

## Synthesis and structural studies of bis(macrocyclic) dimetal (II) complexes based on 14-18 membered pentaaza unit

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Bis(macrocyclic) binuclear metal complexes of the type  $[M_2LCl_4]$  [where  $M = Fe(II)$ ,  $Co(II)$ ,  $Ni(II)$ ,  $Cu(II)$  and  $Zn(II)$ ;  $L = L_1 - L_6$ ] have been synthesised by the template condensation reaction of ethylenediamine or 1, 3-diaminopropane, with formaldehyde, benzidine and acetylacetone or dibenzoylmethane or phthalaldehyde in 4:4:1:2 molar ratio. All these complexes have been characterized by elemental analysis, IR,  $^1H$  NMR, EPR and UV/VIS and conductivity data as well as magnetic susceptibility measurements. An octahedral geometry is suggested for all the complexes.

A large number of binuclear macrocyclic complexes have been synthesised where one of the metals exhibit coordinative saturation and the other acts as coordinatively unsaturated site<sup>1</sup>. Such type of complexes have been largely employed for the redox behaviour accompanying dioxygen binding to metals. The preparation of bis macrocyclic N-donor ligands with binucleating properties towards transition metals has attracted much interest and the variety of systems have been reported<sup>2-4</sup>. Recent studies proved that bis cyclams are a better electrocatalyst than those of the corresponding mononuclear species<sup>5,6</sup>. Several articles have been reported in recent years on the coordination chemistry of bis macrocyclic molecules in which two potentially coordinating tetraaza subunits are linked together by bridging the amine nitrogen or carbon atom of the ligands backbone<sup>7,8</sup>.

Our interest was to generate a rare situation where both macrocyclic rings are far away from each other in which the two proximate metal centers act as independently as possible especially with regard to the magnetic behaviour. We have recently reported the synthesis and characterization of various mononuclear cyclam<sup>9</sup>, dioxo cyclam<sup>10</sup> and other related<sup>11,12</sup> polyazamacrocyclic systems. In this note we report the synthesis of a new series of bis macrocyclic complexes where both the tetraaza units are bridged through the nitrogen of the benzidine moiety.

### Materials and Methods

The metal salts, ethylenediamine, 1, 3-diaminopropane and formaldehyde were purchased from

E. Merck. Benzidine was purchased from SD's fine chemicals.

### Synthesis of complexes

*Tetrachloro*[1,1'-phenylbis(1,3,6,10,13-pentaazacyclotetradecane-7,9-dimethyl-6,9-diene)]dimetal(II) and *tetrachloro*[1,1'-phenyl bis(1,3,7,11,15-pentaazacyclohexadecane-8, 10-dimethyl-7, 10-diene)]dimetal(II),  $[M_2L_1Cl_4]$  and  $[M_2L_2Cl_4]$  [ $M = Fe(II)$ ,  $Co(II)$ ,  $Ni(II)$ ,  $Cu(II)$  and  $Zn(II)$ ]

To a stirred methanolic solution of benzidine (0.01 mol) taken in a two-necked round bottomed flask was added simultaneously, formaldehyde (0.04 mol) and ethylenediamine or 1, 3-diaminopropane (0.04 mol) followed by the addition of methanolic solution of metal salts (0.02 mol). The resulting mixture was kept on stirring for 2 h and finally acetylacetone (0.02 mol) was added to the reaction vessel where a change in colour of the solution was noticed. Furthermore, the reaction mixture was refluxed for 7 h. The resultant product obtained was filtered, washed with methanol and dried *in vacuo*.

*Tetrachloro*[1,1'-phenyl bis(1, 3, 6, 10, 13-pentaazacyclotetradecane-7, 9-diphenyl-6, 9-diene)]dimetal(II) and *tetrachloro*[1,1'-phenyl bis(1, 3, 7, 11, 15-pentaazacyclohexadecane-8, 10-diphenyl-7, 10-diene)]dimetal(II),  $[M_2L_3Cl_4]$  and  $[M_2L_4Cl_4]$  [ $M = Fe(II)$ ,  $Co(II)$ ,  $Ni(II)$ ,  $Cu(II)$  and  $Zn(II)$ ].

These compounds were prepared by adopting the same procedure as stated above. Here, instead of acetylacetone dibenzoylmethane (0.02 mol) was added.

