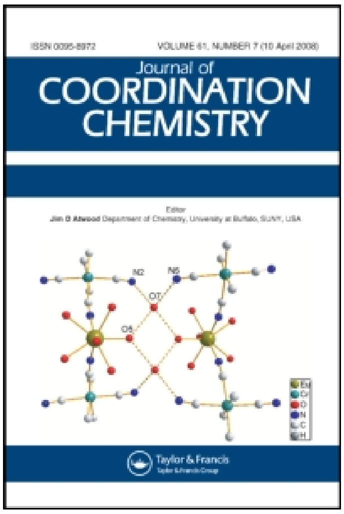

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METAL COMPLEXES OF *N, N, N', N'*-TETRAKIS-(*n*-PROPYL)-1,2-PHENYLENEDIOXYDIACETAMIDE AND RELATED LIGANDS

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METAL COMPLEXES OF *N,N,N′,N′*-TETRAKIS-(*n*-PROPYL)-1,2-PHENYLENEDIOXYDIACETAMIDE AND RELATED LIGANDS

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N,N,N′,N′-Tetrakis-(*n*-propyl)-1,2-phenylenedioxydiăcetamide and related ligands with four binding sites have been shown to selectively complex Group IIA cations in solution *via* liquid membrane, picrate extraction, and UV spectroscopic techniques. The formation and partial characterization of crystalline complexes of these ligands with various salts of Group IIA, transition metal and rare earth cations is reported. The complexes were characterized by IR and UV spectroscopy, molar electrolytic conductance, elemental analysis, and (in several cases) single crystal X-ray analysis. The accumulated evidence suggests that $[L_2M]^{2+}[MX_4]^{2-}$ (X = Cl, Br, SCN), $[L_2M]^{2+}2X^-$ (X = Cl, Br, SCN, BF_4, ClO_4) or $[LM]^{2+}2X^-$ (X = Cl, Br, SCN) complexes are formed. The $[L_2M]^{2+}$ complexes are eight-coordinate in some cases. Thus these ligands can vary their stoichiometry of complexation depending upon the cation and anion involved. *Trans-N,N,N′,N,*-tetrakis-(*n*-propyl)-1,2-cyclohexanedioxydiacetamide reacts with $MnBr_2$ to form a $[L_2Mn]^{2+}]MnBr_4]^{2-}$ complex which is the *first* example of a structurally characterized molecule corresponding to a McCasland-type diastereomer ($CA^+A^+A^-A^-$), *i.e.* a substance whose optical inactivity can be attributed to fourfold alternating axial molecular symmetry.

INTRODUCTION

We and the Simon group have reported that *N,N,N′,N′*-tetrakis-(*n*-propyl)-1,2-phenylenedioxydiacetamide (**1**), the related naphthalene ligand **2**, and the *cis*- and *trans*-1,2-dioxycyclohexane ligands **3**, **4**, all with four binding sites, show selective Group IIA cation complexation and transport by incorporation into liquid membrane electrodes,[1,2] extraction of picrates from water into methylene chloride,[3a] and by binding studies in methanol or ethanol.[3] The stoichiometry of ligand–metal cation binding for **1–4** in solution was found to be concentration dependent. Stoichiometries of 1 : 1 were found only at ligand concentrations below 2×10^{-4} M.[3] At higher concentrations, ligand–cation ratios >1 were found by studies involving UV absorption,[3b] conductivity (at 10^{-3} M),[4a] and cation-induced proton NMR shift (at 0.1 M)[4b] techniques. Furthermore, Simon *et al.*, found that *N,N,N′,N′*-tetrakis-(*n*-substituted)-1,2-ethylenedioxydiacetamides such as **5** form either 1 : 1 or 2 : 1 ligand–cation complexes in solution, as studied by NMR[5a–c] or differential vapor phase osmometry[5d] techniques. A few complexes of **5** have been isolated and characterized.[5e] The structure of the $MnBr_2$ complex of **4** has been solved by X-ray analysis[6] and shown to be $[L_2Mn]^{2+}][MnBr_4]^{2-}$. Similar structures have been found for the $MnBr_2$ complex of **1**[7a] and the $CaBr_2$ complex of **1**[7b] while the $Ca(SCN)_2$ complex of **1** is $LCa(NCS)_21.0$(solvent).[7a] These complexes of **1** and **4** were previously prepared by us but not otherwise reported. We now report the isolation and partial characterization of a number of crystalline metal cation complexes of **1–4** and the related ligands **6**, **7** (see Figure 1).

