

## Metallic Perchlorate Salts of *N*-Isopropyl- and *N*-Cyclohexyl-2-pyrrolidinone

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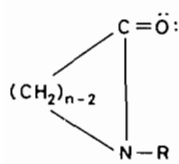
### Abstract

A series of metal perchlorate complexes of *N*-isopropyl-2-pyrrolidinone (NIPP) and *N*-cyclohexyl-2-pyrrolidinone (NCHP) have been synthesized, showing coordination through the carbonyl oxygen atom. These complexes have compositions with the general formulas  $[M(NIPP)_{4 \text{ or } 6}]^{2+}(\text{ClO}_4)_2$  and  $[M(NCHP)_6]^{2+}(\text{ClO}_4)_2$  [ $M = \text{Mn(II), Co(II), Ni(II), Cu(II), Zn(II)}$  and  $\text{Cd(II)}$ ]. They have been characterized by IR spectra, electrical conductivity measurements, magnetic moments, X-ray diffraction patterns and electronic absorption spectra.

### Introduction

A large number of transition metal complexes of amides and cyclic amides have been prepared and characterized [1-6]. Drago and others [7] have systematically studied the spectroscopic properties of octahedral Ni(II) and Cr(III) perchlorate complexes of several amides and cyclic amides. They found that the ligand field parameters did not follow the order of amide basicity towards phenol. This was attributed to a steric interaction between the substituted groups of adjacent ligands when the carbonyl carbon and amide nitrogen atoms contained alkyl substituents.

Bright and coworkers [8] have investigated the donor properties of cyclic amides containing five-, six-, and seven-membered rings of the general formula:



where  $n = 5, 6, 7$  and  $R = \text{H}$  or  $\text{CH}_3$ .

It was found for the Ni(II) perchlorate complexes that the donor strengths were in the order of 5- < 6- = 7-membered ring, when  $R = \text{H}$ . The order of basicity for these cyclic amides was reported to be in the

order of a 5-  $\ll$  7- < 6-membered ring [9]. It appeared then that the donor strengths of these complexes approximately followed the order of basicity of the cyclic amides. When  $R = \text{CH}_3$ , the crystal-field splitting energy,  $Dq$ , was lower than that of the analogous Ni(II) perchlorate complex when  $R = \text{H}$ . The order of the ring size in relation to the donor strength of the Ni(II) perchlorate complexes was found to be 5- > 6- = 7-membered ring, when  $R = \text{CH}_3$ . The lower crystal-field splitting energy and the reversal of the donor strengths, when the nitrogen substituent was  $\text{CH}_3$ , were attributed to a steric interaction involving the methyl group.

This steric interaction has been investigated in complexes of 2-pyrrolidinone (NHP =  $\gamma$ -butyrolactam) and *N*-methyl-2-pyrrolidinone (NMEP = NBuL = *N*-methyl- $\gamma$ -butyrolactam) [10, 11]. Both cyclic amides were found to form complexes with the dipositive cations of the first transition series rather readily. The complexes of 2-pyrrolidinone were found to form six-coordinate species when they were prepared as perchlorate salts with Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II). In contrast, *N*-methyl-2-pyrrolidinone formed four-coordinate complexes when prepared as the perchlorate salts of Cu(II) and Zn(II), and six-coordinate complexes when prepared as the perchlorate salts of dipositive manganese, cobalt, nickel and cadmium. Madan [12] was able to isolate both four- and six-coordinate complexes for the Co(II) perchlorate salts of *N*-methyl-2-pyrrolidinone.

To further investigate this steric effect, dipositive manganese, nickel, cobalt, copper, zinc and cadmium perchlorate salts of *N*-isopropyl- and *N*-cyclohexyl-2-pyrrolidinone were synthesized. The compounds have been characterized by their IR spectra, electrical conductivity measurements, magnetic susceptibility measurements, X-ray diffraction patterns and electronic absorption spectra.

