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Physical and Theoretical Studies on Some Solid Complex Diazonium Salts of p-Dimethylaminobenzenediazonium Chloride. I. Magnetic Investigations

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The diazonium chloride salt of p-aminodimethylaniline has been prepared and complexed with the anhydrous chlorides of Fe(III), Mn(II), Co(II), Cu(II), Zn(II), Cd(II), Sb(V), Bi(III), Sn(IV) and Te(IV). The magnetic susceptibilities of these compounds have been determined and the diamagnetic anisotropies and magnetic moments deduced. Effective radii for the π-electron orbits of the diazonium ion in the complexes were obtained from the anisotropy data, and the resulting values are found to be several tenths to one Ångstrom greater than the π-radius of the uncomplexed diazonium ion. Also the magnetic moments of the $FeCl_4^-$, $MnCl_4^{-2}$, $CoCl_4^{-2}$ and $CuCl_6^{-4}$ ions present in some of the complexes are found to be significantly greater than the moments of these anions in CsCl lattices. It is suggested that the observed magnetic effects are due at least in part to a charge transfer interaction involving the metal chloro anion and the diazonium cation.

Introduction

This is the first of several papers oriented toward an attempt to elucidate the mechanism of bonding between p-dimethylaminobenzenediazonium chloride and a number of metal chlorides incorporated as stabilizing agents for this salt.

Although aromatic diazonium salts and their metal chloride-stabilized counterparts are well known, little work has been done in probing the nature of the interaction whereby coprecipitation with certain metal chlorides imparts both thermal and/or photochemical stability to the diazonium salt; the latter being otherwise generally unstable. For this reason a concerted effort was undertaken to prepare and study solid metal chloride complexes of at least one diazonium salt. The techniques used include magnetochemical, spectral, thermochemical and X-ray methods, involving both experimental and theoretical aspects.

In the light of modern coördination theory it is commonly accepted that the compounds in question are characterized by the general formula $[ArN_2]_{(n-q)}^+$ $[M^qCl_n]^{-(n-q)}$, in which an aryldiazonium cation and a metal chloro complex anion are involved. Although a limited number of physiochemical studies in solution fail to show any appreciable interaction between the diazonium cation and the metal chloro anion, similar studies in the solid phase indicate quite the contrary.

Gremillion, Jonassen and O'Connor[3] studied p-dimethylaminobenzenediazonium chloride complexed with a variety of metal chlorides, by infrared spectral and thermochemical techniques. They concluded that, aside from the normal static charge effects, a partial charge transfer between cation and anion is involved. Their findings were confirmed by Kazitsyna, Reutov and Buchkovskii,[4] and also by Nuttall, Roberts and Sharp,[5] who recorded and analyzed the infrared spectra of a variety of diazonium salts and their metal chloride complexes. The latter authors also suggest some definite covalent interaction between the π-electrons of the diazonium ion and the chloride ligands of the metal complex anions.

An exhaustive survey of the literature reveals that except for one photochemical investigation in solution,[6] there are no reports wherein the magnetic properties of diazonium salts and their complexes have been determined. Thus the magnetic susceptibilities and diamagnetic anisotropies of these compounds have been measured in an effort to show that the observed results are reasonably consistent with what one might expect if charge transfer interaction is involved.

Experimental

To substantiate the claim that the data reported here are in accord with the findings of previously mentioned investigators, we have taken the precautions to prepare carefully and purify all compounds studied. Thus we report somewhat complete analytical data for all samples.

Preparation of Compounds.—$C_8H_{10}N_3Cl$ (p-dimethylaminobenzenediazonium chloride) is obtained in excellent yield by the diazotization of p-dimethylaminoaniline in anhydrous ethanolic solution according to the procedure of Koenigs.[7] The desired metal chloride complex salts are easily prepared by simply adding together equimolar solutions (alcoholic) of both the diazonium salt and the desired anhydrous metal chloride. The product precipitates immediately and is recovered, washed, dried and analyzed. All experimental operations were carried out in a dark room to avoid contamination by photodecomposition of the samples.

$C_8H_{10}N_3Cl$, Calcd.: N, 22.80; C, 52.30; H, 5.45; Cl, 19.35. Found: N, 22.76; C, 52.26; H, 5.37; Cl, 19.35.

$(C_8H_{10}N_3)FeCl_4$, Calcd.: Fe, 16.20; N, 12.20; Cl, 41.00. Found: Fe, 15.88; N, 12.20; Cl, 39.90.

