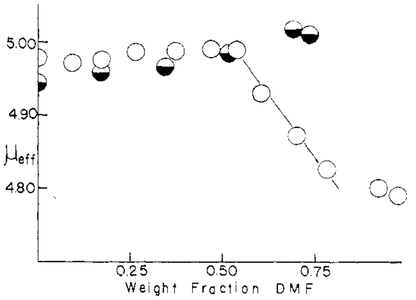

Figure 3.—Magnetic moment of Co(II) in water–DMF mixtures at 25°: ○, 1 *M* CoCl$_2$; ◒, 1 *M* Co(NO$_3$)$_2$.

weight fraction DMF of about 0.5 and then decreases approximately linearly to 0.80 weight fraction, becoming constant again at about 4.80 BM. Bull[35] has reported a value of 4.71 BM[26] for the solid CoCl$_2$DMF$_2$, suggesting that in the present study, even in the DMF-rich mixtures, some of the Co(II) is still in an octahedral field. In contrast to the chloride, the nitrate salt shows a slight increase in μ_{eff} over this solvent composition range, the value being consistent with octahedral coordination.

Dunn,[36] in a spectrophotometric study of CoCl$_4^{2-}$ and CoCl$_2$ in DMF, has suggested that there is strong solute–solvent interaction in these systems leading to both four- and six-coordinate complexes: CoCl$_2$DMF$_2$, CoCl$_3$DMF$^-$, Co(DMF)$_6^{2+}$, and Co(DMF)$_5$Cl$^+$. Popov[37] has found a pronounced dependence of the Co(II) spectra in DMF on the anion, finding the chloride and nitrate to have different spectra, consistent with the present study.

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Metal Complexes of 4-Methylthiazole

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A recent publication[1] has reported the preparation of a number of complexes of alkyl-substituted thiazoles. We are interested[2] in the preparation of model compounds for thiazole– and thiamine–metal ion interactions in biological processes and have examined the coordination behavior of 4-methylthiazole (4-MeT) with cobalt(II), nickel(II), copper(II), zinc(II), and palladium(II) salts. Our results with cobalt(II), zinc (II), and copper(II) halides agree with those of Hambright, *et al.*, but we have prepared several additional complexes with these metals and also with nickel(II). Certain of our conclusions differ from those previously reported.

Results and Discussion

Table I lists the new complexes we have prepared, together with our results for certain of those already reported.[1] Diffuse reflectance electronic spectra and room-temperature magnetic moments are also given. In certain cases we were unable to obtain magnetic moment data. Far-infrared spectra (666–222 cm^{-1}) are listed in Table II, together with ν_{M-N} and ν_{M-X} assignments where possible.

Nickel Complexes.—We had already prepared a blue complex, Ni(4-MeT)$_2$Br$_2$, to which we had assigned a tetrahedral stereochemistry. Hambright, *et al.*, reported the formation of a light blue complex of this stoichiometry and suggested it has an octahedral structure. We have repeated their preparation and have obtained a blue complex identical with the one we had obtained earlier. We have repeated the preparation a number of times under widely varying conditions and have always obtained the same product, with the blue color varying somewhat in intensity from preparation to preparation. The electronic spectrum is slightly different from that quoted earlier.[1] We assign the spectrum in T_d symmetry, bands at 9.65 and 17.3 kK corresponding to transitions ${}^3T_1(F) \rightarrow {}^3A_2$ and ${}^3T_1(F) \rightarrow {}^3T_1(P)$, respectively. The tetrahedral stereochemistry is supported by the fact that blue Ni(4-MeT)$_2$Br$_2$ and tetrahedral Co(4-MeT)$_2$Br$_2$ are isomorphous. In acetone solution, in the presence of a slight excess of ligand, this complex retains its tetrahedral structure. Using the method of Ballhausen[3] we calculate values of $Dq = 450$ cm^{-1} and $B = 772$. We have also prepared the tetrahedral complex [(C$_2$H$_5$)$_4$N$^+$][Ni(4-MeT)Br$_3^-$] which has a spectrum with band positions intermediate between those of Ni(4-MeT)$_2$Br$_2$ and NiBr$_4^{2-}$.