### Experimental

#### Materials

*N*-isopropyl-2-pyrrolidinone (NIPP) and *N*-cyclohexyl-2-pyrrolidinone (NCHP) were obtained from

TABLE I. Analytical Data and some Physical Properties of the Metal Perchlorate Complexes of *N*-isopropyl-2-pyrrolidone and of *N*-cyclohexyl-2-pyrrolidone

Complex	Theoretical		Experimental		Color	Yield (%)	Melting point (°C)	$\mu_{\text{eff}}$ (BM)				
	%C	%H	%M	%ClO <sub>4</sub>								
[Mn(C <sub>7</sub> H <sub>13</sub> NO) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	49.60	7.75	5.40	19.56	49.59	7.50	5.41	19.27	white	86	96-7	5.96
[Co(C <sub>7</sub> H <sub>13</sub> NO) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	49.41	7.72	4.67	19.48	49.36	7.68	4.74	19.40	raspberry	92	131	5.18
[Co(C <sub>7</sub> H <sub>13</sub> NO) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	43.87	6.85	7.69	25.95	43.85	6.61	7.69	25.76	violet	89	152	4.42
[Co(C <sub>7</sub> H <sub>13</sub> NO) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>2</sub> · H <sub>2</sub> O	42.86	6.77	7.51	25.35	42.69	6.70	7.61	25.17	violet	-	152	4.62
[Ni(C <sub>7</sub> H <sub>13</sub> NO) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	49.42	7.75	4.67	19.49	49.29	7.65	4.74	19.55	yellow-green	88	166-8	3.27
[Cu(C <sub>7</sub> H <sub>13</sub> NO) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	43.60	6.81	8.24	25.79	43.32	6.62	8.28	25.50	aqua-blue	94	172	2.13
[Zn(C <sub>7</sub> H <sub>13</sub> NO) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	43.50	6.79	8.46	25.73	43.50	6.94	8.50	25.38	white	82	178-80	diamagnetism
[Cd(C <sub>7</sub> H <sub>13</sub> NO) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	46.95	7.33	10.46	18.51	46.99	7.20	10.50	18.36	white	83	103-4	diamagnetism
[Mn(C <sub>10</sub> H <sub>17</sub> NO) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	57.31	8.19	4.37	15.82	57.05	8.13	4.42	15.81	white	81	162	5.86
[Co(C <sub>10</sub> H <sub>17</sub> NO) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	57.14	8.17	4.67	15.77	56.93	8.22	4.74	15.58	raspberry	93	165-7	5.31
[Ni(C <sub>10</sub> H <sub>17</sub> NO) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	57.14	8.17	4.66	15.77	57.20	8.32	4.64	15.50	yellow	94	175-6	3.39
[Cu(C <sub>10</sub> H <sub>17</sub> NO) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	56.92	8.14	5.02	15.71	56.94	8.20	4.94	15.30	green-blue	90	115-6	2.09
[Zn(C <sub>10</sub> H <sub>17</sub> NO) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	56.84	8.13	5.16	15.69	56.81	8.17	5.26	15.48	white	85	123	diamagnetism
[Cd(C <sub>10</sub> H <sub>17</sub> NO) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	54.81	7.84	8.55	15.13	54.69	7.80	8.63	14.97	white	91	175-7	diamagnetism

GAF Corporation in technical grade form and purified using vacuum distillation (NIPP: 84 °C, 5 mmHg; NCHP: 137-8 °C, 5 mmHg). All other reagents were at least reagent grade.

#### Preparation of NIPP Complexes

The metal perchlorate complexes of NIPP were synthesized in a nitrogen atmosphere as described for the manganese compound, with the exception of [Co(NIPP)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub>.