(1) Extracted in part from the Ph.D. Dissertation of Edward A. Boudreaux, submitted March, 1962.

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(3) A. F. Gremillion, H. B. Jonassen and R. J. O'Connor, J. Am. Chem. Soc., **81**, 6134 (1959).

(4) L. A. Kazitsyna, O. A. Reutov and Z. F. Buchkovskii, Russ. J. Phys. Chem., **34**, 404 (1960).

(5) R. H. Nuttall, E. R. Roberts and D. W. A. Sharp, Spectrochim. Acta, **17**, 947 (1961).

(6) E. A. Boudreaux and E. Boulet, J. Am. Chem. Soc., **80**, 1588 (1958).

(7) E. Koenigs, Ann., **509**, 149 (1934).

($C_8H_{10}N_3$)$_2$MnCl$_4$, Calcd.: Mn, 11.10; N, 16.50; Cl, 29.00.
Found: Mn, 11.20; N, 17.00; Cl, 28.85.
($C_8H_{10}N_3$)$_2$CoCl$_4$, Calcd.: Co, 11.91; N, 16.80; Cl, 28.60.
Found: Co, 12.10; N, 16.60; Cl, 28.30.
($C_8H_{10}N_3$)CuCl$_3$, Calcd.: Cu, 20.00; N, 13.40; Cl, 33.50.
Found: Cu, 19.9; N, 13.30; Cl, 33.30.
($C_8H_{10}N_3$)$_2$ZnCl$_4$, Calcd.: Zn, 13.0; N, 16.70; Cl, 28.2.
Found: Zn, 12.8; N, 16.70; Cl, 28.3.
($C_8H_{10}N_3$)CdCl$_3$, Calcd.: Cd, 30.6; N, 11.5; Cl, 29.1.
Found: Cd, 30.6; N, 11.6; Cl, 28.7.
($C_8H_{10}N_3$)SbCl$_6$, Calcd.: Sb, 25.3; N, 8.7; Cl, 44.1; C, 20.0;
H, 2.1. Found: Sb, 25.5; N, 8.9; Cl, (42.0); C, 20.8; H, 2.3.
($C_8H_{10}N_3$)SnCl$_6$, Calcd.: Sn, 18.9; N, 13.4; Cl, 34.0; C,
30.6; H, 3.2. Found: Sn, 19.4; N, 12.9; Cl, 33.7; C, 30.7;
H, 3.2.
($C_8H_{10}N_3$)$_2$TeCl$_6$, Calcd.: Te, 20.1; N, 13.4; Cl, 33.4.
Found: Te, (20); N, 13.1; Cl, 33.2.
($C_8H_{10}N_3$)BiCl$_4$, Calcd.: Bi, 41.8; N, 8.4; Cl, 28.5. Found:
Bi, 41.6; N, 8.6; Cl, 29.0.

Magnetic Measurements.—All susceptibility measurements
were made with a standard Gouy balance carefully calibrated
(over a period of two years) with a number of standards both
paramagnetic and diamagnetic (*i.e.*, HgCo(NCS)$_4$, CuSO$_4$·5H$_2$O,
Mohr's salt, benzoic acid, naphthalene, etc.).

Subsequent to calibration, a number of susceptibility measure-
ments were made on each of a large variety of very pure com-
pounds for which good susceptibility data were available. From
these data it was established that the maximum error in deter-
mining magnetic moments of finely powdered samples did not
exceed ±0.02$_{(5)}$ B.M., and observed diamagnetic susceptibilities
are accurate to at least ±1%. Also, the diazonium compounds
employed were of sufficiently high purity to ensure that this es-
tablished accuracy was maintained. Furthermore, an inde-
pendent set of measurements, using another apparatus, at three
different field strengths failed to exhibit any dependence of the
observed susceptibility on field strength.

All susceptibility and other physical measurements were con-
ducted in a cool, dark room illuminated only by a small yellow
light, so as to ensure no contamination by either photo or
thermal decomposition. The densities required for calculating
molar susceptibilities and polarizabilities were determined by
the standard flotation method using inert liquids.

Dielectric Constant Measurements.—Static dielectric con-
stants of all the compounds studied were measured at one mega-
cycle with a model 1690-A solid dielectric sample cell manufac-
tured by the General Radio Corporation. The samples were
pressed into thin circular disks and their capacitances determined
according to the procedure outlined by the manufacturer. All
reported values are accurate to better than ±0.05 unit.

