Synthesis of Imidazole-Containing Ligands and Studies on Metal Complexes

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1,5-Di(imidazol-1-yl)-3-[2-(imidazol-1-yl)ethyl]pentane, 1,7-di(imidazol-1-yl)-4-[3-(imidazol-1-yl)propyl]heptane, *N*,*N*′,*N*″ -tris[2-(imidazol-4-yl)ethyl]benzene-1,3,5-tricarboxamide, and 1,3,5-tris[3-(imidazol-1-yl)propyl]benzene (TIPB) have been synthesized for a study of the formation and characteristics of zinc complexes. TIPB forms a crystalline zinc complex, not a tetrahedral complex but an octahedral complex. Other ligands form either microcrystalline complexes or polymer complexes with zinc.

Zinc complexes of imidazole ligands are widely studied as models for zinc-containing enzymes, and the complexes have been characterized in aqueous solution and the solid state.[1,2] Information from model studies has contributed a great deal to the understanding of the relations between their structures, electronic properties, and functions.[2—6] In a series of Zn(II) coordination compounds with imidazole ligands, no zinc coordination polymer has been synthesized, presumably because of difficulties in synthesizing the imidazole moiety and dealing with the extremely low solubility. The coordination polymers are of interest, among other things, in connection with material science. To develop zinc polymer chemistry, new polymidazole ligands should be synthesized. Thus we have recently synthesized new three-imidazole-containing ligands, 1,5-di(imidazol-1-yl)-3-[2-(imidazol-1-yl)ethyl]pentane (DIIEP), 1,7-di(imidazol-1-yl)-4-[3-(imidazol-1-yl)propyl]heptane (DIIPH), *N*,*N*′,*N*″-tris[2-(imidazol-4-yl)ethyl]benzene-1,3,5-tricarboxamide (TIEBT), and 1,3,5-tris[3-(imidazol-1-yl)propyl]benzene (TIPB). These organic molecules can't only serve as an example for a biomimetic ligand, but are also expected to have the characteristic tridentate-bridging without deprotonation in a polymeric system through incorporation of the three imidazole nitrogen donor functions. This paper describes the synthesis, structure, and properties of the first polynuclear Zn(II) complex with these ligands.

Results and Discussion

Syntheses of Ligands. 1,5-Di(imidazol-1-yl)-3-[2-(imidazol-1-yl)ethyl]pentane (DIIEP) 6. Wittig olefination of dimethyl 3-oxopentanedioate and methyl triphenyl-λ^5-phosphoranylideneacetate afforded dimethyl 3-(methoxycarbonyl)methylpent-2-enedioate **2**, which was hydrogenated to yield dimethyl 3-(methoxycarbonyl)methylpentane-1,5-dioate **3** (86%). Reduction of **3** with $LiAlH_4$ afforded (86%) the triol **4**, which was brominated with carbon tetrabromide and triphenylphosphine to give 1,5-dibromo-3-(2-bromoethyl)pentane **5** (59%). Treatment of **5** with sodium imidazolide in DMF afforded DIIEP **6** in 57% yield as colorless needles (Scheme 1). The structure was confirmed by spectral data and by X-ray crystallographic analysis (Fig. 1).

1,7-Di(imidazol-1-yl)-4-[3-(imidazol-1-yl)propyl]heptane (DIIPH) 11. The tertiary nitro group of 1,5-dicyano-3-(2-cyanoethyl)-3-nitropentane **7**[7] was reduced by tributyltin hydride[8] to afford 1,5-dicyano-3-(2-cyanoethyl)pentane **8** in 90% yield. Acid catalyzed alcoholysis of **8** followed by reduction with $LiAlH_4$ afforded 4-(3-hydroxypropyl)heptane-1,7-diol **9** in 87% yield from **8**. Treatment of **9** with hydrogen bromide-saturated acetic acid yielded 1,7-dibromo-4-(3-bromopropyl)heptane **10** (84%). The reaction of **10** with sodium imidazolide in DMF afforded **11** as a colorless

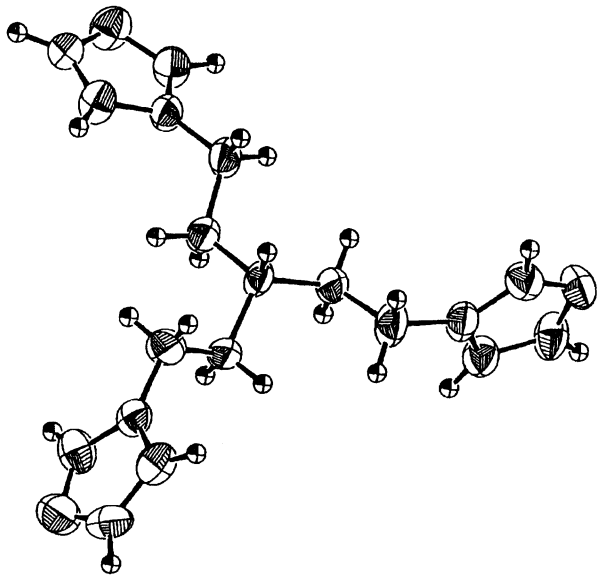
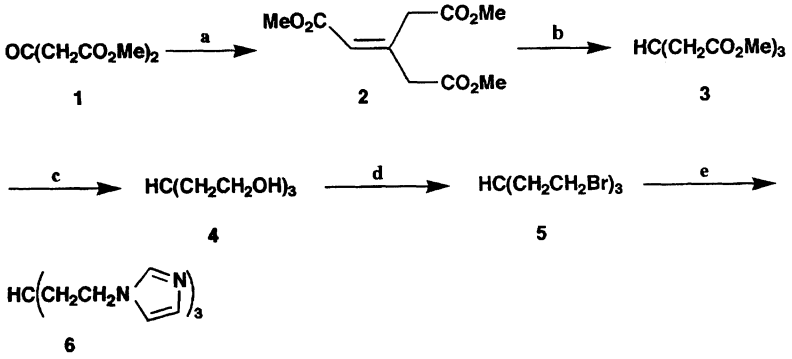
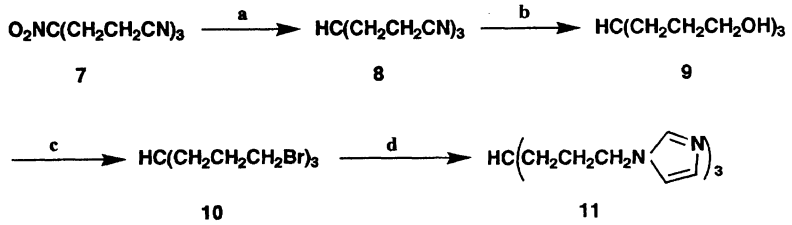


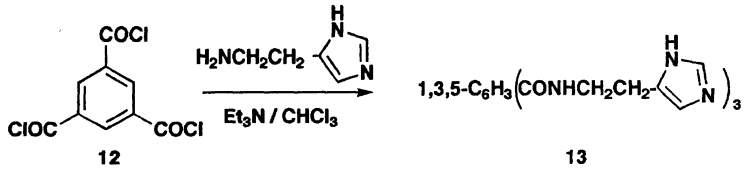
Fig. 1. The structure of DIIEP.



