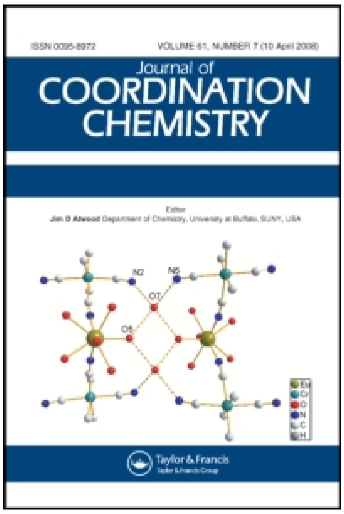

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2-Dimensional and computational analysis of the ^{1}H NMR spectrum of the bis(2,2′-bipyridine)carbonatocobalt(III) ion[†]

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The use of COSzY and NOESY ^{1}H NMR techniques allows for the assignment of ^{1}H NMR chemical shifts for the bis(2,2′-bipyridine)carbonatocobalt(III) ion. These assignments are further confirmed by DFT GIAO-NMR calculations using the model chemistry B3LYP/6-31G(d,p) and invoking the IEF-PCM representing acetone. These computations also allow for initial quantification of a *cis* influence on the chemical shift due to anisotropic ring currents and a much less pronounced *trans* influence on the chemical shift due to inductive effects. The computational model employed is also compared to previously accepted models for anisotropic effects.

Keywords: Cobalt(III) complex; ^{1}H NMR; GIAO-DFT calculations; *cis* influence; *trans* influence

1. Introduction

^{1}H nuclear magnetic resonance (NMR) spectroscopy is an essential tool for structural elucidation of hydrogen containing species including solution phase cobalt(III) complex ions [1]. While it is generally accepted that the ligands have an influence on each other's chemical shift, which also can be affected by their relative geometries, there has not been a concerted effort to quantitate these *cis*/*trans* influences [2]. The bis(2,2′-bipyridine)carbonatocobalt(III) ion (**1**), has been chosen to begin this type of study due to the ion being diamagnetic and kinetically inert and its ^{1}H NMR spectrum being fully resolved.

Using routine Correlation Spectroscopy (COSY) and Nuclear Overhauser Effect Spectroscopy (NOESY) assignments for the ^{1}H chemical shifts can be made. These empirically determined assignments can be confirmed using Gauge Including Atomic Orbital (GIAO) Density Functional Theory (DFT) calculation methods. Interest in this

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[†]In memory of Professor Emeritus Jay H. Worrell.

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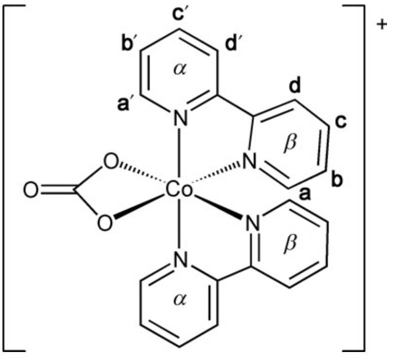

Figure 1. $[Co(CO_3)(bpy)_2]^+$ (**1**).

ion is to ascertain the *cis*/*trans* influence evident in the ^{1}H chemical shifts of the 2,2′-bipyridine (bpy) ligands.

The known structure of Complex **1** is shown in figure 1 [3–5]. Due to C_2 symmetry both bpy ligands are magnetically equivalent, but the two pyridine rings of each bpy are not equivalent (labelled α and β for discussion). The pyridine rings labelled α are *cis* to the carbonate ligand and *trans* to each other. The β pyridine rings are both *cis* and *trans* to the carbonate ligand and *cis* to each other.

Previous ^{1}H NMR spectra on similar systems has focused on the free bpy ligand [6], tris(2,2′-bipyridine)cobalt(III) ion [7], and α-*cis*-$[Co(bpy)(trien)]^{3+}$ where trien is triethylenetetraamine [8]. In these three cases the two pyridine rings of the bpy are magnetically equivalent due to symmetry and show four resonances (two doublets and two triplets) indicative of a 2-substituted pyridine ring. Recently the complex $[Co_2(bpy)_4(thM)]^{2+}$ has been reported which can be described as a binuclear complex containing a *bis*(catecholate) bridging ligand connecting two bis(bpy)Co^{3+} moieties (H_4thM is 3,3′,4,4′-tetrahydroxy-5,5′-dimethoxybenzaldazine) [9]. Due to loss of symmetry with respect to the bpy ligands, the ^{1}H NMR is somewhat more involved than complex **1**.

