BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 1—7 (1967)

The ESR Study of the Ion Pair Complexes of *m*-Iodonitrobenzene with Alkali and Alkaline Earth Metals

Kazuo NAKAMURA[*1]

Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto

(Recieved February 8, 1966)

The ESR spectra of the ion-pair complexes of the *m*-iodonitrobenzene anion with alkali and alkaline earth cations were measured. Cation-induced variations in the nitrogen and proton splitting constants were found. When the observed alkali metal splittings were related to the back-transferred charge, ρ, on the ns-shell of each metal, ρ increased in the sequence: Li<Na<K<Rb<Cs at 20°C. The solvent and the temperature effects on alkali-metal splitting varied with the alkali metal. The Cs and Rb splitting constants increased in the sequence: DME<THF<THP solutions, and were independent of the temperature. The Na and Li splitting constants decreased in the above sequence of solvents. With a lowering of the temperature, the Na splitting constant decreased while the Li splitting constant increased. The K splitting constant was independent of both the temperature and the solvent. These results were found in the ion pairs of other halogeno-nitrobenzenes, also.

Electron-spin-resonance (ESR) studies of aromatic polynitro anion radicals in solution, first by Ward[1] and afterward by Glarum *et al.*,[2] have clearly shown that there exists a strong association between the metal cation and the nitro group of the anion.

This association was expected also to be found in an aromatic mononitro anion radical produced chemically. There has been, however, little information as to the interaction of mononitro anions with metal cations, except for Ward's observation of the sodium hyperfine interaction in the nitrobenzene-sodium complex.[1]

This paper will describe several features of the cation-anion interaction obtained from an ESR study of the ion pair of the *m*-iodonitrobenzene anion with the metal cation, *i. e.*, the effect of the cationic field on the spin distribution of the anion, and the solvent and temperature effects on the hyperfine interaction of alkali metal.

In order to confirm these results, some ESR studies of other halogeno-nitrobenzene anions will also be referred to.

Experimental

The preparation of the radicals, the purification of the solvents, and other experimental procedures were carried out in a conventional manner.[3] The reduction of *m*-iodonitrobenzene was performed at room temperature in several solvents, such as tetrahydrofuran (THF), dimethoxyethane (DME) and tetrahydropyran (THP). The reducing agents used were five alkali metals: lithium, sodium, potassium, rubidium, and cesium, and four alkaline earth metals: magnesium, calcium, strontium, and barium. Lithium and alkaline earth metals were employed in the amalgamated form.

The other halogeno-nitrobenzenes examined were the entire series of chloro- and bromo-nitrobenzene and *o*- and *p*-iodonitrobenzene. All were reduced with potassium, sodium, or lithium, in DME or in THF.

The spectra were measured over the range from room temperature to −70°C using a JES 3B-type ESR spectrometer with a 100-kc field modulation and a JES 12-inch magnet.

Results and Discussion

The contact of a *m*-iodonitrobenzene with alkali or alkaline earth metal resulted in the immediate formation of a dark brown solution, which gave an ESR signal.

Although the ESR spectrum of the anion produced with magnesium or calcium was only a single broad line, the anions produced with seven other metals exhibited rather well resolved spectra. If the additional lines from the metal nuclei are disregarded, these spectra may be interpreted in terms of one nitrogen splitting, two equivalent ortho-proton splittings, and one para- and one meta-proton splittings, like the spectra of *m*-chloro- and *m*-bromo-nitrobenzene anions previously reported.[4,5] Several examples of the spectra are shown in Figs. 1(a), (b) and (c).

[*1] Present address: Marine Technical College, Ashiya City, Hyogo.

1) R. L. Ward, *J. Am. Chem. Soc.*, **83**, 1296 (1961).

2) S. L. Glarum and J. H. Marshall, *J. Chem. Phys.*, **41**, 2183 (1964).

3) D. B. Paul and L. Lipkin and S. I. Weissmann, *J. Am. Chem. Soc.*, **78**, 116 (1956).

4) T. Fujinaga, Y. Deguchi and K. Umemoto, This Bulletin, **37**, 822 (1964).

