When *N,N'*-dimethyl-*m*-xylylenediamine is used as the spanning reagent in these reactions, complex **10** is produced in good yield (66%). The methylated species was synthesized (complex **11**) and also isolated in good yield (80%). The UV–vis and electrochemical characterization of these complexes matches identically with that found for the previously synthesized spanned species, complexes **6–9**. The NMR data collected for complexes **10** and **11** are consistent with the incorporation of the *m*-xylylenediamine unit into the cyclized ligand. However, the conductivities that were measured for these complexes indicate that they are dimeric species, **10** being a 1:2 salt and **11** being a 1:6 salt. The chemical behavior of these complexes agree with this assignment, as the highly charged complex **11** is found to be soluble only in very polar solvents. The formation of the dimeric species selectively for the *m*-xylylenediamine spanning reactions is probably due to the rigid nature of the *m*-xylylene linkage, which does not allow for the spanning chain to bridge across the chloride ligand and form the monomeric spanned complex.

Acknowledgment. This work was supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and both the Biomedical Research Support Grant and the Research Development Fund of the SUNY at Buffalo. J.J.G. gratefully acknowledges Gettysburg College for his sabbatical leave at SUNY at Buffalo.

Registry No. **1**, 112817-37-5; **2**, 112924-02-4; **3**, 112793-32-5; **4**, 112793-34-7; **5**, 112793-36-9; **6**, 112793-38-1; **7**, 112793-40-5; **8**, 112817-39-7; **9**, 112793-42-7; **10**, 112793-44-9; **11**, 112817-41-1; *trans*-[(trpy)$Ru^{II}(PPh_3)_2(Cl)](PF_6)$, 72905-27-2; $Ru^{III}(trpy)(Cl)_3$, 72905-30-7; 1,3-bis{[methyl(*p*-tolylsulfonyl)amino]methyl}benzene, 112793-45-0; *N,N'*-dimethyl-1,5-pentanediamine, 56992-95-1; diphenyl{*p*-[(tetrahydropyranyloxy)methyl]phenyl}phosphine, 112793-46-1; *p*-bromobenzyl alcohol, 873-75-6; dihydropyran, 110-87-2; *N,N'*-dimethyl-*m*-xylylenediamine, 23399-62-4; diphenylchlorophosphine, 1079-66-9; *N,N'*-dibenzyl-*N,N'*-dimethyl-1,6-hexanediamine, 59406-44-9; 1,5-pentanediamine, 462-94-2; diphenyl[*p*-(hydroxymethyl)phenyl]-phosphine, 7187-90-8; *p*-[(chloromethyl)phenyl]diphenylphosphine, 59891-92-8; *N,N'*-dimethyl-1,6-hexanediamine, 13093-04-4; [1,6-hexanediylbis[(methylimino)methylene-4,1-phenylene]]bis[diphenylphosphine], 112793-47-2; methyl iodide, 74-88-4; [1,5-pentanediylbis-[(methylimino)methylene-4,1-phenylene]]bis[diphenylphosphine], 112793-48-3; [*m*-xylylenediylbis[(methylimino)methylene-4,1-phenylene]]bis[diphenylphosphine], 112793-49-4.

Contribution from the Department of Organic Chemistry, Facultad de Química, Universidad Complutense, 28040 Madrid, Spain, and the Instituto de Estructura de la Materia, CSIC, Serrano, 119, 28006 Madrid, Spain

^1H and ^{13}C NMR Coordination-Induced Shifts in a Series of Tris(α-diimine)ruthenium(II) Complexes Containing Pyridine, Pyrazine, and Thiazole Moieties

Guillermo Orellana,[†] Carlos Alvarez Ibarra,*[†] and Jorge Santoro[‡]

Received March 9, 1987

^1H and ^{13}C NMR chemical shifts of a series of ruthenium(II) tris chelates containing the heterocyclic ligands 2,2'-bipyridine, 2-(2-pyridyl)thiazole, 2-(2-pyrazyl)thiazole, and 2,2'-bithiazole are reported and compared to those of the corresponding free ligands. Calculated coordination-induced shifts (CIS, $\delta_{complexed} - \delta_{free}$) range from +0.41 to −1.00 ppm for ^1H and from +5.8 to −3.7 ppm for ^{13}C nuclei. These values are discussed on the basis of the various effects (charge perturbation and field interactions) that arise upon chelation: electronic σ-donation to the metallic center via the nitrogen lone pair, d–π* back-donation to the ligand, van der Waals interactions, and magnetic anisotropy of the spectator ligands. Semiquantitative values of each effect at the different positions have been proposed, taking theoretical calculations of steric and anisotropic contributions as the starting point. Shielding van der Waals interaction between proximate atoms influences only the H(3') CIS of six-membered moieities, but to a very low extent (<0.15 ppm). Magnetic anisotropy of proximate ring currents practically determines the CIS of the α positions for all the complexed ligands examined (upfield shifts from −0.8 to −1.0 ppm), has a lower influence on external β positions (<0.2 ppm), and is negligible for γ-protons. σ-donation deshields all the positions, its contribution increasing as protons separate from the coordinated nitrogen atom (up to 0.4 ppm). π-back-bonding is a weaker effect (<0.2 ppm upfield contribution) that operates mainly on the γ position of the pyridine and α and β positions of the pyrazine rings. For complexes containing unsymmetrical ligands, full assignment of meridional and facial isomers has been performed by the use of high-field and ^1H–^1H correlation 2D-NMR techniques. Although assignment of individual carbon atoms could not be achieved, average ^{13}C CIS values provide additional support to the above conclusions.

