

CONTRIBUTION FROM THE CLIPPINGER LABORATORIES,
DEPARTMENT OF CHEMISTRY, OHIO UNIVERSITY, ATHENS, OHIO 45701**Complexes of 1,8-Naphthyridines. IV. Alkaline Earth Perchlorate Complexes of 1,8-Naphthyridine and Its 2,7-Dimethyl Derivative¹**

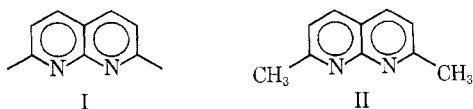
BY RICHARD L. BODNER AND DAVID G. HENDRICKER

Received November 10, 1969

Alkaline earth-perchlorate complexes of the types $M(I)_2(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$ and $M(II)_2(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$ ($M = \text{Mg, Ca, Sr, Ba}$; $0 \leq x \leq 3.5$), where I is 1,8-naphthyridine and II is 2,7-dimethyl-1,8-naphthyridine, have been synthesized. The white crystalline compounds have been characterized by elemental analyses, molar conductances, and infrared ($4000\text{--}200\text{ cm}^{-1}$) and pmr spectroscopy. The steric influence of the methyl groups of II does not affect the resulting stoichiometry. In a polar solvent, the compounds exhibit the expected three-ion conductances. As deduced from the solid infrared spectra, some of the perchlorates are distorted toward C_{3v} symmetry. Distortion of the perchlorate in the crystal lattice and/or a weak interaction of the metal ion and the perchlorate are offered as possibilities for this reduction in symmetry. In view of the known 1,10-phenanthroline complexes of the same metal ions, where as many as four chelates are associated, the present work indicates that the coordination number of the metal ion is strongly dependent on the intramolecular nitrogen-nitrogen distance in the chelating heterocycle.

The area of isolable alkaline earth metal complexes has been studied primarily by analytical chemists interested in the selective precipitation of the group IIa ions. Most commonly used ligands, such as EDTA, contain negatively charged oxygen donor atoms.² However, Pfeiffer, *et al.*,³ prepared alkaline earth complexes involving nitrogen donor ligands such as ammine, 1,10-phenanthroline, and 2,2-bipyridine. Their results with phen suggest a possible coordination number of 8 for several of the alkaline earth as well as transition metal ions.⁴

In our studies of transition metal complexes of 1,8-naphthyridine, I, we too have found evidence for coordination number 8.⁵



This unusual stoichiometry is not obtained when the sterically hindered 2,7-dimethyl derivative, II, is used.⁶ The size of the metal ion appears to play an important role in determining the coordination number. Comparison of the chelating properties of the naphthyridine system with that of five-membered ring chelates led to the investigation of other complexes which exhibit unusual coordination with phen. Thus a study of alkaline earth perchlorate complexes of I and II was undertaken to observe the effect of large dipositive cations on coordination.

Experimental Section

Materials.—Calcium, strontium, and barium perchlorates

(1) Presented in part at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 12, 1969; see Abstracts, No. INOR 221.

(2) F. L. Carvin in "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor, Ed., Academic Press, New York, N. Y., 1946, pp 298-300.

(3) P. Pfeiffer, E. Schmitz, F. Dominik, A. Fritzen, and B. Werdeimann, *Z. Anorg. Allgem. Chem.*, **264**, 188 (1951).

(4) W. Brandt, F. P. Dwyer, and E. C. Gyarfás, *Chem. Rev.*, **54**, 959 (1954).

(5) D. G. Hendricker and R. L. Bodner, *Inorg. Nucl. Chem. Letters*, in press.

