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# Rational Design of Linear Trinuclear Metal Complexes

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# Rational Design of Linear Trinuclear Metal Complexes

## **Abstract**

A great deal of interest in multi metallic complexes derives from the special chemical and physical properties resulting from the mutual interaction of two or more metal centers.<sup>1</sup> Of particular interest are one-dimensional chains of metal complexes.<sup>2</sup> Materials of this type have exhibited unusual magnetic, optical, and conduction properties.<sup>3</sup> Despite the great interest in this area, the development of widely applicable, rational methods for synthesis of desired metal chain complexes remains elusive.

## **Disciplines**

Chemistry

## **Comments**

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may probably best be described as a square-planar chromium(II) ion-paired to fluorine (the cationic moiety having  $D_4$  and the anions  $C_{4v}$  symmetry, respectively) or alternatively as an octahedron elongated due to Jahn-Teller distortion of the  $d^4$  system. This interaction is likely to be responsible for the small lengthening of the bond between the bridging fluorine atom and phosphorus (about 0.05 Å with respect to the other P-F bonds) [this could suggest that **1** is a precursor to **2** in a Cr(II)  $\rightarrow$  Cr(III) oxidation process, where Cr(I) could be the oxidant<sup>2c</sup>].

A comparison of the orientation of the planes of the pyridine ligands in **1** and **3**, respectively, reveals that while **1** contains a four-bladed propeller, thus lowering the steric repulsions between the *o*-H's,<sup>4b</sup> an unusual overall disposition is found in **3**, similar to that observed in *trans*-PPh<sub>3</sub>F<sub>2</sub>.<sup>18</sup> The hypothesis of F...H attractive interactions<sup>19</sup> could explain the observed less tilted orientation of the pyridine rings in **3** with respect to **1** (the dihedral angle between the Cr-N<sub>4</sub> and individual py planes is 58.1 (1)° in **1**, while it is 69.3 (1) and 73.2 (1)° for py1 and py2, respectively, in **3**). C-H...F hydrogen bonds could be postulated in **3**, the H...F distances resembling the H...O contacts found in some bent C-H...O hydrogen bonds.<sup>21</sup>

**Registry No.** 1, 136342-74-0; 2, 136342-72-8; 3, 136342-71-7; bis-( $\eta^6$ -benzene)chromium hexafluorophosphate, 51160-14-6.

**Supplementary Material Available:** For **1** and **3**, text describing the structure determination procedure and parameters and tables listing positional and thermal parameters, bond distances and angles, and least-squares planes (15 pages); tables listing observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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 (19) The F...H distances (Table II) are shorter than the sum of the van der Waals radii of fluorine and hydrogen.<sup>20</sup>  
 (20) Bondi, A. J. *Phys. Chem.* 1964, 68, 441.  
 (21) Taylor, R.; Kennard, O. J. *Am. Chem. Soc.* 1982, 104, 5063. In the lack of structural data for C-H...F hydrogen bonds, a cautious comparison to the C-H...O case could be proposed, on the basis of the similar van der Waals radii of O and F.<sup>20</sup>

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## Rational Design of Linear Trinuclear Metal Complexes

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Received February 13, 1991

### Introduction

A great deal of interest in multimetallic complexes derives from the special chemical and physical properties resulting from the mutual interaction of two or more metal centers.<sup>1</sup> Of particular interest are one-dimensional chains of metal complexes.<sup>2</sup> Materials of this type have exhibited unusual magnetic, optical, and conduction properties.<sup>3</sup> Despite the great interest in this area,

the development of widely applicable, rational methods for synthesis of desired metal chain complexes remains elusive.

As part of a program to prepare metal-containing polymers, we have synthesized multichelating ligand systems. We recently reported the synthesis of a new binucleating ligand, *cis*-5,15-bis[*o*-( $\beta$ -alanyl-amido)phenyl]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin, [H<sub>2</sub>(DPE)](NH<sub>2</sub>)<sub>2</sub>,<sup>4</sup> and showed that the porphyrin core of this ligand can be metalated to produce mononuclear building blocks.<sup>5</sup> We now report that these complexes can be readily used to prepare linear trinuclear metal complexes.