Table 1—Characterization data of the complexes

| Compounds<br>Colour                                                   | M.Pt<br>(°C) | $\Lambda_M$<br>$\text{cm}^2\Omega^{-1}\text{mol}^{-1}$ | Found (Calc.), % |              |                |                |                | $\mu_{\text{eff}}$<br>(BM) | Electronic<br>spectral data<br>$\lambda_{\text{max}}$ ( $\text{cm}^{-1}$ ) |
|-----------------------------------------------------------------------|--------------|--------------------------------------------------------|------------------|--------------|----------------|----------------|----------------|----------------------------|----------------------------------------------------------------------------|
|                                                                       |              |                                                        | C                | H            | N              | M              | Cl             |                            |                                                                            |
| [Fe <sub>2</sub> L <sub>1</sub> Cl <sub>4</sub> ]<br>Brick red        | 341          | 11                                                     | 47.5<br>(47.8)   | 5.8<br>(6.1) | 16.1<br>(16.4) | 13.3<br>(13.2) | 16.1<br>(16.5) | 5.60                       | 11,600                                                                     |
| [Co <sub>2</sub> L <sub>1</sub> Cl <sub>4</sub> ]<br>Orange           | 238          | 20                                                     | 47.2<br>(47.5)   | 5.6<br>(6.0) | 15.5<br>(16.0) | 13.3<br>(13.7) | 16.4<br>(16.5) | 4.05                       | 22,300<br>14,200                                                           |
| [Ni <sub>2</sub> L <sub>1</sub> Cl <sub>4</sub> ]<br>Brown            | 320          | 13                                                     | 47.0<br>(47.5)   | 5.8<br>(6.0) | 15.8<br>(16.3) | 13.0<br>(13.6) | 16.1<br>(16.6) | 3.11                       | 27,600<br>20,500<br>11,250                                                 |
| [Cu <sub>2</sub> L <sub>1</sub> Cl <sub>4</sub> ]<br>Dark brown       | 295          | 24                                                     | 49.5<br>(49.9)   | 5.6<br>(5.9) | 16.1<br>(16.0) | 14.2<br>(14.6) | 16.5<br>(16.3) | 1.70                       | 20,500<br>16,350                                                           |
| [Zn <sub>2</sub> L <sub>1</sub> Cl <sub>4</sub> ]<br>White            | 311          | 13                                                     | 46.0<br>(46.5)   | 5.5<br>(5.9) | 15.6<br>(15.9) | 15.1<br>(15.5) | 16.0<br>(16.2) | —                          | —                                                                          |
| [Fe <sub>2</sub> L <sub>2</sub> Cl <sub>4</sub> ]<br>Red              | 278          | 15                                                     | 50.0<br>(50.1)   | 6.2<br>(6.6) | 15.0<br>(15.4) | 12.2<br>(12.3) | 15.1<br>(15.6) | 5.41                       | 11,400                                                                     |
| [Co <sub>2</sub> L <sub>2</sub> Cl <sub>4</sub> ]<br>Yellowish brown) | 262          | 18                                                     | 49.2<br>(49.8)   | 6.4<br>(6.5) | 15.1<br>(15.3) | 12.5<br>(12.7) | 15.2<br>(15.5) | 4.23                       | 21,900<br>13,800                                                           |
| [Ni <sub>2</sub> L <sub>2</sub> Cl <sub>4</sub> ]<br>Grey             | 296          | 10                                                     | 49.5<br>(49.8)   | 6.4<br>(6.6) | 15.0<br>(15.3) | 12.6<br>(12.8) | 15.3<br>(15.5) | 3.10                       | 27,800<br>20,000<br>11,150                                                 |