Calculations and Results

Evaluation of Diamagnetic Anisotropy.—The dia-
magnetic anisotropy is related to the average molar sus-
ceptibility by the expression[8]

$$\chi_M = \frac{1}{3}(2\chi_{||} + \chi_{\perp}) = \chi_{||} + \frac{1}{3}\Delta\chi \qquad (1)$$

where χ_M is the observed molar susceptibility, $\chi_{||}$ and
$\chi_{\perp}$ the principal susceptibilities with the molecular
plane parallel and perpendicular to the magnetic field,
respectively, and $\Delta\chi$ the anisotropy. Since the π-
electrons are not involved in $\chi_{||}$, this quantity can be
determined by applying Pascal's rules. On applying
the additivity law, the susceptibility of the diazonium
ion is: $\chi_{Dz^+} = \chi_M(DzCl) - \chi(Cl^-) = (-125 +
23.4) \times 10^{-6} = -101.6 \times 10^{-6}$ e.m.u./g.-ion, where
the symbol Dz$^+$ is the representation for the p-dimeth-
ylaminobenzenediazonium ion. Thus $\Delta\chi$ for the
diazonium ion is given by

$$\Delta\chi = 3(\chi_{Dz^+} - \chi_{||}) \qquad (2)$$

It may be considered that an important resonance form
contributing to the over-all electronic structure of the
diazonium ion is[9]
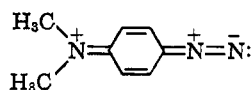
hence $\chi_{||}$ by Pascal's rules becomes

$\chi_{||} = 8\chi_0 + 10\chi_B + 3\chi_N + \lambda(N{=}N) + 2\lambda({>}C{=}N) +$
$\lambda(ring) + 2\lambda(N{-}C)$

(8) H. Watanabe, K. Ito and M. Kubo, *J. Am. Chem. Soc.*, **82**, 3294
(1960).
(9) L. C. Anderson and J. W. Stedly, *ibid.*, **76**, 5144 (1954).

∴ $\chi_{||} = 8(-6.0) + 10(-2.9) + 3(-5.6) +$
$$(1.85) + 2(+8.2) + 2(-2.95)$$
$$= -73.3 \times 10^{-6} \text{ e.m.u./g.-ion}$$

All values of the above constants were taken from the
literature,[10,11] with the exception of λ(ring) which was
evaluated from the experimental susceptibility of p-di-
methylaminonitrosobenzene. Substitution of the value
for $\chi_{||}$ and the previously determined value of χ_{Dz^+}
into eq. 2 gives $\Delta\chi = -85 \times 10^{-6}$ e.m.u./mole.

A similar procedure was also used in evaluating $\Delta\chi$
for the diazonium salt complexes. However, the ob-
served molar susceptibilities were corrected for the sus-
ceptibilities of the various metal chloro-anions, which
were obtained from the observed susceptibilities of their
alkali chloride double salts. In those cases where ex-
perimental data were not available, the values were
estimated from additivity relationships. The suscep-
tibility data and the $\Delta\chi$ values obtained for the dia-
magnetic compounds are given in the top half of
Table I.

TABLE I

DIAMAGNETIC SUSCEPTIBILITIES, ANISOTROPIES AND EFFECTIVE
π-RADII OF DIAZONIUM SALT COMPLEXES

Compound[a]	$-\chi_M \times 10^{-6}$	$-\chi_{An}[b] \times 10^{-6}$	$-\chi_{Dz^+} \times 10^{-6}$	$-\chi_{||} \times 10^{-6}$	$-\Delta\chi[c] \times 10^{-6}$	$\bar{r}_\pi$, Å.[d]
DzCl	125	23.4	101.6	73.3	85	1.35
(Dz)$_2$SnCl$_6$	383	156	114.0	73.3	121	1.61
(Dz)$_2$ZnCl$_4$	342	109	116.7	73.3	130	1.67
(Dz)$_2$TeCl$_6$	376	143	117.0	73.3	132	1.70
(Dz)SbCl$_6$	275	150	125.0	73.3	155	1.75
[(Dz)CdCl$_3$]$_2$[f]	235	92	143.0	73.3	209	1.97
(Dz)BiCl$_4$	265	119	146.0	73.3	216	2.05
[(Dz)CuCl$_3$]$_2$[f]	(180)[e]	73	107.0	73.3	101	1.50
(Dz)FeCl$_4$	(215)	104	111.0	73.3	113	1.55
(Dz)$_2$CoCl$_4$	(332)	106	113.0	73.3	119	1.59
(Dz)$_2$MnCl$_4$	(337)	108	114.5	73.3	124	1.62