### Experimental Section

All solvents and metal salts used in the syntheses were of analytical grade. Synthesis and characterization of [H<sub>2</sub>(DPE)](NH<sub>2</sub>)<sub>2</sub> and its Zn(II), Cu(II), and Ni(II) complexes were accomplished by literature procedures.<sup>5</sup> Elemental analysis was performed by Galbraith Laboratories, Inc., Knoxville, TN. Visible spectra were recorded at room temperature on a HP 8452A diode array spectrophotometer using chloroform as solvent. Infrared spectra were recorded as Nujol mulls on an IBM IR-98 Fourier transform infrared spectrophotometer. <sup>1</sup>H NMR spectra were recorded on a Nicolet NIC 300 spectrometer using CD<sub>2</sub>Cl<sub>2</sub> as solvent. Chemical shifts (in ppm) are reported relative to CD<sub>2</sub>Cl<sub>2</sub> (5.32 ppm). EPR spectra were recorded in frozen CHCl<sub>3</sub> solution on an IBM ER-200 EPR spectrometer. Molecular weights were determined in CHCl<sub>3</sub> solutions with a Knauer vapor pressure osmometer.

**[[Ni<sup>II</sup>(DPE)](NH<sub>2</sub>)<sub>2</sub>]<sub>2</sub>Zn(ClO<sub>4</sub>)<sub>2</sub>.** A methanolic solution (4 mL) of Zn(ClO<sub>4</sub>)<sub>2</sub> (22.0 mg, 0.06 mmol) was added to [Ni<sup>II</sup>(DPE)](NH<sub>2</sub>)<sub>2</sub> (100.0 mg, 0.12 mmol) dissolved in 10 mL of CHCl<sub>3</sub>/CH<sub>3</sub>OH (9:1). The resulting mixture was stirred at room temperature for 4 h and then heated at reflux for 24 h. After removal of the solvent under reduced pressure, the crude solid was dissolved in 5 mL of CH<sub>3</sub>OH, and the solution was treated with 16.3 mg (0.12 mmol) of NaClO<sub>4</sub> in 2 mL of CH<sub>3</sub>OH. The mixture was stirred at room temperature for 4 h and was subsequently evaporated to dryness. Water (15 mL) was added to the resulting crude [[Ni(DPE)](NH<sub>2</sub>)<sub>2</sub>]<sub>2</sub>Zn(ClO<sub>4</sub>)<sub>2</sub>, and the suspension was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3  $\times$  40 mL). The combined organic layers were dried over anhydrous MgSO<sub>4</sub> and filtered. Removal of the solvent under reduced pressure yielded 86 mg (73%) of pure purple product. UV/vis (CHCl<sub>3</sub>): 408 (Soret), 532, 568 nm. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 9.38 (s, 4 H, meso H), 8.25 (d, 4 H, aryl), 8.01 (d, 4 H, aryl), 7.64 (t, 4 H, aryl), 7.45 (t, 4 H, aryl), 6.89 (s, b, 4 H, NH), 3.62 (q, 16 H, CH<sub>2</sub>CH<sub>3</sub>), 3.47 (s, b, 8 H, NH<sub>2</sub>), 2.19 (s, 24 H, CH<sub>3</sub>), 2.08 (t, 8 H, CH<sub>2</sub>CH<sub>2</sub>), 1.55 (t, 24 H, CH<sub>2</sub>CH<sub>3</sub>), 1.30 (t, 8 H, CH<sub>2</sub>CH<sub>2</sub>). IR (mull):  $\nu$ (ClO<sub>4</sub><sup>-</sup>) = 1107, 623 cm<sup>-1</sup>. Anal. Calcd for C<sub>100</sub>H<sub>112</sub>N<sub>16</sub>O<sub>12</sub>Cl<sub>2</sub>Ni<sub>2</sub>Zn: C, 60.55; H, 5.65; N, 11.30. Found: C, 60.92; H, 6.04; N, 10.99. Molar conductance (acetone): 190.6 mhos mol<sup>-1</sup> cm<sup>2</sup>.

