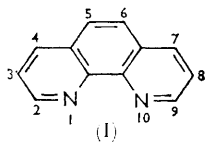


583. The Proton Magnetic Resonance Spectra of *ortho*-Phenanthroline and Some of its Metal Complexes

By J. D. MILLER and R. H. PRINCE

The nuclear magnetic resonance spectra of *ortho*-phenanthroline, the tris-*o*-phenanthroline complexes of Co^{III}, Fe^{II}, Ru^{II}, and Zn^{II} and the tetrakis-*o*-phenanthroline complexes of Ca^{II} and Mg^{II} in aqueous solution are described. The spectra are analysed in terms of an AA'MM'SS'X₂ model and coupling constants are derived. A high-field shift for the 2 and 9 ring protons, probably due to a metal-non-bonded hydrogen interaction, is shown to occur in the metal complexes. A method of determining the changes in charge at the other ring positions when chelation occurs is suggested.

PHENANTHROLINE [*o*-phen, (I)] is a well-known bidentate ligand.^{1,2} It forms complexes with many metal ions, and its complexes are frequently used as oxidation-reduction indicators, the best known being the ferrous-tris-*o*-phenanthroline complex. The ligand possesses donor *sp*² orbitals on the nitrogen atoms, and low-energy, antibonding π -orbitals associated with the aromatic ring systems;^{3,4} therefore it is possible that *ortho*-phenanthroline may act both as a donor and an acceptor of electrons. There is some evidence for the existence of such a synergic effect in the bonding



of *o*-phenanthroline complexes, for example, the preparation of such low oxidation states as Co(I) in [Co(*o*-phen)₃]ClO₄,⁵ and the many related dipyrindyl complexes prepared by Herzog *et al.* Also the stability of M(*o*-phen)₃²⁺ is generally greater than that of M(*o*-phen)₃³⁺ where M is a transition metal such as Mn, Fe, Ru, Os, or Co. However, this stabilisation of lower oxidation states is not always the case, as Ag^I can be stabilised by *o*-phenanthroline.⁶

For a better understanding of the metal-ligand interactions in these complexes, and the mechanism of electron transfer in their reactions, we studied the proton nuclear magnetic resonance (n.m.r.) spectra of *o*-phenanthroline, some substituted phenanthrolines, and some diamagnetic metal complexes in aqueous solution. Little previous work has been reported; the electron paramagnetic resonance spectrum of tris-*o*-phenanthroline-copper(II) has been reported⁷ and the tris-complexes of Fe^{II} and Fe^{III} have been studied by n.m.r. by Wahl *et al.*,^{8,9} but mainly with the object of determining rates of electron transfer between the two oxidation states. In the present Paper, the spectra presented are analysed and some conclusions as to the metal-ligand interactions are reached.

RESULTS AND DISCUSSION

o-Phenanthroline in *m*-Acid.—To assist in the identification of the various peak systems in the spectrum of *o*-phenanthroline, the spectra of the unsubstituted molecule and the 3,4,7,8- and 3,5,6,8-tetramethyl derivatives were obtained in *m*-sulphuric acid (Figure 1). The positions of the various peaks are in Table 1, with their relative area ratios.

The spectrum of *o*-phenanthroline and of all its complexes studied here can be analysed as an AA'MM'SS'X₂ system which implies that there is no coupling between positions 4 and 5 (and 6 and 7). From the symmetry of the molecule the 5 and 6 protons are chemically

¹ W. W. Brandt, F. P. Dwyer, and E. C. Gyarfás, *Chem. Rev.*, 1954, **54**, 959.

² "Chelating Agents and Metal Chelates," ed. F. P. Dwyer and D. P. Mellor, Academic Press, New York, 1964.

³ Hückel orbitals of *o*-phenanthroline calculated by A. Hudson and G. R. Luckhurst, personal communication.

⁴ J. S. Brinen, D. D. Rosebrook, and R. C. Hirt, *J. Phys. Chem.*, 1963, **67**, 2651.

⁵ N. Maki, M. Yamagami, and H. Itatani, *J. Amer. Chem. Soc.*, 1964, **86**, 514.

⁶ "An Introduction to Advanced Inorganic Chemistry," P. J. Durrant and B. Durrant, Longmans, London, 1962, p. 1071.

⁷ H. C. Allen, G. F. Kokoszka, and R. G. Inskeep, *J. Amer. Chem. Soc.*, 1964, **86**, 1023.

⁸ M. W. Dietrich and A. C. Wahl, *J. Chem. Phys.*, 1963, **38**, 1591.

⁹ D. W. Larson and A. C. Wahl, *J. Chem. Phys.*, 1964, **41**, 908.

