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Electrochemical Reduction and Electron Spin Resonance Studies of Organozinc Complexes

M. F. EL-SHAZLY*

Department of Chemistry, Faculty of Science, Science Center for Advancement of Post Graduate Studies, Alexandria University, Alexandria, Egypt

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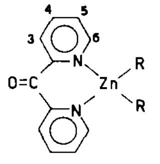
The electrochemical behaviour of organozinc complexes with di-2-pyridylketone, 1,2-bipyridine and 1,10-phenanthroline as ligands were investigated. The complexes showed two reductive waves in 1,2-dimethoxyethane (DME) as a solvent and tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte. Controlled potential electrolysis at the plateau of the first wave produced coloured radical anions. The esr spectra of the radical anions showed that the unpaired electron is delocalized mainly over the ligand π-system.

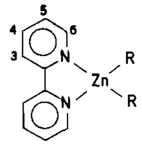
Introduction

In recent years, there has been a growing interest in organozinc compounds due to the fact that they are of biological importance. Metal chelates of Zn(II) together with a variety of ligands such as 2,2-bipyridine and 1,10-phenanthroline were prepared [1, 2], and their biological activities were tested. It is a common fact that most zinc complexes are colourless but recently coloured organozinc compounds have been prepared [3–5]. Organozinc complexes of the general structure R_2LZn (L = 2,2-bipyridine or 1,10-phenanthroline) were found to be of different colours, depending on the nature of the R-group. The colours of these compounds were attributed to the charge-transfer from the filled d-electron orbitals to the vacant π-type ligand orbitals.

These investigations deal with the electrochemical reduction of these compounds. The electrochemical reduction of organozinc complexes with di-2-pyridylketone (I), 2,2-bipyridine (II) and 1,10-phenanthroline (III) was investigated with 1,2-dimethoxyethane as a solvent.



I



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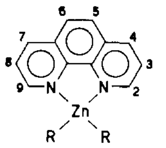

III

Where R = C_2H_5 or C_6H_5

Experimental

The organozinc complexes of 2,2-bipyridine and 1,10-phenanthroline were prepared in a nitrogen atmosphere according to the methods reported in the literature [3–5].

Preparation of Organozinc Complexes with Di-2-pyridylketone

Diethyl(di-2-pyridyl)zinc

To a solution of 0.01 mol di-2-pyridylketone in 50 ml dry monoglyme, 0.01 mol of diethyl zinc was added by means of a syringe under nitrogen. A dark orange solution resulted, which was then cooled overnight. Yellow–orange crystals separated and were washed with dry ether (m.p. 70–72 °C (dec)). *Anal.* Calcd. for $C_{15}H_{18}N_2O$ Zn: C, 64; H, 6.00 and N, 9.0%. Found: C, 63.95; H, 6.20 and N, 8.89%.

Diphenyl(di-2-pyridylketone)zinc

A solution of 0.01 mol di-2-pyridylketone in 50 ml dry monoglyme was mixed with 0.01 mol diphenylzinc. The resulting dark yellow solution was left overnight under nitrogen to give yellow crystals (m.p. 200 °C (dec)). *Anal.* Calcd. for $C_{23}H_{18}N_2O$ Zn: C, 68; H, 4.00 and N, 7.00%. Found: C, 67.60; H, 3.98 and N, 6.87%.

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*Present address: Chemistry Department, Northeastern University, Boston, Massachusetts 02115, U.S.A.

TABLE I. Polarographic Reduction Data for Organozinc Complexes.

