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Dicompartmental Ligands with Hexa- and Tetradentate Coordination Sites: One-Step Synthesis of Ligands and Metal Complexes and Their X-ray Structure Analysis

Elena V. Rybak-Akimova,[†] **Nathaniel W. Alcock,**[‡] **and Daryle H. Busch***[,†]

Departments of Chemistry, University of Kansas, Lawrence, Kansas 66045, and University of Warwick, Coventry CV4 7AL, United Kingdom

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Examples of interesting ligands previously requiring lengthy synthetic procedures have been prepared by one-step routes, opening the way to more extensive studies of their complexes and to possible applications. New dicompartmental ligands bearing picolyl pendant arms on the amine nitrogen donors have been synthesized, via the Mannich condensation, from 5-substituted salicylaldehydes, formaldehyde, and *N*,*N*′-bis(2-pyridylmethyl)-1,2-diaminoethane. The protonated acyclic ligand salt, two mononuclear complexes of a macrocyclic ligand with a second compartment featuring a Schiff base, and one of the decomposition products resulting from a retro-Mannich reaction have been structurally characterized. The ligand salt (**L1b**) has an extended conformation with the ethylenediamine fragment displaying the trans configuration, very different from that of the corresponding closed-site macrocyclic complexes $\mathrm{NiH_2}$(**L2b**)$^{2+}$ and $\mathrm{ZnH_2}$(**L2b**)$^{2+}$. The mononuclear macrocyclic complex $\mathrm{NiH_2}$(**L2b**)$^{2+}$ has a much smaller ligand twist than the corresponcing Zn(II) complex. The degree of ligand distortion is correlated with the M−N bond length between the metal ions and the pyridine nitrogens; longer M−N bonds cause the pyridine rings to tilt and twist the phenolic rings out of the main ligand plane. The ability of the macrocyclic ligand **L2b** to accommodate a second metal ion has been demonstrated by successful synthesis of dinuclear complexes. The free carbonyl groups of the open-site ligand were transformed into oxime groups, and the corresponding dinuclear bis(nickel) complex has been prepared. Acetal formation by the free carbonyl groups of ligand and retro-Mannich rearrangements are found to be possible pathways for the decomposition of this family of dicompartmental ligands.

Introduction

The chemistry of metal complexes with dicompartmental ligands has become a rapidly growing area of research, because of their importance in biomimetic studies of binuclear metalloproteins, their interesting catalytic properties, their ability to stabilize unusual oxidation states and mixed-valence compounds, and the possibilities for magnetic interaction between the two metal ions, leading to the design of molecular magnetic materials.[1−4] The Robson-type ligands (**I**−**III**, Figure 1) derived from 4-substituted 2,6-diformylphenol (or analogous ketones) and a variety of α,ω-diamines are among the most accessible dicompartmental compounds.[5,6] The essentially planar structures of the ligands provide efficient pathways for metal−metal interactions through bridging phenolic oxygen atoms. The planarity of the complexes, however, results in the relatively low solubilities of these compounds,[4,7] limiting their possible applications (although the solubilities of the complexes can be increased by varying the substituents in the 4-positions of the phenolic rings[4,7,8]). Another problem of traditional Robson dicompartmental complexes is the scrambling of metal ions between the different coordination sites, during the synthesis of heterodinuclear complexes.[8b,9] An elegant development of the Robson design suggested recently by Bosnich and coworkers[10−16] makes use of picolyl pendant arms attached to nitrogen donor atoms in one of the compartments of the

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[†] University of Kansas.

[‡] University of Warwick.

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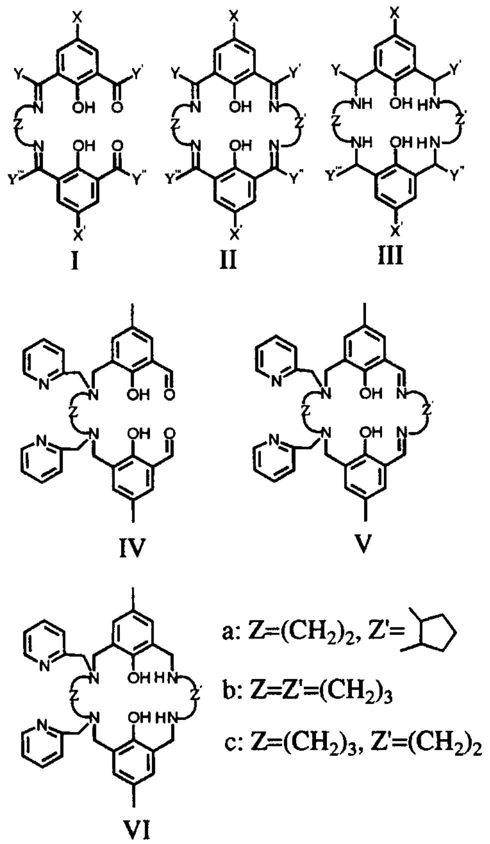

Figure 1. Dicompartmental ligands.

macrocycle (**IV** and **V**, Figure 1). The resulting compounds have one 6-coordinate, hexadentate site and one 4-coordinate, tetradentate site. It has been demonstrated that metal ions in the hexadentate site are substantially less labile than those in either tetradentate site of the parent ligands **I**−**III** (Figure 1).[12] The solubilities of these nonplanar Bosnich complexes are also higher than the solubilities of planar Robson compounds.[10−16] Such binuclear complexes with asymmetric ligands having hexa- and tetradentate coordination sites are expected to be effective mimics of redox enzymes.[10,15,16] The metal ion at the tetradentate site could act as a binding center, while the coordinatively saturated metal ion at the hexadentate site could participate in redox process via an outer-sphere mechanism.

Although Bosnich complexes are very promising in many ways, their study and possible applications are limited by their complicated synthetic procedure. The original method[10] requires 9 steps to obtain ligand **IV**, starting from 4-methylphenol. Further, it is difficult to vary the substituents at the 4-positions of the phenolic rings, because the whole 9-step synthesis must be repeated with each distinctive 4-substituted phenol. As a result, only the 4-Me substituted complexes of **IV** and **V** have been described.[10−16] Variation of the 4-substituent X is desirable for control of the solubilities of the complexes[4,7,8] and the redox potentials of the central metal ions.[7c,17,18]

In this paper, we describe a simple 1-step procedure for the synthesis of compound **IV** (ligand **L1**), based on the Mannich reaction (Figure 2). This reaction has been successfully applied to the synthesis and functionalization of a variety of macrocyclic complexes,[19−22] to the synthesis of polydentate (nonmacrocyclic) complexes bearing picolyl arms,[23,24] and to the synthesis of asymmetric Robson-type ligands having two tetradentate compartments.[25,26] Here, we apply the Mannich reaction to the synthesis of dicompartmental ligands having hexa- and tetradentate sites. 5-Substituted salicylaldehydes are used as starting materials in our work, facilitating variation of the substituents on the phenolic moiety and leading to the preparation of a number of new complexes. We report the synthesis and characterization of mononuclear complexes Zn(**L1b**) and Ni(**L1b**) (X = Cl), the isolation of the free ligand H_2**L1b** and its salts, the modification of the open compartment in the **L1b** derivatives (synthesis of mononuclear macrocyclic complexes with an empty Schiff base or dioxime compartment), and the incorporation of two metal ions in the dicompartmental ligands **L1b** and **L2b**. X-ray structures are described for the ligand salt (H_6**L1b**)$(ZnBr_4)_2$, its mononuclear complexes, Zn(**L2b**)·$2HClO_4$ and Ni(**L2b**)·$2HClO_4$, and a bis(nickel) complex resulting from the partial ligand decomposition (Ni_2(**L4**)$_2$-$(ClO_4)_2$). The detailed characterization of the dinuclear complexes with **L2b** will be a subject of future studies.

Results and Discussion

Mannich Condensation for the Synthesis of L1 Derivatives. Mannich condensation between *N,N*′-bis(2-pyridylmethyl)-1,2-diaminoethane, formaldehyde, and 5-Me or 5-Cl-salicylaldehyde gives a mixture of products which contains the target ligand H_2**L1** (Figure 2, reaction 1). The reaction conditions and yields of the products were found to be essentially the same for the 4-Me and 4-Cl derivatives (X = Me, **L1a**; X = Cl, **L1b**). The yield of H_2**L1** depends on the reaction conditions. In methanol the reaction gives an isolated yield of ca. 25%; in ethanol, the yield is about 10%; in ethanol−water (9:1 v/v), black byproducts complicate the work up; in dioxane, only traces of H_2**L1** are formed. Refluxing for 30 h was found necessary for complete reaction. The amine-containing products are separated from the unreacted 4-substituted salicylaldehyde by the precipitation of perchlorate salts (***Caution***: *perchlorates are potentially explosive!*), followed by redissolving in water, addition of an excess of NaOH, and extraction of the free bases into methylene chloride. The ligands H_2**L1a** and H_2**L1b** can be separated from other amine-containing

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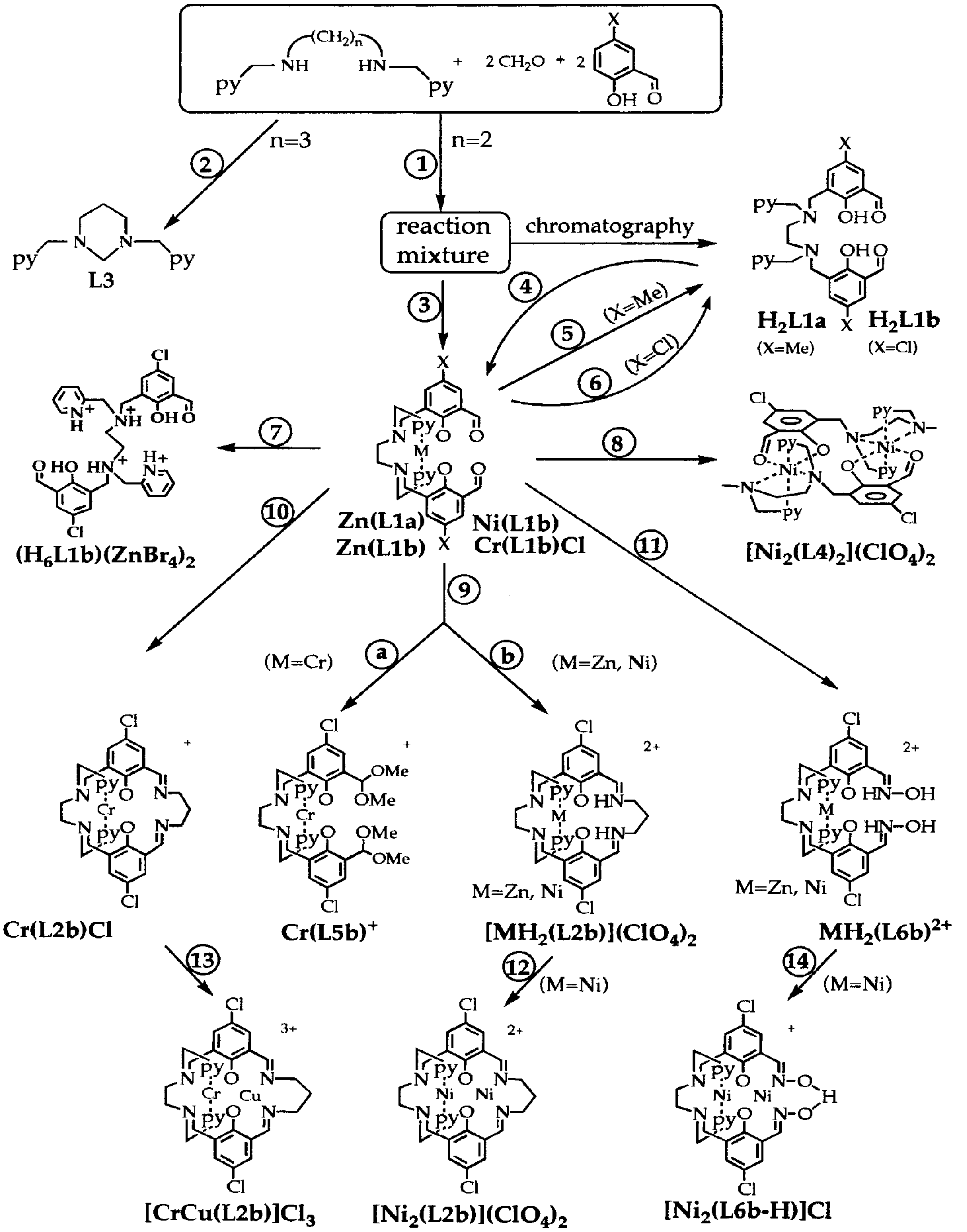