2. Experimental

Standard methods were used for synthesis of complex **1** using reagent grade chemicals purchased from Fisher Chemical and Sigma-Aldrich. The cobalt(III) precursor, $Na_3[Co(CO_3)_3]\cdot 3H_2O$, was synthesized as previously reported [10]. Acid promoted ligand substitution, followed by metathesis with potassium hexafluorophosphate yielded **1** as a PF_6^{1-} salt as shown in figure 2. Acetone-d_6 (99.9%) was purchased from Cambridge Isotope Laboratories containing 0.05% tetramethylsilane (TMS).

2.1. *Bis(2,2′-bipyridine)carbonatocobalt(III)chloride tetrahydrate*

A solution of 2,2′-bipyridine (0.43 g, 2.76 mmol) in 1.0 M hydrochloric acid (4.0 cm^3) was added drop-wise over 30 min at 0°C to sodium triscarbonatocobaltate(III)

$$Na_3[Co(CO_3)_3]{\cdot}3H_2O + 2bpy + 2HCl \xrightarrow{i} [Co(CO_3)(bpy)_2]Cl{\cdot}4H_2O$$

$$[Co(CO_3)(bpy)_2]Cl{\cdot}4H_2O + KPF_6 \xrightarrow{ii} [Co(CO_3)(bpy)_2]PF_6{\cdot}xH_2O$$

Figure 2. (i) H_2O, 0°C, 6 h. 79%; (ii) H_2O, quantitative.

trihydrate (1.0 g, 2.76 mmol). After stirring at room temperature for 12 h, the solution was filtered and reduced to dryness via evaporation. Recrystallization from ethanol yielded bis(2,2′-bipyridine)carbonatocobalt(III)chloride tetrahydrate (0.548 g, 79%) as a pink crystalline solid.

2.2. *Bis(2,2′-bipyridine)carbonatocobalt(III)hexafluorophosphate hydrate*

A solution of potassium hexafluorophosphate (0.20 g, 1.1 mmol) in water (10 cm^3) was added dropwise to a warm aqueous solution (10 cm^3) of bis(2,2′-bipyridine)carbonatocobalt(III)chloride tetrahydrate (0.10 g, 0.19 mmol). Upon slow cooling to 0°C a dark pink precipitate of bis(2,2′-bipyridine)carbonatocobalt(III) hexafluorophosphate hydrate (0.11 g, quantitative) was isolated by filtration and rinsed with small portions of water, ethanol and diethyl ether.

2.3. *NMR spectroscopy*

In this study, ^1H NMR analyses were completed using a Brucker Avance DRX-500 equipped with dual carbon/proton CPDUL cryoprobe. Samples were analyzed in acetone-d_6 as a saturated solution with a concentration of less than 1 μM. Chemical shifts are reported relative to TMS.

2.4. *Computations*

Ab initio calculations were performed in a Windows XP environment using Gaussian 03W/GaussView 3.0 software [11] on a Dell Optiplex GX270 equipped with 4 GB of RAM memory. The model chemistry used for the geometry optimization of complex **1** was B3LYP/6-31++G(d,p) invoking the integral equation formalism – polarisable continuum model (IEF-PCM) representing acetone as the solvent; and the model chemistry employed for the GIAO NMR computations was B3LYP/6-31G(d,p) also invoking the IEF-PCM representing acetone. Sufficient memory was provided by reserving 100 megawords via the Gaussian keyword %mem = 100 MW. The computed chemical shifts were calculated by performing an identical calculation on TMS, and subtracting the isotropic shielding value of the respective proton from the protons in TMS.

