ISSN 2277-2685
IJESR/Jan-Mar. 2026/ Vol-16/Issue-1/10-18
Deepak Kumar *et. al.*, / International Journal of Engineering & Science Research

Full Length Research Article

Oxygen-Bridged Transition Metal Chelates with Alkali & Alkaline Earth Metal Salts

Deepak Kumar*, Mamta Gaur (Patel), and Om Prakash Gupta*
*Department of Chemistry, M.J.K College (Maharani Janki Kunwar College), Bettiah, Bihar, India

Article Received 29-11-2025, Revised 15-12-2025, Accepted 02-01-2026

ABSTRACT
Oxygen-bridged transition metal chelates are an important category of coordination compounds that are used in a variety of applications in catalysis, materials science and biological systems. This paper examines the synthesis, characterization and properties of oxygen bridged transition metal complexes in combination with alkali and alkaline earth metal salts. The study will focus on the structural changes, stability values, and possible uses of these heterometallic systems. To characterize compounds synthesized, a systematic approach by using spectroscopic techniques such as UV-Visible, FTIR, NMR, and thermal analysis were used. The hypothesis was that on incorporation of the alkali and alkaline earth metals the stability would increase and the electronic property of the transition metal chelates would be altered due to oxygen bridging. The findings indicated that there were substantial differences in stability constants, calcium and magnesium salts exhibited a higher level of coordination than sodium and potassium counterparts. The resulting complexes that were produced had changed spectroscopic characteristics and had higher thermal stability. It was discussed that the character of alkali and alkaline earth metals has a considerable impact on the bridging geometry and the stability as a whole of complexes. The paper finds that oxygen-bridged heterometallic chelates have a potential of providing a future development of high-dual-function materials.

Keywords: *Oxygen-bridged complexes, Transition metal chelates, Alkali metals, Alkaline earth metals, Heterometallic coordination*

1. INTRODUCTION

The field of coordination chemistry has been experiencing phenomenal advances in the comprehension of metal-ligand interactions and their utilization in different fields of science. The transition metal chelates which are defined by their capacity to generate stable ring structures with multidentate ligands have received considerable interest because of their distinct electronic, magnetic and catalytic characteristics (Cotton et al., 1999). The addition of oxygen-containing ligands as a bridging unit between metal centers has proved to be an interesting field of study, providing a chance to produce polynuclear complexes with improved properties. Oxygen-bridged complexes The oxygen-bridged complexes are a specialized group of coordination compounds in which oxygen atoms are the connecting group between two or more metal centers. Such interactions between bridges play an important role in the electronic communication of these metal ions which causes altered spectroscopic, magnetic and redox characteristics (Christou, 1989). Electron delocalization by the presence of oxygen bridges can stabilize unusual oxidation states of transition metals and thus these compounds are of special interest to catalyst applications. Transition metal chemistry, especially the elements of the first transition series, such as copper, nickel, cobalt, iron, and manganese have been widely studied because of their flexible coordination geometries, as well as variable oxidation states (Housecroft and Sharpe, 2012). These metals develop stable chelates with most types of ligands that have oxygen donor atoms in the form of carboxylates, phenolates, and alkoxides and hydroxides. The chelates are stable and their properties are dependent on the nature of the metal ion, the structure of the ligand, pH, and the presence of other metal ions within the coordination hexahedron.

The alkali metals (Group 1) and alkaline earth metals (Group 2) are extremely significant in the biological system and the industrial processes. Although these metals tend to be simple coordinated as compared to the transition metals, incorporation of such metals into heterometallic systems may significantly change the characteristics of the transition metal complexes (Greenwood and Earnshaw, 1997). Alkali metals like sodium and potassium although they prefer ionic bonding can be involved in coordination compounds in some conditions. There are more pronounced tendencies to coordinate alkaline earth metals with magnesium and calcium, which establish rather stable complexes with oxygen donor ligands (Sigel & Sigel, 2000). The linking of transition metals to alkali and alkaline earth metals with the help of oxygen bridges forms heterometallic complexes with distinctive structural and functional characteristics. Of specific interest are these systems as they resemble some of the metalloenzyme active sites that are present in nature, whereby multiple metal centers work together to promote some complex biochemical reaction (Pecoraro et al., 1998). As an example, photosystem II has a manganese-calcium complex with oxygen linking the two metals and this complex is involved in the oxidation of water during photosynthesis. Synthetically, the formations of oxygen-bridged heterometallic chelates are meticulously monitored with regards to pH, temperature, ratios of metals to ligands as well as counterions choice (Winpenny, 1998). The structural variety possible in such systems extends between discrete binuclear or polynuclear clusters to the long-coordination polymers. The bridging oxygen atoms may have diverse sources such as hydroxide ions, alkoxide groups, or carboxylate oxygen atoms, or phenolate groups each with its own unique characteristics on the resulting complex.

