A study on ligand design in coordination chemistry to enhance catalytic performance and Solvent extraction selectivity

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Abstract

In an effort to improve the selectivity of the solvent extraction process and the catalytic process, the paper will consider the ligand design as it relates to the field of coordination chemistry. They were formulated as transition metal complexes by the utilization of customized ligand scaffolds comprising diversified fractions of donor atoms, denticity and steric flexibility. Structural characterization was used to study ligand to metal interactions and found a variety of different geometries and electronic conditions to be structurally clear. Preexisting ligand architecture-turnover efficiency correlations were seen in catalytic studies; the most active were late transition metals and polydentate ligands. Extraction studies of the solvents revealed that the efficiencies that depended on pH were affected by the type of donor and structure of the ligand, which also showed a variable behavior of partitions. Rational design of ligands was the versatile factor and was reinforced by the comparative studies that have revealed a direct correlation between electronic density and selective catalytic turnover of extractions. With the dawning of industrial implications on the potential in the revival of rare-earth, hydrometallurgy and green chemistry, mechanics became constructed in significant consideration of striking some balance amid thermodynamic stability and kinetic lability. The results of all these lead to the fact that the ligand design is a common methodology of the environmentally friendly processes of catalysis and separation.

Keywords: *Transition Metal Complexes, Coordination Chemistry, Ligand Design, Homogeneous Catalysis, Solvent Extraction, Green Chemistry*

1. Introduction

A key point about inorganic work in modern times is the design of ligands in coordination chemistry, which offers fine control in terms of reactivity and selectivity of transition metal complexes. Chemists using denticity and steric environments can fine-tune the electronic structures and the partaking pathways and this may simplify the study of the fundamentals and its application in practice (Boros, Marquez, Ikotun and others, 2014). In addition to stabilization of the reactive intermediates, the ligand selection has also been noted to control the shape and electronic distribution of the complex that directly influences the turnover rate of the catalyst and the extraction efficiency (Wilson and Lee, 2013).

The design of the ligand is one of the factors in favor of the adjustment of reactivity and selectivity. In fact, flexible scaffolds provide a conglomeration of binding modes; multifunctionality can also be enhanced by the use of sterically assertive ligands and some coordination geometries may be instigated (Kumar & Gupta, 2013). Having a vital impact on the processes of both solvent extraction and catalysis, ligand architecture

suggests the modulation of the electronics by means of an alteration of donor atoms in which the metal ion activation and selectivity towards the substrate are further to be affected (Sahoo, Sharma, Bera, Crisponi, etc., 2012).

The mechanistic precision that is useful in the scenario of homogeneous catalysis is particularly provided by logical ligand design. The uniform active sites provided by transition metal succinate complexes may be investigated by comprehensive mechanistic investigations and with reproducible turnover rates with customized ligands. The industry will need these catalysts in the types of hydroformylation processes, hydrogenation and polymerization reactions and the geometry of the ligand will determine the performance and success of the final product (Pospech, Fleischer, Franke, et al., 2013). The concept of sustainability is in line with homogeneous catalysis because of the developments in solvent engineering and plant immobilization, which contribute to the improvement in recyclability (Stirling, Nair, Lledoss and Ujaque, 2014).

The solvents, on the other hand, never succeed in choosing ions of chemically identical ions easily. It is possible to answer this question by ligand design with the inclusion of donor atoms and geometries capable of differentiating between target and competing species. The advancement of the ionic liquid and hybrid ligands leads to the evolution of the extraction toolkit, which is a hard task to achieve since there is a need to define an equilibrium between efficiency and selectivity (Panak & Geist, 2013).

