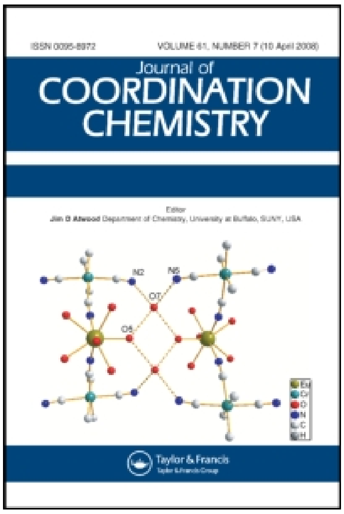

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

NMR STUDIES OF OCTAHEDRAL DI- AND TETRACYANO-(2,2 ' -BIPYRIDINE) IRON(II) COMPLEXES

B. V. Agarwala[a]; K. V. Ramanathan[b]; C. L. Khetrapal[b]
[a] Chemistry Department, University of Allahabad, Allahabad, India [b] Sophisticated Instruments Facility, Indian Institute of Science, Bangalore, India

To cite this Article Agarwala, B. V. , Ramanathan, K. V. and Khetrapal, C. L.(1985) 'NMR STUDIES OF OCTAHEDRAL DI- AND TETRACYANO-(2,2 ' -BIPYRIDINE) IRON(II) COMPLEXES', Journal of Coordination Chemistry, 14: 2, 133 — 137

To link to this Article: DOI: 10.1080/00958978508073899

URL: http://dx.doi.org/10.1080/00958978508073899

J. Coord. Chem. 1985, Vol. 14 pp. 133–137
0095-8972/85/1402-0127 $25.00/0

NOTE

NMR STUDIES OF OCTAHEDRAL DI- AND TETRACYANO-(2,2'-BIPYRIDINE) IRON(II) COMPLEXES

B.V. AGARWALA
Chemistry Department, University of Allahabad, Allahabad 211 002, India.

K.V. RAMANATHAN and C.L. KHETRAPAL†
Sophisticated Instruments Facility, Indian Institute of Science, Bangalore 560 012, India.

(Received December 13, 1984)

Keywords: 2,2'-bipyridine; cyanide; complexes; NMR studies; diimines; coordination geometries

Coordination compounds of the polypyridines, 2,2'-bipyridine (bipy) and 1,10-penanthroline (phen) have offered renewed interest on account of their manifold applications and from the point of view of understanding their structure-reactivity relationships.[1] Iron(II) reacts with them to form *tris*-complexes possessing spin-paired ground states. Cyanide ion greatly enhances the rate of displacement of bipy or phen to form the Schilt class of compounds, $Fe(bipy)_2(CN)_2$ and $Fe(phen)_2(CN)_2$. They display varying colours in solution depending upon the nature of the solvent and react reversibly with acids to form diprotonated species.[2] Magnetic circular dichroism studies have been reported to describe their lowest electronic excitation.[3]

In view of the large number of anomalies and inadequate spectral information available in the literature, detailed NMR studies of dicyanobis(bipy) and tetracyano(bipy) complexes of iron(II) have been undertaken and the results are reported in the present communication. An NMR study of $K_2Fe(phen)(CN)_4$ in DMSO-d_6 and D_2O has been reported earlier.[4] The results indicate the presence of two stable species in D_2O solution. Definitive results concerning the dicyanobis(phen) Fe(II) complex could not be obtained due to its poor solubility.

The complexes were prepared by a standard procedure.[5] The proton and carbon NMR spectra were recorded in DMSO-d_6, D_2O and acetone d_6 + D_2O solutions on a Bruker WH-270 Fourier-transform NMR spectrometer. The operating frequencies were 270 and 67.9 MHz for the ^1H and the ^{13}C-spectra respectively. The chemical shifts were measured with respect to TMS used as internal standard for the DMSO-d_6 solution and DSS for the solution prepared in D_2O or its mixture with acetone-d_6. The spectrum of uncomplexed bipyridine was also recorded for comparison. Typical spectra are shown in Figures 1 to 4.