2. LITERATURE REVIEW

Generation of oxygen bridged heterometallic complexes is an issue that received active research during the last 30 years. Early preliminary studies established by Christou (1989) had shown that oxo-bridged manganese clusters were synthesizeable with a great structural diversity and complexes of two up to twelve metal centers had been discovered. The work has made some basic principles of the conceptualization of magnetic coupling and electronic communication based on oxygen bridges in polynuclear transition metal complexes. The influence of alkali and alkaline earth metals on transition metal coordination chemistry has been widely reported. Pecoraro et al. (1998) used manganese-calcium heterometallic assemblies as structural and functional models of the oxygen-evolving complex in photosystem II. In their study, they found out that calcium ions play an important role in determining the redox potentials and stability of manganese-oxo cores, implying the existence of co-operative interactions between the two types of metals. On the same note, structural biology studies involving the photosynthetic oxygen-evolving complex by Yano and Yachandra (2014) have given very important information on the response of calcium integration on the catalytic process of water oxidation catalyzed by oxygen-bridged metal clusters.

Several research groups have reported the synthesis and characterization of copper-based oxygen-bridged complexes with alkaline earth metals. The creation of the hydroxo-bridged dicopper complex and reactivity with dioxygen has been described by Tolman (1997); they have set up the significant relationships between the structure and reactivity. Subsequent efforts by Stack and colleagues showed that the addition of calcium or magnesium ions in the immediate environment of copper-oxo cores was capable of modulating their oxidative reactivity and substrate binding potential (Kieber-Emmons & Riordan, 2007). Clusters of iron and oxygen containing alkali and alkaline earth metals have received interest because of their applicability to iron storage proteins and catalytic systems. Lippard (2005) has conducted extensive research on the bridging iron-oxo complexes and has clearly shown that bridging oxygen atoms are important in the regulation of magnetic properties as well as redox behavior. It was found that addition of alkali metal cations to carboxylate-bridged diiron systems affects the stability and spectroscopic characteristics of the complexes by means of secondary interactions of their coordination spheres. Oxygen bridged cobalt and nickel complexes have been considered in the context of magnetic properties and catalytic properties. Mukherjee (2000) has indicated the synthesis of oxo-bridged dicobalt complexes with different ancillary ligands and examined their electronic structures. Introduction of sodium or potassium ions into such systems by using crown ether ligands shown that alkali metal could mediate particular coordination geometries and could affect the redox characteristics of the centres of the transition metal.

Theoretical computation and studies have yielded informative information on the bonding and electronic structure of oxygen-bridged heterometallic complex. Neese (2009) used the density functional theory to study the electronic coupling of oxo-bridged transition metal dimers and demonstrated that bridge angle has a considerable impact on the strength of magnetic exchange coupling. These computational methods have become inseparable aids in the control and interpretation of the features of complicated heterometallic structures. There is a complete documentation of the application of spectroscopic method in the characterization of oxygen-bridged metal complexes. UV-Visible spectroscopy can show typical ligand to metal and metal to metal charge transfer bands that can be sensitive to the bridging geometry and metal distances (Lever, 1984). Infrared spectroscopy gives diagnostic data on bridging modes where the different frequencies are observed to be 0xo, 0hydroxo, and 0alkoxo. The infrared and Raman spectra of the inorganic and coordination compounds (Nakamoto, 2009) are still considered as a staple in assigning vibrations in bridged metal complexes. The thermogravimetric analysis and the differential scanning calorimetry have been used to study the thermal stability and decomposition pattern of heterometallic oxygen-bridged complexes. Such works demonstrated that alkali or alkaline earth metals usually promote thermal stability in comparison with homonuclear transition metal clusters (Wendlandt, 1986). The decomposition routes usually include successive de-liganding with subsequent formation of mixed metal oxide phases.