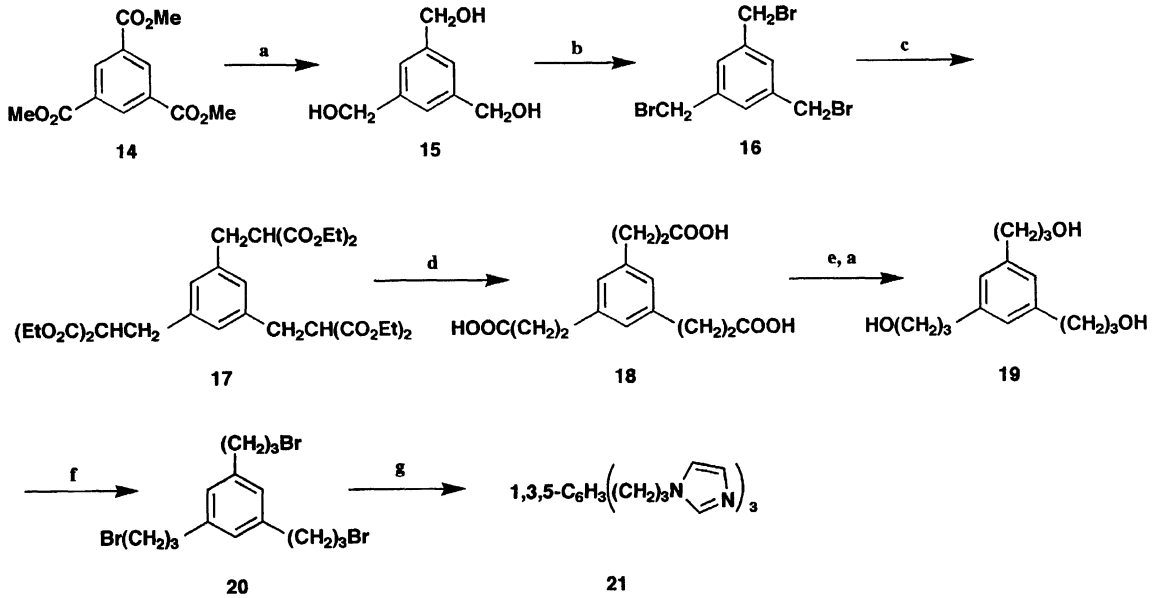
Scheme 1. (a) $Ph_3P{=}CHCO_2Me$, C_6H_6, reflux, 18 h; (b) H_2, PtO_2, EtOH; (c) $LiAlH_4$, THF, 0 °C to r.t., 2 h; (d) Ph_3P, CBr_4, THF, reflux, 2 h; (e) imidazole, NaH, DMF, r.t, 2 h.



Scheme 2. (a) *n*-Bu_3SnH, AlBN, $(CH_2Cl)_2$, reflux, 1.5 h; (b) (i) HCl, EtOH, reflux, 2 h; (ii) $LiAlH_4$, THF, reflux, 2 h; (c) HBr, AcOH, reflux, 3 h; (d) imidazole, NaH, DMF, r.t, 3 h.



Scheme 3.



Scheme 4. (a) $LiAlH_4$, THF, r.t., 1.5 h; (b) HBr, AcOH, reflux, 1 h; (c) $CH_2(CO_2Et)_2$, NaH, THF, r.t., 2 h; (d) (i) KOH, H_2O, reflux, 16 h; (ii) 180 °C, 3h; (e) MeOH, cat. H_2SO_4, reflux, 24 h; (f) (i) MsCl, pyridine, DMAP, THF, r.t., 48 h; (ii) LiBr, acetone, reflux, 20 h; (g) imidazole, NaH, DMF, 0 °C, 3 h.