A synergy effect between catalysis chemistry and extraction chemistry is presented when the ligands are planned to perform two functions. Along with effective selective partitioning and stabilization of catalyst intermediates, multifunctional scaffolds may ease the procedures and reduce waste (Villanneau, Marzouk, Wang, Djamaa, & Proust, 2013). Irrespective of this development, a good research gap is in high abundance inasmuch as few integrated research studies incorporate the connections that exist between the design of the ligands and performance due to catalysis and extraction of the products. Our work fulfills this gap and provides a contribution to the sustainable chemical processes via a methodical investigation of the strategy of ligand design integrating catalytic functionality with selectivity to isolate components by selective assemblies of ligands comprising different functional groups (Maglio, Nastri and Lombardi, 2012).

Objectives

- To design and synthesize novel ligand scaffolds with specific transition metal coordination environment modulations, i.e.,
- each of the donor atom types, each degree of denticity and each degree of steric freedom.
- To establish connections between ligand structure, rate of turnover and pathways of action of these complexes to fully understand the catalytic performance of such complexes in the homogeneous processes.
- To compare the solvent extraction efficiency and selectivity of the same ligand complexes to demonstrate their bivalent nature and to facilitate combined methods of environmentally friendly separation and recovery processes.

2. Theoretical Background and Design Strategy

Principles of coordination geometry and electronic structure Spatial arrangement of ligands around a metal center Ligand coordination geometry has a direct effect on the stability and reactivity. Types of common geometries would be octahedral, tetrahedral and square-planar geometries and each of them is associated with a distinct set of electrical properties. Electronic structural factors such as orbital overlap and d-orbital splitting determine the bond strengths and the catalytic routes. As an example, square-planar geometries are biased towards low-spin states and biased towards selective activation of a substrate and the octahedral complexes tend to stabilize high oxidation states. Since geometry and electronic distribution determine the catalytic turnover and extraction selectivity, there is a need to understand these terms in order to make rational designs of ligands (Maglio, Nastri and Lombardi, 2012).

HSAB theory and selection of donor atoms The Hard-Soft Acid-Base (HSAB) theory is a theory that offers a conceptual understanding of predicting interactions between ligand and metal. Soft acids such as Pd(II) or Pt(II) favor phosphine or sulfur ligands, whereas hard acids such as early transition metals favor oxygen donors. It is important when selective ligands involving the generation of a donor atom intended to discriminate among competitive ions are to be developed. The matching of HSAB enhances efficiency in catalysis by stabilizing catalysis intermediates and transitioning states. Accordingly, rational selection of donor atoms provides that ligands are appropriate to both catalytic and separation activity; there is the connection between fundamental coordination chemistry and applications (Panak & Geist, 2013).

Catalytic activity, the ligand field theory explains the effect of the strength of ligands on the d-orbital splitting, electronic transitions and catalytic activity. The strong-field ligands based on n-heterocyclic carbenes are highly split that stabilize low-spin states and even allow powerfully challenging transformations such as C-H activation. Weak-field ligands, on the other hand, promote high-spin topologies, which promote dynamic catalytic cycles and flexible coordination. Similar effects can be applied to solvent extraction, in which the strength of the ligand field has an influence on the affinity and partitioning behavior of metal ions. Chemists have the opportunity of designing compounds that combine selectivity in extraction and catalytic power through the modulation of the ligand field to facilitate multilet uses (Engle, Wang and Yu, 2010).

Even though they offer endurance, thermodynamically stable compounds can occasionally limit catalytic turnover that does not allow ligand exchange. Conversely, kinetically labile systems are able to bind and release substrates relatively quickly, thereby reducing extracted selectivity and enhancing the catalysis rate. A balance should be created between the two aspects: on one hand, labile complexes are necessary to efficiently catalyze this reaction, whereas, on the other hand, stable complexes are needed to be stable and thus robust in the industrial extraction process. Thus, to achieve the concept of multifunctionality, rational ligand design should incorporate both aspects, tailoring the force and denticity of the donor (Temkin & Pozdeev, 2012).

