steric hindrance and bond strain are introduced when the three groups are not all the same. This strain is probably sufficient to preclude the stable existence of such isomers.

The requirement that the singly attached amine molecules have the same configuration as the bridging molecules should be less stringent. Models show that isomers of the L-(*ddd*)(*llll*) type complexes might possibly occur. We feel that if such isomers would have been present in our mixtures to the extent of several per cent they would have been detected, and so we can only say that our procedure must have formed them only in very small amounts, if at all.

Steric hindrance probably also accounts for the failure to replace the last water molecule on each cobalt despite the presence of large excesses of the amine used in the preparation. Rather severe steric crowding occurs when a third singly attached amine molecule is placed on a given cobalt.

An examination of the possible conformations of other *trans*-1,2-cycloalkanediamines shows that rings containing more than five carbon atoms should be sufficiently flexible to permit unhindered chelation by the two amine groups, while rings containing five or fewer carbons would be expected to introduce considerable steric strain. This predicted difference between the compounds containing five- and six-membered rings is supported by the contrast between the results reported here and the normal behavior of the tris-(*trans*-1,2-cyclohexanediamine)cobalt(III) ion.[19] This difference is also illustrated by the observation[20,21] that *trans*-1,2-cyclopentanediaminetetraacetic acid is a much weaker coordinating agent than *trans*-1,2-cyclohexanediaminetetraacetic acid.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE RADIATION LABORATORY,[1]
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Electric Moments of Complexes of Pyridine and Hexamethylphosphoramide with Metal Halides, Isocyanates, and Isothiocyanates

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Electric moments of bispyridine complexes of CdI_2, NiI_2, $ZnBr_2$, ZnI_2, $Zn(NCO)_2$, and $Zn(NCS)_2$ and of bishexamethylphosphoramide complexes of $CdBr_2$, CdI_2, $CoCl_2$, $CoBr_2$, CoI_2, $Co(NCO)_2$, $Co(NCS)_2$, $ZnCl_2$, $ZnBr_2$, ZnI_2, $Zn(NCO)_2$, and $Zn(NCS)_2$ have been determined in benzene or dioxane solution. The increase in moments from chlorides to iodides corresponds to the order of increasing polarizability. The complexes of cobalt and of zinc containing the NCO group appear to be isocyanates. The P–O–M bond angle in hexamethylphosphoramide complexes is appreciably less than 108°. The order of dipole moments of corresponding complexes is Co > Zn > Cd.

The electric dipole moments of dichlorobis(pyridine)zinc and dichlorobis(γ-picoline)zinc indicate[2] a regular tetrahedral configuration for these complexes in dioxane. As an extension of this study, the moments of other tetrahedral complexes of pyridine and of hexamethylphosphoramide have been determined. The bispyridine complexes of $ZnBr_2$, ZnI_2, $Zn(NCO)_2$, $Zn(NCS)_2$, CdI_2, and NiI_2 proved to be sufficiently soluble in benzene or dioxane for dielectric constant measurements. The nickel complex is the first of its type (containing two Ni–N bonds) for which evidence has been offered[3] for a tetrahedral configuration. Infrared spectra obtained in this laboratory indicate a tetrahedral configuration for the other above compounds also. This configuration for the cadmium iodide complex is in contrast to the bridged, tetragonal structure revealed by infrared and/or X-ray diffraction measurements for the bispyridine complexes of cadmium chloride,[4] bromide, isocyanate,[5] and isothiocyanate. The very low solubility of these complexes in benzene indicates that this solvent does not break these bridges. The low solubility of the complexes of pyridine with cobalt(II) halides in benzene and their reaction with dioxane prevented the determination of their electric moments.

Complexes of hexamethylphosphoramide, $[(CH_3)_2N]_3PO$ (HMPA), with cobalt(II) halides and isothiocyanate have been reported by Donoghue and Drago.[6] Similar compounds of zinc were prepared, along with $Co(NCO)_2(HMPA)_2$ and $Zn(NCO)_2(HMPA)_2$. The preference of palladium(II) for Pd–N bonds and the similar frequencies observed[7] for the NCO symmetric stretching vibration in $M(NCO)_2(C_5H_5N)_2$ complexes (1340, 1348, and 1347 cm.$^{-1}$ for Pd, Co, and Zn,

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[1] The Radiation Laboratory is operated by the University of Notre Dame under contract with the Atomic Energy Commission. This is A.E.C. document No. COO-38-381.