Compound	$-E_{1/2}^{1}$[a], v	(n)	$-E_{1/2}^{2}$, v	Color	
				Neutral	Radical
(Di-2-pyridylketone)Zn$(C_2H_5)_2$	2.30	(1)	2.90	orange	purple
(Di-2-pyridylketone)Zn$(C_6H_5)_2$	2.32	(1)	2.91	orange	purple
(2,2-Bipyridine)Zn$(C_2H_5)_2$	2.76	(1)	3.20	orange–red	green
(2,2-Bipyridine)Zn$(C_6H_5)_2$	2.70	(1)	3.18	pale yellow	green
(1,10-Phenanthroline)Zn$(C_2H_5)_2$	2.40	(1)	3.24	orange–red	green
(1,10-Phenanthroline)Zn$(C_6H_5)_2$	2.35	(1)	3.25	pale yellow	blue
Organic Ligands[b]					
Di-2-pyridylketone	2.31		2.91	colorless	green
2,2-Bipyridine	2.80		3.11	colorless	green
1,10-Phenanthroline	2.72		3.24	colorless	dark green

[a] $E_{1/2}$ with reference to ($10^{-3}M$) Ag/Ag$^+$ in DME and TBAP as a supporting electrolyte. [b] Values taken from reference 9.

The electrochemical work and the preparation of esr samples were performed in a dry box under an argon atmosphere. The electrochemical methods and instrumentation were identical with those described by Dessy and coworkers [6, 7]. The half-wave potential ($E_{1/2}$) values were taken relative to a Ag/Ag$^+$ ($10^{-3}M$) reference solution with 1,2-dimethoxyethane (DME) as a solvent and tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte.

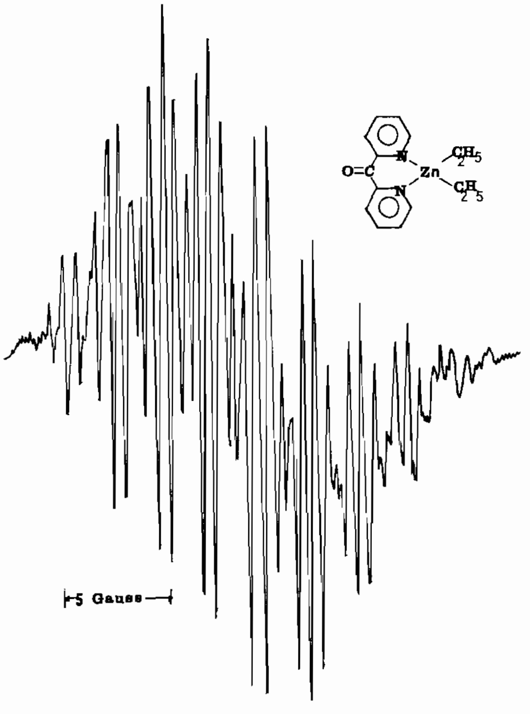


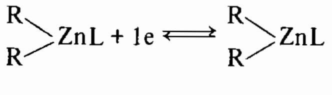
Figure 1. ESR spectrum of diethyl(di-2-pyridylketone)zinc in DME.

Electron Spin Resonance

The radicals generated by electrochemical reduction were placed in a standard esr quartz tube fitted with a Delmar teflon needle valve. The esr spectrophotometer used was a Varian E-3 unit with a variable temperature accessory. The esr spectra were simulated using a program similar to the one described by Stone and Maki [8].

Results and Discussion

The electrochemical reduction of organozinc complexes exhibited two reductive waves in 1,2-dimethoxyethane as a solvent and the results collected are shown in Table I. Analysis of the waves showed that the plots of –E vs. log i/i$_d$ – i from the polarographic data gave a slope close to that expected for a one electron reversible reduction (59 mv) for the first wave while the second wave was irreversible in nature. The half-wave potentials, especially the first one, showed a slight shift by comparison with the $E_{1/2}$ of the free ligands. The exhaustive controlled potential electrolysis at the plateau of the first wave involved a one electron reduction process (n = 1). In all the cases there were changes in the colour of the neutral species upon reduction (Table I).



$$R_2ZnL + 1e \rightleftharpoons R_2ZnL$$

Electron Spin Resonance Results

Di-2-pyridylketone complexes

Electrolysis of a $10^{-3}M$ solution of diethyl(di-2-pyridylketone)zinc in DME at –2.50 volts resulted in a purple solution. A highly resolved esr spectrum of the generated radical is shown in Fig. 1. A large splitting of 4.8 gauss, due to a nucleus of spin I = 1/2 was seen in the spectrum and attributed to the

TABLE II. ESR Data of the Organozinc Complexes.