**[[Zn<sup>II</sup>(DPE)](NH<sub>2</sub>)<sub>2</sub>]<sub>2</sub>CuCl<sub>2</sub>.** A methanolic solution (5 mL) of CuCl<sub>2</sub> (10.0 mg, 0.06 mmol) was added to a solution of [Zn<sup>II</sup>(DPE)](NH<sub>2</sub>)<sub>2</sub> (100.0 mg, 0.12 mmol) dissolved in 10 mL of CHCl<sub>3</sub>/CH<sub>3</sub>OH (9:1). After the mixture was refluxed for 24 h, the solvent was removed under reduced pressure. Water (15 mL) was added to the residue, the suspension was filtered through a Celite pad, and the solid was washed with water. After the Celite pad was dried in vacuo, the product was washed from Celite with CHCl<sub>3</sub>. The solution was concentrated to ca. 5 mL, and 5 mL of hexane was added. After cooling to -10 °C for several days, the solution was filtered to yield 63 mg (53%) of brown-red microcrystals. UV/vis (CHCl<sub>3</sub>): 410 (Soret), 532, 572 nm. EPR (CHCl<sub>3</sub>, 110 K):  $g_{\parallel}$  = 2.21,  $g_{\perp}$  = 2.07,  $a_{Cu}$  = 197.5 G,  $a_N$  = 16.4 G. Anal. Calcd for C<sub>100</sub>H<sub>112</sub>N<sub>16</sub>O<sub>4</sub>Cl<sub>2</sub>Zn<sub>2</sub>Cu-1/2CHCl<sub>3</sub>: C, 62.64; H, 5.88; N, 11.63; Cl, 6.44. Found: C, 62.53; H, 6.01; N, 11.21; Cl, 7.38. Mol wt: calcd, 1865; found, 1742.

**[[Ni<sup>II</sup>(DPE)](NH<sub>2</sub>)<sub>2</sub>]<sub>2</sub>CuCl<sub>2</sub>.** This purple-red compound was prepared in the same fashion as described for [[Zn(DPE)](NH<sub>2</sub>)<sub>2</sub>]<sub>2</sub>CuCl<sub>2</sub> using 100.0 mg (0.12 mmol) of [Ni(DPE)](NH<sub>2</sub>)<sub>2</sub>. Yield: 47 mg (41%). UV/vis (CHCl<sub>3</sub>): 408 (Soret), 532, 568 nm. Anal. Calcd for C<sub>100</sub>H<sub>112</sub>N<sub>16</sub>O<sub>4</sub>Cl<sub>2</sub>Ni<sub>2</sub>Cu-CHCl<sub>3</sub>: C, 61.46; H, 5.73; N, 11.36. Found: C, 61.49; H, 6.37; N, 11.01. Mol wt: calcd, 1852; found, 1881.

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 (4) DPE is derived from diphenyletioporphyrin, the modified common name for 5,15-diphenyl-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin.  
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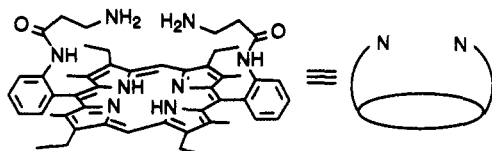


Figure 1. Structure and schematic representation for  $H_2(DPE)(NH_2)_2$ .

**$[Cu^{II}(DPE)](NH_2)_2CuCl_2$ .** A methanolic solution of cupric chloride (10.0 mg, 0.06 mmol in 4 mL) was added to  $[Cu^{II}(DPE)](NH_2)_2$  (100.0 mg, 0.12 mmol) dissolved in 10 mL of  $CHCl_3/CH_3OH$  (9:1). The reaction mixture was refluxed for 24 h. After evaporation of the solvent to dryness, the solid was dissolved in 15 mL of  $CHCl_3$ , and then the solution was poured into 75 mL of water with stirring. The organic layer was separated from the mixture, and the aqueous suspension was extracted with  $CHCl_3$  ( $3 \times 20$  mL). The combined organic layers were dried over anhydrous  $MgSO_4$ , filtered, and concentrated to 5 mL. After addition of 5 mL of hexanes, the flask was cooled to  $-10^\circ C$  for 4 days. The microcrystalline purple solid was filtered out, washed with hexanes, and dried in vacuo to yield 52 mg (45%) of product. UV/vis ( $CHCl_3$ ): 410 (Soret), 534, 570 nm. Anal. Calcd for  $C_{100}H_{112}N_{16}O_4Cl_2Cu_3 \cdot 1/2CHCl_3$ : C, 62.76; H, 5.86; N, 11.66; Cu, 9.92. Found: C, 62.74; H, 5.81; N, 11.04; Cu, 9.47. Mol wt: calcd, 1862; found, 1848.