3. Results

3.1. *^1H NMR analysis*

The ^1H NMR spectrum of complex **1** is shown across the top of figure 3. While consistent assignments have been indicated in figure 3 for all eight hydrogen atoms

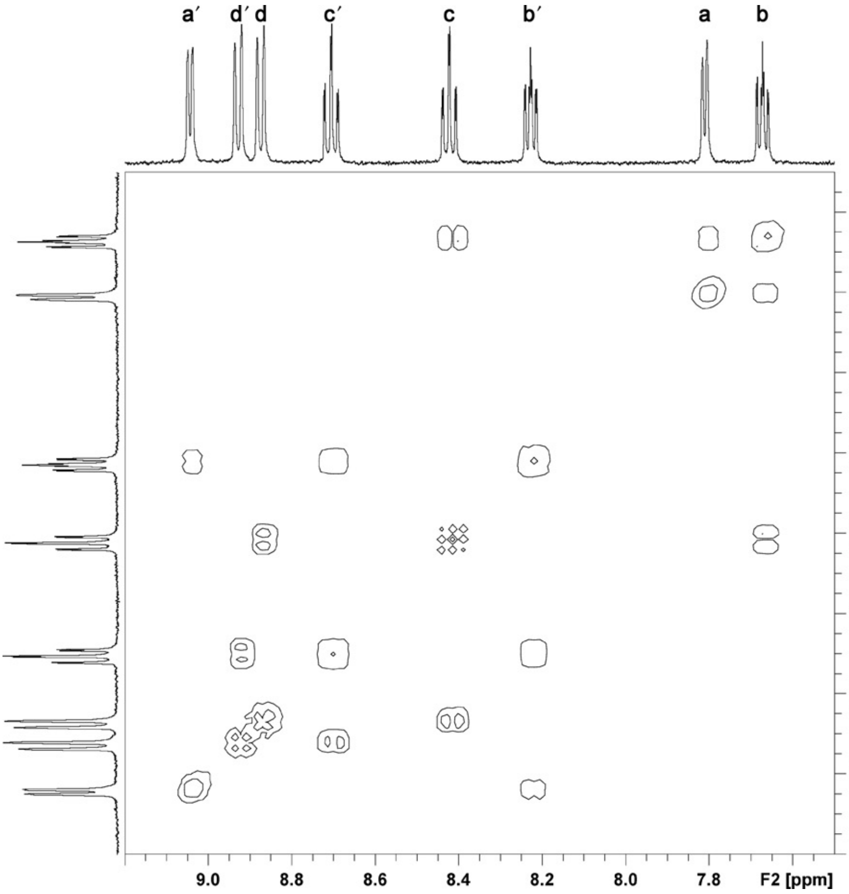

Figure 3. COSY spectrum of complex **1**.

of the bpy ligands, all that can be stated based on the 1-dimensional ^{1}H NMR is that all eight resonances are resolved, and that there are four doublets and four triplets indicative of two non-equivalent 2-substituted pyridine rings (the α and β pyridine rings).

3.2. *Correlation Spectroscopy (COSY)*

Using COSY as shown in figure 3 both four spin systems can be grouped: one set is labelled with a prime, the other is not. The COSY of **1**, however, cannot differentiate between the α or β rings or between hydrogen **a** and **d** or **b** and **c** on each ring.

3.3. *Nuclear Overhauser Effect Spectroscopy (NOESY)*

The overall features of the COSY spectrum and the NOESY spectrum are very similar with one major addition in the NOESY spectrum. There are additional off diagonal cross-peaks which indicate the through space interaction between **d** and **d′**; the location

