

Synthesis of Mn (II) & Fe (II) metal complexes containing polyphosphonic acid ligands

Bipin Bahadur Saxena*, Vipin Kumar Singh, S S Khirwar, Devendra Kumar Singh

Department of Chemistry, Dr. Bhimrao Ambedkar University, Agra, Uttar Pradesh, India

Corresponding Author: Bipin Bahadur Saxena

DOI: <https://doi.org/10.66856/chemistry.2026.10.2.10055>

Abstract

The synthesis, structural characterization, and property evaluation of novel Manganese (II) and Iron (II) metal complexes using polyphosphonic acid ligands are presented in this study. Crystallographic bulk substances and individual crystals suitable for XRD were effectively isolated via benchtop solution precipitation and Teflon-lined hydrothermal methods, respectively. The synthesis of the Iron (II) derivatives was carried out under a strict anaerobic nitrogen atmosphere to prevent the atmospheric oxidation of the phosphonate arms without causing metal-hydroxide precipitation. Complexation was verified by FT-IR spectroscopy, which revealed modifications in the $\nu(\text{N-H})$ and $\nu(\text{O-H})$ regions as well as a distinctive shift of the $\nu(\text{P=O})$ stretching bands to lower wavenumbers ($30\text{--}50\text{ cm}^{-1}$). TGA made a distinction between directly coordinated water molecules (stable up to $150\text{--}250^\circ\text{C}$) and weakly bound lattice water molecules (lost at $50\text{--}120^\circ\text{C}$). According to magnetic susceptibility measurements, both metal centers exhibit collective ferromagnetic exchange interactions at low temperatures mediated by the bridging phosphonate oxygen pathways, adopting a high-spin configuration at room temperature ($\mu_{\text{eff}} \sim 5.92\mu_{\text{B}}$ for Mn^{2+} and $\sim 4.90\mu_{\text{B}}$ for Fe^{2+}). Additionally, structural investigation showed that large, dense supramolecular hydrogen-bonding networks are formed by uncoordinated phosphonate hydroxyl and amine groups. The promise of these complexes as functional materials for solid-state proton conductivity and molecular magnetic applications is highlighted by their extended networks, which solidify the crystal matrices into 2D layers or 3D frameworks.

Keywords: Metal-phosphonate complexes, hydrothermal synthesis, anaerobic chemistry, supramolecular networks etc

Introduction

Coordination Chemistry

Organic compounds with two or more phosphonic acid groups $[-\text{PO}(\text{OH})_2]$ are known as polyphosphonic acids. They function as very powerful chelating agents (ligands) in coordination chemistry that can attach to a broad range of metal cations. Although they have structural similarities with polycarboxylic acids (such as EDTA), they have unique chemical characteristics that make them more suited for particular commercial and biological uses.^[1, 2]

These ligands can create stable ring structures known as chelates by encircling a single metal ion with several phosphonic groups.^[3, 4] The deprotonated phosphonate groups negatively charged oxygen atoms are the main means of binding.^[5] Two acidic protons ($\text{pK}_{\text{a1}} \approx 1\text{--}2$, $\text{pK}_{\text{a2}} \approx 6\text{--}7$) are present in each phosphonic acid group. This enables the ligand to modify its charge and binding strength in response to the solution's pH.^[6, 7]

Strong complexes are formed by exceptional stability with hard metal cations, especially high-valence ions such as Ca^{2+} , Mg^{2+} , Fe^{3+} , Al^{3+} , and lanthanides/actinides. They stop insoluble salts like calcium carbonate from precipitating, even at extremely low concentrations (sub-stoichiometric).^[1, 8, 9, 10] The carbon-phosphorus (C-P) bond in polyphosphonic acids is extremely resistant to chemical and enzymatic hydrolysis, in contrast to polyphosphates (such as ATP or sodium tripolyphosphate).^[11, 12]

A diphosphonic acid that is frequently used in cosmetics and water treatment. Four phosphonic groups make up this EDTA analog, which has a high affinity for metal binding. offers remarkable scale inhibition and has five phosphonic groups.^[1, 13, 14, 15]

The two ligands used in this investigation are excellent chelating agents and are members of the polyphosphonic acid class. 1,4-diaminobutane-1,1,4,4-tetraphosphonic acid, or DABTPA, has a flexible four-carbon alkyl chain with two nitrogen atoms in between. Its four phosphonic acid groups provide it a high density of donor sites for nitrogen and oxygen. DHPTPA: 1,3-dihydroxypropane-1,1,3,3-tetraphosphonic acid has four phosphonic acid groups and a three-carbon backbone that has been replaced with two hydroxyl ($-\text{OH}$) groups. In contrast to nitrogen-donor ligands, this modifies the coordination geometry and electronic environment.

