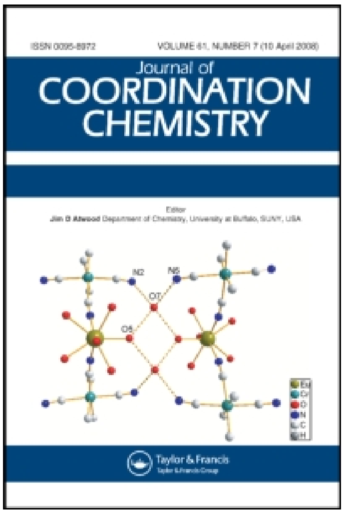

Journal of Coordination Chemistry

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

Mössbauer Parameters of Iron(II) Naphthyridine Complexes[1]

Elaine Dittmar[a]; C. J. Alexander[b]; Mary L. Good[b]
[a] Davis and Elkins College, Elkins, West Virginia [b] Louisiana State University in New Orleans, New Orleans, Louisiana

To cite this Article Dittmar, Elaine , Alexander, C. J. and Good, Mary L.(1972) 'Mössbauer Parameters of Iron(II) Naphthyridine Complexes[1]', Journal of Coordination Chemistry, 2: 1, 69 — 70

To link to this Article: DOI: 10.1080/00958977208072951

URL: http://dx.doi.org/10.1080/00958977208072951

J. Coord. Chem., 1972, Vol. 2, pp. 69–70

SHORT COMMUNICATIONS

Mössbauer Parameters of Iron(II) Naphthyridine Complexes[1]

ELAINE DITTMAR

Davis and Elkins College, Elkins, West Virginia 26241

and

C. J. ALEXANDER and MARY L. GOOD

Louisiana State University in New Orleans, Lakefront, New Orleans, Louisiana 70122

(*Received February* 7, 1972; *in final form April* 5, 1972)

Dear Sir:

We wish to report the Mössbauer parameters and magnetic moment for the only authenticated[2] eight-coordinate iron(II) complex, tetrakis (1,8-naphthyridine) iron(II) perchlorate,[3] and to propose that the Mössbauer data for the compound in solution and after exposure to moisture can be rationalized in terms of a change in ligands with retention of eight-coordination (Table I). Tentative values for the six-coordinate 2,7-dimethyl-1,8-naphthyridine complex are given since we have been unable to prepare the pure material. The spectrum for this compound contains two overlapping doublets with Mössbauer parameters indicative of a mixture of high-spin iron (II) and iron(III) species.

When exposed to moist air, the naphthyridine (napy) complex picks up about 8–9 water molecules and changes in color from a bright orange to a very pale tan. The regeneration of the anhydrous complex is readily accomplished by desiccation. Recovery of the complex from acetonitrile solution is complete and achieved by simple evaporation of the solvent.

Octahedral coordination for the napy species when dissolved in acetonitrile has been proposed based upon the presence of a near infrared spectral band at 9,000 cm^{-1} for the complex in solution and the absence of any band in this spectral region for the anhydrous material.[4] Upon repeating this work, we found a band centered around 10,300 cm^{-1} (Table II) for the anhydrous complex. A similar weak band at 10,500 cm^{-1} has subsequently

TABLE I

Mössbauer Parameters[a] and Magnetic Moments of Fe(II) Naphthyridine Complexes

Complex	δ mm/sec	ΔE_q mm/sec	$\Gamma\frac{1}{2}$[c] mm/sec	d[d] mg Fe/cm^2	μ_{eff}[e] B.M.
$[Fe(napy)_4](ClO_4)_2$	+1.14	4.49	0.29 ± 0.01	1.3	5.05
$[Fe(napy)_4(H_2O)_4](ClO_4)_2 \cdot XH_2O$[b]	+1.35	3.27	0.41 ± 0.06	1.1	
$[Fe(napy)_4(CH_3CN)_4]^{++}$[b] in acetonitrile	+1.29	2.97	0.74 ± 0.19	1.3	
$[Fe(2,7\text{-dmnapy})_3](ClO_4)_2$[f]	+1.04	1.80	~0.29	~3	5.55

[a] Determined at 77°K with respect to iron foil standard.
[b] Proposed coordination.
[c] Width of peak at half height.
[d] Area density.
[e] Determined at room temperature by Gouy method.
[f] Tentative values. $\delta = 0.47$ mm/sec and $\Delta E_q = 0.61$ mm/sec for a contaminating iron(III) species.