RESULTS AND DISCUSSION

The ^1H-NMR spectra of $Fe(bipy)_2(CN)_2$ in acetone-d_6 + D_2O and DMSO-d_6 are shown in Figure 1 along with the spectrum of the ligand. The broad band decoupled ^{13}C spectrum

---

† Author for correspondence

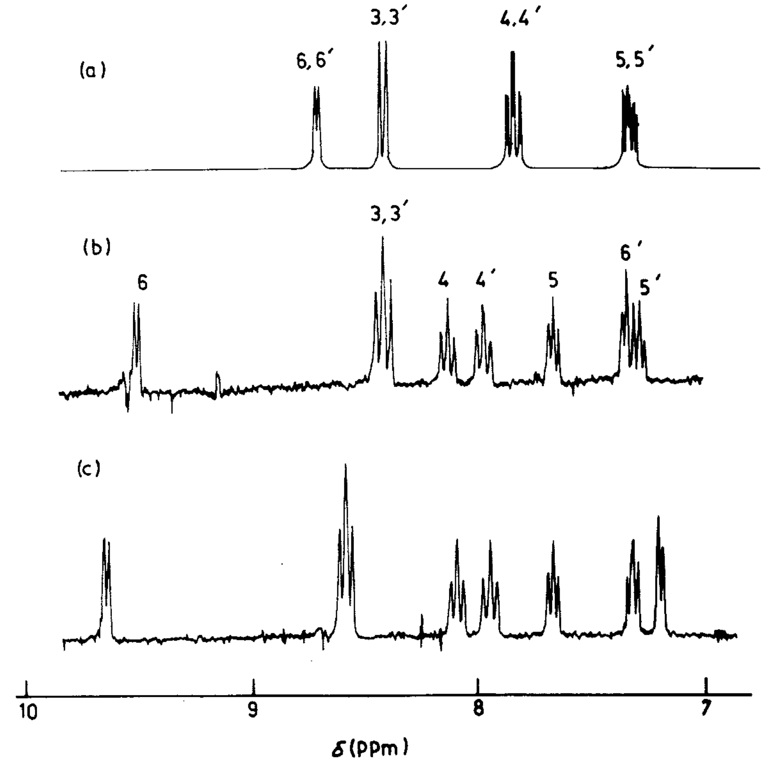

FIGURE 1 ^1H NMR spectra of the ligand (2,2′-bipyridine) and the complex $Fe(bipy)_2(CN)_2$: (a) the ligand spectrum in $CDCL_3$, (b) the spectrum of the complex in acetone-d_6 + D_2O and (c) the spectrum of the complex in DMSO-d_6.

of the complex in acetone-d_6 + D_2O shows ten signals (Figure 2) between 124 ppm and 172 ppm. They arise from the ^{13}C-nuclei of the bipyridyl ligands. Due to the long spin-lattice relaxation times of the cyano carbons, their corresponding signals were not observed

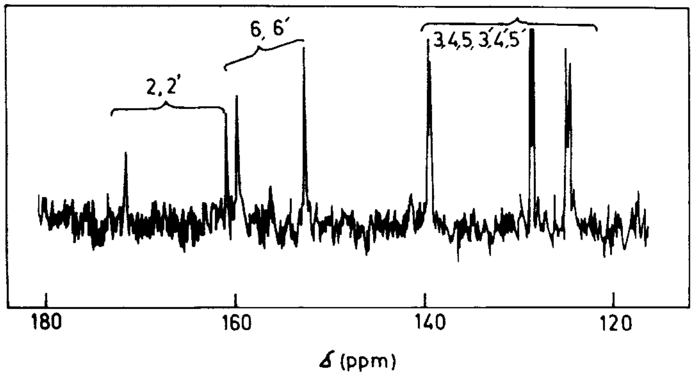

FIGURE 2 Broad band decoupled ^{13}C NMR spectrum of $Fe(bipy)_2(CN)_2$ in acetone-d_6 + D_2O.