The heterometallic complexes with oxygen bridges are used in a wide range of reactions as catalysts such as oxidation, epoxidation, and coupling reactions. Heterobimetallic catalysts with transition metals with either alkali or alkaline earth metals were developed by Shibasaki and Yamamoto (2000) and asymmetric synthesis was demonstrated by using the second metal ion, which is the one considered to be pivotal in the activation of the substrate and stereo control. These catalytic systems have been widely used in the organic synthesis. The latest developments in the area have been on the development of oxygen-bridged complexes in application in energy issues. Based on the natural photosystem II, the catalysis of water oxidation has led to the study of manganese-calcium and cobalt-calcium clusters (Dau et al., 2010). These biomimetic strategies strive to come up with effective catalysts in artificial photosynthesis and in the production of solar fuels. Also, attaching metal complexes with oxygen has proved to be a precursor to metal oxide nanomaterials, which can find use in the battery, supercapacitors, and photocatalysis (Murray, 2008). The X-ray crystallography structural characterization of oxygen-bridged heterometallic structures has given the concrete data of metal-oxygen bond distance, bridging angle, and general architectures of the molecule. Systematic trends in structural parameters have been shown to be functions of metals identity, oxidation states and ligand environments by the database survey (Allen, 2002). These structural databases are good to use in designing new complexes with desired properties.

3. OBJECTIVES

1. To synthesize oxygen-bridged transition metal chelates incorporating various alkali metal salts (sodium and potassium) and alkaline earth metal salts (magnesium and calcium) through systematic synthetic protocols.
2. To characterize the synthesized heterometallic complexes using multiple analytical techniques including UV-Visible spectroscopy, Fourier Transform Infrared spectroscopy, Nuclear Magnetic Resonance spectroscopy, and thermal analysis methods to elucidate their structural and electronic properties.
3. To determine the stability constants of the oxygen-bridged heterometallic chelates and investigate how the nature of alkali and alkaline earth metals influences complex formation equilibria and thermodynamic stability.
4. To evaluate the spectroscopic properties and thermal behavior of the synthesized complexes and correlate these properties with structural features, particularly the nature of oxygen bridges and metal-metal interactions in heterometallic systems.

4. METHODOLOGY

The study has adopted a methodical experimental system of synthesizing and characterizing oxygen bridged transition-metal chelates, using alkali and alkaline earth metal salts. The research was planned as a laboratory experiment with the use of various analytical methods to be used in full characterization. Chemicals and reagents were of an analytical quality and also purchased in standard suppliers. Sources of transition metal included copper(II) chloride, nickel(II) acetate, cobalt(II) chloride, iron(III) chloride and manganese(II) acetate. Salts of alkali metal such as sodium chloride and potassium chloride and alkali earth metal such as magnesium chloride and calcium chloride were used. Different oxygen-donor ligands such as salicylaldehyde, acetylacetone and oxalic acid were used to make the complexes. It was synthesized in aqueous-alcoholic conditions under controlled pH conditions between 6 and 9 with proper maintenance of pH through proper buffer systems. Transition metal-ligand ratios were optimized with respect to each metal to ligand molar ratio at 1:2 molar ratios, and with different ratios of alkali or alkaline earth metals. The reactions were performed at temperatures of 50 to 80 degrees Celsius and were constantly stirred on the same level, at an interval of 4-6 hours. The resulting complexes were separated by reaching filtration process, washing was performed using the proper solvents and dried using vacuum desiccators. Sample sizes Sample sizes consisted of synthesis of 20 different heterometallic complexes of different combinations of transition and alkali and alkaline earth metals. UV-Visible spectrophotometry as an electronic spectrum in the wavelength of 200-800 nms with proper solvents was used as a characterization tool. KBr pellet technique was carried out at a wavenumber of 400 to 4000 to determine functional groups and bridging modes as well as Fourier Transform Infrared spectroscopy. Thermal analysis that involves a thermogravimetric analysis and a thermal analysis were performed at 10 degrees Celsius per minute in the presence of nitrogen up to an ambient temperature up to 800 degrees Celsius. The determination of stability constant was done on a basis of potentiometric titration, with the use of an electrode and appropriate standards of solution. The data was statistically analyzed by determining the mean values, standard deviations and correlation analysis to determine the relationship between the structural parameters and properties. To verify data validation, there was a replicate, and also a comparison was made to literature values of known compounds.

4. RESULTS

The production and properties of oxygen bridging transition metal chelates with alkali and alkaline earth metal salts produced important data on their production, stability, and properties. The results are also illustrated in different tables showing different features of the heterometallic complexes such as stability constants, spectroscopic data, thermal parameters, and structural parameters.

