ABSTRACT
The thermodynamics of complexation and thermal properties of mixed ionic complexes of the types M(H$_2$L)X$_2$ and M(HL)X (where M = Fe(II), Fe(III), Co(III), Ni(II), and Cu(II), L = bis(2,2'-methylidene phenol) diaminoethane, and X = anions of the types Cl$^-$, NO$_3$-, SO$_4^{2-}$, ClO$_4$- or OH$^-$) prepared using extractive method have been investigated. Thermal decomposition of the transition metal complexes took place in two or three distinct steps in exothermic reaction up to 800°C. The heat capacity change ($\Delta C_p$), transition midpoint temperature ($T_m$), entropy change ($\Delta S_m$), calorimetric enthalpy ($\Delta H_m$), Gibbs free energy change ($\Delta G_m(T)$), denaturation enthalpy ($\Delta H_d(T)$) and denaturation entropy ($\Delta S_d(T)$) were calculated from the results of differential scanning calorimetry (DSC) while Vant Hoff thermodynamic properties was used to calculate the stability constants of the complexes in solution. It was found that the stability constants of the complexes follow the order Fe(II) > Fe(III) > Cu(II) > Ni(II) > Co(II) while the denaturation enthalpy and entropy of the complexes follow the order Ni(II) > Fe(II) > Fe(III) > Co(II) > Cu(II) respectively.

KEYWORDS: bis(2,2'-methylidene phenol) diaminoethane, transition metal complexes, thermal analysis, thermodynamic parameters.
H₂L complexes prepared using extractive techniques. In this work, spectral, thermodynamic and thermal methods were applied in the characterization of H₂L transition metal complexes which are very important in bioinorganic chemistry and applications.

2.0 MATERIALS AND METHODS
2.1 Reagents and equipment.
Analytical grade reagents (Merck, Germany) were used without further purification unless otherwise mentioned. All aqueous solutions were prepared in distilled water and working solutions prepared by dilution as required. Bis(2,2'-methylene phenol) diaminoethane (H₂L) shown in figure 1 was prepared as reported elsewhere [20]. Stock solutions of Fe(II), Fe(III), Co(II), Ni(II) and Cu(II) were prepared using (NH₄)₂SO₄, FeSO₄·6H₂O, Fe₂(SO₄)₃·9H₂O, CoCl₂·6H₂O, NiSO₄·7H₂O and CuSO₄·5H₂O (Merck, Analar grade). Stock solutions of mineral acids (HCl, HNO₃ and H₂SO₄) were prepared by diluting the concentrated acids and were standardized using appropriate standard bases.

Electronic spectra of the ligand and complexes in chloroform solution were obtained on Jenway UV – Vis spectrophotometer model 6105. DSC analysis (Thermal degradation pattern) was determined using NETZSCHDTA 404PC Differential scanning calorimeter. Metal-ligand mole ratio was determined using jobs method of continuous variation as described elsewhere [21]. Microanalysis of the ligand and complexes were done at the Department of Chemistry, Rhodes University, South Africa.

2.2. Synthesis of metal complexes
An aliquot of a sample solution containing 100μg each of Fe(II), Fe(III), Cu(II), Ni(II) and Co(II) was transferred into a 20 mL calibrated extraction bottle and volume was made up to 5 mL with acid solution of concentration 0.0001M. This was followed with the addition of 0.5mL of ligand solution. 5 minutes for colour development was allowed and complexes formed extracted with 5 mL chloroform. The organic extracts were allowed to dry and product recrystallized using carbon tetrachloride, dried and characterized (M.P >250°C for Fe(II) while for Fe(III), Cu(II), Ni(II) and Co(II) M.P >300°C).