We have also obtained a yellow form of the complex Ni(4-MeT)$_2$Br$_2$ from ethanol solution. This reverts to the blue isomer at room temperature and rapidly so on heating. We assume that the yellow form corresponds to an octahedral halogen-bridged complex with axial 4-methylthiazole groups. The magnetic moment of 2.98 BM is consistent with such a structure.

The previously reported octahedral complex Ni(4-MeT)$_3$(NO$_3$)$_2$ appears to be stable in solution in the presence of excess ligand or excess metal nitrate, there being no evidence for the formation of the 1:4 or 1:2 species. The infrared spectrum clearly shows that the nitrate group is coordinated; thus the ν_3 band is split into broad bands at 1445 and 1288 cm^{-1}. The complex probably has one monodentate and one bidentate nitrate group as suggested[4] for Ni(py)$_3$(NO$_3$)$_2$.

We have also prepared Ni(4-MeT)$_2$I$_2$ and Ni(4-MeT)Br$_2$. The former complex is isomorphous with the corresponding cobalt analog, of tetrahedral stereochem-

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TABLE I
DIFFUSE REFLECTANCE ELECTRONIC SPECTRA AND MAGNETIC MOMENTS

Complex	Color	μ_{eff}, BM	Electronic spectra,[a] kK
$Ni(4\text{-}MeT)_2Br_2$	Blue	3.22	17.3 s, 15.8 sh, 11.35 sh, 9.65 m, 7.25 sh, 6.1 m
$Ni(4\text{-}MeT)_2Br_2$[b]	Yellow	2.95	22.1 s, 18.9 s, 16.6 w, 12.71 s, 9.8 sh, 5.0 m
$[(C_2H_5)_4N^+][Ni(4\text{-}MeT)Br_3^-]$[b]	Blue		26.2 m, 18.8 sh, 15.2 s, br, 8.3 s, 5.9 m
$Ni(4\text{-}MeT)_2I_2$[b]	Green		24.1 br, 20.3 m, br, 15.8 m, 10.4 sh, 9.33 m, 6.3 m
$Ni(4\text{-}MeT)_3(NO_3)_2$	Green	3.36	25.5 s, 15.6 s, 9.1 m
$Ni(4\text{-}MeT)Br_2$[b]	Pink		20.3 s, 18.3 sh, 11.0 s, br, 7.4 w, 5.6 w
$Cu(4\text{-}MeT)_2Cl_2$	Green	1.86	13.1 s, br, 11.5 sh
$Cu(4\text{-}MeT)_2Br_2$[b]	Green	1.85	23.1 s, br, 14.6 s, br
$Cu(4\text{-}MeT)_2(NO_3)_2$[b]	Blue	1.88	15.1 s, 13.1 s
$Cu(4\text{-}MeT)Cl_2$[b]	Yellow-brown	1.86	~20.6 sh, 12.6 sh, 11.0 s
$Co(4\text{-}MeT)_2(NO_3)_2$[b]	Purple	4.59	18.6 s, br, 8.3 m, br
$Co(4\text{-}MeT)_2(NCS)_2$[b]	Blue		17.4 sh, 16.4 s, 9.0 m, 7.8 m, 6.9 m
$Co(4\text{-}MeT)_2Cl_2$	Blue	4.75	16.8 s, 16.0 sh, 15.75 s, 9.0 m, 7.0 m, 5.9 m
$Co(4\text{-}MeT)_2Br_2$	Blue	4.68	16.6 s, 15.6 sh, 15.2 s, 8.6 m, 6.75 m, 5.75 m
$Co(4\text{-}MeT)_2I_2$	Green	4.46	16.0 s, 14.9 s, 14.3 s, 8.2 m, 6.5 m, 5.65 m
$Pd(4\text{-}MeT)_2Cl_2$[b]	Yellow	...	26.3 sh, 24.6 s, br

[a] Abbreviations: s, strong; m, medium; br, broad; sh, shoulder. [b] New compound.

