

**STUDIES ON COMPLEXES AND LIGANDS.
PART II. COMPLEXES OF MERCURY(II) AND ZINC(II) WITH
PRIMARY AROMATIC AMINES: INFRA-RED SPECTRA
AND BONDING***

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OPSOMMING

'n Reeks koördinasieverbindings is deur reaksie van kwiksilwer en sinkchloried met primêre aromatiiese amiene berei. 'n Volledige toeskrywing van die infrarooifrekwensies binne die omvang 4000-625 cm^{-1} word aangegee. Die simmetriese en asimmetriese N-H rekwensies volg die verhouding

$$\nu(\text{sim}) = 345.5 + 0.876\nu(\text{asim}).$$

Die C-N rekwensies bewys 'n lineêre verhouding met die Hammett σ -funksies van die *m*- en *p*-substitueerde amiene.

SUMMARY

A series of amine complexes has been prepared by reaction of zinc chloride and mercuric chloride with primary aromatic amines. A detailed assignment of the bands in the infra-red spectra of the complexes in the range 4000-625 cm^{-1} is presented. The symmetric and asymmetric N-H stretching frequencies follow the relationship

$$\nu(\text{sym}) = 345.5 + 0.876\nu(\text{asym}).$$

The C-N stretching frequencies exhibit a linear relationship with the Hammett σ -functions for the *m*- and *p*-substituted amines.

There is much current interest in the infra-red spectra of co-ordination compounds but the spectra of complexes of metals with primary aromatic amines have received little attention. In this paper we report the results of an investigation of the spectra of several zinc and mercury complexes of general formula $[\text{MCl}_2\text{L}_2]$ ($\text{M} = \text{Zn}, \text{Hg}$; $\text{L} =$ primary aromatic amine).

Zinc(II) and mercury(II), with d^{10} configuration, are expected to yield a tetrahedral distribution of ligands about the metal. In almost all cases where complexes of these 4-co-ordinate metals have been studied by X-ray diffraction methods, tetrahedral structure has been confirmed. Exceptions arise only where the stereochemical requirements of the ligand forces an alternative configuration to be adopted, e.g. the square-planar phthalocyanines. We believe the presently-described molecules to be tetrahedral complexes since square-planar structure would lead to the existence of geometric isomers. As a result, the crude products would melt over a wide temperature range with sharpening of the melting point after repeated recrystallization; no such effects were observed. Furthermore, the infra-red spectra of the crude and analytically-pure compounds were identical, indicating the absence of geometric isomers.

*Part I: Haigh, van Dam and Thornton, *Zeit. anorg. allgem. Chem.*, 1967, (in the press).

Molecular weight determination of the aniline-zinc chloride complex, the comparatively low melting points of all the complexes, their highly crystalline character and their solubility in certain organic solvents all point to mononuclear composition for these molecules.

TABLE I

Infra-red spectral data for mercury and zinc complexes (cm⁻¹)