Figure 2. Synthetic transformations. The following reagents/conditions were used. Reaction 1: reflux in methanol. Reaction 2: reflux in methanol or ethanol. Reaction 3: $Zn(OAc)_2{\cdot}2H_2O$ or $Ni(OAc)_2{\cdot}4H_2O$, triethylamine (2 equiv); ethanol or methanol. Reaction 4: $Zn(OAc)_2{\cdot}2H_2O$ or $Ni(OAc)_2{\cdot}4H_2O$, triethylamine (2 equiv) or $CrCl_2$, followed by aerial oxidation; KOH (1 equiv); methanol or ethanol. Reaction 5: Zn(**L1a**), H_2S (gas). Reaction 6: Zn(**L1b**) in CH_2Cl_2, $H_2C_2O_4$ in water, extraction of the ligand in methylene chloride. Reaction 7: Zn(**L1b**), HBr(gas) in ethanol. Reaction 8: $NiCl_2{\cdot}6H_2O$, CH_3CN; $NaClO_4$; crystallization from acetonitrile/ethanol. Reaction 9: (a) Cr(**L1b**)Cl, HOAc (2 equiv), 1,3-diaminopropane (or 1,3-diamino-2-propanol); methanol. (b) Zn(**L1b**) or Ni(**L1b**), HOAc (2 equiv), 1,3-diaminopropane; $NaClO_4$. Reaction 10: Cr(**L1b**)Cl, 1,3-diaminopropane; DMF. Reaction 11: Zn(**L1b**) or Ni(**L1b**), $NH_2OH{\cdot}HCl$ (2 equiv); $NaClO_4$; ethanol. Reaction 12: $[NiH_2($**L2b**$)](ClO_4)_2$, $Ni(OAc)_2{\cdot}4H_2O$, reflux in CH_3CN/methanol. Reaction 13: $CuCl_2{\cdot}2H_2O$; DMF. Reaction 14: $[NiH_2($**L6b**$)]^{2+}$, $NiCl_2{\cdot}2H_2O$, triethylamine (3 equiv); ethanol.

products by column chromatography. Alternatively, the zinc(II) or nickel(II) complexes can be prepared in situ by the addition of the metal acetate and 2 equiv of triethylamine to the ethanol solution of the amine-containing mixture (Figure 2, reaction 3); the neutral complexes with the deprotonated ligand **L1** precipitate from solution and are easily isolated.

Carrying out the Mannich condensation in a different manner, e.g. by slow dropwise addition of *N*,*N*′-bis(2-pyridylmethyl)-1,2-diaminoethane to the refluxing mixture of substituted salicylaldehyde and formaldehyde or by slow simultaneous dropwise addition of the *N*,*N*′-bis(2-pyridylmethyl)-1,2-diaminoethane and formaldehyde to the refluxing solution of salicylaldehyde, did not improve the yield of the desired product. A slight improvement in the yield of **L1b** (up to 32%) has been accomplished by the slow dropwise addition of the bis(2-methylpyridine)ethylenediamine to a refluxing solution containing 5-Cl-salicylaldehyde, formaldehyde, and triethylamine (in 1:2:1 molar ratio); the purification of the ligand H_2**L1b** or its metal complexes was, however, more complicated in this case. Although the yields of the H_2**L1** and Zn(**L1**) from this procedure are not high, they exceed the overall yield of the original 9-step Bosnich synthesis (16.5%, despite excellent yields for most of the individual steps),[10] and the isolation of the product is simple and straightforward.

While the proposed method is applicable for different 4-substituted salicylaldehydes, thereby providing facile variation of the substituents X, it is sensitive to the diamine component of the reaction. Our attempts to use *N,N′*-bis(2-pyridylmethyl)-1,3-diaminopropane, in place of the corresponding 1,2-diaminoethane derivatives, failed to produce the dicompartmental ligand. Instead, a simple heterocycle **L3** was formed (Figure 2, reaction 2), as established by elemental analysis, NMR, and mass spectroscopy. The same byproduct was obtained in attempts to develop a two-step procedure for the Mannich condensation, although such a procedure has been used successfully to prepare substituted aza-crowns.[20]

Compounds H_2**L1a** and Zn(**L1a**) (X = Me) were found to be identical with the compounds originally described by Bosnich and co-workers.[10] Analogous compounds H_2**L1b** and Zn(**L1b**) (X = Cl) gave NMR and IR spectra very similar to those of the Me-substituted derivatives, suggesting their similar structures. The identities of the **L1b** derivatives have also been proven by elemental analysis. Room-temperature magnetic succeptibility measurements showed that nickel(II) complex Ni(**L1b**) is a high-spin species ($\mu = 3.37\ \mu_B$), which is typical of 6-coordinate nickel(II) complexes.

Preparation of L1 from Its Zn Complexes. It has been shown earlier[10] that the free ligand H_2**L1a** is not very stable but that it can be stored for relatively longer periods of time in the form of its zinc(II) complex. In our case, the need to isolate the ligands H_2**L1a** and H_2**L1b** from the reaction mixture by column chromatography results in substantial loss of the product. However, the zinc(II) complexes can be isolated much more easily, without loss. Therefore, it was necessary to develop a convenient method for the demetalation of the zinc complexes. As previously reported,[10] H_2S gas can be used successfully for the demetalation of Zn(**L1a**) (Figure 2, reaction 5). This method, however, does not work for the Zn(**L1b**) complex (having Cl subsituents in the phenolic rings). Of the other approaches examined, the most successful procedure for isolation of H_2**L1b** uses the precipitation of insoluble zinc(II) oxalate upon treatment of Zn(**L1b**) with an equivalent amount of $H_2C_2O_4$ in a two-phase water/chloroform system (Figure 2, reaction 6). The protonated ligand, in the form of its tetrabromozincate salt (H_6**L1a**)$(ZnBr_4)_2$, can also be isolated, in this case by treating an ethanol suspension of Zn(**L1b**) with HBr gas (Figure 2, reaction 7).

Crystal Structure of [H_6L1b]$^{4+}$([$ZnBr_4$]$^{2-}$)$_2$·2H_2O. The ligand cation in this compound is tetraprotonated, on all four nitrogen atoms; the two hydrogen atoms attached to the phenolic oxygens also dissociate upon complexation with metal ions. All of these protons have been identified in difference Fourier maps, as have the two protons of each H_2O molecule. The structural diagram (Figure 3) shows the cation with its two hydrogen-bonded water molecules. In the ligand cation, the conformation is strikingly different from that found in metal complexes of Robson-type ligands, with the ethylenediamine fragment in a trans-conformation (dihedral angle N(1)−C(15)−C−N = 180.00°). The overall impression is that of a badly damaged fragment of a network of hexagons. This extended conformation probably arises from repulsions between the four positively charged atoms. The structure is stabilized by intramolecular stacking interactions between the pyridine and phenolic rings (C(4)−C(10) = 2.964 Å, C(7)−C(13) = 3.821 Å); the angle between the plane of the pyridine ring and that of the phenolic ring is 13.3°.

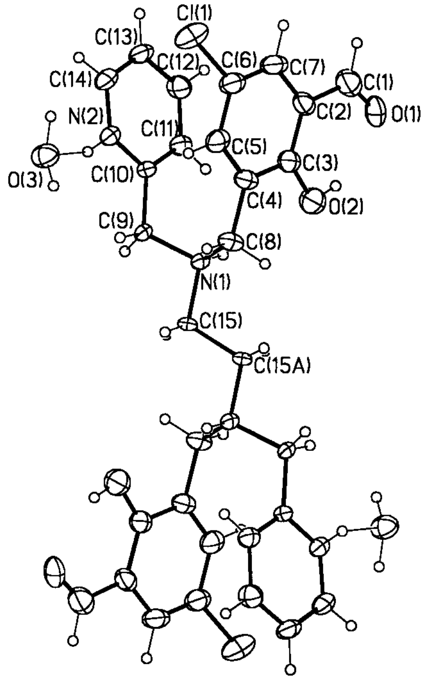


Figure 3. Crystal structure of the protonated ligand, [H_6**L1b**]$^{4+}$[$ZnBr_4$]$^{2-}$·2H_2O (front view of the cation).

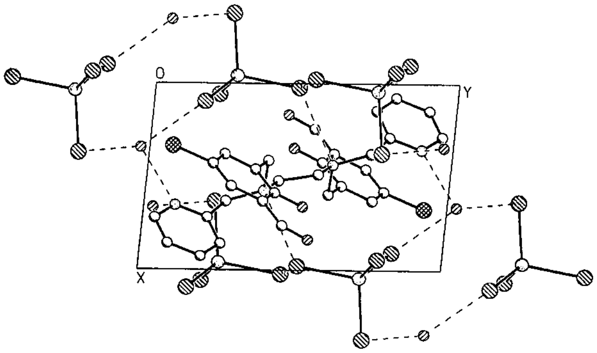


Figure 4. Crystal structure of the protonated ligand, [H_6**L1b**]$^{4+}$[$ZnBr_4$]$^{2-}$·2H_2O (packing diagram).