Compound*	g	Hyperfine Coupling Constant a_i, gauss	
(di-2-pyridyl)ZnR_2	2.0026	$a_{H_{5,5}}$	4.80
		$a_{N,N}$	2.46
		$a_{H_{3,3}}$	1.24
		$a_{H_{4,4}}$	0.87
		$a_{H_{6,6}}$	0.45
(2,2-bipyridine)ZnR_2	2.0024	$a_{H_{5,5}}$	4.91
		$a_{N,N}$	2.48
		$a_{H_{3,3}}$	1.40
		$a_{H_{4,4}}$	0.70
		$a_{H_{6,6}}$	0.68
(1,10-phenanthroline)ZnR_2	2.003	$a_{H_{3,8}}$	5.38
		$a_{N,N}$	2.72
		$a_{H_{5,6}}$	0.20

*R = C_2H_5 or C_6H_5. The assignments of the hyperfine coupling constants are based on successful computer simulation; where a possible ambiguity exists the assignment is based on known assignments in model compounds.

protons 5 and 5′. The second largest splitting of 2.46 gauss was assigned to the nitrogen atoms (I = 1). The splitting from protons 3,3′ was found to be equal to 1.24 gauss and small splitting of 0.87 and 0.45 gauss resulted from protons 4,4 and 6,6 respectively. The assigned hyperfine coupling constants are given in Table II. Computer simulation supports such assignments. Reduction of diphenyl(di-2-pyridylketone)-zinc gave a purple radical anion with similar esr spectrum. Both compounds showed an isotropic g-factor of 2.0026.

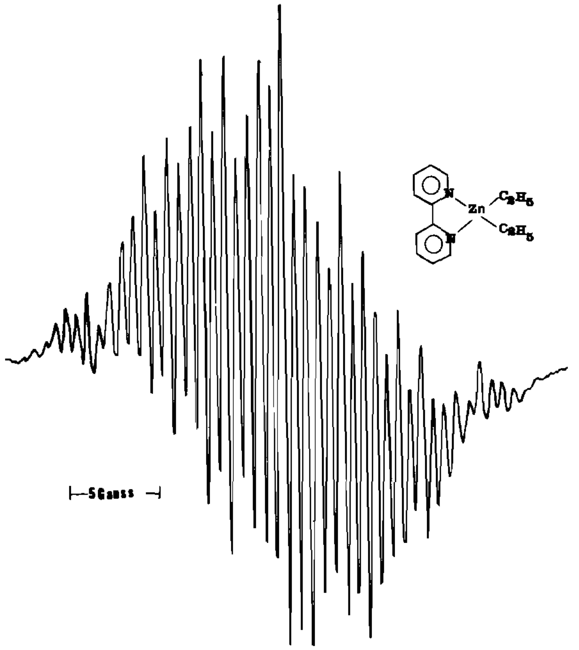


Figure 2. ESR spectrum of diethyl(2,2-bipyridine)zinc in DME.

1,2-bipyridine complexes

Diethyl(2,2-bipyridine)zinc: Electrolysis at −2.85 volts yielded first a dark red colour which then changed to green. A well resolved esr spectrum with an isotropic g-value of 2.0024 is shown in Fig. 2. The spectrum has a total width of about 29.0 gauss and there are considerable hyperfine overlappings. The assigned hyperfine coupling constants, based on computer simulations, are given in Table II.

Diphenyl(2,2-bipyridine)zinc: Reduction at −2.80 volts gave a green radical anion with an esr spectrum similar to the above mentioned.