#### [Mn(NIPP)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub>

Hydrated manganese perchlorate Mn(ClO<sub>4</sub>)<sub>2</sub> · 6H<sub>2</sub>O, (0.3557 g, 0.00098 mol) was dehydrated by magnetic stirring for 2 h at room temperature with 500% excess of 2,2-dimethoxypropane (3.07 g, 0.029 mol) [13], NIPP (0.7504 g, 0.0059 mol) was added dropwise to the solution while stirring. The resulting solution was stirred magnetically for an additional fifteen minutes. An equal volume of anhydrous ethyl ether was then added with continuous stirring. After the reaction mixture was triturated vigorously for 20 min, additional NIPP was added dropwise (approximately 0.971 g, 0.0076 mol), until a beige precipitate formed. The precipitate was washed with several portions of anhydrous ethyl ether, and dried in a nitrogen atmosphere at room temperature in the presence of P<sub>4</sub>O<sub>10</sub>. The white crystalline substance was then stored under nitrogen.

#### [Co(NIPP)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub>

Approximately 2 g of [Co(NIPP)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub> were placed into a drying pistol. This sample was heated to 80.0 °C at 5 mmHg in the presence of P<sub>4</sub>O<sub>10</sub> for 96 h. The raspberry colored crystals turned to a deep violet after 96 h of drying. The resulting crystals were extremely hygroscopic.

#### Preparation of NCHP Complexes

The syntheses of the metal perchlorate complexes of NCHP were similar to that for [Mn(NIPP)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub>.

#### Chemical Analysis

Carbon and hydrogen analyses were done by MicAnal Organic Microanalysis of Tucson, Ariz. Metal ion analyses were performed by complexometric titration with EDTA, as described by Flaschka [14]. Perchlorate analyses were completed utilizing a gravimetric procedure based upon the precipitation of nitron perchlorate.

#### Physical Measurements

These were carried out as previously described [10-12].

TABLE VII. Band Shifts in the Infrared Spectra upon Coordination

Complex	Assignment					
	$\nu\text{CO}$	$\Delta\text{CO}$	$\nu\text{CN}^{\text{a}}$	$\Delta\text{CN}$	$\nu\text{CN}^{\text{b}}$	$\Delta\text{CN}$
$\text{C}_7\text{H}_{13}\text{NO}$ (neat)	1687		1287		1239	
$[\text{Mn}(\text{C}_7\text{H}_{13}\text{NO})_6][\text{ClO}_4]_2$	1638	-49	1299	+12	1225	-14
$[\text{Co}(\text{C}_7\text{H}_{13}\text{NO})_6][\text{ClO}_4]_2$	1630	-57	1301	+14	1227	-12
$[\text{Co}(\text{C}_7\text{H}_{13}\text{NO})_4][\text{ClO}_4]_2$	1610	-77	1308	+21	1223	-16
$[\text{Ni}(\text{C}_7\text{H}_{13}\text{NO})_6][\text{ClO}_4]_2$	1628	-59	1300	+13	1228	-11
$[\text{Cu}(\text{C}_7\text{H}_{13}\text{NO})_4][\text{ClO}_4]_2$	1615	-72	1304	+17	1225	-14
$[\text{Zn}(\text{C}_7\text{H}_{13}\text{NO})_4][\text{ClO}_4]_2$	1611	-76	1308	+21	1222	-17
$[\text{Cd}(\text{C}_7\text{H}_{13}\text{NO})_6][\text{ClO}_4]_2$	1625	-62	1304	+17	1228	-11
$\text{C}_{10}\text{H}_{17}\text{NO}$ (neat)	1682		1283		1209	
$[\text{Mn}(\text{C}_{10}\text{H}_{17}\text{NO})_6][\text{ClO}_4]_2$	1622	-60	1298	+15	1207	-2
$[\text{Co}(\text{C}_{10}\text{H}_{17}\text{NO})_6][\text{ClO}_4]_2$	1620	-62	1298	+15	1208	-1
$[\text{Ni}(\text{C}_{10}\text{H}_{17}\text{NO})_6][\text{ClO}_4]_2$	1615	-67	1297	+14	1204	-5
$[\text{Cu}(\text{C}_{10}\text{H}_{17}\text{NO})_6][\text{ClO}_4]_2$	1628	-54	1298	+15	1205	-4
$[\text{Zn}(\text{C}_{10}\text{H}_{17}\text{NO})_6][\text{ClO}_4]_2$	1627	-55	1299	+16	1206	-3
$[\text{Cd}(\text{C}_{10}\text{H}_{17}\text{NO})_6][\text{ClO}_4]_2$	1621	-61	1299	+16	1205	-4