The packing diagram shown in Figure 4 reveals a variety of intermolecular interactions. Each water molecule is hydrogen-bonded to a protonated pyridine nitrogen (N(2)−O(3) distance = 2.716 Å) and to Br atoms in two different $ZnBr_4^{2-}$ anions (O−Br distances 3.287 and 3.300 Å, with O−H−Br angles of 148.68 and 152.33°, respectively). The protonated aliphatic amine is also hydrogen-bonded to the $ZnBr_4^{2-}$ anion (N(1)−Br distance 3.240 Å, N(1)−H−Br angle = 144.93°). Secondary Br−Br contacts between different $ZnBr_4^{2-}$ anions can also be found (Br−Br distance = 3.785 and 4.231 Å). $\pi-\pi$ stacking between the carbonyl group in one ligand cation and the phenolic ring in another ligand cation can also be identified (C(1)−C(2)′ distance = 3.419 Å, O(1)−C(7)′ = 3.501 Å).

Analysis of the molecular structure of the ligand salt H_6**L1b**$^{4+}$ provides an important insight into the chemical reactivity of the compound. Protons have often be used, instead of metal ions, for the template synthesis of macrocyclic ligands or their acyclic precursors.[27,28] However, with our ligands, the distance between the carbonyl groups in the tetraprotonated ligand H_6**L1b**$^{4+}$ is clearly unfavorable for ring closure reactions.

Consequently, protonation of the ligands **L1** will not assist cyclization. Complexation with metal ions is therefore essential to position the two carbonyl groups preparatory to macrocycle formation (corresponding reactions 9 and 10, Figure 2, are discussed below).

Synthesis of Mononuclear Complexes of Acyclic Ligands L1. Although the complete characterization (including crystal structure determination) of the salt (H_6**L1b**)$(ZnBr_4)_2$ was highly instructive, the presence of the zinc ions in the anion makes the compound of doubtful value for the synthesis of mononuclear complexes with different metal ions (the competition between the incoming metal ion and the zinc ion could lead to scrambling and to the formation of binuclear species of uncertain composition). However, the free ligand prepared by reaction 6 (Figure 2) has been successfully used for the synthesis of complexes with other metal ions, e.g., nickel(II) and chromium(III) (Figure 2, reaction 4). Because it is insoluble in alcohols, the nickel(II) complex can also be prepared directly from the reaction mixture obtained in the workup of the Mannich condensation (reaction 3); however, the soluble chromium(III) complex cannot be separated from byproducts, and the synthesis of the chromium(III) complex requires the preparation of pure ligand H_2**L1b**. Two other features of our procedure for the synthesis of [Cr(**L1b**)]Cl are worth mentioning. (1) $CrCl_2$, rather than chromium(III) salts, was used as a chromium source. Kinetically inert chromium(III) ions would require elevated temperature and extended reaction time, for incorporation into the polydentate ligand. These reaction conditions are acceptable for Salen derivatives[29] but not for fragile ligands having free aldehyde groups, like **L1**. In contrast, chromium(II) compounds are kinetically labile and amenable to the mild conditions for metal ion incorporation. Oxidation of chromium(II) to chromium(III) occurs even in the absence of O_2 (phenolic protons probably serve as the oxidizing agents). The overnight aerial oxidation of the reaction mixture was used to ensure completion of this process. (2) When triethylamine was used to deprotonate the ligand, we could not separate the resulting chromium complex from triethylammonium chloride (the two had very similar solubilities in many common solvents). We therefore carried out the complexation in ethanol, using KOH as the base. KCl precipitated from the reaction mixture and did not contaminate the product.

Reactivity of Mononuclear M(L1b) Complexes. We were interested in the possibility of incorporating a second metal ion in the empty O_4 compartment of M(**L1b**) complexes and in modifications of the carbonyl groups targeted toward synthesis of dinuclear and polynuclear complexes. Both types of reactions have been explored for Robson-type complexes.[1a,6]

For open-side Schiff base ligands having N_2O_2 and O_4 compartments (**I**, Figure 1), dinuclear complexes have been synthesized starting from the corresponding mononuclear complex and a metal salt.[6] Our attempts to apply a similar approach to the M(**L1b**) complexes did not give satisfactory results. The incorporation of the second metal ion probably occurs upon treatment of Zn(**L1b**) with solutions of $Zn(OAc)_2$ or $ZnCl_2$ or upon treatment of Ni(**L1b**) with solutions of $Ni(OAc)_2$, $NiCl_2$, or $Ni(ClO_4)_2$, as indicated by the increased solubility of the starting material in the solvents used (methanol, ethanol, or acetonitrile). The molecular ions corresponding to the binuclear species have also been observed in the mass spectra. The isolated products, however, did not correspond to the individual dinuclear species and, rather, represented mixtures of several materials. Recrystallization of the mixture isolated from the Ni(**L1b**)/$Ni(ClO_4)_2$ system (Figure 2, reaction 8) gave a crystalline decomposition product suitable for X-ray diffraction studies. This compound, Ni_2(**L4**)$_2(ClO_4)_2$, is derived from the ligand H**L4** which has lost one of the phenolic rings of **L1b** (structure **VII**), suggesting a retro-Mannich rearrangement as a probable pathway for decomposition of ligand **L1b**.

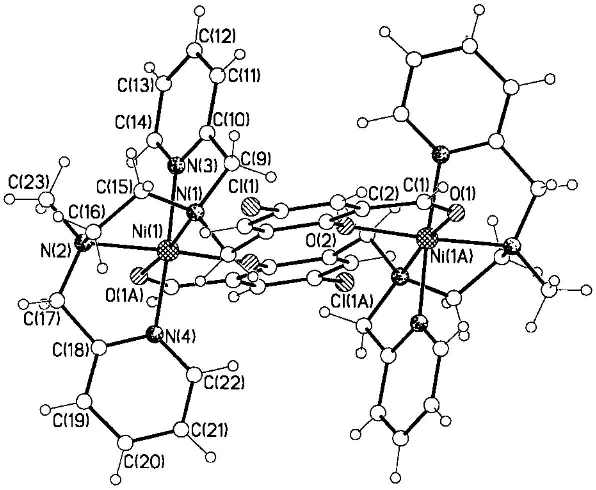
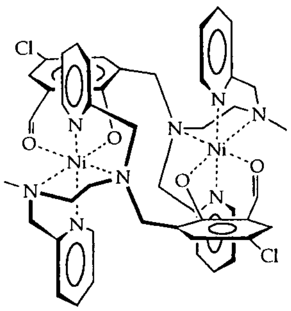


Figure 5. Crystal structure of the complex $[Ni_2(\mathbf{L4})_2](ClO_4)_2$.



Structure VII

Crystal Structure of Ni$_2$(L4)$_2$(ClO$_4$)$_2$. The structure of this unexpected dinuclear complex is shown in Figure 5. Each nickel(II) ion is bound to two tertiary amine nitrogen donors, two pyridine nitrogen donors, and the deprotonated phenolic oxygen and carbonyl oxygen from another ligand. Two phenolic groups bridge the dimeric complex. The nickel(II) ions in the dimer are separated by 6.253 Å, which is too far for significant metal−metal exchange interactions. The coordination geometry around nickel(II) ions is that of a slightly distorted octahedron, with Ni−O bond lengths of 1.994 and 2.027 Å, Ni−N(pyridine) bond lengths of 2.070 and 2.077 Å, and Ni−N(amine) bond lengths of 2.134 and 2.131 Å; the Ni−N(amine) bonds are longer than the Ni−N(pyridine), which is usual for these types of donor atoms. These dimensions are typical for high-spin nickel(II) complexes.[30] The ligand can be considered to be a substituted *N*,*N*′-bis(2-pyridylmethyl)-1,2-diaminoethane

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for $[Ni_2(\mathbf{L4})_2](ClO_4)_2$[a]

Ni(1)−O(2)#1	1.993(6)	Ni(1)−N(3)	2.078(8)
Ni(1)−O(1)#1	2.033(7)	Ni(1)−N(1)	2.129(8)
Ni(1)−N(4)	2.071(9)	Ni(1)−N(2)	2.136(8)
O(2)#1−Ni(1)−O(1)#1	91.3(3)	N(4)−Ni(1)−N(1)	100.1(3)
O(2)#1−Ni(1)−N(4)	95.4(3)	N(3)−Ni(1)−N(1)	80.5(3)
O(1)#1−Ni(1)−N(4)	87.1(3)	O(2)#1−Ni(1)−N(2)	172.8(3)
O(2)#1−Ni(1)−N(3)	88.0(3)	O(1)#1−Ni(1)−N(2)	93.8(3)
O(1)#1−Ni(1)−N(3)	92.2(3)	N(4)−Ni(1)−N(2)	79.9(3)
N(4)−Ni(1)−N(3)	176.5(3)	N(3)−Ni(1)−N(2)	96.8(3)
O(2)#1−Ni(1)−N(1)	91.0(3)	N(1)−Ni(1)−N(2)	84.6(3)
O(1)#1−Ni(1)−N(1)	172.3(3)		

[a] Symmetry transformations used to generate equivalent atoms: (#1) −*x*, −*y*, −*z* + 1.

bearing a bidentate pendant arm. As it binds in a tetradentate manner to one of the metal ions, the coordinated ligand adopts cis-α conformation, with the two pyridine nitrogen donors in positions trans to each other. The remaining two cis-positions on that metal ion are occuppied by the bidentate residue of a second ligand, i.e., bound through phenolic and carbonyl oxygen atoms. α-cis-orientation of bis(picolylethylenediamine) derivatives is quite common among their metal complexes,[31] although the alternative *β*-cis-orientation (with two pyridine nitrogen donors cis to each other) has also been found in a few cases.[31a,g] Selected bond lengths and angles are given in Table 1.

Synthesis of Mononuclear Macrocyclic Complexes of L2b. The Schiff base condensation between diamines and the two carbonyl groups present in $M(N_2O_2)(O_4)$ complexes with dicompartmental acyclic ligands (**I**, Figure 1) has traditionally been used to prepare macrocyclic compounds.[1−16] Here, we followed the procedure previously suggested by Bosnich and co-workers for M(**L1a**) complexes.[10,14] When Ni(**L1b**) or Zn(**L1b**) was used as starting material, the condensation with 1 equiv of 1,3-diaminopropane in the presence of 2 equiv of acetic acid in ethanol, followed by the addition of excess $NaClO_4$, leads to the formation of the expected macrocyclic products (Figure 2, reaction 9b). In both cases, it has been established by X-ray crystallography that the metal ion occupies the hexadentate site.

The conditions for the ring closure reactions at the open site of the mononuclear complexes M(**L2b**) depend on the metal ion (M) bound in the hexadentate compartment. With M = Zn or Ni, this Schiff base condensation in the presence of 2 mol of acetic acid in alcohol solutions produces the desired macrocycle (Figure 2, reaction 9b); however, no macrocycle is obtained, under the same conditions, with M = chromium(III). Instead (Figure 2, reaction 9a), the free aldehyde groups form acetals, as is seen from the mass spectra of the products; the same molecular ion, M = *m/e* 720, was found, when two different diamines, 1,3-diaminopropane or 1,3-diamino-2-propanol, were used in the reaction. The formation of acetals from the carbonyl groups of acyclic Robson-type complexes has been observed earlier,[32] but proper selection of solvent favors the Schiff base condensation; DMF was found reasonably satisfactory for the synthesis of the chromium(III) complex (Figure 2, reaction 10).