TABLE II

Comparison of Near Infrared Spectral Results

Complex	This Work (cm^{-1})	Previous Work (cm^{-1})	
		Ref. 4	Ref. 5
$[Fe(napy)_4](ClO_4)_2$	10,300[a]	none	10,500
$[Fe(napy)_4(H_2O)_4](ClO_4)_2.XH_2O$	9,500[a]	——	——
$[Fe(napy)_4(CH_3CN)_4]^{++}$ in acetonitrile	9,100	9,000	9,170
$[Fe(2,7\text{-dmnapy})_3](ClO_4)_2$	10,300[a]	10,100[b]	——
$[Fe(2,7\text{-dmnapy})_3]^{++}$ in acetonitrile	10,100	——	——

[a] Determined in nujol mulls.

[b] In nitromethane solution.

been reported by Bodner and Hendricker for the eight-coordinate species.[5]

The isomer shift values (δ) shown in Table I are within the range found for other high-spin iron(II) compounds in which the bonding is considered to be of the outer-sphere type. The increase in δ for the hydrated species, and species in solution, over that found for the anhydrous complex cannot readily be explained as resulting from a change in coordination from eight to six. An increase in s-electron density at the iron nucleus would be expected to result from such a change and, indeed, the 2,7-dmnapy complex, which is believed to be 6-coordinate,[6] does show an increase. (For iron an increase in s-electron density produces a decrease in δ.) The data are consistent with the retention of 8-coordination and the possible substitution of some ligand sites by water or acetonitrile molecules.

The iron-nitrogen bond distances at the A-positions of the dodecahedron, which the napy complex assumes, are all greater than those at the B-positions.[2] Possibly in the presence of moisture and in solution the bidentate ligand becomes monodentate, remaining coordinated in the B-positions, with water or acetonitrile coordinated in the now vacant A-positions. The iron-water and iron-acetonitrile bond distances would be expected to be shorter than the original iron-napy bonds at the A-positions. For the aquo complex, this shortening could result in a τ-bond strength approximately the same as the iron-napy, producing no change in s-electron density at the iron nucleus from this source. However, possible ligand to metal π-bonding from the aquo oxygen would increase the electron density of the d-orbitals which would result in the decreased s-electron density observed. For the acetonitrile complex, the linearity of the coordinating portion of the molecule permits τ-bond formation free of any steric effects. This increased σ-bonding could produce the decrease in δ observed. Reedijk observed a change in the same direction and of the same magnitude between octahedral complexes of water and acetonitrile.[7]

The quadrupole splitting for the napy complex is the largest reported for any iron compound. The complex is very distorted[2] so that the contribution of the lattice term to ΔE_q should be quite significant. The largest splittings previously reported have been for compounds with large distortions from symmetric species.[8,9] The observed trend, i.e. a reduction in the splitting for the aquated species and a further reduction for the solvated species, is consistent with a reduction in the asymmetry of the electronic environment about the iron nucleus caused by the equalization of metal-ligand bond lengths (and bond strengths). Again, the direction and magnitude of change is the same as that observed between aquo and aceto-nitrile complexes.[7]

Further studies intended to clarify the bonding, coordination number, solvent effects, and lattice term electric field contribution in these naphthyridine complexes are in progress.[10]

ACKNOWLEDGEMENTS

We would like to thank Donna Howland for the determination of the magnetic data and Dr Ronald Prados for help with the Mössbauer runs.

REFERENCES

1. Presented in part at the Southwest Regional Meeting, American Chemical Society, San Antonio, Texas, December, 1971.
2. P. Singh, A. Clearfield, and I. Bernal, *J. Coord. Chem.* **1**, 29 (1971).
3. Abbreviations: napy, 1,8-naphthyridine; 2,7-dmnapy, 2,7-dimethyl-1,8-naphthyridine.
4. D. G. Hendricker and R. L. Bodner, *Inorg. Nucl. Chem. Letters* **6**, 187 (1970).
5. R. L. Bodner and D. G. Hendricker, *Inorg. Chem.*, in press. The manuscript was made available by Prof. Hendricker during the review of this article.
6. D. G. Hendricker and R. L. Bodner, *Inorg. Chem.* **9**, 273 (1970).
7. J. Reedijk, *Recl. Trav. Chem. Pay-Bas* **88**, 499 (1969).
8. J. P. Jesson, J. F. Weiher, and S. Trofimenko, *J. Chem. Phys.* **48**, 2058 (1968).
9. P. H. Merrell, V. L. Goedken, D. H. Busch, and J. A. Stone, *J. Am. Chem. Soc.* **92**, 7590 (1970).
10. Note added in proof. Mossbauer parameters for the solid napy complex have been reported since this communication was submitted. See: E. Konig, G. Ritter, E. Lindner and I. P. Lorenz, *Chem. Phys. Letts.* **13**, 70 (1972).