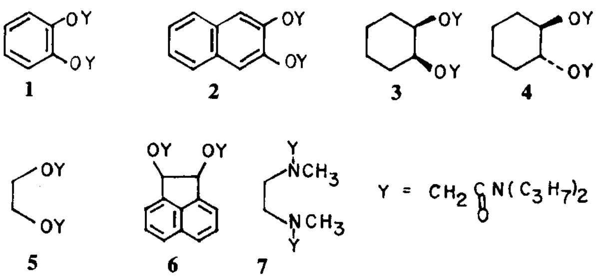

FIGURE 1 Structures of the ligands.

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EXPERIMENTAL

General Information

Solvents used were dried by distillation over molecular sieves, calcium hydride, or lithium aluminum hydride. Proton NMR spectra were recorded on Varian A-60A or Perkin Elmer R-12 spectrometers at 60 MHz, using $(CH_3)_4Si$ as an internal standard. Infrared spectra were taken on Perkin Elmer 300 and 467 spectrophotometers. UV and visible spectra were recorded on Perkin Elmer 402 and Varian Spectroscan-3 spectrophotometers. Conductivity measurements were done with a Beckman RC-19 conductivity bridge and Yellow Springs Instruments Model 3401 conductivity cell, using nitromethane as a solvent. Chemical analyses were by Galbraith Laboratories, Knoxville, Tenn. and Schwarzkopf Laboratories, Queens, New York.

Preparation of the Ligands

Most of the ligands used have been previously prepared.[1d,3a,8] *N,N,N',N'*-Tetrakis-(*n*-propyl)-3,6-di(*N*-methyl)azaoctanediamide (**7**) was obtained in 50% yield as a viscous yellow oil from the alkylation under nitrogen of *N,N'*-dimethylethylenediamine with *N,N*-di-(*n*-propyl)chloroacetamide, KI and K_2CO_3 in acetone.[8] It was chromatographed on silica gel, eluted with benzene-triethylamine (9 : 1) and distilled at bp 180–182°C (0.1 mm): IR(neat) 1640 cm^{-1}; NMR($CDCl_3$) δ0.9 (t, 12, $CH_3CH_2CH_2$), 1.2–1.7 (m, 8, CH_3CH_2), 2.32 (s, 6, CH_3N), 2.62 (s, 4, CH_2N), 3.25 (s, 4, $NCH_2C{=}O$), and 3.3 (t, 8, $NCH_2CH_2CH_3$). Calcd for $C_{20}H_{42}N_4O_2$: C, 64.82; H, 11, 42; N, 15.12. Found: C, 64.54; H, 11, 42; N, 14.91

Preparation of the Complexes

a) The metal salt (5×10^{-4} to 10^{-3} mol) was added to methanol (20 ml) which contained 2,3-dimethoxypropane (1 ml) to ensure absence of moisture, and the solution was heated with stirring for 30 min. An equimolar amount of ligand was then added and the solvent was evaporated to a small volume. The remaining solid or liquid was dissolved in an appropriate solvent, filtered through a sintered glass funnel and allowed to crystallize. The resultant crystals were filtered, dried *in vacuo* at 25°C for 24 h, and recrystallized again for analysis (Tables I and II). The presence of hydrates was inferred from the analytical data. The absence of methanol as a ligand was directly determined in one case. Special procedures are indicated in Tables I and II.

b) The procedure was the same but 2,2-dimethoxypropane was omitted. The complexes were best prepared in methanol or ethanol. They could not be prepared in acetonitrile or other solvents. The presence of water of crystallization in some of the salts led to hydrates for some of the complexes. Most of the complexes were isolated in *ca*. 80% yields.

RESULTS AND DISCUSSION

For **1**, and to a lesser extent for **2–4** and **6**, **7** complexes were obtained with the chlorides, bromides and thiocyanates of Group IIA, transition metal and lanthanide cations (see Tables I and II for some examples). No complexes with Group IA cations were isolated. The complexes are unstable to water. The ligand–salt ratios were mostly 1 : 1 by chemical analysis. In comparison, the perchlorate or tetrafluoroborate salts of cobalt(II) or manganese(II) gave complexes with **1** which analyzed as 2 : 1 ligand–salt.

Molar electrolytic conductance data in nitromethane for the complexes with metal halide or thiocyanate salts are in the range for 1 : 1 electrolytes[9,10] while the perchlorate or tetrafluoroborate complexes give greater values appropriate to 3-particle electrolytes[9] (Table III). The values for some of the metal halide complexes are somewhat low, as previously observed with other amide-metal halide complexes.[10,11] Several lanthanide complexes were found to have very low conductivity, rendering this method useless for the determination of the nature of these complexes. These complexes include **1**.$GdCl_3$, **4**.$GdCl_3$ and **4**.$YbCl_3$. We believe that the transition metal cation complexes are probably all 8-coordinate $[L_2M]^{2+}$ types with either $[MX_4]^{2-}$ (X = Cl, Br, NCS) or $2X^-$ ($X = BF_4$, ClO_4) anions. Such structures would explain the conductivity results. Anions of the $[MX_4]^{2-}$ type have been previously postulated as present in the complexes of transition metal halides with caprolactam.[10] Our evidence for the presence of $[MX_4]^{2-}$ anions and for 8-coordinated dodecahedral cations follows.