<sup>a</sup>Carbonyl carbon-nitrogen stretch.<sup>b</sup>Amide nitrogen substituted carbon stretch.

## Results

The analytical data, color, yield, melting points and magnetic moments for the complexes of NIPP and NCHP are given in Table I.

The powder X-ray diffraction data can be found in Tables II–VI\*. In Table VII, the changes in the carbonyl and carbon–nitrogen stretching frequencies are given. The infrared spectra for the four- and six-coordinated complexes of NIPP can be found in Table VIII\*. The IR spectra of the NCHP complexes can be found in Table IX\*. The electronic absorption spectra of the six-coordinated complexes of NIPP and NCHP were obtained using acetone, nitromethane, Nujol mulls, and solid reflectance, in order to determine whether the primary absorbing species was the same in the solid as in the solution. Methylene chloride was the solvent used for the four-coordinate species of NIPP. In order to prevent solvolysis of the complexes of NIPP and NCHP, ligand was added to the solvents. The spectral band assignments for the cobalt(II) complexes of NIPP and NCHP are given in Table X\*. The spectral data for the nickel(II) complexes of NIPP and NCHP are given in Table XI\*. The spectral data for the NIPP and NCHP complexes of copper(II) and manganese(II) can be found in Table XII\*. The solvent used to determine the electronic absorption spectra of the manganese complexes was methanol.

## Discussion

The analytical results indicate that the complexes of NCHP are six-coordinate, while the complexes of NIPP are six- and/or four-coordinate. The possibility that the perchlorate ion is coordinated in the complexes can be ruled out by the evidence from the electrolytic conductance measurements and the IR spectra. Geary [15] has compiled acceptable ranges for complexes of the various electrolyte types at concentrations of approximately  $10^{-3}$  M in nitromethane. The ranges are suggested as 1:1, 75–95; 2:1, 150–180; 3:1, 200–260; 4:1, 290–330  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ . The specific conductances for all the complexes of NIPP and NCHP in nitromethane fall in the range for 2:1 electrolyte types. The molecular conductivity of  $9.27 \text{ ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$  for tetra(NIPP) cobalt(II) perchlorate in methylene chloride is comparable to the values of  $8.47 \text{ ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$  for  $[\text{Ni}(\text{py})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2$  [16],  $12.1 \text{ ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$  for  $[\text{Co}(\text{DMA})_4](\text{ClO}_4)_2$  [16], and  $11.4 \text{ ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$  for  $[\text{Co}(\text{NIPP})_4](\text{ClO}_4)_2$  [12], which were all interpreted as being 2:1 electrolytes.

Hathaway and Underhill [17] have shown that for a unidentate coordinated perchlorate, the symmetry of the perchlorate ion is lowered from  $T_d$  to  $C_{3v}$  in the complex. The lowering of symmetry results in the splitting of a broad band into two intense peaks in the  $1200\text{--}900 \text{ cm}^{-1}$  region of the IR spectrum. For the complexes of NIPP and NCHP there is only one broad peak between  $1200\text{--}900 \text{ cm}^{-1}$  in the IR spectrum, with the exception of  $[\text{Cu}(\text{NIPP})_4](\text{ClO}_4)_2$  (Tables VIII and IX)\*. The

\*See 'Supplementary Material'.