$Ru(\alpha\text{-diimine})_3^{2+}$ complexes (where the α-diimine moiety is inserted in a heterocyclic system) continue to attract wide interest because of their unusual properties. These complexes have found extensive application as catalysts in photoinduced electron-transfer processes[1] and, especially, as photosensitizers in solar energy conversion by water photoreduction processes.[2]

Herein we report an investigation on metal–ligand interactions that arise upon chelation to ruthenium(II), evaluated in using ^1H and ^{13}C NMR spectroscopy. This study completes ground-state characterization of a series of tris chelates containing five- and six-membered heterocyclic moieties: 2,2'-bipyridine (**1**), 2-(2-pyridyl)thiazole (**2**), 2-(2-pyrazyl)thiazole (**3**), and 2,2'-bithiazole (**4**) (Chart I). Excited-state properties of these complexes will be published elsewhere.[3,4]

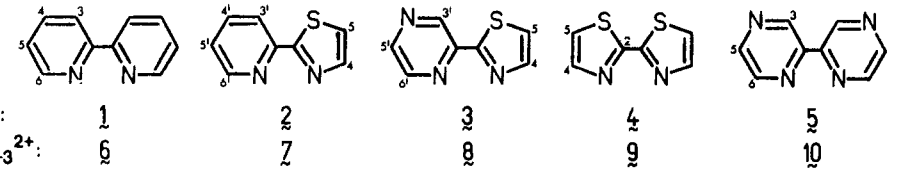
Several authors have found NMR spectroscopy useful to study the interactions that develop in coordination of heterocyclic ligands to transition metals. Normally, these reports have dealt with octahedral complexes with an arrangement of five small spectator ligands (cyanide or ammonia) and one nitrogen heterocycle (pyridines,[5–7] diazines,[5] imidazoles,[8] or pyrazoles[8b]) around the

[†] Universidad Complutense.
[‡] CSIC.

(1) (a) Balzani, V.; Bolletta, F.; Gandolfi, M. T.; Maestri, M. *Top. Curr. Chem.* **1978**, *75*, 1–64. (b) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159–244. (c) Rillema, D. P.; Allen, G.; Meyer, T. J.; Conrad, D. *Inorg. Chem.* **1983**, *22*, 1617–1622 and references therein.
(2) See for example: (a) Grätzel, M., Ed. *Energy Resources Through Photochemistry and Catalysis*; Academic: New York, 1983. (b) Braun, A. M., ed. *Photochemical Conversions*; Proceedings of the IOCD-UNESCO Seminar, Presses Polytechniques Romandes: Lausanne, Switzerland, 1983.
(3) Orellana, G.; Quiroga, M. L.; Braun, A. M. *Helv. Chim. Acta* **1987**, *70*, 2073–2086.
(4) Orellana, G.; Quiroga, M. L.; Braun, A. M., to be submitted for publication in *J. Photochem.*

0020-1669/88/1327-1025$01.50/0

Chart I



metal center (cobalt, iron, ruthenium). Such complexes offer an opportunity to study metal–ligand interactions for isolated nitrogen heterocycles. Several research groups have also reported (and only in a few cases discussed) NMR chemical shifts of iron, ruthenium, or osmium complexes including heterocyclic chelates with the α-diimine moiety.[9-15] Evaluation of the changes in electron density within ligands occurring upon chelation has been based on the NMR coordination-induced shifts (CIS) obtained by substracting chemical shifts of each nucleus in the complexed and the free ligand (CIS = $\delta_{complexed} - \delta_{free}$).

In spite of all these studies, a wide consensus about the main factors that determine the observed CIS has not been reached yet. Among the different effects affecting CIS are σ- and π-electron polarization in coordinated heterocycles, magnetic anisotropy of neighboring ligands and metal–ligand bonds, van der Waals interactions, residual paramagnetism of the metal center, and solvent effects.[8d,10a,13b,15b] This paper provides further insight about these interactions within the family of ruthenium(II) polypyridyl complexes. In addition, ^{1}H NMR signals of meridional (*mer*) and facial (*fac*) isomers, which arise from the unsymmetrical nature of some ligands used, have been fully assigned for the first time.

Experimental Section

1. Compound Preparation. Synthesis of ligands **2–4** was accomplished by formation of the thiazole moiety from the corresponding thioamides (prepared by the method of Karrer and Schukri,[16] except commercial dithiooxamide) following the procedure of Glover and Thomas.[17] They were finally purified twice by high-vacuum sublimation (yields from 30 to 60%) before use. Analytical grade 2,2′-bipyridine was purchased from Merck.

Commercial ruthenium trichloride hydrate (Fluka) and 20% excess of ligand were used for the synthesis (under dinitrogen) of the corresponding metal tris chelates. Complexes **6** and **7** were prepared by Palmer and Piper's method[18] (yields 80–90%) in ethanol at reflux,

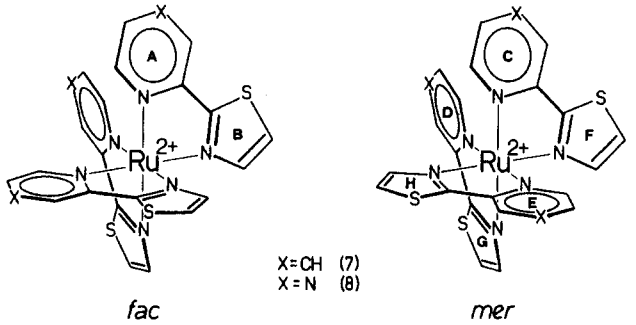


Figure 1. *mer* and *fac* isomers of ruthenium(II) tris chelates with unsymmetrical bidentate ligands **2** and **3**.

whereas complexes **8** and **9** were obtained by using the conditions of Rillema, Allen, Meyer, and Conrad[1c] in ethylene glycol (yields 92–99%). In every case they were isolated as hexafluorophosphate salts and purified twice by slow reprecipitation from acetonitrile with diethyl ether. Anal. (**7–9**; $RuC_{24}H_{18}N_6S_3P_2F_{12}$, $RuC_{21}H_{15}N_9S_3P_2F_{12}$, and $RuC_{18}H_{12}N_6S_6P_2F_{12}$, respectively) C, H, N, S.