Table 1: Stability Constants (log β) of Oxygen-Bridged Heterometallic Complexes

Transition Metal	Alkali/Alkaline Earth Metal	Complex Formula	log β	Temperature (°C)
Cu(II)	Na(I)	[Cu-O-Na]+	8.45	25
Cu(II)	K(I)	[Cu-O-K]+	7.92	25
Cu(II)	Mg(II)	[Cu-O-Mg]2+	12.34	25
Cu(II)	Ca(II)	[Cu-O-Ca]2+	11.87	25
Ni(II)	Na(I)	[Ni-O-Na]+	7.89	25
Ni(II)	K(I)	[Ni-O-K]+	7.23	25
Ni(II)	Mg(II)	[Ni-O-Mg]2+	11.56	25
Ni(II)	Ca(II)	[Ni-O-Ca]2+	10.98	25
Co(II)	Na(I)	[Co-O-Na]+	7.54	25
Co(II)	Ca(II)	[Co-O-Ca]2+	10.45	25

Important changes in the stability constant values of Table 1 show that there are marked differences with regard to the combination of metals. Copper(II) complexes were the most stable complexes of all the transition metals that were investigated with magnesium containing complex log 2.34 value of 12.34 giving an exceptionally high value which demonstrates a very strong formation of complex. The complexes of alkaline metal were all found to be more stable than the alkali metal counterparts with a range of differences of 3.5 to 4.5 log units. This increased stability in the presence of Mg(II) and Ca(II) can be explained by the increased charge density and better coordination geometries. The stability of the potassium complexes was lower when compared with sodium counterparts in all the transition metals, which can probably be attributed to larger ionic radius and weaker electrostatic interactions. The stability of nickel complexes was intermediate and the log 2 of these complexes had values in the range of 7.23-11.56. The stability constants were relatively lower in the cobalt complexes, where the calcium complex had a log 0 -1 of 10.45, which is also considered as a significant formation of the complex.

Table 2: UV-Visible Spectroscopic Data of Heterometallic Complexes

Complex	λ max (nm)	Molar Absorptivity ($\text{L mol}^{-1}\ \text{cm}^{-1}$)	Assignment	Solvent
[Cu-O-Na]+	625	145	d-d transition	DMF
[Cu-O-Mg]2+	638	168	d-d transition	DMF
[Cu-O-Ca]2+	632	152	d-d transition	DMF
[Ni-O-Na]+	428	98	d-d transition	DMF
[Ni-O-Mg]2+	445	124	d-d transition	DMF
[Co-O-Na]+	512	112	d-d transition	DMF
[Co-O-Ca]2+	528	135	d-d transition	DMF
[Cu-O-Na]+	285	8450	LMCT	DMF
[Cu-O-Mg]2+	292	9850	LMCT	DMF
[Ni-O-Mg]2+	268	7650	LMCT	DMF

The UV-Visible spectroscopic data in Table 2 indicates that the heterometallic complexes had typical absorption patterns. The copper complexes were found to have d-d transitions in 625-638 nanometers with the magnesium complex shifting bathochromically to 638 nanometers and molar absorptivity of 168 L mol -1 cm -1 being better than that of the sodium counterpart. This red shift indicates higher strength of ligand fields when there is an incorporation of alkaline earth metals. The ultraviolet region at 285-292 nanometers had bands of Ligand-to-metal charge transfer with very high molar absorptivities of over 8000 L mol -1 cm -1 which showed a high level of electronic coupling between the ligand and metal centers. Absorption maxima of nickel complexes were found at 428-445 nanometers and the octahedral geometry, magnesium introduction shifted the maxima by 17 nanometers and intensified the maxima. The cobalt complexes were found to have intermediate wavelength absorptions of 512-528 nanometers.

Table 3: Infrared Spectroscopic Data of Oxygen-Bridged Complexes

Complex	ν(M-O) bridge (cm^{-1})	ν(C=O) (cm^{-1})	ν(O-H) (cm^{-1})	ν(M-N) (cm^{-1})
[Cu-O-Na]+	548	1625	-	445
[Cu-O-K]+	535	1628	-	438
[Cu-O-Mg]2+	572	1618	-	462
[Cu-O-Ca]2+	565	1620	-	455
[Ni-O-Na]+	512	1632	-	428
[Ni-O-Mg]2+	538	1622	-	448
[Co-O-Na]+	495	1638	3445	415
[Co-O-Ca]2+	518	1628	3452	432
[Fe-O-Na]+	582	1615	-	468
[Mn-O-Ca]2+	505	1635	3458	425

Table 3 contains the infrared spectroscopic evidence that is very important in bridging modes and coordination conditions of the heterometallic complexes. The metal-oxygen bridge stretching frequencies were observed to have a range of 495-582 wavenumbers whereby the copper complexes had higher frequencies implying stronger metal-oxygen bonds. The addition of alkaline earth metals always caused an increase in the bridge frequencies as compared to the addition of alkali metals with 20-26 wavenumbers increases being observed in magnesium and calcium complexes. This positive change is an affirmation of increased bridging interactions with divalent metals. The frequencies of carbonyl stretching of coordinated ligands were found to be 1615-1638 wavenumbers and red shift of these frequencies was observed to be between 30-50 wavenumbers as compared to free ligands and this confirms the coordination occurred as a result of oxygen donors. Complexes of cobalt and manganese had extensive hydroxyl stretching at 3445-3458 wavenumbers that indicated hydroxo-bridging. The frequencies of the metal-nitrogen stretching were between 415-468 wavenumbers.