**$[Ni^{II}(DPE)](NH_2)_2Zn(NCS)_2$ .** A methanolic solution of  $Cu(ClO_4)_2$  (21.6 mg, 0.06 mmol in 4 mL) was added to  $[Ni^{II}(DPE)](NH_2)_2$  (100 mg, 0.12 mmol) dissolved in 10 mL of  $CHCl_3/CH_3OH$  (9:1). After the reaction mixture was stirred at ambient temperature for 1 h, it was heated at reflux for 24 h. After evaporation of the solvents to dryness, the resulting solid was dissolved in 5 mL of  $CH_3OH$ , and the mixture was treated with a solution of  $NaSCN$  (10.54 mg, 0.13 mmol) in 2 mL of  $CH_3OH$ . After 2 h of stirring at ambient temperature, the solvent was evaporated to dryness and 50 mL of water was added. The suspension was filtered through a well-packed Celite pad, and the solid was washed with water and dried. The product was washed from Celite with  $CHCl_3$  until the washings were clear. The solution volume was concentrated to 5 mL. After addition of 5 mL of hexane, the mixture was cooled to  $-10^\circ C$  for several days. A dark red microcrystalline solid was isolated by filtration and dried in vacuo under reduced pressure (58 mg, 49% yield). UV/vis ( $CHCl_3$ ): 408 (Soret), 530, 566 nm. IR (mull):  $\nu(SCN) = 2064$   $cm^{-1}$ . EPR ( $CHCl_3$ , 110 K):  $g_{||} = 2.27$ ,  $g_{\perp} = 2.06$ ,  $a_{Cu} = 156.7$  G,  $a_N = 25.3$  G. Anal. Calcd for  $C_{102}H_{112}N_{18}O_4Ni_2Cu \cdot CHCl_3$ : C, 61.28; H, 5.60; N, 12.49. Found: C, 61.42; H, 6.18; N, 12.06. Mol wt: Calcd, 1897; found, 1953.

## Results

The binucleating ligand,  $[H_2(DPE)](NH_2)_2$ , is shown in Figure 1. Metalation of the porphyrin core of this ligand with Ni(II), Cu(II), and Zn(II) has been previously described.<sup>5</sup> Treatment of  $[Ni(DPE)](NH_2)_2$  with 0.5 equiv of  $Zn(ClO_4)_2$  in refluxing  $CHCl_3/CH_3OH$  produces the new trinuclear species  $\{[Ni(DPE)](NH_2)_2Zn\}(ClO_4)_2$  (**1**) in 73% yield as a dark purple solid. The  $^1H$  NMR spectrum of this new complex dissolved in  $CD_2Cl_2$  shows distinctive changes in its proton resonances relative to those of the starting mononuclear species  $[Ni(DPE)](NH_2)_2$ .<sup>6</sup> As expected, the most notable changes involve the shifts of the protons of the chelating appendages. For example, the aryl protons of the trinuclear  $Ni_2Zn$  complex appear as four distinct signals at 8.25 (d, 4 H), 8.01 (d, 4 H), 7.64 (t, 4 H), and 7.45 ppm (t, 4 H). In  $[Ni(DPE)](NH_2)_2$ , these same protons resonate at 8.33 (d, 4 H), 7.69 (t, 2 H), and 7.56 ppm (t, 2 H). In addition, the methylene protons of the  $\beta$ -alanyl linkages of the  $Ni_2Zn$  complex have slightly shifted to  $\delta$  2.08 and 1.30 from their original positions of  $\delta$  2.19 and 1.28 in the starting material. Although these spectral changes are also consistent with a single nickel porphyrin chelate bound to zinc in a binuclear complex, the composition of complex **1** was established by several independent techniques. The IR spectrum of **1** exhibits bands at 1107 and 623  $cm^{-1}$ , indicating that the  $ClO_4^-$  counterions are uncoordinated.<sup>7</sup> The ionic nature