TABLE II
INFRARED SPECTRA (666–222 cm^{-1})

Complex	Ligand vibrations	ν_{M-X}	ν_{M-L}	Other bands
4-MeT	483 s, 337 s			
$Ni(4\text{-}MeT)_2Br_2$ (blue)	485 m, 366 m	266 m	245 s	
$Ni(4\text{-}MeT)_3(NO_3)_2$	488 m, 370 m	290 m	230 m	255 m
$Cu(4\text{-}MeT)_2Cl_2$	486 m, 364 m	311 s, 278 m	260 s	
$Cu(4\text{-}MeT)_2Br_2$	483 m, 361 s	265 s	254 sh	
$Cu(4\text{-}MeT)_2(NO_3)_2$	486 m, 373 m	307 sh, 296 s	245 w, 252 w	
$Cu(4\text{-}MeT)Cl_2$	487 m, 363 m	?	?	290 m, 280 m 253 m, 248 m
$Co(4\text{-}MeT)_2(NO_3)_2$	489 s, 367 m	306 m, 282 m	250 m	
$Co(4\text{-}MeT)_2(NCS)_2$	485 m, 365 s	330 m, 282 m	244 m	δ_{NCS} 476
$[Zn(4\text{-}MeT)_4](ClO_4)_2$	488 s, 365 s	...	238 m	
$Pd(4\text{-}MeT)_2Cl_2$	488 m, 368 m	353 s	265 m	

istry, and its electronic spectrum may be assigned in T_d symmetry, ν_1 and ν_3 appearing at 9.33 and 15.8 kK, respectively. The latter complex is prepared by heating the 1:2 species. It is pink and appears to have a pseudooctahedral stereochemistry. The electronic spectrum is similar to that of $Ni(py)Br_2$ and it may well have a similar structure,[5] although in this case 4-methylthiazole does have a second potential donor atom and the possibility of halogen and ligand bridging should be considered. Solutions of the complex in acetone are blue, the electronic spectrum confirms a tetrahedral structure, and addition of excess ligand results in the formation of the spectrum characteristic of blue $Ni(4\text{-}MeT)_2Br_2$.

Copper(II) Complexes.—We have prepared three new copper(II) complexes, $Cu(4\text{-}MeT)_2X_2$ ($X = Br$, NO_3) and $Cu(4\text{-}MeT)Cl_2$. It has been suggested[1] that the complex $Cu(4\text{-}MeT)_2Cl_2$ is a six-coordinate polymeric chloride-bridged structure, and the far-infrared spectrum is assigned in terms of copper–chlorine (short-bond) and copper–chlorine (long-bond) stretching modes at 305 and 259 cm^{-1}, respectively, with ν_{Cu-N} at 274 cm^{-1}. We suggest that the assignment of the copper–chlorine (long-bond) stretching frequency to 259 cm^{-1} is uncertain and that this should appear at lower frequency.[6] The corresponding bromo complex also appears to have a similar six-coordinate structure, with an electronic spectrum similar to that of $Cu(4\text{-}MeT)_2Cl_2$. The far-infrared spectrum of this complex shows, in addition to ligand bands, bands at 265 (s) and 254 cm^{-1} (sh). We assign the latter band to metal–nitrogen and the former band to metal–bromine stretch. The ratio $\nu_{Cu-Br}/\nu_{Cu-Cl} = 0.87$, which is similar to that observed for other analogous chloro and bromo species of this type.

The nitrato complex is also a distorted octahedral species with bidentate nitrato groups. We assign metal–oxygen bands at 307 and 296 cm^{-1}. We suggest that the 1:1 complex with $CuCl_2$ is probably a four-coordinate dimeric species with bridging halogen and terminal halogen and 4-methylthiazole. We are unable to assign the far-infrared spectrum of this complex.