5) P. B. Ayscough, F. P. Sargent and R. Willson, *J. Chem. Soc.*, **1963**, 5418.

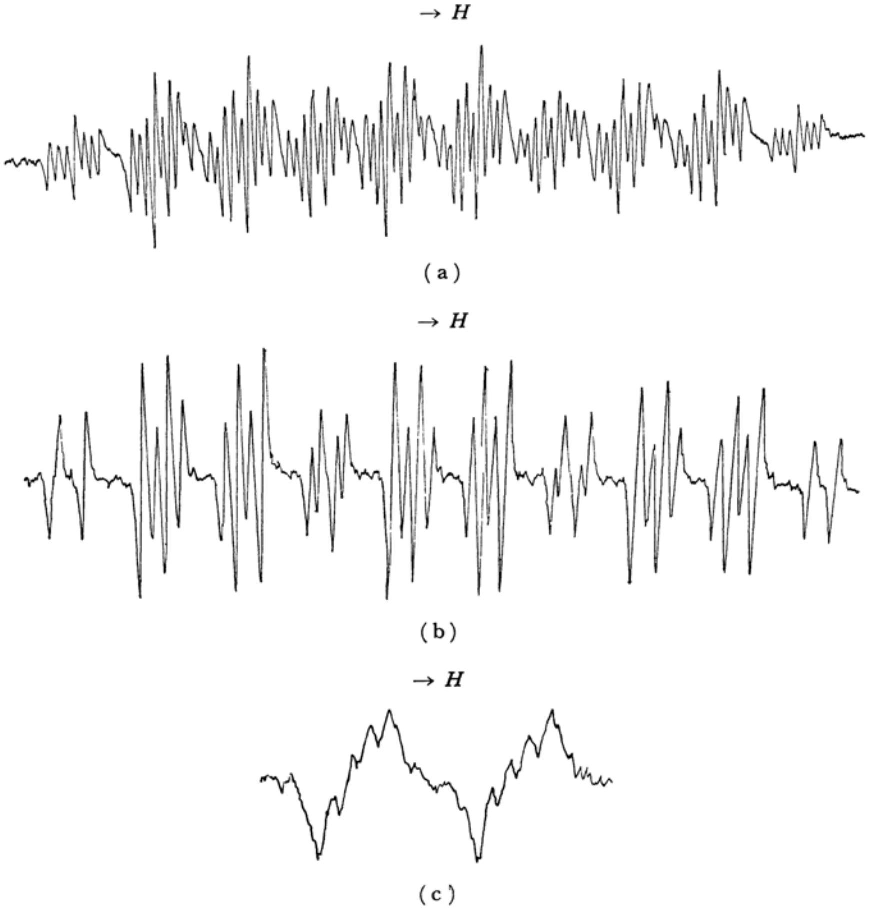


Fig. 1. ESR spectra of the ion-pair complex of *m*-iodonitrobenzene anion.
(a) Sodium ion in DME (at 20°C)
(b) Lithium ion in THF (at 20°C)
(c) Lithium hyperfine splitting in low field-end part of (b) (at −40°C)

TABLE 1. PROTON AND NITROGEN SPLITTING CONSTANTS IN METAL COMPLEXES OF THE *m*-IODONITROBENZENE (in gauss)

Position	Metal						
	Cs	Rb	K	Na	Li	Ba	Sr
N	9.3	9.5	9.72	10.07	10.65	11.24	11.84
H_p	4.15	4.15	4.13	4.05	4.01	3.89	3.84
H_o	3.33	3.33	3.36	3.36	3.40	3.46	3.50
H_m	1.03	1.03	1.05	1.10	1.10	1.13	1.15

N: Nitrogen splitting constant.
H_p, H_o and H_m: para-proton splitting constant and so on.

The Effect of the Cationic Field on the Anion. The proton and nitrogen splittings did not exhibit any solvent or temperature dependence, while both changed when the counter cation was altered, as Table 1 shows. From this table it can be seen that the change in the nitrogen splitting is much more appreciable than those in the proton splittings. The nitrogen, ortho-, and meta-proton splitting constants increased, and the para-proton splitting constant decreases, with the decrease in the cationic radius and with the increase in the cationic charge, both of which changes are related to the increase in the cationic field strength.