The UV spectrum of **1**.$MnBr_2$ shows the relatively strong absorption of tetrahedral Mn(II)[12,13] in the solid state, while the UV of **1**.$Mn(ClO_4)_2$ has only very weak absorption (Table IV, Figure 2). The strong absorption of the $MnBr_2$ complex persists in acetonitrile but is converted to the characteristic weaker absorption for octahedral Mn(II) in methanol.[12a,14] We believe that the tetrahedral-type absorption of the **1**.$MnBr_2$ complex is due to $[MnBr_4]^{2-}$ which overshadows the absorption of 8-coordinated $[L_2Mn]^{2+}$ which is also present. Eight-coordinated Mn(II) is known to have weak absorption[15] and is probably present as the sole

TABLE I
Analytical data of the complexes of **1**[a]

Complex	Method[b] (solvent)	Ligand/ salt	MP(°C) (color)	Formula	Calcd (%) C	Calcd (%) H	Calcd (%) Other	Found (%) C	Found (%) H	Found (%) Other
1.Ca(SCN)$_2$	B CHCl$_3$	1 : 1	248–250°	$C_{24}H_{36}N_4O_4S_2Ca$ $.H_2O$	50.86	6.76	S, 11.31 N, 9.88	51.04	6.85	S, 10.83 N, 9.65
1.CaBr$_2$	B CHCl$_3$[c]	1 : 1	244–245°	$C_{22}H_{36}N_2O_4CaBr_2$ $.H_2O$	43.29	6.28	Br, 26.18 CH$_3$O, 0.0	43.58	6.46	Br, 26.15 CH$_3$O, 0.3
1.CaBr$_2$	A CHCl$_3$	2 : 1[d]	229–231°	$C_{44}H_{72}N_4O_8CaBr_2$ $.H_2O$	52.68	7.44		52.34	7.26	
1.CoCl$_2$	B CH$_3$NO$_2$	1 : 1	216–218° blue	$C_{22}H_{36}N_2O_4CoCl_2$	50.58	6.80	Cl, 13.58	50.52	7.16	Cl, 13.43
1.Co(SCN)$_2$	A CH$_2$Cl$_2$/ CH$_3$OH	1 : 1	202–203° blue	$C_{24}H_{36}N_4O_4S_2Co$	50.79	6.40	S, 11.30	50.82	6.30	S, 11.16
1.Co(BF$_4$)$_2$	A *i*-PrOH	2 : 1[e]	220–221° purple-blue	$C_{44}H_{72}N_4O_8CoB_2F_8$ $.H_2O$	51.01	7.20	Co, 5.69	51.35	7.14	Co, 6.21
1.Mn(ClO$_4$)$_2$	A ChCl$_3$	2 : 1	224–225°	$C_{44}H_{72}N_4O_{16}MnCl_2$	50.86	6.99	Mn, 5.29	51.11	6.73	Mn, 4.80
1.MnBr$_2$	B CH$_3$NO$_2$	1 : 1	297–299° yellow cubes	$C_{22}H_{36}N_2O_4MnBr_2$	43.51	5.93	Br, 26.34	43.55	5.91	Br, 26.54
1.CuBr$_2$	B CH$_3$CN/ *i*-PrOH	1 : 1	177–178° yellow green needles	$C_{22}H_{36}N_2O_4CuBr_2$ $.H_2O$	41.68	6.00	Br, 25.23	41.57	5.99	Br, 25.48
1.CdBr$_2$	B CH$_3$OH/ EtOAc	1 : 1	216–217° white	$C_{22}H_{36}N_2O_4CdBr_2$	39.75	5.46	Br, 24.04	39.94	5.31	Br, 23.81
1.ZnCl$_2$	A CH$_3$NO$_2$	1 : 1	174–175° white	$C_{22}H_{36}N_2O_4ZnCl_2$	49.97	6.86	Cl, 13.41	49.93	7.08	Cl, 13.47
1.Ba(SCN)$_2$	B *i*-PrOH	1 : 1	132–135°	$C_{24}H_{36}N_4O_4S_2Ba$ $.2H_2O$	42.26	5.91	S, 9.75	42.11	6.05	S, 9.40
1.NiCl$_2$	B CH$_3$OH/ EtOAc	1 : 1	285° dec orange pwd	$C_{22}H_{36}N_2O_4NiCl_2$	50.61	6.95	Cl, 13.58	50.40	6.78	Cl, 13.84
1.LaCl$_3$	A *i*-PrOH	1 : 1	209–211° hygroscopic, white	$C_{22}H_{36}N_2O_4LaCl_3$ $.H_2O$	40.29	5.84	Cl, 16.22	40.51	5.95	Cl, 16.66
1.NdCl$_3$	A *i*-PrOH/ CH$_3$OH	1 : 1	244–245°	$C_{22}H_{36}N_2O_4NdCl_3$ $.H_2O$	39.97	5.80	Cl, 16.09 16.54[f]	39.68	6.05	Cl, 17.19
1.GdCl$_3$	A i-PrOH/ CH$_3$OH	1 : 1	265–266°	$C_{22}H_{36}N_2O_4GdCl_3$	40.27	5.53	Cl, 16.21	40.09	5.71	Cl, 16.30
1.YbCl$_3$	A Ch$_3$NO$_2$/ *i*-PrOH	1 : 1	281–283° white	$C_{22}H_{36}N_2O_4YbCl_3$ $.H_2O$	38.30	5.55	Yb, 25.08 25.75[f] N, 4.06	38.77	5.72	Yb, 25.65 N, 3.93