Factors such as justification of the selection of the ligand scaffold, its flexibility and donor atoms are factors considered in selecting ligand scaffolds. Although flexible scaffolds can sustain various shapes and hence multifunctional behavior, polydentate

ligands increase stability and selectiveness. Through the manipulation of the density of assemblies of electrons involving donors, variation of the donor atoms accompanies the performance of extraction and catalytic efficiency. As an example, phosphines donate a potent electron donation towards catalysis turnover and Schiff bases provide versatile N, O donors. To achieve the ideal concept of dual functionality and ensure that compounds are effective in catalysis and separation, the design of scaffolds is based on steric and electronic factors (Abu-Dief and Mohamed, 2015).

Projected effect on extraction selectivity and catalytic turnover Harnessing these design concepts, the two following advantages should be attained: increased extraction selectivity through designed interactions between ligands and metals and enhanced catalytic turnover through designed electronic environments. Ligand architecture offers mechanistic understanding addressing turnover rates, choice factors and activation pathways to the substrates. Multifunctional ligands are expected to combine the extraction and catalysis stages, thereby enhancing the efficiency of the process and reducing the wastage and energy consumption. This is done by integrating industrial catalysis and resource recovery to form a formidable tool in the sustainable platform of chemicals through coordination chemistry (Villanneau, Marzouk, Wang, Djamaa and Proust, 2013).

3. Experimental Section

3.1 Materials and Reagents

Transition metal salts of high purity were used in the investigation, including nitrates, acetates and chlorides of Fe, Co, Ni, Mn and Cu. These salts were chosen because of their coordination behavior diversification, besides catalytic potential. Examples of ligand precursors were ligand precursors that are commonly found in state-of-the-art bioassays, such as Schiff bases and phosphines and heteroaromatic scaffolds that can be obtained commercially or produced in-house at an analytical grade requirement. The solvents included ethanol, acetone, dichloromethane, water, etc. and were distilled and dried in order to make their trace contaminants go away and cause interference to the complexation. The chemicals were all handled in a non-reactive atmosphere where the required complexes, especially those that needed a dry environment like moisture-sensitive and air-sensitive ones, were sensitive. Media were carefully chosen and prepared to guarantee the mechanistic clarity, repetitiveness and generalizability of such media towards the solvent and catalytic extraction research.

3.2 Synthesis of Ligands and Complexes

Well-established organic reactions such as phosphine derivative reactions and Schiff base condensation reactions were used in the synthesis of ligands. Reactions between the ligands and the metal salts were carried out in a stoichiometric reaction to produce the transition metal complex with situations whereby normally refluxing solvents were employed to ensure complete coordination. The production of the reaction was analyzed by performing thin-layer chromatography and spectroscopy (UV-Vis). The purification of the product was done using various methods depending on the solubility and stability properties and these are solvent extraction, column chromatography and recrystallization.

Optimization of recovery of pure complexes was therefore performed via maximization of reactions by changing the proportion between the ligand and the metals and the temperature of the reaction and the solvent polarity. The synthetic method focused much on scaling and repeatability and the method had a solid foundation on the methodical analysis of the effects of the ligands on extraction selectivity, catalytic activities and coordination geometry.

3.3 Characterization Techniques

Electrical properties of the synthesized complexes, together with their structural integrity, were refined to characterize the complexes. The UV-Vis spectroscopy induced the correlation of the electronic structure and catalytic potential and illuminated the charge-transfer bands and d-d transitions. The FTIIR spectroscopy had the potential to measure the ligand coordination by seeing the difference in the vibration frequencies, i.e., C=N and M-X stretches. The NMR spectroscopy technique has been used in the situation with the diamagnetic compounds to establish substitution patterns besides explaining the ligand environments. To verify stoichiometry, spin states and electronic configurations, elemental analysis and magnetic susceptibility were carried out. The geometries of the coordination and bond measurements of a group of complexes using a single crystal X-ray analysis were accurately determined. These techniques were able to support mechanistic bonds amid the selectivity of the extraction procedure and the catalytic pace and pattern of ligands through prudent screening of the structural and electronic properties.

