

*trans*-Dichlorodinitroethylenediamineplatinum(IV) was prepared by passing Cl<sub>2</sub> gas for 2 hr through a suspension of 0.51 g (1.5 mmol) of Pt(en)(NO<sub>2</sub>)<sub>2</sub> in 5 ml of water. The yellow crystals which formed were recrystallized from hot, very dilute hydrochloric acid and vacuum dried. The yield was 0.40 g (65%). *Anal.* Calcd for Pt(C<sub>2</sub>N<sub>2</sub>H<sub>8</sub>)(NO<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>: Pt, 46.66; Cl, 16.98. Found: Pt, 46.65; Cl, 16.77.

*trans*-Dibromodinitroethylenediamineplatinum(IV) was prepared by repeatedly contacting a 0.51-g (1.5-mmol) sample of Pt(en)(NO<sub>2</sub>)<sub>2</sub> with 10 ml of an aqueous solution containing 1 drop of HBr (48%) which was kept saturated with bromine. The yellow crystalline product was recrystallized from a very dilute HBr solution and vacuum dried. The yield was 0.40 g (50%). *Anal.* Calcd for Pt(C<sub>2</sub>N<sub>2</sub>H<sub>8</sub>)(NO<sub>2</sub>)<sub>2</sub>Br<sub>2</sub>: Pt, 38.46; Br, 31.56. Found: Pt, 38.29; Br, 32.28. Platinum analyses were done by ignition; halide analyses, by a modified Volhard titration procedure.

**Kinetic Measurements.**—Kinetics were followed spectrophotometrically on a Beckman DU spectrophotometer modified with a Gilford 220 absorbance indicator. The cell compartment was thermostated to better than ±0.02°. The reactions were studied under pseudo-first-order conditions by using at least a 50:1 excess of entering anion. Unless otherwise indicated the ionic strength of the solutions was maintained with NaClO<sub>4</sub>. Perchloric acid was used to adjust solution acidity. Bromide ion was provided as NaBr except in 90 and 99% methanol solution where N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>Br was used. Chloride ion was provided

as NaCl except in the runs in pure methanol where N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>Cl was used. Fresh platinum(II) and -(IV) solutions were prepared each day kinetics were run. In many cases duplicate kinetic runs were carried out and average values are reported in Tables I–III. Duplicate runs reproduced quite well with deviations seldom being greater than ±3%. Infinite-time absorbances on kinetic solutions were consistent with those expected from the spectra of the reaction products.

The reactions were studied at wavelengths at which large absorbance changes were observed. In most cases the very intense ultraviolet maximum of the *trans*-dibromo compounds was used. Reaction 4 was studied at 233 mμ except for the dioxane solutions which were studied at 250 mμ. Reaction 9 was studied at 235 mμ and the reverse of reaction 4 was studied at 226 mμ, an isosbestic point for *trans*-Pt(en)(NO<sub>2</sub>)<sub>2</sub>Br<sub>2</sub> and *trans*-Pt(en)(NO<sub>2</sub>)<sub>2</sub>ClBr.

Rate data were analyzed by a Gauss–Newton nonlinear least-squares fit to the equation  $A = A_0 + (A_\infty - A_0) \exp(-kt)$ . Absorbance vs. time data covering 4½ half-lives were in general used and the fit to the equation was in general within the uncertainty of the absorbance measurements.

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## Complexes of Thiazoles. I. Zinc(II), Cobalt(II), Copper(II), Nickel(II), and Platinum(II) Derivatives of Alkyl-Substituted Thiazoles

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Nineteen complexes of 4- and 2,4-dialkyl-substituted thiazoles with copper(II), nickel(II), cobalt(II), zinc(II), and platinum(II) containing various anions have been synthesized and are generally of the form MX<sub>2</sub>L<sub>2</sub>. The electronic and far-infrared spectra and the temperature dependence of the magnetic moments are reported. All of the zinc and cobalt derivatives are tetrahedral, the 4-methyl copper and nickel species are octahedral, while the dialkyl complexes of copper and nickel, as well as the platinum complexes, are square planar. The four-coordinate dialkyl complexes follow the crystal field stabilization energy predictions as to the relative tendency to form tetrahedral as opposed to square-planar forms *i.e.*, Zn > Co > Cu > Ni. There was no evidence for ambidentate behavior; all of the complexes showed metal–nitrogen as opposed to metal–sulfur coordination.

