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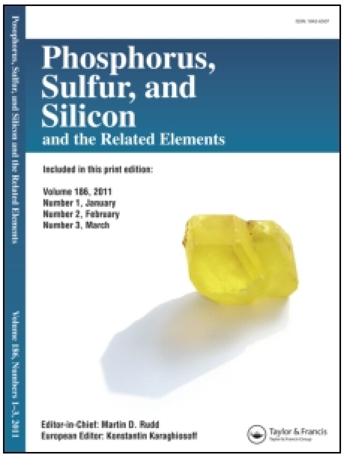

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Ligand Design for Stabilization of Group 2 Element Compounds by Intramolecular Coordination

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Aesthetically pleasing, interlocked ring systems (catenanes) accumulate charge, as they are prepared from neutral ligands and cations. A new approach to the fabrication of charge neutral catenanes, based on designed dianionic ligands and divalent cations is presented. Ba_2L_2(H_2L = 3,5,25,27-tetraoxo-6,7,12,15,18,21,24-heptaoxanonaeisane) represents a new member of the class of helical metal containing catenanes. Each ligand in Ba_2L_2 acts as a double-stranded heterotopic catenand. The two helicates are interlocked to form a [2] catenane. Ba_2L_2 is a rare example of a heterotopic, homodinuclear catenane. Most heterotopic catenates hold two different metal centers, the binding environments being tailored for each metal; *e.g.*, a metal with preference for 4-coordination binding two bipyridyls and one with preference for 6-coordination binding two terpyridyls. The coordinative flexibility of Ba^{2+} permits coordination both to the pseudo-crown ether portion of the catenand, as well as to the anionic ketoester moieties. Ba_2L_2 also is a rare example of an alkaline earth containing catenane, and is the first crystallographically characterized group 2 catenane.

Keywords: Ligand; alkaline earth; intramolecular; catenane; volatility; thermal stability

One of the most difficult challenges facing main group coordination chemists is the charge to size ratio of the heavy p-block elements.[1] Most specifically, in the case of group 2 elements the coordination number preferred for the metal cation is always substantially above two. Thus, either two monoanionic multidentate ligands, or one dianionic oligodentate ligand must be assembled to satisfy its electronic neutrality and coordination number constraints. Approaches involving intermolecular coordination to achieve these objectives in group 2 element chemistry have met with somewhat limited success; however, intramolecular coordination approaches have demonstrated promising results.

One motivation for the exploration of group 2 element chemistry is the prevalence of these species in electronic materials.[2] The optimum preparation method for most electronic devices is chemical vapor processing, a technique which demands volatile molecules having thermal robustness and displaying vapor phase integrity under processing conditions, whilst cleanly decomposing to result in the desired film at substrate temperatures suitable for growth. As one component of continuing

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investigations aimed at the preparation of electronic materials containing group 2 elements, it was required to investigate the extent of suitability of intramolecular coordination of the heavy group 2 elements. This report summarizes the components of this investigation, which resulted in the formation of intramolecularly coordinated inorganic ring systems containing group 2 elements.

Perhaps the simplest group 2 element-containing inorganic ring system is the well-studied β-diketonate class of compounds. In its bidentate monoanionic form, two β-diketonate ligands combine with one group 2 element to achieve electronic neutrality and render a four coordinate species. Even for the early members of the group, such as magnesium, such coordination numbers are insufficient to completely satisfy the saturation requirements (FIGURE 1).

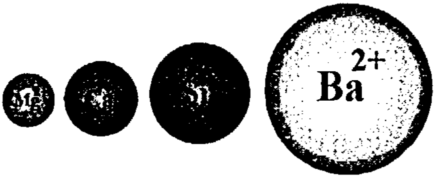


FIGURE 1: Comparison of the ionic radii of the group 2 elements Mg, Ca, Sr and Ba.

By the time one arrives at barium, with its preferred coordination number of 9-12, then substantial intermolecular coordination by solvent molecules or introduced Lewis bases must occur in order to form a stable monomeric arrangement. In the absence of such added intermolecular species, polymeric compositions often result.[3] Some examples of Lewis bases employed in intermolecular coordination and various β-diketonate ligands for barium are given in FIGURE 2A and 2B, respectively.

