Inorg. Chem. **1987**, *26*, 4331–4335

The green solution changed to orange-red. The stirring was continued for 15 min. The solution was evaporated to dryness on a steam bath. The mass was washed with water and dried in vacuo over P_4O_{10}, affording **8a** in quantitative yield. Reduction of **9b** furnished **8b** similarly.

Acknowledgment. Financial support received from the Department of Science and Technology, New Delhi, India, and from the Council of Scientific and Industrial Research, New Delhi, India, is gratefully acknowledged. We are thankful to a reviewer for bringing ref 13 to our attention.

Registry No. **3a**$^+$, 111267-45-9; **3a**, 111321-91-6; **3a**$^-$, 111267-50-6; **3b**$^+$, 111267-46-0; **3b**, 111267-16-4; **3b**$^-$, 111267-51-7; **4a**$^+$, 111267-22-2; **4a**, 111267-17-5; **4a**$^-$, 111267-52-8; **4b**$^+$, 111267-24-4; **4b**, 111267-18-6; **4b**$^-$, 111267-53-9; **4c**$^+$, 111267-47-1; **4c**, 111267-19-7; **4c**$^-$, 111267-54-0; **4d**$^+$, 111267-48-2; **4d**, 111267-20-0; **4d**$^-$, 111267-55-1; **4e**$^+$, 111267-49-3; **4e**, 111267-21-1; **4e**$^-$, 111267-56-2; **5a**, 111267-23-3; **5b**, 111267-25-5; **6a**, 111267-26-6; **6a**$^{2-}$, 111267-59-5; **6b**, 111267-27-7; **6b**$^{2-}$, 111267-60-8; **6c**, 111290-88-1; **6c**$^{2-}$, 111267-61-9; **6d**, 111267-28-8; **6d**$^{2-}$, 111267-62-0; **7a**, 111267-30-2; **7b**, 111267-32-4; **7c**, 111267-34-6; **7d**, 111267-36-8; **8a**$^+$, 111267-38-0; **8a**, 111321-92-7; **8a**$^-$, 111267-63-1; **8b**$^+$, 111267-40-4; **8b**, 111267-37-9; **8b**$^-$, 111267-64-2; **9a**, 111267-39-1; **9b**, 111267-41-5; **10a**$^+$, 111267-57-3; **10a**, 111267-42-6; **10a**$^-$, 111267-65-3; **10b**$^+$, 111267-58-4; **10b**, 111267-43-7; **10b**$^-$, 111267-66-4; Ru(acac)$_3$, 14284-93-6; CoQ$^1{}_3$, 87583-61-7; CoL$^1{}_3$, 111267-44-8; $(NH_4)_2OsCl_6$, 12125-08-5; $(NH_4)_2OsBr_6$, 24598-62-7; $Ce(SO_4)_2$, 13590-82-4; N_2H_4, 302-01-2.

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Ionophoric Binding of Alkaline-Earth-Metal Cations (A^{2+}) by Tris(arylazo oximato)iron(II) Anions (RL^-): The Trinuclear $A(RL)_2$ Family

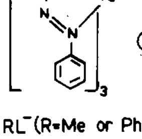
Samudranil Pal and Animesh Chakravorty*

Received December 30, 1986

Reaction of $NaRL{\cdot}H_2O$ and $A(ClO_4)_2{\cdot}xH_2O$ in ethanol or of HRL with ACO_3 in acetone affords $A(RL)_2$, in ≥90% yield (R = Me, Ph; A = Mg, Ca, Sr, Ba). Two complexes are formed as hydrates: $Sr(MeL)_2{\cdot}4H_2O$ and $Ba(MeL)_2{\cdot}5H_2O$. These furnish the anhydrous species upon heating. The $A(RL)_2$ chelates have been characterized with the help of molecular weight, IR, ^1H NMR, electrochemical, and manganese(II)-doped complex EPR data. It is concluded that in $A(RL)_2$ the A^{2+} ion is centrally held in an O_6 environment provided by the oximato oxygen atoms of the pair of facial RL^- anions (**1**–**3**), which act as tridentate ligands. The complexes are soluble in polar organic solvents. Quantitative ionophoric transport of 1 mol of A^{2+} from water to dichloromethane can be achieved with the help of 2 mol of PhL^-. When the aqueous phase is made acidic with 2 mol of H^+, $A(PhL)_2$ is decomposed into A^{2+} and HPhL and A^{2+} is returned to this phase. The equilibrium constants (K_{AMg}) of reactions of type $Mg(PhL)_2(o) + A^{2+}(a) \rightleftharpoons A(PhL)_2(o) + Mg^{2+}(a)$ are as follows: A = Ca, 5.10; A = Sr, 9.52; A = Ba, 24.72 (at 298 K; the abbreviations o and a signify dichloromethane and aqueous phases, respectively). This implies that the equilibrium constants K_A of reactions of type $2PhL^-(o) + A^{2+}(a) \rightleftharpoons A(PhL)_2(o)$ are in the order $K_{Ba} > K_{Sr} > K_{Ca} > K_{Mg}$. The difference ($\Delta\Delta G^\circ{}_f$) of the free energies of formation of $Mg(PhL)_2$ and $A(PhL)_2$ is found to be proportional to the difference ($\Delta\Delta G^\circ{}_h$) in the hydration free energies of Mg^{2+} and A^{2+} as well as to the difference ($\Delta\Delta G^\circ{}_l$) of the lattice energies of crystalline MgO and AO: $\Delta\Delta G^\circ{}_f/\Delta\Delta G^\circ{}_h = 0.99$; $\Delta\Delta G^\circ{}_f/\Delta\Delta G^\circ{}_l = 0.82$.