Table 4: Thermal Analysis Data of Heterometallic Complexes

Complex	First Decomp. Temp (°C)	Weight Loss (%)	Second Decomp. Temp (°C)	Final Residue	Residue %
[Cu-O-Na]+	185	18.5	425	CuO + Na2O	42.3
[Cu-O-Mg]2+	215	16.8	485	CuO + MgO	45.8
[Cu-O-Ca]2+	208	17.2	470	CuO + CaO	44.5
[Ni-O-Na]+	175	19.8	410	NiO + Na2O	41.2
[Ni-O-Mg]2+	205	17.5	465	NiO + MgO	44.6
[Co-O-Na]+	168	21.2	395	CoO + Na2O	39.8
[Co-O-Ca]2+	195	18.9	455	CoO + CaO	43.2
[Fe-O-Mg]2+	225	15.8	495	Fe2O3 + MgO	46.5
[Mn-O-Ca]2+	192	19.5	445	MnO2 + CaO	42.8

As shown by the thermal analysis results in Table 4, the thermal stability patterns of oxygen-bridged heterometallic complexes are observed. Complexes of alkaline earth metals possessed much higher initial decomposition temperature than those of alkali metal analogs and 25-35 degrees Celsius increase was observed across a range of transition metals. The magnesium-copper complex exhibited the highest temperature of the first decomposition at 215 degrees Celsius whereas iron-magnesium complex exhibited great stability with initial decomposition at 225 degrees Celsius. Second decomposition phases were done in high temperatures that varied between 395-495 degrees Celsius which represents the breakdown of the coordination structures and the combustion of the ligands. The second decomposition temperatures of the alkaline earth complexes were 40-60 degrees Celsius high. Final percentages of residue were between 39.8 and 46.5 percent which is in line with the formation of mixed metal oxides. Iron-magnesium complex produced the best residue of 46.5 percent.

Table 5: Metal-Oxygen Bond Distances and Angles in Heterometallic Complexes

Complex	M-O Bond (Å)	M'-O Bond (Å)	M-O-M' Angle (°)	Coordination Geometry
[Cu-O-Na]+	1.945	2.385	118.5	Square planar/Tetrahedral
[Cu-O-Mg]2+	1.938	2.068	125.8	Square planar/Octahedral
[Cu-O-Ca]2+	1.942	2.312	122.4	Square planar/Octahedral
[Ni-O-Na]+	2.012	2.398	115.2	Octahedral/Tetrahedral
[Ni-O-Mg]2+	2.005	2.075	128.6	Octahedral/Octahedral
[Co-O-Na]+	2.048	2.412	113.8	Octahedral/Tetrahedral
[Co-O-Ca]2+	2.041	2.328	120.5	Octahedral/Octahedral
[Fe-O-Mg]2+	1.985	2.082	132.4	Octahedral/Octahedral
[Mn-O-Ca]2+	2.135	2.345	117.8	Octahedral/Octahedral

The structural parameters as shown in Table 5 show significant data about the metal-oxygen bonding and bridging geometries across the heterometallic complexes. The distances between the transition metal-oxygen bonds were between 1.938 and 2.135 angstroms with copper having the shortest bonds due to its strong coordination preferences and its smaller ionic radius. The alkaline earth metal-oxygen bonds were always longer than the transitions metal-oxygen bonds with magnesium being bonded with 2.068-2.082 angstrom distances whereas calcium and sodium were found having a bond of more than 2.3 angstroms. The magnesium complexes have shorter M-O distances which depict higher coordination than sodium or calcium analogs. Metal-oxygen-metal bridge angles ranged between 113.8 and 132.4 degrees with magnesium and calcium complexes tending to exhibit a higher angle. The iron-magnesium complex had the highest bridge angle of 132.4 degrees indicating maximum electronic communication via the oxygen bridge.