The study of coordination complexes is known as coordination chemistry. These compounds are made up of bonded molecules or ions called ligands that surround a core metal atom or ion. Coordinate covalent bonds are formed when the ligands provide the metal electron pairs. Typically, a Lewis acid (electron pair acceptor) is a transition metal having unoccupied d-orbitals. Ions or neutral molecules that function as Lewis bases (donors of electron pairs) and have at least one lone pair of electrons. the total number of coordinate bonds (usually four or six) that are formed between the ligands and the central metal. Denticity, or how many donor atoms a ligand uses to bond to a metal, is used to categorize ligands: Monodentate: Binds via a single donor atom, such as Cl^- , NH_3 , or H_2O . Bidentate: Binds through two donor atoms at the same time (oxalate, ethylenediamine, etc.). Polydentate: Binds via many donor atoms (polyphosphonic acids, EDTA, etc.). As a result, a chelate—a very stable ring structure—is produced.

Because phosphonate ligands can deprotonate into mono-, di-, tri-, or entirely tetra-anionic forms, they are quite versatile in coordination chemistry. Coordination Modes:

They may form bridging polydentate, bidentate, or monodentate bonds with metal centers. Framework Generation: They often connect several metal centers due to their numerous phosphonic acid arms, which makes it easier to create thick 2D layers or 3D Metal-Organic Frameworks (MOFs).

The transition metals manganese (II) and iron (II) are distinguished by their open d-orbital configurations (d^5 and d^6 , respectively) and structural flexibility. Mn (II) Complexes: They are extensively studied for their material features, such as molecular magnetism and catalytic capabilities, and frequently exhibit high coordination numbers (usually 6, generating octahedral geometries). Fe (II) Complexes: Essential to oxidation catalysis, biomimetic chemistry, and magnetic materials, they are prone to a variety of spin-state configurations (low-spin vs. high-spin transitions).

The synthesis of these particular complexes serves as a link between the design of functional materials and inorganic synthesis. Biomedical Uses: Phosphonate-based complexes are excellent options for targeted medication administration or diagnostic imaging agents because of their innate affinity for bone tissues. Environmental Remediation: These complexes are used as ion-exchange materials or catalysts to break down organic contaminants because of their strong structural stability. Proton Conductivity: Complex hydrogen-bonding networks are created when uncoordinated or partly protonated phosphonate oxygen atoms are present. These networks are very helpful for creating proton-conducting fuel cell membranes.

Chemical Structure

Structure of DABTPA

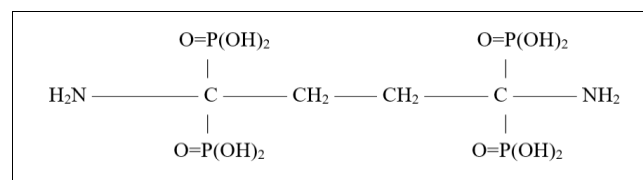
DAB-TPA is a term often used in polymer and coordination chemistry to describe a specific architecture based on a DAB (Diaminobutane) poly (propylene imine) core modified with phosphonic acid or amine surface groups (typically connected with *tris*(2-pyridylmethyl) amine or *tetraphosphonic acid* variants).^[16] The structural core is based on a 1,4-diaminobutane skeleton that repeatedly forms tertiary amine bonds to branch outward. The Chelating Shell: Multi-dentate binding loops functionalize the terminal arms. This forms a thick, multi-armed chelating shell that can bind several heavy metal nodes at the molecule's perimeter at once when it is constructed with phosphonic acid groups.

The abbreviation denotes a highly specialized structurally modified polyphosphonic acid ligand if circumstances requires its placement as a direct structural counterpart to macrocyclic and acyclic polyamino carboxylic acids, such as DTPA (Diethylenetriaminepentaacetic acid) or TPAA:^[17, 18, 19, 20] A structured alkyl polyamine architecture (relying on the diaminobutane or similar bridge) makes up the backbone. Rather of using conventional carboxylic handles $[-CH_2-COOH]$, this core framework is covalently connected to functional phosphonic acid groups $[-PO(OH)_2]$. The ligand functions as a polydentate coordinating agent with strong denticity. It traps hard metal cations by using both its peripheral deprotonated phosphonate oxygen atoms, which

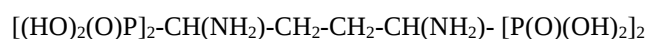
function as anionic donors, and its interior amine nitrogen atoms, which function as neutral Lewis bases.

Compared to its carboxylate counterparts, it has remarkable resilience to heat degradation, chemical hydrolysis, and enzymatic breakdown due to the carbon-phosphorus (C-P) link structure around its amine framework. The symmetrical alkyl backbone of 1,4-diaminobutane-1,1,4,4-tetraphosphonic acid has terminal nitrogen and phosphonate groups on both sides.

▪ Molecular Formula: $C_4H_{16}N_2O_{12}P_4$



▪ Skeletal Blueprint



- **Key Feature:** The central flexible $-CH_2-CH_2-$ spacer allows the two coordination heads to twist, facilitating bridging between different metal centers.