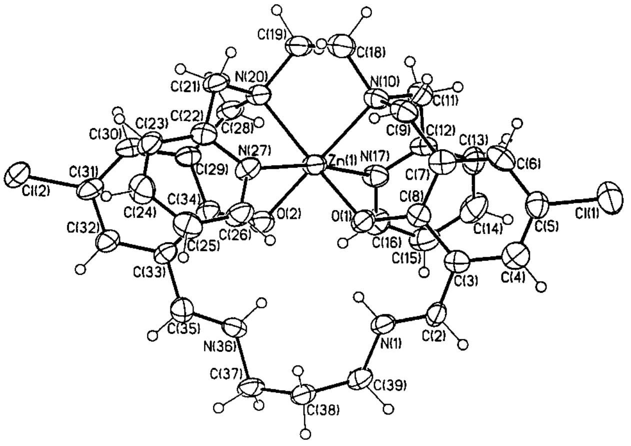

Figure 6. Crystal structure of the complex $[ZnH_2(\mathbf{L2b})](ClO_4)_2 \cdot 0.5CH_3CN$ (front view of the cation).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[MH_2(\mathbf{L2b})]^{2+}$

bond/angle	M = Zn	M = Ni
M−O(1)	2.056(4)	2.051(5)
M−O(2)	2.089(4)	2.025(5)
M−N(20)	2.174(5)	2.100(5)
M−N(10)	2.196(5)	2.106(5)
M−N(17)	2.202(5)	2.097(5)
M−N(27)	2.232(5)	2.095(5)
O(1)−M−O(2)	98.7(2)	91.1(2)
O(1)−M−N(20)	161.7(2)	170.1(2)
O(2)−M−N(20)	92.4(2)	92.1(2)
O(1)−M−N(10)	90.5(2)	92.2(2)
O(2)−M−N(10)	161.7(2)	170.1(2)
N(20)−M−N(10)	83.2(2)	86.2(2)
O(1)−M−N(17)	87.3(2)	89.6(2)
O(2)−M−N(17)	86.6(2)	90.2(2)
N(20)−M−N(17)	108.0(2)	99.8(2)
N(10)−M−N(17)	77.9(2)	80.5(2)
O(1)−M−N(27)	88.8(2)	90.1(2)
O(2)−M−N(27)	84.8(2)	90.2(2)
N(20)−M−N(27)	77.6(2)	80.5(2)
N(10)−M−N(27)	111.3(2)	99.5(2)
N(17)−M−N(27)	170.0(2)	179.7(2)

Crystal Structure of $[ZnH_2(L2b)]^{2+}([ClO_4]^-)_2 \cdot {}^1/_2CH_3CN$ (Figures 6 and 7). The ligand is significantly distorted when compared to Robson macrocyclic complexes lacking pendant arms, which are essentially planar. The zinc(II) ion is pseudo-octahedrally coordinated to two amine nitrogen donors, two phenolic oxygen donors, and two trans pyridine nitrogens. For charge balance, the two Schiff base nitrogens in the open site of the dicompartmental ligand are presumed to be protonated, with hydrogen bonds between O(1) and N(1) and also O(2) and N(36).

The Zn−donor atom bond lengths (Table 2) are similar to those found previously for analogous complexes,[11,13,15,33] although the Zn−N(py) bonds are slightly longer. The angle N(10)−Zn(1)−N(20) (the bite angle of the five-membered

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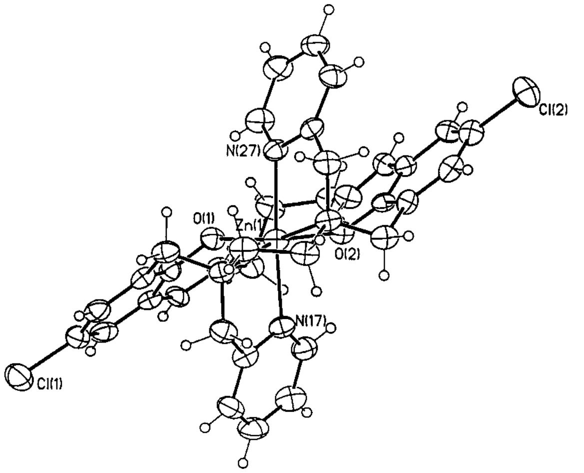

Figure 7. Crystal structure of the complex $[ZnH_2(\mathbf{L2b})](ClO_4)_2{\cdot}0.5CH_3CN$ (side view).

chelate ring) is rather small (83.2°) and the opposite O(1)−Zn(1)−O(2) angle is relatively large (98.7°); these are almost identical to the angles (82.8°) in the Zn complex with ligand **Va** (Figure 1, $Z = (CH_2)_2$, $Z' =$ 1,2-bis(CH_2)-cyclopentane).[11] However, with a trimethylene bridge (Vb, $Z = Z' = (CH_2)_3$), the bite angle of the six-membered chelate ring is significantly greater (93.8°).[13]

The cavity at the unfilled site of the ligand has "diagonal" distances of 3.957 Å (N(1)−O(2)) and 4.261 Å (N(36)−O(1)), which should be suitable for a second 3d-transition metal ion, for which M−N and M−O bond lengths are generally close to 2 Å. These dimensions are comparable to the open cavity size in the C(2)−C(4) bridged macrocycle Zn(**Va**) (diagonal distances for this complex 3.9 and 4.4 Å),[11] although the open site in the C(3)−C(3) bridged complex Zn(**Vb**) is significantly smaller (diagonal dimensions are 3.6 and 3.7 Å).[13]

Although the main N_2O_2 ligand unit is reasonably planar (±0.32 Å), and the zinc ion is not displaced out of the plane (Zn−{N_2O_2} plane 0.011 Å), the Zn−N(py) directions are far from perpendicular to this plane (Figure 7). This is clearly due to the pendant arms being shorter than ideal and is exemplified in the chelate N(amine)−Zn−N(py) angles of 77−78° and in the pyridine rings being canted with respect to the N(py)−Zn−N(py) axis (Figure 7) (angles between the Zn−N directions and the N−C midlines of the pyridine ring of 20−22°). As a consequence, the amine nitrogen atoms (N(10) and N(20)) are pulled to opposite sides of the O(1)−Zn−O(2) plane. Following on from this, the phenyl rings are markedly twisted out of the main ligand plane (dihedral angles to ZnO_2 plane of 38−41°). This distortion from planarity is also demonstrated by the displacements of the terminal chlorine atoms of the phenolic rings out of the N_2O_2 plane (1.90−2.13 Å).

Crystal Structure of $[NiH_2(L2b)]^{2+}([ClO_4]^-)_2$ (Figure 8). Overall, the structure of the nickel(II) complex is similar to that just described; the atom-numbering scheme is the same as shown in Figure 6 for the zinc complex. The Ni−donor atom bond lengths are typical of high spin nickel(II) complexes, with almost equal Ni−N(amine) and Ni −N(pyridine) distances. The metal atom is displaced by ±0.17 Å from the N_2O_2 plane. The dimensions of the open site in Ni(**L1b**) (diagonal distances N(1)−O(12) = 4.117 Å and N(36)−O(11) = 4.045 Å) are again suitable for a second 3d-metal ion. The rather smaller Ni has the effect of increasing the bite angle of the five-membered ethylenediamine chelate ring by 3° compared to the Zn complex; as a result, the O(1)−Ni−O(2) angle (91.1°) is smaller and probably more favorable for complexation with a second metal ion.

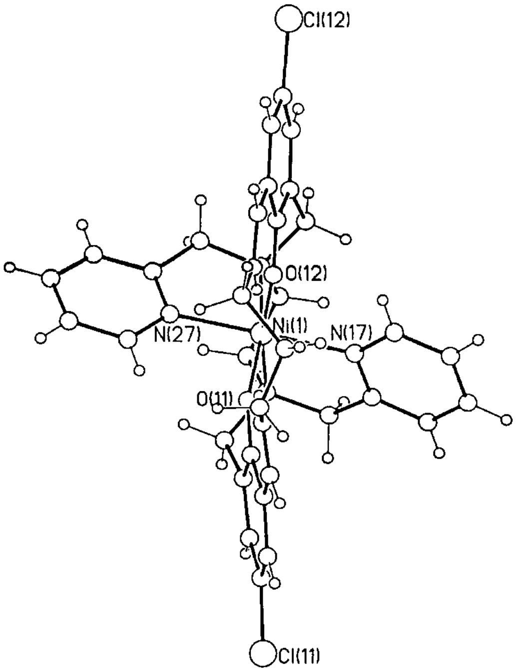

Figure 8. Crystal structure of the complex $[NiH_2(\mathbf{L2b})](ClO_4)_2$.

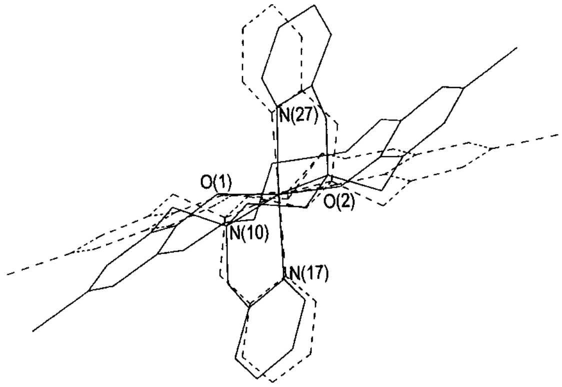

Figure 9. Overlay of the X-ray structures of $[ZnH_2(\mathbf{L2b})](ClO_4)_2{\cdot}0.5CH_3CN$ (solid line) and $[NiH_2(\mathbf{L2b})](ClO_4)_2$ (dotted line).

The decrease in size of the central metal atom also has a notable effect on the overall structure, as can clearly be seen if the two structures are overlaid (Figure 9). The chelate N(py)−Ni−N(amine) angles are about 3° larger than in the zinc complex; the py rings are less oblique (inclined at 6−12° to the Ni−N lines). As a result, the displacement of the phenyl rings is greatly reduced (dihedral angles to NiO_2 of 13−20°); the contrast can also be seen in the smaller displacements of the Cl atoms from the N_2O_2 plane (0.06−0.64 Å). The increased planarity of this complex allows intermolecular stacking interactions between pyridine rings, which can be seen in the packing diagram down crystallographic *c* axis (Figure 10).