The above changes in the splitting constants are in accord with those induced by the increase in the Coulomb integral parameter for oxygen atoms

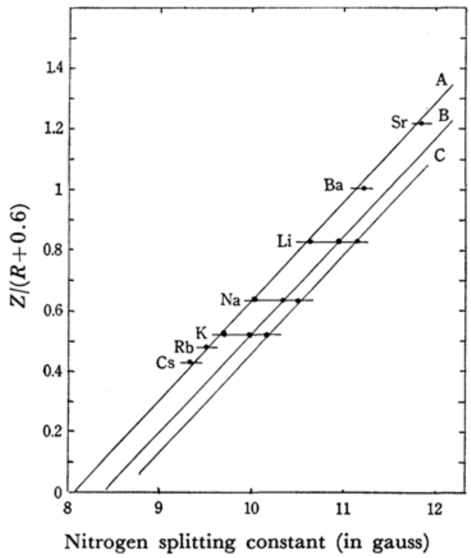


Fig. 2. Nitrogen splitting constant *vs.* $Z/(R+006)$ plots.

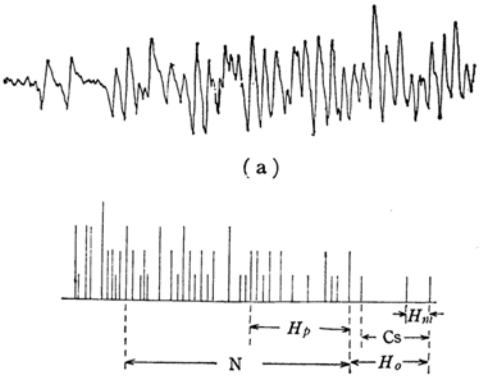
A *m*-Iodonitrobenzene complex
B *p*-Chloronitrobenzene complex
C *o*-Chloronitrobenzene complex

Cationic radii R used⁷⁾ (in Å): Li, 0.60. Na, 0.95. K, 1.33. Rb, 1.48. Cs, 1.69. Sr, 1.13. Ba, 1.35.

in the nitro group, as was calculated by Rieger and Fraenkel.⁶⁾ This accordance will suggest that the metal cation is located in the neighborhood of the oxygen atoms.

It seems of interest to find a definite relationship between the nitrogen splitting constant and the cationic field and to estimate, if possible, the nitrogen splitting constant free from the effect of this field. After several attempts, it was found that there was a good linear relationship between the nitrogen splitting constant and the term of $Z/(R+0.6)$, where Z is a charge number of the cation and R is Pauling's cationic radius in Å.⁷⁾ Figure 2 represents this linear relationship. The extrapolation of this plot to an infinite R gives the nitrogen splitting of about 8.1 gauss for zero cationic strength. This value seems to be appropriate for the nitrogen splitting without any electrostatic influence from the environment, except for the effect of weak solvation.

The General Features of Alkali Metal Splittings. It was observed with alkali metal complexes that each line from the free anion was split into $2I+1$ lines due to the hyperfine interaction of a metal nucleus, the one exception being the THP solution of the lithium complex, where I is the spin number of a metal nucleus. In particular, the spectrum of the rubidium complex consisted of two sorts of hyperfine patterns, corresponding to two rubidium isotopes: ^{85}Rb ($I=5/2$ and natural abundance $A=72.15\%$) and ^{87}Rb ($I=3/2$ and $A=27.75\%$); the intensity ratio of the hyperfine pattern from ^{85}Rb to that from ^{87}Rb, 1.75 closely agreed with the $A/(2I+1)$ ratio of each isotope. Figures 3 (a) and (b) and Figs. 4 (a) and (b) show the low-field end parts of the ESR spectra of the cesium and the rubidium complexes respectively, together with the corresponding reconstructions based on the splitting constants listed in Tables 1 and 2.



(a)

(b)

Fig. 3. (a) The low field end part of ESR spectrum of *m*-iodonitrobenzene - cesium complex in DME
(b) The reconstruction corresponding to (a)

Table 2 represents the splitting constants of alkali metals in DME, THF, and THP at 20°C. It seems difficult to derive from this table a definite relationship between the splitting constants in the same solvent and any physical quantity.