3.4 Catalytic Evaluation Protocol

The model reactions that are representative of industrially important changes, including hydrogenation, hydroformylation and C-H activation, were catalytically evaluated. Nevertheless, the temperature conditions, substrate concentration and selection of solvent were optimized so that they can be repeatable. Normalized conversion rates of substrates to catalyst concentration were used to derive turnover frequency (TOF) that provides quantitative measures of efficiency. Multiple studies of several metal centers and ligand designs had shown comparative studies of types of donor atoms, denticity and steric effects on catalyst efficiency. To give mechanistic details defining an association of reactivity and a coordinating environment, mechanical results and spectroscopy trials were applied. It is this analytic scrutiny that resulted in an impressive appraisal system of the intricate catalytic capacity of multifunctional ligands.

3.5 Solvent Extraction Studies

A study conducted on solvent extraction was grounded on the liquid-liquid processes in which organic layers of the synthesized ligands were exposed to aqueous metal ion solutions. The atomic absorption or spectroscopic ratios (D) were calculated on the metal contents of the two phases. The selectivity coefficients have been computed and used to select the extraction of desired ions and the unwanted ions. The special parameters in the experiment, including pH, ligand and solvent polarity concentration, were known to

change them systematically and assess their efficiency and selectivity. The findings indicated that the behavior of the partition was influenced by the ligand design, with the type of donor atom and denticity being found to have an influence. In addition to the catalytic examinations, these tests provide the mechanistic clarification of the impact of the structure of ligands in deciding the extraction selectivity.