Precisely the same distortion effects can also be seen in the previously reported structures of three closely related complexes, and the relevant dimensions are summarized in Table 3. Not surprisingly, all five structures show a close correlation between M−N(py) distance and N(amine)−M−N(py) mean angle. More important for the overall geometry, the metal size clearly also controls the out-of-plane distortion of the phenyl groups. This ranges from the maximum of 49° for the highly nonplanar manganese complex with **Va**[11] to 17° for Ni(**L2b**) as discussed

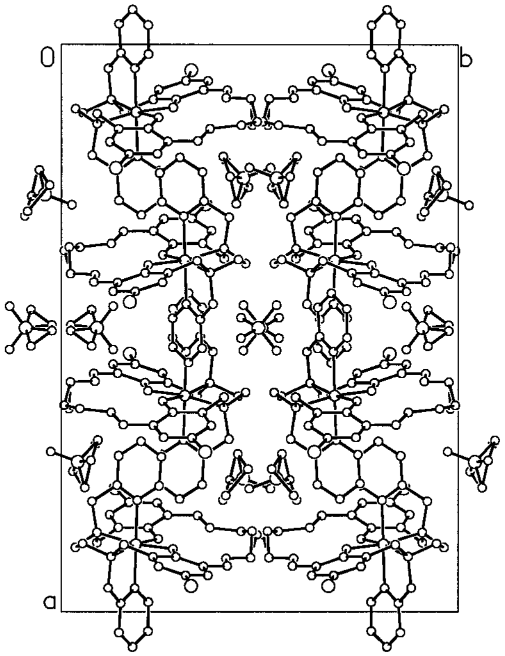

Figure 10. Crystal structure of the complex $[NiH_2(\mathbf{L2b})](ClO_4)_2$ (packing diagram down crystallographic *c* axis).

Table 3. Correlation of Metal Size with Complex Dimensions

compd	M−N(py) (mean)	N(ring)− M−N(py) angle (mean)	interplane angle Ph to {MO2} (mean)	ref
Co(**VIc**) (Figure 1)	1.955	83.5	34.9	15
Ni(**L2b**)	2.096	80.5	16.8	this work
Zn(**Va**) (Figure 1)	2.163	78.2	29.9	11
Zn(**L2b**)	2.217	77.8	39.5	this work
MnL(**Va**) (Figure 1)	2.267	74.9	49.2	11

above. It would be expected that the complex with an even smaller cobalt(III) central ion (ligand **VIc**, Figure 1) would be still less distorted, but other modes of distortion seem to set in here.[15] The Co−N(amine) distances are 0.08 Å longer than those to N(py), (although in the zinc complexes these are almost equal), and the phenyl group is twisted about its axis. It appears that the size of the high-spin Ni(II) ion fits best into the hexacoordinate compartment; Zn(II) and Mn(II) are too large, and the Co(III) is too small for the undistorted ligand conformation.

The different ligand conformations in the zinc and nickel complexes give rise to different vibrational frequencies for C=N stretches: 1621 cm^{-1} for the Zn complex and 1656 cm^{-1} for the Ni complex. This can be attributed to different degree of conjugation between C=N groups and phenolic rings in the nickel and zinc complexes caused by the different twist angles of the phenolic rings. The $\nu_{C=N}$ frequencies (or $\nu_{C=O}$ in the parent acyclic complexes) have often been used to distinguish between empty metal-occupied compartments and compartments.[34] Although in the absence of structural information the IR data might be useful in determining the coordination geometry of Robson-type complexes,[34] our result suggests that the interpretation of such IR spectra requires caution.

Although the crystalline $Zn(\mathbf{L2b})\cdot 2HClO_4$ complex does not have precise C_2 symmetry, the solution NMR spectra (in CD_3CN or in DMSO-d_6) show a C_2-symmetrical coordination site for the zinc ion (e.g., indistinguishable pyridine rings). The same behavior has been observed previously for similar mononuclear zinc(II) or cobalt(III) complexes.[10] The nickel(II) complex is a high-spin compound (room-temperature magnetic moment of the solid sample $\mu = 3.32\ \mu_B$), as expected for 6-coordinate nickel(II).

Preparation of the Dinuclear Complexes of L2b and L6b. The value of the newly synthesized mononuclear complexes $MH_2(\mathbf{L2b})^{2+}$ for the preparation of dinuclear complexes has been demonstrated. The interaction of $NiH_2(\mathbf{L2b})^{2+}$ with nickel(II) acetate, in the presence of 2 equiv of triethylamine, leads to the formation of the homodinuclear complex $[Ni_2(\mathbf{L2b})](ClO_4)_2$ (Figure 2, reaction 12). Similarly, interaction of the monochromium(III) complex with copper(II) chloride produced the heterodinuclear complex $[CrCu(\mathbf{L2b})]Cl_3$ (Figure 2, reaction 13). In the latter case, no dichromium or dicopper complexes were formed, confirming the absence of scrambling of different metal ions. The structures and properties of these and other dinuclear complexes will be the subject of future research.

The free carbonyl groups present in M(**L1**) complexes (and in similar Robson-type complexes) provide many opportunities for the modification of the ligands. Macrocycle formation via Schiff base condensation provides the most popular route; the application of this reaction to the synthesis of M(**L1b**) complexes has been discussed above. The formation of oxime groups offers special promise[32,35] because the oxime nitrogens can coordinate to the metal ion in the second compartment of the dicompartmental ligand, while the oxime oxygens can be used to bridge between these dinuclear units or to connect them to additional metal complexes.[32,35] We have successfully synthesized mononuclear zinc(II) and nickel(II) complexes with the ligand **L6b**, by the reaction between the corresponding M(**L1b**) and hydroxylamine hydrochloride in the presence of triethylamine (Figure 1, reaction 14). The dinuclear nickel(II) complex with the dicompartmental oxime-containing ligand **L6b** has been obtained by either incorporation of the second metal ion in the preformed $Ni(\mathbf{L6b})^+$ or by the interaction of Ni(**L1b**) with 1 equiv of nickel(II) salt, followed by the addition of hydroxylamine hydrochloride and triethylamine. The successful preparation of mono- and dinuclear complexes with the oxime-containing ligand **L6b** demonstrates that the open-site precursor **L1b** is well-suited for the exploration of the chemistry of polynuclear complexes and their aggregates. Studies on these complexes will be reported separately.

Conclusions. The Mannich condensation provides a simple route to the synthesis of complicated dicompartmental ligands bearing picolyl pendant arms. The salt of the protonated acyclic ligand **L1b**, two mononuclear complexes of a macrocyclic ligand **L2b**, and one of the decomposition products resulting from the retro-Mannich reaction ($Ni_2(\mathbf{L4})_2{}^{2+}$) have been structurally characterized. Remarkably, the salt of an open-site ligand **L1b** has a conformation very different from that for corresponding closed-site macrocyclic complexes $NiH_2(\mathbf{L2b})^{2+}$ and $ZnH_2(\mathbf{L2b})^{2+}$. The mononuclear complex $Ni(\mathbf{L2b})\cdot 2HClO_4$ has a much reduced ligand twist compared to that for some similar complexes and is well suited for the incorporation of the second metal ion in the Schiff base compartment. The potential of the macrocyclic ligand **L2b** to accommodate the second metal ion has been demonstrated by the successful synthesis of examples of dinuclear complexes. Free carbonyl groups in M(**L1b**) complexes have also been transformed into oxime groups, and the corresponding dinuclear nickel(II) complex has been pre-

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pared. Acetal formation from the free carbonyl groups of ligand **L1b** and the retro-Mannich rearrangements are found to be possible side reactions in the chemistry of **L1b** complexes; these reactions should be avoided in the syntheses of **L2b** derivatives. The exploration of the rich chemistry of dinuclear complexes derived from **L2**, **L6**, and other related ligands is a subject for our future research.

Experimental Section

Infrared spectra (potassium bromide disks) were recorded using a Perkin-Elmer model 1600 FTIR instrument; only strong peaks are given. Magnetic moments were determined with the Johnson Matthey magnetic susceptibility balance. Fast atom bombardment (FAB) mass spectra were obtained with a VG Analytical, Ltd., ZAB HS mass spectrometer equipped with a Xenon gun operated at 8 keV and 0.8 mA emission using, as the sample-containing matrix, either a mixture of 3:1 dithiothreitol and dithioerythriol (FAB/MB) or 3-nitrobenzyl alcohol (FAB/NBA) or a mixture of thioglycerol/glycerol (FAB/TG-G). NMR spectra were obtained on a General Electric QE-300 spectrometer. Signal positions are reported in parts per million (ppm) relative to residual solvent signals.

All inert-atmosphere manipulations were performed either on a vacuum/argon Schlenk line in Schlenk-type glassware or in a nitrogen-filled Vacuum Atmospheres Corp. (VAC) glovebox equipped with a gas circulation and dioxygen removal system.

The solvents and reagents used in these studies were reagent grade or better. The solvents used in preparation of chromium complexes were degassed by successive freeze−pump−thaw cycles prior to use. *N*,*N*′-Bis(2-pyridylmethyl)-1,2-diaminoethane and *N*,*N*′-bis(2-pyridylmethyl)-1,3-diaminopropane were synthesized according to the published method,[36] and 5-methylsalycilaldehyde, according to ref 37.

Mannich Condensation. (a) Synthesis of Zn(L1a). *N*,*N*′-bis(2-pyridylmethyl)-1,2-diaminoethane (3.9 g, 16.1 mmol) and 5-methylsalicylaldehyde (4.4 g, 32.2.mmol) were dissolved in 70 mL of methanol, paraformaldehyde (0.97 g) was added, and the reaction mixture was refluxed for 30 h (during the first 1 h, all solid paraformaldehyde was dissolved). The solvent was removed by rotary evaporation, the oily residue was redissolved in a minimum amount of ethanol, and an aqueous solution of 50% $HClO_4$ was added dropwise (do not allow the temperature of the solution to exceed 40 °C), until the reaction mixture became acidic. After standing for 1 h, the liquid phase was decanted from the oily residue. The residue was washed several times with ethanol (without stirring!), then treated with an excess of aqueous $NaHCO_3$ (ca. 100 mL), and extracted with methylene chloride (3 × 70 mL). The combined extracts were dried over anhydrous sodium sulfate overnight. After filtration, the solvent was evaporated, leaving 5.2 g of the oily material. This was dissolved in 50 mL of ethanol, and a solution of 2.11 g of $Zn(OAc)_2{\cdot}2H_2O$ in 30 mL of methanol was added, followed by 2.5 mL of triethylamine (the amount of zinc acetate was calculated by assuming that the oil is essentially pure ligand H_2**L1a**). A yellow precipitate started to form in 1 h. The reaction mixture was left at room temperature overnight, and then the precipitate was collected, carefully washed with ethanol and diethyl ether, and dried in vacuo (1.2 g). Additional product (1.1 g) was isolated from the filtrate by refluxing for 3 h and evaporation of $^3/_4$ of the solvent. The NMR is identical with that described in ref 10. MS (NBA): *m/e* 601 (isotopic pattern corresponds to the molecular ion). An analytically pure sample was obtained by dissolving the complex in methylene chloride and reprecipitating it with ethanol (as described in ref 10). Anal. Calcd for $C_{32}H_{32}N_4O_4Zn$: C, 63.84; H, 5.36; N, 9.31. Found: C, 63.56; H, 4.99; N, 9.18.

