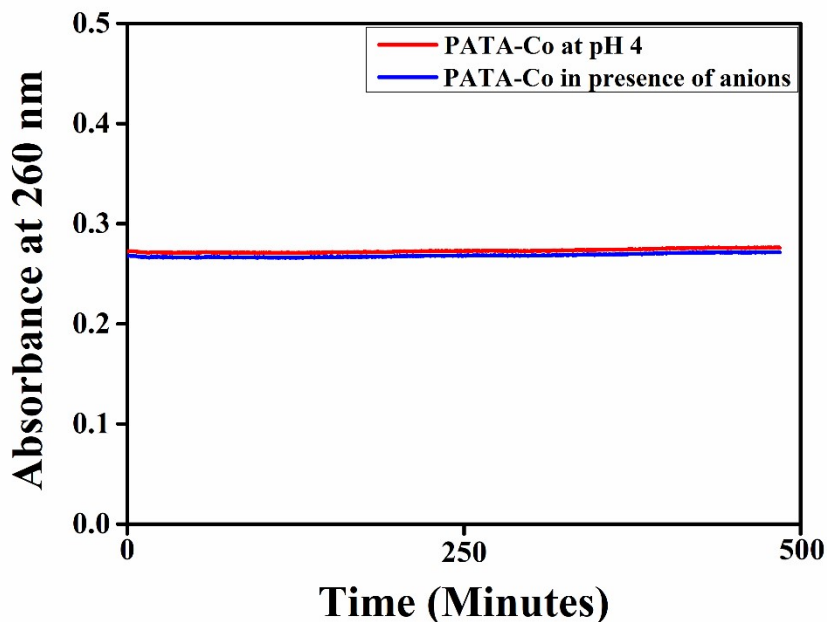


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