### Introduction

The general metal ion requirements noted in many thiamine-dependent enzyme systems<sup>2,3</sup> and the catalytic hydrogen wave produced by cobalt–ammonia buffer solutions of thiamine during polarography<sup>4</sup> lend support for some type of metal–thiamine interaction. Several studies have been carried out involving the thiamine analog thiazole (I). Metal complexes of thia-

zole,<sup>5</sup> benzothiazole,<sup>6</sup> and its 2-methyl derivative<sup>7</sup> have already been reported. Thiazole has both nitrogen and sulfur as possible donor sites, and whereas the majority of complexes have been found to be nitrogen bonded, a case of sulfur coordination has been postulated.<sup>8</sup>



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TABLE I  
 ANALYTICAL DATA, COLOR, AND MELTING POINTS

Compounds <sup>a</sup>	% calcd					% found					Mp, °C	Color
	Metal	Anion	C	H	N	Metal	Anion	C	H	N		
CoCl <sub>2</sub> (4-MeT) <sub>2</sub>	17.9	21.6	29.3	3.07	8.54	18.1	22.1	28.7	3.19	8.61	179-181	Royal blue
CoBr <sub>2</sub> (4-MeT) <sub>2</sub>	14.14	38.2	23.0	2.42	6.71	13.96	38.2	...	...	...	211-213	Royal blue
CoI <sub>2</sub> (4-MeT) <sub>2</sub>	11.54	49.5	18.8	1.97	5.47	11.82	49.7	...	...	...	202-204	Sea green
CoCl <sub>2</sub> (2,4-DMeT) <sub>2</sub>	16.7	19.9	33.7	3.96	7.87	16.7	20.2	33.5	4.32	7.43	168-170	Royal blue
CoCl <sub>2</sub> (2-Et-4-MeT) <sub>2</sub>	15.3	18.5	37.5	4.72	7.29	15.3	18.7	37.4	4.90	6.78	115-118	Royal blue
ZnCl <sub>2</sub> (4-MeT) <sub>2</sub>	19.6	21.2	28.7	3.01	3.17	20.2	21.3	29.4	3.13	3.12	184-187	Colorless
ZnBr <sub>2</sub> (4-MeT) <sub>2</sub>	15.4	37.7	22.7	2.39	6.63	15.5	37.7	...	...	...	213-215	Colorless
ZnI <sub>2</sub> (4-MeT) <sub>2</sub>	12.7	48.9	22.0	2.59	5.14	12.7	48.8	22.2	2.68	4.77	202-204	Colorless
ZnCl <sub>2</sub> (2,4-DMeT) <sub>2</sub>	18.1	19.6	33.1	3.90	7.73	18.1	19.5	...	...	...	...	Colorless
ZnI <sub>2</sub> (2,4-DMeT) <sub>2</sub>	12.0	46.5	18.6	1.95	5.37	12.1	46.3	18.7	2.02	5.41	189-191	Colorless
CuCl <sub>2</sub> (4-MeT) <sub>2</sub>	18.2	20.3	30.9	3.45	7.99	18.3	20.4	29.4	3.27	7.78	162-163	Green
CuCl <sub>2</sub> (2,4-DMeT) <sub>2</sub>	17.6	19.7	33.3	3.91	7.77	17.6	19.6	33.6	4.02	7.73	168-170	Purple
Ni(NO <sub>3</sub> ) <sub>2</sub> (4-MeT) <sub>2</sub>	12.2	<i>b</i>	30.0	3.15	14.6	12.2	<i>b</i>	29.3	3.33	14.5	122-124	Green
NiBr <sub>2</sub> (2-Et-4-MeT) <sub>2</sub>	12.5	33.8	30.5	3.84	5.92	12.7	33.9	28.6	4.17	5.61	<i>c</i>	Light blue
NiBr <sub>2</sub> (2,4-DMeT) <sub>2</sub>	13.2	36.0	26.9	3.17	6.28	13.3	36.1	25.1	3.67	5.56	<i>c</i>	Light blue
NiBr <sub>2</sub> (4-MeT) <sub>2</sub>	14.1	38.4	23.1	2.43	6.74	14.3	38.5	19.7	3.27	5.20	<i>c</i>	Light blue
PtCl <sub>2</sub> (4-HT) <sub>2</sub>	44.72	16.25	16.50	1.38	6.42	45.31	...	16.45	1.55	6.28	<i>d</i>	Yellow
PtCl <sub>2</sub> (4-MeT) <sub>2</sub>	42.02	15.27	20.67	2.17	6.03	43.23	...	20.98	2.33	5.95	<i>d</i>	Yellow
PtBr <sub>2</sub> (4-MeT) <sub>2</sub>	35.26	28.90	17.36	1.83	5.06	...	...	17.21	2.31	4.85	<i>d</i>	Yellow

<sup>a</sup> Names: 4-MeT, 4-methylthiazole; 2,4-DMeT, 2,4-dimethylthiazole; 2-Et-4-MeT, 2-ethyl-4-methylthiazole; 4-HT, thiazole. <sup>b</sup> Per cent N includes nitrate. <sup>c</sup> Color change; no melting below 300°. <sup>d</sup> Decomposed above 220°.

We reported the synthesis and characterization of 19 complexes of divalent zinc, platinum, cobalt, nickel, and copper with thiazole and 4- or 2,4-dialkyl-substituted thiazoles, containing various anions. The nature and position of the substituents were found to have a profound effect on the stereochemistry of the resulting complexes. The question of ambidentate behavior in the metal thiazoles is also considered.