No.	aniline		benzylamine		<i>p</i> -toluidine		<i>p</i> -anisidine		<i>p</i> -chloro-aniline Zn	<i>p</i> -bromo-aniline Zn
	Hg	Zn	Hg	Zn	Hg	Zn	Hg	Zn		
1	3289s	3268s	3311s	3300s	3300s	3300m	3284m	3279m	3295s	3279s
2	3226s	3223s	3257sh	3236m	3231s	3236s	3226s	3230m	3236s	3231s
3	3125m	3123m			3135m	3133w	3128w	3125w	3135m	3133m
4	3040m	3040m	3035m	3030m	3030w	3030w				
5			2950vw	2933vw	2924w	2928w	2920w	2924m		
6							2841m	2845w		
7	1603s	1602s		1592sh	1612s	1603sh	1613s	1616m	1603sh	1595sh
8	1570m	1567s	1563s	1567s	1584s	1579s	1563m	1582s	1575s	1577s
9										
10	1489s	1492s	1495s	1494s	1508s	1513s	1511s	1515s	1493s	1488s
11								1470w	1456w	1453w
12			1456m	1450s	1449sh	1449vw	1456w	1451m		
13	1470m	1467m	1445m	1443m			1439m	1441m	1427s	1424s
14			1361m	1366m						
15			1351m	1356m						
16							1299m	1300m		1316m
17							1250s	1250s		
18	1228s	1214m	1208m	1200sh	1222s	1209m	1216m	1209m	1224s	1220s
19	1175m	1175w	1176w	1176w						
20					1178sh		1179s	1176m	1174w	1175w
21										
22										
23				1149s						
24		1099s	1098s	1100w						
25					1090w	1091sh	1099wb	1103s	1095s	1088s
26										
27										
28										
29	1064sh	1066w	1072m	1072m						
30						1073s			1074s	1074s
31	1037s	1021m	1033w							
32					1020s		1031s	1035s	1012s	1012s
33										
34										
35										
36	999m	1000vw	989s	993s	999s				946w	950w
37	899s	898m			925m	926vw	917w		927w	931w
38	831w	831vw			833vw				826sh	
39	814m	815vw			820w	821m	821s	822s	821s	820s
40	798s	792m			806s	808s			808sh	803sh
41	754s	752s	750s	738s						
42					734m	731w	731s	728s		
43										
44										
45	690s	691s	694s	692s	702m	702w			701m	700s
46										
47					647m	660m	657wb	662mb	661s	661s
48						633m		630m	628m	626s
49	647mb	660m	625s	630s						

Intensity abbreviations: s=strong, m=moderate, w=weak, v=very, b=broad, sh=shoulder.

TABLE I—continued
Infra-red spectral data for mercury and zinc complexes (cm⁻¹)

<i>m</i> -toluidine Hg		<i>m</i> -chloro- aniline Zn	<i>o</i> -toluidine Hg		<i>o</i> -anis- idine Hg	Assignment	No.
3311m	3274s	3268m	3333m	3300m	3333s	ν N-H; asym.	1
3236s	3226s	3224m	3257s	3247s	3242s	ν N-H; sym.	2
3140m	3125w	3130w		3130w		ν N-H . . . Cl (intermol.)	3
3030w	3030w					ν C-H; aromatic	4
2929w	2924w		2920w	2933w	2933w	ν C-H; aliphatic	5
	2841vw		2857w		2837w	ν C-H; aliphatic	6
1613m	1595m	1613sh	1617s	1592s	1612s	ν C=C (1); aromatic	7
1587s	1569s	1600s	1592s	1575s	1558m	δ N-H; scissor	8
		1572sh				ν C=C (2); aromatic	9
1513s	1493s	1479m	1497s	1496s	1495s	ν C=C (3); aromatic	10
		1449m					11
1447wb			1467m	1465m	1465m	δ C-H; aliphatic	12
1447wb		1427w			1450m	ν C=C (4); aromatic	13
						δ C-H; CH ₂ scissor	14
						δ C-H; CH ₂ scissor	15
						β C-H; 1, 4-disubst.	16
					1258s	ν C-O-C; ethers	17
1224s	1253w	1230w	1236s	1235m	1214m	ν C-N	18
						β C-H; monosubst.	19
						β C-H; 1, 4-disubst.	20
1179w	1167vw	1163vw				β C-H; 1, 3-disubst.	21
			1192m	1189w	1180w	β C-H; 1, 2-disubst.	22
							23
						β C-H; monosubst.	24
						β C-H; 1, 4-disubst.	25
1089w	1097s	1099s				β C-H; 1, 3-disubst.	26
		1086s	1081w	1075s	1093w	β C-H; 1, 2-disubst.	27
					1085m		28
							29
						β C-H; 1 4-disubst.	30
						β C-H; monosubst.	31
						β C-H; 1, 4-disubst.	32
1021s			1015sb	1042w	1042w	β C-H; 1, 3-disubst.	33
				1013w		β C-H; 1, 2-disubst.	34
							35
1001s		952vw	998sb	992sh	969sb	NH ₂ bend	36
926w	915w	870s		935w	913vw		37
833sh			833w	831m	847m	γ C-H	38
821m					821w	NH ₂ bend (rock)	39
808s	778sh				800m		40
						γ C-H; monosubst.	41
						γ C-H; 1, 4-disubst.	42
735m	773s	775s				γ C-H; 1, 3-disubst.	43
			757s	756s	740s	γ C-H; 1, 2-disubst.	44
702w	686s	679s	712m	712m			45
647m				640m			46
						γ C-H; 1, 4-disubst. (?)	47
							48
							49