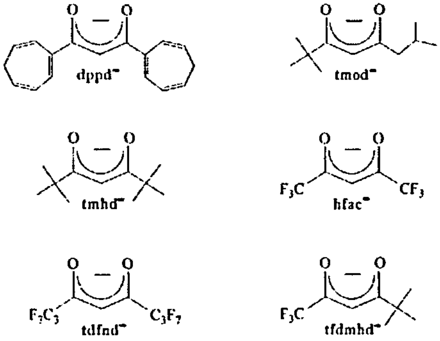


FIGURE 2A: Variably substituted β-diketonate ring systems as designed ligands for formation of group 2 element complexes.

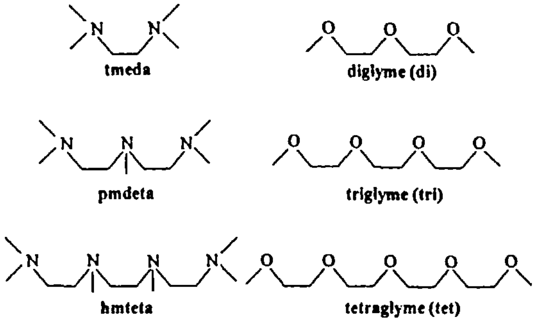


FIGURE 2B: Charge neutral Lewis base examples as intermolecularly coordinating species of group 2 element complexes.

Substantial investigation of the suitability of compounds such as those created by the intermolecular stabilization of barium *bis*(β-diketonate) molecules is summarized in FIGURE 3. The condensed phase of the intermolecularly-coordinated species (be it liquid or solid) must undergo only a single transformation to the vapor phase of the same compound. As represented in the lower horizontal equilibrium (FIGURE 3), no condensed phase dissociation of the intermolecular Lewis base must occur.

$$\begin{tikzcd}
\mathbf{Ba(\beta\text{-}diketonate)_2 \cdot LB_{(g)}} \arrow[r, leftrightarrow] \arrow[d, leftrightarrow] & \mathbf{Ba(\beta\text{-}diketonate)_{2(g)}} \arrow[r, phantom, "+"] \arrow[d, leftrightarrow] & \mathbf{LB_{(g)}} \arrow[d, leftrightarrow] \\
\mathbf{Ba(\beta\text{-}diketonate)_2 \cdot LB_{(s,l)}} \arrow[r, leftrightarrow] & \mathbf{Ba(\beta\text{-}diketonate)_{2(s,l)}} \arrow[r, phantom, "+"] & \mathbf{LB_{(s,l)}}
\end{tikzcd}$$

FIGURE 3: Intermolecular stabilization of barium *bis*(β-diketonate) complexes by Lewis base addition.

The siphoning off of these products, no matter how small (to the right side) is gained by the conversion of the Lewis base from its condensed phase into a vapor phase. The Lewis bases employed exhibit substantial volatility, therefore the net result is an accumulation of the condensed phase of an unligated barium *bis*(β-diketonate) species which often is oligomeric in nature, and exhibits substantially reduced vapor pressure. A minor equilibrium is in place between the vapor phase monomeric barium *bis*(β-diketonate) and its condensed phase polymeric structure. Although the ability to tolerate minor amounts of vapor phase dissociation of intermolecular adducts (as demonstrated in the upper horizontal equilibrium), may be acceptable for certain cases, in general, it is preferred to have no dissociation other than in the boundary layer immediately above the accreting epitaxial film on the desired substrate. Thus, overall, the challenge in addressing intermolecular coordination for barium *bis*(β-diketonate) compounds is summarized by the competitiveness of these equilibria, and the desire to maintain vapor phase integrity of the intermolecular adduct.