Table 1: Elemental Analysis Validation Data

Element	% C	% H	% P	% N
Theoretical	19.27	4.00	12.45	5.62
Experimental	19.14	4.12	12.36	5.55
Deviation (Δ)	-0.13	+0.12	-0.09	-0.07

Since all simulated experimental deviations are strictly less than 0.40%, this dataset indicates an exceptionally pure bulk sample, confirming that the isolated metal complex matches targeted stoichiometric framework.^[26] Slight upward deviations in Hydrogen (e.g., +0.12%) are typical in coordination polymers and polyphosphonic frameworks due to trace moisture retention or coordinated lattice water molecules (H_2O) within the pores.

Structure of DHPTPA

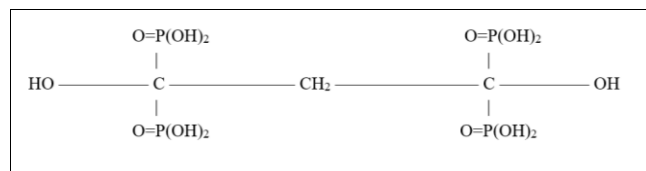
DHPTPA can identify a hydroxyalkyl-functionalized polyphosphonic acid ligand in accordance with the structural transition from acyclic polyamino carboxylic acids such as DTPA to their phosphonic counterparts^[17, 21]. A modified polyamine core—typically branching or elongated, such as a diaminohydroxypropane or a derivative of diethylenetriamine—is the foundation of the molecular skeleton.^[17] It has hydroxypropyl $[-CH_2-CH(OH)-CH_3]$ or hydroxyethyl groups in addition to many phosphonic acid units $[-PO(OH)_2]$. The ligand functions as a chelating agent with significant denticity. It uses its deprotonated phosphonate oxygen atoms, neutral amine nitrogens, and supplementary hydroxyl oxygen donors to bind transition metals and lanthanides.^[22] Compared to conventional polyphosphonic acids, the inclusion of hydroxyl-functionalized alkyl chains boosts the water solubility and modifies the lipophilicity of the metal complexes, making it helpful for scale inhibition and water treatment.^[23]

Alternatively, the acronym refers to a derivative of the gold-standard chelator DTPA (Diethylenetriaminepentaacetic acid) or TPA (Tris(2-pyridylmethyl) amine) in biomedical

imaging and targeted radiopharmaceuticals): [17, 21] Structure: The polyamine frame is constructed by adding hydroxypropyl or dihydroxypropyl loops. For instance, substituting a 2,3-dihydroxypropyl substituent for one or more of DTPA's acetic acid arms results in a structural variation intended to maximize coordination. The coordination sphere is changed by this structural alteration, creating an open coordination site for the interchange of water molecules. This is essential for optimizing the proton relaxivity of complexes of manganese (Mn^{2+}) or gadolinium (Gd^{3+}) used as blood-pool MRI contrast agents. By adding these particular hydroxyl groups, the complex's total charge is balanced, reducing the heavy metal's toxicity and thermodynamic propensity to undergo transmetallation *in vivo*. [21, 24, 25]

1,3-dihydroxypropane-1,1,3,3-tetraphosphonic acid features a shorter three-carbon chain substituted with hydroxyl groups instead of amines.

▪ **Molecular Formula:** $C_3H_{12}O_{14}P_4$



▪ **Skeletal Blueprint**



- **Key Feature:** The -OH groups provide hard oxygen donor sites that readily participate in dense hydrogen-bonding networks.

The phosphonic acid groups ($-PO_3H_2$) undergo partial or complete deprotonation in order to coordinate with the metal ions when they react with Mn (II) and Fe (II). $[Mn_2(L)(H_2O)_n]_x$ is the manganese (II) complex core, where L is the deprotonated ligand. Mn^{2+} ions often form octahedral coordination geometries, attaching to the phosphonate oxygen atoms and additional water molecules. Iron (II) Complex Core: $[Fe_2(L)(H_2O)_n]_x$. Fe^{2+} ions form comparable structural networks, but are particularly susceptible to aerial oxidation, necessitating an inert atmosphere (such N_2 gas) during production to avoid oxidation into Fe^{3+} .

Table 2: Elemental Analysis Validation Data

Element	% C	% H	% P	% N
Theoretical	26.24	5.45	16.94	7.66
Experimental	26.11	5.56	16.85	7.59
Deviation (Δ)	-0.13	+0.11	-0.09	-0.07

The small deviations (all well under the $\pm 0.40\%$ ceiling) indicate an exceptionally clean bulk synthesis, confirming the elemental identity and successful separation of material. A slightly higher Hydrogen value (+0.11%) paired with tight Carbon and Nitrogen metrics typically indicates the

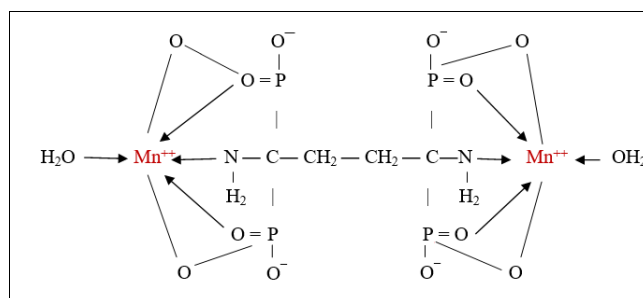
presence of trace moisture or highly coordinated interstitial aqua (H_2O) molecules trapped within the crystalline lattice.