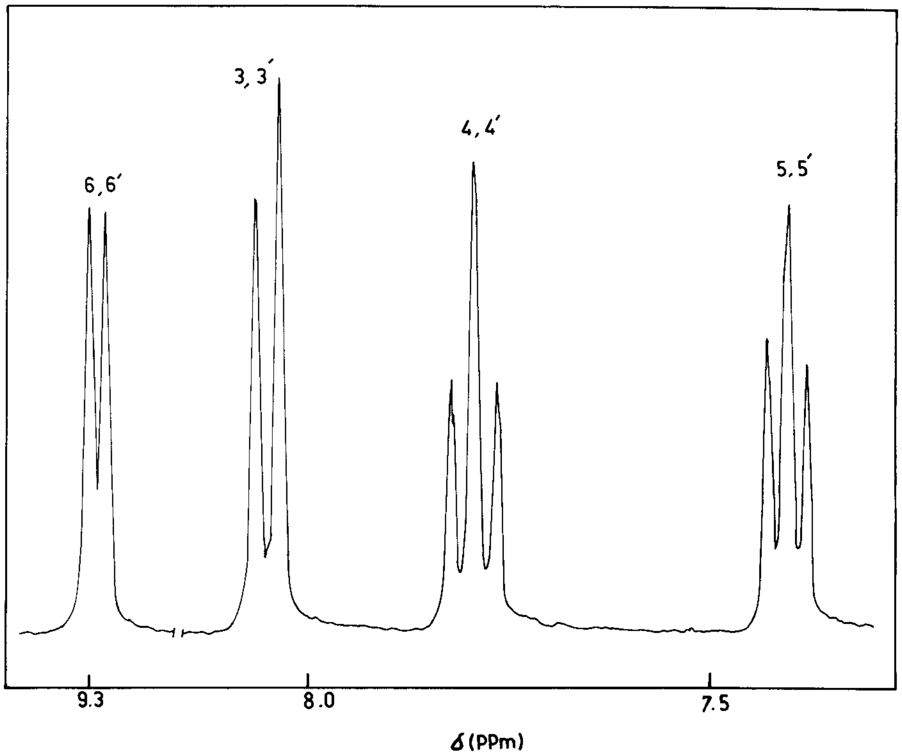

FIGURE 3 Proton NMR spectrum of $K_2Fe(bipy)(CN)_4$ in D_2O.

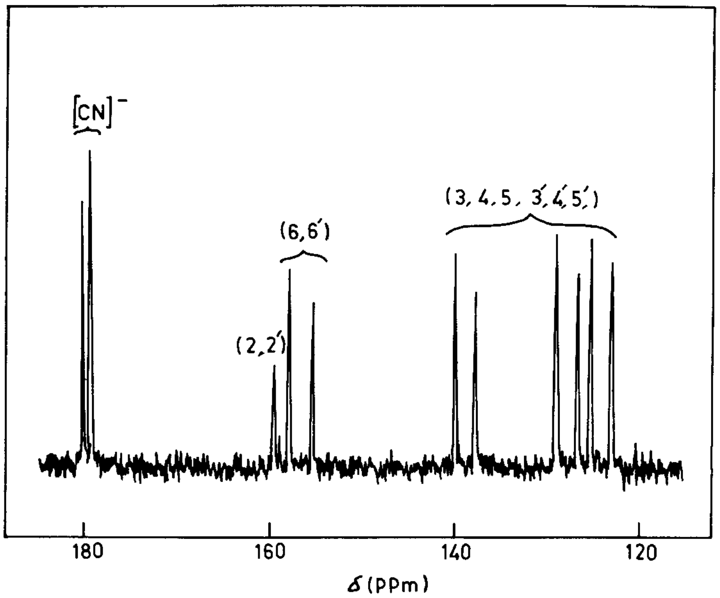

FIGURE 4 Off-resonance decoupled ^{13}C NMR spectrum of $K_2Fe(bipy)(CN)_4$ in D_2O.

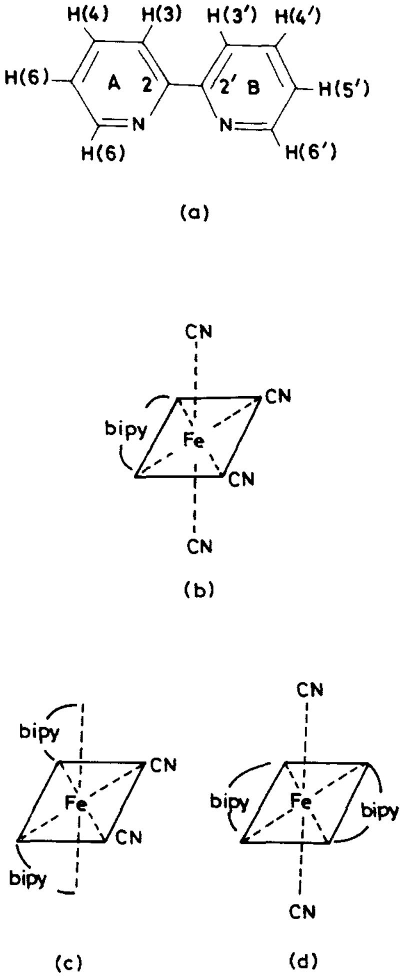

FIGURE 5 Structures of 2,2-bipyridine (a), tetracyano (b) and *cis* (c) and *trans* (d) dicyano-complexes of iron(II).