In a systematic exploration of numerous compounds of this composition, it has been observed that only in the specific case where the β-diketonate is derived from a fluorinated dione is vapor phase integrity of the intermolecular adduct achieved.[4] This may be explained by the substantial electron withdrawing nature of the fluorine substituents of the β-diketonate ring, which leaves a residual positive charge on the metal center. This uncompensated latent Lewis acidity on the metal serves to draw the lone pair of electrons on the oxygen atoms of the glyme ether more strongly to the metal center. This increased electrostatic attraction is demonstrated by the metrical parameters of a series of compounds, which were examined in the solid state by single crystal X-ray diffraction. The overall shortening of the intermolecular barium-oxygen distances results in a retention of this intermolecular adduct in the vapor phase. Despite its success in coordination chemistry for achieving monomeric vapor phase intermolecular species, this approach was unsuccessful in the preparation of suitable electronic materials by chemical vapor processing. The substantial accumulation of barium fluoride in resultant electronic materials rendered them unsuitable for application as device films. Although the concentration of fluoride in these films may be reduced by the addition of substantial water during the vapor phase processing, inclusion of up to 10^5 parts of water per part of barium has proven to be, as of this date, unsuccessful in totally removing the last traces of the electronically undesirable fluoride from these films. Thus, a challenge for intermolecular coordination still exists in the case of barium *bis*(β-diketonate) compounds, appropriate for vapor phase processing of electronic materials.

For intramolecular formation of inorganic ring systems containing group 2 elements, one initial approach was based on the clam shell motif of oligoether alcohols[5] (FIGURE 4A) or oligoether thiols[6] (FIGURE 4B).

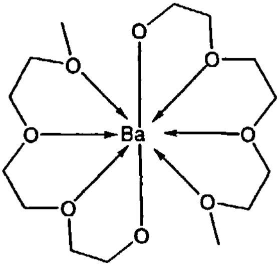


FIGURE 4A: Multidentate and monoanionic oligoether alkoxide ligand as electronically saturating species designed for barium complexation.

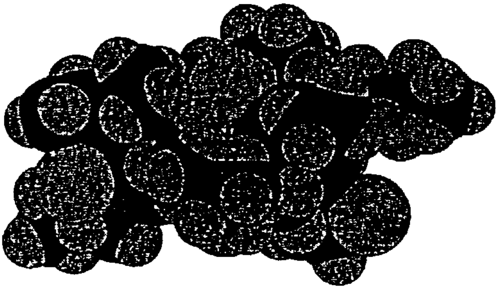


FIGURE 4B: Space-filling molecular model of $[Ba(S(CH_2CH_2O)_2(CH_2)_3CH_3)_2]_2$, as calculated utilizing the CSC Chem 3D Plus program from Cambridge Scientific Computing, Inc.

This approach, although yielding monomeric species of high purity for barium, was not successful in yielding stable vapor phase compounds. One alternate approach, also resulting in the formation of intramolecular coordination to encapsulate barium in an inorganic ring systems, was based on the cyclopentadienido ligand platform[7] (FIGURE 5A), whilst another approach employed bulky tetraphenyldithioimidodiphosphinate ligand[8] (FIGURE 5B).

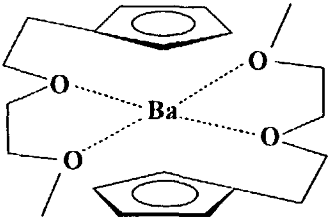


FIGURE 5A: Oligoether substituted cyclopentadienyl barium complex.

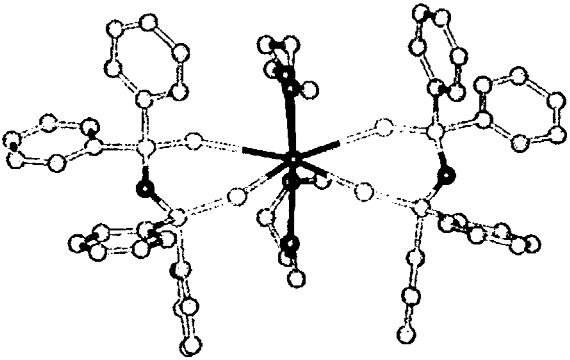


FIGURE 5B: Ball-and-stick representation of the solid state structure of $Ba[(SP(Ph)_2N]_2 \cdot 2DME$, as determined by single crystal X-ray diffraction.

