INVESTIGATIONS ON ORGANOZINC COMPOUNDS

II*. SYNTHESIS AND ABSORPTION SPECTRA OF SOME 2,2'-BIPYRIDINE AND 1,10-PHENANTHROLINE COMPLEXES OF ORGANOZINC COMPOUNDS

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INTRODUCTION

Most coordination complexes of zinc dialkyls and diaryls with mono- and bidentate ligands are colourless[1–5], but certain complexes with 2,2'-bipyridine and 1,10-phenanthroline are reported to be coloured[6–8]. Dimethyl(2,2'-bipyridine)zinc and dimethyl(1,10-phenanthroline)zinc, first mentioned by Coates and Green[6,7], are yellow, whereas complexes of dimethylzinc with a number of tertiary and ditertiary amines, recently isolated by Thiele[5], are colourless.

The present paper deals with the preparation and light absorption behaviour of a variety of coloured 2,2'-bipyridine and 1,10-phenanthroline organozinc complexes.

RESULTS

From the reaction between a number of dialkylzinc compounds and diphenylzinc with 2,2'-bipyridine in an inert solvent, coloured solutions were obtained from which crystalline 1:1 complexes were isolated. The colour of these organozinc complexes depends on the nature of the organic groups bound to zinc, *e.g.* red for R = isopropyl and slightly yellow for R = phenyl. This effect was further checked by the preparation of the 2,2'-bipyridine complex of recently reported bis(pentafluorophenyl)zinc[1]; this complex is colourless. For the sake of comparison, the 2,2'-bipyridine complex of zinc bromide was included in the experiments. In order to investigate the influence of the nature of the ligand in this type of complex a few 1,10-phenanthroline complexes were synthesized as well. The synthetic results are summarized in Table 1.

Contrary to the corresponding dimethylzinc complexes, which are relatively stable[7,8], the higher alkyl- and phenylzinc complexes are extremely sensitive towards air and moisture, especially in dilute solution.

Absorption spectra of these complexes have been recorded in the UV and visible region. The spectra of some of the complexes are shown in Figs. 1 and 2. The values of λ_{max} and log ε_{max} of the long-wavelength absorptions and the colours of the complexes are presented in Table 2. The excitation energies of the electronic transition involved may be calculated from λ_{max}. For correlation purposes the electronegativity values

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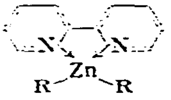
* Part I: ref. 1.

TABLE 1

SOME 2,2'-BIPYRIDINE AND 1,10-PHENANTHROLINE COMPLEXES OF ORGANOZINC COMPOUNDS

Complex	*R*	*M.p.* (°*C*)	*Formula*	*Zinc* %	
				Calcd.	*Found*
	(I, a) iso-C_3H_7	100–101	$C_{16}H_{22}N_2Zn$	21.28	21.45
	(I, b) *n*-C_4H_9	57–58	$C_{18}H_{26}N_2Zn$	19.47	19.31
	(I, c) C_2H_5	114–115	$C_{14}H_{18}N_2Zn$	23.40	23.48
	(I, d) C_6H_5	199–201	$C_{22}H_{18}N_2Zn$	17.40	17.56
	(I, e) C_6F_5	~ 250 (dec.)	$C_{22}H_8F_{10}N_2Zn$	11.78	11.54
	(I, f) Br	> 360	$C_{10}H_8Br_2N_2Zn$	17.15	17.20
	(II, a) *n*-C_4H_9	73–74	$C_{20}H_{26}N_2Zn$	18.17	17.86
	(II, b) C_2H_5	123 (dec.)	$C_{16}H_{18}N_2Zn$	21.55	22.06
	(II, c) C_6H_5	197–199	$C_{24}H_{18}N_2Zn$	16.36	16.41
	(II, d) C_6F_5	*	$C_{24}H_8F_{10}N_2Zn$	11.29	11.18

* Gradual decomposition without melting starts at ~ 140°.

x_R according to Pritchard and Skinner[9] of the substituent groups bound to zinc are given as well.