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TABLE I

POLARIZATIONS AND ELECTRIC MOMENTS AT 25° [a]

Compound	Solvent	$1000wf_2$	$\Delta\epsilon/wf_2$	$\Delta d/wf_2$, g./ml.	$P_{2\infty}$, ml.	$1.15MR_D$, ml.	μ, D.
$CdI_2(C_5H_5N)_2$	B	2.9–3.8	17.5	0.35	1832	102	9.19
$NiI_2(C_5H_5N)_2$	B	3.3–4.7	21.2	0.37	1969	99	9.6
$NiI_2(C_5H_5N)_2$	D	2.5–3.2	24.8	0.51	1987	99	9.6
$ZnBr_2(C_5H_5N)_2$	D	2.5–3.0	28.9	0.44	1883	86	9.37
$ZnI_2(C_5H_5N)_2$	B	3.0–3.3	22.3	0.45	2080	98	9.84
$Zn(NCO)_2(C_5H_5N)_2$	B	3.3–4.9	34.1	0.24	2046	84	9.82
$Zn(NCS)_2(C_5H_5N)_2$	D	2.3–4.1	43.3	0.53	2395	102	10.6
Hexamethylphosphoramide	B	17–43	11.2	0.08	384	52.7[b]	4.31
$CdBr_2(HMPA)_2$	B	4.5–6.2	14.9	0.27	1924	145	9.32
$CdI_2(HMPA)_2$	B	3.8–9.9	14.9	0.47	2145	157	9.85
$CoCl_2(HMPA)_2$	B	6.4–28.9	19.9	0.19	1955	136	9.43
$CoBr_2(HMPA)_2$	B	3.6–7.1	17.7	0.25	2055	140	9.67
$CoI_2(HMPA)_2$	B	2.1–9.5	18.5	0.35	2475	154	10.7
$Co(NCO)_2(HMPA)_2$	B	2.5–3.2	21.7	0.14	2190	122	10.0
$Co(NCS)_2(HMPA)_2$	B	4.2–5.9	24.4	0.33	2561	158	10.8
$ZnCl_2(HMPA)_2$	B	2.7–6.4	18.0	0.30	1789	134	8.99
$ZnBr_2(HMPA)_2$	B	4.2–7.1	16.8	0.42	1949	140	9.40
$ZnI_2(HMPA)_2$	B	4.9–7.5	16.5	0.46	2215	152	10.0
$Zn(NCO)_2(HMPA)_2$	B	3.3–4.9	20.9	0.27	2115	139	9.82
$Zn(NCS)_2(HMPA)_2$	B	4.5–7.0	23.9	0.34	2543	156	10.8

[a] wf_2 is the weight fraction of solute, $\Delta\epsilon$ and Δd are the changes in dielectric constant and density, respectively, from solvent to solution, $P_{2\infty}$ is the total polarization of solute at infinite dilution, and μ is the electric dipole moment. B, D, and HMPA represent benzene, dioxane, and hexamethylphosphoramide. [b] $1.10MR_D$.

respectively, and 1331 cm.$^{-1}$ for $Co(NCO)_2(HMPA)_2$) suggest that these complexes are isocyanates. In support of this interpretation, infrared spectra indicate Si–N bonding in $Si(NCO)_4$.[8] Infrared spectra reveal that the zinc and cobalt complexes with the NCS group are isothiocyanates.

Experimental

Preparation and Purification of Compounds.—The complexes of pyridine with the iodides of zinc, cadmium, and nickel and the bromides and isothiocyanates of zinc were prepared by Glonek.[9] The complexes of the isocyanates of cobalt and zinc with pyridine were prepared by Petra.[7]

Anal. Calcd. for $CdI_2(C_5H_5N)_2$: Cd, 21.43; I, 48.39. Found: Cd, 21.29; I, 48.25. Calcd. for $ZnBr_2(C_5H_5N)_2$: Zn, 17.05; Br, 41.43. Found: Zn, 16.81; Br, 41.08. Calcd. for $ZnI_2(C_5H_5N)_2$: C, 25.16; H, 2.11. Found: C, 25.07; H, 2.19. Calcd. for $Zn(NCS)_2(C_5H_5N)_2$: C, 42.45; H, 2.94; Zn, 19.24. Found: C, 42.69; H, 3.21; Zn, 19.69. Calcd. for $Zn(NCO)_2(C_5H_5N)_2$: C, 46.84; H, 3.25; Zn, 21.26. Found: C, 45.55; H, 3.41; Zn, 21.51.