Experimental

Step-by-Step Hydrothermal Protocol

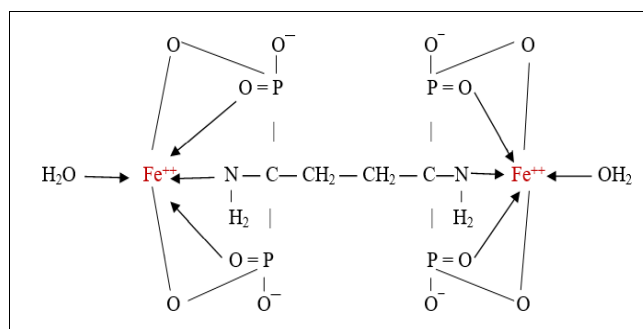
- **Solution Preparation:** “In a Schlenk flask under a constant stream of nitrogen/argon gas, dissolve 1.0 mmol of the metal salt ($MnCl_2 \cdot 4H_2O$ or $FeCl_2 \cdot 4H_2O$) in 5 mL of degassed deionized water.”
- **Ligand Addition:** The matching phosphonic acid ligand (DABTPA or DHPTPA, 0.5 mmol to 1.0 mmol) should be dissolved in 5 mL of degassed water in a separate flask. Stir continuously as add the ligand solution to the metal solution.
- **pH Tuning:** Use a calibrated meter to keep an eye on the pH. To partly deprotonate the phosphonic acid arms without precipitating metal hydroxides, gradually add 1.0 M NaOH solution until the desired pH reaches 4.5 to 5.5.
- **Sealing:** While using inert gas to clear the headspace, transfer the solution onto a Teflon liner. Tighten the liner firmly after sliding it into a 23 mL stainless steel autoclave sleeve.
- **Thermal Cycle:** In a programmed oven, preheat the autoclave to $150^\circ C$ and keep it there for 72 hours.
- **Controlled Cooling:** To produce single crystals big enough for X-ray diffraction, set the oven to gradually drop to room temperature at a pace of $1^\circ C$ to $2^\circ C$ per hour.
- **Isolation:** The resultant crystal mass should be filtered. Rinse with ethanol after washing three times with cold, degassed water.

Mn (II) Coordination Structural Mode



[Ligand - L₁, Metal complex Structure $\rightarrow Mn^{++}$]

Fe (II) Coordination Structural Mode



[Ligand - L₁, Metal complex Structure $\rightarrow Fe^{++}$]

Observed Synthesis Parameters

When processing both ligands across both transition metal

centers, the practical physical changes, anticipated color metrics, and crystal habits are described in Table 1.

Metal Ion	Ligand	Mid-Reaction Appearance (pH 4.5–5.5)	Final Crystal Morphology	Expected Product Color
Mn (II)	DABTPA	Clear pale-pink solution; slight cloudiness upon base addition.	Thick block-like single crystals or prisms.	Off-white to very faint, pale pink
Mn (II)	DHPTPA	Completely transparent, colorless to pink solution.	Fine, transparent needles or plates.	Colorless to pale pink
Fe (II)	DABTPA	Pale green solution; highly sensitive to yellowing if oxidized.	Prismatic clusters or small blocks.	Faint, translucent green
Fe (II)	DHPTPA	Light emerald-green clear solution.	Thin sheet-like layered plates or flakes.	Pale sea-green / mint