The complexes were prepared by reaction of the appropriate amine with the metal chloride (in a molar proportion of 2.2 : 1) in ethanol. Zinc chloride was somewhat more versatile in its complexing ability than mercuric chloride. Thus, *p*-chloroaniline, *p*-bromoaniline and *m*-chloroaniline failed to form complexes with mercuric chloride

while *o*-anisidine failed to react with zinc chloride. The limited reactivity of the halogen-substituted anilines can be readily explained in terms of their positive Hammett σ -functions, indicative of low electron density at the carbon atom *para* (or *meta*) to the halogen substituent. This argument presupposes the reasonable assumption that the mesomeric effect of the halogen substituent is transmitted to the nitrogen atom and hence affects its donor capacity for the metal. For similar reasons it is not surprising that *o*-, *m*-, and *p*-nitroaniline (with their high positive σ -functions) failed to react with either zinc chloride or mercuric chloride. The failure of *o*-anisidine to form a complex with zinc chloride may be due to the steric hindrance imposed by the bulky methoxyl group *ortho* to the donor nitrogen atom. This effect would be more marked with the small zinc atom than with mercury.

INFRA-RED SPECTRA

The infra-red absorption frequencies for the complexes are given in Table 1 together with the vibrational assignments. Evidence for the assignments is presented below. The similar character of the spectra, which is in support of a structural similarity, enables the discussion to be based on the various regions of absorption.

The 3400-2700 cm⁻¹ region. From four to six well-resolved bands of moderate to strong intensity appear within this range of frequencies. The two bands of highest frequency can be unambiguously assigned to the asymmetric and symmetric N-H stretching vibrations. The N-H stretching frequencies of the free amines are lowered by 150-100 cm⁻¹ due to co-ordination. This shift is of similar magnitude to that observed for co-ordinated ammonia in complex amines.^{1, 2, 3} A noteworthy feature of the observed frequencies is their good agreement with the linear relationship

$$\nu(\text{sym}) = 345.5 + 0.876\nu(\text{asym})$$

reported⁴ to hold for free amines. It appears from our results that the validity of this relationship is unaffected by co-ordination of the amine.

On the other hand, the relationship

$$\nu(\text{sym}) = 1023 + 0.682\nu(\text{asym})$$

described⁵ as valid for *m*- and *p*-substituted anilines exhibits a more marked deviation from the observed frequencies for the co-ordinated amines. The discrepancies between the observed and calculated frequencies are shown in Table 2.

No well-defined relationship appears to exist between the Hammett σ -functions for the amines and the N-H stretching frequencies of the complexes. If the chief contribution to the strength of the metal-nitrogen bond arises from σ -bonding, a correlation between the σ -values and frequencies would be anticipated. On the other hand, if a mechanism similar to π -bonding were operative in these complexes, such a correlation would not be expected. Classical π -bonding concepts cannot account for metal-ligand π -bonding between a d¹⁰ metal ion and the nitrogen atom of a