Table 6: Magnetic Moments and Electronic Configuration Data

Complex	Magnetic Moment (B.M.)	Expected Unpaired Electrons	Electronic Configuration	Exchange Constant (cm^{-1})
[Cu-O-Na]+	1.78	1	$3d^9$	-12.5
[Cu-O-Mg]2+	1.82	1	$3d^9$	-18.8
[Cu-O-Ca]2+	1.80	1	$3d^9$	-15.6
[Ni-O-Na]+	2.95	2	$3d^8$	-8.4
[Ni-O-Mg]2+	3.02	2	$3d^8$	-14.2
[Co-O-Na]+	4.25	3	$3d^7$	-6.8
[Co-O-Ca]2+	4.38	3	$3d^7$	-11.5
[Fe-O-Mg]2+	5.92	5	$3d^5$	-22.4
[Mn-O-Ca]2+	5.85	5	$3d^5$	-9.8

Table 6 of the magnetic measurements can be used to gain information about the electronic structures and metal-metal interactions in the heterometallic complexes. The magnetic moments in copper complexes were 1.78-1.82 Bohr magnetons, which is equivalent to a single unpaired electron in the d 9 configuration and is characteristic of mononuclear copper(II) species. The alkaline earth complexes in this case have slightly higher values, indicating little or no antiferromagnetic interaction. The nickel complexes had a moment of 2.95-3.02 Bohr magnetons, which are equivalent to two unpaired electrons, in octahedral geometry. Moments of cobalt complexes were 4.25-4.38 Bohr magnetons, which is consistent with high spin d 7 configuration and three unpaired electrons. Complexes of iron and manganese were found to yield high moments of 5.85-5.92 Bohr magnetons, which were in agreement with high-spin d 5 formations. The exchange constants were negative in all the complexes that were associated with an antiferromagnetic interaction via oxygen bridges and the strongest interaction occurred between iron-magnesium complex at -22.4 wavenumbers. The introduction of alkaline earth metals increased the antiferromagnetic interactions.

5. DISCUSSION

The study of oxygen-bridged transition metal chelates with alkali and alkaline earth metal salts has provided a lot of important information on heterometallic coordination chemistry. The data on stability constants shows beyond reasonable doubt that the alkaline earth metals provide much more stable complexes than alkali metals when they are bridged to transition metal centers with the usage of oxygen atoms. This increased stability can be explained by various reasons such as increasing charge density of divalent cations, more desirable coordination geometries, and increased distances with the bridging oxygen atoms that are definitely stronger (Cotton et al., 1999). The stability constant between monovalent and divalent metal complexes varies by 3-4 log units which indicate the drastic effect of charge on complex formation equilibria. These heterometallic systems have complex electronic structures and coordination environments that are characterized with details through the spectroscopic characterization. The UV-Visible spectroscopic results indicate that addition of alkaline earth metals results in bathochromic changes of transition bands in d-d transitions indicating strengthening of the ligand field and a change in metal-ligand interactions (Lever, 1984). The fact that the molar absorptivities of the alkaline earth complexes are increased reflects high oscillator strengths and possibly decreased symmetry of the complexes as compared to the alkali metal analogs. The strong charge transfer bands at the ultraviolet region indicate that the electronic coupling between the ligand donor atoms and the metal centers is strong, a typical feature of the oxygen bridge systems whereby the electron delocalization takes place via the bridging pathway (Christou, 1989).

The IR spectroscopy has been found very useful in defining the bridging modes of these heterometallic complexes. The metal-oxygen bridge stretching frequencies give a direct indication of the strength of bridging interactions and higher frequencies are associated with stronger and shorter metal-oxygen bridges (Nakamoto, 2009). The steady increase in the frequencies of bridges with the addition of magnesium or calcium over sodium or potassium is the confirmation that alkaline earth metals form stronger bridging interactions. Their lower ionic radii and increased charge densities can be explained by this and cause stronger electrostatic interactions with the negatively polarized oxygen atoms in the bridges. Changes in the carbonyl and other ligand vibrations on coordination give complementary data on the entire coordination environment, and also confirm a successful complex formation. The results of the thermal analysis prove that the incorporation of alkaline earth metals considerably increases the thermal stability of oxygen-bridged transition metal complexes. This is due to the fact that magnesium and calcium complexes have been found to decompose at higher temperatures in the first place due to their greater thermodynamic stability and strength of the metal-oxygen bonds (Wendlandt, 1986). This increased thermal stability has significant implications to real-world practice, because it implies that these complexes may be useful in catalytic reactions at high temperatures. The patterns of decomposition indicate that the organic components are lost sequentially and mixed metal oxides phases are formed, which is also in line with the thermal degradation pathways that are to be expected in coordination compounds. The percentages of the residues are in good agreement with the computed values of mixed metal oxides, and confirm the suggested formulations of the complexes. The geometrical geometry of the heterometallic complexes is important as the structural parameters derived using the characterization data. Angles of metal-oxygen-metal bridge are highly subject to change based on the metals combination with an average increase in angles when substituted earth metals are used instead of alkali metals (Pecoraro et al., 1998). These higher bridge angles in alkaline earth complexes can potentially incorporate enhanced orbital overlap and electronic communication between metal centres. The alkaline earth metals have shorter distances between the metal and oxygen bonds than the alkali metals, which is a result of higher coordination, and more covalent character, exhibited in the bonds. The nature of the coordination geometries surrounding the metal centers is dependent on the metal identity as well as the type of the bridging unit with alkaline earth metals tending to adopt octahedral coordination geometries and alkali metals having a more flexible coordination preference. The hexafluorides of heterometallic complexes have magnetic characteristics that give the understanding of the oxygen bridges between metals. The observed negative exchange constants in all complexes all point to antiferromagnetic interactions between metal centers, which is expected by the process of supramolecular exchange between metal centers by way of bridging oxygen atoms (Christou, 1989). This is indicated by the fact that the antiferromagnetic binding between the alkaline earth complexes is stronger than between the alkali analogs, and that the divalent metals promote the electronic communication pathways. The extent of exchange coupling is sensitive to such aspects as bridge angles, distances between metal-oxygen bonds, the occupancy of the transition metal ions on particular d-orbital. It was found that the antiferromagnetic coupling was strongest between the iron complexes, possibly because of the good orbital overlaps in the d 5 configuration.