[a] The symbol Dz$^+$ represents the p-dimethylaminobenzene-
diazonium ion. [b] The susceptibilities of the complex anions as
deduced from experimental data on other compounds or esti-
mated from the values given in ref. 11, p. 20. [c] Calculated ac-
cording to eq. 2. [d] Calculated according to eq. 3. The radii
for the diamagnetic compounds have an average error of about
±3%; those for the paramagnetic compounds (bottom half of
table) are accurate to only about ±5%. [e] All calculated from
eq. 6 using the data provided in Table II. [f] Preliminary X-ray
studies indicate that the structures of these compounds are
analogous to the known structures of CsCdCl$_3$ and CsCuCl$_3$,
which are dimeric.

Evaluation of π-Electron Radii.—The effective
average values of the radii of the π-electron orbits, $\bar{r}_\pi$,
in the diazonium cation was evaluated from the well
known Larmor–Langevin formula

$$\bar{r}_\pi = [\Delta\chi/4.248 \times 10^{10}(n)]^{1/2} \qquad (3)$$

where n is the total number of π-electrons in the diazo-
nium cation. (For the Dz$^+$ ion, n is given the value of
eleven, since the nitrogen lone pair electrons are un-
doubtedly involved in the total delocalization of the π-
electron system.) The $\bar{r}_\pi$ values of the diamagnetic com-
pounds calculated according to 3 are presented in the
last column of the top half of Table I. It is estimated
that the reported values are accurate to about 3%.

**Estimation of Underlying Diamagnetism in Para-
magnetic Compounds.**—In order that there be a com-
plete set of data for comparative purposes, it is also
desirable to have $\bar{r}_\pi$ values for those diazonium salt com-
plexes containing paramagnetic metal ions. This, how-
ever, requires a knowledge of the diamagnetism of such
compounds if eq. 3 is to be applied. Since direct meas-

(10) G. Foex, "Constantes Selectionees diamagnetisme et paramag-
netisme," Masson and Cie, Paris, 1957.
(11) P. W. Selwood, "Magnetochemistry," Interscience Publishers Inc.,
New York, N. Y., 1956, p. 78.

urement of the underlying diamagnetism is not possible and a mere estimation of it has little or no significance for our purposes, it is advisable to evaluate the diamagnetism from some other related measurable property.

It has been shown that the molar diamagnetism of isotropic molecules can be closely correlated to the molar electronic polarizability through the relationship[12]

$$\chi_M = \frac{-Ne^2 a_0^{1/2}}{4mc^2} (k\alpha_M)^{1/2} \quad (4)$$

where k is the total number of electrons in the molecule, α_M the molar polarizability and the other terms have their usual significance. For planar anisotropic molecules eq. 4 can be rewritten to give

$$\chi_M = \frac{-Ne^2 \bar{r}_0^{1/2}}{2mc^2} (k\bar{\alpha}_M)^{1/2} \quad (5)$$

where $\bar{r}_0$ is an average effective radius of the planar orbit and $\bar{\alpha}_M$ the average molar polarizability. For a given system in which $\bar{r}_0$ is constant, (5) can be rewritten in the form

$$\chi_M = -C \times 10^6 (k\bar{\alpha}_M)^{1/2} \quad (6)$$

where C is determined empirically, $\bar{\alpha}_M$ is obtained from the observed static dielectric constant, ϵ, according to the relationship[13]

$$\frac{\epsilon - 1}{\epsilon + 2} (M/d) = \frac{4}{3}\pi N_{\bar{\alpha}_M} \quad (7)$$

where M and d are the molecular weight and density of the compound, respectively. It is not expected that (7) will give the exact polarizability of a crystalline solid, but since we are primarily interested in relative changes in $\bar{\alpha}_M$ an exact determination of it is not essential. Furthermore, for rigid lattices such as these, $\bar{\alpha}_M$ is truly a representation of the distortion polarization and no complications from anisotropic orientation polarization effects are involved. Thus the constant in (6) was determined from observed values of χ_M and $\bar{\alpha}_M$ for those diazonium complexes containing Zn(II), Cd(II), Sb(V), Bi(III), Sn(IV) and Te(IV) ions. The results are given in the top half of Table II. From these data it is found that the best value for C in (6) is 2.1 with an average deviation of about ±5%.