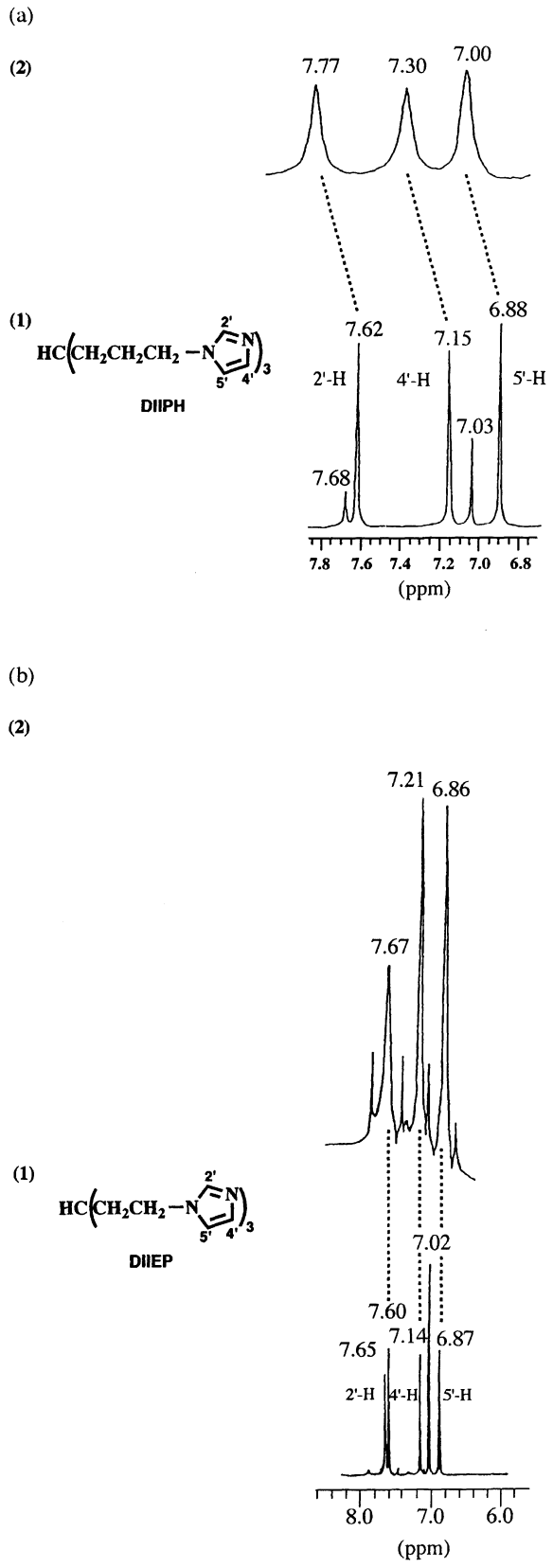


Fig. 2. (a) ^{1}H NMR spectra of Zn(II)–DIIPH complex and free ligand (DMSO-d_6), (1) Free ligand, (2) $[Zn^{2+}]/[L] = 1/1$. (b) ^{1}H NMR spectra of Zn(II)–DIIEP complex and free ligand (DMSO-d_6), (1) Free ligand, (2) $[Zn^{2+}]/[L] = 1/1$.

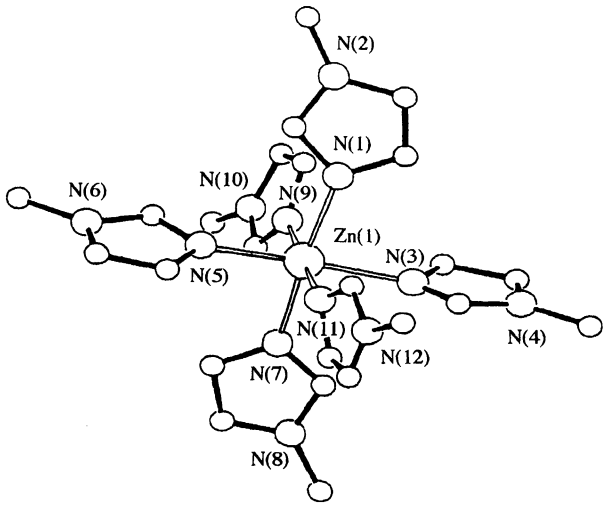


Fig. 3. Molecular structure of $[Zn(TIPB)_2]^{2+}$.

oil (52%) (Scheme 2).

***N,N′,N″*- Tris[2- (imidazol- 4- yl)ethyl]benzene- 1, 3, 5- tricarboxamide (TIEBT) 13.** TIEBT was prepared by the reaction of trimestic acid chloride with histamine (96%) (Scheme 3).

1,3,5-Tris[3-(imidazol-1-yl)propyl]benzene (TIPB) 21. Trimethyl trimesate was reduced with $LiAlH_4$ to afford the triol **15**, which was then treated with hydrogen bromide in acetic acid to yield 1,3,5-tris(bromomethyl)benzene **16** in 92% overall yield. Treatment of **16** with sodiomalonic ester followed by base hydrolysis and decarboxylation yielded 1, 3,5-benzenetripropanoic acid **18** (44% yield from **16**). The esterification and reduction of **18** yielded the triol **19** (77%). Mesylation and bromination of **19** afforded the tribromide **20** (90%). The reaction of **20** with sodium imidazolide in DMF afforded TIPB in 96% yield as a colorless oil (Scheme 4).

Syntheses and Structures of Metal-Ligand Complexes. Many of the biologically active zinc metalloproteins contain Zn(II) ion bound to one or more imidazoles of the amino acid residue of histidine. For this reason, a large number of studies have been done over an extended period on Zn(II) complexes with imidazole, substituted imidazoles, histidine, and related ligands, and these complexes have a large literature base.[9] To our knowledge, no X-ray single crystal structure of the Zn(II) complexes with the ligands containing three imidazoles has been reported. So we have explored the syntheses of Zn(II) complexes with these new ligands.

The reaction of $Zn(ClO_4)_2$ and DIIPH or DIIEP in acetonitrile afforded Zn-ligand 1:1 complexes as white precipitates. Both precipitates were not suitable for X-ray crystallographic analysis. The ^{1}H NMR spectra of both complexes in DMSO-d_6 showed coordination shifts of the imidazole protons. The coordination shift, $\Delta\delta$ [δ(complex)$-\delta$(free ligand)], were 0.15, 0.15, 0.12 ppm in Zn–DIIPH complex and 0.07, 0.07, -0.01 ppm in Zn–DIIEP complex for each 2′-H, 4′-H, and 5′-H of the imidazole protons, respectively (Fig. 2). The IR spectrum showed a strong band due to the absorption of ClO_4^- anion at 1100 cm^{-1} in both complexes. The smaller coordination shift values in the Zn–DIIEP complex indicates

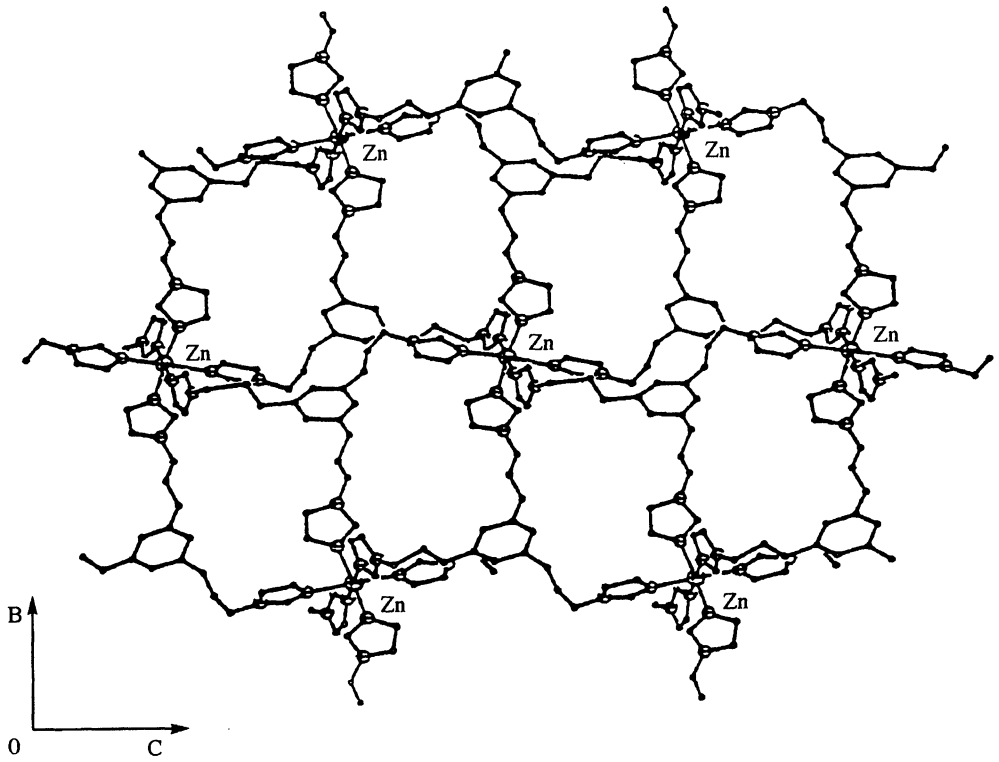


Fig. 4. A segment of two-dimensional structure of $[Zn(TIPB)_2]^{2+}$.