Cobalt(II), Zinc(II), and Palladium(II) Complexes.—The following new cobalt complexes have been prepared: purple $Co(4\text{-}MeT)_2(NO_3)$ and blue $Co(4\text{-}MeT)_2(NCS)_2$. The former complex has a distorted octahedral structure, with bidentate nitrato groups, of a now familiar type.[7,8] Coordination of the nitrate group is confirmed by substantial splitting of the ν_3 nitrate mode into bands at 1500 and 1270 cm^{-1}. The

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TABLE III

ANALYTICAL RESULTS

Complex	% calcd C	H	N	M	% found C	H	N	M
Ni(4-MeT)$_2$Br$_2$ (blue)	23.0	2.40	6.72	14.1	22.7	2.40	6.52	14.1
Ni(4-MeT)$_2$Br$_2$ (yellow)				14.1				14.0
Ni(4-MeT)$_2$I$_2$	18.8	1.96	5.48	11.5	18.5	2.06	5.49	11.4
Ni(4-MeT)$_3$(NO$_3$)$_2$	30.0	3.15	14.6	12.2	29.9	3.16	14.5	12.1
Ni(4-MeT)Br$_2$				18.5				18.6
Cu(4-MeT)$_2$Cl$_2$	28.9	3.01	8.42	19.1	28.8	3.13	8.29	19.2
Cu(4-MeT)$_2$Br$_2$	22.8	2.37	6.64	15.1	22.6	2.40	6.62	14.8
Cu(4-MeT)$_2$(NO$_3$)$_2$	24.9	2.59	14.5	16.5	24.6	2.60	14.5	16.5
Cu(4-Me)Cl$_2$	20.5	2.17	5.99	27.2	20.7	2.14	6.14	27.0
Co(4-MeT)$_2$(NCS)$_2$	32.2	2.68	14.7	15.8	31.9	2.63	14.7	15.6
Co(4-MeT)$_2$Cl$_2$	29.3	3.05	8.54	18.0	29.4	3.12	8.69	18.0
Co(4-MeT)$_2$Br$_2$	23.0	2.40	6.72	14.1	22.8	2.41	6.66	14.0
Co(4-MeT)$_2$I$_2$	18.8	1.96	5.48	11.5	18.6	2.02	5.42	11.6
Pd(4-MeT)$_2$Cl$_2$	25.6	2.66	7.45		25.5	2.41	7.24	
Zn(4-MeT)$_4$(ClO$_4$)$_2$	29.0	3.03	8.47	9.90	29.1	3.01	8.39	9.81

complex Co(4-MeT)$_2$(NCS)$_2$ has N-bonded thiocyanate ($\nu_{C\equiv N}$ at 2027, 2037 cm^{-1}, δ_{NCS} at 476 cm^{-1}) and has a tetrahedral stereochemistry as confirmed by the intensities and band positions in the electronic spectrum. We have listed the electronic spectra of a number of other cobalt(II) complexes as we appear to have achieved better resolution of the near-infrared band. The isothiocyanate complex has only slight splitting of this band, reflecting the closer approximation of this species to tetrahedral symmetry. We have also prepared tetrahedral [Zn(4-MeT)$_4$](ClO$_4$)$_2$, which is a 1:2 electrolyte in nitromethane (Λ = 187; 10^{-3} *M* solution), while the infrared spectrum shows no indication of perchlorate coordination. In diamagnetic square-planar Pd(4-MeT)$_2$Cl$_2$ the ligand still appears to be N bonded rather than S bonded and we assign bands in the far-infrared spectrum to ν_{Pd-N} and ν_{Pd-Cl}. The far-infrared spectrum indicates a trans structure, there being only one ν_{Pd-Cl} band.