2. NMR Experiments. All spectra were taken in 99.95 atom % Me_2SO-d_6, by using concentrations of 30% (w/v) for ligands and 0.20 M for ruthenium(II) complexes, at room temperature. Fourier transform ^{1}H NMR (at 80 MHz) and ^{13}C NMR (at 20 MHz) spectra were recorded in a Varian FT-80A spectrometer using respectively 32- and 10-μs pulse widths, 800- and 5000-Hz spectral windows, 16K data points, and, for ^{13}C NMR, 3-s recycle time.

^{13}C NMR spectra at 50 MHz were obtained with a Bruker WH-200 spectrometer under the same conditions described above for the 20-MHz apparatus, except that a 2-μs pulse width was used. ^{1}H NMR spectra at 360 MHz were recorded with a Bruker WM-360 spectrometer. Conditions were as follows: 8 μs pulse width (90° flip angle), 4000-Hz spectral window (600–900 Hz in the expanded spectra), 16K data points, and 3-s recycle time (10 s in the expanded spectra). For the two-dimensional COSY experiments time domain data matrices of 1024 × 256 size, covering 600–900 spectral widths, were collected. Before Fourier transformation, a sine-bell window function was applied in both dimensions and one level of zero filling was used in the t_1 dimension. The final 2D spectra, developed in 512 × 512 data matrices with digital resolutions of 1.2–1.8 Hz, were further improved by triangular symmetrization.

Results and Discussion

^{1}H and ^{13}C NMR spectra of the ligands 2,2′-bipyridine (**1**), 2-(2-pyridyl)thiazole (**2**), 2-(2-pyrazyl)thiazole (**3**), and 2,2′-bithiazole (**4**) and of their Ru(II) complexes **6–9** (Chart I) have been analyzed in this paper. For the sake of comparison, ^{1}H NMR data of the ligand **5** and its complex **10** have been taken from the literature[19] and presented here. However, it should be stressed that these data have been recorded under experimental conditions different from those used in the present work.

1. Assignments. ^{1}H and ^{13}C NMR chemical shifts of free ligands and their tris complexes in DMSO-d_6, in addition to their corresponding CIS values, have been collected in Tables I and II. Measured NMR parameters for **1** and **6** agree with those previously reported.[11-15]

Pyridine protons H(3′)–H(6′) of ligand **2** form an ABCD spin system (at 80 MHz), so their NMR parameters have been calculated from a modified version of the LAOCOON III iterative computer program.[20] Chemical shifts of H(3′), H(5′), and H(6′) of the pyrazine ring of ligand **3** have been determined by analysis of the ABX system. Protons of heterocyclic moieties in the free

(5) (a) Lavallee, D. K.; Fleischer, E. B. *J. Am. Chem. Soc.* **1972**, *94*, 2583–2599. (b) Lavallee, D. K.; Baughman, M. D.; Phillips, M. P. *J. Am. Chem. Soc.* **1977**, *99*, 718–724.
(6) Figard, J. E.; Paukstelis, J. V.; Byrne, E. F.; Peterson, J. D. *J. Am. Chem. Soc.* **1977**, *99*, 8417–8425.
(7) Malin, J. M.; Schmidt, C. F.; Toma, H. E. *Inorg. Chem.* **1975**, *14*, 2924–2928.
(8) (a) Shepherd, R. E. *J. Am. Chem. Soc.* **1976**, *98*, 3329–3335. (b) Johnson, C. R.; Henderson, W. W.; Shepherd, R. E. *Inorg. Chem.* **1984**, *23*, 2754–2763. (c) Storm, C. B.; Turner, A. H.; Rowan, N. S. *Inorg. Chem.* **1985**, *24*, 1269–1271. (d) Henderson, W. W.; Shepherd, R. E.; Abola, J. *Inorg. Chem.* **1986**, *25*, 3157–3163.
(9) (a) Miller, J. D.; Prince, R. H. *J. Chem. Soc.* **1965**, 3185–3194. (b) Miller, J. D.; Prince, R. H. *J. Chem. Soc.* **1965**, 4706–4709.
(10) (a) Castellano, S.; Günther, H.; Ebersole, S. *J. Phys. Chem.* **1965**, *69*, 4166–4176. (b) Tänzer, C.; Price, R.; Breitmaier, E.; Jung, G.; Voelter, W. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 963–964.
(11) Lytle, F. E.; Petrosky, L. M.; Carlson, L. R. *Anal. Chim. Acta* **1971**, *57*, 239–247.
(12) (a) Bryant, G. M.; Ferguson, J. E. *Aust. J. Chem.* **1971**, *24*, 441–444. (b) Constable, E. C.; Lewis, J. *Inorg. Chim. Acta* **1983**, *70*, 251–253.
(13) (a) Cook, M. J.; Lewis, A. P.; McAuliffe, G. S. G.; Thomson, A. *Inorg. Chim. Acta* **1982**, *64*, L25–L28. (b) Cook, M. J.; Lewis, A. P.; McAuliffe, G. S. G. *Org. Magn. Reson.* **1984**, *22*, 388–394.
(14) (a) Ohsawa, Y.; DeArmond, M. K.; Hanck, K. W.; Moreland, C. G. *J. Am. Chem. Soc.* **1985**, *107*, 5383–5386. (b) Baggott, J. E.; Gregory, G. K.; Pilling, M. J.; Anderson, S.; Seddon, K. R.; Turp, J. E. *J. Chem. Soc., Faraday Trans. 2* **1983**, *79*, 195–210.
(15) (a) Steel, P. J.; LaHousse, F.; Lerner, D.; Marzin, C. *Inorg. Chem.* **1983**, *22*, 1488–1493. (b) Marzin, C.; Budde, F.; Steel, P. J.; Lerner, D. *Nouv. J. Chim.* **1987**, *11*, 33–41.
(16) Karrer, P.; Schukri, J. *Helv. Chim. Acta* **1945**, *28*, 820–824.
(17) Glover, E. E.; Thomas, T. R. *J. Chem. Soc. C* **1967**, 463–466.
(18) Palmer, R. A.; Piper, T. S. *Inorg. Chem.* **1966**, *5*, 864–878.
(19) Crutchley, R. J.; Lever, A. B. P. *Inorg. Chem.* **1982**, *21*, 2276–2282.
(20) Castellano, S.; Bothner-By, A. A. *J. Chem. Phys.* **1964**, *41*, 3863–3869.