(b) Synthesis of Zn(L1b). The procedure described above for the synthesis of Zn(**L1a**) was repeated, started with 5 g of 5-chlorosalicylaldehyde. The same workup gave rise to 2.6 g of zinc complex. NMR ($CDCl_3$): 10.23 (s, 2H); 8.88 (d, 2H); 7.52 (t, 2H), 7.31 (d, 2H), 7.15 (m, 2H), 6.96 (d, 2H), 6.79 (d, 2H), 4.05 (d, 2H), 3.94 (d, 2H), 3.72 (d, 2H), 3.30 (d, 2H), 2.83 (s, 4H). IR: 1657, 1603, 1543, 1458, 1430, 1268, 1205, 1102, 992, 879, 761, 677 cm^{-1}. MS (MB or TG-G): *m/e* 643 (isotopic pattern corresponds to the calculated for the molecular ion). It should be noted that, in NBA, another peak with M = *m/e* 748 (molecular ion + 105) was sometimes observed. This peak seems to originate from the interaction of the complex with the matrix or its fragments, because it was not observed in other matrixes. The analytically pure product was obtained, as described above. Anal. Calcd for $C_{30}H_{26}N_4O_4Cl_2Zn$: C, 56.05; H, 4.08; N, 8.72. Found: C, 55.80; H, 3.88; N, 8.60.

The procedure can be scaled up (≤20 g of 5-Cl-salicylaldehyde) or down (≥0.65 g of 5-Cl-salicylaldehyde), without substantial changes in the % yield of the zinc complex. ***Caution***: *$HClO_4$ should not be used in a large scale preparation! It can be replaced with HBF_4, leading to a small reduction (by ca. 20%) of the overall yield.*

(c) Synthesis of Ni(L1b). The procedure described above for the synthesis of Zn(**L1a**) was repeated, started with 3.13 g of 5-Cl-salicylaldehyde. $Ni(OAc)_2{\cdot}4H_2O$ was used, instead of $Zn(OAc)_2{\cdot}2H_2O$. A 1.1 g amount of brown-green Ni complex was isolated. Anal. Calcd for $C_{30}H_{26}N_4O_4Cl_2Ni$: C, 56.64; H, 4.12; N, 8.81. Found: C, 56.61; H, 4.40; N, 8.70. MS (MB): *m/e* 637; isotopic pattern corresponds to the molecular ion. MS (NBA): *m/e* 637, 742 (as in the case of the zinc complex with **L1b**, another peak corresponding to molecular ion + 105 is sometimes observed, when nitrobenzyl alcohol is used as a matrix). IR: 1653, 1458, 1432, 1416, 1204, 936, 761 cm^{-1}.

(d) Isolation of the Pure Ligand H_2L1b. The same procedure described above for the synthesis of the zinc complex was repeated, but instead of the addition of $Zn(OAc)_2{\cdot}2H_2O$, the oily mixture containing the free ligand was dissolved in a minimum amount of methylene chloride and loaded on the top of a chromatography column packed with SiO_2(neutral)/CH_2Cl_2. Ethyl acetate was used as an eluent. The first band which moved with the solvent front was found to be unreacted 5-Cl-salicylaldehyde. The second narrow band has not been identified; the third band contains the pure desired ligand. It was isolated as a yellow solid (mp 122−124 °C); yield, ca. 15%. MS (NBA): *m/e* 579. NMR ($CDCl_3$): 10.16 (s, 2H), 8.52 (d, 2H), 7.63 (t, 2H), 7.55 (d, 2H), 7.15−7.3 (m, 6H), 3.76 (s, 4H), 3.64 (s, 4H), 2.72 (s, 4H). Anal. Calcd for $C_{30}H_{28}N_4O_4Cl_2$: C, 62.18; H, 4.87; N, 9.67. Found: C, 62.43; H, 4.56; N, 9.34. *Note*: the success of the chromatography depends on the quality of SiO_2. Old samples of SiO_2 worked much better than fresh SiO_2 from newly opened containers. In the latter case, the sorbent was dry and too active, and the ligand could not be eluted from the column with ethyl acetate. Moreover, the decomposition of the ligand on the column was evident from a color change (from yellow to dark reddish-brown). In this case, the treatment of the sorbent with methylene chloride containing 2% of water before packing the column was necessary for successful isolation of H_2**L1b**. Running a small pilot column is recommended.

(e) Formation of L3 from *N*,*N*′-Bis(2-pyridylmethyl)-1,3-diaminopropane. Attempts were made to carry out the Mannich reaction, starting with 0.77 g of *N*,*N*′-bis(2-pyridylmethyl)-1,3-diaminopropane, 0.94 g of 5-Cl-salicylaldehyde, and 0.18 g of paraformaldehyde in 25 mL of methanol and from 0.51 g of *N*,*N*′-bis(2-pyridylmethyl)-1,3-diaminopropane, 0.54 g of 5-methyl-salicylaldehyde, and 0.12 g of paraformaldehyde in 20 mL of methanol. In both cases, the reaction mixtures were refluxed for 25 h, then the solvent was evaporated, the residue was redissolved in ethanol, and treated with aqueous $HClO_4$, and the resulting oil was treated with aqueous $NaHCO_3$ and extracted into methylene chloride (the same procedure has been described above for the synthesis of Zn(**L1a**)). The extract was dried over Na_2SO_4, and methylene chloride was removed. After addition of ethanol to the residue, an off-white precipitate was formed. It was filtered out, washed with ethanol, and dried in vacuo. Yield: 0.45 g for 5-Cl-salicylaldehyde or 0.26 g for 5-methylsalicylaldehyde. Analysis of the product showed that, in both cases, the same compound L3 was formed. Anal. Calcd for $C_{16}H_{20}N_4$: C, 71.61; H, 7.51; N, 20.88. Found: C, 71.32; H, 7.83; N, 20.27. MS (NBA): *m/e* 269. NMR ($CDCl_3$): 8.74 (d, 2H), 7.80 (t, 2H), 7.47 (d, 2H), 7.37 (t, 2H), 4.67 (s, 2H), 4.40 (s, 4H), 3.32 (t, 4H), 1.52 (quint, 2H).

Synthesis of H_2L1a from Zn(L1a). The treatment of Zn(**L1a**) with H_2S gas, previously described by Bosnich and co-workers,[10] gave the

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(36) Goodwin, H. A.; Lions, F. *J. Am. Chem. Soc.* **1960**, *82*, 5013.

(37) Casiraghi, G.; Casnati, G.; Puglia, G.; Sartori, G.; Terenghi, G. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1862.

desired product. The observed NMR spectrum was identical with that described in ref 10.

Synthesis of H_2L1b from Zn(L1b). For the chloro-substituted compound, treatment of Zn(**L1b**) with H_2S gas in a variety of solvents (chloroform, methylene chloride, carbon tetrachloride, carbon disulfide, 1,2-dichloroethane, ethanol, dioxane) did not produce the desired ligand H_2**L1**. Instead, sulfur-containing reaction products were formed. We also could not obtain the ligand by the reactions of Zn(**L1b**) (suspended in methylene chloride or chloroform) with aqueous solutions of EDTA (disodium salt), $NaHCO_3$, or $NH_4H_2PO_4$. The reaction with $H_2C_2O_4$ proved to be successful. Zn(**L1b**) (0.5 g) was suspended in 250 mL of methylene chloride. $H_2C_2O_4$ (0.1 g) was dissolved in 250 mL of water, and the aqueous solution was added to the suspension of zinc complex. The two-phase system was shaken for 16 h (overnight) (extensive mixing of the phases is essential). At the end, the organic phase was yellow, and a white precipitate (zinc oxalate) had formed. The precipitate was filtered out, the layers were separated, and the organic layer was dried with Na_2SO_4. The organic solvent was removed under reduced pressure, the yellow solid was redissolved in ethanol, and the minor impurity of undissolved and unreacted zinc complex was filtered. The ethanol was removed by rotary evaporation, and the yellow oil was dried *in vacuo*. Yield: 0.35 g (78%). NMR ($CDCl_3$): 10.16 (s, 2H), 8.52 (d, 2H), 7.63 (t, 2H), 7.55 (d, 2H), 7.15−7.3 (m, 6H), 3.76 (s, 4H), 3.64 (s, 4H), 2.72 (s, 4H). MS (NBA): *m/e* 579 (the absence of the peak with M = *m/e* 643 indicates an absence of the zinc complex). *Note*: large volumes of methylene chloride and water in the two-phase system are essential for a high yield of the product.

Synthesis of $[H_6L1b](ZnBr_4)_2 \cdot 2H_2O$. Zn(**L1b**) (0.5 g) was suspended in 20 mL of ethanol, and HBr (gas) was bubbled through the mixture for 5 min whereupon all solids dissolved. The light-yellow (almost colorless) solution was evaporated slowly, and colorless crystals formed after several days. They were separated from solution, carefully washed with a minimum amount of ethanol, and air-dried. Yield: 0.18 g (17%). Anal. Calcd for $C_{30}H_{36}N_4O_6Cl_2Zn_2Br_8$: C, 25.93; N, 4.03; H, 2.61. Found: C, 26.28; N, 3.88; H, 2.45. MS (NBA): *m/e* 579. NMR (DMSO): 9.95 (s, 2H), 8.58 (d, 2H), 8.09 (t, 2H), 7.5−7.8 (m, 8H), 4.31 (s, 4H), 4.07 (s, 4H), 3.26 (s, 4H). Some of the crystals proved to be suitable for X-ray diffraction analysis.

Synthesis of Ni(L1b) from the Free Ligand. H_2**L1b** (0.58 g, 1 mmol) was dissolved in 40 mL of warm ethanol. $Ni(OAc)_2 \cdot 4H_2O$ (0.25 g, 1 mmol) was dissolved in 15 mL of warm ethanol and added to the ligand solution, followed by the addition of 0.2 g (2 mmol) of triethylamine. The mixture was stirred in warm ethanol (40 °C) for 2 h, during which time a yellow precipitate was formed. The reaction mixture was left overnight at room temperature; then the precipitate was filtered out, washed with ethanol and diethyl ether, and dried in vacuo. Yield: 0.28 g (44%). Anal. Calcd for $C_{30}H_{26}N_4O_4Cl_2Ni$: C, 56.64; H, 4.12; N, 8.81. Found: C, 56.82; H, 4.02; N, 9.13. MS (MB): *m/e* 637; isotopic pattern corresponds to the molecular ion. MS (NBA): *m/e* 637, 742. IR: 1653, 1458, 1432, 1416, 1204, 936, 761 cm^{-1}.