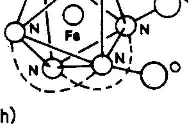
Introduction

Ionophoric transport of alkaline-earth-metal cations (A^{2+}) from the aqueous to the organic phase is of current interest in relation to biological membrane action.[1,2] Ionophores have both polar (inside) and nonpolar (outside) regions. The polar interior binds cations, and the nonpolar exterior ensures solubility in organic phases. Oxygen donors have high affinity for A^{2+}.[3] The polar parts of most natural and synthetic A^{2+}-transporting ionophores are therefore rich in oxygen.[1,3,4] In the present work we have explored the feasibility of using the anionic complex tris(arylazo oximato)iron(II) (RL^-, **1**) for ionophoric binding of A^{2+}.

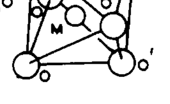


RL^- (R=Me or Ph)

1



2



3

Complex **1** has the facial stereochemistry **2**.[5-7] The oximato oxygen atoms are correctly disposed to span a triangular face of another polyhedron. In other words, RL^- should be able to act as a facial O_3 ligand. Two such ligands can be aligned to define an O_6 coordination sphere as shown schematically in **3**, in which the O_3 and O'_3 faces correspond to the two ligands. This structural situation has been realized in the 3d ion (M^{n+}, n = 2, 3) complexes of type $M(RL)_2{}^{(n-2)+}$.[5,6]

We now report that A^{2+} can be very efficiently transported from aqueous to organic media and vice versa by utilizing the formation and decomposition of complexes of type $A(RL)_2$. A study of this phenomenon as well as the synthesis and characterization of the remarkable group of alkaline-earth-metal complexes is described.

Results and Discussion

A. Synthesis. Two methods were used for preparing $A(RL)_2$ in ≥90% yields: (i) the reaction of $NaRL{\cdot}H_2O$[5-7] with hydrated $A(ClO_4)_2$ in ethanol (eq 1) and (ii) reaction of HRL[7] with ACO_3

$$2NaRL + A(ClO_4)_2 \xrightarrow{EtOH} A(RL)_2 + 2NaClO_4 \tag{1}$$

$$2HRL + ACO_3 \xrightarrow{Me_2CO} A(RL)_2 + H_2O + CO_2 \tag{2}$$

suspended in boiling acetone (eq 2). The eight complexes synthesized are listed in Table I. All complexes except $Sr(MeL)_2{\cdot}4H_2O$ and $Ba(MeL)_2{\cdot}5H_2O$ are isolated in the anhydrous form. The two hydrated species lose water completely in a continuous thermogravimetric step over the temperature range

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Table I. Characterization Data

compd	anal. data,[a] % Fe	C	H	N	UV-vis data[b] λ, nm (ϵ, M^{-1} cm^{-1})	ν_{NO},[c] cm^{-1}
$Mg(MeL)_2$	10.10 (10.08)	51.86 (51.98)	4.29 (4.33)	22.68 (22.74)	800[d] (780), 605 (12 900), 390 (43 300), 260 (57 960)	1260
$Ca(MeL)_2$	9.75 (9.94)	51.33 (51.26)	4.32 (4.27)	22.26 (22.42)	800[d] (710), 610 (12 200), 390 (44 350), 260 (49 700)	1260
$Sr(MeL)_2 \cdot 4H_2O$[e]	9.00 (8.98)	46.56 (46.33)	4.48 (4.50)	19.96 (20.27)	820[d] (730), 610 (11 300), 390 (42 050), 265 (47 450)	1250
$Ba(MeL)_2 \cdot 5H_2O$[e]	8.70 (8.52)	43.55 (43.94)	4.40 (4.42)	19.07 (19.22)	820[d] (750), 605 (12 150), 390 (44 750), 260 (50 000)	1255
$Mg(PhL)_2$	7.68 (7.55)	62.96 (63.24)	4.02 (4.05)	16.93 (17.03)	820[d] (650), 610 (16 000), 560[d] (15 200), 410 (29 200), 265 (120 000)	1280
$Ca(PhL)_2$	7.59 (7.47)	62.61 (62.58)	4.18 (4.01)	16.74 (16.85)	830[d] (730), 610 (16 060), 410 (32 500), 270 (118 300)	1270
$Sr(PhL)_2$	7.40 (7.24)	60.84 (60.65)	3.99 (3.89)	16.32 (16.33)	820[d] (770), 610 (16 200), 410 (34 200), 275 (117 300)	1280
$Ba(PhL)_2$	7.20 (7.01)	58.82 (58.76)	3.84 (3.77)	15.73 (15.81)	820[d] (810), 610 (16 160), 410 (35 100), 275 (115 200)	1260

[a] Calculated values are in parentheses. [b] Solvent is acetonitrile. [c] In KBr disks. ν_{NO} is broad and strong. [d] Shoulder. [e] In thermogravimetry the percentage weight losses were 5.79 and 6.87 for the Sr and Ba compounds, respectively, in the temperature range 330–390 K.

Table II. Molecular Weight[a] and ^1H NMR[b] Data

compd	M_r[c]	δ_{Me}	compd	M_r[c]
$Mg(MeL)_2$	1116 (1108)	2.87	$Mg(PhL)_2$	1450 (1480)
$Ca(MeL)_2$	1137 (1124)	2.80	$Ca(PhL)_2$	1518 (1496)
$Sr(MeL)_2$	1156 (1171)	2.72	$Sr(PhL)_2$	1570 (1543)
$Ba(MeL)_2$	1070 (1221)	2.70	$Ba(PhL)_2$	1490 (1593)

[a] The solvent is chloroform. [b] In $CDCl_3$; tetramethylsilane is used as standard. [c] Molecular weight; calculated values are in parentheses.