### Experimental Section

Thiazole (4-HT),<sup>8</sup> 4-methylthiazole (4-MeT),<sup>8</sup> 2,4-dimethylthiazole (2,4-DMeT),<sup>9</sup> and 2-ethyl-4-methylthiazole (2-Et-4-MeT)<sup>9</sup> were synthesized by modifications of literature procedures. The complexes of Co(II), Cu(II), Zn(II), and Ni(II) were prepared by slowly adding a saturated methanolic solution of the hydrated metal salt to a concentrated stirred methanolic solution of the thiazole. The ratio of thiazole to metal ion was always greater than 6:1. The complexes either precipitated immediately, or were forced out of solution with ether. They were all recrystallized from ether-methanol. The *cis* Pt(II) complexes were prepared by a modification of the procedure for Pt(II)-py complexes.<sup>10</sup> The platinum(II) bromide complex was prepared by adding a 200% excess of KBr to an aqueous solution of K<sub>2</sub>PtCl<sub>4</sub>, stirring for 72 hr, and then proceeding as with the chloro derivative.

C, H, N, and Pt analyses were made by Aldridge Associates, Washington, D. C. Metal ion determinations were carried out *via* EDTA titrations, and the halide determinations, *via* the Volhard method.

The magnetic susceptibilities were measured by a previously described Faraday method.<sup>11</sup> The infrared spectra were determined on a Perkin-Elmer 621 using KBr or CsI pellets and/or Nujol mulls between polyethylene sheets or NaCl crystals. The liquids were observed in 0.1-mm polyethylene cells. Electronic spectra were recorded on a Cary 14 spectrophotometer with a standard reflectance attachment, using MgCO<sub>3</sub> as a reference.

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### Results

**Zinc Complexes.**—The zinc chloride, bromide, and iodide complexes of 4-MeT and 2,4-DMeT analyzed as ZnX<sub>2</sub>L<sub>2</sub> (Table I) and were observed to be diamagnetic. The thiazole zinc derivatives have the same stoichiometry found for most heterocyclic amine-zinc complexes, which are tetrahedral.<sup>6,12-14</sup> Table II shows the infrared spectra of the zinc derivatives from 500 to 200 cm<sup>-1</sup>. These complexes had essentially the same spectra in CsI pellets as in Nujol mulls. The observed thiazole spectra are similar to those of zinc-pyridine derivatives.<sup>12</sup> Thus ZnX<sub>2</sub>(py)<sub>2</sub> has  $\nu(\text{Zn-Cl})$  at 329 (s) and 296 (s) cm<sup>-1</sup>,  $\nu(\text{Zn-Br})$  at 254 (s) and 220 (m) cm<sup>-1</sup>, and  $\nu(\text{Zn-I})$  at 220 (m) cm<sup>-1</sup>. The corresponding  $\nu(\text{Zn-N})$  frequencies are *ca.* 220 cm<sup>-1</sup>. For the ZnX<sub>2</sub>(4-MeT) derivatives,  $\nu(\text{Zn-Cl})$  is assigned as 320 (s) and 290 (s) cm<sup>-1</sup>,  $\nu(\text{Zn-Br})$  as 245 (s) and 220 (s) cm<sup>-1</sup>, and  $\nu(\text{Zn-I})$  as 208 (s) cm<sup>-1</sup>.  $\nu(\text{Zn-N})$  is tentatively assigned as 239 (s) cm<sup>-1</sup> for the chloride and iodide and 240 (sh) cm<sup>-1</sup> for the bromide.

The 4-MeT ligand itself has peaks at 495 (s), 335 (m), and 230 (s) cm<sup>-1</sup>. In the ZnX<sub>2</sub>(4-MeT)<sub>2</sub> complexes, the bands at *ca.* 495 (s), 364 (s), and 230 (s) cm<sup>-1</sup> are assigned to ligand vibrations, as they occur in both the zinc and cobalt derivatives, as well as in the uncomplexed ligand, assuming that the ligand 335-cm<sup>-1</sup> band moves up about 30 cm<sup>-1</sup> upon complexation.

With ZnCl<sub>2</sub>(2,4-DMeT)<sub>2</sub>, 400 (s) and 270 (w) cm<sup>-1</sup> are assigned to ligand vibrations, which occur at 374 (s) and 263 (m) cm<sup>-1</sup> in the free ligand.  $\nu(\text{Zn-Cl})$  is at 305 (s) cm<sup>-1</sup> and  $\nu(\text{Zn-N})$  is at 240 (s) cm<sup>-1</sup>.