primary aromatic amine. Nevertheless, there is much evidence that a mechanism similar in its effects to π -bonding may be operative in metal-amine complexes. Chatt and Gamlen⁶ found that trimethylamine complexes of platinum(II) are, despite the combined inductive effect of the three methyl groups, less stable than those of less-methylated methylamines. It has also been found⁷ that in a series of complexes *trans*-[Pt (or Pd) X₂(*p*-toluidine) (PPr₃)] (X = Cl, Br, I) the N-H stretching frequencies vary with X in a manner opposite to that which would be expected on the basis of the relative halogen electronegativities. If Pt-N π -bonding were possible and significant with respect to the stability of the molecule, the more electronegative chlorine atom would reduce the efficacy of such bonding and favour the observed lowering of the N-H frequency. Anderegg⁸ has compared the stabilities of a series of complexes comprising ligands capable of π -bonding (*e.g.* picolinic acid) with those of an analogous ligand (*e.g.* glycine) in which such additional stabilization is not formally possible. Contrary to expectation, the stability relative to the aliphatic ligand is greatest for the alkali earth metals rather than for the transition metals. Da Silva and Calado⁹ have used data pertaining to a series of silver(I)-amine complexes to calculate so-called stabilization factors which are functions of the stability constants of the complexes and the ionization constants of the bases. The stabilization factors, plotted against σ , exhibit a linear relationship with slope opposite to that for pKa - σ plots indicating stabilization by electron-withdrawing substituents.

TABLE 2

Difference of observed (ν_0) and calculated (ν_c) symmetric N-H stretching frequencies of co-ordinated amines.

Amine	Mercury complexes		Zinc complexes	
	$\nu_c - \nu_0^*$	$\nu_c - \nu_0^\dagger$	$\nu_c - \nu_0^*$	$\nu_c - \nu_0^\dagger$
aniline	0		-19	
benzylamine ..	-12		0	
<i>o</i> -toluidine ..	+ 7		-11	
<i>m</i> -toluidine ..	+ 9	+45	-14	+29
<i>p</i> -toluidine ..	+ 5	+43	0	+38
<i>o</i> -anisidine ..	+22			
<i>p</i> -anisidine ..	- 4	+37	-13	+30
<i>m</i> -chloroaniline			-16	+28
<i>p</i> -chloroaniline			- 4	+35
<i>p</i> -bromoaniline			+14	+29

*Calculated values from the relationship of Bellamy and Williams⁴

†Calculated values from the relationship of Krueger and Thompson⁵

In the spectra of many of the complexes, a band of moderate to weak intensity occurs at $3130 \pm 10 \text{ cm}^{-1}$. This is probably due to splitting of the N-H stretching band by intermolecular hydrogen bonding: N-H. . . . Cl. The observation of this band in a series of platinum-amine complexes has been reported² and its assignment to this type of bond made on the basis that it is of moderate intensity when the spectrum is taken in the solid state or in concentrated solution but is considerably weakened in dilute solution.

The aromatic C-H stretching frequencies of the complexes occur near 3033 cm^{-1} in agreement with the value reported,¹⁰ while the aliphatic C-H stretching vibration lies within the range $2950\text{--}2837 \text{ cm}^{-1}$ in accordance with the range proposed by Fox and Martin.¹¹ Co-ordination of the amines has no significant effect on the positions of these bands.

The 2700—1480 cm^{-1} region. No bands are observed in the range $2700\text{--}1650 \text{ cm}^{-1}$. For free primary aromatic amines, some confusion exists in the literature in respect of suggested assignments below 1650 cm^{-1} . This is the result of overlap of the reported ranges of $1620\text{--}1560 \text{ cm}^{-1}$ for the N-H bending (scissoring) vibration and $1,625\text{--}1575 \text{ cm}^{-1}$ for the first of the four infra-red-active aromatic ring stretching modes. Furthermore, there is little published information on the frequencies of the former vibration. Nevertheless, assignment of the bands in this region is assisted by several features.

The highest frequency aromatic ring stretching band is very little influenced by substitution in the ring.¹² It would therefore be expected that co-ordination of aromatic amines through the nitrogen atom (*i.e.* at a point removed from the ring) would have negligible effect on this frequency. In the compounds described here, there are two bands in this region to consider. These are at mean frequencies of 1612 and 1574 cm^{-1} for the mercury complexes and at 1603 and 1574 cm^{-1} for the zinc complexes. The first aromatic stretch for *p*-chloroaniline and *p*-bromoaniline has been reported at 1604 and 1597 cm^{-1} , *i.e.* within 2 cm^{-1} of our values for the co-ordinated amines if the *higher* frequency band is assigned to this mode. The intensity of this band, weak in solution spectra, is enhanced in solid state spectra, particularly in 1, 4-disubstituted benzenes;¹³ the present findings are in agreement with this.