the difficulty of stable complex formation when the arms of the ligand are shorter.

The reaction of $Zn(ClO_4)_2$ and TIEBT in methanol afforded microprisms and its elemental analysis indicated Zn–TIEBT 1:1 complexes. Unfortunately, the crystals were again not suitable for X-ray crystallographic analysis.

Structure of $\{[Zn(TIPB)_2](ClO_4)_2\}_\infty$. The reaction of $Zn(ClO_4)_2$ and TIPB in methanol–water using a solvent diffusion method afforded Zn–TIPB 1:2 complexes as colorless crystals. The molecular structure of $\{[Zn(TIPB)_2](ClO_4)_2\}_\infty$ is shown in Fig. 3. The Zn atom is octahedrally coordinated to six imidazole nitrogens, the N–Zn–N bond angles being in the range of 86.8° to 94.2°. The Zn–N bond distances ranging from 2.14 to 2.21 Å are longer than the distances of 1.99 and 2.00 Å for tetrahedral Zn(II) complexes.[10] The TIPB molecule functions as a bridge to connect three Zn ions to give the first polymeric coordination complex of imidazole with a two-dimensional structure as shown in Fig. 4. This finding indicates that TIPB ligands stereochemically favor a bridging mode rather than a tripod mode, at least on coordination to Zn(II). Structural analysis of Zn(II) complexes with imidazoles showed that the central Zn readily undergoes the structural change between tetrahedral and octahedral geometries; the Zn ion in $[Zn(imidazole)_4](ClO_4)_2$[11] is tetrahedrally coordinated by four imidazoles, but the Zn atom in $[Zn(imidazole)_6]Cl_2$[12] is octahedrally coordinated by six imidazoles. In addition, Zn(II) complexes are generally labile and have low stability.[9] Therefore, multiple and rigid chelating ligands such as the tripod ligand[13,14] should be used to control the structure and functionality of Zn(II) complexes with imidazoles.

Experimental

The melting points were measured on a micro hot-stage Yanaco MP-S2 and are uncorrected. IR spectra were recorded on either a JASCO A-100 or a Shimadzu FTIR-8100 spectrometer and ^{1}H NMR spectra were recorded on either a Hitachi R-600L or a JEOL GX-270FT spectrometer in $CDCl_3$ using TMS as the internal standard unless otherwise noted. Mass spectra were measured on a JEOL LMS-HX 100 spectrometer. X-Ray diffraction data were measured on Rigaku AFC-6B and AFC-5R four-circle diffractometers. Silica-gel TLC and column chromatography were done on a Merck precoated TLC #5715 and Merck Kieselgel 60 #7734 or #9385, respectively. Air- and/or moisture sensitive reactions were done under an argon or nitrogen atmosphere. The organic solvents were purified and dried using appropriate procedures.

Dimethyl 3-(Methoxycarbonyl)methylpent-2-enedioate 2. A solution of methyl triphenyl-λ^5-phosphoranylideneacetate (11.23 g, 33.6 mmol) and dimethyl 3-oxopentanedioate (4.50 g, 25.8 mmol) in 30 ml of dry benzene was refluxed for 18 h under an argon atmosphere. The solvent was removed and the residue was extracted twice with hot hexane. The combined extracts were evaporated and the crude product was purified by column chromatography (SiO_2, benzene–ethyl acetate 4:1) to afford the alkenetricarboxylate **2** (5.21 g, 88%) as a pale yellow oil. ^{1}H NMR ($CDCl_3$) $\delta = 3.24$ (d, $J = 1.8$ Hz, 2H), 3.66 (s, 9H), 3.84 (s, 2H), 5.91 (br, 1H);IR (neat) 3001, 2955, 2847, 1740, 1710, 1659, 1436, 1331, 1259, 1198, 1167, 1034, 1007 cm^{-1}. Found: C, 51.80; H, 6.14%. Calcd for $C_{10}H_{14}O_6$: C, 52.17; H, 6.13%.

Dimethyl 3-(Methoxycarbonyl)methylpentanedioate 3. A mixture of the alkenetricarboxylate **2** (4.4 g, 19 mmol) and 1% PtO_2 on carbon (40 mg) in 15 ml of ethanol was hydrogenated in a hydrogen atmosphere. After removal of the catalyst, the solvent was evaporated and the residue was purified by column chromatography

(SiO_2, benzene–ethyl acetate 85:15) to afford 4.37 g (99%) of the triester **3** as a colorless oil. ^{1}H NMR ($CDCl_3$) δ=2.48 (d, J=6.7 Hz, 6H), 2.79 (hep, J=6.7 Hz, 1H), 3.67 (s, 9H); IR (neat) 3002, 2955, 2849, 1748, 1728, 1437, 1264, 1210, 1163, 999 cm^{-1}. Found: C, 51.21; H, 6.97%. Calcd for $C_{10}H_{16}O_6$: C, 51.72; H, 6.94%.

3-(2-Hydroxyethyl)pentane-1,5-diol 4. To a suspension of lithium aluminum hydride (0.179 g, 4.72 mmol) in 10 ml of dry THF was added the solution of **3** (0.610 g, 2.63 mmol) in 10 ml of THF at 0 °C. The mixture was stirred for 2 h at room temperature and then 0.18 ml of water, 0.18 ml of 15% aqueous NaOH solution and 0.54 ml of water were added. After filtration of the mixture, the filter cake was continuously extracted with hot THF. Combined filtrate and extracts were dried over anhydrous magnesium sulfate and the solvent was evaporated. The residue was purified by column chromatography (SiO_2, chloroform–methanol 4:1) to afford 0.334 g (86%) of the triol **4** as a colorless oil. ^{1}H NMR (CD_3OD/$CDCl_3$) δ = 1.52 (q, J = 6.3 Hz, 6H), 1.81 (hep, J = 6.6 Hz, 1H), 3.65 (t, J = 6.3 Hz, 6H), 3.89 (s, 3H); IR (neat) 3400, 2950, 2870 cm^{-1}.