The similarity in the spectra of the zinc thiazole complexes with those of known tetrahedral derivatives

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TABLE II  
 ABSORPTION FREQUENCIES (CM<sup>-1</sup>) OF COMPLEXES OF METAL HALIDES WITH SUBSTITUTED THIAZOLES (RANGE 500–200 CM<sup>-1</sup>)

Compounds	Substituted thiazole ring vibrations			$\nu(\text{M-X})$	$\nu(\text{M-L})$	Unassigned
4-MeT	495 s	335 m	230 m	...	...	...
CoCl <sub>2</sub> (4-MeT) <sub>2</sub>	495 s	375 s	230 m	345 s	245 s	...
				305 sh		
CoBr <sub>2</sub> (4-MeT) <sub>2</sub>	495 s	367 s	230 sh	270 s	240 s	...
CoI <sub>2</sub> (4-MeT) <sub>2</sub>	490 s	365 s	230 m	220 sh	240 s	...
				210 s		
ZnCl <sub>2</sub> (4-MeT) <sub>2</sub>	494 s	346 s	Ca. 230 sh	320 s	239 s	420 w
				290 s		
ZnBr <sub>2</sub> (4-MeT) <sub>2</sub>	495 s	365 s	235 s	245 sh	240 sh	210 m
ZnI <sub>2</sub> (4-MeT) <sub>2</sub>	495 s	363 s	230 sh	220 sh	239 s	...
				208 s		
CuCl <sub>2</sub> (4-MeT) <sub>2</sub>	487 s	362 m	237 sh	305 s	274 m	248 w
				259 m		
Ni(NO <sub>3</sub> ) <sub>2</sub> (4-MeT) <sub>3</sub>	495 s	373 s	230 m	...	255 m	288 s, 225 sh
<i>cis</i> -(4-MeT) <sub>2</sub> PtCl <sub>2</sub>	492 m	382 m	230 w	336 vs	264 w	
				326 s	252 w	284 sh
<i>cis</i> -(4-MeT) <sub>2</sub> PtBr <sub>2</sub>	490 m	376 m	232 s	219 vs	262 s	
				205 m	243 w	...
2,4-DMeT	...	374 s	263 m	...	...	...
CoCl <sub>2</sub> (2,4-DMeT) <sub>2</sub>	...	400 m	270 sh	330 s		
				310 sh	240	...
ZnCl <sub>2</sub> (2,4-DMeT) <sub>2</sub>	...	400 s	270 w	305 s	240 s	...
CuCl <sub>2</sub> (2,4-DMeT) <sub>2</sub>	...	395 w	265 sh	302 s, br	242 m	...
2-Et-4-MeT	...	371 w	342 w, 227 m, br	...	...	...
CoCl <sub>2</sub> (2-Et-4-MeT) <sub>2</sub>	...	370 w	345 sh, 220 w, br	305 s	241 m	...
NiBr <sub>2</sub> (2-Et-4-MeT) <sub>2</sub>	...	380 s	339 s, 230 m	312 s	258 m	415 w, 450 w
<i>cis</i> -(4-HT) <sub>2</sub> PtCl <sub>2</sub>	...	...	...	328 vs	250 m	
				321 vs	243 m	455 w

implies the same stereochemistry and the absence of zinc-sulfur bonding.

**Cobalt Complexes.**—The royal blue cobalt chloride and bromide and the sea green iodide derivatives of 4-MeT, 2,4-DMeT, and 2-Et-4MeT had the stoichiometry CoX<sub>2</sub>L<sub>2</sub> (Table I). The infrared spectra of the complexes and the ligand frequency shifts were similar to those of the zinc thiazole derivatives and tetrahedral forms of cobalt complexes of pyridine or substituted pyridines.<sup>12,13,15–17</sup> The  $\nu(\text{Co-X})$  and  $\nu(\text{Co-N})$  frequencies are shown in Table II.

The reflectance spectra of the solid thiazole complexes (Table III) and the absorption spectra of CoCl<sub>2</sub>(4MeT)<sub>2</sub> in nitromethane (also in acetone and dichloromethane) are typical of tetrahedral cobalt species.<sup>16</sup> While the disubstituted complexes immediately decomposed in solution, the similarity of the solution and solid-state spectra (Figure 1) of the 4-MeT complex indicates the same forms are present in both phases.

The spectra of tetrahedral and pseudotetrahedral complexes are in general quite similar. The bands from 25,000 to 17,000 cm<sup>-1</sup> are probably spin-forbidden transitions.<sup>16</sup> For CoCl<sub>2</sub>(4-MeT)<sub>2</sub>, the estimated center of gravity for  $\nu_2(^4A_2 \rightarrow ^4T_1(\text{F}))$  was 8076 cm<sup>-1</sup> and for  $\nu_3(^4A_2 \rightarrow ^4T_1(\text{P}))$  it was 16,450 cm<sup>-1</sup>. Using the method of Cotton and Goodgame,<sup>18</sup> the mean ligand field strength parameter  $\Delta_0$  was 4740 cm<sup>-1</sup> and the Racah interelectronic repulsion integral  $B'$