Complexes of hexamethylphosphoramide were prepared by addition of anhydrous metal halide or thiocyanate to an excess of HMPA with slight heating to effect dissolution; the complexes precipitated on the addition of petroleum ether and the products were washed with petroleum ether. The isocyanates were prepared by dissolving $Co(NCO)_2(C_5H_5N)_2$ and $Zn(NCO)_2(C_5H_5N)_2$ in HMPA, precipitating with petroleum ether, and washing with ethyl ether and petroleum ether. Infrared spectra revealed that the products were pyridine-free. All complexes were dried under vacuum.

Anal. Calcd. for $CoCl_2(HMPA)_2$: Co, 12.07; Cl, 14.52. Found: Co, 11.91; Cl, 14.16. Calcd. for $CoBr_2(HMPA)_2$: Co, 10.21; Br, 27.68. Found: Co, 10.90; Br, 26.89. Calcd. for $CoI_2(HMPA)_2$: Co, 8.63; I, 37.81. Found: Co, 8.43; I, 36.09. Calcd. for $Co(NCO)_2(HMPA)_2$: C, 33.53; H, 7.23. Found: C, 33.73; H, 7.34. Calcd. for $Co(NCS)_2(HMPA)_2$: C, 31.51; H, 6.75; Co, 11.05. Found: C, 31.86; H, 7.00; Co, 11.03. Calcd. for $CdBr_2(HMPA)_2$: Cd, 17.82; Br, 25.34. Found: Cd, 17.94; Br, 24.99. Calcd. for $CdI_2(HMPA)_2$: Cd, 15.51; I, 35.02. Found: Cd, 16.02; I, 34.74. Calcd. for $ZnCl_2(HMPA)_2$: Zn, 13.21; Cl, 14.33. Found: Zn, 12.78; Cl, 14.30. Calcd. for $ZnBr_2(HMPA)_2$: Zn, 11.20; Br, 27.39. Found: Zn, 10.63, Br, 27.04. Calcd. for $ZnI_2(HMPA)_2$: Zn, 9.65; I, 37.46. Found: Zn, 9.92; I, 36.08. Calcd. for $Zn(NCO)_2(HMPA)_2$: C, 33.20; H, 7.12; Zn, 12.87. Found: C, 32.10, H, 7.19; Zn, 12.44. Calcd. for $Zn(NCS)_2(HMPA)_2$: C, 31.14; H, 6.72. Found: C, 31.22; H, 6.97.

Measurements and Calculations.—Dielectric constant and density measurements and calculations of electric moments were carried out as in previous investigations.[10] A few of the dielectric constants were obtained with an oscillator similar to that described by Estok.[11] The value of MR_D for HMPA, 47.86, was obtained from index of refraction and density measurements at 25°. The refractions of the complexes were taken as the sum of the refractions of the ligands and the metal halides, isocyanates, and isothiocyanates. The following refractions were used in the calculations: Co 10.5,[12] Ni 10.0,[12] Cd 13.0,[13] Zn 9.3,[13] NCO 8.0,[14] pyridine 24.07,[15] and Vogel's[16] values: Cl 5.9, Br 8.7, I 13.9, and NCS 15.6. The distortion polarizations of the complexes were taken as $1.15MR_D$ and that of HMPA as $1.10 MR_D$. As the dielectric constant was practically a linear function of concentration for solutions of all complexes, average values of $\Delta\epsilon/wf_2$ (for at least three different concentrations) were used in calculating solute polarizations. Polarizations and electric moments are listed in Table I.

Discussion

Pyridine Complexes.—The moments of the bispyridine complexes of zinc chloride, bromide, and iodide are 9.20, 9.37, and 9.84 D., respectively. This is the reverse order of moments of the majority of simple halides. For example, the moments of the arsenic and antimony trihalides decrease from chloride to iodide.[17]

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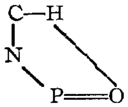
On complex formation with dioxane, however, a greater increase in moment is observed for arsenic and antimony tribromides than for the corresponding chlorides.[18] This is attributed to the greater polarizability of bromine. In the formation of the bispyridine complexes the electron release from nitrogen to zinc is counteracted by an electron withdrawal by the halogen atoms. The moments reveal that this withdrawal is greatest for iodine; this is very probably related to the order of polarizabilities: iodine > bromine > chlorine. Venanzi and co-workers[19] have observed a general increase in the moments of bistriarylphosphine complexes with nickel halides from chloride to iodide. They have attributed this in part to increased polarizability, but chiefly to decreasing X–Ni–X bond angles. This latter suggestion appears to us to be very unlikely.