Several workers have attributed the origin of alkali metal splitting to the back-transfer of an unpaired electron to the ns-shell of a cation;⁸⁻¹¹⁾ the magnitude of this back-transfered spin density, ρ, has been simply estimated from the metal-splitting constant, a_m, and the Q value, which represents a hyperfine splitting due to an electron on the ns-shell of each metal.¹²⁾ In contrast to its splitting constant, the ρ in DME decreases from cesium to lithium in the order of decreasing

---

6) P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 609 (1963).

7) L. Pauling, "Nature of the Chemical Bond," Cornel University Press, Cornel (1940), p. 340.

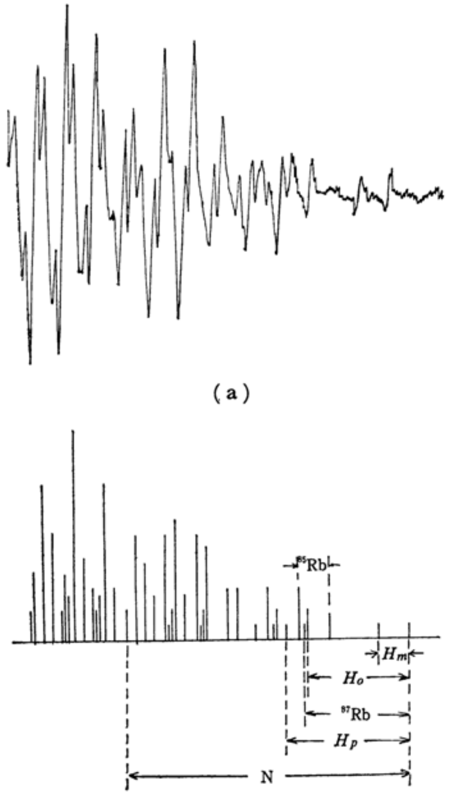
8) N. M. Atherton and S. I. Weissmann, *J. Am. Chem. Soc.*, **83**, 1296 (1961).

9) H. Nishiguchi, Y. Nakai, K. Nakamura, K. Ishizu, Y. Deguchi and H. Takagi, *Mol. Phys.*, **9**, 153 (1965).

10) C. A. McDowell and K. F. G. Paulus, *Can. J. Chem.*, **43**, 224 (1965).

11) S. Aono and K. Oohasi, *Progr. Theoret. Phys. Kyoto*, **30**, 162 (1962).

12) P. Kush and H. Taub, *Phys. Rev.*, **75**, 1477 (1949).



(a)

(b)

Fig. 4. (a) The low field end part of ESR spectrum of *m*-iodonitrobenzene - rubidium complex in THF
(b) The reconstruction corresponding to (b)

TABLE 2. ALKALI METAL SPLITTING CONSTANT OF THE *m*-IODONITROBENZENE COMPLEX AT 20°C

Metal	Spin number	Solvent DME	THF	THP	DME/THF
^{133}Cs	7/2	2.05	2.85	3.12	1.38
^{85}Rb	5/2	0.95	1.04	1.06	1.08
^{87}Rb	3/2	3.20	3.45	3.53	1.08
^{39}K	3/2	0.18	0.18	0.18	1.00
^{32}Na	3/2	0.37	0.28	0.21	0.75
^{7}Li	3/2	0.105	*ca.* 0.07*	<0.05**	0.66

* Unresolved at 20°C, but resolved below 0°C.
** Unresolved in the range of 20°C to −70°C.

ionic radius and in the order of increasing ionization potential, as Table 3 shows. Especially, an abrupt change in ρ between potassium and sodium is observed. This tendency becomes even more appreciable in THF and THP solutions.