 TABLE III  
 ELECTRONIC SPECTRA<sup>a</sup>

Compound	Medium	Freq, cm <sup>-1</sup>
4-MeT	Liquid	37,100
CoCl <sub>2</sub> (4-MeT) <sub>2</sub>	Solid	37,100, 20,800 sh, 18,900 sh, 17,200 br, 15,700 br, 9000 br
	Nitromethane	17,000 (493), 15,600 (682), 15,200 (656), 9000 br
CoCl <sub>2</sub> (2,4-DMeT) <sub>2</sub>	Solid	37,100, 21,300 sh, 19,650 sh, 17,250 br, 15,650 br, 9000 br
NiBr <sub>2</sub> (2-Et-4-MeT) <sub>2</sub>	Solid	37,100, 27,000, 16,400 br
Ni(NO <sub>3</sub> ) <sub>2</sub> (4-MeT) <sub>3</sub>	Solid	37,100, 25,600, 15,600, 8750
CuCl <sub>2</sub> (4-MeT) <sub>2</sub>	Solid	37,100, 25,600, 13,300 br
CuCl <sub>2</sub> (2,4-DMeT) <sub>2</sub>	Solid	37,100, 25,600, 19,250, 17,250
NiBr <sub>2</sub> (4-MeT) <sub>2</sub>	Solid	26,300, 18,900, 15,400, 9500

<sup>a</sup> Abbreviations: sh, shoulder; br, broad.

was 687 cm<sup>-1</sup>. These values are slightly larger than those obtained in cobalt-pyridine analogs.

The magnetic moments of the complexes, obtained either from room-temperature data using the observed diamagnetic susceptibilities of substituted thiazoles<sup>19</sup> or from temperature studies from 300 to 77°K, are listed in Table IV. Figure 2 shows typical susceptibility data. The moments of the cobalt derivatives are in the range usually found for tetrahedral species (4.4–4.8 BM).<sup>20</sup> Thus, all evidence points to tetra-

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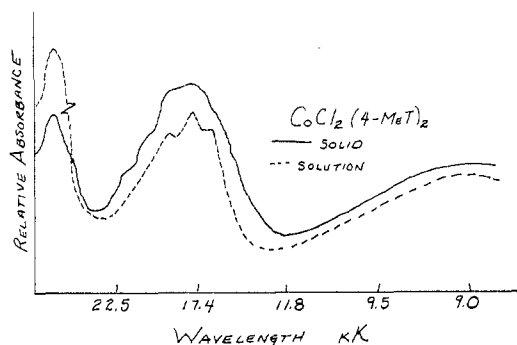


Figure 1.—Electronic spectra of  $\text{CoCl}_2(4\text{-MeT})_2$  in the solid state and in nitromethane solution.

TABLE IV  
MAGNETIC MOMENTS

	$\mu$ , BM	$\theta$ , deg
$\text{CuCl}_2(4\text{-MeT})_2^a$	1.86	...
$\text{CuCl}_2(2,4\text{-MeT})_2$	1.93	0
$\text{CoCl}_2(4\text{-MeT})_2$	4.67	0
$\text{CoBr}_2(4\text{-MeT})_2$	4.48	0
$\text{CoI}_2(4\text{-MeT})_2^a$	4.61	...
$\text{CoCl}_2(2\text{-Et-4-MeT})_2$	4.69	0
$\text{CoCl}_2(2,4\text{-DMeT})_2$	4.78	0
$\text{NiBr}_2(2,4\text{-DMeT})_2^a$	Diam	...
$\text{NiBr}_2(2\text{-Et-4-MeT})_2^a$	Diam	...
$\text{NiBr}_2(4\text{-MeT})_2$	3.22	45
$\text{Ni}(\text{NO}_3)_2(4\text{-MeT})_3$	3.36	0

<sup>a</sup> Room-temperature measurement, all others from 77 to 300°K.

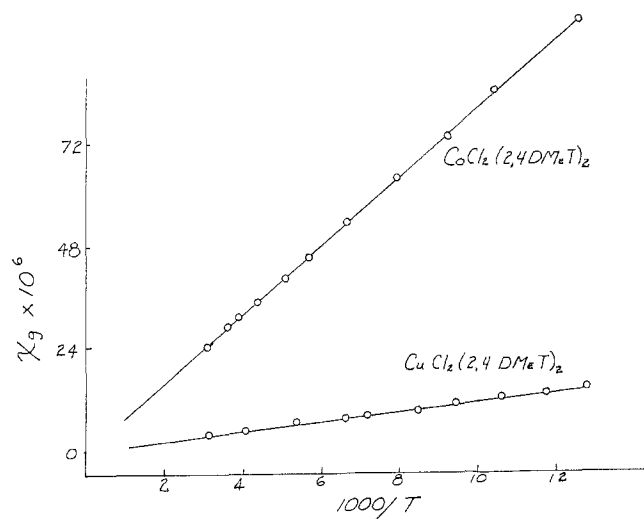


Figure 2.—Magnetic susceptibility data for  $\text{CoCl}_2(2,4\text{-DMeT})_2$  and  $\text{CuCl}_2(2,4\text{-DMeT})_2$ .

hedral, nitrogen-bonded, high-spin cobalt(II) species.