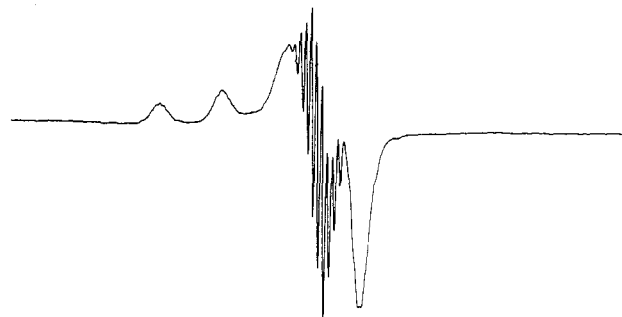
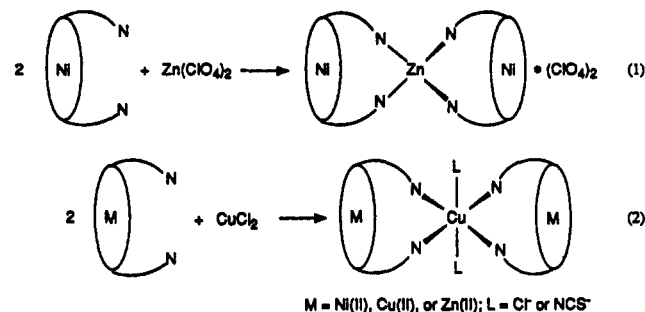


Figure 2. X-Band EPR spectrum for  $\{[Zn(DPE)](NH_2)_2\}_2CuCl_2$  in  $CHCl_3$  at 110 K with a field strength of 3300 G (center field) and a sweep width of 2000 G.

of complex **1** was further verified by conductivity measurements in acetone. The measured molar conductance of 190.6  $mhos\ mol^{-1}\ cm^2$  is indicative of a 1:2 electrolyte. (The expected range for a 1:2 electrolyte is 160–200  $mhos\ mol^{-1}\ cm^2$ .<sup>8</sup>) Finally, the trinuclearity of complex **1** was ascertained by a molecular weight determination using vapor pressure osmometry. Since complex **1** is a 1:2 salt, the measured value (found: 672) is an average molecular weight for the three ions in solution (calcd:  $1982/3 = 660$ ). A binuclear 1:2 salt,  $\{[Ni(DPE)](NH_2)_2\}Zn(ClO_4)_2$ , would yield an average molecular weight of 375.

A variety of trinuclear complexes have been prepared in a similar manner. Equations 1 and 2 schematically represent the



formation of these complexes and illustrate that homometallic as well as heterometallic complexes can be fabricated. Thus, when  $CuCl_2$  is treated with 2 equivalents of  $[Zn(DPE)](NH_2)_2$  in refluxing  $CHCl_3/CH_3OH$ , the trinuclear complex  $\{[Zn(DPE)](NH_2)_2\}_2CuCl_2$  (**2**) is produced in 53% yield. This  $CHCl_3$ -soluble complex shows an anisotropic EPR spectrum (Figure 2) in a frozen solution which is characteristic of tetragonal  $Cu(II)$  complexes. The  $g$  values for complex **2** are  $g_{||} = 2.21$  and  $g_{\perp} = 2.07$ , and the copper hyperfine coupling is 197.5 G. In addition, a nine-line nitrogen superhyperfine splitting is observed with a  $^{14}N$  superhyperfine coupling of 16.4 G. The experimentally determined molecular weight for complex **2** was found to be 1742 (calcd: 1865).

It is possible to modify the coordination sphere of the central metal by simple substitution chemistry. For example, the axial chlorides in  $\{[Ni(DPE)](NH_2)_2\}_2CuCl_2$  can be replaced with thiocyanate ligands by treating the  $Ni_2Cu$  complex with excess  $NaSCN$  in methanol. The resulting product exhibits a new IR stretching frequency at 2064  $cm^{-1}$  arising from the coordinated S-bound thiocyanates.<sup>9</sup> The EPR spectrum of  $\{[Ni(DPE)](NH_2)_2\}_2Cu(SCN)_2$  in frozen  $CHCl_3$  is similar to that of the dichloride analogue with  $g_{||} = 2.27$ ,  $g_{\perp} = 2.06$ ,  $a_{Cu} = 156.7$  G, and  $a_N = 25.3$  G.