330–390 K. Anhydrous $Sr(MeL)_2$ and $Ba(MeL)_2$ were prepared by heating the hydrated complexes to 373 K in vacuo. Anhydrous complexes alone were used in all experiments reported below.

B. Characterization and Structure. We have failed to grow X-ray-quality single crystals for any of the $A(RL)_2$ complexes. Evidence cited below, however, proves beyond doubt that these are structural analogues of $M(RL)_2$ (M = bivalent 3d ion).[6]

(a) Molecular Weight. In acetonitrile solution $A(RL)_2$ has molar electrical conductivity in the range 4–36 Ω^{-1} cm^2 mol^{-1}. There is a gradual increase from $Mg(RL)_2$ to $Ba(RL)_2$. Dissociation of the complexes to constituent ions is therefore very small in acetonitrile. In chloroform it should be even less. Osmometric molecular weights for the complexes were determined in chloroform, and the data (Table II) agree well with the $A(RL)_2$ formulation. The barium complexes are slightly dissociated, leading to somewhat low molecular weights.

(b) Spectra. The infrared spectra (4000–400 cm^{-1}) of $A(RL)_2$ are closely alike to those of the 3d congeners[6] $M(RL)_2$. Oximato NO stretches at ~1250 cm^{-1} characteristic[5-7] of five-membered arylazo oxime chelate rings are uniformly present. In $CDCl_3$, $A(MeL)_2$ displays a single sharp ^1H methyl NMR signal (Table II). This is in agreement with the facial geometry of bound MeL^-.[6] Further, instantaneous dissimilarities between the two bound MeL^- ligands, if any, are averaged out on the NMR time scale. An interesting result is that the signal shifts to higher fields as the radius of A^{2+} increases and its polarizing power correspondingly decreases. There is an approximate linear correlation between δ_{Me} and the charge-to-radius ratio[8] of A^{2+}.

(c) Electroactivity. When two MeL^- ligands bind to a central metal atom, a characteristic pair of one-electron cyclic voltammetric responses are observed below –0.7 V vs SCE. These arise from successive reductions of azo functions of the two MeL^- ligands.[6] The $A(MeL)_2$ species satisfy this criterion excellently as can be seen in Figure 1.

In acetonitrile solution $NaRL \cdot H_2O$ and Ph_4AsRL display a reversible iron(III)/iron(II) couple (eq 3), near 0.3 V vs SCE.[5,6]

$$RL + e^- \rightleftharpoons RL^- \qquad (3)$$

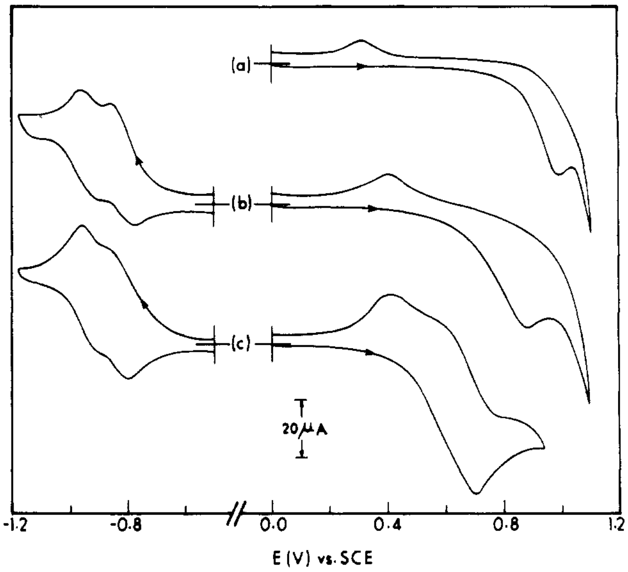

Figure 1. Cyclic voltammograms (scan rate 50 mV s^{-1}) of ~10^{-3} M solutions of (a) $Ni(MeL)_2$, (b) $Mg(MeL)_2$, and (c) $Ca(MeL)_2$ in acetonitrile (0.1 M TEAP) at a platinum electrode (298 K).

Table III. Electrochemical[a,b] Data at 298 K

compd	E_{pa}, V[c] Fe(III)/Fe(II)	$-E^\circ_{298}$, V (ΔE_p, mV)[c] ligand redn
$Mg(MeL)_2$	0.88	0.82 (70), 0.93 (60)
$Ca(MeL)_2$	0.68	0.83 (60), 0.93 (60)
$Sr(MeL)_2$	0.64	0.93,[d] 1.01 (60)
$Ba(MeL)_2$	0.63	0.92,[d] 1.04 (80)
$Mg(PhL)_2$	0.92	0.69 (100), 0.89 (60)
$Ca(PhL)_2$	0.74	0.76 (160), 0.96 (120)
$Sr(PhL)_2$	0.70	0.70 (80), 0.96 (120)
$Ba(PhL)_2$	0.69	0.71 (100), 0.98 (120)

[a] Conditions: solvent, acetonitrile; supporting electrolyte, TEAP (0.1 M); working electrode, platinum; reference electrode, SCE. [b] Definitions: E_{pa}, anodic peak potential; E_{pc}, cathodic peak potential; $\Delta E_p = E_{pa} - E_{pc}$; E°_{298}, calculated as the average of anodic and cathodic peak potentials. [c] Cyclic voltammetric data; scan rate 50 mV s^{-1}. [d] Cathodic peak potential (E_{pc}); on scan reversal the anodic peak potential (E_{pa}) is not observed.