| [Cu <sub>2</sub> L <sub>2</sub> Cl <sub>4</sub> ]<br>Green            | 319          | 20                                                     | 49.0<br>(49.3)   | 6.1<br>(6.4) | 14.8<br>(15.1) | 13.5<br>(13.7) | 15.1<br>(15.3) | 1.61                       | 20,100<br>16,200                                                           |
| [Zn <sub>2</sub> L <sub>2</sub> Cl <sub>4</sub> ]<br>Cream            | 171          | 16                                                     | 48.3<br>(48.8)   | 6.0<br>(6.4) | 14.7<br>(14.9) | 15.0<br>(15.2) | 14.2<br>(14.6) | —                          | —                                                                          |
| [Fe <sub>2</sub> L <sub>3</sub> Cl <sub>4</sub> ]<br>Reddish brown    | 272          | 19                                                     | 58.4<br>(58.8)   | 5.0<br>(5.4) | 12.2<br>(12.7) | 10.0<br>(10.2) | 12.3<br>(12.9) | 5.39                       | 11,800                                                                     |
| [Co <sub>2</sub> L <sub>3</sub> Cl <sub>4</sub> ]<br>Brown            | 220          | 21                                                     | 58.1<br>(58.5)   | 5.2<br>(5.4) | 12.2<br>(12.6) | 10.2<br>(10.6) | 12.4<br>(12.8) | 4.11                       | 21,600<br>14,300                                                           |
| [Ni <sub>2</sub> L <sub>3</sub> Cl <sub>4</sub> ]<br>Dark grey        | 286          | 12                                                     | 58.1<br>(58.4)   | 5.0<br>(5.4) | 12.3<br>(12.6) | 10.1<br>(10.5) | 12.3<br>(12.8) | 3.05                       | 27,850<br>20,600<br>11,150                                                 |
| [Cu <sub>2</sub> L <sub>3</sub> Cl <sub>4</sub> ]<br>Light green      | 252          | 22                                                     | 57.7<br>(58.0)   | 5.0<br>(5.3) | 12.1<br>(12.5) | 11.2<br>(11.4) | 12.5<br>(12.7) | 1.60                       | 19,800<br>16,400                                                           |
| [Zn <sub>2</sub> L <sub>3</sub> Cl <sub>4</sub> ]<br>White            | 211          | 16                                                     | 57.2<br>(57.5)   | 5.0<br>(5.3) | 12.0<br>(12.4) | 12.0<br>(12.2) | 12.2<br>(12.6) | —                          | —                                                                          |
| [Fe <sub>2</sub> L <sub>4</sub> Cl <sub>4</sub> ]<br>Red              | 265          | 17                                                     | 63.3<br>(63.8)   | 5.0<br>(5.3) | 12.0<br>(12.4) | 11.8<br>(12.2) | 12.2<br>(12.6) | 5.45                       | 11,500                                                                     |
| [Co <sub>2</sub> L <sub>4</sub> Cl <sub>4</sub> ]<br>Pink             | 226          | 21                                                     | 63.0<br>(63.4)   | 4.8<br>(5.2) | 10.5<br>(10.9) | 8.9<br>(9.2)   | 10.7<br>(11.2) | 4.20                       | 22,000<br>14,100                                                           |
| [Ni <sub>2</sub> L <sub>4</sub> Cl <sub>4</sub> ]<br>Grey             | 263          | 15                                                     | 63.2<br>(63.5)   | 5.0<br>(5.3) | 10.2<br>(10.9) | 8.8<br>(9.2)   | 10.5<br>(11.1) | 3.15                       | 27,700<br>20,200<br>11,200                                                 |
| [Cu <sub>2</sub> L <sub>4</sub> Cl <sub>4</sub> ]<br>Bluish green     | 275          | 19                                                     | 62.5<br>(62.9)   | 4.8<br>(5.2) | 10.5<br>(10.8) | 9.6<br>(9.8)   | 10.7<br>(11.0) | 1.59                       | 19,900<br>16,200                                                           |