[a]Yields were 70–80%, generally. Ligand/salt ratios of 1 : 1 were mixed. [b]Recrystallization solvent is indicated. Mixed solvents: better solvent listed first; other solvent added to turbidity. Method A included 2,2-dimethoxypropane and method B omitted it. [c]Also: CH_3CN, $CHCl_3—CH_3OH$. [d]Yield 20% after many recrystallizations from $CHCl_3$. [e]Ligand/salt = 1.5 was used; 51% yield. [f]Value for anhydrous complex.

chromophore in the **1**.Mn(ClO$_4$)$_2$ complex. The $[MnBr_4]^{2-}$, and possibly also $[L_2Mn]^{2+}$, convert to 6-coordinated octahedral Mn(II) in methanol. The absence of tetrahedral Mn(II) absorption in the perchlorate complex rules out the presence of tetrahedral Mn(II) cations in any of the manganese complexes. Definitive evidence for the $[L_2Mn]^{2+}$-$[MnBr_4]^{2-}$ structure was obtained by single crystal X-ray analyses on the MnBr$_2$ complexes of **1**[6] and **4**.[7a]

For other transition metal complexes of **1**, including those of Co(II), Ni(II), and Cu(II), the UV absorption can be interpreted as that of either tetrahedral $[MX_4]^{2-}$ anions or tetrahedral $[LM]^{2+}$ cations. The interpretation of the data for Co(II) complexes is complicated by the fact that dodecahedral (8-coordi-

TABLE II
Analytical data of the complexes of **2–4**, **6**, **7**[a]

Complex	Method[b] (solvent)	Ligand/ salt	MP (°C) (color)	Formula	Calcd (%)			Found (%)		
					C	H	Other	C	H	Other
2.Ca(SCN)$_2$	B CH_3OH	1 : 1	250° dec	$C_{23}H_{38}N_4O_4S_2Ca$ $.H_2O$	56.16	6.40	S, 10.70 mw 598.8	55.99	6.20	S, 10.68 mw 303[c]
2.Ba(SCN)$_2$	B $CHCl_3$/EtOAc	2 : 1	159–161°	$C_{54}H_{76}N_6O_8S_2Ba$ $.H_2O$	56.08	6.80	S, 5.54	56.00	7.01	S, 5.42
2.MnBr$_2$	A $CHCl_3$/EtOAc	1 : 1	297–299°	$C_{26}H_{38}N_2O_4MnBr_2$ $.H_2O$	46.24	6.00	Br, 23.66	46.81	6.08	Br, 23.70
2.Co(SCN)$_2$	A CH_2Cl_2/ CH_3OH	1 : 1	219–221°	$C_{29}H_{38}N_4O_4S_2Co$	54.45	6.20	S, 10.38	54.28	6.22	S, 10.09
3.Ca(SCN)$_2$	B EtOAc	1 : 1	105–110°	$C_{24}H_{42}N_4O_4S_2Ca$	51.95	7.63	S, 11.56	52.49	7.88	S, 11.43
4.Ca(SCN)$_2$	B $CHCl_3$/THF	1 : 1	145–155°	$C_{28}H_{50}N_4O_5S_2Ca$ (1 : 1 + C_4H_8O(THF))	53.64	8.04	N, 8.94 S, 10.23	53.60	7.93	N, 8.85 S, 9.86
4.MnBr$_2$	A CH_3OH	1 : 1	255–256° lt green	$C_{22}H_{42}O_4N_2MnBr_2$	43.08	6.85	Br, 26.11	43.17	6.95	Br, 26.24
4.Co(SCN)$_2$	A CH_2Cl_2/ CH_3OH	1 : 1	207–208° blue	$C_{24}H_{42}N_4O_4S_2Co$	50.25	7.38	S, 11.18	49.73	7.23	S, 10.85
4.CuBr$_2$	A CH_3CN/EtOAc	1 : 1	130–132° purple	$C_{22}H_{42}N_2O_4CuBr_2$	42.49	6.81	Br, 25.69	42.15	6.68	Br, 25.35
4.GdCl$_3$	B Ch_3OH/EtOAc	1 : 1	261–262°	$C_{22}H_{42}N_2O_4GdCl_3$	39.90	6.40	Cl, 16.08	39.90	6.40	Cl, 16.16
6.MnBr$_2$	B CH_2Cl_2/ CH_3OH	1 : 1	258–260° beige	$C_{28}H_{40}N_2O_4MnBr_2$	49.21	5.90	Br, 23.39	49.27	6.19	Br, 23.07
7.Co(SCN)$_2$	A CH_2CL_2/CH_3OH	1 : 1	257–259° dark pink	$C_{22}H_{42}N_6O_2S_2Co$	48.42	7.76	S, 11.75	48.68	7.80	S, 11.86
7.CaBr$_2$	A EtOAc	2 : 1	174–177°	$C_{40}H_{84}N_8O_4CaBr_2$ $.3H_2O$	48.27	9.12		48.24	8.92	
7.MnBr$_2$	A *i*-PrOH	1 : 1	218–220° violet-pink	$C_{20}H_{42}N_4O_2MnBr_2$	41.04	7.23	Br, 27.30	41.05	7.12	Br, 27.59
7.CuBr$_2$	B CH_3CN/ EtOAc + Et_2O	1 : 1	152–155° dark green	$C_{20}H_{42}N_4O_2CuBr_2$	40.45	7.13	Br, 26.91	40.59	7.14	Br, 27.19
7.NiCl$_2$	A $CHCl_3$/EtOAc	1 : 1	234–236°	$C_{20}H_{42}N_4O_2NiCl_2$ $.H_2O$	46.36	8.56	Ni, 11.33	45.90	8.77	Ni, 11.60