The corresponding anodic peak potentials (E_{pa}) in $A(RL)_2$ occur at much higher potentials (Table III). The reductive response on scan reversal is poorly defined. The one-electron nature of the oxidative response was established by coulometry at potentials 200 mV more positive than E_{pa}. The electron stoichiometry is found to lie in the range 0.9–1.1 for the entire group of complexes.

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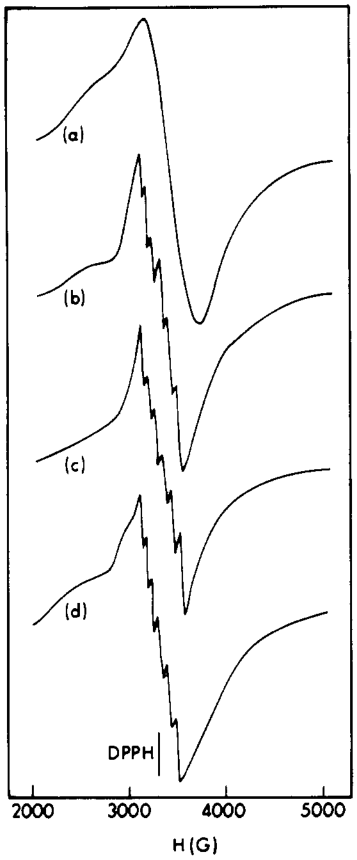

Figure 2. X-Band EPR spectra (298 K) of polycrystalline (a) Mn-$(MeL)_2$, (b) $Mg(Mn)(MeL)_2$, (c) $Ba(Mn)(MeL)_2$, and (d) Ca(Mn)-$(PhL)_2$.

The very similar voltammograms of $Mg(MeL)_2$ and X-ray-characterized[6] $Ni(MeL)_2$ are compared in Figure 1. The smaller ion (Ni^{2+}, $r = 0.68$ Å; Mg^{2+}, $r = 0.78$ Å) makes E_{pa} more positive. This trend continues into $Ca(MeL)_2$ and $Sr(MeL)_2$ and then levels off (Figure 1). The positively charged central cation is expected to hinder electron loss from bound ligands, hence the increase in E_{pa} in going from free RL^- (eq 3) to $A(RL)_2$. The effect decreases with increasing ionic size as expected.

(d) Manganese(II)-Doped Complex EPR Spectra. We have earlier demonstrated that in $Mn(MeL)_2$ the central manganese(II) atom has a nearly octahedral O_6 environment closely alike to that of structurally characterized nickel(II) in $Ni(MeL)_2$.[6] The A-$(MeL)_2$ lattice is found to accept the manganese(II) complex as a guest. The doped complex is designated as $A(Mn)(MeL)_2$. The gross features of the EPR spectra of pure $Mn(MeL)_2$ and A-$(Mn)(MeL)_2$ are very similar, as seen in the representative examples of Figure 2. The doped complex, however, displays ^{55}Mn hyperfine structure, which is not resolved in the pure complex. Clearly in $A(Mn)(MeL)_2$, $Mn(MeL)_2$ occurs as part of the host lattice. If it formed a separate phase, a spectrum without hyperfine structure like that of the pure complex would have resulted. The results of Figure 2 strongly suggest that in $A(RL)_2$ the A^{2+} ions are bound in grossly octahedral AO_6 geometry.

(e) Conclusion. Evidence cited above leads to the conclusion that the anhydrous $A(RL)_2$ complexes uniformly have AO_6 coordination of type **3**;[9,10] while this coordination is common[3] for oxygen donor complexes of magnesium(II) and is not unusual[11] for those of calcium(II), coordination numbers in excess of 6 (7–10) usually characterize complexes of strontium(II) and barium(II).[3] The $A(RL)_2$ complexes are thus quite remarkable, and in cation coordination they resemble the oxides AO, which have the rock-salt structure.[12] The radius of the O_6 cavity formed by two RL^- units is tunable to the requirement of any of the A^{2+} ions ($r = 0.78$–1.43 Å).[8] The real limits of tunability are actually wider since Fe^{3+} ($r = 0.53$ Å) is easily accommodated as in $Fe(RL)_2^+$.[5]

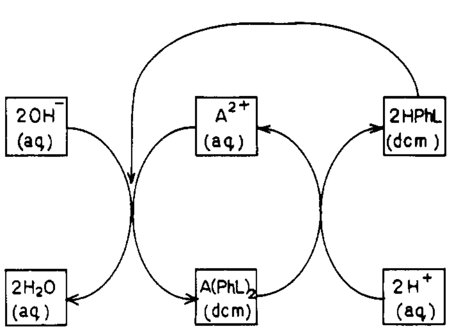

Figure 4. Scheme for transport of alkaline-earth-metal ions (A^{2+}) back and forth from the aqueous to the organic phase.

The O_3 face of RL^- probably carries most of the negative charge, and two such moieties are able to create a sufficiently polar environment for smooth binding of A^{2+} by displacement of aqua ligands present in hydrated A^{2+}. The formation of chelate rings no doubt facilitates the process. On the other hand, the numerous pendant R and Ph groups of $A(RL)_2$ ensure its solubility in organic media. Thus, the pair of RL^- ligands satisfy the polar-inside-nonpolar-outside criterion[1] for ionophoric activity well and are able to transport A^{2+} from aqueous to organic media efficiently as shown below.