1,5-Dibromo-3-(2-bromoethyl)pentane 5. To a solution of triphenylphosphine (2.16 g, 8.24 mmol, azeotropically dried with benzene) and carbon tetrabromide (2.73 g, 8.23 mmol) in 5 ml of dry THF was added a solution of **4** (0.313 g, 2.11 mmol, azeotropically dried from benzene) in 5 ml of dry THF and the mixture was refluxed for 2 h. The mixture was diluted with hexane, filtered, and evaporated. The residue was filtered through a short silica-gel pad to afford 0.425 g (59%) of the tribromide **5** as a colorless oil. This bromide was used in the next step without further purification. ^{1}H NMR (DMSO-d_6/$CDCl_3$) δ = 1.89 (m, 7H), 3.41 (t, J = 6.9 Hz, 6H); IR (neat) 3030, 2960, 2930, 675, 650 cm^{-1}.

1,5-Di(imidazol-1-yl)-3-[2-(imidazol-1-yl)ethyl]pentane 6. To a suspension of sodium hydride (60% dispersion in mineral oil, 0.146 g, 3.68 mmol) in dry DMF (5 ml) was added imidazole (0.374 g, 5.51 mmol) and after the mixture had been stirred for 30 min at 50 °C, a solution of **5** (0.415 g, 1.23 mmol) in 5 ml of dry THF was added at room temperature over 30 min, and the resulting mixture was stirred for 2 h. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (Al_2O_3, chloroform) to afford 0.207 g (57%) of **6** as colorless prisms. Mp 124.0—127.0 °C; ^{1}H NMR ($CDCl_3$) δ = 1.17 (sept, J=6.9Hz, 1H), 1.70 (q, J=6.8 Hz, 6H), 3.81 (t, J=6.8 Hz, 6H), 6.70 (t, J=1.1 Hz, 3H), 7.02 (s, 3H), 7.29 (s, 3H); IR ($CHCl_3$) 1660 cm^{-1}; EIMS (*m/z*) 298, 217, 203, 123 (base peak). Found: C, 62.04; H, 7.25; N, 26.82%. Calcd for $C_{16}H_{22}N_6 \cdot 1/2H_2O$: C, 62.51; H, 7.54; N, 27.34%. Crystal data: $C_{16}H_{22}N_6$, M=298.39, Orthorhombic, Space group $Pna2_1$ (#33), Z=4, D=1.233 g cm^{-3}, F_{000}=640, λ(Mo $K\alpha$) = 0.73 cm^{-1}, a=13.791(3), b=11.066(4), c=10.532(3) Å, V=1607(1) Å^3, R = 0.044, R_W = 0.045.

1,5-Dicyano-3-(2-cyanoethyl)pentane 8. A mixture of 1,5-dicyano-3-(2-cyanoethyl)-3-nitropentane **7** (4.55 g, 20.6 mmol), tributyltinhydride (7.19 g, 24.8 mmol), and azobisisobutyronitrile (0.976 g, 4.13 mmol) in 20 ml of 1,2-dichloroethane was heated under reflux for 1.5 h. The solvent was removed under reduced pressure and the residue was diluted with hexane to afford a crude crystalline product. Recrystallization from dichloromethane-hexane afforded **8** as colorless crystals. Purification of the crude product from the mother liquid of recrystallization by chromatography (SiO_2, chloroform–methanol 9 : 1) afforded further crops. The total yield was 3.25 g (90%). Mp 81.0—81.9 °C; ^{1}H NMR ($CDCl_3$) δ = 1.77 (dt, J = 6.0, 7.1 Hz, 6H), 1.81 (m, 1H), 2.43 (t, J = 7.1 Hz, 6H) ; IR (KBr) 2961, 2938, 2903, 2891, 2242, 1474, 1460, 1435, 1427, 1358, 1248, 754 cm^{-1}; EIMS (*m/z*) 174, 147, 135, 121 (base peak), 108, 94, 82, 67, 54, 41. Found: C, 67.98; H, 7.51; N, 23.97%. Calcd for $C_{10}H_{13}N_3$: C, 68.54; H, 7.48; N, 23.98%. HRMS found: *m/z* 175.1124. Calcd for $C_{10}H_{13}N_3$: M, 175.1109.

4-(3-Hydroxypropyl)heptane-1,7-diol 9. A solution of **8** (1.69 g, 9.65 mmol) in 15 ml of hydrogen chloride saturated ethanol was heated under reflux for 3 h. After filtration the solvent was removed under reduced pressure. The residue was diluted with water and the mixture was extracted with chloroform. The organic phase was dried and evaporated to afford the crude triethyl ester (3.01 g).

To a suspension of lithium aluminum hydride (1.20 g, 30.0 mmol) in 25 ml of dry THF was added the solution of the above triethyl ester (2.94 g) in 10 ml of THF at 0 °C. After the mixture had been refluxed for 2 h, water (1.2 ml), 15% aqueous NaOH solution (1.2 ml), and water (3.6 ml) were successively added and then the mixture was filtered. The filter cake was extracted with small portions of hot THF. The combined filtrate and extracts were dried and evaporated. The residue was purified by column chromatography (SiO_2, chloroform–methanol 85 : 15) to afford 1.55 g (87% from **8**) of the triol **9** as a colorless oil. ^{1}H NMR (DMSO-d_6/$CDCl_3$) δ = 1.28—1.44 (m, 7H), 1.48—1.59 (m, 6H), 3.16 (br.s, 3H), 3.55 (t, J = 6.8 Hz, 6H); IR (neat) 3326, 2936, 2866, 1456, 1057, 1032, 754 cm^{-1}; EIMS (*m/z*) 191, 160, 142, 129, 113, 101, 95 (base peak), 82, 71, 67, 55, 41. HRMS Found: *m/z* 190.1593. Calcd for $C_{10}H_{22}O_3$: M, 190.1569.