(6) D. G. Hendricker and R. L. Bodner, *Inorg. Chem.*, **9**, 273 (1970).

purchased from G. F. Smith Chemical Co., Columbus, Ohio, and magnesium perchlorate from J. T. Baker Chemical Co., Phillipsburg, N. J., were used without further purification. Commercially available ethyl acetate was dried before use.⁷ Practical grade 2,2-dimethoxypropane (dmp) was obtained from Eastman Chemicals. Purity of 1,8-naphthyridine and 2,7-dimethyl-1,8-naphthyridine, prepared by the method of Paudler and Kress,⁸ was verified by pmr spectroscopy.

Instrumentation.—The infrared spectra ($4000\text{--}200\text{ cm}^{-1}$) and conductance measurements in absolute methanol were obtained as previously described.⁶ A Varian Model HA-100 nmr spectrometer was used to obtain the pmr spectra of the complexes in absolute methanol with tetramethylsilane as the internal standard. Carbon, hydrogen, and nitrogen contents were ascertained by combustion.

Complex Preparation.—The requisite amount of hydrated alkaline earth perchlorate (0.38 mmol for I and 0.42 mmol for II) was dehydrated in 25 ml of ethyl acetate by adding 5 ml of dmp and stirring for 1 hr. To this solution was added the ligand (1.52 mmol of I or 1.26 mmol of II), which had been dissolved in 12 ml of hot ethyl acetate. After the specified time (Table I), the mixture was cooled to 0° , filtered, washed with 10 ml of chloroform, purified by the appropriate method (Table I), and dried *in vacuo* over phosphorus pentoxide for 1 week. Analytical data were obtained within 24 hr.

Results and Discussion

Analytical and conductance data for the newly prepared complexes reported in Table I indicate that in the three-ion salts 2 mol of ligand is associated with each metal ion. The use of methanol as a conductance solvent may produce dissociation of weakly bonded perchlorates. Owing to low solubility in less polar solvents, the nature of the perchlorates in solution, whether bonded or nonbonded to the metal ion, cannot be inferred. The white crystalline compounds are indefinitely stable, although water of hydration may be adsorbed on standing in air. Thermal stability was not examined because of the presence of perchlorate.

We recorded and analyzed the infrared spectra ($4000\text{--}200\text{ cm}^{-1}$) of the reported complexes. In Tables II and III are listed selective ligand modes which change on

(7) L. F. Fieser, Ed., "Experiments in Organic Chemistry," 3rd ed, D. C. Heath and Co., Boston, Mass., 1957, p 287.

(8) W. W. Paudler and T. J. Kress, *J. Heterocycl. Chem.*, **4**, 284 (1967).

TABLE I
 ANALYTICAL, CONDUCTANCE, AND PREPARATIVE DATA

Compound	% calcd			% found			Conductance ^a		Reaction time, hr	Purification method
	N	C	H	N	C	H	Δ molar, cm ² mho	Concn $\times 10^3$, M		
Mg(I) ₂ (ClO ₄) ₂ ·H ₂ O	11.17	38.31	2.82	10.99	38.55	3.55	151	0.85	0.25	c
Mg(II) ₂ (ClO ₄) ₂ ·3.5H ₂ O	9.30	39.85	4.52	9.31	40.00	4.71	185	1.20	24	b
Ca(I) ₂ (ClO ₄) ₂ ·0.25H ₂ O	11.12	38.14	2.51	11.08	38.20	2.78	171	1.14	0.25	c
Ca(II) ₂ (ClO ₄) ₂	10.09	43.25	3.64	10.03	43.20	3.63	181	0.86	0.25	c
Sr(I) ₂ (ClO ₄) ₂ ·0.25H ₂ O	10.16	34.85	2.29	10.18	34.71	2.31	172	1.30	1	c
Sr(II) ₂ (ClO ₄) ₂	9.29	39.84	3.35	9.44	39.87	3.18	175	1.10	0.25	d
Ba(I) ₂ (ClO ₄) ₂ ·0.25H ₂ O	9.12	31.27	2.30	8.90	30.94	2.10	195	0.88	1	c
Ba(II) ₂ (ClO ₄) ₂	8.59	36.80	3.09	8.72	36.92	3.04	180	1.12	0.25	e