Contd.

Table 1—Characterization data of the complexes

| Compounds<br>Colour                                               | M.Pt<br>(°C) | $\Lambda_M$<br>$\text{cm}^2\Omega^{-1}\text{mol}^{-1}$ | Found (Calc.), % |              |                |                |                | $\mu_{\text{eff}}$<br>(BM) | Electronic<br>$\lambda_{\text{max}}$ ( $\text{cm}^{-1}$ ) |
|-------------------------------------------------------------------|--------------|--------------------------------------------------------|------------------|--------------|----------------|----------------|----------------|----------------------------|-----------------------------------------------------------|
|                                                                   |              |                                                        | C                | H            | N              | M              | Cl             |                            |                                                           |
| [Zn <sub>2</sub> L <sub>4</sub> Cl <sub>4</sub> ]<br>Light violet | 220          | 12                                                     | 62.0<br>(62.5)   | 4.9<br>(5.1) | 10.6<br>(10.7) | 10.0<br>(10.6) | 10.3<br>(10.9) | —                          | —                                                         |
| [Fe <sub>2</sub> L <sub>5</sub> Cl <sub>4</sub> ]<br>Dark red     | 241          | 17                                                     | 51.9<br>(52.1)   | 4.7<br>(5.2) | 14.8<br>(15.2) | 11.6<br>(12.0) | 15.0<br>(15.4) | 5.50                       | 11,400                                                    |
| [Co <sub>2</sub> L <sub>5</sub> Cl <sub>4</sub> ]<br>Orange brown | 252          | 15                                                     | 51.4<br>(51.7)   | 4.8<br>(5.1) | 14.6<br>(15.1) | 12.2<br>(12.7) | 15.0<br>(15.3) | 4.15                       | 22,100<br>14,300                                          |
| [Ni <sub>2</sub> L <sub>5</sub> Cl <sub>4</sub> ]<br>Green        | 278          | 23                                                     | 51.6<br>(51.8)   | 4.9<br>(5.2) | 14.5<br>(15.1) | 12.2<br>(12.6) | 15.0<br>(15.3) | 3.25                       | 27,650<br>20,100<br>11,150                                |
| [Cu <sub>2</sub> L <sub>5</sub> Cl <sub>4</sub> ]<br>Grey         | 238          | 20                                                     | 49.6<br>(51.2)   | 4.7<br>(5.1) | 14.6<br>(14.9) | 13.3<br>(13.5) | 14.6<br>(15.1) | 1.65                       | 20,300<br>16,400                                          |
| [Zn <sub>2</sub> L <sub>5</sub> Cl <sub>4</sub> ]<br>Light cream  | 205          | 15                                                     | 49.8<br>(50.1)   | 4.4<br>(5.0) | 14.6<br>(14.8) | 14.3<br>(14.5) | 14.4<br>(14.9) | —                          | —                                                         |
| [Fe <sub>2</sub> L <sub>6</sub> Cl <sub>4</sub> ]<br>Red          | 297          | 11                                                     | 53.7<br>(53.9)   | 5.2<br>(5.7) | 14.0<br>(14.3) | 11.3<br>(11.4) | 14.1<br>(14.5) | 5.56                       | 11,700                                                    |
| [Co <sub>2</sub> L <sub>6</sub> Cl <sub>4</sub> ]<br>Dark pink    | 275          | 19                                                     | 53.4<br>(53.6)   | 5.5<br>(5.7) | 14.0<br>(14.2) | 11.6<br>(11.9) | 14.2<br>(14.4) | 4.18                       | 22,200<br>14,000                                          |
| [Ni <sub>2</sub> L <sub>6</sub> Cl <sub>4</sub> ]<br>Green        | 265          | 15                                                     | 53.5<br>(53.7)   | 5.3<br>(5.6) | 14.0<br>(14.2) | 11.5<br>(11.9) | 14.2<br>(14.5) | 3.09                       | 27,800<br>20,300<br>11,250                                |
| [Cu <sub>2</sub> L <sub>6</sub> Cl <sub>4</sub> ]<br>Grey         | 250          | 12                                                     | 52.6<br>(53.1)   | 5.4<br>(5.6) | 13.7<br>(14.0) | 12.6<br>(12.8) | 14.0<br>(14.3) | 1.60                       | 20,100<br>16,350                                          |
| [Zn <sub>2</sub> L <sub>6</sub> Cl <sub>4</sub> ]<br>White        | 228          | 21                                                     | 52.4<br>(52.6)   | 5.2<br>(5.5) | 13.5<br>(13.9) | 13.4<br>(13.6) | 13.8<br>(14.1) | —                          | —                                                         |

*Tetrachloro*[1, 1'-phenyl bis(1, 3, 6, 11, 14-pentazacyclopentadecane-8, 9 phenyl-6, 10-diene)]-dimetal(II) and *tetrachloro*[1, 1'-phenyl bis(1, 3, 7, 12, 16-pentazacycloheptadecane-9, 10-phenyl-7, 11-diene)]dimetal(II), [M<sub>2</sub>L<sub>5</sub>Cl<sub>4</sub>] and [M<sub>2</sub>L<sub>6</sub>Cl<sub>4</sub>] [M = Fe(II), Co(II), Ni(II), Cu(II) and Zr(II)]