With this result and the observed values of $\bar{\alpha}_M$, the underlying diamagnetic susceptibilities of the diazonium salt complexes containing Fe(III), Mn(II), Co(II) and Cu(II) ions were evaluated from eq. 6. The values thus obtained for χ_M and the other pertinent data are presented in the bottom half of Table II. From these χ_M the $\Delta\chi$ were obtained as discussed previously and the $\bar{r}_\pi$ calculated according to (3). The final results are given in the bottom half of Table I. It is estimated that the probable average error in the reported values of $\bar{r}_\pi$ for the paramagnetic compounds is about ±5% whereas that for the diamagnetic compounds is about ±3% as mentioned earlier.

Discussion

Diamagnetic Properties.—It has been pointed out by McGlynn[14] that the molar diamagnetic susceptibilities of charge transfer complexes are greater than the sum of the susceptibilities of their components, i.e.

$$\chi_M(D^+A^-) > \chi_M(D) + \chi_M(A)$$

where $\chi_M(D^+A^-)$ is the observed molar susceptibility of the complex, and $\chi_M(D)$ and $\chi_M(A)$ are the observed molar susceptibilities of the donor and acceptor species, respectively. It is assumed that the most important

(12) Y. G. Dorfman, *Doklady Akad. Nauk S.S.S.R.*, **119**, 305 (1960).

(13) This equation can be found in any good advanced physical chemistry text.

(14) S. P. McGlynn, *Chem. Rev.*, **58**, 1113 (1958).

TABLE II

RELATIONSHIPS BETWEEN POLARIZABILITIES AND DIAMAGNETIC SUSCEPTIBILITIES OF DIAZONIUM SALT COMPLEXES

Compound	ϵ^a	$\bar{\alpha}_M$, Å.^{3b}	k^c	$-\chi_M \times 10^{-6}$	C^d
DzCl	8.33	39.7	96	125	2.03
(Dz)$_2$SnCl$_6$	6.50	91.9	310	383	2.27
(Dz)$_2$ZnCl$_4$	8.97	93.5	256	342	2.21
(Dz)$_2$TeCl$_6$	10.09	111.5	312	376	2.01
(Dz)SbCl$_6$	10.77	79.5	232	275	2.03
[(Dz)CdCl$_3$]$_2$	11.19	59.1	178	235	2.29
(Dz)BiCl$_4$	14.99	72.3	230	265	2.10
[(Dz)CuCl$_3$]$_2$	5.41	44.6	159	(180)^f	2.1)^e
(Dz)FeCl$_4$	8.63	60.3	173	(215)	(2.1)
(Dz)$_2$CoCl$_4$	9.05	97.6	253	(332)	(2.1)
(Dz)$_2$MnCl$_4$	10.69	101.4	251	(337)	(2.1)

^{a} The static dielectric constant measured on the powdered sample at one megacycle. Reported values are accurate to ±0.05 unit. ^{b} The average molar polarizability calculated according to eq. 7. ^{c} Total number of electrons in the molecule according to 6. ^{d} The constant appearing in eq. 6. ^{e} The average value of C in 6. ^{f} Calculated according to 6.

single factor affecting the susceptibility is the increased delocalization of the electrons in the dative bonded structure. According to McGlynn, rough calculations support the conclusion that the increase in orbital extent due to the dative bond–no bond resonance is the basis for the observed increase in diamagnetism. It is found in the charge transfer complexes of polyacene with trinitrobenzene, for example, that the diamagnetic susceptibility of the complex is as high as 17 × 10^{-6} e.m.u./mole greater than the sum of the component susceptibilities.[15]

An inspection of the data in Table I reveals that there is a rather large increase in the observed diamagnetism of the diazonium salt complexes, as evidenced by the large increases in $\Delta\chi$ above that for the uncomplexed diazonium salt. Furthermore, it follows that the $\bar{r}_\pi$ values given in Table I for these complexes are all greater than that for the uncomplexed diazonium ion. While it is true that the actual numerical values of these radii are themselves not highly accurate, the observed relative trends are indicative of some process in which a considerable delocalization of the π-electron cloud of the diazonium ion has taken place. It seems reasonable therefore to conclude that the most important single factor leading to such a sizable increase in the orbital extent of the π-electrons might well be due to a charge transfer interaction between the diazonium cation and the metal halo-anion. Although this may not be the only mechanism whereby the observed effects could result, it is nevertheless the simplest and most logical one to expect in these cases. Further evidence substantiating these conclusions is to be found in the spectra of these compounds as presented in part II of this publication series.