Table I. ^{1}H NMR Chemical Shifts in DMSO-d_6 for Free Ligands and $Ru(L)_3(PF_6)_2$ Complexes and Coordination-Induced Shifts (CIS)[a]

	H(4)	H(5)	H(3′)	H(4′)	H(5′)	H(6′)	confign	field, MHz
1			8.52	7.99	7.48	8.78		80
2[b]	8.11	7.92	8.27	8.01	7.53	8.73		80
3[c]	8.16	8.03	9.41		8.83	8.77		80
4[d]	8.07	7.96						80
5[e]			9.53		8.84	8.84		60
6			8.86	8.19	7.55	7.79		80
7[f]	7.365 [B[g]]	8.309 [B[g]]	8.637 [A]	8.146 [A]	7.565 [A]	7.777 [A]	*fac*	360
	7.293 [G]	8.330 [G]	8.648 [D]	8.153 [D]	7.586 [D]	7.760 [D]	*mer*	
	7.366 [F[g]]	8.330 [F[g]]	8.626 [C]	8.150 [C]	7.555 [C]	7.867 [C]	*mer*	
	7.305 [H]	8.307 [H]	8.637 [E]	8.158 [E]	7.573 [E]	7.855 [E]	*mer*	
8[f]	7.646 [B]	8.409 [B]	9.786 [A]		8.658 [A]	7.792 [A]	*fac*	360
	7.273 [G]	8.401 [G]	9.783 [D]		8.667 [D]	7.775 [D]	*mer*	
	7.666 [F]	8.401 [F]	9.783 [C]		8.662 [C]	8.178 [C]	*mer*	
	7.287 [H]	8.393 [H]	9.783 [E]		8.640 [E]	8.159 [E]	*mer*	
9	7.34	8.33						80
10[e]			10.17		8.76	8.03		60
6 − 1			+0.34	+0.20	+0.07	−0.99		
7 − 2[f]	−0.75 [B[g]]	+0.39 [B[g]]	+0.37 [A]	+0.14 [A]	+0.04 [A]	−0.95 [A]	*fac*	
	−0.82 [G]	+0.41 [G]	+0.38 [D]	+0.14 [D]	+0.06 [D]	−0.97 [D]	*mer*	
	−0.74 [F[g]]	+0.41 [F[g]]	+0.36 [C]	+0.14 [C]	+0.03 [C]	−0.86 [C]	*mer*	
	−0.81 [H]	+0.39 [H]	+0.37 [E]	+0.15 [E]	+0.04 [E]	−0.88 [E]	*mer*	
8 − 3[f]	−0.51 [B]	+0.38 [B]	+0.38 [A]		−0.17 [A]	−0.98 [A]	*fac*	
	−0.89 [G]	+0.37 [G]	+0.37 [D]		−0.16 [D]	−1.00 [D]	*mer*	
	−0.49 [F]	+0.37 [F]	+0.37 [C]		−0.21 [C]	−0.59 [C]	*mer*	
	−0.87 [H]	+0.36 [H]	+0.37 [E]		−0.19 [E]	−0.61 [E]	*mer*	
9 − 4	−0.73	+0.37						
10 − 5			+0.64		−0.08	−0.81		

[a] In ppm from TMS; concentrations 300 mg/mL (ligands) and 0.20 M (complexes), unless otherwise stated. [b] Coupling constants in hertz: $J_{3'4'} = 7.85$; $J_{3'5'} = 1.07$; $J_{3'6'} = 1.29$; $J_{4'5'} = 7.44$; $J_{4'6'} = 1.41$; $J_{5'6'} = 4.83$; $J_{45} = 3.17$. [c] Coupling constants in hertz: $J_{3'5'} = 0$; $J_{3'6'} = 1.36$; $J_{5'6'} = 2.59$; $J_{45} = 3.20$. [d] Coupling constants in hertz: $J_{45} = 3.21$. [e] Reference 19; these data are not exactly comparable because of the different concentration (ca. 3×10^{-2} M). [f] Capital letters refer to the individual rings (see Figure 1) of the isomers. [g] Interchangeable assignments.