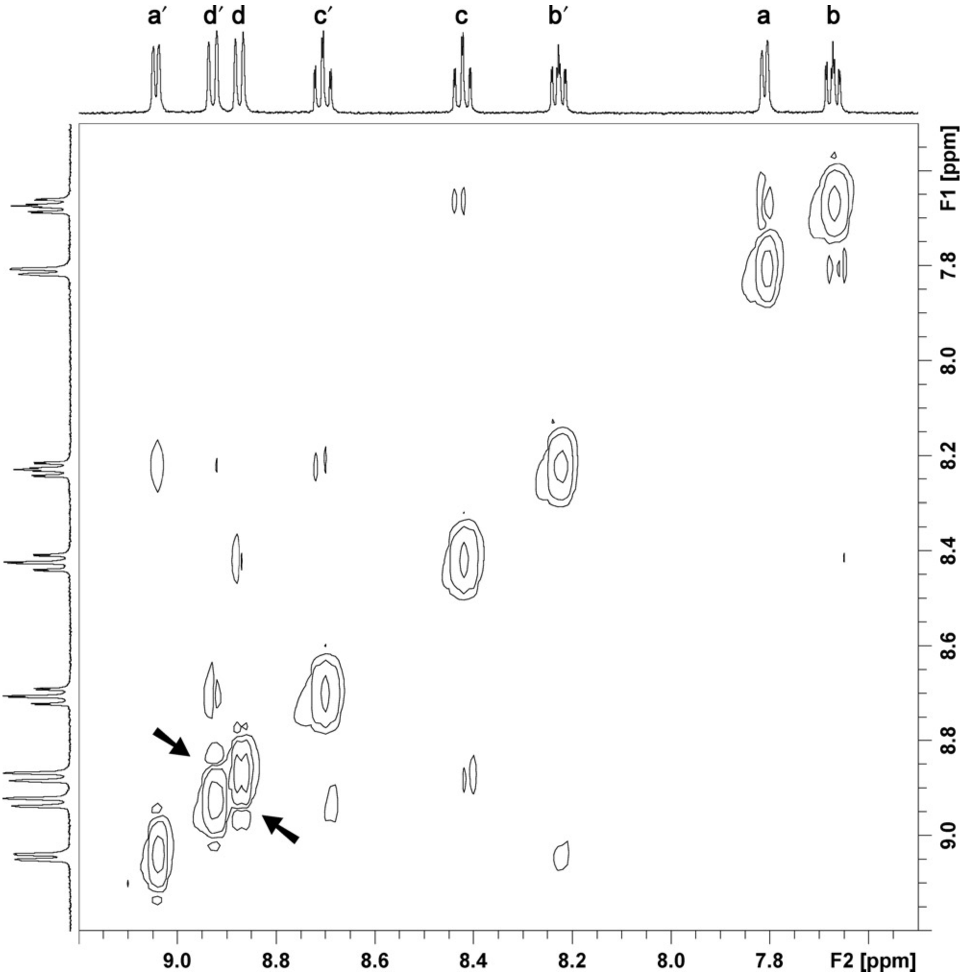

Figure 4. NOESY spectrum of complex **1**.

of which is shown in figure 4. While this resolves the identity of protons **a** *versus* **d** and **b** *versus* **c** in both of the four spin systems, this does not conclusively assign the α or β pyridine ring as the un-primed or primed four spin system based on ^{1}H NMR data.

3.4. *Gauge Including Atomic Orbital (GIAO) Density Functional Theory (DFT) calculations*

In order to make the distinction between the α and β pyridine rings and determine *cis/trans* influences, *ab initio* calculations were performed. The model chemistries reported gave the best correlation and fit to experimental results;[1] the results are summarized in table 1.[2]

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[1] The computational values show a systematic error as previously described in the literature [12, 13].

[2] Computed atomic coordinates are available as supplemental information.

4. Discussion

With the assignment of the chemical shifts, a comparison was made between the hydrogens of the α and β pyridine rings as shown in table 2. Two different influences appear by comparing the differences between analogous hydrogen atoms ($\alpha - \beta$ in table 2).

The largest difference is between the **a′** and **a** hydrogen atoms, and the difference decreases going towards the **d′** and **d** hydrogen atoms. Due to their orientation, the ring currents from the α pyridine ring of one of the bpy ligands shields the β pyridine ring of the other bpy ligand – an anisotropic *cis* influence. The extent of this shielding is compared to the theoretical model of McConnell [14] and computational results of Martin [15]. Although both models were developed for significantly different systems, there is good correlation and a trend of aromatic ring shielding for hydrogen atoms **a**, **b**, and **c** on the β pyridine. Hydrogen **d** is distant from the influence of the α pyridine and very close to the "magic angle" where $3\cos^2\theta = 1$. The *cis* ring is predicted by the McConnell equation to have a deshielding influence, if any, on this atom. (Martin's equation does not model deshielding: it was derived from methane above and within the plane of the benzene ring.)

Rather than a shielding influence of the *cis* α pyridine, the shift of **d** relative to **d′** may be attributed to an inductive *trans* influence. The α pyridine ring is *trans* to the other α pyridine ring, whereas the β pyridine ring is *trans* to one of the oxygen atoms of the carbonate ligand. The carbonate ligand donates more electron density to the Co^{3+} than the bpy ligands, thus weakening the Co–N bond *trans* to the carbonate. This influence can be seen in the calculated Co–N bond lengths which are 1.95 Å to the α pyridine ring

Table 1. Summary of ^{1}H NMR assignments.[a]

Pyridine ring	H	Experimental	Computational	Deviation[b]
α	**a′**	9.04	9.59	0.55
	b′	8.23	8.34	0.11
	c′	8.71	8.84	0.13
	d′	8.93	8.95	0.02
β	**d**	8.88	8.89	0.01
	c	8.42	8.63	0.21
	b	7.67	7.91	0.24
	a	7.81	7.99	0.18

[a] All values are in ppm.