The lower frequency band with mean wave number 1574 cm^{-1} for both the mercury and zinc complexes is ascribed to the N-H scissoring vibration. The mean value lies towards the lower frequency end of the range normally attributed to this mode in free primary aromatic amines. This is to be expected for complexed amines since they have a 4-covalent nitrogen atom and the frequency might therefore be expected to lie closer to the value associated with quaternary ammonium salts. For such ions this frequency is often encountered^{14, 15} near 1580 cm^{-1} in excellent agreement with our mean value of 1574 cm^{-1} .

The second aromatic ring stretching frequency variously reported^{12, 16} at $1590\text{--}1570$ and $1571 \pm 11 \text{ cm}^{-1}$, is frequently absent, weak or obscured in phenyl compounds¹² except where conjugation with, for example, a carbonyl group enhances its intensity.¹³ It is obscured in the spectra of the present compounds by the N-H

deformation band except for the zinc complex of *m*-chloroaniline, which, with its high N-H scissoring frequency, permits of its observation at 1572 cm^{-1} .

If the second ring stretching mode yields a weak band, the third such band is normally strong. This is true of our complexes. We can unambiguously assign the band at 1501 ± 12 (mercury complexes) and $1496 \pm 20\text{ cm}^{-1}$ (zinc complexes) to this vibration. The reported ranges^{12, 16} are 1522-1469 and $1512 \pm 12\text{ cm}^{-1}$. The influence of co-ordination on this consistently strong band is, as expected, negligible. Thus the frequencies of this band for the zinc complexes of *p*-substituted anilines (with the reported values¹² for the free amines in parentheses) are: *p*-toluidine, 1513 (1512); *p*-anisidine, 1516 (1510); *p*-chloroaniline, 1493 (1491); *p*-bromoaniline, 1488 (1487) cm^{-1} .

The 1480-1260 cm⁻¹ region. Two bands occur for most of the complexes within the range 1470-1424 cm^{-1} . This is the region of expected aliphatic C-H deformation and the fourth aromatic ring stretching vibration. Thus the complexes of aniline, with no methyl or methylene group, show only one band in this region which can be unambiguously assigned to the fourth ring stretch. However, the complexes derived from halogen-substituted anilines also exhibit two bands within the range and ambiguity in assignment arises. We tentatively suggest that (with the exception of the halogen-substituted anilines) the upper frequency band is due to the methyl (or methylene) deformation in agreement with Raman evidence¹⁷ and with the accepted frequency of approximately 1460 cm^{-1} for this mode. In support of this assignment is the fact that, for the complexes containing *p*-substituted anilines, the frequencies are low, in agreement with previous observations^{12, 13} for the unco-ordinated amines.

The 1260-1200 cm⁻¹ region. The complexes of *o*- and *p*-anisidine yield bands within the range 1258-1250 cm^{-1} as normally reported¹⁸ for alkyl aryl ether C-O-C groups.

A band of variable intensity but usually moderate to strong, at 1221 ± 15 (mercury complexes) and $1220 \pm 33\text{ cm}^{-1}$ (zinc complexes) is ascribed to the C-N stretching mode of the co-ordinated amines. Colthup¹⁸ assigns moderate to strong absorption in the range 1340-1250 cm^{-1} as due to the C-N stretching vibration in aromatic amines; usually the band is near 1260 cm^{-1} . This assignment is based on his own unpublished work and no papers have dealt in detail with these particular correlations. Two features: its persistence in the same approximate frequency range for primary, secondary and tertiary amines and the fact that, on deuteration, the band is shifted¹⁹ to near 1350 cm^{-1} support this assignment. The present results also agree with this assignment since co-ordination of the amine with a metal would lead to a shift to lower frequencies: the observed lowering is approximately 40 cm^{-1} .