peak is broad with a maximum at  $1090\text{ cm}^{-1}$ , which is characteristic of ionic perchlorate. For  $[\text{Cu}(\text{NIPP})_4](\text{ClO}_4)_2$ , there are two relatively intense peaks, one at  $1119\text{ cm}^{-1}$ , and the other at  $1090\text{ cm}^{-1}$ , which are characteristic of monodentate coordinated perchlorate. It was observed that a color change from blue to brown took place when  $[\text{Cu}(\text{NIPP})_4](\text{ClO}_4)_2$  was prepared either as a Nujol mull, using NaCl or CsBr plates, or as a KBr pellet. Since the molecular conductivity indicated that the complex was a 2:1 electrolyte type in solution, and because of the change in color of the complex when placed under pressure, it appears that the perchlorate ion became coordinated during sample preparation.

The decrease of the carbonyl and the corresponding increase in the carbonyl carbon–nitrogen stretching frequencies is indicative of coordination through the carbonyl oxygen atom (Table VII) [18]. The decrease in the stretching frequency of the bond between the substituted group and the amide nitrogen, upon coordination, suggests a decrease in the bond order. This indicates an electron-donation by the alkyl group and is more pronounced for the complexes of NIPP than for those of NCHP. It is apparent from these data that coordination occurs through the carbonyl oxygen, not the amide nitrogen, and the bond between the amide nitrogen and the isopropyl group is significantly weakened.

The magnetic moments for the six-coordinate complexes of Mn(II), Co(II), Ni(II) and Cu(II) NIPP and NCHP fall within the ranges of magnetic moments previously reported for octahedral high-spin complexes [19] with the exception of  $[\text{Co}(\text{NIPP})_6](\text{ClO}_4)_2$  (Table I). The range of accepted magnetic moments for octahedral high-spin Co(II) complexes has been reported to be 4.8–5.2 BM. The magnetic moment of 5.31 BM for  $[\text{Co}(\text{NCHP})_6](\text{ClO}_4)_2$  is slightly higher than the upper limit of this range, but can be thought of as indicative of an octahedral high-spin complex. The magnetic moments of 4.42 and 4.62 BM for the four-coordinate Co(II) complexes of NIPP are well within the range of 4.2–4.8 BM accepted for tetrahedral Co(II) complexes. Drago and others [16] have reported a magnetic moment of 4.68 BM for  $[\text{Co}(\text{DMA})_4](\text{ClO}_4)_2$ , and Madan [12] has found a magnetic moment of 4.80 BM for  $[\text{Co}(\text{NMEP})_4](\text{ClO}_4)_2$ . The authors assigned a distorted tetrahedral geometry to the complexes in each case. The magnetic moment of 2.13 BM for  $[\text{Cu}(\text{NIPP})_4](\text{ClO}_4)_2$  is close to that of 2.10 BM for  $[\text{Cu}(\text{NMEP})_4](\text{ClO}_4)_2$  as reported by Sturr [10], and both these numbers approach the value of 2.2 BM, which is that predicted for the Cu(II) complexes of tetrahedral geometry. Predictions of the geometry of Cu(II) complexes on the basis of magnetic moments must be done with caution, however, because of the small changes in the magnetic measurements.