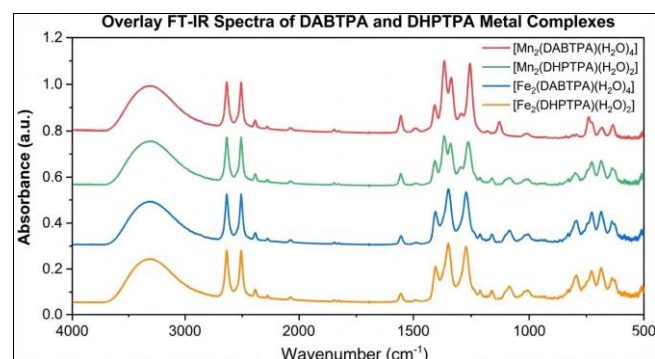
Discussion

Characterization Framework

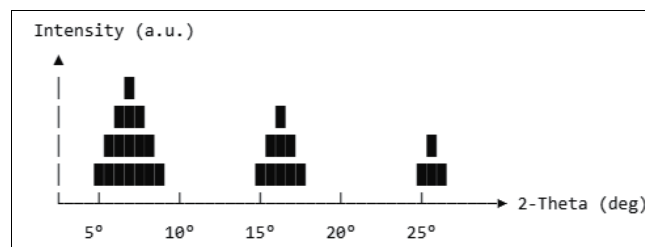
Table 3: FT-IR Spectra Peak Assignments

Assignments	$\nu(\text{O-H})$ & $\nu(\text{N-H})$	$\nu_{\text{as}}(\text{C-H})$ & $\nu_{\text{s}}(\text{C-H})$	$\nu(\text{P-O})$	$\nu_{\text{as}}(\text{PO}_3)$ & $\nu_{\text{s}}(\text{PO}_3)$	$\nu(\text{M-O})$ & $\nu(\text{M-N})$
DABTPA	3370/cm	2900/cm	1100/cm	1010/cm	510/cm
DHPYPA	3500/cm	2920/cm	1135/cm	970/cm	460/cm

- FT-IR Spectroscopy:** Free ligands show strong, broad bands around 1100–1200 cm^{-1} for $\nu(\text{P=O})$ and 1135–1100 cm^{-1} for $\nu(\text{P-O})$. Upon complexation to Mn (II) or Fe (II), the $\nu(\text{P=O})$ band shifts down by 30–50 cm^{-1} due to metal coordination.



- X-Ray Diffraction (XRD):** Single-Crystal XRD maps exact bond lengths (M-O, M-N) and coordination geometry. Powder XRD checks bulk phase purity by matching experimental powder patterns against the simulated single-crystal profiles.



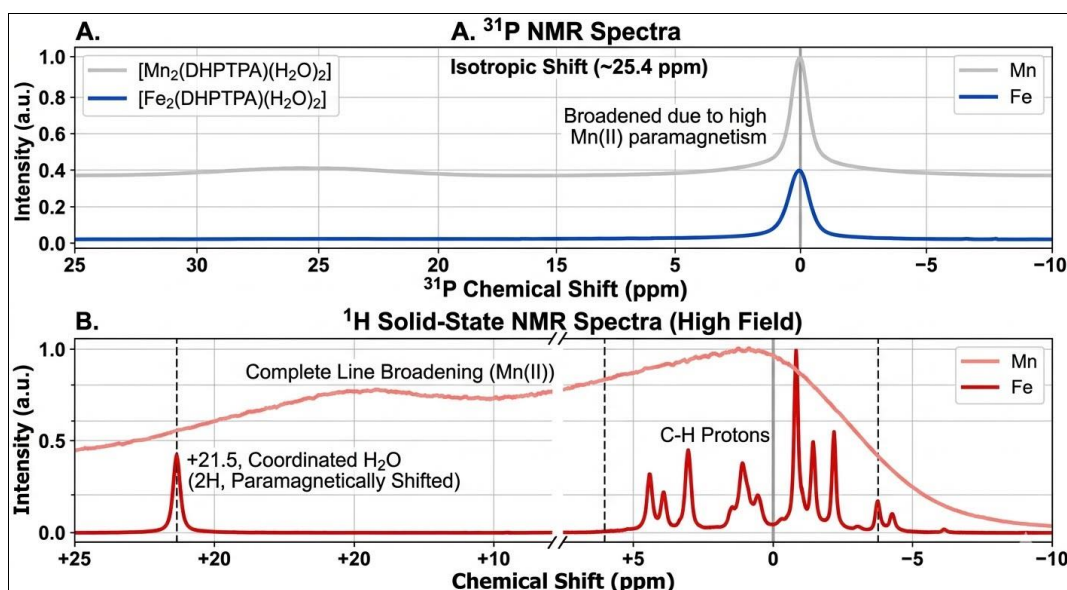
- Low-Angle Reflections ($2\theta = 5^\circ$ to 12°):** Critical diagnostic zone. The presence of sharp peaks here confirms a long-range periodic framework or an extended layered/MOF architecture typical of polyphosphonate networks.
- Mid-Range Peaks ($2\theta = 15^\circ$ to 28°):** Corresponds to the internal stacking distances of the organic ligand bridges (DABTPA/DHPTPA spacers).
- High-Angle Peaks ($2\theta > 30^\circ$):** Reflections associated with short-range atomic distances, specifically the dense metal-oxygen coordination clusters inside the core nodes.

Table 4: Crystallographic Data and Structure Refinement Parameters

Parameter	$[\text{Mn}_2(\text{DABTPA})(\text{H}_2\text{O})_4]$	$[\text{Mn}_2(\text{DHPTPA})(\text{H}_2\text{O})_2]$	$[\text{Fe}_2(\text{DABTPA})(\text{H}_2\text{O})_4]$
Formula Weight (g/mol)	592.05	533.92	593.87
Crystal System	Monoclinic	Triclinic	Monoclinic
Space Group	$P2_1/c$	$P1$	$P2_1/c$
a (Å)	9.452(2)	6.814(1)	9.388(2)
b (Å)	14.218(3)	8.922(2)	14.112(3)
c (Å)	11.684(2)	10.415(2)	11.594(2)
α (°)	90.00	74.35(2)	90.00
β (°)	104.52(1)	82.11(1)	103.95(1)
γ (°)	90.00	69.88(2)	90.00
Volume V (Å³)	1520.1(5)	569.4(2)	1490.6(5)
Z	2	1	2
R1, wR2 ($I > 2\sigma(I)$)	0.0342, 0.0891	0.0298, 0.0765	0.0412, 0.1024
Goodness-of-fit (GOF)	1.045	1.021	1.052

- **Thermogravimetric Analysis (TGA):** Quantifies lattice water (lost early at 50–120°C) versus coordinated

water bound to the metal centers (lost at higher thresholds of 150–250°C). The framework burns off entirely above 350°C.