In marked contrast with the lack of correlation between the Hammett σ -function and the N-H stretching frequency, a notable linear relationship is found to exist between the σ -function and the C-N stretching frequency for the co-ordinated *m*- and *p*-substituted anilines (Fig. 1). The electronic effects in a complex containing an electron-withdrawing substituent R *para* to the amino group (positive σ) are illustrated in the diagram (I). Thus amines with a positive σ -function would yield a high C-N

stretching frequency in agreement with our observations. Apparently, the mesomeric effects of the substituents R are transmitted to the C-N bond but beyond this point they are perturbed by the electron drift from the metal-donor atom.

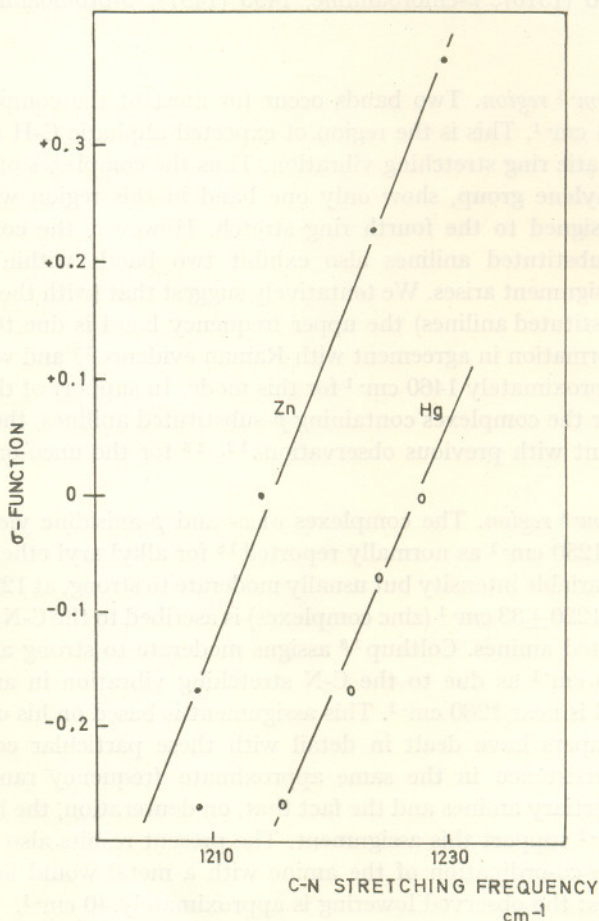
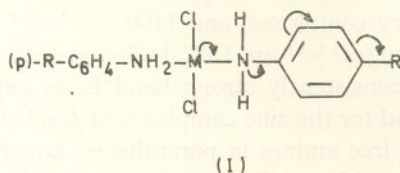


Fig. 1. Relationship between Hammett σ -function and C-N stretching frequency for co-ordinated *m*- and *p*-substituted anilines.

The 1200-950 cm⁻¹ region. In the higher frequency portion of this region the normal in-plane aromatic C-H bending vibrations occur. In all cases agreement with the reported values for the free amines is good.

A band which occurs at 993 ± 24 (mercury complexes) and 972 ± 28 cm^{-1} (zinc complexes) is probably due to a deformation mode associated with the NH_2 twist, about which very little is known. It has been reported for aniline²⁰ at 1054 cm^{-1} .

The 950-625 cm^{-1} region. Accurate assignments in this region are characteristically difficult due to lack of the required information resulting from the work of others and complication of the spectra by the various aromatic substitution patterns. Nevertheless some salient features emerge.

The B_2-B_{3u} out-of-plane aromatic C-H bending mode for 1, 4-disubstituted benzenes has been variously reported^{12, 16, 18, 21} as causing absorption in the ranges 857-808, 817 ± 13 , 860-800 and 833-810 cm^{-1} for substituents of the type present in our complexes. The frequencies are raised by strongly electron-withdrawing substituents.¹² On the other hand, the NH_2 rocking frequency has been ascribed to the 800 cm^{-1} region for quaternary ammonium compounds²² and to the range 850-800 cm^{-1} for metal amines.^{23, 24, 25}

For the amines in the present study, the C-H out-of-plane bending frequency would be expected to be practically unaffected by co-ordination while the NH_2 rocking frequency would be lowered. Between one and three prominent bands are observed for the complexes in the range 850-778 cm^{-1} . On the basis of the above evidence the highest frequency band (at 835 ± 12 cm^{-1} for mercury complexes and 829 ± 3 cm^{-1} for zinc complexes) is tentatively ascribed to the C-H out-of-plane deformation and those at 819 ± 5 and 803 ± 5 cm^{-1} (mercury complexes) and 820 ± 5 and 798 ± 20 cm^{-1} (zinc complexes) to the deformation of the amino group.