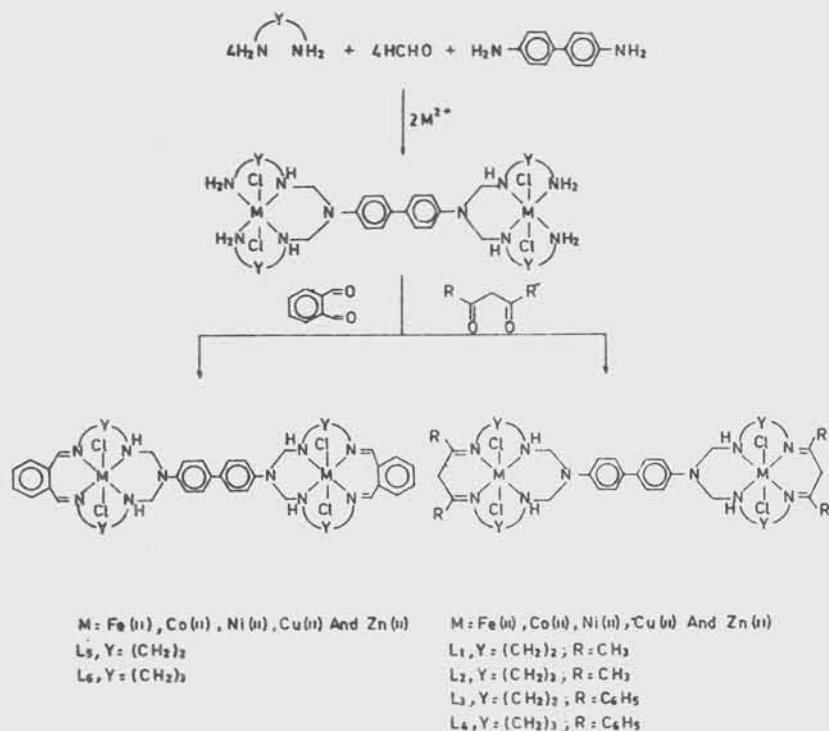
The procedure adopted was the same as discussed earlier except that here phthalaldehyde (0.02 mol) was added in the final step.

The elemental analysis were obtained from the Microanalytical laboratory of CDRI, Lucknow, <sup>1</sup>H NMR spectra in DMSO-*d*<sub>6</sub> using a Bruker AC 200 E spectrometer with Me<sub>4</sub>Si as an internal standard were obtained from GNDU, Amritsar, India. The estimation of chloride was done gravimetrically<sup>13</sup> and the metals were estimated by titrating with standard EDTA solution<sup>14</sup>. The IR spectra (4000-200 cm<sup>-1</sup>) were recorded as KBr

discs on an IR 408 Shimadzu spectrophotometer. The electronic spectra of compounds in DMSO were recorded on a Pye-Unicam 8800 spectrophotometer. EPR spectra of solid complexes at room temperature were recorded on a Jeol JES RE2X EPR spectrometer. Magnetic susceptibility measurements were carried out using a Faraday Balance at 25°C. The electrical conductivities of 10<sup>-3</sup>M solutions in DMSO were obtained on a Systronic type 302 conductivity bridge equilibrated at 25 ± 0.05°C.

## Results and Discussion

A new series of bis macrocyclic complexes [M<sub>2</sub>LCl<sub>4</sub>] [M = Fe(II), Co(II), Ni(II), Cu(II) and Zn(II); L = L<sub>1</sub> - L<sub>6</sub>] have been synthesized from the template reaction of primary diamines, formaldehyde and benzidine followed by the addition of



Scheme 1

diketones or phthalaldehyde in 4:4:1:2 molar ratio (Scheme 1). All the complexes are stable to atmosphere and polycrystalline in nature. Elemental analysis (Table 1) agree well with the bis macrocyclic complexes (Scheme 1). The molar conductance values are indicative<sup>15</sup> of non-electrolytic nature of all these complexes.