TABLE I
Observed peak positions for *o*-phenanthroline in $M-H_2SO_4$ given in τ units relative to the main solvent peak

<i>o</i> -Phen		3,4,7,8-Tetramethyl- <i>o</i> -phen		3,5,6,8-Tetramethyl- <i>o</i> -phen		Assignment (protons)
τ	Area ratio	τ	Area ratio	τ	Area ratio	
-3.72	0.53	-2.98	1.00	-3.00	1.00	2 and 9
-3.70						
-3.64	0.50					
-3.62						
-3.40	0.51			-2.49	1.14	4 and 7
-3.38						
-3.26	0.51					
-3.24						
-2.80	0.51	+2.93 *		+2.85 †		3 and 8
-2.71						
-2.67	0.81					
-2.59	0.52					
-2.47	1.11	-1.99	1.19	+3.42 †		5 and 6

* Methyl-H signals which cannot be assigned. † Methyl-H signals.

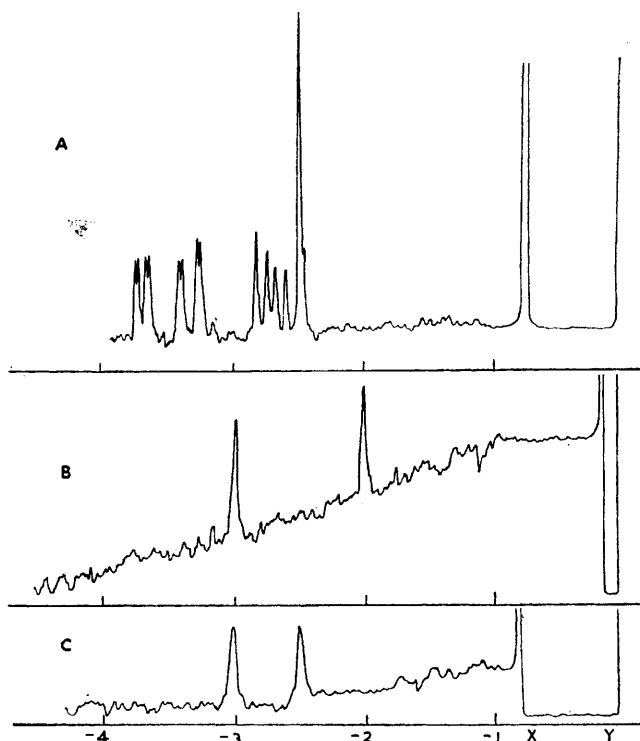


FIGURE 1. N.m.r. spectra of *o*-phenanthrolines in M -sulphuric acid: shifts in p.p.m. downfield from the main solvent peak

A, *o*-Phenanthroline. B, 3,4,7,8-Tetramethyl-*o*-phenanthroline. C, 3,5,6,8-Tetramethyl-*o*-phenanthroline. X, Spinning side band. Y, Main solvent peak.

equivalent and since they do not couple with any other nuclei they are also magnetically equivalent; therefore, although they couple, no splitting of the peak due to these protons is observed. Such a phenomenon has been reported by Pople, Schneider, and Bernstein¹⁰ for naphthalene, where no coupling occurs between neighbouring protons on different rings. Approximate coupling constants derived from these spectra for *o*-phenanthroline are of the

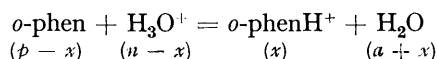
¹⁰ J. A. Pople, W. G. Schneider, and H. J. Bernstein, *Canad. J. Chem.*, 1957, **35**, 1060.

order of $J_{2,3} = 5.0$ c./sec., $J_{2,4} = 1.2$ c./sec., and $J_{3,4} = 8.1$ c./sec. A more accurate determination of these coupling constants is quoted below and a comparison between the coupling constants derived here and those of naphthalene and pyridine^{11,12} show a close similarity and provide additional verification for the assignment of the spectrum (see Table 4).

The centres of the peak systems of the various protons in *o*-phenanthroline do not occur at the same values as those in the substituted phenanthrolines, which may be due to the effect of the methyl groups on the electron distributions in the occupied molecular orbitals.

The spectrum of *o*-phenanthroline in water could not be obtained, and therefore, to compare this spectrum with those of the metal complexes in solution, a series of solutions of 0.0567M-*o*-phenanthroline, over a range of nitric acid concentrations, was studied in order to allow an extrapolation of τ -values to zero acid concentration. *t*-Butyl alcohol (TBA) was added as an internal standard. A preliminary set of spectra were obtained of the alcohol at various acid concentrations using an added, external, acetone standard to study the variation of the alcohol peak position with acid concentration. These spectra show that the effect of acid concentration, over the range 0—2.5M, on the peak position is very slight, the change in τ over this range being 8.78—8.81.