**Copper Complexes.**—While a number of copper-containing thiazole complexes were obtained, only the green  $\text{CuCl}_2(4\text{-MeT})_2$  and purple 2,4-DMeT derivatives could be isolated having no water molecules present. The reflectance spectrum of  $\text{CuCl}_2(4\text{-MeT})_2$  is characteristic of six-coordinate Cu(II)<sup>21,22</sup> and is similar to that of  $\text{CuCl}_2(\text{py})_2$ , which has a polymeric, chloride-bridged structure.<sup>23</sup> The magnetic moment of the derivative, 1.83 BM, is usual for octahedral

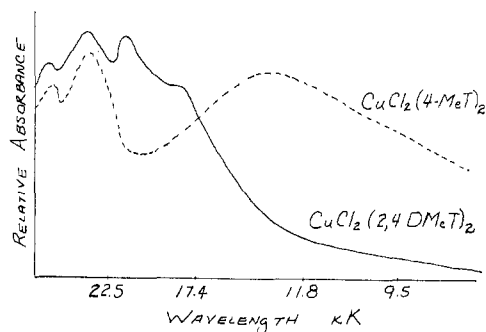


Figure 3.—Reflectance spectra of  $\text{CuCl}_2(4\text{-MeT})_2$  and  $\text{CuCl}_2(2,4\text{-DMeT})_2$ .

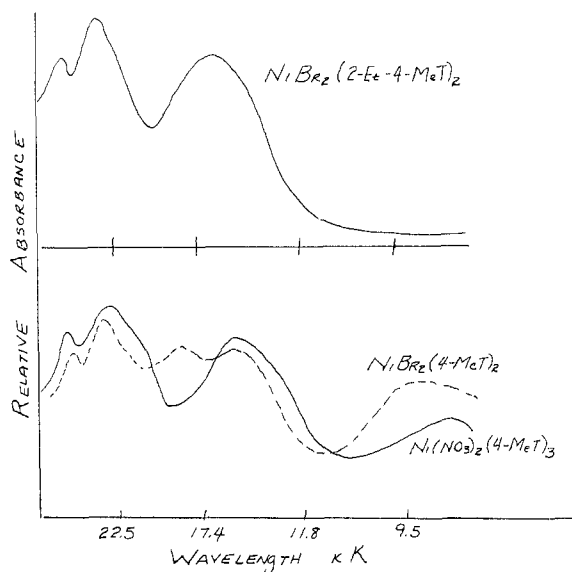


Figure 4.—Reflectance spectra of the nickel thiazole complexes.

Cu(II). For  $\text{CuCl}_2(4\text{-Mepy})_2$ ,<sup>23,24</sup> the terminal  $\nu(\text{Cu-Cl})$  is 296 (s)  $\text{cm}^{-1}$ ,  $\nu(\text{Cu-N})$  is 285 (m)  $\text{cm}^{-1}$ , and the bridge  $\nu(\text{Cu-Cl})$  is assigned as 259 (s)  $\text{cm}^{-1}$ . For our  $\text{CuCl}_2(4\text{-MeT})_2$ , we find bands at 305 (s), 274 (m), and 259 (m)  $\text{cm}^{-1}$  that closely correspond to those of substituted pyridine complexes.

In contrast,  $\text{CuCl}_2(2\text{-4-DMeT})_2$  gave no evidence of a  $\nu(\text{Cu-Cl})$  bridge frequency. The 302 (s, br)  $\text{cm}^{-1}$  band is assigned to the terminal  $\nu(\text{Cu-Cl})$ , and  $\nu(\text{Cu-N})$  is at 242 (m)  $\text{cm}^{-1}$ . The reflectance spectra (Figure 3) resemble neither six-coordinate nor tetrahedral copper species and are similar to that reported for square-planar Cu(II)<sup>25,26</sup> species. The observed moment of 1.93 BM is consistent with such a structure.<sup>25</sup>

**Nickel Complexes.**—The nickel thiazoles show the most diverse behavior as the thiazole substituent and anion was varied. All of the complexes had the form  $\text{NiX}_2\text{L}_2$ , with the exception of the nitrate, which was  $\text{Ni}(\text{NO}_3)_2(4\text{-MeT})_3$ .

From the reflectance spectra, the nitrate complex appears to be octahedral (Figure 4). The band at 25,600  $\text{cm}^{-1}$  is  $\nu_3(^3A_{2g} \rightarrow ^3T_{1g}(\text{P}))$ , that at 15,600  $\text{cm}^{-1}$  is  $\nu_2(^3A_{2g} \rightarrow ^3T_{1g}(\text{F}))$ , and  $\nu_1(^3A_{2g} \rightarrow ^3T_{2g}(\text{F}))$  is at 8750

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TABLE V  
 STEREOCHEMISTRIES OF METAL THIAZOLES

	Thiazole <sup>5</sup>	Benzothiazole <sup>6</sup>	4-Methylthiazole	2,4-Dialkylthiazoles	2-Methylbenzothiazole <sup>7</sup>
ZnX <sub>2</sub> L <sub>2</sub>	...	Tetrahedral	Tetrahedral	Tetrahedral	...
CuX <sub>2</sub> L <sub>2</sub>	Polymeric octahedral	Polymeric octahedral	Polymeric octahedral	Planar	...
CoX <sub>2</sub> L <sub>2</sub>	Polymeric octahedral	Tetrahedral	Tetrahedral	Tetrahedral	...
NiX <sub>2</sub> L <sub>2</sub>	...	Polymeric octahedral	Polymeric octahedral	Planar	Planar
PtX <sub>2</sub> L <sub>2</sub>	Planar	...	Planar	...	...