These species, though monomeric in solution and synthesizable in good yields with high purity, did not lend substantial vapor phase integrity to the resultant compound. Approaches based on partial intramolecular substitution of β-diketones[9] (FIGURE 6A) or β-ketoiminates[10] (FIGURE 6B)

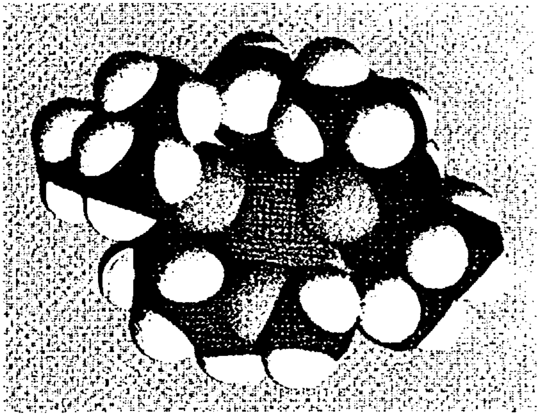


FIGURE 6A: Space-filling model of the proposed structure of $Ba(dmmod)_2$ [dmmod = $Me_3CCOCH_2CO(CH_2)_3OMe$].

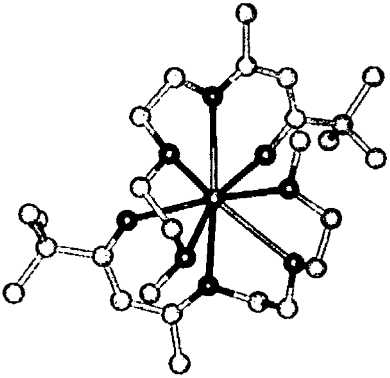
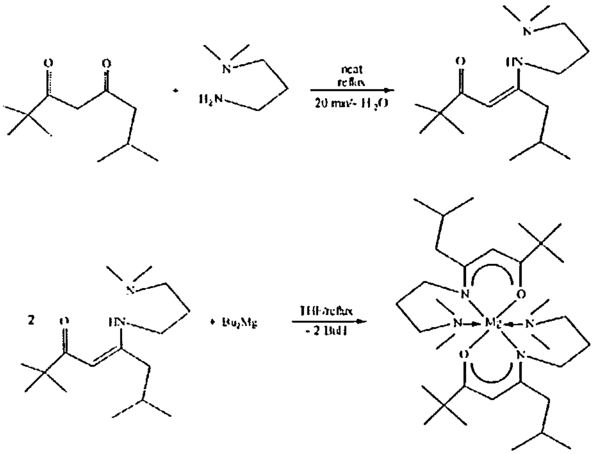


FIGURE 6B: Ball-and-stick representation of the solid state structure of $Ba(diki)_2$, as determined by single crystal X-ray diffraction.

were both successful in providing additional stabilization to the barium center, above that rendered by an unsubstituted bidentate β-diketone or -ketoimine; however, in neither approach was substantial vapor phase integrity of the resultant compounds reported. Presumably, this is due (in each case) to the lack of adequate coordinative saturation of the barium metal center by the ligand system employed.

Quite recently, compounds containing pendant tertiary amine groups have been reported on amide ligands[11], as well as on a β-ketoimine backbone.[12] The synthesis of these later compounds is presented in SCHEME 1.

SCHEME 1



The crystal structure of the six coordinate magnesium compound (FIGURE 7A) may be compared to that of a similar example with intermolecular coordination in FIGURE 7B.

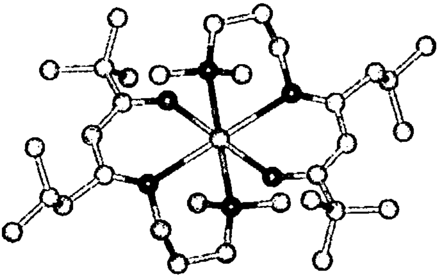


FIGURE 7A: Ball-and-stick representation of the solid state structure of *bis*[5-N-(N,N-dimethylaminopropyl)-2,2,7-trimethyl-3-octanonato] magnesium, as determined by single crystal X-ray diffraction.

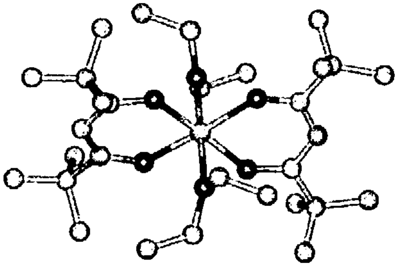


FIGURE 7B: Ball-and-stick representation of the solid state structure of $Mg(tmhd)_2 \cdot 2Et_2O$, as determined by single crystal X-ray diffraction.