In a weakly acid solution of *o*-phenanthroline there exists the equilibrium:



There will be rapid exchange between the ligand and its protonated derivative, and therefore the spectrum observed for the solution will obey the simple equation

$$\omega_{\text{mean}} = P_{o\text{-phen}}\omega_{o\text{-phen}} + P_{o\text{-phenH}^+}\omega_{o\text{-phenH}^+} \quad (\text{i})$$

where P is the fractional population of a given species and ω is the resonance frequency. Therefore, since $n > p$, we have

$$\omega_{\text{mean}} = \omega_{o\text{-phen}} + \frac{Kn}{a}(\omega_{o\text{-phenH}^+} - \omega_{o\text{-phenH}}) \quad (\text{ii})$$

As n is the total added acid concentration, and all other terms on the right-hand side of equation (ii) are constants, the observed peak positions, ω_{mean} , should vary linearly with total added acid concentration and extrapolation to $n = 0$ should give the peak positions of the unprotonated molecule in water.

TABLE 2

Observed centres of peak systems for pairs of protons in the *o*-phenanthroline molecule in acid solutions, 0.567M in *o*-phen

Added HNO ₃ (moles/l.)	τ (obs.) for protons				
	2 and 9	3 and 8	4 and 7	5 and 6	TBA
0.2	1.00	2.01	1.33	2.13	8.78
0.3	1.01	2.03	1.35	2.15	8.78
0.4	1.04	2.06	1.38	2.19	8.79
0.5	1.02	2.04	1.36	2.17	8.79
0.6	1.04	2.06	1.37	2.18	8.79
0.7	1.01	2.04	1.35	2.17	8.79
0.8	1.05	2.06	1.40	2.20	8.79
0.9	1.03	2.06	1.37	2.18	8.79
1.0	1.04	2.06	1.39	2.20	8.80
1.1	1.04	2.06	1.38	2.19	8.80
1.2	1.05	2.07	1.40	2.20	8.80

The observed results for the spectra in various acid concentrations are quoted in Table 2, where for simplicity only the centres of the peak systems for each pair of protons are given. There is only a slight variation in peak positions with acid concentration and therefore the error in any measurement is of the order of its change in position. The extrapolation to

¹¹ W. G. Schneider, H. J. Bernstein, and J. A. Pople, *Canad. J. Chem.*, 1957, **35**, 1487.

¹² W. G. Schneider, H. J. Bernstein, and J. A. Pople, *Ann. N.Y. Acad. Sci.*, 1958, **70**, 806.

$[\text{HNO}_3] = 0$ will, however, be only slightly less accurate than a directly measured spectrum. This extrapolation gives $\tau_{2,9} = 0.98$, $\tau_{3,8} = 2.00$, $\tau_{4,7} = 1.31$, $\tau_{5,6} = 2.12$.

The values given for the centre of the 3 and 8 proton signal systems are less reliable than the other values as there is overlap between the right-hand end of the system and the stronger singlet of the 5 and 6 protons. From an expanded spectrum of the solution of *o*-phenanthroline in 0.9M-acid, accurate coupling constants were obtained. The estimated error in these values is ± 0.08 c./sec. These coupling constants are quoted in Table 3 together with those from the experiments described later, for which the error may be of the order of 0.3 c./sec.

It is interesting that the τ -value for the centre of the peak system for a given pair of protons varies inversely with the relative net charges at the various ring positions as calculated by Longuet-Higgins and Coulson¹³ (Table 4).

TABLE 3
Coupling constants (c./sec.) for various species

Species	$J_{2,3}$	$J_{2,4}$	$J_{3,4}$	Ref.
Naphthalene *	6.0	1.4	8.6	10
Pyridine	5.5	1.9	7.5	11, 12
<i>o</i> -Phen in 0.9M-HNO ₃	5.0	1.6	8.4	
Ferrous-tris- <i>o</i> -phen ion	5.4	—	7.8	
Ruthenous-tris- <i>o</i> -phen ion	5.4	1.2	8.1	
Cobaltic-tris- <i>o</i> -phen ion	6.0	—	8.4	
Zinc-tris- <i>o</i> -phen ion	5.1	—	7.8	
Calcium-tetra- <i>o</i> -phen ion	4.7	1.5	8.2	
Magnesium-tetra- <i>o</i> -phen ion	4.6	—	8.6	

* The numbering of the naphthalene rings has been altered to compare with that of the *o*-phenanthroline molecule.

TABLE 4
Centre of signal system for ring positions and calculated net charge on these positions in *o*-phenanthroline

	2 and 9	4 and 7	3 and 8	5 and 6
τ	0.98	1.31	2.00	2.12
Relative net charge	0.138	0.120	0.019	0.015

While not perfect, the correlation suggests that the charge on the neighbouring carbon atom has a major influence on the position of a given proton's resonance frequency and that the dependence upon the charge is approximately linear.