Table II. ^{13}C NMR Chemical Shifts in DMSO-d_6 for Free Ligands and $Ru(L)_3(PF_6)_2$ Complexes and Coordination-Induced Shifts (CIS)[a]

	C(2)	C(4)	C(5)	C(2′)	C(3′)	C(4′)	C(5′)	C(6′)	field, MHz
1				155.6	120.7	137.2	124.1	149.3	20
2	168.5	144.2	122.5	150.7	119.2	137.5	124.9	149.6	20
3	165.7	144.6	123.4	146.0	140.6		145.5	144.3	20
4	160.8	144.0	122.4						20
6				156.6	124.5	138.0	127.9	151.3	20
7	165.02	142.91	127.67	152.98	124.87	138.20	127.88	152.57	50
	164.94	142.91	127.67	152.98	124.76	138.20	127.88	152.57	
	164.94	142.63	127.56	152.98	124.67	138.20	127.88	152.25	
	164.85	142.63	127.47	152.98	124.54	138.20	127.79	152.25	
8	163.56	143.55	129.22	149.28	145.10		147.88	147.36	50
	163.20	143.43	128.97	149.20	144.98		147.66	147.36	
	163.01	142.92	128.80	148.89	144.92		147.66	147.36	
	162.65	142.82	128.55	148.89	144.81		147.66	147.27	
9	159.4	143.0	128.0						20
6 − 1				+1.0	+3.8	+0.8	+3.8	+2.0	
7 − 2	−3.5	−1.3	+5.2	+2.3	+5.7	+0.7	+3.0	+3.0	
	−3.6	−1.3	+5.2	+2.3	+5.6	+0.7	+3.0	+3.0	
	−3.6	−1.6	+5.1	+2.3	+5.5	+0.7	+3.0	+2.8	
	−3.7	−1.5	+5.0	+2.3	+5.3	+0.7	+2.9	+2.8	
8 − 3	−2.1	−1.1	+5.8	+3.3	+4.5		+2.4	+3.1	
	−2.5	−1.2	+5.6	+3.2	+4.4		+2.2	+3.1	
	−2.7	−1.7	+5.4	+2.9	+4.3		+2.2	+3.1	
	−3.1	−1.8	+5.2	+2.9	+4.2		+2.2	+3.0	
9 − 4	−1.4	−1.0	+5.6						

[a] In ppm from TMS; concentrations 300 mg/mL (ligands) and 0.20 M (complexes).

ligands **2–4** were assigned by comparison to literature data for similar compounds,[21] whereas the assignment of ^{13}C NMR signals was accomplished from both chemical shifts and carbon–proton coupling constants reported for several 2-substituted heterocyclic rings.[22]

For the Ru(II) tris chelates **7–9**, the assignment of ^{1}H and ^{13}C chemical shifts has been based on published NMR data for the 2,2′-bipyridine complex **6**[11–15] and the bipyrazine complex **10**.[19] Signals of the thiazole protons were assigned by comparison of the observed CIS values of H(4) and H(5) with those of pyridine or pyrazine protons H(6′) and H(5′), respectively, which occupy equivalent positions. ^{13}C chemical shifts of the coordinated ligands have been unequivocally assigned from those of the free compounds and the ^1J carbon–proton coupling constants.

Full assignment of the complex ^{1}H resonance patterns of *mer* and *fac* isomers resulting from tris chelates with unsymmetrical bidentate ligands **7** and **8** (Figure 1), is first described in this paper. This assignment (24 nonequivalent protons in complex **7** and 20

(21) (a) Zanger, M.; Simons, W. W. *Anal. Chem.* **1974**, *46*, 2042–2045. (b) Marx, G. S.; Spoerri, P. E. *J. Org. Chem.* **1972**, *37*, 111–114. (c) Metzger, J. V., Ed. *Thiazole and Its Derivatives*; Chemistry of Heterocyclic Compounds 34; Wiley: New York, 1979; pp 66–81.

(22) (a) Retcofsky, H. L.; Friedel, R. A. *J. Phys. Chem.* **1968**, *72*, 2619–2622. (b) Hansen, M.; Jakobsen, H. J. *J. Magn. Reson.* **1973**, *10*, 74–84. (c) Turner, C. J.; Cheeseman, G. W. H. *Org. Magn. Reson.* **1974**, *6*, 663–666.

in complex **8**) has been performed by analysis of their homonuclear correlation $^1H-^1H$ (COSY) two-dimensional NMR spectra[23] and will be discussed later.

The decoupled 50-MHz ^{13}C NMR spectra of complexes **7** and **8** show individual signals for C(3′) of the former and for C(2), C(4), C(5), and C(3′) of the latter, corresponding to *mer* and *fac* isomers, and partially resolved or unresolved signals for the remaining carbons (Table II). The assignment of the carbon shifts to the individual moieties of these isomers could not be achieved due to the small differences between the observed CIS values of equivalent carbon atoms of each isomer.

2. Analysis of the Observed CIS. Coordination-induced shifts $\delta_{complexed} - \delta_{free}$) are collected in Tables I (^1H) and II (^{13}C). Positive values refer to downfield shifts. CIS of the different nuclei in the heterocyclic moieties can be interpreted by considering the main effects that operate on each position.

The most outstanding effect is σ-withdrawal of electron density via the nitrogen lone pair ("σ-donation"). This effect includes deshielding contributions from both polarization of the σ-framework (σ-effect) and resonance within the π-framework (π-effect). However, whereas the former is attenuated by the distance to the coordinated nitrogen, the latter should predominate at the γ and α positions.