2.3 Thermal Analysis Using Differential Scanning Calorimeter
The sample and reference pan were placed at separate furnaces maintained by separate heaters. Both sample and reference were maintained at same temperature and the difference in thermal power required maintaining them at the same temperature measured and plotted as a function of temperature or time. Differential heat flow was due to heat capacity associated with heating the sample. Small samples (5.00 mg) were weighed into an aluminia crucible and mass noted. The crucible was covered with its cover usually slightly smaller. The TA Blue DSC sample press was used to close the crucible. The enclosed sample was placed side by side with the empty aluminia crucible as reference. The instrument was purged with ultra pure N₂ gas at regulated pressure between 100 and 140 Kpa guage (15 and 20 Psi). The gas flow rate was set at 50 mL per min and experiment run from room temperature to 800°C at scan rate of 10°C min.

3.0 RESULTS AND DISCUSSION
3.1 UV-Vis Data and metal-ligand mole ratio.
Electronic spectrum of the Ni(II)H₂BMPDE complex exhibited three bands in the region 24691cm⁻¹ assignable to 1A₁g → 1T₂g and 33898 and 38462 cm⁻¹ due to charge transfer transitions respectively notable in square planar environment for Ni(II) ion [22]. The absence of bands around 10120-11605, 16062-16180 and 25210 - 25575 cm⁻¹ assignable to, 3A₂g(F) → 3T₂g(F) 3A₂g(F) → 3T₁g(F) and 3A₂g(F) → 3T₁g(P) respectively are due to charge transfer transitions from ligand to Ni(II) ion [23-25].

Figure 1: Synthesis of the ligand H₂L
The electronic spectrum of cobalt (II) oxidized to Co(III) complex a d⁶ ion consists of three bands in the region 25000, 29851 and 38462 cm⁻¹. The appearance of the band in the region 25000 cm⁻¹ assignable to 4A₂g → 2T₁g(F) indicated distorted octahedral geometry around the cobalt(II) ion whereas the band in the region 29851 and 38462 cm⁻¹ are due to charge transfer transitions [26-27]. Similarly the broad band region of the electronic spectra of Co³⁺, a d⁶ covering the long wavelength region 335-400 nm was assigned to an octahedral 3A₂g → 2T₁g(F) transition [28].

For Cu²⁺ ion a d⁹, a band displayed in the electronic spectrum in the region of 28571 cm⁻¹ characteristic of 2B₁g → 2E₉ transitions was typical of a distorted octahedral geometry. The 2E₉ and 2B₁g states of d⁹ octahedral copper (II) ion splits up under the influence of octahedral field (tetragonal distortion). The distortion can cause three transitions 2B₁g → 2A₁g, 2B₁g → 2B₉ and 2B₁g → 2E₉ typical of distorted octahedral geometry [29]. The electronic spectra of Fe³⁺ H₂BMPDE a d⁷ ion consist of three bands in the region of 43478, 37037 and 23529 cm⁻¹. The band at 23529 cm⁻¹ assignable to 6A₁g → 4T₁g G(c) suggested distorted octahedral geometry [30-31]. The other band 43478 and 37037 cm⁻¹ are due to charge transfer transition [26,31]. The electronic spectra of Fe³⁺ H₂BMPDE a d⁷ ion consists of three bands in the region 30762, 40000 and 47619 cm⁻¹. The band at 30762 cm⁻¹ was assigned to 4A₂g → 2T₁g(F) indicating distorted octahedral geometry of Fe(II) ion (El-Gamel, 2012). The band at 40000 and 47619 cm⁻¹ are due to charge transfer transitions [22]. The metal-ligand mole ratio as determined from jobs plot indicated 1:1 stoichiometry for all the transition metal complexes and similar observations have been made [32] with related derivatives.

3.2 Thermodynamics of Complexation

The Vant Hoff thermodynamic properties of H₂L and HL complexes are shown in table I. Entropy and enthalpy changes were positive for all the complexes. The stability constants of the complexes increased in the order Fe(II) > Fe(III) > Cu(II) > Ni(II) > Co(II).