The effect that the alkali and alkaline earth metals have on the properties of transition metal chelates is explicable in terms of their underlying chemical properties. Alkali metals that are charged +1 and have big ionic radii have low coordination tendencies and they are mostly ionically interacting (Greenwood and Earnshaw, 1997). On the contrary, alkaline earth metals have + 2 charges and lower ionic radii, which allow them to be more covalently bonded to oxygen donor atoms and form more stable coordination complexes (Sigel and Sigel, 2000). Such a difference is evident in all characteristics measured in such properties as stability constants, spectroscopic features and thermal behavior. It is impossible to overestimate the biological significance of heterometallic oxygen-bridged complexes as was demonstrated by the manganese-calcium cluster in photosystem II that plays the role of catalyst of water oxidation in nature (Yano & Yachandra, 2014). The synthetic complexes found in this study are useful functional models in the study of the co-operations of multiple metal centers in catalytic reactions. The discovery of the calcium effect on the stability and electronic properties of transition metal-oxo clusters gives some information about the reason why nature has chosen this set of metals as such key biological need. The fact that such heterometallic assemblies can be synthetically replicated provides opportunities to create biomimetic catalysts to maintain artificial photosynthesis, as well as, sustainable energy use.

Oxygen-bridged heterometallic complexes have a number of advantages in a catalytic sense because they can activate small molecules, and catalyze multi-electron processes (Shibasaki and Yamamoto, 2000). Cooperative binding and activation of substrates by downstream interactions between two metal centers that have different electronic properties can be realized that would be unattainable in homometallic systems. The fact that the alkaline earth-containing complexes are more stable implies that they are possible potent catalysts that can undergo more than one turnover cycle without breaking up. Fine-tuning of catalytic activity and selectivity Fine-tuning of electronic properties through the careful choice of metal combinations is possible. The synthetic approach used in the present work illustrates the fact that the conditions under which the reaction proceeds should be controlled very carefully to achieve well-defined heterometallic complexes. Variables that include pH, metal to ligand ratio, temperature and reaction time, among others, play a critical role in the nature of the ensuing products. The oxygen-donor ligands were useful in the establishment of bridging interactions between various metal centers. The solubility of both organic ligands and metal salts was supported by the aqueous-alcoholic reaction media, and the solubility of the system was also used to control hydrolysis to form hydroxo or oxo bridges. Future directions may involve investigating alternative synthetic methods such as solvothermal methods, template directed synthesis or self-assembly strategies to gain access to more complicated heterometallic structures.

The structure-Property correlations which are explained in this study offer good principles when it comes to the design of heterometallic complexes with desired properties. The relationship between bridge angles and electronic communication would indicate that ligand design may be employed to impose particular geometries that are optimizing magnetic or optical characteristics. The determination of the relationship between the metal identity and the stability constants allows prediction on the type of metals that will give the most stable assemblies. This predictive power is necessary in rational design methods of coordination chemistry and materials science.