Paramagnetic Properties.—While it is true that the paramagnetic compounds involved in this study are of the high spin type, it is nevertheless of interest to make careful and accurate determinations of their magnetic moments, inasmuch as it has been suggested that a considerable orbital contribution to the magnetic moment may result if charge transfer interaction is involved.[16]

Because of highly selective chemical reactivity, there are only a few metal chloride salts containing paramagnetic cations that will complex with p-dimethylaminobenzenediazonium chloride. This necessarily imposes severe limitations on the number of complexes that can be studied, thus leaving the conclusions drawn from

(15) R. Ch. Sabney, S. L. Aggarwal and M. J. Singh, *J. Indian Chem. Soc.*, **23**, 335 (1946).

(16) S. P. McGlynn, private communication.

TABLE III

REPORTED MAGNETIC DATA FOR CHLORO COMPLEXES OF Fe(III), Mn(II), Co(II) AND Ce(II)

Compound	$\chi_M^{obs} \times 10^{-6}$	$\chi_D^a \times 10^{-6}$	$10Dq$, cm.$^{-1}$	$\chi_{tip}^e \times 10^{-6}$	$\chi_M^{eff} \times 10^{-6}$	T, °K.	μ_{eff}, B.M.^{d}	Ref.
Cs[FeCl$_4$]^f	14,837	−137	...	...	14,974	293	5.95	f
Cs$_3$MnCl$_5$	15,097	−174	...	...	15,271	300	6.08	18
Cs$_3$[CoCl$_4$]Cl	9,188	−135	3,200^b	622	8,661	298.6	4.56	24
[CsCuCl$_3$]$_2$	2,854	−229	6,500^c	480	1,303^g	290	1.75	10 (p. 58)

^{a} Obtained from ref. 11. ^{b} Obtained from ref. 20. ^{c} Obtained from ref. 21. ^{d} It appears that these moments reported in the literature are within an accuracy of about ±1%. ^{e} Calculated according to procedure in ref. 19. ^{f} This compound was prepared and measured in our laboratory. It has previously been reported by H. L. Friedman (*J. Am. Chem. Soc.*, 74, 5 (1952)) and cited in private communication with W. Klemm. The structure of this compound is unknown, but in the light of modern coördination theory it is probable that a tetrahedral FeCl$_4^-$ complex is involved. ^{g} Value is for 1 gram-ion of Cu^{+2}.

TABLE IV

MAGNETIC DATA FOR DIAZONIUM SALT COMPLEXES WITH FeCl$_3$, MnCl$_2$, CoCl$_2$ AND CuCl$_2$

Compound	$\chi_M^{obs} \times 10^{-6}$	$\chi_D^a \times 10^{-6}$	$10Dq,^b$ cm.$^{-1}$	$\chi_{tip}^c \times 10^{-6}$	$\chi_M^{eff} \times 10^{-6}$	T, °K.	$\mu_{eff} \pm$ 0.02, B.M.	$\Delta\mu_{eff}^d$
(Dz)FeCl$_4$	15,426	−205	...	...	15,631	298.7	6.13	0.18 ± 0.08
(Dz)$_2$MnCl$_4$	16,214	−311	...	...	16,525	297.9	6.32	.24 ± .08
(Dz)$_2$CoCl$_4$	9,580	−309	3,200	662	9,227	297.5	4.75	.19 ± .07
[(Dz)CuCl$_3$]$_2^e$	3,322	−366	6,500	480	1,604^f	296.7	1.96	.21 ± .04

^{a} The diamagnetic correction for the Dz$^+$ ion was obtained from Table I. All other corrections were obtained from ref. 11. ^{b} For references to values reported here see Table III. ^{c} Calculated according to the procedure in ref. 19. ^{d} These are the differences between the μ_{eff} values reported here and those in Table III. The uncertainties reported in these values were estimated from the maximum probable error of values given in Table III and the established error of the values in Table IV. ^{e} Preliminary X-ray data indicate that the structure of this compound is similar to that of [CsCuCl$_3$]$_2$ as determined by A. F. Wells, *J. Chem. Soc.*, 1662 (1947). ^{f} Value is for 1 gram-ion of Cu^{+2}.

the relatively few compounds studied open to question. Nevertheless, it is felt that the data reported here are of fundamental interest and may also serve as a stimulus to initiate similar investigations.