*Tris-*o*-phenanthroline-Metal Complexes.*—The spectra of aqueous solutions of the diamagnetic complexes $\text{Fe}(\textit{o}\text{-phen})_3^{2+}$, $\text{Fe}(\text{3,4,7,8-tetra-methyl-}\textit{o}\text{-phen})_3^{2+}$, $\text{Fe}(\text{3,5,6,8-tetra-methyl-}\textit{o}\text{-phen})_3^{2+}$, $\text{Co}(\textit{o}\text{-phen})_3^{3+}$, $\text{Ru}(\textit{o}\text{-phen})_3^{2+}$, and $\text{Zn}(\textit{o}\text{-phen})_3^{2+}$ have been obtained and are summarised in Table 5. Those of the ferrous complexes are also illustrated in Figure 2.

TABLE 5
Observed resonance peaks in the n.m.r. spectra of metal complexes (in τ -units) relative to TBA taken as τ 8.78

Complex/Protons	2 and 9	3 and 8	4 and 7	5 and 6
$\text{Fe}^{\text{II}}(\textit{o}\text{-phen})_3$	* (2.17, 2.24, 2.37, 2.47) *		1.29(b), 1.41(b)	1.75
$\text{Fe}^{\text{II}}(\text{3,4,7,8-tetra-methyl-}\textit{o}\text{-phen})_3$	2.67	7.58 †	7.95 †	2.03
$\text{Fe}^{\text{II}}(\text{3,5,6,8-tetra-methyl-}\textit{o}\text{-phen})_3$	2.69	7.58 †	1.84	7.93 †
$\text{Co}^{\text{III}}(\textit{o}\text{-phen})_3$	2.27(b)	1.90, 2.00	0.81(b)	1.49
	2.37(b)	2.04, 2.14	0.99(b)	
$\text{Ru}^{\text{II}}(\textit{o}\text{-phen})_3$	1.90, 1.92	2.36, 2.45	1.42, 1.44	1.84
	1.99, 2.01	2.50, 2.59	1.55, 1.57	
$\text{Zn}^{\text{II}}(\textit{o}\text{-phen})_3$	1.65 ‡	2.17, 2.25	1.16(b)	1.81
		2.29, 2.38	1.30(b)	

* Overlapping signals (see Fig. 2). † Methyl H signals. ‡ Broad unresolved peak.
(b) Broadened line.

¹³ H. C. Longuet-Higgins and C. A. Coulson, *J.*, 1949, 971.