According to the second-order perturbation, ρ is approximately proportional to the overlap integral between the ns-shell of a cation and the orbital of an unpaired electron on an anion; also,

TABLE 3. SPIN DENSITY ON THE ns-SHELL OF ALKALI METAL IN DME AT 20°C AND −70°C

Metal	Q value gauss	Spin density (×10^3) (20°C)	(−70°C)
^{133}Cs	820.1	2.68	2.68
^{85}Rb	361.0	2.62	2.62
^{87}Rb	1219.4	2.62	2.62
^{39}K	82.4	2.19	2.19
^{23}Na	316.2	1.39	0.53
^{7}Li	143.3	0.75	1.43

it increases with an increase in the ionization potential of a parent metal.[11] Thus, the present decrease of ρ with an increase in the ionization potential suggests that there is a remarkably large decrease in the overlap in the same series. One part of this decrease is probably due to the decrease in the spread of the ns-orbital. However, it may also be ascribed to some other process, one which depends on the relative location of a cation to an anion.

The Solvent Effect on Alkali Metal Splittings. Contrary to what was found for splittings from the anion, the alkali metal splitting changed with the solvent. Table 2 shows that the solvent effect is different for each alkali metal; *i. e.*, the cesium and rubidium splitting constants increase in the order of DME<THF<THP, while the sodium and lithium splitting constants increase in the reverse order of solvents. Lying between these two groups, the potassium splitting is independent of the solvents used. The ratio of a metal splitting constant in DME to that in THF decreases from 1.38 for cesium to 0.68 for lithium.

Except for the complex of tetramethylpyrazine with potassium,[10] the solvent effect on alkali metal splittings obtained so far have shown that the splitting constants increase in the order of DME<THF<THP solutions. Furthermore, Powell and Warhurst observed the bathochromic shift from THF to DME in the electronic spectra in the visible range of several ketyls.[13] They attributed this solvent effect to an increasing separation between the anion and the metal cation due to the increase in the solvating power of the cation from THF to DME. Their explanation seems also to be applicable to the ordinary solvent effect of alkali metal splitting, because the overlap decreases with an increase in the separation distance. However, if different solvents induce a change in the relative location of a cation, such as a shift along the aromatic plane or a dislocation from the "above" aromatic plane to the proximity of lone-pair electrons, other than that of the separation distance, then there is a possibility of an upset of

---

[13] D. G. Powell and E. Warhurst, *Trans. Faraday Soc.*, **58**, 953 (1962).

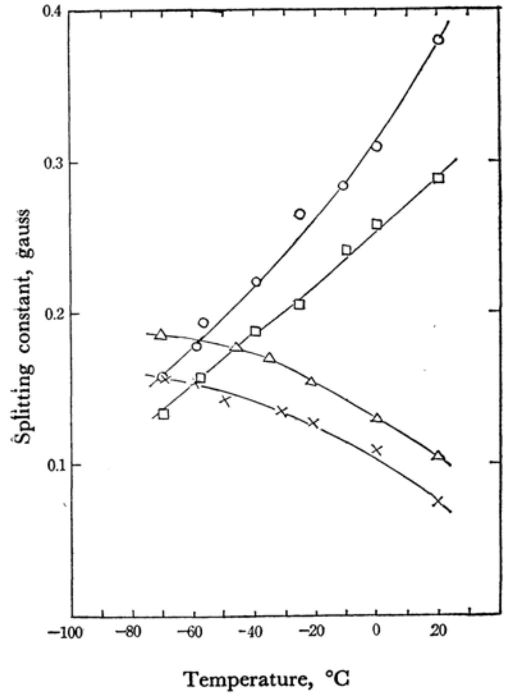


Fig. 5. Temperature dependence of sodium and lithium splitting constants.

○: Na in DME △: Li in DME
□: Na in THF ×: Li in THF

TABLE 4. TEMPERATURE DEPENDENCE OF ALKALI METAL SPLITTING CONSTANTS (in gauss)

Metal	Solvent	Temperature (20°C)	(−20°C)	(−70°C)
Na	DME	0.38	0.26	0.16
Na	THF	0.28	0.22	0.13
Na	THP	0.21	0.13	*
Li	DME	0.105	0.15	0.18
Li	THF	*ca.* 0.07	0.13	0.15

* Unresolved.

the ordinary solvent effect on alkali-metal splitting. The anomaly in the solvent effect on the sodium and lithium splittings may be ascribed to a change in such a relative location.