1,10-phenanthroline complexes

Electrochemical reduction at −2.50 volts gave a blue solution in case of R = phenyl, while for R = C_2H_5, the orange solution turned to a green colour.

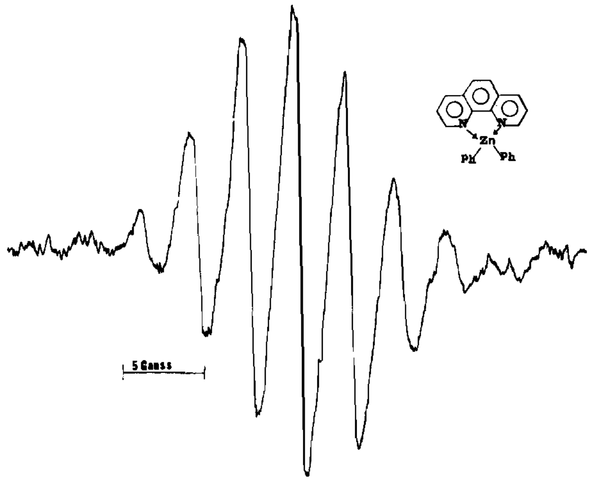


Figure 3. ESR spectrum of diphenyl(1,10-phenanthroline)-zinc in DME at −50 °C.

The esr spectrum of diphenyl(1,10-phenanthroline)-zinc at −50 °C is shown in Fig. 3. Attempts have been made to obtain a well resolved spectrum at very low temperatures, but without success. The line broadening may be due to the increased delocalization of the ligand π-system which leads to more overlapping hyperfine components. The assigned hyperfine coupling constants for R = phenyl and ethyl are in Table II.

Therefore, the esr results for the produced radical anions showed no evidence for any hyperfine interaction with the moiety ZnR_2. The hyperfine coupling constant (Table II) of the radical anions are in good agreement with those reported for the free ligand radical anions [6, 9, 10], which indicates that upon reduction the electron is mainly delocalized over the ligand π-orbitals.

Obviously, the coordination with organozinc compounds, ZnR_2, leads to the stabilization of the ligand free radical anions. The same phenomenon has been found in the electrochemical and chemical reduction of β-diketone ligands with non-transition metals such as BR_2 moiety [11, 12] and reduction of β-diketone metal complexes with Grignard reagents [13].

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References

1 A. Shulman and F. P. Dwyer, in "Chelating Agents and Metal Chelates", Ed. F. P. Dwyer and D. P. Mellor, Academic Press (1964) p. 383.
2 M. F. Dunn, *Structure and Bonding, 23,* 61 (1975).
3 G. E. Coates and S. I. E. Green, *Proc. Chem. Soc.,* 376 (1961).
4 G. E. Coates and S. I. E. Green, *J. Chem. Soc.,* 3340 (1962).
5 J. G. Noltes and J. W. E. Van Den Hurk, *J. Organometal. Chem., 3,* 222 (1965).
6 R. E. Dessy, R. B. King and M. Waldrup, *J. Am. Chem. Soc., 88,* 5112 (1966).
7 R. E. Dessy, W. Kitching and M. Waldrup, *J. Am. Chem. Soc., 88,* 453 (1966).
8 F. W. Stone and A. H. Maki, *J. Chem. Phys., 38,* 1999 (1963).
9 R. E. Dessy and L. Wieczorek, *J. Am. Chem. Soc., 91,* 4963 (1969).
10 R. E. Dessy, J. C. Charkoudian and A. L. Rheingold, *J. Am. Chem. Soc., 94,* 738 (1972).
11 R. E. Dessy, M. F. El-Shazly and J. C. Schug. To be published.
12 M. F. El-Shazly, *Ph. D. Dissertation,* Virginia Polytechnic and State University, Virginia (1972).
13 C. L. Kwan and J. K. Kochi, *J. Am. Chem. Soc., 98,* 4903 (1976).