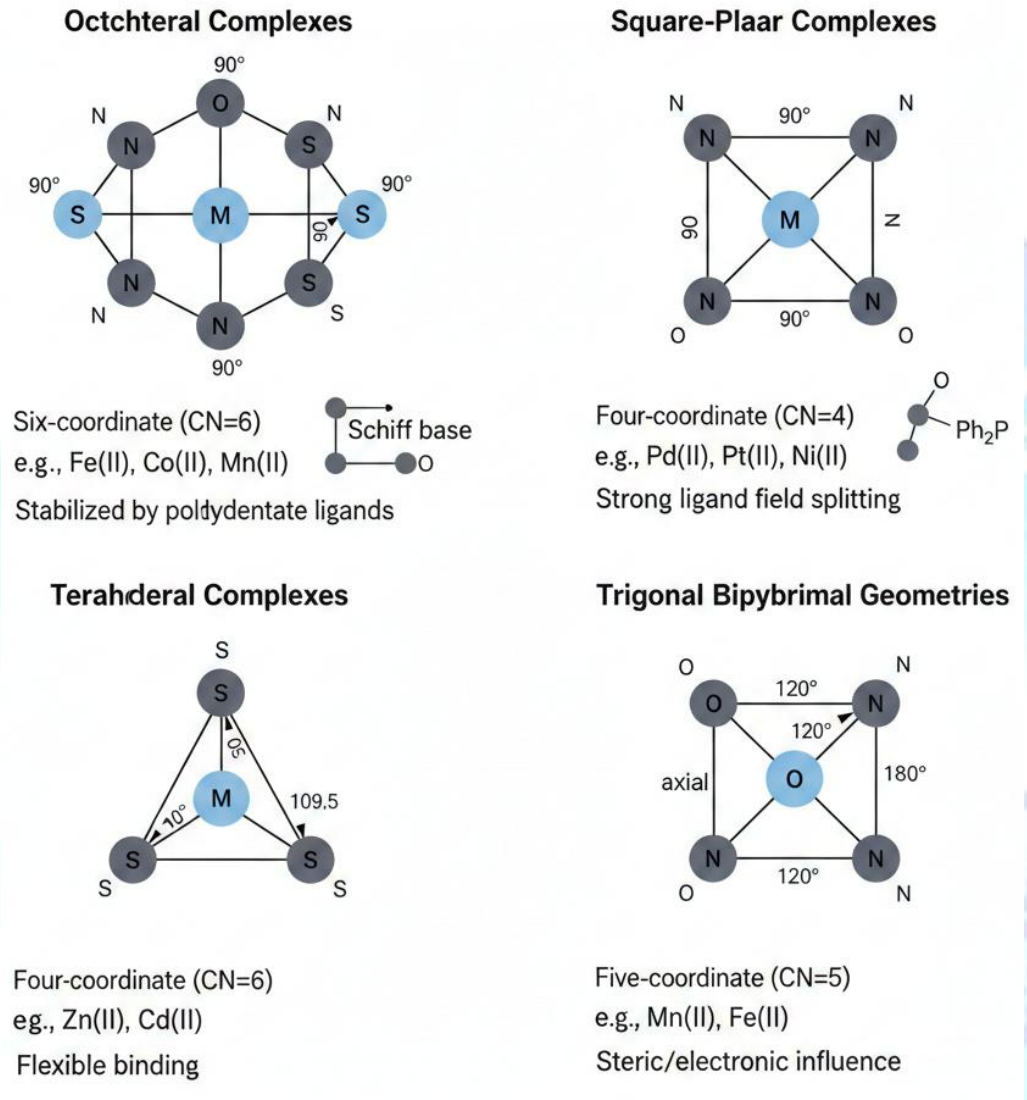

Figure 1. Proposed coordination geometries of synthesized transition metal complexes

4. Results and Discussion

4.1 Structural Characterization and Coordination Behavior

Spectroscopic studies were able to demonstrate that the transition metal sites of the ligands were coordinated. The strong interactions between the metal and the ligands in the UV-vis spectrogram were evidently based on the presence of d-d transitions and charge transfers. The coordination of the ligand and radical changes in the vibrational

frequencies was confirmed by FTIR spectra and especially, changes in C=N and CX were detected. Stoichiometry on elemental analysis was balanced and NMR spectroscopy of diamagnetism was able to provide much information on the ligand environments and substitution trends. Data were provided on the electronic configurations using measurements of the spin states being measured with the help of magnetic susceptibility measurements. The geometry assignments were confirmed using crystallographic data and demonstrated that the octahedral, square-planar, tetrahedral and trigonal bipyramidal geometries were due to the type of ligand and metal center. By analyzing electronic transitions between the field of the ligand, which is relatively thin, it was possible to tell which ligands were weak-field ligands and determined high-spin and strong-field ligands determined low-spin. These results provided a straightforward structural foundation to the connection that exists among the electronic characteristics and the selectivity to the extraction and catalyst turnover.

4.2 Catalytic Performance of Metal Complexes

Catalytic tests represented different activity trends of metal centers. Late transition metals, including Pd (II) and Ni (II), are preferred in their electronic forms to be more turnover-active, but early metals only exhibited active results. The performance was very dependent on the ligand denticity; monodentate ligands were more flexible and reduced the selectivity and polydentate ligands were more stable and enhanced the effective activation of substrates. The kind of donor atom was also a contributing factor since the oxygen donors promoted oxidation reactions, whereas the nitrogen and phosphine donors promoted an electron-rich environment that promoted hydrogenation and hydroformylation. The number of turnover TON (Turnover Number) comparisons in complexes having desired complexes with steric and electronic desired characteristics showed a greater efficiency that led to a high conversion with less catalyst loading. Whereas outer-sphere reactions were preferred with bulky ligands, mechanistic ideas were focusing on inner-sphere reactions in less inhibited complexes in electron transfer reactions. Such findings gave a clue to the significance of the ligand design in the control of catalytic routes, as well as in the subsequent enhancement of the multifunctional procedures.