The second effect results from metal back-bonding to the vacant π^* orbitals of the ligands ("π-back-donation"). The magnitude of this contribution will depend on the nature of the transition metal and on the energy of the heterocyclic π^* orbitals with symmetry appropriate to combine with filled t_{2g} orbitals. This effect shields the different positions according to their π^*-orbital coefficients into which the back-bonding occurs. On the other hand, the crowding of ligands around the metal center of tris chelates causes strong field effects on external positions due to anisotropy of neighboring heterocyclic rings ("ring current effect").[11,13b,15b] Chelation of ligands formed by two heterocyclic moieties imposes a planar conformation of both rings, giving rise to van der Waals steric interactions between proximate atoms.[12b,24]

Two other effects are worth noting: solvent effects and magnetic anisotropy of the metal–ligand bonds. The first can be neglected if the spectra of free and complexed ligands are recorded in the same solvent (DMSO-d_6, which helps to reduce the magnitude of solvent effects[8d]). The second has also a minimal influence on the observed CIS of complexed nitrogen heterocycles.[8d,25]

Consequently, σ- and π-back-donations, ring current anisotropy, and van der Waals interactions have been semiquantitatively evaluated from the ^1H and ^{13}C CIS within our series of related metal chelates (Chart I). This evaluation has been carried out by a priori calculation of ring current and steric effects on each nucleus from reported empirical equations (vide infra). Estimation of the remaining contributions can be made by the difference from the observed CIS values.

A. ^1H NMR. The observed proton CIS values (Table I) appear to be positive, except those for H(4) and H(6′) of complexes **6–9** and H(5′) of complex **8**. These results reflect the expected deshielding of ligand positions as result of coordination via ligand-to-metal σ-donation, which should be always greater than deshielding caused by metal π-back-donation. For H(4) and H(6′), located at positions α from the coordinated nitrogen atoms, there is an additional shielding contribution resulting from neighboring heterocyclic ring anisotropy.

H(3′). The influence of metal-to-ligand π-back-donation over β positions of the pyridine moiety should be essentially null, inasmuch as the coefficients of vacant π^* orbitals with symmetry appropriate to interact efficiently with the filled ruthenium t_{2g} orbitals are zero at such positions.[5a,26a] However, the pyrazine ring presents nonzero (but small) coefficients of the vacant π^* orbital,[5a,26b] and therefore, there should be a slight increase in the electron density at this position due to a back-donation effect.

On the other hand, the deshielding contribution to H(3′), caused by the electronic circulation in the remaining heterocyclic moiety of each coordinated chelate, should not contribute to the observed CIS, considering that it is the same in the free or complexed ligand provided a planar conformation of the two constituting rings is assumed for both situations.[10a,27]

^1H NMR studies[11,12b] and chemical reactivity data of the tris(2,2′-bipyridine) complex **6**[24] have led some authors to propose that the most important effect, caused by chelation, on the chemical shift of H(3′) is the steric interaction between this proton and H(3). This effect arises from the s-cis conformation of both rings for the complexed ligand in opposition to the nitrogen s-trans conformation, which predominates in the dissolved ligand.[10a,27]

We have estimated the deshielding caused by this van der Waals effect on H(3′) (in complex **6**) having a maximum value of +0.18 ppm, on the basis of the distance between the protons H(3′) and H(3) (2.07 Å)[28] and the empirical equation proposed by Cheney.[29] Therefore, the maximum contribution of this effect to the total CIS should amount to ca. 50% in the most favorable case.

H(3′) CIS values are practically coincident in all the complexes (Table I). Taking into account that the covalent radius of the sulfur atom (1.04 Å)[30] has approximately the same value as the C–H bond distance (1.08 Å),[29] the interaction between H(3′) and the unshared electron pair of the thiazole sulfur atom, in complexes **7** and **8**, should be the same as that calculated above for complex **6** (ca. +0.15 ppm). Therefore, a value of +0.25 ppm is proposed for the σ-donation contribution to H(3′) CIS within this series of complexes.

H(4′). The location of this proton causes either van der Waals or ring current effects of neighboring heterocycles to be negligible. Consequently, σ- and π-back-donations are the only effects to be considered. Exact separation and evaluation of these effects are very difficult because both interact synergistically via "back-bonding".[31] However, they can be estimated separately from the

Table III. Calculated Ring Current Effects (ppm) for H(3′)–H(6′) Caused by Different Pyridine Units in the $Ru(1)_3^{2+}$ Complex[a]

ring[b]	H(3′)	H(4′)	H(5′)	H(6′)
I	0.00	−0.06	−0.25	−1.08
II	−0.04	−0.09	−0.11	−0.01
V	+0.04	+0.06	+0.08	+0.13
VI	+0.03	+0.03	+0.04	+0.08
total	+0.03	−0.06	−0.24	−0.88

[a] For calculation details, see ref 32; a positive value always indicates deshielding (shift to lower field). [b] For ring numbering, see Figure 2; the effect of ring III has not been computed because it is supposed to be practically identical for the free and complexed ligand (assuming a planar conformation in both cases) and thus does not contribute to the observed CIS.

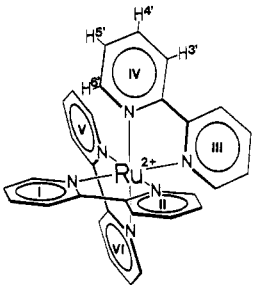


Figure 2. Perspective drawing of the tris(2,2′-bipyridine) complex for evaluation of ring current effects.