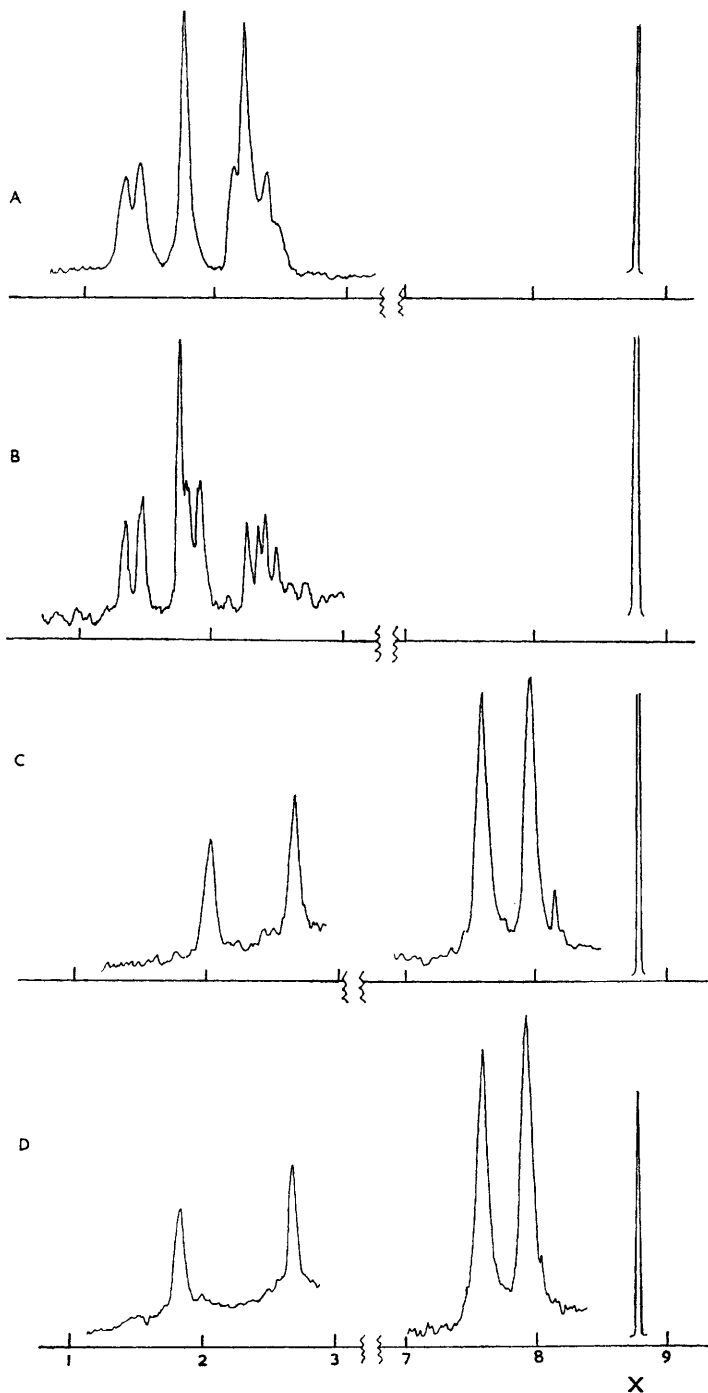


FIGURE 2. N.m.r. spectra of some metal-tris-*o*-phenanthroline complexes in aqueous solution measured in τ units relative to τ for *t*-butyl alcohol taken as 8
 A, $\text{Fe}(\textit{o}\text{-phen})_3^{2+}$. B, $\text{Ru}(\textit{o}\text{-phen})_3^{2+}$. C, $\text{Fe}(3,6,7,8\text{-tetra-Me-}o\text{-phen})_3^{2+}$.
 D, $\text{Fe}(3,5,6,8\text{-tetra-Me-}o\text{-phen})_3^{2+}$. X, *t*-Butyl alcohol.

The spectra of the ferrous complexes and the values derived for coupling constants show that the assignment of signals to individual protons is correct for the complexes, as it was for the uncomplexed ligand. In the majority of cases the fine splitting caused by the coupling between the 2 and 4 (and the 7 and 9) positions is seen only as a line broadening, and here the centre of the broadened line is quoted. In the case of the zinc complex, the signal for the 2 and 9 protons was observed only as a very broad peak at τ 1.65.

N.m.r. spectra of some iron complexes have already been reported: Dietrich and Wahl⁸ studied the rate of electron transfer between $\text{Fe}^{\text{II}}(o\text{-phen})_3$ and $\text{Fe}^{\text{III}}(o\text{-phen})_3$, but only described the spectrum of the ferrous complex as showing three peaks in the narrow region between -150 and -50 c./sec. relative to HDO in $3\text{M-D}_2\text{SO}_4$: these results were obtained on a 56.4 Mc./sec. spectrometer. More recently, Larson and Wahl⁹ have studied some methyl-substituted ferriins and ferriins from the viewpoint of electron transfer rates and also of proton contact shifts in the iron(III) complexes. Although they distinguish between the peak systems of the given ring positions, no spectrum or analysis is presented. At present there are no other spectra reported for this family of complexes.

The 2 and 9 Protons.—Large alterations in position occur for the signal of the 2 and 9 protons in the various complexes. These variations are much more pronounced than those occurring for any other proton signal, and are most readily explained by postulating a metal–non-bonded hydrogen interaction. The distance of these hydrogen atoms from the central metal ion is of the order of 2.8 – 2.9 Å, while the only other nearby atom, excluding the attached carbon atom, is the equivalent hydrogen atom on another ligand; and the H–H distance between such atoms is appreciably greater than twice the van der Waals's radius^{14a} of 1.2 Å and therefore the only atoms capable of affecting this hydrogen are its attached carbon atom and the central metal atom. Such high-field shifts can be explained either by movement of electrons in the C–H bond towards the proton, under the influence of the electric field of the metal ion, or the field due to water molecules closely attached to this ion:¹⁵ or alternatively, by postulating an M–H interaction of the type observed in directly bonded transition-metal hydrides, *e.g.*, in ref. 16 and 17. In Table 6, the centre of the 2 and 9 proton signal systems are compared with the "single bond radii" of the central metal ions, and also their "octahedral covalent radii," as given by Pauling.¹⁴

TABLE 6

Central metal ion	Co ^{III}	Fe ^{II}	Ru ^{II}	Zn ^{II}
τ_{29}	2.32	ca. 2.3	1.95	1.65
"Single bond radius" (Å)	1.162	1.165	1.246	1.249
"Octahedral covalent radius" (Å)...	1.22	1.23	1.33	

From this comparison, it can be seen that the 2 and 9 proton signal tends to move to high field as the size of the central metal ion decreases, *i.e.*, as the M–H distance decreases. The correlation shown in Table 6 agrees qualitatively with the theoretical predictions of Buckingham and Stephens¹⁷ for directly-bonded hydrogen atoms and the predictions of Buckingham¹⁵ for field effects. But the metal–hydrogen separations are not known accurately enough to enable the relationship between the shift in resonance frequency, and the M–H distance, to be deduced. Also, the effect of change in charge at the ring positions would need to be known accurately before any law could be shown to be obeyed.