The six-coordinate environment, satisfactory for magnesium, is insufficient for the heavier congeners of group 2, as demonstrated by thermogravimetric analysis plots (FIGURE 8).

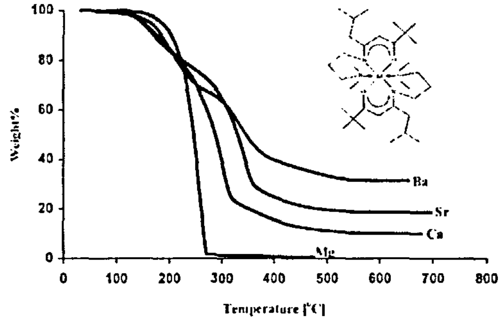


FIGURE 8: Thermogravimetric analyses of *bis*(dimethylaminopropyl) β-ketoiminate complexes of Mg, Ca, Sr and Ba.

These data indicate that, as the ligand constraint remains constant at tridentate and the metal size increases going down the group, the ability of two ligands to satisfy preferred coordination number is diminished, and overall relative vapor phase stability is not enhanced. Shown in FIGURE 9 is a recently obtained intermolecular coordination compound based on a malonate derivative on barium with tetraglyme.[13]

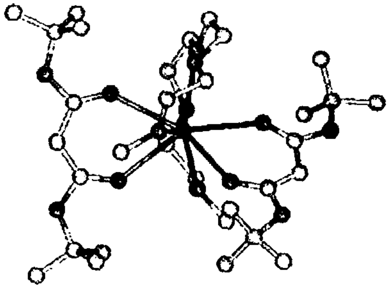
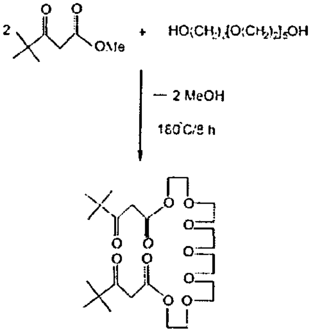


FIGURE 9: Ball-and-stick representation of the solid state structure of *bis*(di^{t}butylmalonato-O,O')barium • tet, as determined by single crystal X-ray diffraction.

This compound, whilst not stable in the vapor phase, was the inspiration for a study to stitch together the two β-diketone ligands with the tetraglyme and form a dianionic nonadentate ligand (SCHEME 2).[14]

SCHEME 2



This synthetic approach was patterned after comparable earlier work that resulted in the formation of β-ketoester derivatives in good yield.

As shown in FIGURE 10, the solid state structure of this compound was quite surprising.

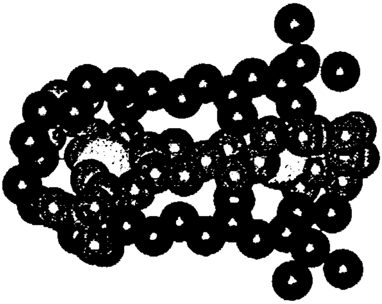


FIGURE 10: Space-filling representation of the solid state structure of dibarium-*bis*(3,5,25,27-tetraoxo-6,9,12,15,18,21,24-heptaoxanoeisanate).

The formation of two inorganic based interlocking rings in demonstrated by the quadruply-stranded homo bi-metallic catenene. Although bi-metallic catanenes had been reported earlier,[15] they were hetero di-nuclear species, which had coordination environments tailored for one four- and one six-coordinate species. Additionally, although quadruply stranded catenenes[16] are not unprecedented, they are quite rare in the literature, and, to date, all develop substantial charge on the molecule. This positive charge on the overall quadruply stranded helicate is compensated for by ionic ligands external to the bound ligands. Thus, the neutral quadruply stranded inorganic ring system formed here is unusual in that it is highly soluble in non-polar organic solvents.

Most catenanes are based on transition metals,[17] and main group elements have, to date, played little role in catenane chemistry. In fact, only one other group 2 inorganic ring system-based catenane is present in the literature, and it did not lend itself to structural characterization.[18] Thus, the molecule represented in FIGURE 10 is an entrée into a related family of inorganic ring systems based on dianionic nonadentate ligands. Additional results will be presented as they become available.

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