signed primarily to the ν_{Zn-Cl} vibration. This vibration shifts to 214 cm^{-1} (ν_{Zn-Br}) in the bromide and 187 cm^{-1} in the iodide (ν_{Zn-I}). None of these vibrations is pure, since ligand vibrations are probably also involved. A medium-intensity band which is present in all three complexes occurs at 243–245 cm^{-1} and is assigned to the ν_{Zn-N} vibration, while a medium band at 164–167 cm^{-1} present in all of the complexes is assigned to the δ_{Zn-N} vibration. Assignments for the δ_{Zn-X} vibrations involve the same complications discussed for the bipyridyl complexes.

Table IV records all of the assigned metal to ligand vibrations for the three series of complexes. In the pyridine and bipyridyl complexes the frequency of the ν_{Zn-X} vibrations is very similar. This is understandable since both series of complexes have a tetrahedral structure[14] and a coordination number of four. These complexes differ only in the fact that the pyridine is monodentate while the bipyridyl is bidentate. Thus, differences ought to be observed in the metal–nitrogen vibrations, and this is confirmed. The added stabilization through chelation is reflected by the shift of the ν_{Zn-N} vibration to higher frequencies for the bipyridyl complexes. Chelation also causes the N–Zn–N bend in the bipyridyls to be at a higher frequency than for the monodentate complexes. For the terpyridyl complexes, several changes occur. The structure changes to a trigonal bipyramid,[15] the coordination number becomes five, and the ligand is now terdentate. This is reflected by a shift to lower frequencies of the ν_{Zn-X} vibrations as expected for an increase in coordination number.[16] The shift of the ν_{M-N} vibration is the net result of two opposing factors: a shift to lower frequencies due to the increase in coordination number and to higher frequencies due to an increase in chelation. Actually, the ν_{M-N} occurs at slightly lower frequencies than for the bipyridyl complexes indicating that the influence of change in coordination number is the predominant factor.

TABLE IV
COMPARISON OF METAL–LIGAND VIBRATIONS FOR Zn(II) HALIDE COMPLEXES (CM^{-1})

Complex	ν_{ZnCl}	ν_{ZnBr}	ν_{ZnI}	ν_{MN}	δ_{ZnCl}	δ_{ZnBr}	δ_{ZnI}	δ_{ZnN}
$Zn(py)_2Cl_2$	326,293			218	200			154
$Zn(py)_2Br_2$		260sh,254		219		182		153
$Zn(py)_2I_2$			210	222			167	147,159
$Zn(bipy)Cl_2$	323			241				192
$Zn(bipy)Br_2$		261		250				190
$Zn(bipy)I_2$			217	250				194
$Zn(terp)Cl_2$	287,278			244				167
$Zn(terp)Br_2$		222,213		243				167
$Zn(terp)I_2$			187	245				167

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Metal Complexes of N,N,N′,N′-Tetramethylated Diamines. II.[1] Copper(II) and Iron(II) Complexes

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Complexes of N,N,N′,N′-tetramethylated ethylenediamine (Me_4en), 1,2-propylenediamine (Me_4pn), and trimethylenediamine (Me_4tn) with copper(II) and iron(II) halides of the type $M(diamine)X_2$ have been prepared and investigated. The Fe(diamine)Br_2 and $Cu(Me_4tn)Br_2$ complexes are pseudo-tetrahedral, but the Me_4en and Me_4pn derivatives of copper(II) are essentially planar in solution and probably also in the solid state. The ligand field spectra of the compounds have been discussed on the basis of their stereochemistry.

Introduction

In a previous paper[1] the complexes formed by Co(II) and Ni(II) halides with some N,N,N′,N′-tetramethylated alkylenediamines, those of ethylenediamine (Me_4en), 1,2-propylenediamine (Me_4pn), and trimethylenediamine (Me_4tn), were described and characterized: $(CH_3)_2NCH_2CH_2N(CH_3)_2$, Me_4en; $(CH_3)_2NCH(CH_3)CH_2N(CH_3)_2$, Me_4pn; $(CH_3)_2NCH_2CH_2CH_2N(CH_3)_2$, Me_4tn. Most of these complexes, which have the formula $M(diamine)X_2$, were assigned a pseudo-tetrahedral structure with C_{2v} microsymmetry. In the solid state only the complexes $Ni(Me_4en)Cl_2$ and $Ni(Me_4pn)Cl_2$ attain six-coordination by polymerization, and in inert solvents such as dichloromethane and dichlorobenzene there is an equilibrium between associated six-coordinated species and tetrahedral species. The formation of pseudo-tetrahedral complexes was attributed to steric hindrance about the donor atoms of these ligands.