Experimental Section

4-Methylthiazole was supplied by Koch-Light Laboratories. All other materials were AnalaR or the best grade available. Analytical results for the complexes are presented in Table III. The complexes were prepared as follows.

Cu(4-MeT)$_2$Cl$_2$.—A 0.99-g sample of ligand (0.01 mol) was added to 0.42 g of CuCl$_2$·2H$_2$O (0.0025 mol) dissolved in the minimum volume of ethanol. Precipitation of the complex occurred. The product was filtered off and washed with ethanol and ether.

The following complexes were also made by this method; in all cases 0.0025 mol of metal salt and 0.01 mol of ligand were used: **Cu(4-MeT)$_2$Br$_2$** (using anhydrous CuBr$_2$), **Cu(4-MeT)$_2$(NO$_3$)$_2$** (from Cu(NO$_3$)$_2$·3H$_2$O), yellow **Ni(4-MeT)$_2$Br$_2$** (from NiBr$_2$·3H$_2$O), and **Co(4-Me)T$_2$Cl$_2$** and **Co(4-MeT)$_2$Br$_2$** (from CoCl$_2$·6H$_2$O and anhydrous CoBr$_2$, respectively). **Blue Ni(4-MeT)$_2$Br$_2$** was prepared using methanol as the solvent.

The best preparative method for **Ni(4-MeT)$_3$(NO$_3$)$_2$** appears to be that quoted by Hambright, *et al.*[1]

Ni(4-MeT)$_2$I$_2$.—This was prepared by dissolving 0.005 mol of NiI$_2$ in the minimum volume of 50:50 1-butanol–ethanol, slowly adding 0.02 mol of ligand, and refluxing for 1 hr. On standing, crystals formed and were filtered off and washed with ethanol and petroleum ether (bp 30–40°). These were very hygroscopic.

Co(4-MeT)$_2$(NCS)$_2$.—A 0.005-mol sample of Co(NCS)$_2$ was dissolved in the minimum volume of acetone and 0.03 mol of ligand was added. The solution was boiled and evaporated to a small bulk, cooled, and filtered. The product was washed with acetone and light petroleum ether. **Co(4-MeT)$_2$I$_2$** was obtained by adding 0.02 mol of ligand to 0.005 mol of CoI$_2$·2H$_2$O in acetone and washing the precipitated product with ethanol and petroleum ether. The complexes **Co(4-MeT)$_2$(NO$_3$)$_2$** and **[Zn(4-MeT)$_4$](ClO$_4$)$_2$** were both prepared by refluxing ethanol–2′,2″-dimethoxypropane solutions of the metal salt hexahydrates (0.005 mol) with excess ligand (0.03 mol) for 30 min and then allowing them to stand. The products were filtered off and washed with ethanol and ether.

Both **Cu(4-MeT)Cl$_2$** and **Ni(4-MeT)Br$_2$** were obtained by heating the corresponding 1:2 complex at 140° *in vacuo* to constant weight. Correct weight losses were observed. The complex **Pd(4-MeT)$_2$Cl$_2$** was prepared by dissolving 0.005 mol of bis(benzonitrile)palladium(II) chloride in the minimum volume of benzene, adding 0.01 mol of 4-methylthiazole. The precipitated complex was washed with benzene.

Instrumentation was as described in earlier papers.[2,8] The diamagnetic correction for 4-methylthiazole was obtained from the literature.[9]

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1:1 Adducts of Tetracyanoethylene with Methylplatinum(II) Complexes

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The unique properties of tetracyanoethylene, TCNE, due to the highly electronegative cyano-group substituents of the olefin have prompted much recent interest in its complexes with transition metals.[1]

We have found that TCNE forms stable 1:1 adducts with *trans*-PtXCH$_3$L$_2$ (L = tertiary phosphine or arsine, X = halogen). The complexes isolated are given in Table I. They melt sharply with blackening and effervescence in the range 150–190° and are generally insoluble in common organic solvents. The structure (I)

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