The effect described here is sufficiently large to mask all other causes of a shift in the 2 and 9 proton signals, and therefore the values of spin density on the 2 and 9 carbon atoms in the ferric complexes, as derived by Larson and Wahl,⁹ are not reliable. Further proof of this is that the theoretically derived "Hückel orbitals" of *o*-phenanthroline³ quoted

¹⁴ L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, 3rd edn., 1960, (*a*) pp. 260, 249; (*b*) p. 256.

¹⁵ A. D. Buckingham, *Canad. J. Chem.*, 1960, **38**, 300.

¹⁶ J. Chatt and R. G. Hayter, *J.*, 1963, 6017.

¹⁷ A. D. Buckingham and P. J. Stephens, *J.*, 1964, 2747.

below suggest that the spin density for the 2 and 9 carbon atoms should be considerably less than their quoted value.

Other Aromatic Protons.—It has been shown for charged pyridine molecules¹⁸ and benzene ions¹⁹ that, to a good approximation, the change in the chemical shift of an aromatic proton, on putting a charge on the aromatic system, is directly proportional to the change in charge on the neighbouring carbon atom. The correlation between resonance frequency and relative net charge for the various positions on *o*-phenanthroline, shown above, implies that this may be a reasonable approximation in the present case. Smith and Schneider¹⁸ derived equation (iii) for pyridine

$$\Delta s = k \cdot \Delta d \quad (\text{iii})$$

where Δs is the change in chemical shift, Δd is the change in electron density at the adjacent carbon atom and k is a constant equal to 9.5 per million. In Table 7 this equation has been assumed to hold for the systems we have studied and changes in charge on going from uncomplexed ligand to the various complexes for ring positions 3 to 8 have been calculated. A positive sign implies a change to greater positive charge.

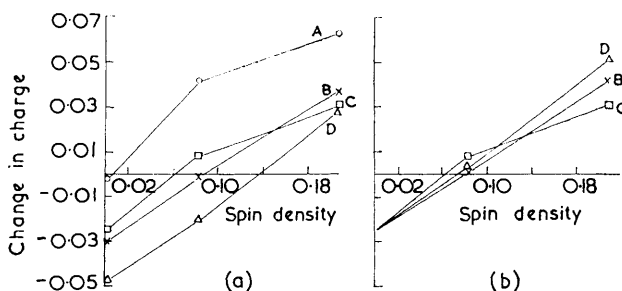


FIGURE 3. Relationship between change in charge as calculated from equation (iii), and the spin densities for the same ring positions for the highest bonding orbital of the uncomplexed ligand

A, Co^{III} . B, Fe^{II} . C, Zn^{II} . D, Ru^{II} .

When an *o*-phenanthroline molecule becomes complexed to a metal ion, there occurs a change in its environment which could cause a change in the chemical shifts of the ring protons distinct from the specific effects associated with the bonding of the complexed

TABLE 7

Change in charge on going from *o*-phen to the complexes

Complex	Positions 3 and 8	4 and 7	5 and 6
$\text{Co}^{\text{III}}(\text{o-phen})_3$	-0.002	+0.041	+0.063
$\text{Fe}^{\text{II}}(\text{o-phen})_3$	ca. -0.03 *	-0.004	+0.037
$\text{Ru}^{\text{II}}(\text{o-phen})_3$	-0.048	-0.020	+0.028
$\text{Zn}^{\text{II}}(\text{o-phen})_3$	-0.027	+0.008	+0.031

metal ion. Therefore, even if the assumption that equation (iii) holds is valid, the values derived in Table 7 will not be absolute. The "Hückel orbitals" for *o*-phenanthroline have been calculated for us by A. Hudson and G. R. Luckhurst: the spin densities found for the highest bonding and lowest antibonding orbitals are quoted in Table 8 together with the spin densities for $\text{Fe}^{\text{III}}(\text{o-phen})_3$ derived by Larson and Wahl⁹ (the M-H interaction for the 2 and 9 positions is well illustrated in this Table). If, as in Figure 3a, the change in charge given in Table 7 is plotted against the spin densities in the highest bonding orbital of the uncomplexed ligand, it can be seen that the calculated change in charge, at a given position, increases as the spin density at that position increases.

¹⁸ I. C. Smith and W. G. Schneider, *Canad. J. Chem.*, 1961, **39**, 1158.