[a] Yields were 70–80%, generally. Ligand/salt ratios of 1 : 1 were mixed in CH_3OH. [b] Recrystallization solvent is indicated. Mixed solvents are listed with the major one (complex more soluble in it) first; other solvent added to turbidity. Method A included 2,2-dimethoxypropane in the preparation of the complex and Method B omitted it. [c] Vapor phase osmometric method; the result probably indicates the presence of two particles/complex.

nated) Co(II) cations have UV spectra similar to those of tetrahedral Co(II) cations.[15a] While single crystal X-ray analysis would provide a definitive answer, in its absence[16] we suggest that the identical UV-visible "tetrahedral-type" spectra of the $CoCl_2$ and $Co(BF_4)_2$ of **1**, (Figure 3) together with the observed 2- and 3-particle conductivity values, respectively, are best explained by assuming $[L_2Co]^{2+}$ $[CoCl_4]^{2-}$ and $[L_2Co]^{2+}$ 2 $[BF_4]^{2-}$ structures.

The **1**.$NiCl_2$ complex has similar, but not identical, UV absorption to $[NiCl_4]^{2-}$ literature values in nitromethane.[12b,17] Eight-coordinate Ni(II) is known to have weak absorption,[15a] so that, as with 8-coordinate Mn(II), the absorption of the $[L_2Ni]^{2+}$ cation believed to be present may be obscured by that of the $[NiCl_4]^{2-}$ anion. The low conductivity of **1**.$NiCl_2$ was not informative (Table III). It is an orange powder in solid form which dissolves in nitromethane or acetonitrile to give a blue solution and in methanol to give a green solution. The spectrum in methanol is similar to that of octahedral $[Ni(H_2O)_6]^{2+}$.[14] The data suggest that this complex may be square planar (orange) in the solid state,[12c] becoming octahedral (green) by coordination with solvent molecules in methanol, and becoming $[L_2Ni]^{2+}$ $[NiCl_4]^{2-}$ in nitromethane.

TABLE III
Molar conductance of the complexes in nitromethane.[a]