In this paper the preparation and study of the complexes formed by copper(II) and iron(II) halides with Me_4en, Me_4pn, and Me_4tn are reported. Complexes of the general formula $M(diamine)X_2$, where X = Cl or Br, were obtained. Of these only $Cu(Me_4en)Br_2$ had previously been described,[2] and on the basis of its absorption spectrum it had been assigned a tetragonal

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TABLE I

ANALYTICAL AND PHYSICAL DATA FOR THE N,N,N′,N′-TETRAMETHYLDIAMINE COPPER(II) AND IRON(II) COMPLEXES

Compound	Mp, °C	% nitrogen		% halogen		Molar conductance, cm²/ohm mole[a]		
		Calcd	Found	Calcd	Found	Nitroethane	Dichloroethane	i^b
$Cu(Me_4en)Cl_2$	145–148	11.18	11.30	28.29	27.95	2.0	0.6	0.92
$Cu(Me_4pn)Cl_2$	127–130	10.58	11.00	26.79	26.78	1.3	0.8	0.94
$Cu(Me_4en)Br_2$	112–113	8.26	8.20	47.06	46.93	2.0	0.6	1.05
$Cu(Me_4pn)Br_2$	100–105	7.92	7.60	45.19	45.08	3.3	0.7	1.08
$Cu(Me_4tn)Br_2$	95–99	7.92	7.68	45.19	45.34	6.5	0.5	
$Fe(Me_4en)Br_2$		8.44	8.53	48.15	48.33			
$Fe(Me_4pn)Br_2$		8.10	8.10	46.20	45.89			

[a] For *ca.* 10^{-3} *M* solutions at 25°. Reference values in nitroethane and dichloroethane, respectively, are 68 and 16 for $[(n\text{-}C_4H_9)_4N]I$.
[b] van't Hoff coefficients for *ca.* 5×10^{-3} *M* solutions at 37°.

six-coordinated structure in the solid state attained by means of bromine bridges between adjacent copper atoms.

Experimental Section

Preparation of the Compounds.—Me_4en [bp 121–122 (758 mm), lit.[3] bp 119.5° (724 mm)], Me_4pn [bp 139–140 (758 mm), lit.[4] bp 138–139° (745 mm)], and Me_4tn [bp 143–145° (755 mm), lit.[5] bp 145–146° (755 mm)] were prepared by the formaldehyde–formic acid methylation of the appropriate diamines.[3,4] All of the complexes were prepared by the following general method. A solution of 10 mmoles of the diamine ligand in 10 ml of dry butanol was added to a boiled solution of 10 mmoles of the appropriate metal halide salt in 100 ml of butyl alcohol. The metal halides were anhydrous with the exception of copper chloride. In some case cyclohexane was added to promote precipitation. The crystals were collected on a funnel and dried in a stream of dry nitrogen. The iron(II) compounds were prepared and filtered in a pure nitrogen atmosphere. White crystals were obtained when Me_4tn ligand was added to a hot solution of the $FeBr_2$ and cooled. The compound is very unstable and it was not possible to perform any measurements.

Physical Measurements.—The absorption spectra were recorded in the range 4000–30,000 cm^{-1} with a Beckman DK-2 spectrophotometer and 1-cm silica cells. The diffuse reflectance spectra were measured using the standard Beckman reflectance attachment with magnesium oxide as the reference. The magnetic measurements were performed by the Gouy method with the apparatus and experimental technique already described.[6] The sample tube was calibrated with $Co[Hg(SCN)_4]$[7] and freshly distilled water. Diamagnetic corrections were calculated from Pascal constants.[8] Molecular weights were determined in 1,2-dichloroethane at 37° with a Mechrolab Model 301 A vapor pressure osmometer calibrated with benzyl. Scale readings were made 3 min after a drop of the solution was placed on the thermistor. Concentrations of the solution were *ca.* 5×10^{-3} *M*. The conductivity values were measured on a WTW Model LBR/B conductance bridge. Concentrations of the solutions were *ca.* 10^{-3} *M*.

