January, 1980] © *The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, ***53***, *271—272 (1980)*

Electron Spin Resonance Spectra of Square Planar Cobalt(II) Complexes with Various N_4-Macrocyclic Ligands

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(Received May 18, 1979)

Synopsis. ESR spectra of square planar cobalt(II) complexes with various N_4-macrocyclic ligands were measured, the results being discussed in relation to the π-basicity and π-conjugation of the macrocyclic ligands.

Square planar low-spin cobalt(II) complexes can be classified into complexes of the $(d_{xy})^2(d_{z^2})^1$ ground state(Type I) and those of the $(d_{xy})^2(d_{yz})^1$ ground state(Type II).[1–5] The diagnosis of the compounds can be carried out by means of ESR spectra; $|A_3|$ (g_3 is the ESR peak observed at the highest field) is always larger than 100×10^{-4} cm^{-1} in Type I complexes but much smaller than this in Type II compounds. A number of compounds were subjected to analysis on this basis. From the results, it was found that complexes with electrically neutral ligands, phthalocyanine and porphyrins belong to Type I, and those with dinegatively charged ligands to Type II. This is interpreted as Type I complexes being formed with π-neutral or very weak π-basic ligands, and Type II complexes with fairly strong π-bases.[6]

In this study, we have measured the ESR spectra of square planar cobalt(II) complexes with tetraazamacrocyclic ligands (Fig. 1 (e)—(j)) in order to confirm this view.

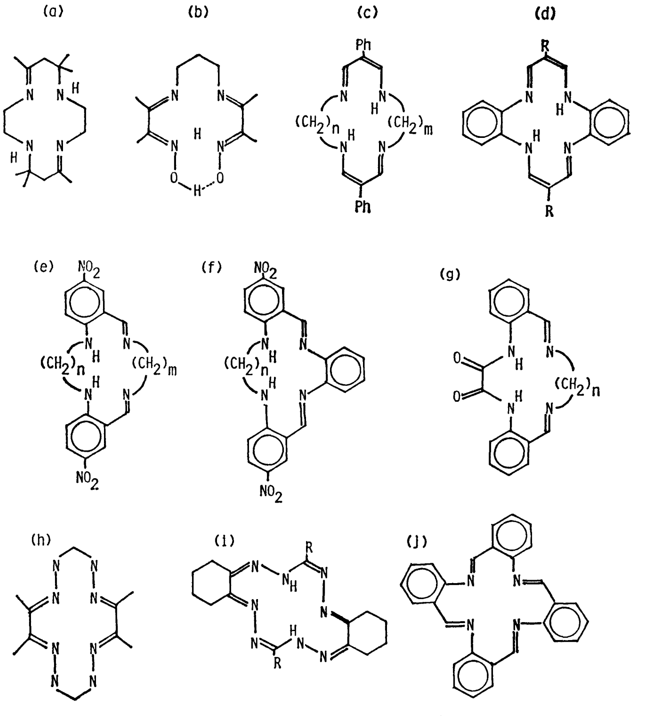

Fig. 1. N_4-Macrocyclic ligands cited in this paper. Abbreviations are: (a); (a-14), (b); H(b-14), (c); H_2(c-14), $n=m=2$, H_2(c-15), $n=2$, $m=3$, (d); H_2(d-14), R=phenyl, H_2(d-14′), R=*p*-tolyl, (e); H_2(e-14), $n=m=2$, H_2(e-15), $n=2$, $m=3$, H_2(e-15′), $n=3$, $m=2$, (f); H_2(f-14), $n=2$, H_2(f-15), $n=3$ (g); H_2(g-14), $n=2$, H_2(g-15), $n=3$, (h); (h-14), (i); H_2(i-14), $R=CH_3$, H_2(i-14′), $R=C_2H_5$, (j); (j-16).

Experimental

Preparation. The ligands and their metal complexes were prepared according to the methods reported. ((e),[7] (f),[7] (g),[8] (h),[9] (i),[10] and (j)[11]). New compounds were prepared as follows.

[Co(i-14)]: To a methanol solution (20 ml) of cobalt(II) acetate (0.001 mol) was added a benzene solution (10 ml) of the ligand, H_2 (i-14) (*cf.* Fig. 1, $R=CH_3$) (0.001 mol) under an atmosphere of nitrogen, and the resulting solution was warmed at 60 °C for 1 h. After the solution had been cooled, violet crystals deposited.

H_2 (f-14) and H_2 (f-15): A DMF solution (100 ml) of $[Mn(py)_4(NCS)_2]$[12] (0.001 mol), *N,N′*-bis(2-formayl-4-nitrophenyl)ethylenediamine[7] (0.001 mol) (or its 1,3-propanediamine derivative) and *o*-phenylenediamine (0.002 mol) was refluxed for several hours. After the solution had beed cooled, yellow crystals deposited. Analytical data of the compounds are given in Table 1.