under the conditions of the experiments. No special attempt was made to observe these signals since the desired information could be obtained from the signals due to the ring carbons. The proton and the off-resonance decoupled ^{13}C spectra of the tetracyano complex are shown in Figures 3 and 4 along with assignments of lines to specific nuclei (Figure 5) based on assignments in the ligand.[6,7] The broad band proton decoupled ^{13}C spectrum of the tetracyano complex shows five lines between 120–160 ppm arising from the five non-equivalenat bipyridine carbons. The off-resonance proton decoupled ^{13}C spectrum of the complex (Figure 4) shows doublets for each carbon resonance having protons directly attached to them and singlets for those where there are no directly bonded protons. The spectra shown in Figures 3 and 4 clearly establish the presence of single species with equivalence of the two halves of the bipyridyl ligand.

The spectra of the dicyano compound are more complex (Figure 1 and 2). They show nearly double the number of lines/groups. Analogous observations have been made for the other similar complexes Fe(5,5′-Me_2bipy)$_2$$(CN)_2$ and Pt(bipy)$_2$ OH^+.[8,9] The results cannot be interpreted in terms of a single *trans* species since in such a situation spectra similar to those for the tetracyano compound would have been expected. On the other hand, complex patterns as shown in Figure 1 and 2 indicate either the nonequivalence of the two halves of the bipyridyl ligand or the existence of two species where the two halves are equivalent as in the tetracyano phenanthroline complex.[4] A study of the temperature, concentration and solvent dependences of the spectra of the dicyano complex did not reveal any changes in spectral patterns or relative intensities. Furthermore, in the proton spectra the intensities of the lines due to different groups were nearly equal.

The results indicate the presence of a single species and this is assigned as the *cis* form. The two halves of the bipyridyl ligand are not equivalent for such a configuration and the doubling of the lines can, therefore, be easily explained. Assignments of the resonance (Figures 1, 2 and 5) due to different nuclei can be made on the basis of ring current effects. ring (B) of one of the bipyridyl ligands lies above ring (A) of the other and this results in upfield shifts of the resonances of the protons of the (B) ring with respect to those of the (A) ring (Figure 5). The magnitude of the shift is dependent upon the distance of the particular proton in ring (B) from ring (A). Though a quantitative calculation of the shift is not attempted, it is qualitatively observed that the 6′ proton is closest to ring (A) and the 3′ proton is furthest. Thus for the 6′ proton, the upfield shift is at a maximum and the 3′ proton is virtually unaffected. Similarly, the shift of the 5′ proton is more than that of the 4′ proton.

ACKNOWLEDGEMENTS

The authors are grateful to Drs. E.D. Becker and O.A. Gansow (USA) and Dr. G. Nord (Denmark) for helpful discussions.

REFERENCES

1. N. Serpone, G. Ponterini and M.A. Jamieson, *Coord. Chem. Rev.*, **50,** 209 (1983).
2. A.A. Schilt, *J. Amer. Chem. Soc.*, **82,** 5779 (1960); **85,** 904 (1963).
3. H. Kobayashi, B.V. Agarwala and Y. Kaizu, *Bull. Chem. Soc. Japan*, **48,** 465 (1975).
4. B.V. Agarwala, K.V. Ramanathan and C.L. Khetrapal, *Bull. Mag. Reson.*, **5,** 224 (1983).
5. A.A. Schilt, *J. Amer. Chem. Soc.*, **82,** 3000 (1960).
6. F.A. Kramer and R. West, *J. Phys. Chem.*, **69,** 673 (1965).
7. S. Castellano, H. Gunther and S. Ebersold, *J. Phys. Chem.*, **69,** 4166 (1965).
8. R.D. Gillard, C.T. Hughes, L.A.P. Kane-Maguire and P.A. Williams, *Trans. Met. Chem.*, **1,** 114 (1976).
9. O. Farver, O. Monsted and G. Nord, *J. Amer. Chem. Soc.*, **101,** 6118 (1979).