(23) Bax, A.; Freeman, R. *J. Magn. Reson.* **1981**, *44*, 542–561.
(24) Constable, E. C.; Seddon, K. R. *J. Chem. Soc., Chem. Commun.* **1982**, 34–36.
(25) Faust, R. D.; Ford, P. C. *J. Am. Chem. Soc.* **1972**, *94*, 5686–5696.
(26) Jorgensen, W. L.; Salem, L. *The Organic Chemist's Book of Orbitals*; Academic: New York, 1983; (a) pp 263–265; (b) pp 266–268.
(27) Bolotin, A. B.; Bolotin, V. A.; Gineityte, V. L. *Int. J. Quantum Chem.* **1979**, *16*, 839–845.
(28) Rillema, D. P.; Jones, D. S.; Levy, H. A. *J. Chem. Soc., Chem. Commun.* **1979**, 849–851.
(29) Cheney, B. V. *J. Am. Chem. Soc.* **1968**, *90*, 5386–5390.
(30) Wells, A. F. *Structural Inorganic Chemistry*; Clarendon: Oxford, England, 1975; p 236.
(31) Ernst, S.; Kaim, W. *J. Am. Chem. Soc.* **1986**, *108*, 3578–3586.

Table IV. Summary of Semiquantitative Values (ppm) of the Contributions to ^{1}H NMR Coordination-Induced Shifts (CIS) for Tris(α-diimine)ruthenium(II) Complexes **6–9**

effect	sign[a]	H(4)	H(5)	H(3′)	H(4′)	H(5′)	H(6′)
σ-donation	+	≤0.1	0.4	0.25[b]	0.3–0.4	0.2[b]	≤0.1
π-back-donation	−	0.1	0	0[c]	0.1–0.2	0[c]	≤0.1
ring current anisotropy	−	0.8–0.9[e]	≤0.1	0[d]	0	0.2[e]	0.9[e]
van der Waals	+	0	0	≤0.15	0	0	0

[a] Positive sign refers to downfield effect. [b] Slightly lower for pyrazine due to its weaker σ-donor character. [c] Ca. −0.1 ppm for pyrazine protons (see text). [d] Net contribution to the observed CIS is null, assuming a planar conformation of both rings in the free and complexed ligand. [e] These values refer to protons located above a six-membered heterocycle; lower values have to be considered for protons above thiazole rings.

present study. The contribution of ligand-to-metal σ-donation to the H(4′) CIS (γ position) should be greater than that calculated above for H(3′) (+0.25 ppm, β position), following the reported changes of the chemical shifts at these positions induced on protonation of the free pyridine.[5b] Nevertheless, when we take into account the small values of the C(4′) CIS (Table II) and the fact that the γ position is the most sensitive to the balance of σ and π back charge donations that occur upon coordination,[5,13b] the latter should not be very large either. Therefore, a σ contribution between +0.3 and +0.4 ppm to the H(4′) CIS is proposed, which leads to the value ranging from −0.1 to −0.2 ppm for the back-donation effect.

H(5′). No van der Waals effect should be expected at this proton either. On the other hand, the contribution of anisotropy induced by electron circulation in the spectator heterocyclic rings has been evaluated from a computer program based on Johnson and Bovey's equation.[32] Calculations applied to complex **6** yield an estimate of −0.2 ppm (Table III, Figure 2). Considering that shielding is mainly caused by the ring placed just below H(5′) (Figure 2) and assuming equal Ru–N bond distances for identical heterocyclic rings, this result has been extended to complexes **7** and **8**. The hypothesis is confirmed by the similar CIS values of this proton obtained for complexes **6** and **7**.

According to the observed CIS, σ-donation contribution to H(5′) attached to a pyridine ring (complexes **6** and **7**) can be therefore estimated as +0.2 ppm (π-back-donation has been neglected as in the case of H(3′)). A comparison with the value obtained for H(3′) shows an asymmetry of the σ-donation effect at these positions. Further confirmation is provided by the ^{13}C NMR CIS of C(3′) and C(5′) in complexes **6–8** (Table II).

Nevertheless, the H(5′) CIS value of complex **8** appears to be negative, in contrast to those values of complexes **6** and **7**. As discussed for H(3′), a small negative contribution from π-back-donation operates on the β positions of the pyrazine rings. This shielding effect is compensated by σ-donation (which is lower for a pyrazine ring compared to that for a pyridine ring due to the lesser basicity of the former[31]). It thus results that the upfield shift observed in H(5′) of complex **8** is caused by ring current anisotropy.

H(6′). We assume that no CIS originate from steric effects for this proton. The large negative CIS observed can only be ascribed to predominance of the strong shielding effect induced by the electron current of the heterocyclic ring placed just below H(6′) in the octahedral arrangement of ligands (Figure 2). The total anisotropic contribution to this proton has been evaluated in the same way as for H(5′) (Table III),[32] and the resulting value (−0.9 ppm) is extended to complexes **7** and **8**. This value is valid for H(6′) protons located above a pyridine or pyrazine ring, but the effect should be less when H(6′) is above a thiazole moiety due to the lower aromaticity of this heterocycle.[33] Therefore, the estimated shielding effect on this proton is practically coincident with the observed CIS (Table I).