TABLE 2

UV AND VISIBLE SPECTRA OF SOME 2,2'-BIPYRIDINE AND 1,10-PHENANTHROLINE ORGANOZINC COMPLEXES

Complex[a]		*Colour*	λ_{max} (*mμ*)	*log*ε_{max}	*E* (*kcal/mole*)	x_R
(I, a)	iso-C_3H_7	dark red	480	2.63	59	1.97
			365	2.70	78	
(I, b)	*n*-C_4H_9	red	425	2.56	67	—
(I, c)	C_2H_5	orange red	420	2.77	68	2.10
(I, d)	C_6H_5	sl. yellow	350	2.91	82	2.38
(I, e)	C_6F_5	colourless	309	4.15	92	(2.76)[b]
			298	4.14	96	
(I, f)	Br	colourless	310	4.13	92	2.76
			301	4.13	95	
(II, a)	*n*-C_4H_9	red	440	2.79	65	—
(II, b)	C_2H_5	orange red	427	2.95	67	2.10
(II,c)[c]	C_6H_5	sl. yellow	361	3.01	78	2.38

[a] Compare Table 1. [b] Compare refs. 11 and 12. [c] Complex (II, d) is colourless.

DISCUSSION

(In cooperation with Dr. J. A. VLIEGENTHART, Laboratory for Organic Chemistry, University of Utrecht.)

The colour of the complexes, which may be varied from dark red to colourless simply by changing the organic group bound to zinc, cannot be explained from the spectra of the individual components. The long-wavelength absorption maximum of 2,2'-bipyridine is found at 282 mμ (log $\varepsilon = 4.17$). Organozinc compounds do not absorb beyond this wavelength. The spectra of the 2,2'-bipyridine complexes (I, a–d) display a new, broad band in the 300–500 mμ region (Figs. 1 and 2). This band shows two maxima for the isopropyl complex (I, a). Similarly, the spectra of the 1,10-phenanthroline complexes (II, a–c) display a new broad band (Fig. 2).

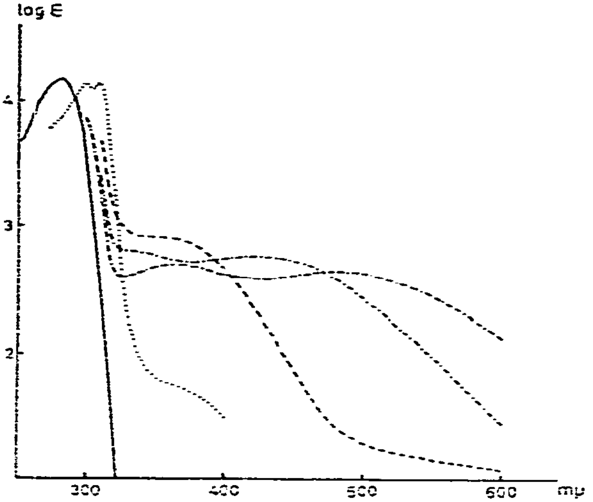


Fig. 1. UV and visible absorption spectra of —— 2,2'-bipyridine, ——·—— (I, a), —·—·— (I, c), ——— (I, d) and ----- (I, e) (compare Table 1).

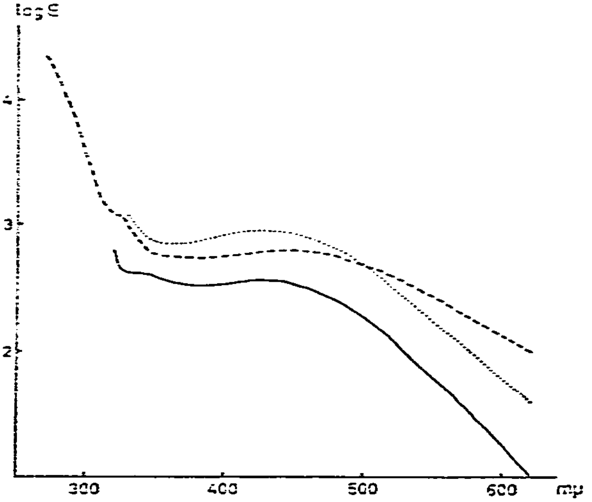


Fig. 2. UV and visible absorption spectra of —— (I, b), ------ (II, a) and ····· (II, b) (compare Table 1).

The data in Table 2 clearly show that the new absorption band shifts to shorter wavelength when the groups bound to zinc become more electron-attracting. Pritchard and Skinner have calculated from thermochemical data pertaining to the gas-phase redistribution reaction $HgR_2 + HgX_2 \rightarrow 2RHgX$ electronegativity values x_R for a number of organic radicals[9]. A plot of the excitation energy of the long-wavelength absorption *versus* x_R for the corresponding group bound to zinc provides the linear relationship shown in Fig. 3. The data in Table 2 show that the dibutylzinc complex (I, b) fits this graph, the butyl group being slightly more electropositive than the ethyl group[9, 10].