Complex	Conc. (mol/L)	λM^b	No. particles; ($Z^+ : Z^-$)	Lig/salt by analysis[c]
$[(\text{Caprolactam})_6\text{Co}]^{2+}\ 2\text{ClO}_4^-$	10^{-3}	157[d]	3 (1 : 2)	6 : 1
$[(\text{Caprolactam})_6\text{Co}]^{2+}\ [\text{Co(SCN)}_4]^{2-}$	5×10^{-4}	92[d]	2 (1 : 1)	3 : 1
1.$CaBr_2$	5×10^{-4}	150	3 (1 : 2)	2 : 1
1.$MnBr_2$	7×10^{-4}	88	2 (1 : 1)	1 : 1
1.$CuBr_2$	10^{-3}	54	2 (1 : 1)	1 : 1
1.$ZnCl_2$	10^{-4}	83	2 (1 : 1)	1 : 1
1.$CdBr_2$	10^{-4}	51	2 (1 : 1)	1 : 1
1.$Co(SCN)_2$	7×10^{-4}	67	2 (1 : 1)	1 : 1
1.$NiCl_2$	5×10^{-4}	10	–	1 : 1
1.$Mn(ClO_4)_2$	5×10^{-4}	150	3 (1 : 2)	2 : 1
1.$Co(BF_4)_2$	5×10^{-4}	151	3 (1 : 2)	2 : 1
2.$Ba(SCN)_2$	10^{-4}	196	3 (1 : 2)	2 : 1
2.$Co(SCN)_2$	10^{-4}	102	2 (1 : 1)	1 : 1
4.$Co(SCN)_2$	10^{-4}	29[e]	2?	1 : 1
4.$MnBr_2$	10^{-3}	74	2 (1 : 1)	1 : 1
6.$MnBr_2$	10^{-4}	75	2 (1 : 1)	1 : 1
7.$CaBr_2$	10^{-4}	170	3 (1 : 2)	2 : 1
7.$NiCl_2$	10^{-4}	66	2 (1 : 1)	1 : 1
7.$Co(SCN)_2$	10^{-4}	56	2 (1 : 1)	1 : 1

[a] Solvent conductivity = 1.35–5 × 10^{-6} Ω^{-1}, generally. [b] In Ω^{-1} cm^2 M^{-1}; corrected for solvent conductivity. [c] Stoichiometry of the complexes (Tables I, II). [d] Model compounds. Lit. value 175 for ClO_4^- complex.[10] Lit. values (range, average) of 60–115 (89) and 115–250 (167) for λM for 2 and 3 particles, respectively, were used to determine the number of particles.[9] [e] Low value probably due to the low solubility of this complex.

The $CuBr_2$ complex of **1** was formed in anhydrous (purple) and hydrated (yellow-green) forms with similar but not identical IR spectra. The data suggests that the complex may have distorted octahedral symmetry, at least in methanol.[14]

The IR spectra of the complexes and ligands have mutually exclusive bands, as expected for true complexation.[18] All of the complexes exhibit downfield carbonyl shifts of 20 to 50 cm^{-1} compared to the ligands (see Table V for data on the complexes of **1**). This suggests coordination of the cation with oxygen of the amide group.[10,19] These coordination sites are proven for the $CaBr_2$, $Ca(SCN)_2$ and $MnBr_2$ complexes of **1**[7] and the $MnBr_2$ complex of **4**[6] by single crystal

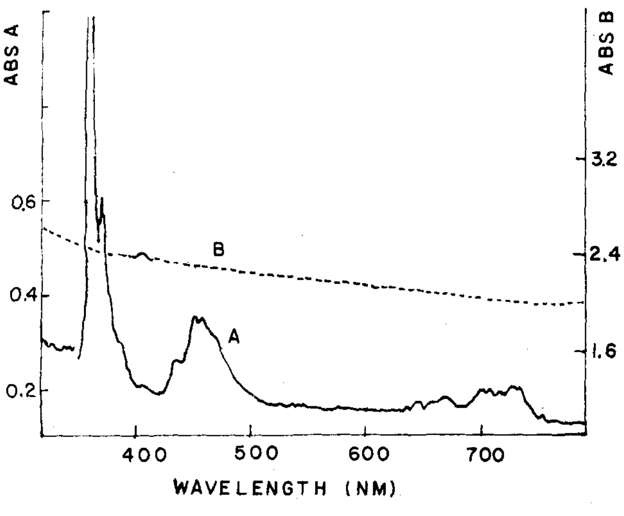

FIGURE 2 Absorption spectra of A (**1**.$MnBr_2$, 50%) and B (**1**.$Mn(ClO_4)_2$, 30%) in KBr pellets.

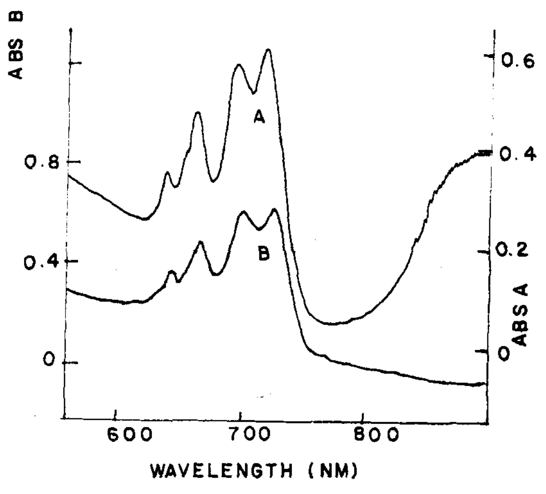

FIGURE 3 Absorption spectra of A (**1**.$Co(BF_4)_2$) and B (**1**.$CoCl_2$) in KBr pellets (0.8% each).