C. Biphasic Transport of A^{2+}. Dichloromethane (dcm) was used as the organic solvent in all experiments. Since $A(PhL)_2$ is insoluble in water while $A(MeL)_2$ is slightly soluble, PhL^- was uniformly chosen as the ionophore.

In one experiment aqueous solutions of hydrated $A(ClO_4)_2$ were shaken with dcm containing progressively increasing amounts of dissolved $NaPhL{\cdot}H_2O$. The complete transport of A^{2+} from the aqueous to the organic layer was rapid and quantitative when the ratio of initial concentrations of A^{2+} and PhL^- is $\leq 1/2$. When this ratio exceeded 1/2, the excess A^{2+} was left behind in the aqueous solution. Equation 4 correctly represents the observations.

$$2NaPhL(o) + A(ClO_4)_2(a) \rightarrow A(PhL)_2(o) + 2NaClO_4(a) \quad (4)$$

$$2HPhL(o) + A(OH)_2(a) \rightarrow A(PhL)_2(o) + 2H_2O(a) \quad (5)$$

The abbreviations o and a respectively refer to organic and aqueous phases.

The acid–base reaction of eq 5 represents a second experiment. Again 1 mol of A^{2+} is transported into dcm for every 2 mol of HPhL present. The progressive transport of A^{2+} with increasing relative concentration of PhL^- can be monitored spectrophotometrically (Figure 3, supplementary material).

The *reverse transport* of A^{2+} bound as $A(PhL)_2$ in dcm back into the aqueous phase can be achieved with the help of eq 6.

$$A(PhL)_2(o) + 2HCl(a) \rightarrow 2HPhL(o) + ACl_2(a) \quad (6)$$

When incremental amounts of acid are added, the pH of the aqueous phase changes little until 2 mol of acid has been added for each 1 mol of $A(PhL)_2$ originally present. Thereafter there is a rapid decrease of pH (Figure 3, supplementary material). The complete transport of A^{2+} into the aqueous phase after addition of 2 mol of acid was confirmed analytically.

With the help of eq 5 and 6 the endless transport of A^{2+} between aqueous and organic phases can be achieved (Figure 4) by al-

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(9) In the hydrated complexes ($Sr(MeL)_2{\cdot}4H_2O$ and $Ba(MeL)_2{\cdot}5H_2O$) the central metal ion may have coordination number greater than 6 as in the hydrated barium salt of tris(dihydrogen violurato)ruthenate(II) ($BaRu_2(H_2Vi)_6{\cdot}9H_2O$). In this compound Ba^{2+} is nine-coordinated (BaO_9).[10] Among the nine oxygen atoms, five come from water molecules, three come from one facial $Ru(H_2Vi)_3^-$ unit, and the last one comes from the other $Ru(H_2Vi)_3^-$ unit.

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(12) Huggins, M. L.; Sakamoto, Y. *J. Phys. Soc. Jpn.* **1957**, *12*, 241–251.

Table IV. Equilibrium Constants (K_{AMg}) and Related Data at 298 K

A	K_{AMg}[a]	log K_{AMg}	$\Delta G°$ [b]	$\Delta\Delta G°_h$[b,c]	$\Delta\Delta G°_l$[b,d]	$\Delta\Delta G°_f$[b]	
						e	*f*
Ca	5.10 (0.25)	0.71	−0.97	−75	−90	−74	−74
Sr	9.52 (1.34)	0.98	−1.33	−115	−138	−114	−113
Ba	24.72 (1.81)	1.39	−1.89	−140	−169	−139	−139

[a] Numbers in parentheses are root mean square deviations. [b] In kcal/mol. [c] Values from ref 13. [d] Values from ref 14. [e] Calculated from eq 16. [f] Calculated from eq 17.

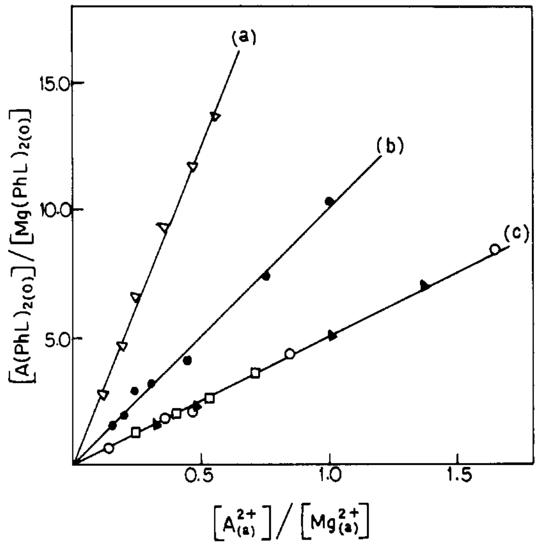

Figure 5. Least-squares plots of $[A(PhL)_2(o)]/[Mg(PhL)_2(o)]$ vs $[A^{2+}(a)]/[Mg^{2+}(a)]$: (a) A = Ba, (△) data obtained from the reaction of $Mg(PhL)_2(o)$ with $Ba^{2+}(a)$; (b) A = Sr, (●) data obtained from the reaction of $Mg(PhL)_2(o)$ with $Sr^{2+}(a)$; (c) A = Ca, (○) data obtained from the reaction of $Mg(PhL)_2(o)$ with $Ca^{2+}(a)$, (□) data obtained from the reaction of $Ca(PhL)_2(o)$ with $Mg^{2+}(a)$, and (▲) data obtained from the reaction of $PhL^-(o)$ with $Mg^{2+}(a) + Ca^{2+}(a)$.

ternatively making the aqueous phase acidic and alkaline.