[b] Deviation = Computational − Experimental.

Table 2. Comparison of the α and β pyridine rings.

H	$\alpha - \beta$ (ppm)[a]	Distance (Å)[b]	Angle[b]	McConnell[c] [14]	Martin (ppm)[15]
a′–a	1.23	3.15	32.5°	0.036	1.61
b′–b	0.56	5.55	24.8°	0.0086	0.30
c′–c	0.29	7.40	39.8°	0.0019	0.10
d′–d	0.05	7.53	58.7°	−0.00044	0.11

[a] Experimental data.

[b] Computed dimensions for the hydrogen on β ring relative to the center of the α ring and the perpendicular axis through the center of the α ring.

[c] Value reported is $(3\cos^2\theta - 1)r^{-3}$ which is proportional to ppm.

and 1.99 Å to the β pyridine ring. The weakening of the bond to the β pyridine ring can also be seen in the calculated average Mulliken charge for each of the pyridine rings which are +0.233 on the α rings and +0.223 on the β rings. The lower average Mulliken charge on the β ring corresponds to the chemical shift being further up-field and is due to induction of electron density from the *trans* carbonate ligand. As the α rings are *trans* to each other and *cis* to the carbonate, they experience much smaller inductive effects.

5. Conclusions

Using 2-dimensional ^{1}H NMR techniques and *ab initio* calculation methods conclusive assignments have been made for all hydrogen atoms on the bis(2,2′-bipyridine)carbonatocobalt(III) ion, **1**. Evidence has been presented for both a *cis* influence due to the ring currents of the α pyridine ring shielding the β pyridine ring of the second bpy ligand and a *trans* influence due to induction of electron density from the carbonate ligand to the β pyridine ring.

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References

[1] M.R. McClure, K.W. Jung, J.H. Worrell. *Coord. Chem. Rev.*, **174**, 33 (1998).

[2] J.M. Pratt, R.G. Thorp. In *Advances in Inorganic Chemistry and Radiochemistry*, J. Emeléus, A.G. Sharpe (Eds), pp. 375–427, Academic Press, New York (1969).

[3] D.A. Buckingham, C.R. Clark. *Inorg. Chem.*, **33**, 6171 (1994).

[4] E.C. Niederhoffer, A.E. Martell, P. Rudolf, A. Clearfield. *Inorg. Chem.*, **21**, 3734 (1982).

[5] V.F.M. Jaeger, J.A. van Dijk. *Z. Anorg. Allg. Chem.*, **227**, 273 (1936).

[6] S. Castellano, H. Günther, S. Ebersole. *J. Phys. Chem.*, **69**, 4166 (1965).

[7] C.R. Kanekar, C.L. Khetrapal, S.V. Nipankar. *J. Phys. Chem.*, **73**, 276 (1969).

[8] M.R. McClure, J. Holcombe. *J. Coord. Chem.*, **57**, 907 (2004).

[9] Y. Suenaga, C.G. Pierpont. *Inorg. Chem.*, **44**, 6183 (2005).

[10] H.F. Bauer, W.C. Drinkard. In *Inorganic Syntheses*, H.F. Holtzclaw Jr (Ed.), pp. 202–204, McGraw-Hill, New York (1966).

[11] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr, T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople. *Gaussian 03*, *Revision C.02*, Gaussian, Inc., Wallingford, CT (2004).

[12] T.H. Sefzik, J.M. Fidler, R.J. Iuliucci, J.C. Facelli. *Magnet. Reson. Chem.*, **44**, 390 (2006).
[13] J.R. Cheeseman, Æ. Frisch. *Gaussian Technical Support Information*, "Predicting Magnetic Properties with Chem Draw and Gaussian" http://www.gaussian.com/g_whitepap/nmrcomp.htm (accessed 9 November 2006).
[14] H.M. McConnell, R.E. Robertson. *J. Chem. Phys.*, **29**, 1361 (1958).
[15] N.H. Martin, N.W. Allen III, J.C. Moore. *J. Mol. Graphics Mod.*, **18**, 242 (2000).