^a Conductivities obtained in absolute methanol solutions at 25°. The following compounds and their molar conductances were used for comparison: [(CH₃(CH₂)₃)₄N]Br, 83; [(CH₃(CH₂)₃)₄N]NO₃, 82; [Co(II)₃](ClO₄)₂, 190. ^b Dissolve in ethanol-chloroform mixture (1:1) and reprecipitate with diethyl ether. ^c Dissolve in ethanol-ethyl acetate mixture (1:1) and reprecipitate with chloroform-diethyl ether mixture (1:1). ^d Recrystallize from ethyl acetate-ethanol mixture (1:2). ^e Recrystallize from ethanol.

 TABLE II
 SELECTED INFRARED ABSORPTIONS FOR COMPLEXES OF II (4000-200 CM⁻¹)^a

II	Mg(II) ₂ ²⁺	Ca(II) ₂ ²⁺	Sr(II) ₂ ²⁺	Ba(II) ₂ ²⁺	Assignment ^b
	~3500 m, b	~3500 w, br	~3500 w, b		O-H str
1598 s	1609 m	1615 s	1611 s	1606 s	II + H ₂ O bend
1532 s	1550 w	1568 w	1562 m	1558 m	II
1360 s	1380 m	1378 m	1375 m	1370 m	II
		1152 vs, b	1154 vs, b	1150 vs, b	ν_4
1145 m	1140 vs, b	1135 vs, b	1137 vs, b	1132 vs, b	II
1128 w					
		1098 vs, b	1105 vs, b	1100 vs, b	ν_3'
	(1090) vs, b	1087 vs, b	1083 vs, b	1068 vs, b	ν_1 (ν_6')
1033 w		1057 sh	1040 sh		II
948 w	(926) m	954 m	(949) m	(941) m	II (+ ν_1')
		949 m	867 s	860 s	ν_2 (+II)
848 s	857 m	863 s	867 s	860 s	II
778 vs	790 m, sh	798 s	795 s	790 s	II
720 w	720 w	725 w	722 w	721 w	II
622 m	(622) s	635 s	632 s	628 s	II + ν_3 (II + ν_4')
		620 s, sh	618 m	615 m	ν_5 + ν_4'
440 m	442 m	453 s	451 s	448 s	II + ν_6
343 s	360 w	365 m	362 m	358 m	II
	308 w	320 w			II
240 s	263 w	265 s	255 s	250 s	II

^a Abbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder; b, broad. ^b See ref 6 for assignments of II; ν_2 assigned on basis of C_{3v} perchlorate; ν_2' assigned on basis of T_d perchlorate.

coordination, water-stretching modes, and fundamental frequencies of the perchlorate ions.

The most interesting features of the infrared spectra are found in the Cl-O stretching region. Figure 1 shows this region for typical alkaline earth complexes of I and II and a transition metal complex of II. From the number of bands exhibited in the spectra, it is obvious that the nature of the perchlorate in the alkaline earth complexes differs from that of the transition metal complex. Hathaway and Underhill⁹ have listed the vibrational modes for three different symmetries of the perchlorate ion. Ross¹⁰ has advanced three possible mechanisms by which symmetry lowering of the perchlorate may occur: (1) covalent bonding through one or more of the oxygen atoms, (2) distortion in the crystal lattice and, (3) a nonuniform field created by the ligand molecules which surround the metal ion. Several examples of authentic perchlorate bonding to a metal ion are found in the literature.^{9,11-15}

