874. *The Proton Magnetic Resonance Spectra of* o-*Phenanthroline and Some of its Metal Complexes in Non-aqueous Solution*

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The nuclear magnetic resonance (n.m.r.) spectra of *o*-phenanthroline, the tris-*o*-phenanthroline complexes of cobalt(III), iron(II), ruthenium(II), and osmium(II), and that of the biscyanobis-*o*-phenanthroline complex of ruthenium(II), in dimethyl sulphoxide solution are described, as is that of the cobalt(III) complex in light petroleum. The spectra are shown to be similar to those in aqueous solution, thus providing additional information about the nature of the metal-ligand and complex-solvent interactions occurring.

In a previous Paper,[1] the spectra of *o*-phenanthroline and some metal chelate complexes in aqueous solution were reported. This work is extended here to non-aqueous solutions of some of the complexes, in an attempt to gain more information on the nature of the shift to high field observed for the 2- and 9-protons on chelation to metal ions; and also to obtain larger concentrations of complex, so enabling the spectrum of the tris-*o*-phenanthroline complex of osmium(II) to be obtained. Even with the best solvent found, dimethyl sulphoxide, it proved possible to obtain only a weak spectrum of the neutral complex Ru(*o*-phen)$_2$CN$_2$. For more accurate comparison of the spectra in the various solvents, it was found necessary to fit part of the ferroin spectra to an ABX model.

Results and Discussion

The spectrum of tris-*o*-phenanthrolinecobalt(III) in light petroleum (b. p. 60—80°), and those of *o*-phenanthroline and the tris-complexes of cobalt(III), iron(II), osmium(II), ruthenium(II), and the complex biscyanobis-*o*-phenanthrolineruthenium(II) in dimethyl sulphoxide are shown in Table 1: that of the cyanide complex is weak and incompletely resolved. As found previously, the fine splitting caused by coupling between protons in positions 2 and 4 (and 7 and 9) is often incapable of resolution when the ligand is complexed, although resolution is possible for the free ligand. In most cases, these unresolved doublets were seen to be appreciably broader than the singlet peaks.

Table 1

Peak positions in the n.m.r. spectra of *o*-phenanthroline complexes in nonaqueous solvents. (Values given in p.p.m. relative to the stated standard); " *o*-phen " = *o*-phenanthroline.

Sample	Solvent	Protons				Standard
		2- & 9-	3- & 8-	4- & 7-	5- & 6-	
Co(*o*-phen)$_3$$^{3+}$	Petrol	−5·64, −5·56	−6·09, −5·99, −5·95, −5·86	−7·17, −7·02	−6·52	Main petrol peak
o-Phen	DMSO	−6·65, −6·62, −6·58, −6·56	−5·34, −5·27, −5·19, −5·13	−6·05, −6·02, −5·91, −5·88	−5·47	Main DMSO peak
Co(*o*-phen)$_3$$^{3+}$	DMSO	−5·17, −5·11	−5·56, −5·48b, −5·34	−6·71, −6·58	−6·04	,,
Fe(*o*-phen)$_3$$^{2+}$	DMSO	−5·27, −5·23,	−5·18, −5·13 *	−6·37, −6·30, −6·27, −6·21	−5·89	,,
Os(*o*-phen)$_3$$^{2+}$	DMSO	−5·55, −5·47	−5·30, −5·20, −5·16, −5·07	−6·13, −6·00	−5·89	,,
Ru(*o*-phen)$_3$$^{2+}$	DMSO	−5·59, −5·51	−5·33, −5·29, −5·20, −5·15	−6·31, −6·18b	−5·86	,,
Ru(*o*-phen)$_2$CN$_2$	DMSO	−5·48b	−5·34, −5·26, −5·16b, −5·08	−6·03, −5·90	−5·68	,,

b = broad.

* Overlapping band system.

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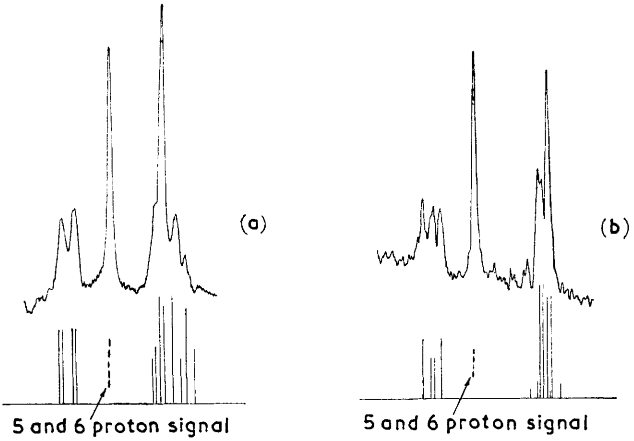
[1] J. D. Miller and R. H. Prince, *J.*, 1965, 3185.