D. Relative Affinities. Since 2 mol of PhL^- transports 1 mol of A^{2+} completely into the organic phase, the equilibrium constant K_A (eq 7) of the transfer reaction (eq 8) could not be reliably determined. Using biphasic (water–dcm) competition and exchange experiments, it is however possible to estimate the relative affinities of various aquated A^{2+} ions for PhL^- in terms of the redistribution equilibrium of eq 9 involving two alkaline-earth-metal ions (Mg^{2+} and A^{2+}). The corresponding equilibrium constant K_{AMg} (eq 10) equals K_A/K_{Mg}.

$$K_A = [A(PhL)_2(o)]/[PhL^-(o)]^2[A^{2+}(a)] \tag{7}$$

$$2PhL^-(o) + A^{2+}(a) \rightleftharpoons A(PhL)_2(o) \tag{8}$$

$$Mg(PhL)_2(o) + A^{2+}(a) \rightleftharpoons A(PhL)_2(o) + Mg^{2+}(a) \tag{9}$$

$$K_{AMg} = [A(PhL)_2(o)][Mg^{2+}(a)]/[Mg(PhL)_2(o)][A^{2+}(a)] \tag{10}$$

We first consider the case of A = Ca. The equilibrium was approached from either side, i.e., starting with either $Mg(PhL)_2(o)$ and $Ca^{2+}(a)$ or with $Ca(PhL)_2(o)$ and $Mg^{2+}(a)$. Alternatively $PhL^-(o)$ (sodium salt) was equilibrated with a mixture of $Mg^{2+}(a)$ and $Ca^{2+}(a)$ while the initial concentration of $PhL^-(o)$ was kept considerably below the level at which the whole of Mg^{2+} and Ca^{2+} would get transported. The equilibrium concentration ratios $[Ca^{2+}(a)]/[Mg^{2+}(a)]$ and $[Ca(PhL)_2(o)]/[Mg(PhL)_2(o)]$ obtained in this manner show a good linear correlation (Figure 5). The slope of the line affords K_{CaMg}. The equilibrium constants K_{SrMg} and K_{BaMg} were similarly determined, and data are collected in Table IV. In summary, $K_{Ca} \approx 5K_{Mg}$, $K_{Sr} \approx 10K_{Mg}$, and $K_{Ba} \approx 25K_{Mg}$.

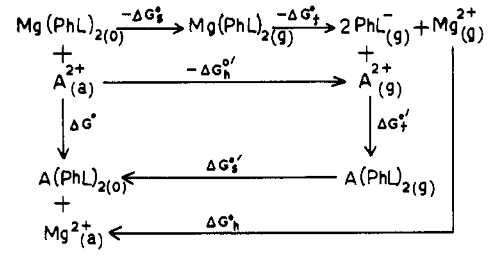

Figure 6. Born–Haber cycle representing the reaction $Mg(PhL)_2(o) + A^{2+}(a) \rightarrow A(PhL)_2(o) + Mg^{2+}(a)$.

The factors contributing to K_{AMg} can be analyzed with the help of the cycle shown in Figure 6. The quantities $\Delta G°_s$, $\Delta G°_h$, and $\Delta G°_f$ are respectively the free energies of solvation of $Mg(PhL)_2$, of hydration of Mg^{2+}, and of the formation of $Mg(PhL)_2$; $\Delta G°_s{'}$, $\Delta G°_h{'}$, and $\Delta G°_f{'}$ similarly apply to the A species. The net free energy change ($\Delta G°$, Table IV) of reaction 9 is related to K_{AMg} as in eq 11 (T = 298 K). The free energies of solvation of $Mg(PhL)_2$ and $A(PhL)_2$ in dcm should be nearly equal. Making the approximation $\Delta G°_s = \Delta G°_s{'}$ and using Figure 6, we can derive eq 12. The terms on the right-hand side of eq 12 have the meanings as defined by eq 13. The combination of eq 11 and 12 affords eq 14. Values of $\Delta\Delta G°_h$ are in Table IV.[13] While corresponding $\Delta\Delta G°_f$ values are unknown, the present work allows an indirect estimate as follows. The plot of log K_{AMg} vs $\Delta\Delta G°_h$ is satisfactorily linear and has a zero intercept (Figure 7, supplementary material). In terms of eq 14 this means that $\Delta\Delta G°_f$ is proportional to $\Delta\Delta G°_h$. Setting $\Delta\Delta G°_f/\Delta\Delta G°_h = c$, eq 14 transforms to eq 15. From the slope of the log K_{AMg} vs $\Delta\Delta G°_h$ line, one obtains c = 0.99. Thus $\Delta\Delta G°_f$ is very nearly equal to $\Delta\Delta G°_h$ (eq 16), hence the relatively small values of $\Delta G°$ (Table IV).

$$-\log K_{AMg} = \Delta G°/2.303RT = 0.74(\Delta G°) \tag{11}$$

$$\Delta G° = \Delta\Delta G°_h - \Delta\Delta G°_f \tag{12}$$

$$\Delta\Delta G°_i = \Delta G°_i - \Delta G°_i{'} \tag{13}$$

$$\log K_{AMg} = 0.74(\Delta\Delta G°_f - \Delta\Delta G°_h) \tag{14}$$

$$\log K_{AMg} = 0.74(c - 1)\Delta\Delta G°_h \tag{15}$$

$$\Delta\Delta G°_f = 0.99(\Delta\Delta G°_h) \tag{16}$$

The proportionality between $\Delta\Delta G°_f$ and $\Delta\Delta G°_h$ is significant since oxygen coordination is involved in either case. The logic can be extended to the lattice energy of crystalline oxides (Figure 7, supplementary material).[14] We define $\Delta\Delta G°_l$ as the lattice energy of MgO minus that of AO. The quantities $\Delta\Delta G°_h$ and $\Delta\Delta G°_l$ (Table IV) are proportional to each other with $\Delta\Delta G°_l/\Delta\Delta G°_h$ = 1.21. When this is combined with eq 16, eq 17 results.

$$\Delta\Delta G°_f = 0.82(\Delta\Delta G°_l) \tag{17}$$

The $\Delta\Delta G°_f$ values calculated from eq 16 and 17 are in Table IV.