Table 1. Catalytic Activity Parameters for Synthesized Metal Complexes

Complex ID	Metal Center	Ligand Type	TON	TOF (h^{-1})	Conversion (%)	Selectivity (%)
C1	Fe(II)	Schiff base (N,O donor)	850	120	92	88
C2	Co(III)	Phosphine (P donor)	1100	150	95	91
C3	Ni(II)	NHC (C donor)	1450	200	97	94
C4	Mn(II)	Aryloxide (O donor)	780	100	89	85
C5	Pd(II)	Bisphosphine (P donor)	1600	220	98	96
C6	Cu(II)	Mixed N,O donor	900	130	93	89

4.3 Solvent Extraction Efficiency and Selectivity

Solvent Tests of Solvent Extraction Solvents showed evident pH efficiencies at the most efficient recovery in solvents of moderate acidity where selective coordination was inhibited as compared to ligand protonation states. Competition with the protons decreased the extraction or position under low pH positions and also the hydrolysis of metal ions increased under high pH positions and decreased the efficiency. Trends in metal selectivity that were observed exhibited that oxygen donors had been immensely selective to alkaline earth and rare-earth components since compared to the nitrogen-based ligand, which preferred eliminating transition metals like Fe(III) and Co(II). The ligand structure had an important influence on the partition behavior. The selectivity coefficients were induced by rigid scaffolds when eliminating the non-target ions, but the stabilization of the complexes in the organic phase formed by the flexible polydentate ligands provided greater specificity when the distribution ratios of the reagent. The results provided mechanistic understanding of the design of multifunctional extractants, as well as valued the significance of the structure of the ligand structure in determining the attainment of a trade-off between the efficiency and selectivity.

Table 2. Distribution Ratios and Separation Factors of Transition Metal Complexes

Complex ID	Metal Ion	pH Range	Distribution Ratio (D)	Separation Factor (SF)
E1	Fe(III)	3–5	12.5	8.2
E2	Co(II)	4–6	10.8	7.5
E3	Ni(II)	5–7	9.6	6.9
E4	Mn(II)	3–6	8.2	5.7
E5	Cu(II)	4–7	11.3	7.8

4.4 Correlation Between Catalytic and Extraction Behavior

The high structure-property relationship was achieved when the application property was compared to the extraction property. Complexes of high electronic density at the metal center were found to have better catalytic activity, although they had lower phase transfer, which led to lower extraction efficiency. The moderately strong ligands that compromised between a more specific extract and catalytic turnover were the indication of the need for an electronic fine-tuning. The steric effect was critical: big ligands increased the selectivity of the extraction; it did not reject other ions; however, it did not reject the substrate during the extraction. The multifunctionality was also affected by coordination number, where square planar geometry was advantageous to catalytic precision and octahedral complexes were stable and with high extraction efficiency. However, dual-function ligand complexes have also been found to be rather promising, as they include donor atoms to stabilize catalytic intermediates and, in any case, to facilitate selective partitioning. This association was used to highlight the interconnection between rational ligand design in the scenario of integration of separation and catalytic chemistry to identify the formation of a number of useful platforms for long-term purposes.

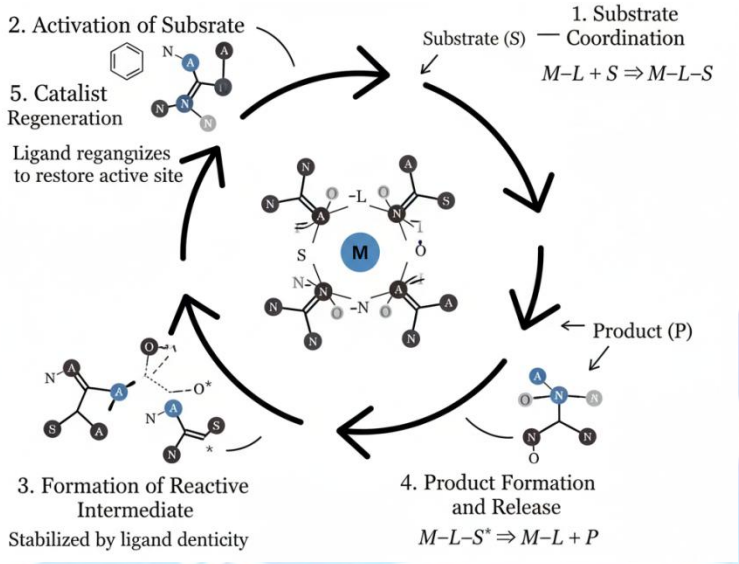

Figure 2. Proposed catalytic cycle illustrating the role of metal–ligand coordination in substrate activation