The Temperature Effect of the Metal Splittings. The temperature dependences of lithium and sodium splittings were also peculiar. The splitting constants of potassium, rubidium, and cesium did not change in the range from 20°C to about −60°C, while those of lithium and sodium changed markedly. Further, the sign of the slope of metal splitting *vs.* the temperature curve was positive for sodium and negative for lithium, and at −60°C the lithium splitting constant became larger than the sodium one, as shown in Table 4 and Fig. 5. It is worth noting that the ρ value of the lithium was less than that of potassium, even at −70°C. These features were independent of the solvent.

Since a cation is considered to be oscilating in the potential valley, the observed alkali-metal splitting should be an average of its splittings at all states of the valley.[14] From this point of view, the lack of the temperature dependence of the cesium and rubidium splittings indicates that the valleys for these ions are shallow and have only a single minimum.

There seems to be a close relation between the anomalies of the solvent and of the temperature effects on the sodium and lithium splittings. Although it is difficult at this stage to obtain any definite interpretation of these two anomalies, they are probably related to the presence of double minimums in the valleys. If the level of one minimum relative to that of the other varies with the solvent and the alkali metal, the rapid temperature-dependent equilibrium of the cation between the minimums may lead to the present anomalies. Furthermore, it may be supposed that the equilibrium location of the larger cation lies above the plane of the nitro group and midway between the two oxygen atoms, while the smaller ion tends to be localized at either of the two oxygen atoms, where the lone-pair electrons of the oxygen atoms will play an important role. This tendency of the smaller ion may be related to the presence of double minimums in the lithium and sodium ions.

The Results Concerning Other Halogenonitrobenzene Anions. Among the halogenonitrobenzene anions examined, the anions produced from *o*- and *p*-iodonitrobenzene exhibited complex spectra, probably because of the coexistence of several species of radicals. The ESR spectra of the anion from *o*-bromonitrobenzene decayed fast. No definite interpretations of these spectra have yet been obtained, but, on the other hand, the anions from *o*-, *p*- and *m*-chloronitrobenzene and *m*- and *p*-chloronitrobenzene exhibited rather well-resolved spectra. The results obtained are listed in Table 5, and some interesting features are as follows.

The Stabilities of the Radicals. Since the contact of halogeno-benzene with alkali metal resulted in a quick dehalogenation from the benzene ring, the ESR spectra of aromatic radicals containing halogen atoms produced with alkali metals have not yet been reported. In this case, however, the radicals produced maintained their ESR signal for a fairly long period, from several days for the *m*-iodonitrobenzene anion to several months for the *o*- and *p*-chloronitrobenzene anions. Although the electrolytic procedure has produced halogeno-nitrobenzene anions from their parent

---

14) S. Aono and K. Oohasi, *Progr. Theoret. Phys. Kyoto,* **31**, 1 (1964).

TABLE 5. SPLITTING CONSTANTS OF METAL COMPLEXES OF HALOGENO NITROBENZENE ANIONS (in gauss)

Material	Metal	N	H_p	H_o	H_m	a_m	a_{Cl}
p-Chloronitrobenzene	K	9.96		3.42	1.10	*	*
	Na	10.35		3.48	1.10	0.376	0.22
	Li	10.93		3.48	1.10	*	*
o-Chloronitrobenzene	K	10.15	4.0	3.38	1.10	*	*
	Na	10.55	4.01	3.38	1.10	0.378	0.18
	Li	11.16	3.95	3.4	1.12	*	*
m-Chloronitrobenzene	K	9.65	4.0	3.40	1.04	0.18	*
	Na	10.02	4.0	3.40	1.06	0.38	*
	Li	11.60	3.9	3.4	1.06	*	*
p-Bromonitrobenzene	Na	10.30		3.42	1.10	0.38	
m-Bromonitrobenzene	K	9.7	4.0	3.4	1.0	*	
	Na	10.0	4.0	3.4	1.0	0.4	

a_m: Alkali metal splitting constant at 20°C.
a_{Cl}: Chlorine splitting constant.
*: Unresolved.

compounds in polar solvents, such as acetonitrile and dimethylformamide,[4,15] the electrolysis of *m*-iodonitrobenzene resulted in the formation of the nitrobenzene anion on account of the prompt relacement of the iodo atom.[4] Hence, the present results may be ascribed to the fact that the cation forms a tightly-bound ion-pair at the nitro group, so that it has little chance of migrating near the halogen atom. In addition, ethereal solvents exhibit only a weak interaction with a halogen atom, and the negative charge on the halogen atom considerably diminishes as a result of the electron-attracting character of the nitro group.