## Discussion

Although a number of multichelating porphyrins are now readily available, the majority of these ligands have sufficiently bulky appendages or superstructures which limit them to binding

(6)  $^1H$  NMR of  $[Ni(DPE)](NH_2)_2(CD_2Cl_2)$ : 9.39 (s, 2 H, meso H), 8.33 (d, 4 H, aryl), 7.69 (t, 2 H, aryl), 7.56 (t, 2 H, aryl), 7.01 (s, b, 4 H,  $NH_2$ ), 5.69 (s, 2 H, NH), 3.67 (q, 8 H,  $CH_2CH_3$ ), 2.77 (t, 4 H,  $CH_2CH_3$ ), 2.19 (s, 12 H,  $CH_3$ ), 1.59 (t, 12 H,  $CH_2CH_3$ ), 1.28 (t, 4 H,  $CH_2CH_3$ ).

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only two metals.<sup>10</sup> The ligand employed here,  $[\text{H}_2(\text{DPE})](\text{NH}_2)_2$ , consists of two  $\beta$ -alanyl appendages, positioned on one face of the porphyrin plane, which serve as chelating sites for additional metals. This is a flexible system designed to promote the formation of trimetallic complexes. Thus, when a central metal is chelated by a pair of these ligands, formation of linear trinuclear arrays is possible. Synthetically, it is convenient to insert a metal into the porphyrin core of  $[\text{H}_2(\text{DPE})](\text{NH}_2)_2$  in the first step. Subsequent introduction of an additional metal to link two porphyrin complexes affords the desired trinuclear complexes.

Preparation of  $\{[\text{Ni}(\text{DPE})](\text{NH}_2)_2\}_2\text{Zn}(\text{ClO}_4)_2$  was achieved by following the above strategy. The solution  $^1\text{H}$  NMR spectrum of this species clearly indicates that a new complex has formed. The presence of one resonance at 2.19 ppm (s) for the four pyrrole methyl substituents, one diastereotopic  $\text{CH}_2$  multiplet at 3.62 ppm, and one triplet at 1.55 ppm for the four pyrrole ethyl groups indicates that the porphyrin ligand retains its  $\text{C}_2$  symmetry in this complex. This is consistent with the expected tetrahedral geometry involving the central  $\text{d}^{10}$  zinc ion.

The trimetallic nature of all of the complexes described here has been confirmed by molecular weight measurements. Unfortunately, the trinuclear complexes reported here have not yet been amenable to mass spectral or X-ray diffraction analysis. However, a particularly useful alternative was the use of  $\text{Cu}(\text{II})$  as the central, linking metal in this system and as an EPR probe for structure and composition. Thus  $\{[\text{Zn}(\text{DPE})](\text{NH}_2)_2\}_2\text{CuCl}_2$  exhibits an EPR spectrum with  $a_{\text{Cu}} = 197.5$  G,  $g_{\parallel} = 2.21$ , and  $g_{\perp} = 2.07$ . This is consistent with an axially symmetric complex.<sup>11</sup> In addition, the nine-line  $^{14}\text{N}$  superhyperfine splitting requires that four nitrogens bind to Cu in equivalent positions. These EPR data unambiguously indicate that the structure of the Cu core must be tetragonal, with chlorides occupying the axial positions and the four terminal amines of the two  $[\text{Ni}(\text{DPE})](\text{NH}_2)_2$  chelates residing in the equatorial plane.

### Conclusions

Preparation of trinuclear species generally leads to the formation of triangular complexes.<sup>12</sup> Few rational methods for preparing linear trinuclear complexes are known, and these are not readily extendable to more than one type of metal system.<sup>13</sup> With the use of specially designed ligands, we have devised a general method for the synthesis of linear arrays of transition-metal complexes. The versatility of our multichelating ligands demonstrates that controlled syntheses of complex multinuclear molecules are readily achievable. For example, by judicious choice of metals, a series of homo- and heteronuclear trimetallic complexes can be prepared. Furthermore, additional modification can be achieved by altering the axial ligands bound to the central metal of these complexes. The compounds prepared here can be viewed as truncated portions of one-dimensional chains. Thus, in principle, it should be possible to prepare increasingly sophisticated materials with deliberately tailored properties. Further investigation of the physical and chemical properties of these novel complexes as well as extension of this work to polymeric systems is underway.