The moments of the bispyridine complexes of ZnI_2 and CdI_2, 9.84 and 9.18 D., respectively, indicate a greater N–M–I resultant for the zinc complex. The N–H proton magnetic resonance spectra[20] of ZnI_2(*p*-toluidine)$_2$ and CdI_2(*p*-toluidine)$_2$ reveal a greater chemical shift (to low field) for the former complex, indicating a greater polarity for the N–Zn bond than for the N–Cd bond. These dipole moment and n.m.r. results indicate similar polarities for the Zn–I and Cd–I bonds. The moment of the nickel iodide complex is seen to be only slightly lower than that of the zinc iodide complex and independent of the solvent.

The moments of ethyl chloride, isocyanate, and isothiocyanate in benzene solution are 2.0,[17] 2.8,[17] and 3.31 D.[21] The moments of the bispyridine complexes of zinc chloride, isocyanate, and isothiocyanate are 9.20, 9.82, and 10.6 D., respectively. The difference between the latter two moments, 0.8 D., is about the expected value (for tetrahedral zinc bond angles) for Zn–NCO and Zn–NCS bonding; this is further evidence for an *iso*cyanate. M–OCN bonding is expected to result in a larger moment than M–NCO bonding (alkylthiocyanates have moments 0.3 D. larger than those of alkylisothiocyanates[21]) and in the event of Zn–OCN bonding the above difference would be reduced. The magnitude of the moment of the isothiocyanate, compared to that of the chloride, indicates very little, if any, contribution of the $\overset{-}{\mathrm{Zn}}{=}\overset{+}{\mathrm{N}}{=}\mathrm{C}{=}\mathrm{S}$ structure which would involve the use of 4d orbitals of zinc in forming π-bonds.

HMPA Complexes.—Steric effects and electrostatic



interaction probably results in a conformation of the $N(CH_3)_2$ groups in HMPA corresponding to minimum moment. The moment observed for this compound, 4.31 D., compares with a value of 4.25 D. for tripropylphosphine oxide obtained some years ago in this laboratory. It suggests some $^{+}N{=}P{-}O^{-}$ character in the NPO bonds.

The P—O—M bond angle in $MX_2(HMPA)_2$ complexes is expected to be less than 180° because of the spatial requirements of the unshared pair of oxygen electrons. The C═O—Cd bond angle in complexes of cadmium chloride with acetamide, urea, and monomethylurea ranges from 134 to 128°.[22] The calculation of the moments of HMPA complexes in various conformations requires a knowledge of the pertinent bond moments. There is no reliable value known to the authors for the moment of the PO→M dative bond. The following comparisons are helpful for estimating the difference between the N→–M bond moment in pyridine complexes and the O→–M bond moment. The moment of BCl_3–dioxane is 4.9 D.[23] The moment of BCl_3–pyridine is 7.5 D.[2] Subtracting the moment of pyridine, 2.3 D. (slightly enhanced in the complex from its normal value of 2.2 D.), yields 5.2 D. for the sum of the N→–B→–Cl dipoles, 0.3 D. greater than the sum of the O→–B→–Cl dipoles in the dioxanate. Assuming that this difference holds for the N→–Zn and O→–Zn dipoles in the pyridine and HMPA complexes, one can calculate the moment of $ZnCl_2(HMPA)_2$ assuming tetrahedral zinc bond angles and 180° as the oxygen bond angle. This value is the moment of dichlorobis(pyridine)zinc $+ 1.16\mu_{\mathrm{HMPA}} - 1.16(0.3) - 1.16\mu_{\mathrm{pyridine}}$ This sum is 11.3 D. compared to the experimental value of 8.99 D., indicating that the P–O–Zn bond angle is not 180°. The moments of the HMPA complexes thus depend on the equilibrium conformations of the HMPA ligands. Construction of Fisher–Hirschfelder models indicates that there can be different unstrained conformations of these ligands resulting from rotation about the O–Zn bonds. Assuming 125° as the oxygen bond angle, the calculated moment corresponding to minimum moment (and minimum repulsion between the methyl groups of the same complex) is 3.3 D., much less than the observed value. If one ligand is in the conformation of minimum moment and the other in the conformation of maximum moment, the calculated moment is 9.9 D.

In the HMPA complexes of both cobalt and zinc halides, the increases in moment from chlorides to iodides are greater than for the pyridine complexes with the zinc halides. This suggests that in addition to polarizability factors, steric effects are operative. The spatial requirements of the large iodine atoms cause the HMPA molecules to assume conformations more favorable for large over-all dipole moments.

The difference between the moments of the HMPA complexes of the isothiocyanates and isocyanates is 0.8–1.0 D., again indicating that the latter are *iso*cyanates. The moments of all cobalt complexes are greater than those of the corresponding zinc complexes.

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