Results

The complexes obtained are all crystalline. The copper complexes are intensely colored, and those of iron are practically colorless. The analytical data and some physical properties are given in Table I. The copper complexes of Me_4en and Me_4pn are stable in air, but the $Cu(Me_4tn)Br_2$ complex is very sensitive to moisture. These complexes are readily soluble in the common organic solvents such as chloroform, symmetrical dichloroethane, and nitroethane. Solutions of the Me_4tn derivative become cloudy after a short time. The iron complexes are not stable in air, and even under pure nitrogen they decompose in a few days. These compounds are not very soluble and they decompose even in anhydrous and deaerated solvents.

Magnetic measurements were made on the solid compounds (Table II). The magnetic moments of the copper complexes at room temperature range between 1.82 and 2.06 BM. Those of the iron complexes are *ca.* 5.40 BM. The magnetic susceptibility of the complex $Fe(Me_4en)Br_2$ between 80 and 300°K follows the Curie–Weiss law with a Weiss constant of −11°.

TABLE II

MAGNETIC SUSCEPTIBILITY DATA FOR THE N,N,N′,N′-TETRAMETHYLDIAMINE COPPER(II) AND IRON(II) COMPLEXES

Compound	Temp, °C	$10^6\chi_g$, cgs units	$10^6\chi_M$, cgs units	μ_{eff}, BM
$Cu(Me_4en)Cl_2$	19	5.58	1,546	1.91
$Cu(Me_4pn)Cl_2$	19	5.09	1,506	1.88
$Cu(Me_4en)Br_2$	19	3.63	1,401	1.82
$Cu(Me_4pn)Br_2$	19	4.07	1,619	1.96
$Cu(Me_4tn)Br_2$	19	4.43	1,747	2.06
$Fe(Me_4en)Br_2$	18	36.72	12,356	5.38
$Fe(Me_4pn)Br_2$	19	35.38	12,420	5.41

Electrical conductivities of 10^{-3} *M* solutions of copper complexes, measured at 25° in nitroethane and dichloroethane, indicate that the complexes are less than 10% dissociated in solution (Table I). The molecular weights found for copper complexes are within 10% of the calculated value for the monomers (Table I). These measurements indicate that all of the complexes are present in solution predominantly as nonionic monomeric species.

The spectra of the copper complexes (Figures 1 and 2) were measured in the solid state and in solution. The absorption maxima and their molar absorption coefficients are shown in Table III. The spectra of the solids are similar to those obtained in solution, although there is some displacement of the absorption maxima. Reflectance spectra were also obtained for the iron com-

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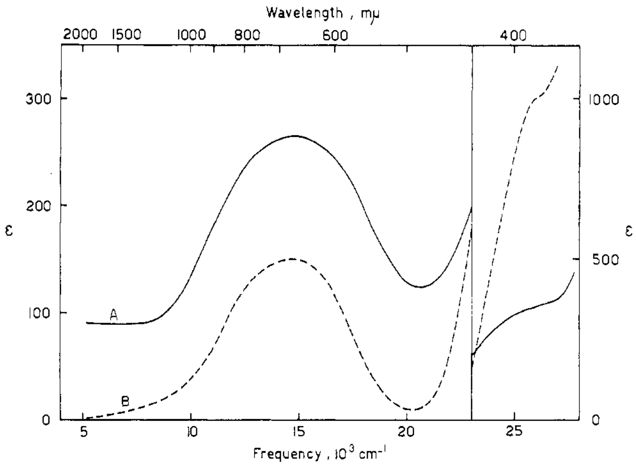

Figure 1.—Reflectance spectrum of $Cu(Me_4en)Cl_2$ (curve A) and absorption spectrum in $C_2H_4Cl_2$ (curve B).

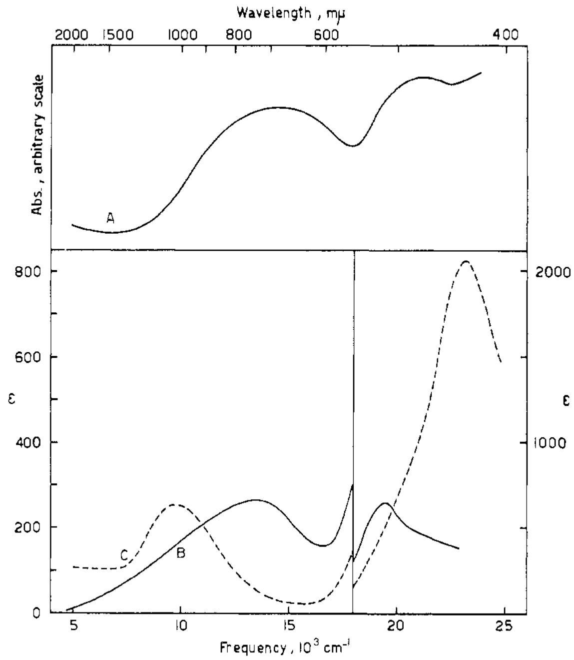

Figure 2.—Reflectance spectrum of $Cu(Me_4en)Br_2$ (curve A); absorption spectra in $C_2H_4Cl_2$ of $Cu(Me_4en)Br_2$ (curve B) and $Cu(Me_4tn)Br_2$ (curve C).