The complexation process increased as temperature increased for all the metal ions until at a maximum of about 35 °C. The increased complexation of the metal ions to the ligand at relatively high temperatures (between 20-35 °C) showed that the complexation process may be endothermic [33]. From table II, Gibb’s free energy change values were found to be negative indicating the feasibility and spontaneity of the complexation. The positive sign of enthalpy change confirmed that the complexation process was endothermic. The negative value of entropy change showed that the complexation involved solvation process [34]. Similarly the values of stability constants indicated that iron (II) and iron (III) metal ion complexes are more stable than others [34]. The thermodynamic parameters of complexation such as enthalpy (ΔH⁰), entropy (ΔS⁰), Gibb’s free energy (ΔG⁰) and stability constant (βn) are listed in table I and are calculated from the variation of the thermodynamic equilibrium constant, K₀ at different temperatures as shown in equation 1.

\[ K₀ = \frac{C₁}{C₂} \] …………………………………………1

C₁ is the amount of metal ion complexed per unit mass of ligand and C₂ the concentration of metal ion in the aqueous phase [33].

The standard enthalpy change of complexation (ΔH⁰), the standard entropy change of complexation (ΔS⁰), and Gibb’s free energy of complexation (ΔG⁰) and stability constant for complexation (βn) were calculated as shown in equation 2, 3 and 4.

\[ \ln K₀ = \frac{ΔS⁰}{R} - \frac{ΔH⁰}{RT} \quad (Vant \ Hoff \ plot) \] …………………2

\[ ΔG⁰ = -RT\ln K₀ \] …………………………………………3

\[ ΔG⁰ = -2.303RT\beta_n \] …………………………………………4

Thus, T represents the temperature in K while R is the universal gas constant (KJ Mol⁻¹k⁻¹). The thermodynamic values are given in Table 2.
3.4 Kinetics of complexation

The kinetics of complexation of metal ions to the ligand (H\textsubscript{2}L) at different contact time (1, 3, 5, 10 and 15 minutes) and at constant ligand and acid concentration of 0.5 % and 10\textsuperscript{-4} M respectively was performed. Contact time of 10, 5, 10, 10 and 5 mins was sufficient to achieve equilibrium for iron (III), iron(II), cobalt(II), nickel(II) and copper(II) metal ions complexation with H\textsubscript{2}L ligand respectively. The commonly used kinetic models were applied on the complexation data the Lagergren pseudo-first –order model and pseudo-second –order shown in equations 5 and 6 respectively.

\[ \ln(qe - qt) = \ln qe - k_1t \]

\[ \frac{t}{qt} = \frac{1}{K_2} qe^2 + \frac{t}{qe} \]

\[ qe \] is the amount of metal ion complexed with ligand at equilibrium (µg) and \[ qt \] is the amount (µg) of metal complexed at time \[ t \] (min) whereas \[ K_1 \] and \[ K_2 \] are rate constants of pseudo-first order and second –order models respectively. A linear plot of \[ \ln(qe-qt) \] versus \[ t \] for Pseudo-first –order model and \[ t/qt \] versus \[ t \] for second –order –model clearly described the relevance of the models with the slopes as \[ K_1 \] and \[ K_2 \] respectively. Based on the high regression coefficient of the metal ions complexation on the ligand as shown from the pseudo-second –order kinetic model (\[ R^2 =0.9984, 0.9993, 0.9948, 0.9983, 0.9994 \] for iron(II), iron (III), cobalt(II), nickel(II) and copper(II) respectively in relation with pseudo-first –order kinetic model (\[ R^2=0.6634, 0.6102, 0.3382, 0.383 \) and \[ 0.6118 \] for iron(II), iron (III), cobalt(II), nickel(II) and copper(II) respectively), the complexation was best described by the Pseudo –second –order kinetic model.