Chlorine Hyperfine Interaction. In the ESR spectra of the *o*- and *p*-chloronitrobenzene anions produced with sodium in DME, each line arising from the hyperfine interactions of the protons and of the nitrogen and sodium nuclei was split further into several lines, although these lines were not clearly resolved. This additional splitting can be understood in terms of the hyperfine interaction of the chlorine nucleus (^{35}Cl and ^{37}Cl, $I=3/2$). Figure 6 shows several lines at the low field end of the spectrum of the *o*-chloronitrobenzene anion, together with the corresponding reconstruction based on the splitting constants in Table 5. The chlorine splitting constants of 0.22 and 0.18 gauss for the *p*- and *o*-chloronitrobenzene anions respectively are in good agreement with those obtained by Ayscough *et al.*[5] This interpretation is supported by the fact that no such additional splitting could be observed in the spectrum of *p*-bromonitrobenzene anion produced with sodium. The bromine splitting is estimated from the line width to be less than 0.06 gauss. The spectra of *p*- and *o*-chloronitrobenzene anions produced with lithium or potassium did not exhibit a well-resolved hyperfine splitting from the metal nucleus, probably because the potassium and lithium splitting constants were of the same order as the chlorine splitting constants.

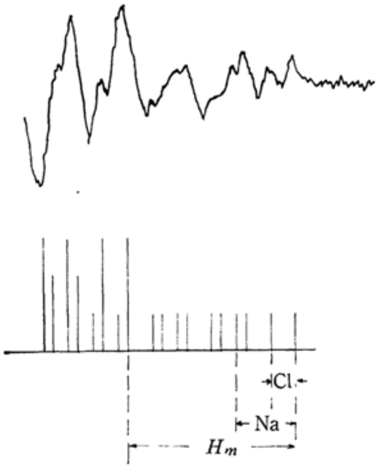


Fig. 6. The low field end part of ESR spectrum of *o*-chlornitrobenzene-sodium complex in DME at 20°C.

The Effect of the Cationic Field on the Anions. The linear plots of the nitrogen splitting constant *vs.* $Z/(R+0.6)$ for *p*- and *o*-chloronitrobenzene were parallel to that for *m*-iodonitrobenzene, as is shown in Fig. 2. This parallelism indicates that the differences in nitrogen splitting constants among these anions will remain even at zero cationic field strength, and that, regardless of the anion, the replacement of the potassium ion by the sodium ion and that of the sodium ion by the lithium ion increase the nitrogen splitting constant by about

---

15) A. H. Maki and D. H. Geske, *J. Am. Chem. Soc.*, **83**, 1852 (1962).

0.3 and 0.5 gauss respectively. It is interesting that the proton and nitrogen splitting constants of the *m*-chloro- and *m*-bromo-nitrobenzene anions are nearly identical with those of the *m*-iodonitrobenzene anion.

Alkali Metal Splitting. Although the increase in line-width due to the chlorine or bromine hyperfine interaction made the estimation of alkali metal splitting difficult, the sodium and potassium splitting constants obtained were nearly identical with those of *m*-iodonitrobenzene complexes.

It may safely said, therefore, that the features of the cation-anion interaction observed in the *m*-iodonitrobenzene complex will also be found in the complexes of other mononitrobenzene derivatives, excluding those containing a group of strong electron-attracting ability, such as a cyano or a carbonyl group.

The author wishes to express his hearty thanks to Professors Hideo Takaki and Ryozo Goto for making the ESR spectrometer available for his study, and to visiting Professor C. A. McDowell for his kind help with the manuscript. He is also much obliged to Dr. Yasuo Deguchi for his helpful discussions and encouragement throughout the course of this work.