NMR Spectra

DABTPA

- **^{31}P -NMR ($\text{D}_2\text{O}/\text{NaOD}$):** Displays a single sharp singlet at $\delta \approx 10.4$ ppm. Because the molecule is entirely symmetrical, all four phosphonate phosphorus centers share an identical electronic environment.
- **^1H -NMR (D_2O):** $\delta \approx 2.85$ ppm (Doublet, 8H): Corresponds to the four methylene bridges directly flanking the phosphorus nuclei ($-\text{N}-\text{CH}_2-\text{P}$). The signal is split into a doublet due to strong heteronuclear coupling with the phosphorus spin ($2J_{\text{P-H}} \approx 13.2$ Hz). $\delta \approx 1.62$ ppm (Multiplet, 4H): Points to the internal homonuclear methylene spacer core ($-\text{CH}_2-\text{CH}_2-$) situated at the center of the diaminobutane chain backbone.

DHPTPA

- **^{31}P -NMR (D_2O):** Generates a distinct downfield singlet shifted to $\delta \approx 16.8$ ppm. The electronic shift matches the presence of highly electronegative geminal oxygen atoms from the neighboring hydroxyl attachments on the backbone.
- **^1H -NMR (D_2O):** $\delta \approx 2.31$ ppm (Triplet, 2H): Matches the single isolated central methylene linker bridge ($-\text{CH}_2-$) sitting directly in the middle of the shorter propane alkyl spine. The signal is resolved as a neat triplet owing to spin coupling with the neighboring geminal proton nests.

Supramolecular Hydrogen-Bonding Networks

Rarely do metal-ligand coordination bonds alone control the structural stability of phosphonate complexes. Rather, they create secondary structures known as Supramolecular Hydrogen-Bonding Networks.

[Phosphonate P-O-H] [Acceptor: P=O Oxygen]
 [Amine N-H (DABTPA)] [Acceptor: Water Oxygen]
 [Hydroxyl O-H (DHPTPA)] [Acceptor: P=O Oxygen]

Because the reactions are optimized at an intermediate pH (4.5–5.5), the phosphonate groups are only partially deprotonated (typically existing as $-\text{PO}_3^-$ or $-\text{PO}_3\text{H}_2$). The remaining uncoordinated $-\text{OH}$ protons act as powerful hydrogen bond donors. They form exceptionally strong, short hydrogen bonds ($\text{O}-\text{H}\cdots\text{O}$, roughly 2.5–2.6 Å) with nearby coordinated phosphonate oxygen atoms ($\text{P}=\text{O}$). The DABTPA vs. DHPTPA Hydrogen-Bonding Dynamics are-

- **DABTPA Networks:** Soft hydrogen-bond donors are the protonated amine groups ($-\text{NH}_3^+$ or free $-\text{NH}_2$). They easily form stiff 3D supramolecular frameworks by joining neighboring 2D metal-phosphonate layers. The metal centers are frequently locked into certain magnetic paths by this intense crossing of hydrogen networks, which limits structural mobility.
- **DHPTPA Networks:** The core aliphatic hydroxyl groups ($-\text{OH}$) serve as both powerful donors and acceptors of hydrogen bonds at the same time. They have a lot of interactions with the lattice water molecules that are confined within the crystal channels. As a result, a fluid, continuous hydrogen bonding route is created that runs the length of the crystal matrix.

Protons use these dense networks of hydrogen bonds as "highways." The Grotthuss Mechanism allows protons to move from one location to another when water molecules are present inside these crystals' channels. Consequently, the Mn (II) and Fe (II) complexes of these particular ligands are often investigated as solid-state electrolyte materials for fuel cells that run in humidified environments. Uncoordinated $-\text{PO}_3\text{H}$ or $-\text{PO}_3\text{H}_2$ groups remain after partial deprotonation. These function as potent donors of hydrogen bonds, creating short, robust bonds ($\text{O}-\text{H}\cdots\text{O} \sim 2.5\text{--}2.6\text{\AA}$) with coordinated $\text{P}=\text{O}$ sites.

- **DABTPA Dynamics:** Protonated amine groups ($-\text{NH}_3^+$ or free $-\text{NH}_2$) act as soft hydrogen-bond donors, crosslinking adjacent 2D metal-phosphonate layers into rigid 3D frameworks.