1,7-Dibromo-4-(3-bromopropyl)heptane 10. A solution of **9** (0.526 g, 2.76 mmol) in 9 ml of hydrogen bromide saturated acetic acid was refluxed for 3 h. The solution was diluted with ice water and extracted with chloroform. The extracts were washed with saturated $NaHCO_3$ solution, dried and evaporated. The residue was purified by column chromatography (SiO_2, benzene–hexane 1:1) to afford 0.875 g (84%) of the tribromide **10** as a colorless oil. ^{1}H NMR ($CDCl_3$) δ = 1.30—1.6 (m, 6H), 1.60—2.10 (m, 6H), 3.40 (t, J=6.3 Hz, 6H); IR (neat) 680 cm^{-1}. Found: C, 31.83; H, 5.14%. Calcd for $C_{10}H_{19}Br_3$: C, 31.69; H, 5.05%.

1,7-Di(imidazol-1-yl)-4-[3-(imidazol-1-yl)propyl]heptane 11. To a suspension of sodium hydride (60% dispersion in mineral oil, 0.236 g, 5.91 mmol) in dry DMF (10 ml) was added imidazole (0.435 g, 6.4 mmol) and after the mixture had been stirred for 30 min at 50 °C, a solution of **10** (0.622 g, 1.64 mmol) in 5 ml of dry THF was added at room temperature over 30 min. The resulting mixture was then stirred for 3 h. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (Al_2O_3, chloroform) to afford 0.29 g of **11** as a colorless oil. ^{1}N NMR ($CDCl_3$) δ = 1.12—1.22 (m, 6H), 1.20—1.36 (m, 1H), 1.56—1.69 (m, 6H), 3.88 (t, J = 6.5 Hz, 6H), 6.87 (s, 3H), 7.45 (s, 3H); IR ($CHCl_3$) 1680 cm^{-1}; EIMS (*m/z*) 340, 259, 245, 231 (base peak). HRMS Found: *m/z* 340.2361. Calcd for $C_{19}H_{28}N_6$: M, 340.2374.

***N,N′,N″*-Tris[2-(imidazol-4-yl)ethyl]benzene-1,3,5-tricarboxamide 13.** To a solution of trimesic acid chloride (2.53 g, 9.53 mmol) and triethylamine (6.7 ml, 48 mmol) in dry chloroform, a solution of histamine (4.23 g, 38 mmol) in dry chloroform was added dropwise at 0 °C. The mixture was stirred at room temperature for 20 h and then refluxed for 2 h. The resulting precipitates were filtered and dissolved in water, and the solution was made alkaline with aqueous NaOH solution. The solution was evaporated under reduced pressure and the residue was extracted with methanol. Evaporation of the solvent gave the crude product as a red-brown viscous oil which was purified by column chromatography (SiO_2, chloroform : methanol : aq ammonia 80 : 20 : 5) to afford 4.46 g (96%) of **13** as a yellow white solid. Mp 253.4—257.3 °C (from methanol); ^{1}H NMR (DMSO-d_6/$CDCl_3$) δ = 2.79 (t, J = 8.1 Hz, 6H), 3.52 (dt, J = 8.1, 5.4 Hz, 6H), 6.76 (s, 3H), 7.47 (dd, J = 10.0,

1.08 Hz, 3H), 8.33 (s, 3H), 8.57 (t, J=5.4 Hz, 3H); IR (KBr) 3250, 2850, 1630, 1560, 754, 690 cm^{-1}; FABMS (negative mode) *m/z* 488. Found C, 58.87; H, 5.59; N, 25.71%. Calcd for $C_{24}H_{27}O_3N_9$: C, 58.87; H, 5.57; N, 25.76%.

Benzene-1,3,5-trimethanol 15. To a suspension of lithium aluminum hydride (3.33 g, 87.7 mmol) in dry THF was added a solution of trimethyl trimesate (8.84 g, 35.1 mmol) in THF at 0°C. The mixture was stirred for 1.5 h at room temperature and then 3 ml of water, 3 ml of 15% aqueous NaOH solution and 9 ml of water were added. The mixture was filtered and the filter cake was washed with THF. The combined filtrate and washings were evaporated and the residue was purified by column chromatography to afford 5.88 g (100%) of **15** as colorless needles. Mp 77.8—78.7 °C; ^{1}H NMR (DMSO-d_6) δ=4.46 (d, J=5.7 Hz, 6H), 5.07 (t, J=5.4 Hz, 3H), 7.11 (s, 3H); IR (KBr) 3600—3200, 3003, 2950, 1612, 1445, 1361, 1168, 1153, 1062, 1029, 860, 725, 657 cm^{-1}; EIMS (*m/z*) 168 (base peak), 150, 137, 119, 104, 91, 79, 65. Found: C, 64.10; H, 6.98%. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19%. HRMS Found: *m/z* 168.0804. Calcd for $C_9H_{12}O_3$: M, 168.0822.

1,3,5-Tris(bromomethyl)benzene 16. A solution of **15** (9.75 g, 58.0 mmol) in 30% hydrogen bromide acetic acid solution (220 ml) was refluxed for 1 h. The solution was diluted with ice-water and extracted with dichloromethane. The organic phase was washed with water and saturated aqueous $NaHCO_3$ solution, dried, and evaporated. The residue was recrystallized from hexane to afford 19.0 g (92%) of **16** as colorless needles. Mp 101.3—102.0 °C ; ^{1}H NMR ($CDCl_3$) δ=4.44 (s, 6H), 7.35 (s, 3H); IR (KBr) 3024, 2972, 1605, 1454, 1435, 1211, 893, 704, 582, 553, 530 cm^{-1}; EIMS (*m/z*) 360, 358, 356, 354, 279, 277 (base peak), 275, 198, 196, 115, 91, 57, 40. Found: C, 30.43; H, 2.48%. Calcd for $C_9H_9Br_3$: C, 30.29; H, 2.54%. HRMS Found: *m/z* 353.8225. Calcd for $C_9H_9Br_3$: M, 353.8254.