Below 775 cm^{-1} the normal aromatic substitution patterns are observed.

EXPERIMENTAL

The compounds were prepared by the addition of the amine (0.022 mole) to the metal halide (0.01 mole) in absolute ethanol. In most cases precipitation of the complex occurred immediately or after shaking. Where no precipitate was formed by this treatment, refluxing of the solution also failed to yield any product; evaporation of the solution yielded only the reactants. The complexes were obtained as colourless crystals, recrystallised from ethanol and dried at $68^\circ/0.1$ mm for 24 hr. prior to analysis and determination of the spectra. Melting points are corrected and were determined on a Kofler hot stage.

$[\text{ZnCl}_2(\text{aniline})_2]$. M.p. 228-230°. (Found: C, 44.9; H, 4.5; Cl, 22.0; N, 8.6%; *M*, 317. Calc. for $\text{C}_{12}\text{H}_{14}\text{Cl}_2\text{N}_2\text{Zn}$: C, 44.7; H, 4.4; Cl, 22.1; N, 8.7%; *M*, 323).

$[\text{ZnCl}_2(\text{benzylamine})_2]$. M.p. 198-200°. (Found: Cl, 19.9; N, 8.4. Calc. for $\text{C}_{14}\text{H}_{18}\text{Cl}_2\text{N}_2\text{Zn}$: Cl, 20.2; N, 8.0%).

$[\text{ZnCl}_2(o\text{-toluidine})_2]$. M.p. 196-198°. (Found: C, 47.0; H, 5.3; Cl, 20.2; N, 8.15. Calc. for $\text{C}_{14}\text{H}_{18}\text{Cl}_2\text{N}_2\text{Zn}$: C, 47.9; H, 5.2; Cl, 20.2; N, 8.0%).

$[\text{ZnCl}_2(p\text{-toluidine})_2]$. M.p. 235-236°. (Found: Cl, 20.1; N, 8.3. Calc. for $\text{C}_{14}\text{H}_{18}\text{Cl}_2\text{N}_2\text{Zn}$: Cl, 20.2; N, 8.0%).

[ZnCl₂(*m*-toluidine)₂]. M.p. 194°. (Found: Cl, 19.7; N, 7.8. Calc. for C₁₄H₁₈Cl₂N₂Zn: Cl, 20.2; N, 8.0%).

[ZnCl₂(*p*-chloroaniline)₂]. M.p. 245-247°. (Found: Ionic Cl, 17.7; N, 7.0. Calc. for C₁₂H₁₂Cl₄N₂Zn: Ionic Cl, 18.1; N, 7.2%).

[ZnCl₂(*m*-chloroaniline)₂]. M.p. 203-205°. (Found: Ionic Cl, 18.0; N, 7.0. Calc. for C₁₂H₁₂Cl₄N₂Zn: Ionic Cl, 18.1; N, 7.2%).

[ZnCl₂(*p*-anisidine)₂]. M.p. 219-221°. (Found: Cl, 18.3; N, 7.7. Calc. for C₁₄H₁₈Cl₂N₂O₂Zn: Cl, 18.5; N, 7.3%).

[ZnCl₂(*p*-bromoaniline)₂]. M.p. 158-160°. (Found: Cl, 14.6. Calc. for C₁₂H₁₂Br₂Cl₂N₂Zn: Cl, 14.8%).

All other compounds synthesized are known.²⁶ The observed melting points were in agreement with those reported. Spectra (KBr discs) were determined on a Beckman IR-8 instrument (reproducibility approximately 2 cm⁻¹ at 1400 cm⁻¹). σ -Functions used were taken from the compilation of Jaffe.²⁷

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