The IR spectra of all the complexes show a single sharp band in the  $3210\text{--}3270\text{ cm}^{-1}$  region which is assigned to the coordinated N-H stretching vibrations of secondary amine moiety. A medium to strong band observed in the region  $1560\text{--}1600\text{ cm}^{-1}$  is due to the coordinated  $\nu(\text{C}=\text{N})$  vibrations and are consistent<sup>16</sup> with that of the analogous compounds. Along with these results, the most remarkable feature is that the IR spectra of the complexes show no bands assignable to primary amine or carbonyl group stretching vibrations. Another band appearing at  $1610\text{--}1640\text{ cm}^{-1}$  is assignable to  $\delta(\text{N-H})$  vibrations. All the complexes gave bands  $\sim 1175\text{ cm}^{-1}$  and can be assigned to  $\nu(\text{C-N})$  vibration. A band  $\sim 460\text{--}510\text{ cm}^{-1}$  region can be ascribed<sup>17</sup> to  $\nu(\text{M-N})$  vibrations.

The room temperature EPR spectra of copper(II) bis macrocyclic complexes show a single broad band with two  $g$  values. The absence of hyperfine splitting signals in these complexes may be

due to the strong dipolar and exchange interactions between the copper(II) ions in the unit cell<sup>18</sup>. The  $g_{\parallel}$  and  $g_{\perp}$  values appeared in the region, 2.135-2.145 and 2.058-2.061 respectively. The observed  $g$  values indicate the presence of an unpaired electron in the  $d_{x^2-y^2}$  orbital, a phenomenon reported in many other complexes. The ratio  $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$  implies the possibility of exchange interaction in the copper complexes<sup>19</sup>. When  $G > 4$ , the exchange interaction is negligible and vice-versa. In the present complexes, the value ranges from 2.21-2.45 which indicate a considerable exchange interaction present in these complexes. It has been reported<sup>20</sup> that  $g_{\parallel}$  is a sensitive function for indicating covalency, for an ionic environment  $g_{\parallel}$  is greater than 2.3 and for a covalent environment,  $g_{\parallel}$  is less than 2.3. In the present complexes,  $g_{\parallel} < 2.3$  is indicative of the covalent nature of the complex.

The  $^1\text{H}$  NMR spectra of all bis macrocyclic zinc complexes show two multiplets in the region 6.28-6.43 and 3.35-3.50 ppm which corresponds<sup>17</sup> to the secondary amino protons and methylene protons of aldehyde moiety ( $\text{C-NH-C}$ , 4H and  $\text{N-CH}_2\text{-N}$ , 8H), respectively. Two more multiplets observed for all the complexes in 2.38-2.48 and 2.62-2.74 ppm regions may be due to the two non-equivalent

methylene protons ( $\text{N}-\text{CH}_2-\text{C}$ , 8H and  $\text{C}-\text{CH}_2-\text{N}=\text{}$ , 8H) of the amine moiety<sup>11</sup>. All the complexes show a multiplet in the region 7.13-7.53 ppm which is assigned<sup>16</sup> to aromatic ring protons. The  $^1\text{H}$  NMR spectra of  $[\text{Zn}_2\text{L}_5\text{Cl}_4]$  and  $[\text{Zn}_2\text{L}_6\text{Cl}_4]$  shows a singlet at 8.34-8.40 ppm range which can be assigned<sup>21</sup> to the four equivalent carboximine protons ( $\text{CH}=\text{N}$ , 4H). Furthermore, another sharp singlet appearing for the complexes  $[\text{Zn}_2\text{L}_1\text{Cl}_4]$  and  $[\text{Zn}_2\text{L}_2\text{Cl}_4]$  in the range 2.14-2.18 ppm may be attributed<sup>8</sup> to the imine methyl ( $\text{CH}_3-\text{C}=\text{N}$ , 12H) protons. The  $^1\text{H}$  NMR spectra of the compounds  $[\text{Zn}_2\text{L}_2\text{Cl}_4]$ ,  $[\text{Zn}_2\text{L}_4\text{Cl}_4]$  and  $[\text{Zn}_2\text{L}_6\text{Cl}_4]$  show an additional multiplet in the region 1.88-1.95 ppm which may be assigned to the middle methylene protons of 1, 3-diaminopropane moiety. However, we did not notice any bands which are assignable to the protons of uncondensed moieties which support the structure of the macrocycles as shown in Scheme 1.

Electronic spectral and magnetic moment data of all the complexes are consistent<sup>22</sup> with their octahedral geometry (Table 1).

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