pounds (Figure 3). The complex $Fe(Me_4en)Br_2$ was also obtained in solution by addition of few drops of free amine in excess; its spectrum is practically indistinguishable from that of the solid. In view of the experimental difficulties, no attempt was made to obtain the molar extinction coefficients.

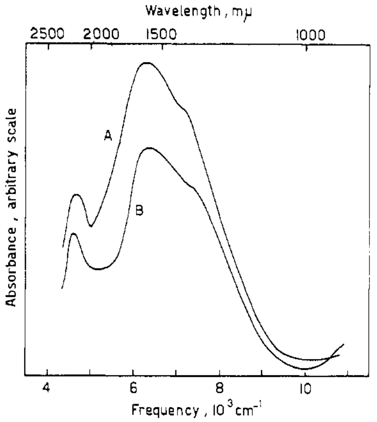

Figure 3.—Reflectance spectra of $Fe(Me_4en)Br_2$ (curve A) and $Fe(Me_4pn)Br_2$ (curve B).

Table III

Spectroscopic Data for the N,N,N′,N′-Tetramethyldiamine Copper(II) and Iron(II) Complexes

Complex	Solvent	Absorption max, cm^{-1} (ϵ_{molar} for soln)
$Cu(Me_4en)Cl_2$		15,000, 27,000 sh
	$C_2H_4Cl_2$	14,300 (144), 26,400 sh
$Cu(Me_4pn)Cl_2$		14,800, 26,400 sh
	$C_2H_4Cl_2$	14,300 (149), 25,600 sh
$Cu(Me_4en)Br_2$		14,500, 21,300
	$C_2H_4Cl_2$	13,300 (265), 19,800 (640)
$Cu(Me_4pn)Br_2$		14,400, 20,500
	$C_2H_4Cl_2$	13,000 (268), 19,800 (612)
$Cu(Me_4tn)Br_2$		10,000, 26,000
	$C_2H_4Cl_2$	9750 (248), 23,000 (2060)
$Fe(Me_4en)Br_2$		4600, 6250, 7100 sh
$Fe(Me_4pn)Br_2$		4600, 6400, 7300 sh

Discussion

Me_4en and Me_4pn Cu(II) Complexes.—In inert solvents the copper complexes exist essentially as nonionic monomers. Thus the coordination number of the Cu(II) ion in these compounds must be four. The spectra of the bromide complexes of Me_4en and Me_4pn in solution have two bands occurring at *ca.* 13,500 and 20,000 cm^{-1} (Figure 2). The chloride complexes in solution have a band at *ca.* 14,500 cm^{-1} and a shoulder at *ca.* 26,000 cm^{-1} (Figure 1). Since the structures of the chloride and bromide complexes are presumably similar in solution, we suggest that the bands at 13,500 and 14,500 cm^{-1} in the bromo and chloro derivatives, respectively, are crystal field bands and that the bands at 20,000 and 26,000 cm^{-1} should be assigned to charge transfer. This is supported by (i) the relatively high intensities (ϵ *ca.* 650) and (ii) charge-transfer bands for halide complexes of Cu(II) which are often assigned to frequencies of this order. In fact, the first charge-transfer bands of the flattened tetrahedral[9] complexes $CuCl_4^{2-}$ and $CuBr_4^{2-}$ have been assigned at *ca.* 25,000 and 18,000–19,000 cm^{-1}, respectively.[10,11] Furthermore a band at *ca.* 25,000 cm^{-1} shown by the compound $[Pt(NH_3)_4][CuCl_4]$ has been assigned[12] to charge transfer of the complex $CuCl_4^{2-}$ which has a planar structure. The d–d bands for complexes for which a planar structure has been proposed occur in the range 14,000–18,000 cm^{-1}.[13-18] When the planar