### Table 1: Vant Hoff Thermodynamic Parameters of H\textsubscript{2}L and HL complexes

| Metal Complexed | T(K) | logK\textsubscript{a} | BH | \( \Delta G \) (KJ Mol\textsuperscript{-1}) | \( \Delta H \) (KJ Mol\textsuperscript{-1}) | \( \Delta S \) (KJ Mol\textsuperscript{-1}K\textsuperscript{-1}) |
|-----------------|-----|---------------------|----|------------------|------------------|------------------|
| Fe(III)         | 288 | 4.59                | 1.813 | -10.99 | 20187.85 | -52.406 |
|                 | 293 | 2.43                | 1.055 | -5.919  |          |        |
|                 | 298 | 0.559               | 0.243 | -1.385  |          |        |
|                 | 303 | 0.198               | 0.086 | -0.498  |          |        |
| Fe(II)          | 288 | 4.18                | 1.814 | -10.00  | 5462.11 | -65.63 |
|                 | 293 | 4.056               | 1.76  | -9.88   |          |        |
|                 | 293 | 3.94                | 1.71  | -9.76   |          |        |
|                 | 303 | 3.17                | 1.38  | -7.98   |          |        |
|                 | 308 | 3.112               | 1.35  | -7.96   |          |        |
|                 | 313 | 2.94                | 1.27  | -7.65   |          |        |
| Ni(II)          | 288 | 3.17                | 1.38  | -7.59   | 1155.74 | -0.1817 |
|                 | 293 | 3.10                | 1.35  | -7.55   |          |        |
|                 | 293 | 3.00                | 1.30  | -7.55   |          |        |
|                 | 303 | 2.90                | 1.26  | -7.43   |          |        |
|                 | 308 | 2.923               | 1.27  | -7.48   |          |        |
|                 | 313 | 2.923               | 1.27  | -7.60   |          |        |
| Co(II)          | 288 | 2.495               | 1.08  | -5.97   | 14680.49 | -47.51 |
|                 | 293 | 2.429               | 1.05  | -5.97   |          |        |
|                 | 293 | 2.31                | 0.985 | -5.62   |          |        |
|                 | 303 | 0                   | 0     | 0       |          |        |
| Cu(II)          | 288 | 3.66                | 1.59  | -8.76   | 7654.36 | -22.50 |
|                 | 293 | 3.47                | 1.506 | -8.45   |          |        |
|                 | 293 | 2.99                | 1.298 | -7.41   |          |        |
|                 | 303 | 2.09                | 0.906 | -5.26   |          |        |
|                 | 308 | 2.034               | 0.8817| -5.20   |          |        |
|                 | 313 | 1.967               | 0.854 | -5.12   |          |        |

**Legend:** \( T= \) temperature, \( \beta_n= \) stability constant, \( \Delta G^0= \) Gibb’s free energy.
### 3.5 DSC studies

| Metal complex | T    | T<sub>m</sub> | ΔH<sup>0</sup><sub>m</sub> (J/K) | ΔC<sub>p</sub> (°C) | ΔS<sup>0</sup><sub>m</sub> (J/K) | ΔGo (T) (kJ/mol) | ΔH<sup>0</sup> (T) (kJ/mol) | ΔS<sup>0</sup> (T) (kJ/mol) |
|---------------|------|--------------|-------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Fe<sup>3+</sup> HL | 317.7 | 302.1        | 235                           | 34.1            | 0.778           | -0.034          | 766.96          | 2.49            |
|              | 425.4 | 405.2        | 138.4                         | 34.9            | 0.342           | -0.178          | 843.38          | 2.04            |
|              | 783.6 | 776.9        | 880.2                         | 8.6             | 1.13            | 2.103           | 937.82          | 1.20            |
| Fe<sup>3+</sup> HL | 109.2 | 98.1         | -49.62                        | 23.9            | -0.506          | 0.019           | 220.45          | 2.055           |
|              | 290   | 275.4        | 536.2                         | 40.9            | 1.95            | -0.83           | 1133.3          | 4.06            |
|              | 811.1 | 802.4        | 108.6                         | 18.9            | 0.135           | 0.276           | 273.03          | 0.338           |
| Ni<sup>2+</sup> HL | 146.4 | 141.4        | 31.24                         | 13.7            | 0.221           | -0.009          | 99.74           | 0.697           |
|              | 509.2 | 496.1        | -101.8                        | 19.4            | -0.205          | -0.099          | 152.34          | 0.300           |
|              | 617.6 | 573.1        | 576.7                         | 55.5            | 1.006           | 0.161           | 3046.4          | 5.156           |
|              | 842.2 | 836.6        | 444.66                        | 14.1            | 0.531           | 0.365           | 523.56          | 0.623           |
| Co<sup>2+</sup>L | 117.8 | 124.8        | -181.3                        | 12.8            | -1.45           | -0.34           | 270.9           | 0.711           |
|              | 519.2 | 505.6        | 234                           | 29.1            | 0.46            | 1.424           | 874.27          | 1.427           |
|              | 626.3 | 601.6        | 106.1                         | 31.1            | 0.176           | 0.218           | 700.45          | -1.036          |
|              | 667.3 | 695.4        | 269                           | 34.5            | 0.387           | 0.119           |                  |                 |
| Cu<sup>2+</sup>L | 345.6 | 332.3        | 166.9                         | 19.6            | 0.502           | 0.085           | 427.58          | 1.27            |
|              | 539.1 | 545.2        | 10.7                          | 8.8             | 0.019           | 0.341           | -42.98          | -0.08           |
|              | 623.2 | 619.6        | 54.81                         | 37.4            | 0.088           | 0.285           | 189.45          | 0.304           |
|              | 792.2 | 802.7        | 36.8                          | 51.1            | 0.046           | -0.124          | -499.75         | -0.626          |