The present results reveal the lack of specificity in the affinity of RL^- for any particular alkaline-earth-metal ion. This is not unexpected since in $A(RL)_2$ the two RL^- units are not mutually constrained and can align to define the O_6 cavity of matching diameter in each ion. The affinities therefore change monotonically.

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E. Concluding Remarks. The efficacy of RL$^-$ as a tridentate O_3 ligand for the binding of alkaline-earth-metal ions has been demonstrated. The $A(RL)_2$ complexes have AO_6 coordination spheres. The A^{2+}, 2 RL$^-$ interaction is not specific for any particular A^{2+} ion—the RL$^-$ pair can create a variable-diameter O_6 cavity. In biphasic equilibria (water–dcm) the bigger A^{2+} ions, having smaller hydration energies, form more stable complexes: $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$. The differential ($\Delta\Delta G°$) free energies of formation (among $A(RL)_2$), of aquation (among A^{2+}), and of lattice formation (among AO) are proportional to one another.

Experimental Section

Materials. Arylazo oximes, NaRL·H_2O and HRL were prepared by using the procedures reported previously.[5-7,15] Hydrated alkaline-earth-metal perchlorates were obtained by dissolving corresponding metal carbonates in 70% aqueous perchloric acid followed by recrystallization. The purification of solvents and preparation of supporting electrolyte (tetraethylammonium perchlorate, TEAP) for electrochemical work were performed as before.[16] All other chemicals and organic solvents used were of reagent grade and were used as supplied.

Measurements. Solution electrical conductivity and pH measurements were performed by using a Philips PR 9500 (India) conductivity bridge and Systronics 335 digital pH meter, respectively. Molecular weights were determined by using a Knauer vapor pressure osmometer with benzil as calibrant. Thermogravimetric measurements were performed by using a Shimadzu DT-30 thermal analyzer. Spectroscopic data were obtained by using the following instruments: IR spectra, Beckman IR-20A or Perkin-Elmer 783 spectrophotometer; electronic spectra, Hitachi 330 spectrophotometer; NMR spectra, Varian EM-390 spectrometer; EPR spectra, Varian E 109C spectrometer. DPPH ($g = 2.0037$) was used as the standard field marker in EPR measurements. Electrochemical experiments were done by using a PAR Model 370-4 electrochemistry system. Cyclic voltammetry was performed by using a PAR 174A polarographic analyzer, 175 universal programmer, and RE 0074 X-Y recorder. The three-electrode measurements were carried out with the use of a planar Beckman Model 39273 platinum-inlay working electrode, a platinum-wire auxiliary electrode, and a saturated calomel electrode (SCE). Controlled-potential coulometry was done by using a PAR 173 potentiostat, PAR 179 digital coulometer, and PAR 377A cell system taken in conjunction with a platinum-wire-gauze working electrode. All measurements were done under a dinitrogen atmosphere and at 298 K. The potentials reported here are uncorrected for junction contribution. Microanalyses (C, H, N) were performed by using a Perkin-Elmer 240C elemental analyzer.

Preparation of Complexes. The complexes reported here were prepared from either NaRL·H_2O or HRL. Details for representative cases are given; other complexes were prepared similarly.

Bis[tris((phenylazo)acetaldoximato)ferrato(II)]magnesium(II), Mg(MeL)$_2$. To an ethanolic solution (25 mL) of NaMeL·H_2O (0.50 g, 0.86 mmol) was added 0.15 g (0.45 mmol) of $Mg(ClO_4)_2 \cdot 6H_2O$, and the mixture was stirred magnetically at room temperature for 1 h. It was then left in the air for slow evaporation to ~8 mL. The dark crystalline solid that separated was collected by filtration, washed thoroughly with ice-cold water, and dried under vacuum over P_4O_{10}; yield 0.44 g (92%).

Bis[tris((phenylazo)benzaldoximato)ferrato(II)]magnesium(II), Mg(PhL)$_2$. To a solution of HPhL (0.50 g, 0.69 mmol) in acetone (30 mL) was added 0.20 g (2.4 mmol) of $MgCO_3$, and the mixture was heated to reflux for 3 h. It was then cooled to 273 K and filtered to remove excess $MgCO_3$. The filtrate was slowly evaporated in air to one-third of the initial volume. The dark crystalline solid that precipitated was collected by filtration, washed with ice-cold water, and dried under vacuum over P_4O_{10}; yield 0.46 g (90%).

Doped Complexes, A(Mn)(RL)$_2$ (A = Mg(II), Ca(II), Sr(II), Ba(II)). These were prepared by the reaction of NaRL·H_2O with $A(ClO_4)_2 \cdot xH_2O$ containing 1% $Mn(ClO_4)_2 \cdot 6H_2O$. Details of the procedure are the same as those described above for synthesis of the pure complex. In the cases of $Sr(Mn)(MeL)_2$ and $Ba(Mn)(MeL)_2$ the products obtained by the above procedure were further dried under vacuum at 373 K to remove water of crystallization.