TABLE IV
Electronic spectra of the complexes of **1**.

Complex	Solvent or KBr; color[a]	Band maxima nm (ε)	Assignment	Reference compounds[12,14]	
1.$MnBr_2$[b] ($[L_2Mn]^{2+}[MnBr_4]^{2-}$)	KBr[c] lt green	361. 368. 436. 454. 470. 664. 670. 704. 730	tetrahedral Mn(II)	$[MnBr_4]^{2-}$	361, 374, 434, 451, 463, 274, 288
	CH_3OH colorless	360. 404 sp. 430. 500–600(0.01–0.1)	octahedral Mn(II)	$[Mn(H_2O)_6]^{2+}$	360, 396 sh, 400 sp, 435, 530(0.01–0.15)
1.$Mn(ClO_4)_2$	KBr colorless	406 w	dodecahedral[15] Mn(II)		
1.$CoCl_2$	CH_3CN blue	573. 590. 632. 660. 685(310)	tetrahedral Co(II)[d]	$[CoCl_4]^-$	593, 613, 635 668(580) 693(660)
	KBr blue	644. 668. 704. 728	tetrahedral Co(II)[d]		
	CH_3OH pink	540(10). 1350	octahedral Co(II)	$[Co(H_2O)_6]^{2+}$	540(10), 1200
1.$Co(BF_4)_2$	KBr blue	465 br. 580 br. 644. 668. 700. 726	tetrahedral or dodecahedral Co(II)		
	CH_3CN blue	620. 634 w. 650 sh. 684			
	CH_3OH pink	342 w. 360. 380. 405. 540 br. 816	octahedral Co(II)		
1.$NiCl_2$	CH_3NO_2 blue	435(35). 570. 618(67). 680	tetrahedral Ni(II)	$[NiCl_4]^{2-}$ (CH_3NO_2)[17]	569 sh, 622 sh, 658(140) 703, 860
	CH_3OH green	408(6). 695. 740(12)	octahedral Ni(II)	$[Ni(H_2O)_6]^{2+}$	395, 667, 714, 725
1.$CuBr_2$	CH_3OH	300 sh. 500–800 br	distorted octahedral Cu(II)?		625

[a] KBr pellets contained 1% Co(II) complex. 30–50% Mn(II) complexes. Bands: sp = sharp, sh = shoulder, w = weak. br = broad. [b] Similar spectra for $MnBr_2$ complexes of **4** and **6**. [c] Similar spectra in CH_3CN. [d] Dodecahedral Co(II) also possible.[15a]

X-ray analysis. Evidence for $[MX_4]^{2-}$ anions was sought in some of the complexes by Raman spectroscopy.[20] The **4**.$MnBr_2$ complex. known to be $[L_2Mn]^{2+}][MnBr_4]^{2-}$ by X-ray analysis[6]. exhibited absorption for $[MnBr_4]^{2-}$ at 155 cm^{-1} in nitromethane.[21] However. the postulated $[CoCl_4]^{2-}$ anion in **1**.$CoCl_2$ could not be observed because of obstruction in the region around 269 cm^{-1} by Rayleigh scattering.[22]

The structures of the calcium complexes of this class of ligands are of great interest because of the selectivity of these ligands for calcium transport.[1,23] Two calcium-containing complexes of **1** have been analyzed by single crystal X-ray techniques.[6,7b] **1**.$Ca(SCN)_2$ was found to have a 7-coordinate calcium cation featuring a flat 4-coordinate ligand (two ether and two amide oxygen groups), two SCN groups (coordinated through nitrogen) above and below the plane of the ligand. and a solvent molecule (probably water. as suggested by chemical analysis). The SCN groups are not crystallographically equivalent, being at 2.48 and 2.42A° from the calcium.[7a] They give rise to two IR peaks at 2050 and 2085 cm^{-1}. The importance of the counter ion and the tendency for **1** to form "sandwich complexes" are illustrated by the different structure found for **1**.$CaBr_2$, compared to **1**.$Ca(SCN)_2$. The interaction of $CaBr_2$ with **1** can give either 1 : 1 or 2 : 1 ligand/cation complexes. The 2 : 1 complex features a calcium sitting on a twofold axis and 8-coordination around the metal by the ether and

TABLE V
Infrared carbonyl shifts for **1** due to complexation.