Table 1. Analytical data of the new compounds

Compound	Found (Calcd) (%)		
	C	H	N
H_2(f-14)	61.19(61.39)	4.18(4.22)	19.47(19.52)
H_2(f-15)	61.89(62.16)	4.50(4.54)	18.90(18.90)
[Co(f-14)][a)]	53.76(53.79)	3.32(3.35)	17.32(17.11)
[Co(f-15)][a)]	55.02(54.58)	3.62(3.59)	16.79(16.63)
[Co(i-14)]	50.10(49.87)	5.92(5.75)	29.53(29.08)
[Co(i-14′)]	52.81(52.30)	6.43(6.34)	27.44(27.11)

a) Obtained by the use of free ligands obtained in this study, and not a new complex.

Measurements. ESR spectra were obtained with a JEOL ESR apparatus model MEX-3X at liquid nitrogen temperature. For ESR measurements, all the cobalt(II) complexes were diluted in the corresponding nickel(II) complexes. The diluted samples were obtained by the use of template reactions except for [Co(f-14)] and [Co(f-15)]. For the latter complexes, the free ligands we prepared were used for obtaining diluted samples.

Results and Discussion

The ESR parameters are summarized in Table 2 together with some related data.[2–4] It is seen that the complexes are satisfactorily classified into Types I and II by their $|A_3|$ values. The results are completely in line with our view that all the complexes with dinegatively charged ligands belong to Type II.

In some Type II pairs of compounds, [Co(c-14)] and [Co(d-14)], [Co(e-14)], and [Co(f-14)], and [Co(e-15)] and [Co(f-15)], π-conjugation is assumed to be

Table 2. ESR parameters of cobalt(II) complexes

Type	Complex	g_1	g_2	g_3	$\lvert A_1\rvert$	$\lvert A_2\rvert$	$\lvert A_3\rvert$	Ref.
					10^{-4} cm^{-1}			
I	[Co(a-14)]$^{2+}$	2.57	2.37	2.02	102	83	138	3
	[Co(b-14)]$^{+}$	2.88	2.28	2.04	199	97	173	4
	[Co(h-14)](ClO$_4$)$_2$	2.47	2.33	1.93	82	60	120	a)
	[Co(j-16)](ClO$_4$)$_2$	2.62	b)	2.02	106	b)	130	a)
II	[Co(c-14)]	2.676	b)	1.97	0	b)	32	4
	[Co(d-14)]	4.256	1.71	1.53	397	30	55	2
	[Co(d-14′)]	4.057	1.70	1.55	352	b)	b)	2
	[Co(e-14)]	3.07	b)	b)	122	b)	b)	a)
	[Co(f-14)]	3.45	1.84	1.84	206	30	30	a)
	[Co(g-14)]	3.862	b)	b)	330	b)	b)	a)
	[Co(i-14)]	3.91	1.67	1.56	341	28	55	a)
	[Co(i-14′)]	3.30	1.91	1.90	165	b)	28	a)
	[Co(c-15)]	2.874	2.04	1.94	47	b)	35	4
	[Co(e-15)]	2.98	2.02	1.99	92	41	22	a)
	[Co(e-15′)]	3.19	1.99	1.90	139	29	24	a)
	[Co(f-15)]	4.00	b)	b)	365	b)	b)	a)
	[Co(g-15)]	3.25	2.16	1.97	190	55	54	a)

a) This work. b) Accurate values not obtained.

more developed in the latter than in the former, because ethylenediamine-ring is substituted for *o*-phenylenediamine-ring in the latter complexes. g_1 and $|A_1|$ (the ESR peak observed at the lowest field) of the latter complexes are larger than those of former complexes. This can be explained by the theoretical interpretation of g and $|A|$ values for square planar cobalt(II) complexes.[3] We showed that g_1 (and also $|A_1|$) corresponds to g_x ($|A_x|$) in Type II complexes, increasing considerably with decrease in Δ_{z^2}, which denotes the energy difference between $(d_{xy})^2(d_{z^2})^1$ and $(d_{xy})^2(d_{yz})^1$ states (*cf.* Fig. 2 in Ref. 3). From the results of X-ray crystal structure determination on analogous complexes,[13] it can be expected that all the 14-membered macrocyclic metal complexes such as [Co(c-14)], [Co(d-14)], [Co(f-14)], and [Co(i-14)], have essentially a planar structure. Thus, the present ESR results suggest that the increase of π-conjugation brings about the decrease of the energy difference between $(d_{xy})^2(d_{z^2})^1$ and $(d_{xy})^2(d_{yz})^1$, *i.e.*, the ground state of Type II compound approaches the cross-over region between Type I and Type II, when π-conjugation of the ligand increases.

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