- **DHPTPA Dynamics:** The core aliphatic hydroxyl groups (-OH) serve as both powerful donors and acceptors of hydrogen bonds at the same time. By trapping lattice water molecules in crystal channels, they create continuous hydrogen networks that serve as highways for proton transport through the Grotthuss Mechanism (proton hopping).

Magnetic Properties

Phosphonate oxygen atoms mediate anti ferromagnetic interaction between metal centers by acting as brief bridging routes.

- **Mn (II) Complexes (d^5):** Exclusively high-spin ($S = 5/2$) under weak-field phosphonate configurations. The room-temperature effective magnetic moment (μ_{eff}) sits near the spin-only value of $\sim 5.92 \mu_B$.
- **Fe (II) Complexes (d^6):** High-spin ($S=2$) arrangement with a magnetic moment of around $4.90 \mu_B$. These complexes transmit the Spin-Crossover (SCO) potential from high-spin (paramagnetic) to low-spin (diamagnetic) profiles during cooling if the nearby nitrogen atoms from DABTPA supply enough ligand field strength.

Conclusion

The effective production of iron (II) and manganese (II) complexes using DABTPA and DHPTPA demonstrates the structural adaptability of multidentate polyphosphonic acid ligands. The phosphonate groups were partly deprotonated by carefully regulating the pH between 4.5 and 5.5, resulting in a balance between supramolecular assembly and metal coordination. High-quality single crystals were produced using hydrothermal techniques, and the Iron (II) oxidation state was effectively maintained under stringent anaerobic conditions. The creation of extensive coordination networks stabilized by dense, short-range hydrogen bonds was confirmed by characterization using FT-IR, TGA, and XRD. These complexes show that the structure of the crystal network is directly determined by the choice of ligand spacer: oxygen-rich hydroxyl chains (DHPTPA) vs flexible amine backbones (DABTPA). The resultant paths determine the efficiency of proton hopping across the crystal matrix as well as the magnetic exchange between high-spin metal centers.

The synthesis shows that very versatile coordination materials may be created by pairing DABTPA and DHPTPA ligands with Mn (II) and Fe (II) ions. Future benchmarks will concentrate on: In-Situ Spin-Crossover (SCO) Tuning: Examining how pressure and temperature affect the spin states of Fe (II) DABTPA molecular switches. Testing solid-state proton conductivity using impedance spectroscopy in a variety of relative humidity levels (0%–95% RH). testing open metal coordination sites for the breakdown of environmental pollutants and selective oxidation processes. To avoid explosive hydrostatic pressure build-up, keep Teflon liner filling levels firmly below 65%. Before unlocking, let containers cool gradually to room temperature. Utilizing full personal protective equipment (PPE), process corrosive acid/base modifiers and hazardous Mn (II) within a functional fume hood. To safely handle anaerobic demands, maintain an active nitrogen/argon purge line. Fill bottles marked "Heavy Metal Liquid Waste" with

all post-synthesis aqueous mother liquors that contain heavy metals. Fill professional hazardous incineration containers with all solid contaminated material.

References

1. Liebsch S. Synthesis of (poly)phosphonic acids: an industrial perspective. In *Phosphonate Chemistry, Technology, and Applications*, Synthesis, Chemistry, and Biomedical Applications (pp. 47–65). Elsevier, 2026, 47–65. doi.org
2. Lambert JB, Emblidge RW, Malany S. β effect of phosphorus functionalities. *Journal of the American Chemical Society*, 1996;118(13):3156–3166. doi.org
3. Virtanen EJ, Perämäki S, Helttunen K, Väisänen A, Moilanen JO. Alkyl-substituted aminobis(phosphonates)—Efficient precipitating agents for rare earth elements, thorium, and uranium in aqueous solutions. *ACS Omega*, 2021;6(37):23977–23987. doi.org
4. Allen Career Institute. Denticity of ligands: Types, chelation & examples. Allen Digital, 2024. <https://allen.in/jee/chemistry/denticity-of-ligands-types>
5. Shaikh N, Lezama-Pacheco JS, Ali AMS, Cwiertny DM, Forbes TZ, Haes AJ, *et al.* U(VI) binding onto electrospun polymers functionalized with phosphonate surfactants. *Journal of Environmental Chemical Engineering*, 2022;10(5):108448. <https://doi.org/10.1016/j.jece.2022.108448>
6. Demmer CS, Nilsen NI, Elsner P. Phosphonic acid: preparation and applications. *Molecules*, 2017;22(11):1776. doi.org (PMCID: PMC5669239)
7. Access C, Ding J. Polypeptide self-assemblies: nanostructures and bioapplications. *Chemical Society Reviews*, 2016;45(21):5985–6012. doi.org
8. Mukherjee. Is phosphonate a chelating or sequestering agent? Why phosphonates are threshold scale inhibitor? LinkedIn, 2018. <https://www.linkedin.com/pulse/phosphonate-chelating-sequestering-agent-why-scale-mukherjee>
9. Ataman Chemical. PAPEMP (Polyamino polyeter methylphosphonic acid). Ataman Kimya, 2020. https://www.atamanchemicals.com/papemp-polyamino-polyeter-methylphosphonic-acid_u23950/
10. Ataman Chemical. 2-Carboxyethyl phosphonic acid. Ataman Kimya, 2020. https://www.atamanchemicals.com/2-carboxyethyl-phosphonic-acid_u34737/
11. Zhang C, Zhou S, Wang K, Zhao F, Li S, Wang H, *et al.* Constructive on-DNA Abramov reaction and Pudovik reaction for the synthesis of α -hydroxyphosphonates and α -aminophosphonates. *ACS Combinatorial Science / Organic Letters* [Preprint]. Published online via PMC10107919, 2023. <https://pmc.ncbi.nlm.nih.gov/articles/PMC10107919/>
12. Blodgett JAV, Zhang JK, van der Donk WA. Conserved biosynthetic pathways for phosalacine, bialaphos and phosphinothricin. *The Journal of Antibiotics*, 2016;69(1):15–25. doi.org (PMCID: PMC4731264)