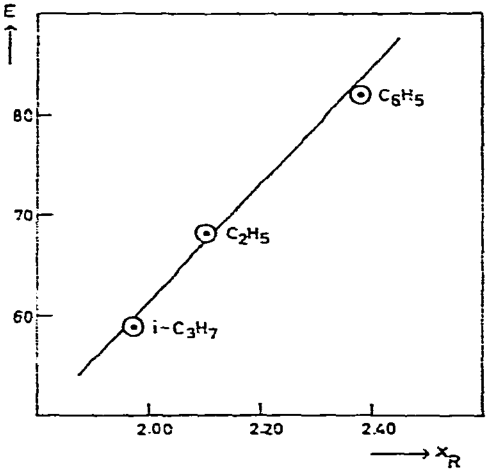


Fig. 3. Correlation of excitation energy E(kcal/mole) with the electronegativity x_R of the substituent groups for some 2,2′-bipyridine organozinc complexes.

The colourless 2,2′-bipyridine complex of bis(pentafluorophenyl)zinc (I, e) shows an identical UV absorption pattern as the zinc bromide complex (I, f), namely a narrow, double band at ~ 300 mμ (Table 2). The different shape of this band is apparent (Fig. 1). As for both complexes no absorption is observed around 280 mμ this band most probably is the long-wavelength absorption of 2,2′-bipyridine shifted to somewhat longer wavelength. The high value of the extinction coefficients supports this view. Recently it has been shown by the study of NMR[11] and Mössbauer[12] spectra of (pentafluorophenyl)tin derivatives that the pentafluorophenyl group and the bromine atom have approximately the same electron-attracting properties. Assuming an x_R-value of 2.76 (electronegativity of bromine[9]) for the pentafluorophenyl complex (I, e) and using the graph in Fig. 3 for extrapolation purposes, the long-wavelength band as found for the other complexes would be expected at ~ 290 mμ. Thus, the possibility that this band is obscured by the bipyridine band cannot be ruled out.

The observation that the 1,10-phenanthroline complexes (II, a–c) absorb at a somewhat longer wavelength than the corresponding 2,2′-bipyridine complexes (Table 2, Fig. 2) suggests that the electronic transition under discussion involves the π-electron system of the ligands. The fact that electronegative groups on zinc increase the required excitation energy indicates that in the excited state of the complex the R_2Zn group acts as an electron-donor.

Similar charge-transfer bands[13] have been observed in the spectra of beryllium complexes of the type BeX_2-2,2'-bipyridine[6,7]. For these complexes both the values of λ_{max} and of the extinction coefficient of the charge-transfer band decrease as the electron-attracting character of the group X attached to beryllium increases. The suggestion was put forward that charge-transfer occurs from one of the Be–X bonds to the lowest unoccupied orbital of 2,2'-bipyridine[7].

Whereas for the organozinc complexes a similar relation exists between electronegativity and wavelength of the charge-transfer band, a reversed trend is observed with respect to the absorption intensities (Table 2).

Participation of *d*-electrons in the charge-transfer, clearly impossible for the organoberyllium complexes, must be considered for the organozinc complexes. With simple M.O.-theory it can be shown that interactions between filled 3*d*-orbitals of zinc with the highest filled and lowest unfilled molecular orbitals of the ligand account for the observed spectral data. It should be remembered that with dicyclopentadienyl- and related π-complexes the origin of the metal *d*-orbitals is also placed in the gap between the filled and unfilled ligand molecular orbitals. The energy of the zinc *d*-orbitals and hence their interaction with the π-molecular orbitals of the ligand will depend on the nature of the alkyl or aryl group attached to the zinc atom. The transition energy (λ_{max}) and transition moment (log ε) will change accordingly.

The absorption spectra of 2,2'-bipyridine and 1,10-phenanthroline complexes of a number of transition metal ions (among which the d^{10}-ion Cu^+) display long-wavelength charge-transfer bands arising from the transition of *d*-electrons to vacant π-type ligand orbitals[14]. Zn^{2+} complexes failed to show such bands[14]. The tendency of d^{10}-transition metal ions towards $d\pi$-bond formation has been correlated with their ionization energies[15]. The role of $d\pi$–$d\pi$ bonding in ditertiary arsine complexes of d^{10}-ions, including the Zn^{2+} ion, has been considered unimportant in view of the high ionization potential of the non-bonding d^{10}-shell of these ions[16]. However, because the zinc–carbon bond has largely covalent character, the formal positive charge of the zinc atom and, accordingly, the ionization energy of a 3*d*-electron will be considerably less for the organo complexes (I, a–d; II, a–c), than for the zinc bromide complex (I, f) which most probably has no charge-transfer band in its spectrum (compare ref. 14).