Inspection of the present spectra in the perchlorate region shows four bands for the complexes of II (except for Mg(II)₂²⁺) in the 1068-1154-cm⁻¹ range (Table II). Unfortunately the spectra are further complicated in this region by the presence of ligand bands. It was found that in the spectra of Pd(II)₂Cl₂¹⁶ and (CH₃)₂-Sn(II)(Cl)₂,¹⁷ the ligand bands at 1145 and 1128 cm⁻¹ appear coupled and result in a single band at approximately 1130 cm⁻¹. If the band at ~1130 cm⁻¹ is subtracted from the present spectra, then only three bands are left to assign to the perchlorates. The highest (ν_4) and lowest (ν_1 —although higher than usually reported at ~1030 cm⁻¹) energy bands are consistent with C_{3v} symmetry as in monodentate perchlorate but the middle band at ~1100 cm⁻¹ is not since only two bands in the 1100-cm⁻¹ region are expected. However

(12) B. J. Hathaway, D. G. Holah, and M. Hudson, *J. Chem. Soc.*, 4586 (1963).

(13) L. E. Moore, R. B. Gayhart, and W. E. Bull, *J. Inorg. Nucl. Chem.*, **26**, 896 (1964).

(14) A. E. Wickenden and R. A. Krause, *Inorg. Chem.*, **4**, 505 (1965).

(15) F. A. Cotton and D. L. Weaver, *J. Am. Chem. Soc.*, **87**, 4189 (1965).

(16) R. L. Bodner and D. G. Hendricker, to be submitted for publication.

(17) D. G. Hendricker, *Inorg. Chem.*, **8**, 2328 (1969).

(9) B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961).

(10) S. D. Ross, *Spectrochim. Acta*, **18**, 225 (1962).

(11) N. T. Barker, C. M. Harris, and E. D. McKenzie, *Proc. Chem. Soc.*, 335 (1961).

TABLE III
 SELECTED INFRARED ABSORPTIONS FOR COMPLEXES OF I (4000-200 cm^{-1})

I	Mg(II) ₂ ²⁺	Ca(II) ₂ ²⁺	Sr(II) ₂ ²⁺	Ba(II) ₂ ²⁺	Assignment ^a
	~3500 s, b	~3500 m, b	~3500 m, b	~3500 m, b	O-H str
1600 s	1601 m	1601 s	1596 s	1598 s	I + H ₂ O bend
1558 s	1578 m	1585 s	1574 s	1572 s	I
	1139 vs, b	1155 vs, b	1140 vs, b	1141 vs, b	ν_4
1128 s	1129 vs, b	1135 vs, b	1120 vs, b	1122 vs, b	I
1105 w	1100 vs, b	1105 vs, b	1090 vs, b	1100 vs, b	I + ν_3'
1045 m	1065 vs, b	1050 vs, b	1048 m, sh	1047 m, sh	I + ν_1
934 w	930 w	924 w	919 w	935 w	I + ν_2
633 w		645 s, sh	630 s, sh	638 s, sh	I + ν_3
600 m	(621) s, b	620 s	620 s	620 s	I + ν_5 (+ ν_3) + ν_4'
480 s, sh	482 m				I
472 s	466 w	471 s	467 s	470 s	I + ν_6
403 s	403 s	415 s	410 s	408 s	I
	229 m				I

^a See ref 19 for assignments of I; ν_2 assigned on basis of C_{3v} perchlorate; ν_2' assigned on basis of T_d perchlorate.

there is no reason to assume that all perchlorates possess the same symmetry. It is possible that the 1100- cm^{-1} band in the present spectra is due to a perchlorate of T_d symmetry. A normal tetrahedral perchlorate gives a broad band centered at ~1100 cm^{-1} as found in the transition metal complexes of II.⁶ The lack of a strong band in the spectra at ~930 cm^{-1} (ν_2) causes concern. This band is stronger than any ligand mode in this region although other reports of C_{3v} perchlorate show ν_2 to be as strong as ν_1 , which is not the case in the present spectra. In addition, more defined splitting in the perchlorate region than is observed here is reported for C_{3v} symmetry.⁹ We conclude that the perchlorate is not distorted to full C_{3v} symmetry in the crystal lattice. Evidence for distortion of the perchlorate, caused by the heterocyclic ligands, was not found in the transition metal perchlorate complexes of II⁶ and thus not believed to be the reason for the distortion here. The distortion may be due to a very weak metal-oxygen bond.