Triethyl α,α',α''- Tris(ethoxycarbonyl)benzene- 1, 3, 5-tripropanoate 17. To a suspension of sodium hydride (5.82 g, 60% dispersion in mineral oil, 243 mmol) in dry THF (100 ml) was added a solution of diethyl malonate (36.4 ml, 240 mmol) in dry THF under a nitrogen atmosphere. After the mixture had been stirred for 30 min at room temperture, a solution of **16** (11.5 g, 32.3 mmol) in dry THF was added and the mixture was stirred for a further 2 h. The mixture was poured into ice-water and the solvent was removed under reduced pressure. The residue was extracted with ethyl acetate and the extracts dried and evaporated. The residue was purified by column chromatography (SiO_2, hexane–ethyl acetate 9:1 to 4:1) to afford 9.84 g (51%) of **17** as a colorless oil. ^{1}H NMR ($CDCl_3$) δ=1.22 (t, J=7.2 Hz, 18H), 3.13 (d, J=7.2 Hz, 6H), 3.56 (t, J=7.2 Hz, 3H), 4.16 (m, J=7.2 Hz, 12H), 6.90 (s, 3H); IR (neat) 3028, 2984, 2939, 1737, 1605, 1464, 1447, 1371, 1337, 1271, 1232, 1178, 1153, 1096, 1036, 860, 757, 667 cm^{-1}; EIMS (*m/z*) 594, 549, 520, 503, 474, 456, (base peak), 446, 429, 410, 401, 382, 337. HRMS Found: *m/z* 594.2649. Calcd for $C_{30}H_{42}O_{12}$: M, 594.2676.

Benzene-1,3,5-tripropanoic Acid 18. A mixture of **17** (10.9 g, 18.4 mmol) and 85% potassium hydroxide (14.5 g) aqueous solution was refluxed for 16 h. The mixture was acidified with conc. hydrochloric acid and extracted with ethyl acetate. The combined extracts were dried and evaporated. The crude product was heated at 100—180 °C for 3 h. The tricarboxylic acid **18** was obtained (4.69 g, 87%) as a brown powder. ^{1}H NMR ($CDCl_3$–DMSO-d_6 4:1) δ=2.53 (t, J=7.2 Hz, 6H), 2.84 (t, J=7.2 Hz, 6H), 6.89 (s, 3H), 8.5—12.5 (br, 3H); IR (KBr) 3600-3100, 3024, 2937, 1701, 1605, 1443, 1296, 1213, 943, 866, 716 cm^{-1}; EIMS (*m/z*) 294, 276, 258, 230 (base peak), 212, 185. HRMS Found: *m/z* 294.1101. Calcd for $C_{15}H_{18}O_6$: M, 294.1102.

Benzene-1,3,5-tripropanol 19. The mixture of **18** (4.69 g, 15.9 mmol) and conc. sulfuric acid (3 ml) in dry methanol (100 ml) was heated under reflux for 23 h. After neutralization with saturated aqueous $NaHCO_3$ solution, the mixture was concentrated under reduced pressure and the residue was extracted with ethyl acetate. The extracts were dried and evaporated and the residue was purified by column chromatography to afford the corresponding triester (4.81 g, 78%) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ=2.60 (t, J=7.5 Hz, 6H), 2.89 (t, J=7.5 Hz, 6H), 3.67 (s, 9H), 6.88 (s, 3H); IR (neat) 2999, 2952, 2864, 1736, 1605, 1437, 1366, 1040, 989, 866, 835, 783, 706 cm^{-1}; EIMS (*m/z*) 336, 304, 276, 244, 212 (base peak), 185. HRMS Found: *m/z* 336.1550. Calcd for $C_{18}H_{24}O_6$:M, 336.1571.

To a suspension of lithium alminum hydride (1.10 g, 29.0 mmol) in dry THF (120 ml) was added the solution of the above triester (3.61 g, 10.9 mmol) in THF at 0 °C. The mixture was stirred for 1h at room temperature and then 1ml of water, 1 ml of 15% aqueous NaOH solution and 3ml of water were added. The mixture was filtered and the filter cake was washed with THF. The combined filtrate and washings were dried and evaporated. The residue was purified by column chromatography (SiO_2, dichloromethane–methanol 9:1 to 85:15) to afford 2.72 g (99%) of **19** as a colorless oil. ^{1}H NMR (DMSO-d_6) δ = 1.45—1.91 (m, 6H), 2.56 (t, J = 7.8 Hz, 6H), 3.13—3.56 (m, 6H), 4.41 (t, J = 5.1 Hz, 3H), 6.81 (s, 3H); IR (neat) 3600—3100, 3010, 2920, 2870, 2825, 1600, 1450, 1225, 1160, 1050, 960, 710 cm^{-1}; EIMS (*m/z*) 252, 208 (base peak), 190, 172, 157, 144, 131, 117. HRMS Found: *m/z* 252.1746. Calcd for $C_{15}H_{24}O_3$: M, 252.1724.

1,3,5-Tris(3-bromopropyl)benzene 20. To a solution of **19** (1.00 g, 3.96 mmol), 4-(*N*,*N*-dimethylamino)pyridine (1.45 g, 11.9 mmol) and pyridine (12.8 ml) in dry THF (50 ml) was added a solution of methanesulfonyl chloride (3.1 ml, 40.1 mmol) in dry THF (15 ml) at 0 °C under a nitrogen atmosphere. After the mixture had been stirred for 48 h at ambient temperature, water was added to this mixture and the solvent was evaporated under reduced pressure. The residue was acidified and extracted with ethyl acetate. The organic layer was washed with 2 M hydrochloric acid (1M = 1 mol dm^{-3}), saturated aqueous $NaHCO_3$ solution, and brine, and dried by evaporation to leave the crude mesylate as a yellow solid.

A mixture of the crude mesylate and LiBr monohydrate (2.49 g, 23.8 mmol) in acetone (60 ml) was refluxed for 20 h. The solvent was evaporated and the residue was diluted with water and extracted with ether. The extracts were dried and evaporated and the residue was filtered through a short silica-gel pad to afford the tribromide **20** (1.58 g, 90%) as a colorless oil. This bromide was used in the next step without further purification. ^{1}H NMR ($CDCl_3$) δ=1.38—2.43 (m, 6H), 2.74 (t, J=7.8 Hz, 6H), 3.39 (t, J=6.6 Hz, 6H), 6.88 (s, 3H); IR(neat) 3000, 2920, 2850, 1600, 1450, 1430, 1240, 1200, 870, 760, 710 cm^{-1}.