As in aqueous solution, the spectrum of the ferroin sample is less simple than that of the other ions studied, and so, for the better comparison of aqueous and nonaqueous results, these spectra were compared with those predicted for an ABX model.[2] The best theoretical fit requires coupling constants that compare closely with those previously reported[1] for other *o*-phenanthroline complexes: in the aqueous solution these constants are $J_{2,3} = 4{\cdot}8$, $J_{2,4} = 1{\cdot}2$, and $J_{3,4} = 8{\cdot}4$ c./sec., while those in the dimethyl sulphoxide solution are $J_{2,3} = 4{\cdot}8$, $J_{2,4} = 1{\cdot}8$, and $J_{3,4} = 8{\cdot}4$ c./sec. The theoretical and experimental spectra are compared in the Figure and Table 2. A better agreement between theoretical and experimental values would be obtained by considering an ABC model, rather than the approximate model used here. In Table 3, the centres of the various peak systems in water and dimethyl sulphoxide are tabulated; those in water are taken from ref. 1.



Comparison of spectra of Fe(*o*-phen)$_3$(CrO$_4$)$_2$ in (a) H_2O and (b) DMSO with predicted spectra

TABLE 2

Comparison of experimental and theoretical spectra of ferroin in water and DMSO. (Values are given in τ units with area ratios in brackets: $\tau_{\text{TBA}} = 8{\cdot}78$ in water and $\tau_{\text{DMSO}} = 7{\cdot}45$ are taken as standards.)

Fe(*o*-phen)$_3{}^{2+}$ in water	2·17(1·7), 2·24(4·9), 2·37(2·0), 2·47(0·5)	1·29(2·1)b, 1·41(2·0)b	1·75(4·0)
ABX model for water	2·15(0·59), 2·18(0·74), 2·23(1·41), 2·26(1·26), 2·35(1·41), 2·48(1·26), 2·43(0·59), 2·56(0·74)	1·27(1·00), 1·30(0·99), 1·40(0·99), 1·43(1·00)	(4·00)
Fe(*o*-phen)$_3{}^{2+}$ in DMSO	2·18(1·2), 2·22(1·2), 2·27(1·6), 2·32(1·2)	1·08(1), 1·15(0·8), 1·18(0·8), 1·24(1)	1·56(3·6)
ABX model for DMSO	2·12(0·11), 2·19(0·29), 2·20(1·89), 2·27(1·71), 2·22(1·89), 2·31(1·71), 2·30(0·11), 2·39(0·29)	1·09(1·00), 1·16(0·66), 1·18(0·66), 1·25(1·00)	(4·00)

The high-field shift for the protons at positions 2 and 9, when the *o*-phenanthroline molecule becomes complexed, is still evident in both solvents used here and, as the values in Table 3 indicate, is not much altered when the solvent is changed. Examination of the resonance frequencies given in Table 3 shows that the frequency for the 2- and 9-protons in the complexes appears to be less affected by the change of solvent than the frequencies of the remaining protons, implying that the high-field shift is largely independent of solvent. Such a phenomenon may be explained by the inability of solvent molecules (including

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[2] "High-Resolution Nuclear Magnetic Resonance," J. A. Pople, W. G. Schneider, and H. J. Bernstein, McGraw-Hill, 1959, p. 133.

water) to penetrate the complex ion sufficiently and so to modify the interaction found between the central ion and the 2- and 9-protons of the ligand, or to the solvent's forming a similar environment to that given by water, though the latter alternative seems less likely.