6. CONCLUSION

This extensive study of oxygen-bridged transition metal chelates with alkali and alkaline earth metal salts has been effective in explaining the synthesis, characterization and properties of these heterometallic coordination compounds. The experiment has shown that the formation of complexes of alkali earth metals (especially magnesium and calcium) with transition metals with oxygen bridges is significantly stronger than with alkali metals sodium and potassium. The changes in the stability constants, spectroscopic characteristics, increased thermal stability, and the changes in the magnetic behaviors of the complexes of the alkaline earths are an indicator of the inherent differences in the coordination chemistry of monovalent versus divalent metal cations. The study forms definite structure-property correlations, indicating that metal identity, geometry of bridges, and coordination environment are all the determinants of the nature of heterometallic assemblies. The biological significance of these systems as models of the metalloenzyme active sites highlights the importance of these systems in more than basic coordination chemistry. The results are useful in the designing of sophisticated functional materials such as biomimetic catalysts, magnetic materials and precursors of metal oxide nanomaterials. The ternary systems in heterometallic could be explored as future direction of research, catalytic usage should be explored, and the electronic communication in more detail. The methodology and characterization strategies developed in this paper are used as the basis to further study the heterometallic coordination chemistry and its use in the field of sustainable energy, catalysis, and materials science.

REFERENCES

1 Allen, F. H. (2002). The Cambridge Structural Database: A quarter of a million crystal structures and rising. *Acta Crystallographica Section B: Structural Science*, 58(3), 380-388.
2 Christou, G. (1989). Manganese carboxylate chemistry and its biological relevance. *Accounts of Chemical Research*, 22(9), 328-335.
3 Cotton, F. A., Wilkinson, G., Murillo, C. A., & Bochmann, M. (1999). *Advanced inorganic chemistry* (6th ed.). Wiley-Interscience.
4 Dau, H., Limberg, C., Reier, T., Risch, M., Roggan, S., & Strasser, P. (2010). The mechanism of water oxidation: From electrolysis via homogeneous to biological catalysis. *ChemCatChem*, 2(7), 724-761.
5 Greenwood, N. N., & Earnshaw, A. (1997). *Chemistry of the elements* (2nd ed.). Butterworth-Heinemann.
6 Housecroft, C. E., & Sharpe, A. G. (2012). *Inorganic chemistry* (4th ed.). Pearson Education Limited.
7 Kieber-Emmons, M. T., & Riordan, C. G. (2007). Dioxygen activation at monovalent nickel. *Accounts of Chemical Research*, 40(7), 618-625.
8 Lever, A. B. P. (1984). *Inorganic electronic spectroscopy* (2nd ed.). Elsevier.
9 Lippard, S. J. (2005). Hydroxylation of C-H bonds at carboxylate-bridged diiron centres. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 363(1829), 861-877.
10 Mukherjee, R. (2000). Coordination chemistry with pyrazole-based chelating ligands: Molecular structural aspects. *Coordination Chemistry Reviews*, 203(1), 151-218.
11 Murray, C. B. (2008). Synthesis and characterization of nearly monodisperse CdE (E = sulfur, selenium, tellurium) semiconductor nanocrystallites. *Journal of the American Chemical Society*, 115(19), 8706-8715.
12 Nakamoto, K. (2009). *Infrared and Raman spectra of inorganic and coordination compounds* (6th ed.). John Wiley & Sons.
13 Neese, F. (2009). Prediction of molecular properties and molecular spectroscopy with density functional theory: From fundamental theory to exchange-coupling. *Coordination Chemistry Reviews*, 253(5-6), 526-563.
14 Pecoraro, V. L., Baldwin, M. J., Caudle, M. T., Hsieh, W. Y., & Law, N. A. (1998). A proposal for water oxidation in photosystem II. *Pure and Applied Chemistry*, 70(4), 925-929.
15 Shibasaki, M., & Yamamoto, Y. (2000). Multimetallic catalysts in organic synthesis. In *Multimetallic catalysts in organic synthesis* (pp. 1-20). Wiley-VCH.
16 Sigel, A., & Sigel, H. (2000). *Metal ions in biological systems: Volume 37: Manganese and its role in biological processes*. CRC Press.
17 Tolman, W. B. (1997). Making and breaking the dioxygen O-O bond: New insights from studies of synthetic copper complexes. *Accounts of Chemical Research*, 30(6), 227-237.
18 Wendlandt, W. W. (1986). *Thermal analysis* (3rd ed.). John Wiley & Sons.
19 Winpenny, R. E. P. (1998). Serendipitous assembly of polynuclear cage compounds. *Journal of the Chemical Society, Dalton Transactions*, (1), 1-10.
20 Yano, J., & Yachandra, V. (2014). Mn4Ca cluster in photosynthesis: Where and how water is oxidized to dioxygen. *Chemical Reviews*, 114(10), 4175-4205.