No fine structure in the perchlorate region of Mg(II)₂²⁺ is observed. Noting that the analytical results show about 3.5 mol of water in this complex, one might speculate that the water is bonded to the metal instead of the perchlorate, but the lack of any significant band in the most sensitive region for coordination water (14 μ)¹⁸ indicates that the water is only present as lattice water. Only two bands are found in the perchlorate region for this complex, one of which is attributed to the ligand and the other (~1090 cm^{-1}) to ν_3 for T_d perchlorate. Either Mg(II)₂²⁺ is of different geometry, which prevents the perchlorate from interacting with the smaller magnesium ion, or the distortion of the perchlorate in the crystal lattice is not as great as in the other complexes.

The infrared spectra of the complexes of I in the perchlorate region are very similar (Table III). Four bands in the 1047-1155- cm^{-1} range are observed. The strong band at ~1125 cm^{-1} is assigned to a strong ligand band at 1128 cm^{-1} . Interpretation of the remaining three bands is again difficult because of two ligand bands present at 1105 (w) and 1145 cm^{-1} (m). The spectra are consistent with C_{3v} symmetry except

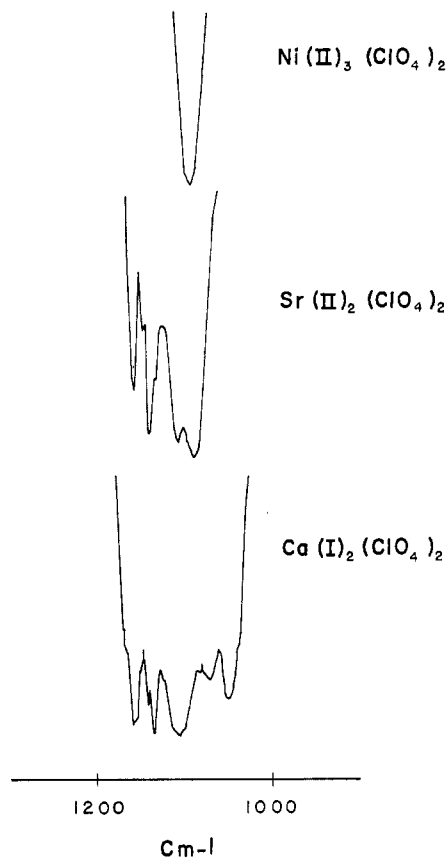


Figure 1.—Typical infrared spectra in the 1200-1000- cm^{-1} region for complexes of I and II.

for the intensity of the band at ~930 cm^{-1} (weak instead of strong) and the magnitude of splitting. The band at ~1100 cm^{-1} may be assigned to a T_d perchlorate coupled with the ligand band at 1105 cm^{-1} . As in the complexes of II, the distortion of the perchlorate toward C_{3v} symmetry is not as great as reported for other authentic monodentate perchlorates.^{9,12-16} Thus it appears that in complexes of both I and II there are two types of perchlorates.

In the remaining portion of the infrared spectra for complexes of II, the presence of water is shown by the broad band at ~3500 cm^{-1} which is of medium intensity for Mg(II)₂²⁺ but only very weak for the calcium and

strontium complexes. In all of the complexes of I, water is detected by a medium broad band in this region. Since no bands in the $14\text{-}\mu$ region are observed, only lattice water is present.¹⁸ The ligand modes for both I ($1700\text{--}650\text{ cm}^{-1}$)¹⁹ and II⁶ were previously assigned. The 403-cm^{-1} band of I and the 240-cm^{-1} band of II decrease in frequency linearly with increasing size of the metal ion except for magnesium.