cm<sup>-1</sup>. Assuming that  $\nu_2$  is approximately  $18Dq$ , the calculated  $Dq$  of 867 cm<sup>-1</sup> is in good agreement with that obtained from  $\nu_1$  (875 cm<sup>-1</sup>). The magnetic moment of 3.36 BM with a zero Weiss constant is in the range of both octahedral<sup>20</sup> (2.93–3.3 BM) and halogen-bridged tetragonal<sup>27</sup> (3.3–4.0 BM) nickel species. The infrared spectra in the nitrate region are complicated by thiazole bands, and although there was some evidence for nitrate coordination, it was not definitive.

The 2,4-DMeT and 2-Et-4-MeT complexes of nickel were of the form NiBr<sub>2</sub>L<sub>2</sub>. Both complexes were hygroscopic, with the dimethyl derivative extremely so. This is reflected in their C, H, and N values. The metal and halogen analyses done immediately after preparation, however, define their composition. While both compounds were initially diamagnetic, they decomposed and became paramagnetic upon standing. The diamagnetism might indicate an essentially square-planar environment about Ni(II), which is in agreement with the reflectance spectra of the 2-Et-4-MeT complex (Figure 4). The usual bands for octahedral<sup>21,22</sup> or tetrahedral<sup>28</sup> nickel were absent, while the characteristic square-planar band near 16,000 cm<sup>-1</sup> was present.<sup>29</sup>

NiBr<sub>2</sub>(4-MeT)<sub>2</sub> was also slightly hygroscopic. The initial moment of 3.22 BM is in the octahedral Ni(II) range.<sup>20,27</sup> Its reflectance spectrum also indicates an octahedral geometry, which could be achieved by polymeric bromide bridging, with *trans* N-bonded thiazole groups, as in the corresponding benzothiazole complex.<sup>6</sup>

No nickel chloride solids of reasonable analysis could be obtained. A variety of paramagnetic yellow solids containing either one or two thiazoles and varying amounts of water and methanol could be isolated. All attempts to desolvate these solids by heating were unsuccessful.

**Platinum Complexes.**—The similarity in positions and splittings of the infrared peaks of the three platinum(II) thiazoles (Table II) as compared to the chloro and bromo derivatives of the analogous pyridine complexes<sup>12,30,31</sup> leads to an assignment of *cis*-planar geometry and N coordination for the thiazoles. Com-

pared to pyridine, the extreme insolubility of the *cis*-platinum thiazoles precluded preparation of the *trans* complexes by the addition of excess ligand to the *cis* species, in aqueous solution.

### Discussion

Thiazole is formally derived from imidazole by replacement of NH by S, which makes imidazole ( $pK = 5.3$ ) more basic than thiazole ( $pK = 2.9$ ). As an extension of previous observations,<sup>5</sup> thiazole complexes resemble pyridine rather than imidazole or amino derivatives. Thus, the maximum ligated copper complexes with imidazole, benzimidazole, 2-methylimidazole, and ammonia are CuCl<sub>2</sub>L<sub>4</sub>, whereas pyridine, thiazole, 4- and 2,4-dialkylated thiazoles, and benzothiazole form predominantly CuCl<sub>2</sub>L<sub>2</sub>. This has been explained in terms of the  $\sigma$ -donor,  $\pi$ -acceptor properties of the ligand in maintaining an effective electroneutrality on the central ion. Thiazole being a weaker  $\sigma$  donor and possibly better  $\pi$  acceptor than imidazole will favor structures in which four halides (MX<sub>2</sub>L<sub>2</sub>) rather than four heterocyclic bases (MX<sub>2</sub>L<sub>4</sub>) are coordinated.

Table V shows the stereochemistries assigned to various substituted thiazoles. Pt and Zn complexes appear insensitive to ring substitution. The thiazole and benzothiazole complexes are more nearly similar to one another than to the dialkylated species. This is presumably a consequence of the steric effect to two groups surrounding the nitrogen center. Thus  $\alpha$ -picolines and  $\alpha$ -lutidines,<sup>32</sup> along with 4-MeT and 2,4-DMeT ligands, form mainly NiX<sub>2</sub>L<sub>2</sub> whereas the  $\beta$ -pyridines, thiazoles, and benzothiazole tend toward NiX<sub>2</sub>L<sub>4</sub>.

It has been predicted that the tendency to stabilize tetrahedral rather than square-planar geometry based on crystal field stabilization energies falls off in the order<sup>25</sup> Zn(II) > Co(II) > Cu(II) > Ni(II). This order is observed with the 2,4-dialkyl substituents, but not with the 4-alkyl or benzothiazole complexes. The probable explanation is that the alkyl groups surrounding the nitrogen are capable of repelling additional halide ions which would give rise to higher coordination numbers and thus overbalance the small magnitude and trend in crystal field effects.