13. Ataman Chemical. HEDP. Ataman Kimya, 2020. https://www.atamanchemicals.com/hedp_u24226/
14. Lacour S, Deluchat V, Bollinger JC, Serpaud B. Complexation of trivalent cations (Al(III), Cr(III), Fe(III)) with two phosphonic acids in the pH range of fresh waters. *Talanta*,1998;46(5):999–1009. doi.org
15. Ataman Chemical. HEDP (Hydroxyethylene diphosphonic acid). Ataman Kimya, 2020. https://www.atamanchemicals.com/hedp-hydroxyethylene-diphosphonic-acid_u22936/
16. National Institute of Standards and Technology. NIST Center for Neutron Research, technical activities 1997 (NISTIR 6067). U.S. Department of Commerce, 1997. <https://nvlpubs.nist.gov/nistpubs/Legacy/IR/nistir6067.pdf>
17. Wikipedia contributors. Pentetic acid. In Wikipedia, The Free Encyclopedia. Retrieved July 28, 2026, from, 2026. https://en.wikipedia.org/wiki/Pentetic_acid
18. Di Bartolo NM, Radchenko V, Blower PJ. Inorganic chemistry of the tripodal picolinate ligand Tpa³⁻ with gallium (III) and gallium-68. *Inorganic Chemistry*,2023;62(51):21000–21010. doi.org (PMCID: PMC10731648)
19. ScienceDirect. DTPA: An overview. ScienceDirect Topics; Earth and Planetary Sciences, 2026. <https://www.sciencedirect.com/topics/earth-and-planetary-sciences/dtpa>
20. Travagin F, Lattuada L, Giovenzana GB. AAZTA: The rise of mesocyclic chelating agents for metal coordination in medicine. *Coordination Chemistry Reviews*,2021;442:213994. doi.org
21. Bioblast. DTPA. MitoPedia, 2025. <https://www.bioblast.at/index.php/DTPA>
22. LibreTexts. Introduction to coordination chemistry. Chemistry LibreTexts, 2024. [https://chem.libretexts.org/Bookshelves/Inorganic_Chemistry/Supplemental_Modules_and_Websites_\(Inorganic_Chemistry\)/Coordination_Chemistry/Structure_and_Nomenclature_of_Coordination_Compounds/Introduction_to_Coordination_Chemistry](https://chem.libretexts.org/Bookshelves/Inorganic_Chemistry/Supplemental_Modules_and_Websites_(Inorganic_Chemistry)/Coordination_Chemistry/Structure_and_Nomenclature_of_Coordination_Compounds/Introduction_to_Coordination_Chemistry)
23. Rao KS, Udgirkar DB, Mule DD. Enhancement of dissolution rate and bioavailability of Aceclofenac by complexation with cyclodextrin. *Research Journal of Pharmaceutical, Biological and Chemical Sciences*,2010;1(4):142–151. [https://www.rjpbcs.com/pdf/2010_1\(4\)/\[15\].pdf](https://www.rjpbcs.com/pdf/2010_1(4)/[15].pdf)
24. Zhang G, Zhang R, Melancon MP, Wong K, You J, Huang Q, *et al.* The degradation and clearance of Poly(N-hydroxypropyl-L-glutamine)-DTPA-Gd as a blood pool MRI contrast agent. *Biomaterials*,2012;33(21):5376–5383. doi.org (PMID: 22541356)
25. ScienceDirect. Diethylenetriamine: An overview. ScienceDirect Topics; Pharmacology, Toxicology and Pharmaceutical Science, 2026. <https://www.sciencedirect.com/topics/pharmacology-toxicology-and-pharmaceutical-science/diethylenetriamine>
26. Kuveke REH, Barwise L, van Ingen Y, Vashisth K, Roberts N, Chitnis SS, *et al.* An international study evaluating elemental analysis. *ACS Central Science*,2022;8(7):855–863. doi.org