1,3,5-Tris[3-(imidazol-1-yl)propyl]benzene 21. To a suspension of sodium hydride (60% dispersion in mineral oil, 0.645 g, 26.9 mmol) in dry DMF (20 ml) was added a solution of imidazole (1.83 g, 26.9 mmol) in dry DMF (12 ml) at 0 °C under a nitrogen atmosphere. After the mixture had been stirred for 30 min at room temperature, a solution of **20** (1.97 g, 4.47 mmol) in dry THF was added at 0 °C and stirring was continued for 3 h. The mixture was poured into ice water and extracted with ether. The extracts were dried and evaporated, and the residue was purified by column chromatography (SiO_2, chloroform–methanol 95:5 to ethyl acetate–methanol 95:5) to afford 1.74 g (96%) of **21** as a colorless

oil ^{1}H NMR ($CDCl_5$) $\delta = 2.10$ (m, 6H), 2.55 (dd, $J = 7.83$, 6.75 Hz, 6H), 3.95 (t, $J = 6.75$ Hz, 6H), 6.77 (s, 3H), 6.92 (d, $J = 1.35$ Hz, 3H), 7.08 (d, $J = 1.35$ Hz, 3H), 7.46 (s, 3H); IR ($CHCl_3$) 3010, 1510, 1480, 1420, 1030 cm^{-1}; EIMS (*m/z*) 402, 373, 333, 321, 308 (base peak), 280, 253, 240, 201, 157. HRMS Found: *m/z* 402.2531. Calcd for $C_{24}H_{30}N_6$: M, 402.2530.

Synthesis of Zn(II)–DIIPH Complex. The complex was prepared by slow diffusion of an acetone solution (1 ml) of $Zn(ClO_4)_2 \cdot 6H_2O$ (5 mmol dm^{-3}) and an acetone solution (1 ml) of DIIPH (5 mmol dm^{-3}) into the upper part of the compartment in an h-shaped glass tube where ether was used as a crystallizing agent. The glass tube was left standing for two weeks at ambient temperature and colorless fine crystals were obtained. The X-ray crystal analysis was not successful. Found: C, 40.70; H, 5.18; N, 14.60%. Calcd for $Zn(ClO_4)_2 \cdot$DIIPH$\cdot CH_3CN$: C, 41.36; H, 4.40; N, 13.79%.

Synthesis of $\{[Zn(TIPB)_2](ClO_4)_2\}_\infty$. The complex was prepared by the slow diffusion of a methanol solution (1 ml) of $Zn(ClO_4)_2 \cdot 6H_2O$ (4 mmol dm^{-3}) and an aqueous solution (1 ml) of TIPB (4 mmol dm^{-3}) into the third compartment in a Y-shaped glass tube where methanol was used as a crystallizing agent. The glass tube was left standing at ambient temperature and colorless brick-shaped crystals were obtained.

X-Ray Data Collections, Structure Solution and Refinement. A crystal of dimensions $0.100 \times 0.080 \times 0.090$ mm^3 was mounted on a Rigaku AFC-5R four-circle diffractometer equipped with a graphite monochrometer Cu $K\alpha$ ($\lambda = 1.54178$ Å) at ambient temperature. Standard reflections were monitored every 25 measurements and no decay in their intensities was observed. Reflection data were corrected for Lorentz and polarization effects. Empirical absorption corrections were applied.

The structures were solved by a direct method[15] and anisotropically refined for non-hydrogen atoms by block-diagonal least-squares calculations. Reliability factors are defined as $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ and $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$. Atomic scattering factors and anomalous dispersion terms were taken from the usual sources.[16] Hydrogen atoms were included as a fixed contribution in the last cycle; their temperature factors were assumed to be isotropic. The calculations were done on a VAX computer using the TEXAN program system.[17] The compound $ZnCl_2O_8N_{12}C_{48}H_{66}$ (FW 1075.421) gave the following data: monoclinic space group $P2_1/n$, $a = 13.529(4)$, $b = 23.463(3)$ Å, $\beta = 93.93(1)°$, $V = 5331(1)$ $Å^3$, $Z = 4$. A total of 8177 reflections were refined to current residual values of $R = 0.147$ and $R_w = 0.159$.

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References

1) R. H. Prince, "Comprehensive Coordination Chemistry," ed by G. Wilkinson, R. D. Gillard, and J. McCleverty, Pergamon, Oxford (1987), Vol. 5, pp. 948—952.

2) X. M. Chen, Z. T. Xu, and X. C. Huang, *J. Chem. Soc., Dalton Trans.*, **1994**, 2331.

3) R. S. Brown, M. Zamkanei, and J. L. Cocho, *J. Am. Chem. Soc.*, **106**, 5222 (1984).

4) R. G. Ball, R. S. Brown, M. Zamkanei, and J. L. Cochoh, *Inorg. Chem.*, **23**, 2315 (1984).

5) R. Breslow, J. T. Hunt, R. Smiley, and T. Tarnowski, *J. Am. Chem. Soc.*, **105**, 5337 (1983).

6) J. L. Pierre, P. Chautemps, S. Refaif, C. Beguin, A. E. Marzouki, G. Serratrice, E. Saint-Aman, and P. Rey, *J. Am. Chem. Soc.*, **117**, 1965 (1995).

7) G. R. Newkome, C. N. Moorefield, and K. J. Theriot, *J. Org. Chem.*, **53**, 5552 (1988).

8) N. Ono, H. Miyake, R. Tamura, and A. Kaji, *Tetrahedron Lett.*, **22**, 1705 (1981).

9) R. H. Prince, "Comprehensive Coordination Chemistry," ed by G. Wilkinson, R. D. Gillard, and J. McCleverty, Pergamon, Oxford (1987), Vol. 5, Chap. 56, pp. 925—1045.

10) C. A. Bear, K. A. Duggan, and H. C. Freeman, *Acta Crystallogr., Sect. B*, **B31**, 2713 (1975).

11) B. C. Cornilsen and K. Nakamoto, *J. Inorg. Nucl. Chem.*, **36**, 2467 (1974).

12) D. D. LeCloux, M. C. Keyes, M. Osawa, V. Reynolds, and W. B. Tolman, *Inorg. Chem.*, **33**, 6361 (1994).

13) M. Ruf, K. Weis, and H. Vahrenkamp, *J. Chem. Soc., Chem. Commun.*, **1994**, 135.

14) N. N. Murthy and K. D. Karlin, *J. Chem. Soc., Chem. Commun.*, **1993**, 1236.

15) a) "MITHRIL-an integrated direct methods computer program," C. J. Gilmore, *J. Appl. Crystallogr.*, **17**, 42 (1984); b) "DIRDIF-Direct methods for difference structures an automatic procedure for phase extension and refinement of difference structure factors," P. T. Beurskens, Technical Report 1984/1, Crystallography Laboratory: Toenhooived, 6525 Nijimegen, The Netherlands (1984).

16) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham, England (1974), Vol. IV.

17) "TEXRAY Structure Analysis Package," Molecular Structure Corp., 1985.