The X-ray diffraction patterns for the complexes of the general formula  $[\text{M}(\text{NIPP})_4](\text{ClO}_4)_2$  (Table II\*) are significantly different from the diffraction patterns for the complexes of the general formulas  $[\text{M}(\text{NIPP})_6](\text{ClO}_4)_2$  (Tables III and IV\*) or  $[\text{M}(\text{NCHP})_6](\text{ClO}_4)_2$  (Tables V and VI\*). Upon closer examination of the diffraction patterns for the four-coordinate complexes, it becomes obvious that  $[\text{Co}(\text{NIPP})_4](\text{ClO}_4)_2$  and  $[\text{Zn}(\text{NIPP})_4](\text{ClO}_4)_2$  are isomorphous. This indicates that the geometries of these two complexes and  $[\text{Cu}(\text{NIPP})_4](\text{ClO}_4)_2$  are different. Although Co(II) and Zn(II) form square-planar complexes with bidentate ligands, they form predominantly tetrahedral complexes with monodentate ligands [20]. Conversely, Cu(II) forms a wide variety of square-planar complexes with monodentate ligands. From this information and the coordination of the perchlorate ion during sample preparation for obtaining the IR spectrum,  $[\text{Co}(\text{NIPP})_4](\text{ClO}_4)_2$  and  $[\text{Zn}(\text{NIPP})_4](\text{ClO}_4)_2$  are tentatively assigned tetrahedral configurations, and  $[\text{Cu}(\text{NIPP})_4](\text{ClO}_4)_2$  is assigned a square-planar geometry. Sturr [11] has recorded the X-ray powder diffraction patterns for  $[\text{Cu}(\text{NMEP})_4](\text{ClO}_4)_2$ . Comparison of these diffraction patterns reveals that the two complexes are isomorphous. It would appear, then, that the relatively large magnetic moments for these complexes are not the result of a tetrahedral configuration.

A comparison of the X-ray powder diffraction patterns for the six-coordinate Mn(II), Co(II) and Ni(II) NIPP complexes shows that the complexes are isomorphous. The X-ray patterns of  $[\text{Cd}(\text{NIPP})_6](\text{ClO}_4)_2$  are significantly different from those of analogous Mn(II), Co(II) and Ni(II) complexes. A similar comparison of the X-ray diffraction patterns of the complexes of the general formula  $[\text{M}(\text{NCHP})_4](\text{ClO}_4)_2$  demonstrates that these complexes are isomorphous with one another. It can be seen that the six-coordinate complexes of NIPP and NCHP are not isomorphous by comparing their respective X-ray data. However, the X-ray diffraction patterns of  $[\text{Cd}(\text{NIPP})_6](\text{ClO}_4)_2$  are similar to those of the complexes of NCHP. A possible explanation of these results may be that the steric interactions of the isopropyl group of the NIPP ligand result in distortion from octahedral configuration for the Mn(II), Co(II) and Ni(II) complexes of NIPP. The larger ionic radius of Cd(II) may relieve some of these interactions for  $[\text{Cd}(\text{NIPP})_6](\text{ClO}_4)_2$ , resulting in a 'purer' octahedral configuration, as in the complexes of NCHP.

The electronic absorption spectral data for the octahedral Co(II) complexes of NIPP and NCHP (Table X\*) show that the primary absorbing species

\*See 'Supplementary Material'.

is the same in the solid as in solution. The molar absorptivities for  $[\text{Co}(\text{NIPP})_6](\text{ClO}_4)_2$  and  $[\text{Co}(\text{NCHP})_6](\text{ClO}_4)_2$  are within the acceptable range for octahedral Co(II) complexes. The molar absorptivity for the tetrahedral Co(II) complex of NIPP (Table X\*), as determined in methylene chloride, is somewhat lower than that found for tetrahedral Co(II) complexes. Madan [12] and Drago [16] have reported similar molar absorptivities for the complexes of  $[\text{Co}(\text{NIPP})_4](\text{ClO}_4)_2$  and  $[\text{Co}(\text{DMA})_4](\text{ClO}_4)_2$ , respectively.

The forbidden two-electron transition,  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}$ , for high-spin octahedral Co(II) complexes is only observed in the solid reflectance spectra of  $[\text{Co}(\text{NIPP})_6](\text{ClO}_4)_2$  at  $14080\text{ cm}^{-1}$  and  $[\text{Co}(\text{NCHP})_6](\text{ClO}_4)_2$  at  $14490\text{ cm}^{-1}$ . This is an indication that the octahedral complexes of NIPP and NCHP experience considerably more distortion in the solid than in solution.