Isolation of $[Ni_2(L4)_2](ClO_4)_2$. Ni(**L1b**) (0.12 g) was suspended in 20 mL of acetonitrile, and 0.048 g of $NiCl_2 \cdot 6H_2O$ was added upon stirring. All solid materials were dissolved in 20 min, giving rise to a green solution. After 3 h, this transparent solution was evaporated on a rotary evaporator (at 35 °C). The resulting green-brown solid (which, according to the mass spectra, contains Ni_2(**L1b**)) was redissolved in 10 mL of CH_3CN. A small amount of insoluble impurity was filtered out, and a solution of 0.3 g of $NaClO_4$ in 2 mL of ethanol was added. A small amount of a fine white precipitate formed; it was filtered out and discarded. Slow evaporation of the solvent from the CH_3CN/ethanol solution gave small but yellow crystals of Ni_2(**L4**)$_2(ClO_4)_2$, which were well-formed and suitable for X-ray diffraction analysis (yield, ca. 10%). MS (NBA): *m/e* 483, 1064 (weak).

Synthesis of $Zn(L2b) \cdot 2HClO_4$. Zn(**L1b**) (0.64 g, 1 mmol) was suspended in 50 mL of ethanol. To the stirred mixture, 0.12 mL (2 mmol) of glacial acetic acid was added, followed by the dropwise addition of the solution of 0.074 g (1 mmol) of 1,3-diaminopropane in 3 mL of ethanol, over a period of 5 min. After being stirred for 20 min, the precipitate was completely dissolved. The yellow solution was stirred for another 1 h, and then a solution of 2.0 g of $NaClO_4$ in a minimum amount of ethanol was added. A yellow precipitate formed immediately. The reaction mixture was allowed to stand for an additional 2 h. The precipitate was filtered out, washed with ethanol and diethyl ether, and dried in vacuo. Yield: 0.38 g (41%). Additional product can be isolated by evaporation of the filtrate, but this portion of the product is not pure and requires recrystallization from acetonitrile/ethanol. Anal. Calcd for $C_{33}H_{34}N_6O_{10}Cl_4Zn$: C, 44.95; H, 3.89; N, 9.53. Found: C, 44.58; H, 4.30; N, 9.26. MS (NBA): *m/e* 682. NMR (CD_3CN): 8.60 (d, 2H), 8.28 (d, 2H), 7.78 (t, 2H), 7.44 (d, 2H), 7.3 (m, 4H), 7.13 (d, 2H), 4.1 (m, 8H), 3.76 (d, 2H), 2.95 (dd, 4H), 2.35 (m, 4H). IR: 3061, 2923, 2860, 1621, 1605, 1549, 1443, 1398, 1344, 1304, 1097, 871, 768, 623 cm^{-1}. X-ray-quality crystals were obtained by slow evaporation of the solvent form the ethanol/acetonitrile solution.

Synthesis of $Ni(L2b) \cdot 2HClO_4$. H_2**L1b** (0.6 g) was dissolved in 25 mL of ethanol. A solution of 0.27 g of $Ni(OAc)_2 \cdot 4H_2O$ in 5 mL of ethanol was added, followed by 0.24 mL of glacial acetic acid. The reaction mixture was heated to 60 °C, and a solution of 0.1 g of 1.3-diaminopropane in 5 mL of ethanol was added dropwise over a period of 10 min. The solution turned brown. Stirring was continued at 60 °C for another 30 min, after which the reaction mixture was cooled to ambient temperature and stirred for an additional 2 h. A solution of 2.0 g of $NaClO_4$ in a minimum amount of ethanol was added; precipitation began immediately. The reaction mixture was stored in the refrigerator overnight, and 0.36 g of orange-brown microcrystalline product was isolated, washed with water, ethanol, and ether, and dried in vacuo. Additional product (0.35 g) was obtained after reducing the volume of the filtrate. Overall yield: 78%. The compound can be recrystallized from acetonitrile/ethanol or acetonitrile/2-propanol. Anal. Calcd for $C_{33}H_{34}N_6O_{10}Cl_4Ni$: C, 45.29; H, 3.92; N, 9.60. Found: C, 45.00; H, 4.09; N, 9.69. MS (NBA): *m/e* 675 (isotopic pattern corresponds to the molecular ion). IR: 3060, 2192, 2860, 1656, 1605, 1546, 1479, 1441,1343, 1261, 1220, 1095, 769, 622 cm^{-1}. The compound can also be prepared in the same manner, starting from the Ni(**L1b**) complex. X-ray-quality crystals were obtained by slow evaporation of the solvent from the ethanol/acetonitrile solution.

Synthesis of $[Ni_2(L2b)]$. $Ni(L2b) \cdot 2HClO_4$ (0.44 g, 0.5 mmol) was dissolved in 10 mL of acetonitrile. Nickel(II) acetate tetrahydrate (0.13 g, (0.5 mmol) was dissolved in a minimum amount of methanol, and this solution was added with stirring to the solution of the mononuclear nickel complex. The reaction mixture was refluxed for 2 h, the solvent volume was reduced in half by evaporation, and the solution was cooled to room temperature. The yellow microcrystalline product was collected, washed with a minimum amount of ethanol, followed by diethyl ether, and dried in vacuo. Yield: 0.24 g (51%). Anal. Calcd for $C_{33}H_{32}N_6O_{10}Cl_4Ni_2$: C, 42.54; H, 3.46; N, 9.02. Found: C, 45.35; H, 3.12; N, 8.71. MS (NBA): *m/e* 732 (Ni_2L^+), 833 ($Ni_2LClO_4^+$).

Synthesis of Cr(L1b)Cl. The first stages of this procedure were performed in an inert-atmosphere (N_2) glovebox. The ligand H_2**L1** (0.58 g, 1 mmol) was dissolved in 100 mL of degassed ethanol. The solution was heated to 60 °C, and a solution of 0.12 g (1 mmol) of $CrCl_2$ in 10 mL of degassed ethanol was added. The resulting brown solution was stirred at 60 °C under N_2 for 1 h and then cooled to the room temperature and taken out of the glovebox. The rest of the workup was performed in the air. KOH (0.056 g, 1 mmol), dissolved in a minimum amount of ethanol, was added to the reaction mixture, and a white precipitate (KCl) was removed by filtration. Air was bubbled through the solution for 10 min, and the solution was left in the air overnight. Rotary evaporation to dryness gave a brown solid that was redissolved in a minimum amount of ethanol. The undissolved residue was filtered out, and the complex was precipitated by the addition of diethyl ether, filtered, washed with a mixture of ethanol with ether, and dried in vacuo. Yield: 0.36 g (55%). Anal. Calcd for $C_{30}H_{26}N_4O_4CrCl_3$: C, 54.19; H, 3.94; N, 8.43; Cr, 7.82. Found: C, 53.73; H, 3.90; N, 8.03; Cr, 7.61. MS (NBA): *m/e* 628, 665. IR: 1660, 1611, 1538, 1441, 1261, 1216, 1057, 1030, 770 cm^{-1}.

Reaction of Cr(L1b)Cl with Diamines in Methanol. An attempt was made to synthesize the monochromium complex with the macrocyclic ligand **L2b**. Cr(**L1b**)Cl (0.13 g, 0.2 mmol) was dissolved in 10 mL of methanol. Glacial acetic acid (0.024 g, 0.4 mmol) and 0.015 g (0.2 mmol) of 1,3-diaminopropane were added. The reaction mixture

Table 4. Crystal Data and Structure Refinement

	$[H_6\mathbf{L1b}]^{4+}([ZnBr_4]^{2-})_2\cdot 2H_2O$	$[Ni_2(\mathbf{L4})_2]^{2+}([ClO_4]^-)_2$	$[ZnH_2(\mathbf{L2b})]^{2+}([ClO_4]^-)_2\cdot 0.5CH_3CN$	$[NiH_2(\mathbf{L2b})]^{2+}([ClO_4]^-)_2$
empirical formula	$C_{30}H_{36}Br_8Cl_2N_4O_6Zn_2$	$C_{23}H_{25}Cl_2N_4NiO_6$	$C_{34}H_{34}Cl_4N_{6.50}O_{10}Zn$	$C_{33}H_{34}Cl_4N_6NiO_{10}$
formula weight	1389.55	583.08	900.85	875.17
temp, K	220(2)	230(2)	180(2)	180(2)
wavelength, Å	0.710 73	0.710 73	0.710 73	0.710 73
cryst system	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$C2/c$
unit cell dimens (Å, deg)	$a = 7.464(5)$, $b = 11.550(6)$, $c = 12.675(8)$, $\alpha =96.14(5)$, $\beta = 101.86(5)$, $\gamma = 94.30(5)$	$a = 11.314(2)$, $b = 16.121(3)$, $c = 13.654(2)$, $\alpha = 90$, $\beta = 100.48(1)$, $\gamma = 90$	$a = 13.434(2)$, $b = 20.2914(5)$, $c = 15.043(1)$, $\alpha = 90$, $\beta = 113.273(5)$, $\gamma = 90$	$a = 28.613(4)$, $b = 18.562(2)$, $c = 14.769(2)$, $\alpha = 90$, $\beta = 111.34(1)$, $\gamma = 90$
reflcns for cell determinatn	23	2601	5785	5748
V (Å^3), Z	1057.9(11); 1	2448.9(2); 4	3766.83(10); 4	7306.3(3); 8
D(calcd), Mg/m^3	2.181	1.581	1.588	1.591
abs coeff, mm^{-1}	8.858	1.058	1.002	0.890
F(000)	666	1204	1846	3600
cryst size, mm	0.44 × 0.24 × 0.45	0.16 × 0.08 × 0.06	0.40 × 0.16 × 0.10	0.32 × 0.22 × 0.10
θ range for data collcn, deg	1.5−25	1.5−23	1.72−22.50	1.34−24.00
limiting indices	$-1 \le h \le 8$, $-12 \le k \le 12$, $-12 \le l \le 12$	$-12 \le h \le 12$, $-17 \le k \le 11$, $-15 \le l \le 15$	$-9 \le h \le 17$, $-24 \le k \le 26$, $-19 \le l \le 14$	$-30 \le h \le 37$, $-15 \le k \le 23$, $-19 \le l \le 16$
reflcns collcd	4343	10 503	14 881	16 966
indepdt reflcns	3509	3467 ($R_{int} = 0.1167$)	4899 ($R_{int} = 0.0789$)	5714 ($R_{int} = 0.0937$)
indepdt reflcns with $I > 2\sigma(I)$	3107	2145	3642	4089
abs corr	analytical	ψ-scan	ψ-scan	ψ-scan
max and min transm	0.23 and 0.12	not recorded	0.72 and 0.63	0.93 and 0.82
data/restrains/param	3502/0/237	3455/0/325	4899/0/505	5714/16/517
goodness-of-fit on F^2	1.057	1.239	1.165	1.217
weighting params[a]	$a = 0.0524$, $b = 2.680$	$a = 0.0000$, $b = 20.0000$	$a = 0.0033$, $b = 16.6383$	$a = 0.0033$, $b = 16.6383$
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0352$	$R1 = 0.0945$	$R1 = 0.0680$	$R1 = 0.0885$
R indices (all data)	w$R2 = 0.1061$	w$R2 = 0.1919$	w$R2 = 0.1275$	w$R2 = 0.1556$
largest diff peak and hole, e Å^{-3}	0.956 and −0.671	0.465 and −0.540	0.593 and −0.382	0.467 and −0.442

[a] The weighting scheme was calculated as $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$.

was stirred at room temperature for 2 h and then rotary evaporated. Mass spectrum: peak at *m/e* 720. IR spectrum: no peaks for the C═N stretch (IR: 2937, 1611, 1442, 1302, 1059, 1032, 769 cm^{-1}). Running the same reaction with 1,3-diamino-2-propanol instead of 1,3-diaminopropane gave a product with the same mass spectrum and IR. Repeating the experiment with the addition of 0.4 mmol of triethylamine before isolation of the product also failed to produce the macrocyclic complex. The product was identified as the corresponding acetal, Cr(**L5b**)$^+$.