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Laboratory. L.K.W. acknowledges support from the NSF in the form of a PYI award.

**Registry No.** 1, 136804-60-9; 2, 136804-61-0;  $\{[\text{Ni}(\text{DPE})](\text{NH}_2)_2\}_2\text{CuCl}_2$ , 136804-62-1;  $\{[\text{Cu}(\text{DPE})](\text{NH}_2)_2\}_2\text{CuCl}_2$ , 136804-63-2;  $\{[\text{Ni}(\text{DPE})](\text{NH}_2)_2\}_2\text{Cu}(\text{SCN})_2$ , 136804-64-3;  $[\text{Ni}(\text{DPE})](\text{NH}_2)_2$ , 136049-49-5;  $[\text{Zn}(\text{DPE})](\text{NH}_2)_2$ , 136049-47-3;  $[\text{Cu}(\text{DPE})](\text{NH}_2)_2$ , 136049-48-4.

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### Nuclearity and Formulation of $\text{SALPN}^{2-}$ Complexes Formed from $\text{M}(\text{O}_2\text{CCH}_3)_2$ : Resolution of Longstanding Problems by X-ray Crystallography

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### Introduction

As part of a program aimed at understanding the synthesis and properties of organocobalt complexes relevant to  $\text{B}_{12}$  coenzymes, we have been investigating the synthesis of complexes based on quadridentate bis(salicylidene) Schiff base ligands.<sup>1,2</sup> Metal complexes of such quadridentate Schiff base ligands have been studied extensively, both as  $\text{B}_{12}$  models<sup>1-3</sup> and also because of the rich coordination chemistry generated by the well-known ability of the two coordinated phenolate oxygen atoms to bridge metal centers.<sup>4</sup> Further interest in these complexes has focused on their usefulness in studying magnetic exchange interactions between bridged paramagnetic metal ions<sup>5,6</sup> and on their application in catalytic processes.<sup>7</sup>

During the course of the investigation, we planned to prepare complexes based on  $\text{SALPN}^{2-}$  (the dianion of  $N,N'$ -bis(salicylidene)propylenediamine) and 2,2-Me<sub>2</sub>SALPN<sup>2-</sup> (the dianion of  $N,N'$ -bis(salicylidene)-2,2-dimethylpropylenediamine). The preparation of  $\text{SALPN}^{2-}$  complexes from  $\text{M}(\text{O}_2\text{CCH}_3)_2$  has been reported to yield analytically impure products for  $\text{Co}(\text{II})$ <sup>8</sup> and  $\text{Fe}(\text{II})$ <sup>9</sup>. This type of preparation for  $\text{Fe}(\text{II})$  has been reported to give a polymeric product on the basis of Mössbauer data,<sup>10</sup> but the reported analytical results cannot be considered acceptable.

In initial studies, we successfully prepared  $\text{Co}(\text{II})$  complexes of the  $\text{SALPN}^{2-}$  class of ligands from  $\text{Co}(\text{O}_2\text{CCH}_3)_2$ . Considering previous uncertainty concerning the nuclearity of the  $\text{Fe}(\text{II})$  species,<sup>10</sup> we extended our synthetic methods to  $\text{Fe}(\text{II})$  compounds.

Two complexes, formulated as  $\text{Co}_3(\text{SALPN})_2(\text{O}_2\text{CCH}_3)_2 \cdot 2\text{DMF}$  (**1**) and  $\text{Fe}_3(\text{SALPN})_2(\text{O}_2\text{CCH}_3)_2 \cdot 2\text{DMF}$  (**2**), were isolated as well-formed crystals. We undertook the structure determination of the complexes in order to establish the coordination geometry about the metal ions. Compounds **1** and **2** proved to have the same trimeric structure, with the metal ions in the +2 oxidation state. The only trimeric structures so far reported with

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