The spectrum obtained for the neutral complex Ru(*o*-phen)$_2$(CN$_2$) in dimethyl sulphoxide is not very satisfactory owing to the limited solubility of the complex. The weak spectrum obtained has been tentatively assigned on the same basis as the other complexes, as shown in Table 1. This assignment, if correct, shows that the frequency of the 2- and 9-protons is nearly the same as that of the charged tris-ruthenium(II) complex, while the other proton frequencies correspond more closely to those of the free ligand. This evidence suggests that the high-field shift occurring for the 2- and 9-protons in complexes is not strongly dependent on the charge of the complex. The variations in resonance frequency for the zinc(II)-, iron(II)-, and ruthenium(II)-tris-*o*-phenanthroline complexes in aqueous solutions may be explained by the occurrence of back π-bonding;[1] such an explanation is possible here for the variation in the resonance frequencies of the 4- and 7-protons in the tris-complexes of iron(II), ruthenium(II), and osmium(II) in dimethyl sulphoxide. No trend is apparent, however, in the frequencies of the 3-, 5-, 6-, and 8-protons, such as one would expect.

TABLE 3

Centres of peak systems for the protons of *o*-phanthroline, in various environments. (Values are given in τ units; $\tau_{\text{TBA}} = 8{\cdot}78$ is taken as standard in both solvents.)

		Protons			
Solute	Solvent	2 & 9	3 & 8	4 & 7	5 & 6
o-Phenanthroline	H_2O	0·98	2·00	1·31	2·12
	DMSO	0·74	2·12	1·39	1·88
Co(*o*-phen)$_3{}^{3+}$	H_2O	2·32	2·02	0·90	1·49
	DMSO	2·21	1·88	0·71	1·31
Fe(*o*-phen)$_3{}^{2+}$	H_2O	2·21	2·45	1·35	1·75
	DMSO	2·14	2·16	1·06	1·46
Os(*o*-phen)$_3{}^{2+}$	DMSO	1·84	2·17	1·29	1·46
Ru(*o*-phen)$_3{}^{2+}$	H_2O	1·95	2·48	1·50	1·84
	DMSO	1·80	2·11	1·21	1·49

While the change in resonance frequencies for positions 3—8 in the metal complexes on changing solvent are similar in both magnitude and sense, those occurring for free *o*-phenanthroline are not so; such a phenomenon can be explained by postulating some interaction between the nitrogen atoms of the organic molecule and the solvent, which changes with solvent.

To summarise, the n.m.r. spectra of *o*-phenanthroline and those complexes studied are little affected by a change in solvent. The changes occurring for the signals of protons 2 and 9 are even smaller than those for the other protons, perhaps because of the absence of closely adjacent solvent molecules. For the series Fe(*o*-phen)$_3{}^{2+}$, Ru(*o*-phen)$^{2+}$, and Os(*o*-phen)$_3{}^{2+}$ in dimethyl sulphoxide, the trend in resonance frequency for the protons 4 and 7 may be caused by increasing back π-bonding as the central metal ion becomes heavier, as was suggested previously for the series Zn(*o*-phen)$_3{}^{2+}$, Fe(*o*-phen)$_3{}^{2+}$, and Ru(*o*-phen)$_3{}^{2+}$ in water: the possibility that this is a solvent effect has not, however, been ruled out.

EXPERIMENTAL

The cationic tris-complexes were dissolved in spectroscopic quality dimethyl sulphoxide as the perchlorates. The preparation of those of Co(III), Fe(II), and Ru(II) have been reported previously.[1]

*Tris-*o*-phenanthrolineosmium*(II) *Perchlorate.*—The complex was prepared by the method of Dwyer *et al.*[3] starting from diammonium hexachloro-osmiate (1 g.): the complex was precipitated

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[3] F. W. Dwyer, N. A. Gibson, and E. C. Gyarfas, *J. and Proc. Roy. Soc., New South Wales*, 1950, **84**, 68.

as the perchlorate [Found: C, 44·6; H, 3·0; N, 8·9. Calc. for Os(*o*-phen)$_3$(ClO$_4$)$_2$,2H$_2$O; C, 44·7; H, 2·9; N, 8·7%].

*Biscyanobis-*o*-phenanthrolineruthenium*(II).—This was prepared by the method of Schilt[4] from commercial ruthenium trichloride (Messrs. Johnson and Matthey) [Found: C, 56·5; H, 3·8; N, 14·5. Calc. for Ru(*o*-phen)$_2$(CN$_2$,3H$_2$O: C, 55·0; H, 3·8; N, 14·8%].

All analyses were performed by the Department of Micro-analysis of the Department of Organic, Inorganic, and Theoretical Chemistry of the University of Cambridge; n.m.r. spectra were recorded on a Perkin-Elmer 60 Mc./sec. R10 spectrometer.

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[4] A. A. Schilt, *J. Amer. Chem. Soc.*, 1963, **85**, 904.