Synthesis of Cr(L2b)Cl in DMF. Cr(**L1b**)Cl (0.33 g, (0.5 mmol) was dissolved in 15 mL of warm (40 °C) DMF, and 0.037 g (0.5 mmol) of 1,3-diaminopropane was added. The reaction mixture was stirred in warm DMF for 2 h and then cooled to ambient temperature, and the product was precipitated by the addition of diethyl ether. It was filtered, carefully washed with ether, and dried in the air. The solid material was redissolved in methanol (10 mL), insoluble residues were filtered, and the product was reprecipitated by the addition of diethyl ether. The complex was filtered, washed with ether, and dried in vacuo. Yield: 0.22 g (59%). Anal. Calcd for $C_{33}H_{32}N_6O_2Cl_3Cr$: C, 56.38; H, 4.59; N, 11.95; Cr, 7.40. Found: C, 55.94; H, 4.71; N, 11.63; Cr, 7.15. MS (NBA): *m/e* 667 (isotopic pattern corresponds to the molecular ion).

Synthesis of CrCu(L2b)Cl₃. Cr(**L1b**)Cl (0.33 g, 0.5 mmol) was dissolved in 15 mL of warm (40 °C) DMF, and 0.037 g (0.5 mmol) of 1,3-diaminopropane was added. After 30 min of stirring at 40 °C, a solution of 0.15 g (0.05 mmol) of $CuCl_2\cdot 2H_2O$ in 3 mL of DMF was added. The reaction mixture was stirred at 40 °C for an additional 2 h, after which an excess of diethyl ether was added and the precipitate was filtered and carefully washed with ether. The product was dried in vacuo, redissolved in a minimum amount of methanol, separated from minor insoluble residues by filtration, and reprecipitated with diethyl ether. The dinuclear complex was filtered, washed with ether, and dried in vacuo over P_2O_5. Yield: 0.32 g (73%). Anal. Calcd for $C_{33}H_{32}N_6O_2Cl_5CrCu$: C, 47.33; H, 3.85; N, 10.04; Cr, 6.21. Found: C, 47.02; H, 4.11; N, 9.72; Cr, 5.95. IR: 1653, 1624, 1441, 1387, 1294, 1076, 1059, 1032, 769 cm^{-1}. MS (NBA): *m/e* 766 (CrCu**L2b**Cl$^+$). No peaks corresponding to mononuclear Cr or Cu complexes or to dichromium or dicopper complexes (which would be formed if the metal ions were scrambled) were observed in the mass spectra.

Synthesis of the Zn(L6)·2HClO₄. Zn(**L1b**) (0.64 g, 1 mmol) and 0.135 g (2 mmol) of $NH_2OH\cdot HCl$ were stirred in 20 mL of ethanol. In 30 min, all solids were dissolved, and the resulting light-yellow solution was stirred for another 2 h. Addition of a solution of $NaClO_4$ (1 g) in ethanol (2 mL) caused the formation of a yellow precipitate. After 3 h, the precipitate was filtered, washed with a mixture of ethanol with ether, and dried in vacuo. Yield: 0.63 g (73%). Anal. Calcd for $C_{30}H_{30}N_6O_{12}Cl_4Zn$: C, 41.24; H, 3.46; N, 9.62. Found: C, 41.00; H, 3.80; N, 9.28. MS (NBA): *m/e* 673 (isotopic pattern corresponds to the molecular ion).

Synthesis of Ni₂(L6)Cl. Ni(L1b) (0.64 g, 1 mmol) and 0.135 g (2 mmol) of $NH_2OH\cdot HCl$ were stirred in 20 mL of ethanol. In 20 min, all solids were dissolved, and 0.25 g (1 mmol) of $NiCl_2\cdot 2H_2O$ was added. The resulting dark green solution was stirred at room temperature for 1 h, after which 0.4 mL (3 mmol) of triethylamine was added and stirring was continued for 2 h. The resulting fine green precipitate was centrifuged, washed ethanol and diethyl ether, and dried in vacuo. Yield: 0.24 g (31%). Anal. Calcd for $C_{30}H_{27}N_6O_4Cl_3Ni_2$: C, 47.45; H, 3.58; N, 11.07; Ni, 15.46. Found: C, 47.78; H, 3.81; N, 10.79; Ni, 15.35. MS (NBA): *m/e* 723 (isotopic pattern corresponds to the molecular ion). IR: 2972, 2926, 1646, 1605, 1574, 1466, 1298, 1208, 1280, 1091, 1047, 878, 823, 762, 715 cm^{-1}.

Crystal Structure Analysis. Crystal data are given in Table 4. For $[H_6\mathbf{L1b}](ZnBr_4)_2\cdot 2H_2O$ the crystals were colorless blocks, for $[Ni_2(\mathbf{L4})_2](ClO_4)_2$, they were orange-red blocks, for $[ZnH_2\mathbf{L2b}](ClO_4)_2\cdot 0.5CH_3CN$, yellow blocks formed, and for $[NiH_2\mathbf{L2b}](ClO_4)_2$, brown blocks formed. Another crystal modification of the second nickel complex was obtained by recrystallization from CH_3CN/2-propanol. The molecular structure of the product was found to be the same as that of the first crystalline form, although the data was of poor quality; this second structure has not been refined.

(A) Data Collection and Processing. For [ZnH$_2$(**L2b**)](ClO$_4$)$_2$·0.5CH$_3$CN, [NiH$_2$(**L2b**)](ClO$_4$)$_2$, and [Ni$_2$(**L4**)$_2$](ClO$_4$)$_2$, a Siemens SMART[38] three-circle system with CCD area detector was used; for [H$_6$**L1b**](ZnBr$_4$)$_2$·2H$_2$O, a Siemens P3R3 four-circle diffractometer, $\omega-2\theta$ mode, was used with scan range of ±1.5° (2θ) around the Kα_1−Kα_2 angles and scan speed 3−29 deg/min, depending upon the intensity of the 2 s prescan. Backgrounds were measured at each end of the scan for 0.25 of the scan time. The temperature was controlled with an Oxford Cryosystem Cryostream Cooler.[39] Cell constants were obtained by least-squares refinement on diffractometer angles for centered reflections (for [H$_6$**L1b**](ZnBr$_4$)$_2$·2H$_2$O) or by least-squares refinement based on reflection positions (for [Ni$_2$(**L4**)$_2$](ClO$_4$)$_2$), [NiH$_2$(**L2b**)](ClO$_4$)$_2$), and [ZnH$_2$(**L2b**)](ClO$_4$)$_2$·0.5CH$_3$CN). For [ZnH$_2$(**L2b**)](ClO$_4$)$_2$·0.5CH$_3$CN, three standard reflections were monitored every 200 reflections and showed no decrease during data collection; for the other three compounds, crystal decay was checked by repeating the initial frames at the end of the collection. None of the crystals showed any decay. For [H$_6$**L1b**](ZnBr4)$_2$·2H$_2$O, reflections were corrected for absorption effects by the analytical method using ABSPSI;[40] for the other compounds, ψ-scan corrections were used.

(B) Structure Analysis and Refinement. For [ZnH$_2$(**L2b**)](ClO$_4$)$_2$·0.5CH$_3$CN, the space group $P\bar{1}$ was chosen from intensity statistics. For [Ni$_2$(**L4**)$_2$](ClO$_4$)$_2$ and [NiH$_2$(**L2b**)](ClO$_4$)$_2$, the systematic absences indicated the space groups uniquely. For [ZnH$_2$(**L2b**)](ClO$_4$)$_2$·0.5CH$_3$CN, the systematic absences indicated either *Cc* or *C*2/*c* space groups. The structure was initially solved in *Cc* but then found to be correctly described as *C*2/*c*.

For [H$_6$**L1b**](ZnBr$_4$)$_2$·2H$_2$O, the structure was solved by direct methods for the Zn and Br positions using SHELXTL PLUS[41] (TREF), and additional light atoms were then found by *E*-map expansion and successive Fourier syntheses. The ligand cation has inversion symmetry, and one water molecule is included in the asymmetric unit. Hydrogen atoms were added at calculated positions and refined using a riding model; all hydrogen atoms on nitrogens were directly identified on Fourier maps, and that for the OH group was positioned to correspond to the maximum electron density position around the O (SHELXTL AFIX 8). Anisotropic displacement parameters were used for all non-H atoms; H-atoms were given isotropic displacement parameters of 0.08 Å^2. An extinction parameter was refined. Refinement was on F^2 (all reflections) using SHELXL93.[42]

For [Ni$_2$(**L4**)$_2$](ClO$_4$)$_2$, [NiH$_2$(**L2b**)](ClO$_4$)$_2$, and [ZnH$_2$(**L2b**)](ClO$_4$)$_2$·0.5CH$_3$CN, the structures were solved by direct methods using SHELXS[43] (TREF) with additional light atoms found by Fourier methods. In the [NiH$_2$(**L2b**)](ClO$_4$)$_2$, the central carbon atom in the diaminopropane bridge (C(38)) is disordered between chair and boat conformations (with occupancies of 0.2 and 0.8); it was treated isotropically with restrained bond lengths. Two ClO$_4^-$ anions are located on a 2-fold axis, and their oxygens are disordered. The remaining perchlorate is in a general position, again with oxygens disordered. In [ZnH$_2$**L2b**](ClO$_4$)$_2$·0.5CH$_3$CN, the crystal lattice includes a solvent molecule (CH$_3$CN) disordered across the center of inversion; disordered solvent hydrogen atoms were not included in the refinement scheme. Hydrogen atoms were added at calculated positions and refined using a riding model with freely rotating methyl groups. Anisotropic displacement parameters were used for all non-H atoms, apart from minor disordered components; H-atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl hydrogen atoms) times the equivalent isotropic displacement parameter of the atom to which the H-atom is attached. Refinement was on F^2 (all reflections) using SHELXL 96.[44]

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Supporting Information Available: Tables listing complete atomic coordinates, full bond lengths and angles, and thermal parameters (30 pages). Ordering information is given on any current masthead page.

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