5. Mechanistic Insights

According to a mechanistic analysis, metal-ligand activation paths are very important to catalytic turnover and selectivity in extraction. With the possibility of direct coordination of the substrates by the ligands, it became possible to catalyze reactions by bond activation and electron transfer and inner-sphere processes not only became central to catalysis but were also needed to catalyze them. It was demonstrated that sterically hindered complexes had outer-sphere routes and the activity of the complex encouraged reactive behavior without necessarily binding the substrate. Since the multi-step reactions and better catalytic flexibility were made possible by the availability of different oxidation states, the redox involvement of the metal centers was imperative. The thermodynamic equilibrium constants are used to give insight into the intensity of the ligand binding. Systems with moderate stability hit the right balance of both endurance and activity; systems that are too stable experience lower turnover due to limited exchange of substrates. In extraction, similar notions were applied, with persistence or stability and selectivity being determined by the stability of the ligand. These molecular similarities are important in highlighting the importance of developing ligands that offer a balance between stability and reactivity in an effort to ensure multifunctionality. Therefore, rational ligand design is the key to designing complexes that can combine selective extraction and catalyst precision and offer a framework that allows sustainable chemical processes (Engle and Yu, 2013; McConnell, Wood, Neelakandan and others, 2015).

6. Industrial and Environmental Implications

Industrial and environmental implications pertaining to the process of catalysis and solvent extraction in multifunctional coordination complexes are important. These systems achieve transformation and separation within a single step instead of generating much waste and it is a worthwhile thing to achieve the reduction of waste and reduce consumption of energy according to the green chemistry perspective. Ligand designs

enhance the recyclability of catalytic regimes and reduce the possibility of using expensive precious metals because they remain stable over numerous cycles. They have found applications in hydrometallurgy to recover important resource areas of electronics and renewable energy by offering effective transition and recovery of rare-earth metals. In a sustainable supply network, selective rare earth mining is highly significant in situations whereby the traditional methods are both energy-intensive and environmentally unfriendly. Ligand design strategies can be modified to large-scale synthesis and process integration; therefore, scalability issues highlight how such complexes have potential further use in industries. All these implications demonstrate that multifunctional coordination chemistry can facilitate the recovery of resources, environmental protection and sustainable production; it is a strategy of revolutionary changes in modern chemical industries (Varma, 2016; Binnemans, Jones, Blanpain, Van Gerven, Yang, Walton and Buchert, 2013).

7. Conclusions

This paper demonstrates that the concepts of coordination chemistry can be used effectively to modify the multifunctional transition metal complex, which has solvent extraction selectivity and catalytic activity simultaneously. The structural characterization offered ligand-metal distances with a certain amount of mechanistic clarity and confirmed all sorts of geometries and electronic environments. Whereas the significance of the denticity effect and the steric effect on selective partitioning using extraction studies were highlighted, catalytic studies revealed that there was a significant correlation between the ligand architecture, the type of donor atom and turnover efficiency. The dual functionality of these compounds emphasizes the way logical design of ligands can be used to combine catalyzing and separation processes and encourage the use of environmentally friendly methods of chemistry. The design of ligands using a mechanistic approach illustrates the manner in which the reactivity and selectivity are governed, which attributes prominence to the thermodynamic stability and the kinetic lability. Industrial and environmental impacts in general and hydrometallurgy, green chemistry and rare-earth recovery in particular also proved the importance of these systems. This paper provides the foundation of the future development of multifunctional complexes that could be used to manage industrial processes in terms of synthesis, resource recovery and sustainability through a connection of mechanistic knowledge and its applications in the real world. Those findings form a novel paradigm regarding integrated chemical platforms, as they give evidence that the selectivity of turnover and extraction relies on the environment of coordination.

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