A nickel(II) bromide-benzothiazole complex has been postulated<sup>5</sup> to involve both its nitrogen and sulfur

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in intermolecular bonding to nickel atoms in different planes, on the basis of infrared studies. However, the infrared frequencies that were assigned to  $\nu(\text{Ni-S})$  are in the range which have been previously assigned to  $\nu(\text{Ni-N})$  in benzoxazole.<sup>14</sup> While ambidentate behavior might have been expected with a class b metal ion (Pt(II)), our data show that both class a and b metal ions only N bond to thiazole. This is presumably be-

cause the important resonance structures for thiazoles place a formal positive charge on the sulfur atom, which would retard  $\pi$  donation from the ligand.

Preliminary work indicates that the N-alkylated derivatives of substituted thiazoles, which could use metal-sulfur bonding, all form complexes of the form  $\text{MX}_2\text{L}_2$ . They appear, however, to involve  $(\text{MX}_4^{2-})\text{-}(\text{L}^+)_2$  rather than metal-sulfur coordination.

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## Complexes of 1,8-Naphthyridines. III. Transition Metal-Perchlorate Complexes of 2,7-Dimethyl-1,8-naphthyridine<sup>1</sup>

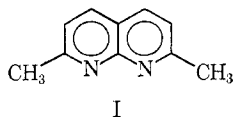
BY DAVID G. HENDRICKER AND RICHARD L. BODNER

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A number of transition metal-perchlorate complexes of the type  $\text{ML}_2(\text{ClO}_4)_2$  ( $\text{M} = \text{Fe}, \text{Cu}, \text{Ni}, \text{Co}, \text{Zn}, \text{and Cd}$ ),  $\text{HgI}_2(\text{ClO}_4)_2$ , and  $\text{AgI}_2\text{ClO}_4$ , where  $\text{I} = 2,7\text{-dimethyl-1,8-naphthyridine}$ , have been synthesized. Elemental analyses, molar conductances, magnetic moments, and infrared and electronic spectral data have been applied to the characterization of the compounds. The resulting ligand field parameters place the present ligand nearer pyridine than 1,10-phenanthroline and 2,2-bipyridine in the spectrochemical series. Since the latter two are very similar in basicity and synergic bonding to  $\text{I}$ , the resulting weak ligand field property is attributed to strain produced in the formation of a four-member chelate ring system.

### Introduction

Complexes of transition metal salts with the nitrogen heterocycles 1,10-phenanthroline (phen), 2,2-bipyridine (bipy), and their numerous derivatives which form a five-member chelate ring system have long been known.<sup>2</sup> The strong crystal field properties of these ligands have been ascribed in part to their ability to participate in  $\pi$  bonding with the metal atom.<sup>3,4</sup> Previously Hendricker and Reed have reported stable complexes of the ligand 2,7-dimethyl-1,8-naphthyridine,  $\text{I}$ ,



which forms a four-member chelate ring system.<sup>5</sup> From the CO stretching frequencies exhibited by group VIb metal carbonyl complexes of the type  $\text{M}(\text{CO})_4\text{I}$  they inferred that the  $\pi$  bonding of  $\text{I}$  is similar to that of phen. The ability of  $\text{I}$  to form stable complexes without  $\pi$  stabilization has also been demonstrated by adduct formation with dialkyltin dihalides.<sup>6</sup> The

$\text{pK}_a$ 's of  $\text{I}$ , phen, and bipy are similar;<sup>5</sup> thus any variation in coordinating ability of the three ligands may not be attributed to differences in basicity. A comparison of the steric requirements of  $\text{I}$  with those of 2,9-dimethyl-1,10-phenanthroline is of interest in light of the documented inability of metal centers to accommodate three molecules of the latter.<sup>7,8</sup> Although reports of metal complexes involving various 1,5-, 1,6-, and 1,7-naphthyridines have appeared in the literature,<sup>9-11</sup> none of these ligands participates in chelation utilizing both heterocyclic nitrogens with the same metal center. Hence, as an integral part of our intensive studies involving a comparison of four- and five-member nitrogen heterocyclic chelate systems, we wish to report the preparation and characterization of some transition metal-perchlorate complexes of  $\text{I}$ .

### Experimental Section

**Materials.**—Metal perchlorates were purchased from G. F. Smith Chemical Co., Columbus, Ohio, and used without further purification. Practical grade 2,2-dimethoxypropane (dmp) and Spectral grade acetonitrile and nitromethane were obtained from Eastman Chemicals. Purity of the ligand 2,7-dimethyl-1,8-naphthyridine, prepared by the method of Paudler and Kress,<sup>12</sup> was verified by pmr.

**Instrumentation.**—The infrared spectra ( $4000\text{--}200\text{ cm}^{-1}$ ) were

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