Gamo,¹⁸ in studying the relationship of the rocking frequency of coordinated water to the M-OH_2 bond distance, also found magnesium not to obey the linear relationship exhibited by the other alkaline earth hydrates. The order $\text{Ca} > \text{Mg} > \text{Sr} > \text{Ba}$ is observed for the complexes of II. This order is described by Williams²⁰ for the stability of group IIa metal complexes. Although we have not determined the stability constants, it seems apparent that one can relate the position of this ligand deformation mode to the strength of the metal-ligand bond and thus the stability of the complex. Additional evidence for this relationship is found in the transition metal complexes of II⁶ where the Irving-Williams order, $\text{Fe} < \text{Co} < \text{Ni} < \text{Cu} > \text{Zn}$, is followed.²¹ One could explain the order $\text{Ca} > \text{Sr} > \text{Ba} > \text{Mg}$ for complexes of I by invoking the possibility of coordinated perchlorate producing steric interaction around the small magnesium ion which would yield a less stable complex. No band attributable to $\nu(\text{M-N})$ was found in complexes of I or II. The $\nu(\text{M-N})$ in $\text{SnCl}_4\text{-(II)}$ ¹⁷ located at 207 cm^{-1} and the lack of $\nu(\text{M-N})$ in transition metal complexes of I¹⁶ and II⁶ lend support to the conclusion that $\nu(\text{M-N})$ in the present work lies below 200 cm^{-1} and is thus not detected.

A study of the pmr spectra of the complexes in absolute methanol was undertaken. For complexes of I and (free I) the chemical shifts in ppm for 2,7-H, 3,6-H, and 4,5-H are 9.07 ± 0.01 (9.05), 7.66 ± 0.01 (7.56), and 8.48 ± 0.02 (8.35), respectively. For complexes

of II and (free II) the values for 2,7-CH₃, 3,6-H, and 4,5-H are 2.74 ± 0.01 (2.70), 7.44 ± 0.02 (7.36), and 8.22 ± 0.02 (8.12), respectively. The coupling constants in the heterocyclic system of the complexes are the same as in the free base. The deshielding of the ligand protons on complex formation indicates electron donation from the heterocycle to the metal ion. The magnitude of deshielding is less than in complexes with Sn(IV) and other metal centers which are stronger Lewis acids.^{16,17} Within experimental error there does not seem to be any relationship between the position of the proton resonances and the size of the alkaline earth metal ion. It is important to note that in the polar solvent methanol, the ligands appear to remain chelated to the metal ion since no free ligand is detected.

Conclusion

The alkaline earth metal complexes of 1,8-naphthyridine and its 2,7-dimethyl derivative are examples of stable four-membered chelate systems and are added to the few known complexes involving nitrogen donor atoms and these metals. Steric hindrance by the methyl groups does not seem to affect the resulting stoichiometry, except in Mg(II)_2^{2+} where ligand crowding probably prohibits a weak interaction of the perchlorate ion with the rather small magnesium ion. The reason for the distortion of the tetrahedral perchlorate toward C_{3v} symmetry is not entirely clear. The data indicate that the resulting coordination number of the alkaline earth metal complexes with nitrogen-chelating heterocycles is strongly dependent on the intramolecular nitrogen-nitrogen distance in the ligand. Because of the similarity of the alkaline earth metal to the rare earth metal ions, we are presently extending our work to the study of rare earth complexes of some naphthyridines.

Acknowledgment.—The authors wish to thank Dr. P. Singh for his helpful discussions and Mrs. P. J. Jones for performing the carbon, hydrogen, and nitrogen analyses.

(19) W. L. F. Armarego, G. B. Barlin, and E. Spinner, *Spectrochim. Acta*, **22**, 117 (1966).

(20) R. J. P. Williams, *J. Chem. Soc.*, 3770 (1952).

(21) H. Irving and R. J. P. Williams, *ibid.*, 3192 (1952).