The spin-orbit coupling constant,  $\lambda$ , for  $[\text{Co}(\text{NIPP})_4](\text{ClO}_4)_2$  has been found to be  $-149\text{ cm}^{-1}$  [21], which is in the  $-130\text{ cm}^{-1}$  to  $-160\text{ cm}^{-1}$  range [22] of Co(II) complexes exhibiting regular tetrahedral geometry. This finding supports the tentative assignment of tetrahedral geometry for  $[\text{Co}(\text{NIPP})_4](\text{ClO}_4)_2$  on the basis of X-ray diffraction and magnetic susceptibility data.

As was found for the Co(II) complexes, the primary absorbing species for the Ni(II) complexes of NIPP and NCHP are the same in solution as they are in the solid. The electronic absorption spectral data for the Ni(II) complexes (Table XI\*) demonstrate that the  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$  transition is split. The splitting of this band is due to the spin-orbit coupling that mixes the  ${}^3\text{T}_{1g}(\text{F})$  and the  ${}^1\text{E}_g$ , which are very close in energy in a weak field complex.

The spectral bands of the manganese complexes (Table XII\*) were located for the complexes in methanol by taking the second derivative spectra on a Perkin-Elmer 559 A spectrophotometer. The molar absorptivities were then calculated from the absorption spectra. The molar absorptivities range between 0.10 and 0.55, which is an order of magnitude higher than the 0.01–0.02 values measured for manganese hexahydrate [19]. Sturr [10] has reported similar behavior for the manganese complexes of 2-pyrrolidinone and *N*-methyl-2-pyrrolidinone. The locations of the spectral bands were similar to those reported for other octahedral Mn(II) complexes.

It is immediately obvious from the spectral data for the Cu(II) complexes (Table XII\*) that  $[\text{Cu}(\text{NIPP})_4](\text{ClO}_4)_2$  has its spectral band centered at 734 nm, but it is shifted to 819 nm for  $[\text{Cu}(\text{NCHP})_6](\text{ClO}_4)_2$ . A transition located at 705 nm

has been reported for  $[\text{Cu}(\text{NMEP})_4](\text{ClO}_4)_2$ , which is similar to the 720 nm reported for  $[\text{Cu}(\text{HMPA})_4](\text{ClO}_4)_2$  [24]. In methylene chloride, however, the band at 734 nm in Nujol for  $[\text{Cu}(\text{NIPP})_4](\text{ClO}_4)_2$  is shifted to 819 nm, which is identical to the transition observed for  $[\text{Cu}(\text{NCHP})_6](\text{ClO}_4)_2$  in Nujol. This may be the result of the coordination of methylene chloride or of the perchlorate ion, which is consistent with assignment of a square planar geometry for  $[\text{Cu}(\text{NIPP})_4](\text{ClO}_4)_2$ .

## Conclusion

The compounds of NIPP and NCHP appear to have a general tendency to form octahedral complexes. The steric effect of the isopropyl group in the complexes of Co(II), Cu(II) and Zn(II) appears to be well established with the formation of four-coordinate species. From a consideration of the X-ray and spectral data, the Co(II) and Zn(II) complexes of NIPP are assigned regular tetrahedral geometry. From the X-ray data alone, the Cu(II) complex of NIPP is assigned a square planar geometry. The ultimate determination of structure would be the single-crystal X-ray spectra. However, the evidence appears sufficiently strong enough to assign the tentative structures, as above.

Furthermore, the complexes of NCHP are more stable because the cyclohexyl ring is in a configuration that is unfavorable for steric interactions to occur. Although the complexes of NIPP exhibit significant steric interactions, they are approximately as stable as the complexes of NMEP, even though the isopropyl group is significantly larger than the methyl group.

## Supplementary Material

Tables II–VI show X-ray diffraction data, Tables VIII and IX contain IR spectral information and Tables X, XI and XII the electronic spectral data (11 pages). Available from the Editor-in-Chief on request.

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