The magnetic data reported in Tables III and IV were obtained at one temperature. We, of course, realize the shortcomings of this, since the μ_{eff} values were calculated from the Curie law, when in all probability the Curie–Weiss law is actually obeyed. This, however, should not amount to any serious error for purposes of comparison, since it has been shown that in other high spin complexes containing the same metal ions involved here the molecular field constant, θ_c, is relatively small (order of magnitude $\leqslant 12°$) and should not significantly alter the observed moments beyond the limits of our experimental error.[17,18]

The χ_M^{eff} values in Tables III and IV are the observed molar susceptibilities completely corrected for diamagnetism in all cases, and for temperature-independent paramagnetism, χ_{tip}, in the cases of the Co(II) and Cu(II) complexes. The diamagnetic correction, χ_D, for the diazonium ion was obtained from Table I. All other χ_D values were obtained from the literature[11]; χ_{tip} for the metal chloro anions of Co(II) and Cu(II) was computed from the expression[19] $\chi_{tip} = 8nN\beta^2/3(10Dq)$, where n is the number of electrons on the metal ion in a cubic field configuraton t^{6-n}e^4, and the other terms have their usual significance. Use was also made of the relationship that a d^n configuration for an ion in a tetrahedral field is d^{10-n} in an octahedral field. The $10Dq$ values required were obtained from the literature.[20,21]

It should be pointed out, however, that theory dictates[22] that for ions having a d^5-orbital configuration and whose magnetic moments are given by the "spin

only" formula (weak field, *i.e.*, FeCl$_4^-$ and MnCl$_4^{-2}$), χ_{tip} actually vanishes for both the free ions and their symmetrical tetrahedral and octahedral complexes. (The non-vanishing of χ_{tip} in CoCl$_4^{-2}$ and CuCl$_6^{-4}$ ions even in the absence of distorted ligand fields is evident, since Co^{+2} and Cu^{+2} have d^7- and d^9-configurations, respectively.) On the other hand, any axial distortion in the cubic symmetry of the field does not quench the l_z component of orbital angular momentum; hence an added orbital contribution to μ_{eff} should result.[22b] This appears to be a factor which may at least partially account for the increases in μ_{eff} values reported for complexes containing Fe(III) and Mn(II) in Table IV.

A rough estimate of the upper limit to the temperature independent paramagnetic contribution arising from the diazonium ion itself may be obtained from the expression

$$\chi_{tip} = \frac{2}{3}N\beta^2 \frac{\langle \pi^* | l^2 | n \rangle}{E_{n-\pi^*}}$$

where the energy for the lowest lying excited state, $E_{n-\pi^*}$, is contained in the singlet–singlet transition of the diazonium group. This is known to occur in the 430 mμ region in the solid state[23] and about 380 mμ in solution.[9] Using this information, χ_{tip} for the diazonium ion is found to be $\leqslant 29 \times 10^{-6}$. Thus it is apparent that this makes a negligible contribution to the total paramagnetism of the complexes involved. Furthermore, since the diamagnetic corrections were made from experimental measurements on the diazonium chloride salt, the actual χ_{tip} for the diazonium ion is contained in this, and the necessary corrections are automatically accounted for.

It is to be noted that the μ_{eff} values for FeCl$_4^-$, MnCl$_4^{-2}$, CoCl$_4^{-2}$ and CuCl$_6^{-4}$ ions in Table IV are about 0.18–0.24 B.M. greater than the moments for these corresponding ions in Table III. Furthermore, these observed increases, $\Delta\mu_{eff}$, are considerably greater than what can be attributed to any experimental error inherent in the moments reported in Tables III and IV. Similar effects have also been pointed out by Cotton, *et al.*,[24] in a variety of complexes containing the CoCl$_4^{-2}$

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ion. In these latter cases it has been suggested that the increases in the moments may possibly arise from compression of the $CoCl_4^{-2}$ ion by the large cations in the crystal, thus causing distortions in the symmetry of the ligand field.[24] While it cannot be argued that this may not be the case, it appears that still another effect may be equally responsible for the observed increases in μ_{eff} values of the diazonium salt complexes. Infrared spectral studies are consistent in showing that aside from the primary charge transfer (i.e., the initial process in which an electron is transferred from the $C_8H_{10}N_3$ radical to the MCl_n fragment to form the ion pair, $[C_8H_{10}N_3]^+$-$[MCl_n]^-$) there is a secondary partial charge transfer from the filled orbitals of the chloride ligands to a vacant π-orbital on the diazonium cation.[5,25] Such a process would conceivably account for distortions in the symmetry of the ligand field about any of the metal ions in question. Pryce[26] has shown that axial distortions in the symmetrical fields of Fe(III) and Mn(II) ions involve energy having an order of magnitude such that would increase the spin orbital contribution to the temperature-dependent paramagnetic susceptibility by an order of magnitude of 10^{-5} e.m.u./g.-ion. At room temperature, this would correspond to a maximum increase in μ_{eff} of about 10^{-1} B.M. It is curious to see that the order of magnitude by which μ_{eff} is increased due to an axial distortion is in agreement with what is observed here.