Biphasic Transport of A^{2+}. (a) Equation 4. An aqueous solution of $Mg(ClO_4)_2$ (3.96×10^{-3} M) was prepared, and 25 mL of this solution was shaken for 15 min with 25 mL of a solution of NaPhL·H_2O in CH_2Cl_2. (From variable-time experiments it was established that 15 min is sufficient to achieve equilibrium in all these and other biphasic experiments reported in this work.) The aqueous phase was quantitatively collected, and the Mg^{2+} in it was estimated. The experiment was repeated with different concentrations of NaPhL·H_2O in the range $(4.15–8.22) \times 10^{-3}$ M. A similar experiment was also performed by using a standard aqueous solution of $Ca(ClO_4)_2$ (4.24×10^{-3} M) and solutions of NaPhL·H_2O ($(4.05–9.05) \times 10^{-3}$ M) in CH_2Cl_2.

(b) Equation 5. A solution of HPhL (0.22×10^{-3} M) in CH_2Cl_2 and an aqueous solution of barium hydroxide (1.00×10^{-3} M) were prepared. Into a 100-mL stoppered conical flask were added 10 mL of HPhL solution, 10 mL of pure CH_2Cl_2, and the required volume of barium hydroxide. The volume of the aqueous phase was made 20 mL by adding water. A series of such mixtures were prepared having the same HPhL concentration (0.11×10^{-3} M) but different barium hydroxide concentrations ($(0.00–0.06) \times 10^{-3}$ M). The flasks were shaken for 15 min, and the electronic spectra of the CH_2Cl_2 phase were then recorded to monitor the extent of transport.

(c) Equation 6. A stock solution of HCl (1.00×10^{-3} M) in water was prepared. Into a 100-mL stoppered conical flask were added 20 mL of a solution of $A(PhL)_2$ of known strength in CH_2Cl_2 and a known volume of the HCl solution. Enough water was then added to make the volume of the aqueous phase 20 mL. Several sets of such mixtures were prepared having the same $A(PhL)_2$ concentration but different HCl concentrations ($(0.00–0.40) \times 10^{-3}$ M). The flasks were shaken for 15 min. After this the phases were separated. The electronic spectra of the organic phases and the pHs of the aqueous phases were recorded. In these experiments concentrations of $Mg(PhL)_2$, $Ca(PhL)_2$, $Sr(PhL)_2$, and $Ba(PhL)_2$ were 0.13×10^{-3}, 0.15×10^{-3}, 0.12×10^{-3}, and 0.10×10^{-3} M, respectively.

Determination of K_{AMg}. (a) Reaction of PhL$^-$(o) with the Mixture of Mg^{2+}(a) and Ca^{2+}(a). An accurately weighed amount of NaPhL·H_2O was dissolved in 50 mL of CH_2Cl_2 in a separating funnel, and 50 mL of an aqueous solution containing known amounts of Mg^{2+} and Ca^{2+} (as perchlorates) was added. The mixture was shaken for 15 min to reach equilibrium. The organic phase was then separated, and in the aqueous phase concentrations of Mg^{2+} and Ca^{2+} were determined. The equilibrium concentrations of $Mg(PhL)_2$ and $Ca(PhL)_2$ in the organic phase were calculated by difference. Several sets of such experiments were performed, with the concentration of NaPhL·H_2O kept fixed (1.56×10^{-2} M) but with the ratio of the initial concentrations of Mg^{2+} and Ca^{2+} varied in the range 0.53–1.98. The ratio of the initial concentration of NaPhL·H_2O to that of $Mg^{2+} + Ca^{2+}$ was set at 1:1 in all experiments.

(b) Equation 9. In a separating funnel a solution (25 mL) of $Mg(PhL)_2$ of known concentration in CH_2Cl_2 was shaken with a standardized aqueous solution (25 mL) of A^{2+} (perchlorate salt) for 15 min followed by separation of the two phases. In the aqueous phase equilibrium concentrations of Mg^{2+} and A^{2+} were determined. Concentrations of $Mg(PhL)_2$ and $A(PhL)_2$ in the organic phase were computed by difference. A series of such experiments were performed with the initial A^{2+} concentration kept constant but with that of $Mg(PhL)_2$ in the CH_2Cl_2 layer varied (in the range $(1.48–10.92) \times 10^{-3}$ M). Initial concentrations of A^{2+} were as follows: Ca^{2+}, 5.53×10^{-3} M; Sr^{2+}, 5.59×10^{-3} M; Ba^{2+}, 4.93×10^{-3} M.

In the case of K_{CaMg}, determination was also carried out by starting from $Ca(PhL)_2$ ($(2.35–6.80) \times 10^{-3}$ M) and Mg^{2+} (4.56×10^{-3} M), the details of the procedure being very similar to those above.

Determination of Metal Ions.[17] Mg^{2+}, Ca^{2+}, and a mixture of Mg^{2+} and Ca^{2+} were determined by the EDTA titration method. Gravimetric procedures were followed for separation (from Mg^{2+}) and determination of Sr^{2+} and Ba^{2+} (as sulfates).

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Supplementary Material Available: UV–vis spectra of a mixture of H(PhL)(o) and $Ba(OH)_2$(a) (Figure 3) and least-squares plots of log K_{AMg} versus $\Delta\Delta G°_h$ and $\Delta\Delta G°_l$ (Figure 7) (2 pages). Ordering information is given on any current masthead page.

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