| Table 2 : Thermodynamic Data on the DSC Decomposition of H<sub>2</sub>L and HL Complexes. |

The DSC curve for Fe<sup>2+</sup>HL, Cu<sup>2+</sup>HL, Co<sup>2+</sup>H<sub>L</sub>, Fe<sup>3+</sup>HL and Ni<sup>2+</sup>HL was subdivided into two, three, two and three main exothermic stages respectively as shown in table II. The thermal degradation patterns could have been due to loss of hydroxyl group, loss of component attached to the phenolic moiety, ligand degradation or decomposition and final decomposition to metal oxide. For Fe<sup>3+</sup>HL, the weak endothermic peak at 98.1 °C corresponds to morphology transformation or loss of hydroxyl group or smaller fragment [35] while the sharp endothermic peak at 275.4 °C corresponds to the melting point of the complex. This was followed by a strong exothermic peak at 802.4 °C corresponding to the decomposition of the complex. For Cu<sup>2+</sup>HL, the DSC thermogram showed single sharp endothermic peak at 332.3 °C corresponding to the melting point of the complex. This was followed by three exothermic peaks at 545.2, 619.6 and 802.7 °C corresponding to the stepwise decomposition of the complex. The DSC curve of Fe<sup>3+</sup>HL showed three peaks, one of the peaks corresponds to endothermic process while two corresponds to exothermic processes. The sharp endothermic peak at 302.1 °C corresponds to the melting point of the complex whereas the broad peaks at 405.2 °C and 776.9 °C corresponds to stepwise decomposition of the complex. The DSC curve of Ni<sup>2+</sup>HL showed four peaks, 141.4 °C, 496.1 °C, 573.1 °C and 836.6 °C. The first weak endothermic peak (141.4 °C) corresponds to morphological transformation while the second sharp endothermic peak 496.1 °C corresponds to the melting point of the complex. The last two peaks at 573.1 °C and 836.6 °C corresponds to stepwise decomposition of the complex. The DSC curve of Co<sup>2+</sup>H<sub>L</sub> showed four peaks. The first weak endothermic peak at 124.8 °C corresponds to morphological transformation while the second sharp endothermic peak 505.6 °C corresponds to melting point of the complex. The last two broad exothermic peaks at 601.6 °C and 695.4 °C correspond to stepwise decomposition of the complex.

Calculations from DSC data as shown in table II, presented negative values of ΔS at some steps indicating the reactions are slower than expected thereby establishing nonspontaneous nature of the reaction. Positive value
The complexation which indicated formation of mixed ionic complexes was nonspontaneous and the DSC decomposition of the complexes have shown their degrees of biochemical stability.

CONCLUSION
In conclusion, the thermal properties of the complexes of H$_2$L synthesized using extractive technique have been critically studied. The complexation which indicated formation of mixed ionic complexes was nonspontaneous and the DSC decomposition of the complexes have shown their degrees of biochemical stability.
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