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structure is distorted toward a tetrahedral configuration, this band diminishes in frequency.[11] Therefore the band observed in the range 13,000–15,000 cm^{-1} for these tetracoordinated copper complexes is consistent with an essentially planar structure. These bands are very broad and presumably contain all four transitions expected in a field of C_{2v} symmetry[19] (*cis* planar). The high intensity of the bands is presumably due to the fact that the molecule does not possess a center of symmetry. In the solid state the frequencies of d–d transitions are displaced toward higher energies by about 1200–1400 cm^{-1} for the bromo complexes and by about 500–700 cm^{-1} for the chloro complexes, the main characteristics of the spectra remaining unaltered. This small displacement can be attributed to a slight distortion of the coordination polyhedron due to lattice effects. Nevertheless a six-coordinated structure very tetragonally distorted cannot be ruled out.

$Cu(Me_4tn)Br_2$.—This complex is orange, but the other bromides are blackish green. The spectrum of this compound is the same in solid state as in solution and differs appreciably from those of the other bromides in its absorption frequency. The band of lowest energy occurs at 10,000 cm^{-1}, that is, at *ca.* 3500 cm^{-1} lower than in the Me_4en and Me_4pn complexes. Since the band at higher energy (23,000 cm^{-1}, ϵ 2060) is assigned to charge transfer, the former is most reasonably interpreted on the basis of a flattened tetrahedral configuration. Furlani, *et al.*,[11] have calculated the energy terms for copper(II) in a flattened tetrahedral complex with D_{2d} symmetry. They demonstrate that a progressive flattening of the tetrahedral structure leads to an increased splitting for both the ground and excited states and a marked displacement toward higher frequencies of the d–d transitions. On this basis it was possible to offer a reasonable explanation for the frequencies 8000–11,000 cm^{-1} observed for the pseudo-tetrahedral complexes CuX_4^{2-} [10,11] and $CuL_{4-n}X_n^{2-n}$ where L is a coordinating solvent such as CH_3CN or CH_3NO_2.[11] Considerable support for the assignment of a pseudo-tetrahedral structure to this compound comes from the value of the magnetic moment, 2.06 BM. This value is close to that found for the pseudo-tetrahedral complexes CuX_4^{2-} (a value of 2.00 BM is found for the complexes Cs_2CuCl_4[20] and $[(C_2H_5)_4N]_2CuCl_4$[21]) and is greater than that found for planar and polymeric octahedral complexes.[20-22] The assumption that the complex $Cu(Me_4tn)Br_2$, unlike the Me_4en and Me_4pn compounds, has a pseudo-tetrahedral structure is consistent with the behavior of the ligand Me_4tn toward the halides of Ni(II) and Co(II) where it definitely favors a tetrahedral structure. This is attributed to steric hindrance.

Complexes of Iron(II).—The reflectance spectra show that these complexes absorb strongly in the range 4500–7000 cm^{-1} with two or more maxima (Figure 3). Such a low value cannot be attributed to a six-coordinated structure attained by polymerization.[23] A tetrahedral configuration, however, would be expected to absorb at frequencies below 5000 cm^{-1}.[24,25] Since the real symmetry of these complexes is at most C_{2v}, the levels ^5E and $^5T_2$ found in T_d symmetry are split into two and three nondegenerate levels, respectively. The fact that it is possible to identify three maxima in the single broad band found in the spectra of these complexes supports this interpretation. These bands are not caused by ligand absorptions as is shown by the spectra of the Zn(II) analogs. It has previously been noted that the pseudo-tetrahedral complexes FeL_2X_2 (L = triphenylarsine oxide, triphenylphosphine oxide; X = Cl, Br)[26] have a broad band at higher frequencies than would be expected assuming an average value of Δ for the four ligands. This can be attributed qualitatively to the fact that the splitting of the ^5E level lowers the energy of the ground state and thus increases the energy of all of the electronic transitions.[26] It is also necessary to consider that in these chelate compounds the departure from T_d symmetry is considerable, because the steric requirements of the chelate ring forces a low value for the N–Fe–N angle. In the compound $Ni(Me_4en)(NO_2)_2$[27] this angle was found to be 85°. The values of the magnetic moments, although they are not decisive in assigning stereochemistry, are consistent with those found for tetrahedral complexes of the type FeX_4^{2-} [24,28] and slightly higher than those found for pseudo-tetrahedral complexes FeL_2X_2.[26] The value of θ found for the Me_4en derivative ($-11°$) is very close to that found for the pseudo-tetrahedral complex $Fe(NCS)_4^{2-}$ and can be attributed to departure from T_d symmetry.[28]

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