¹⁹ V. R. Sandel and H. H. Freedman, *J. Amer. Chem. Soc.*, 1963, **85**, 2328.

TABLE 8

Theoretical and experimental spin densities at various positions for *o*-phenanthroline

Position	2 and 9	3 and 8	4 and 7	5 and 6
Highest bonding orbital	0.0631	0.0030	0.0833	0.2080
Lowest antibonding orbital	0.1330	0.0006	0.1424	0.1385
Fe ^{III} (<i>o</i> -phen) ₃ (ref. 9)	33.6 × 10 ⁻³	6.3 × 10 ⁻³	-0.3 × 10 ⁻³	3.9 × 10 ⁻³

If the difference shown between iron-ruthenium and cobalt-zinc plots is significant, it must be caused by a change in either the strength or the type of metal-nitrogen bond formed. The stability of the ferrous-*o*-phenanthroline complex is anomalously high²⁰ and therefore the ruthenous complex can be expected to show a similarly high stability: this is explained by the formation of a low-spin complex on the addition of the third ligand molecule during the formation of this complex. The stability may also be caused partially by some extra metal-ligand bonding.

If an electron is transferred from the highest bonding orbital to the lowest antibonding orbital of *o*-phenanthroline, then the Hückel values quoted above show that the changes in charge at positions 3, 4, and 5 would be +0.002, -0.059, and +0.070, respectively. The occurrence of back π -bonding and stronger σ -bonding would have such a net effect as this. When the graphs for the Fe^{II} and Ru^{II} complexes shown in Figure 3*a* are superimposed on that of the Zn^{II} complex, as in Figure 3*b*, then the differences at positions 4 and 5, seen in such a plot, could be explained by the occurrence of a greater degree of π -bonding in the Fe^{II} and Ru^{II} cases. The magnitude of the observed effect is Ru^{II} > Fe^{II} > Zn^{II}, which is the order to be expected for a π -bonding effect. There is precedent for this: an increase in π -bonding from Fe to Ru is postulated by Schilt²¹ for M(dipy)₂(CN)₂ from infrared studies of the CN frequencies. While such an explanation is plausible, the evidence presented in this Paper is insufficient to make this explanation more than tentative.

Tetra-o-phenanthroline-Metal Complexes.—The spectra of the calcium- and magnesium-tetra-*o*-phenanthroline complexes have been measured, and are summarised in Table 9.

TABLE 9

N.m.r. resonance frequencies (τ units) relative to TBA
(taken to have τ 8.78)

	Protons 2 and 9	3 and 8	4 and 7	5 and 6
Ca(<i>o</i> -phen) ₄ ²⁺	1.34, 1.36	2.63, 2.71	2.25, 2.28	3.08
	1.42, 1.44	2.77, 2.84	2.40, 2.42	
Mg(<i>o</i> -phen) ₄ ²⁺	1.43, † 1.46	2.64, 2.72	2.24, † 2.27	3.10
	1.52 *	2.78, 2.86	2.40 *	

* Unresolved doublet. † Shoulder.

These spectra have peaks which occur at the same frequencies, within experimental error, for all positions except 2 and 9, where again a metal-hydrogen interaction can be observed. Pauling^{14b} gives the "single bond radii" of Ca and Mg as 1.736 and 1.364 Å, respectively: and so, for these complexes also, the shift to high field for the 2 and 9 proton signals increases with decreasing metal-ion size. The coincidence of the signals for the other ring positions, in these two complexes, suggests that the differences observed in the series of tris-complexes studied are significant, and not just random, or experimental, errors. The shifts for positions 3 to 8 occur at higher fields than in the tris-complexes reported above. Such a phenomenon would be expected from the application of Pauling's electroneutrality rule or may be caused by change in environment.

Conclusion.—The proton n.m.r. spectra of *o*-phenanthroline and all the complexes studied can be analysed on an AA'MM'SS'X₂ model, yielding coupling constants similar to those of the related pyridine and naphthalene molecules. The use of such a model is

²⁰ H. Irving and D. H. Mellor, *J.*, 1962, 5222.²¹ A. A. Schilt, *Inorg. Chem.*, 1964, 3, 1323.

supported by these derived coupling constants, by the consistency of all results obtained from the use of this model, and by the study of tetramethyl-*o*-phenanthrolines and their ferrous complexes.

In all the metal complexes studied, a shift to higher field was found for the 2 and 9 protons, which increases as the central metal-ion size, and therefore the metal-hydrogen distance, decreases. This high-field shift occurring for hydrogen atoms not directly bonded to the metal atom may be analogous to that observed for directly bonded hydrogen atoms reported elsewhere,^{16,17} or that found to arise due to electric fields. It also seems likely that the resonance frequencies for all the aromatic proton signals move to higher field as the ligand molecule becomes chelated into an ion of greater complexity.