It is also established that charge transfer complexes not having a large covalent stabilization of the dative-bond structure have a triplet level lying very close to the ground state.[14] It is not uncommon to find that such complexes exhibit paramagnetism resulting from the thermal population of the well stabilized triplet level. This, for example, has been found in charge transfer complexes of p-phenylenediamine with p-benzoquinones.[27] Thus it is equally possible that magnetic effects reported here may result also from the thermal

population of the low-lying triplet level in the diazonium cation of these complexes.

In view of this and the other data previously mentioned, it is our contention that in complexes of p-dimethylaminobenzenediazonium chloride containing $FeCl_4^-$, $MnCl_4^{-2}$, $CoCl_4^{-2}$ and $CuCl_6^{-4}$ ions the observed increases in μ_{eff} (Table IV) above the μ_{eff} values for analogous ions in CsCl lattices (Table III) are to some extent due to a charge transfer process leading to axial distortions in the ligand field about the metal ions. Such distortion should account for an increase in the spin-orbit coupling contribution to the magnetic moment. Alternately, it is suggested further that thermal population of a low-lying triplet level in the complex may also account for the observed results. Although it is not feasible to attempt any rigorous derivation for demonstrating this, the well known phenomena of orbital spreading and charge delocalization inherent in charge transfer processes could conceivably apply here.

It is not to be denied that other physical processes, including compression of the anions by the cations in the crystal, could lead to a similar effect of increasing the magnetic moment; however, it is felt that in view of this, the anisotropy data, electronic spectral data (appearing in part II) and infrared spectral studies[5,25] indicate that a charge-transfer interaction seems also to be of importance. Other effects may also be involved, but it would be exceedingly difficult at this time to make a quantitative estimate of the various contributing factors. Furthermore, it is not intended that this account be taken as more than qualitative support for charge transfer based on the observed effects.

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Studies of Irreversibility of CF₃ Addition. Reactions with Some cis and trans Isomers and the Problem of cis-trans Isomerization

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Kinetic evidence presented here proves that the addition of CF₃ radicals to a variety of substrates is irreversible at 65° whether the reaction proceeds in solution or in the gas phase. At 150° in the gas phase a small fraction of CF₃·benzene adduct seems to decompose into CF₃ + benzene. No decomposition was observed for the CF₃·CHCl:CHCl adduct radicals. On the other hand, it was shown that under the same conditions, photolysis of 4 mole % of CF₃N₂CF₃ in 99% trans-dichloroethylene may lead to complete isomerization of the ethylene. Further studies indicated that the isomerization is caused by Cl atoms produced through the reactions: CF₃ + CHCl=CHCl → CF₃CHClCHCl· and ·CHClCH(CF₃)Cl → CHCl=CHCF₃ + Cl; i.e., the dissociation of the adduct radical into Cl + CHCl=CHCF₃ takes place while under the same conditions no fission of the ·CHCl-CHCl-CF₃ bond is observed. The dissociation of vibrationally excited radicals is reviewed and the difference between the rupture of a C–R bond (R = polyatomic moiety) and a C–X bond (X = an atom) is considered. Gradation in reactivities of some substrates toward CF₃ addition is discussed.

The relative rate constants of CF₃ addition to various substrates such as olefins, aromatic hydrocarbons, acetylenes, etc., were determined by a technique described in earlier papers.[1–4] The radicals were produced by photolysis of hexafluoroazomethane, and their

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addition to the investigated substrate proceeded simultaneously with the hydrogen abstraction from an aliphatic hydrocarbon used as a solvent (for the liquid phase experiments) or as a diluent (in the gaseous experiments). These two competing reactions are described by eq. 1 and 2.

$$CF_3 + \text{aliphatic hydrocarbon} \longrightarrow$$
$$CF_3H + \text{hydrocarbon radical} \quad (1)$$
$$CF_3 + \text{substrate} \longrightarrow CF_3\text{-substrate·} \quad (2)$$