Compound	$\nu C{=}O$ (cm^{-1})	$\Delta\nu C{=}O$ (cm^{-1}) (complex vs **1**)
1	1660	–
1.$CaBr_2$	1630	−30
1.$Ca(SCN)_2$	1610	−50
	1630	−30
1.$Ba(SCN)_2$	1640	−20
1.$MnBr_2$	1621	−39
1.$CoCl_2$	1612	−48
1.$NiCl_2$	1610	−50
1.$CuBr_2$	1610	−50
1.$ZnCl_2$	1618	−42
1.$CdBr_2$	1620	−40
1.$LaCl_3.H_2O$	1618	−42
1.$NdCl_3.H_2O$	1617	−43
1.$GdCl_3$	1620	−40
1.$YbCl_3$	1620	−40

[a] Spectra recorded in KBr pellets. Similar shifts were shown by the complexes of the other ligands. The aromatic CH band of **1** at 765 cm^{-1} was shifted slightly in the complexes, usually up to 770 cm^{-1}

amide oxygen groups of two ligand molecules. The **1**.$CaBr_2$ and **7**.$CaBr_2$ complexes gave molar conductance values for 3 particles. While they are sensitive to moisture, other $CaBr_2$ complexes were more sensitive and stable conductance values could not be obtained. The conductivity data cannot be used to determine whether or not multiple complexes of **1**.$CaBr_2$ including $[L_2M]^{2+}$ $2X^-$ and $[LM^{2+}]$ $2X^-$ exist in solution, rather than one species per complex. The relationship of the structure(s) of the complexes in solution *vs*. the isolated crystalline complexes is not easily determined. It has been shown that the stoichiometry of the interaction of **1** with Ca^{2+} in solution is concentration dependant.[23] Thus in dilute solution at the beginning of the addition of $CaBr_2$ to **1** in methanol, species with ligand/cation values >1 are present. Only 1 : 1 ligand/cation ratios persist when more $CaBr_2$ is added. A 2 : 1 complex is formed with **3** and **4** forms both 3 : 2 and 1 : 1 complexes in solution.[23] The isolated $Ca(SCN)_2$ complexes of **3** or **4** are 1 : 1 ligand/cation species, possibly reflecting, as with **1**, the stabilizing effect of SCN as a ligand for this system.[7b]

The relationship of the structure of the complexes formed by these ligands in solution or in membranes to the structure of the isolated crystalline complexes reported here remains as an unfinished problem. The similarity of the UV spectra of at least some of the complexes in the solid state and in acetonitrile (see, for example, data for **1**.$MnBr_2$ in Table IV) suggests that the major species is the same in both situations. The isolation of most of the complexes in high yield (*ca*. 80%) supports such a conclusion.

The finding that **1** and related ligands **2–4**, **6**, **7** form complexes with a variety of metal cations prompts further experimentation to define the selectivity of the ligands for Group IIA cations *vs*. these other cations. Previously, the selectivity of **1–5** for sensing Ca^{2+} rather than many other cations was determined by Simon *et al.* in ion-selective electrodes.[24] High selectivity for Ca^{2+} *vs*. Cu^{2+} or Zn^{2+} (500–1000x) was found for **5**, for example. Even though **1** and related ligands can form complexes with numerous cations in a non-competitive situation, the selectivities found in ion-selective electrodes and under other competitive complexation conditions are probably more relevant to *in vivo* conditions. A major justification for our investigating the behavior of the transition metal cations toward **1–4**, **6**, **7** is that these cations have an informative UV spectroscopy when compared to Group IIA cations. Furthermore, the similarity of the crystalline structures of **1**. $MnBr_2$ and **1**. $CaBr_2$[7] strengthens the use of Mn^{2+} as a "probe" cation for Ca^{2+} in the determination of the nature of the interaction of metal cations with ionophores.[25]

Finally, the single crystal X-ray derived structure of the **4**.$MnBr_2$ complex is $[L_2Mn]^{2+}$ $[MnBr_4]^{2-}$.[6] It is the *first* example of a structurally characterized system which corresponds to a McCasland-type *meso* diastereomer $(CA^+A^+A^-A^-)$[26], *i.e.* a substance belonging to the point group S_4 whose optical inactivity could be attributed only to fourfold alternating axial molecular symmetry. According to K. Mislow[27], while a number of species MR_4 have been show to possess molecular structures belonging to the point group S_4, invariably the ground state geometry so adopted is attained through conformational distortion of a conformation belonging to a higher symmetry group, normally D_{2d}.[28]

In summary, we have found that **1** and related ligands generally form 2 : 1 ligand/cation complexes, featuring 8-coordinate cations, which can be isolated. The 8-coordinate "sandwich type" of structures found may be important for the ionophoric behavior of these ligands in that such structures help in solubilizing cations in a nonpolar medium. It is of interest that until the advent of crown ethers,[29] natural ionophores,[29,30] and now our ligands, 8-coordination for Group IIA cations was rarely, if ever, found.[31]

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