There is some evidence supporting the assumption that the chemical shift for a given set of protons in *o*-phenanthroline varies approximately linearly with the charge on the neighbouring carbon atom. Although absolute values for the change in charge at a given ring position on complexing a metal ion to the ligand molecule cannot be obtained by assuming this linearity to hold, the numerical values obtained for the change in charge will be self-consistent for complexes having the same stoichiometry, and suggest that the distribution of charge on the ligand molecule in the Fe^{II} and Ru^{II} tris-complexes may be different from that in the Co^{III} and Zn^{II} tris-complexes. This difference may be tentatively explained by the existence of a greater degree of π -bonding in the iron and ruthenium complexes.

EXPERIMENTAL

o-Phenanthroline (Hopkin and Williams Ltd.) and the 3,4,7,8- and 3,5,6,8-tetramethyl derivatives (G. Frederick Smith Company) were used without purification.

Tetra-o-phenanthrolinecalcium(II) *Cation*.—Anhydrous calcium chloride (70—75%) (0.056 g.) and *o*-phen, H₂O (0.3 g.) were dissolved in 30 ml. of water, acidified with 1 ml. of 2*N*-HCl. After warming for 30 min. the excess of acid was neutralised by adding ammonium hydroxide and boiling off the excess ammonia. For analysis, the complex was precipitated by adding excess of sodium perchlorate, filtering, washing, and drying [Found: C, 57.7; H, 4.6; Cl, 7.3; N, 11.8. Calc. for Ca(*o*-phen)₄(ClO₄)₂, 2H₂O: C, 57.8; H, 3.6; Cl, 7.2; N, 11.3].

Tris-o-phenanthrolinecobalt(III) *Cation*.—This complex was prepared by the method of Ellis *et al.*²² as the chloride, and precipitated as the perchlorate [Found: C, 45.57; H, 3.43; Cl, 13.6; N, 8.65. Calc. for Co(*o*-phen)₃(ClO₄)₃, 3H₂O: C, 45.49; H, 3.16; Cl, 11.2; N, 8.84].

Tris-o-phenanthrolineiron(II) *Cation*.—This was prepared by dissolving analytical reagent grade ferrous ammonium sulphate and *o*-phenanthroline in water in the molar proportions of 1 : 3.1.

Tetakis-o-phenanthroline magnesium(II) *Cation*.—The chloride MgCl₂, 6H₂O (0.1 g.) and 0.3 g. of *o*-phen, H₂O were treated in the same way as the calcium salt and ligand [Found: C, 58.5; H, 4.2; Cl, 6.7; N, 11.9. Calc. for Mg(*o*-phen)₄(ClO₄)₂, 2H₂O: C, 58.9; H, 3.7; Cl, 7.3; N, 11.5].

Tris-o-phenanthrolineruthenium(II) *Nitrate Tetrahydrate*.—Following the given²³ procedure, the complex was precipitated as the iodide. The more soluble nitrate was produced from this by shaking with excess of freshly precipitated silver oxide, filtering, and acidifying the filtrate with nitric acid [Found: C, 46.7; H, 3.1; N, 8.9. Calc. for Ru(*o*-phen)₃I₂, 2H₂O: C, 46.5; H, 3.0; N, 9.0%. Found: C, 50.9; H, 3.7; N, 13.7. Calc. for Ru(*o*-phen)₃(NO₃)₂, 4H₂O: C, 51.5; H, 3.8; N, 13.4%].

Tris-o-phenanthrolinezinc(II) *Sulphate Tetrahydrate*.—Zinc (0.03 g.) was dissolved in dilute hydrochloric acid and 0.3 g. of *o*-phen, H₂O added. After warming for 30 min., the excess of acetic was neutralised with ammonia and the excess ammonia boiled off. Excess of Na₂SO₄ was added and the precipitated complex filtered off, washed, and dried [Found: C, 56.8; H, 4.5; N, 11.2. Calc. for Zn(*o*-phen)₃SO₄, 4H₂O: C, 56.8; H, 4.2; N, 10.9%].

All analyses were by the Micro-analytical Department of the Department of Organic,

²² P. Ellis, R. G. Wilkins, and M. J. G. Williams, *J.*, 1957, 4456.

²³ F. P. Dwyer, J. E. Humpoetz, and R. S. Nyholm, *J. Proc. Roy. Soc. New South Wales*, 1947, 80, 212.

Inorganic, and Theoretical Chemistry of the University of Cambridge. N.m.r. spectra were recorded on a Perkin-Elmer 60 Mc./sec. R. 10 Spectrometer. *t*-Butyl alcohol was used as internal standard.

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