EXPERIMENTAL PART

The organozinc complexes have been prepared in a nitrogen atmosphere using recently described techniques[17].

UV absorption spectra have been recorded in anhydrous toluene solution using a Beckman model DU-spectrophotometer. Solutions were prepared and transferred as described in ref. 17. The spectrum of 2,2'-bipyridine was recorded in cyclohexane.

2,2'-Bipyridine and 1,10-phenanthroline (resublimed) were commercial preparations. Dialkylzincs[18], diphenylzinc[19] and bis(pentafluorophenyl)zinc[1] were prepared according to the literature.

Preparation of complexes (see Table 1)

Di-n-butyl(2,2'-bipyridine)zinc (I, b). To a solution of 1.56 g (10 mmoles) of 2,2'-bipyridine in 75 ml of pentane 2.0 ml (11 mmoles) of di-*n*-butylzinc were added by means of a syringe. A dark-red solution resulted from which upon cooling at —70° orange-red crystals separated. After removal of the supernatant liquid with a syringe the crystals were washed twice with 20 ml of pentane at —80° and after removal of traces of pentane *in vacuo* sealed into ampoules. M.p. 53–54°.

Complexes (I, a) and (I, c) were obtained in essentially the same way.

Diphenyl(2,2'-bipyridine)zinc (I, d). Upon mixing solutions of 1.56 g (10 mmoles) of 2,2'-bipyridine in 50 ml of pentane and of 2.40 g (11 mmole) of diphenylzinc in 30 ml of benzene a yellow solution resulted from which slightly yellow crystals separated immediately. After cooling at 0° and removing the supernatant liquid, the crystals were washed with pentane and after drying sealed into ampoules. M.p. 199–201°.

Bis(pentafluorophenyl)(2,2'-bipyridine)zinc (I, e). This complex precipitated immediately upon mixing solutions of equimolecular amounts of both reactants in pentane. A small quantity of slightly yellow, amorphous, benzene-insoluble material was removed by recrystallization of the complex from benzene–pentane (1:4). Colourless crystals with m.p. ~ 250° (dec.).

Dibromo(2,2'-bipyridine)zinc (I, f). The complex was precipitated by mixing solutions of equimolecular amounts of the reactants in ethanol, collected by filtration, washed with ethanol and dried. Colourless microcrystalline solid with m.p. > 360°.

Di-n-butyl(1,10-phenanthroline)zinc (II, a). To a solution of 2.73 g (15 mmoles) of 1,10-phenanthroline in 20 ml of benzene, 2.9 ml (16 mmoles) of di-*n*-butylzinc were added by means of a syringe. The resulting dark-red solution failed to yield crystals after being kept at —70° and warmed to room temperature. The solvent was evaporated *in vacuo* and the crystalline residue extracted with pentane leaving a chocolate-brown residue. The pentane extract upon cooling at —70° afforded red crystals which after one more crystallization from pentane melted at 73–74°.

Complex (II, b) was obtained similarly.

Diphenyl(1,10-phenanthroline)zinc (II, c). To a solution of 1.80 g (10 mmoles) of 1,10-phenanthroline in 60 ml of benzene kept at 75° 2.40 g (11 mmoles) of diphenylzinc dissolved in 25 ml of benzene was added. The dark-yellow solution thus obtained upon standing afforded slightly yellow crystals which after washing with pentane and drying *in vacuo* melted at 197–199° (dec.).

Complex (II, d) was obtained similarly, but the product was once recrystallized from benzene–pentane (1:3).

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SUMMARY

Coloured 2,2'-bipyridine and 1,10-phenanthroline complexes of a number of organozinc compounds have been prepared. The colour of these complexes deepens

with decreasing electron-attracting character of the organic groups bound to zinc.

The long-wavelength absorption in their UV and visible spectra is discussed in terms of a charge-transfer transition from the organozinc moiety of the complex to the ligand. The role of d_π-interaction of metal and ligand is discussed.

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