According to this result, it appears that the σ and π back electron donations on protons placed at positions α with respect to the coordinated nitrogen atom are nearly balanced. In fact, the back-donation contribution has to be less than that of H(4′) as the result of a lower coefficient for an α-carbon vs that of a γ-carbon in the π* orbital.[5a,26] Consequently, σ-donation at H(6′) should be lower than that estimated for H(3′), H(5′), and H(4′). This variation of the σ-releasing effect with proton site has also been observed in the NMR shifts induced upon protonation of the free pyridine ring,[5b] where no π-back-bonding can occur.

The balance of σ- and π-effects at this position is also found in other tris chelates containing distinct ligands or metal centers. For example, tris(2,2′-bipyridine)iron(II)[10a] and tris[2-(2-pyridylamino)pyridine]ruthenium(II)[34] show a H(6′) CIS of −1.0 ppm, very similar to those values observed in our series of complexes.

H(4). As discussed for H(6′), the predominant effect on the CIS should be anisotropy induced by proximate heterocyclic rings. However, its absolute value has to be lower than that observed for H(6′). This is due to the greater distance of H(4) from the plane of the ring located just below it (Figure 2) since it is attached to a five-membered heterocycle. On the other hand, σ- and π-back-donation effects should be considered to be small and to be balanced as in H(6′) so that their contribution to the CIS is negligible.

H(5). This proton is unaffected by steric interactions. Taking into account that spatial locations of H(5) and H(5′) are equivalent, a shielding ring current effect should influence H(5) CIS. However, this contribution has to be smaller than that calculated for H(5′) in complex **6** (Table III), considering the greater distance of H(5) from the underlying heterocyclic ring in complexes **7–9**. Therefore, the absolute value of the shielding effect operating on H(5) must be less than 0.1 ppm, resulting in σ-donation being the most important factor to its CIS.

The semiquantitative values (in ppm) of the different contributions to ^{1}H NMR CIS of complexes **6–9** are summarized in Table IV.

Assignment of *mer* and *fac* Configurations. Several authors have reported different NMR signals for protons and carbons of *mer* and *fac* isomers of metal tris chelates obtained from unsymmetrical heterocyclic ligands,[13,15] but a full assignment has not been accomplished yet. We have also observed different signals at 360 MHz for protons of *mer* and *fac* isomers of complexes **7** and **8** (Figure 1, Table I). The assignment of the signals to each isomer was impossible to solve by integration since both isomers are obtained in the expected statistical ratio (*mer*:*fac* = 3:1), all the resonances of each type of proton showing the same relative intensity. Nevertheless, the configurational assignment can still be performed by careful analysis of the coordination-induced shifts observed for "probe" protons H(6′) and H(4) (Table I).

The H(6′) and H(4) signals of complexes **7** and **8** appear to be clearly grouped in two pairs, resulting from their spatial location with respect to the different heterocyclic rings. Thus, the pair of H(6′) signals with a larger absolute CIS can be ascribed to protons placed above a six-membered heterocycle (H(6′) of rings A (*fac*) and D (*mer*) in Figure 1) since anisotropy of such rings is larger than that of a thiazole moiety.[33] The remaining pair of H(6′) signals will therefore correspond to protons located above a thiazole ring in the *mer* isomer. Additional confirmation is

(32) Johnson, C. E.; Bovey, F. A. *J. Chem. Phys.* **1958**, *29*, 1012–1014. To compute anisotropic contributions of the pyridine ring, the following values have been taken: ring current, 0.95 of that of benzene, radius of the ring, 1.37 Å. Atomic coordinates of the 2,2′-bipyridine complex have been obtained from ref 28.

(33) Abraham, R. J.; Thomas, W. A. *J. Chem. Soc. B* **1966**, 127–131.

(34) Morris, D. E.; Ohsawa, Y.; Segers, D. P.; DeArmond, M. K.; Hanck, K. W. *Inorg. Chem.* **1984**, *23*, 3010–3017.

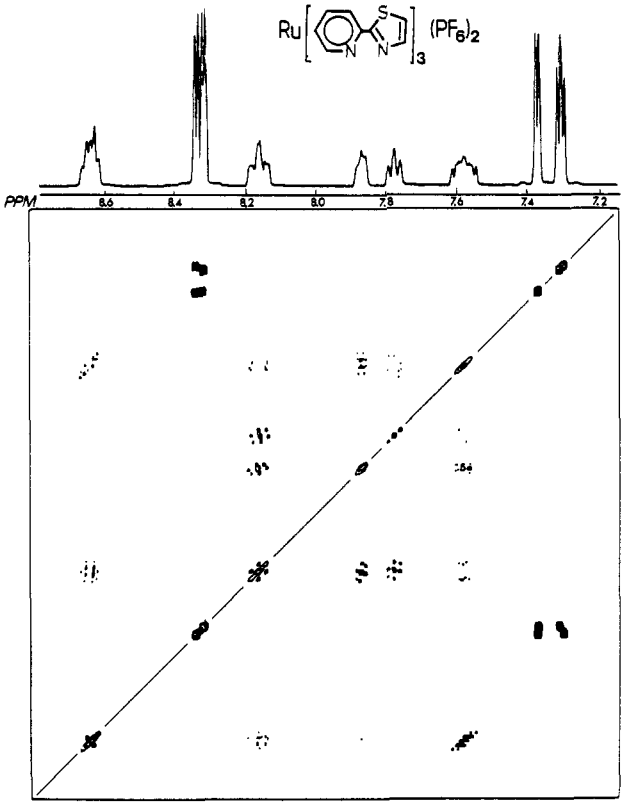


Figure 3. Contour plot of the COSY 2D-NMR spectrum of the tris-[2-(2-pyridyl)thiazole]ruthenium(II) complex.

provided by the CIS values found for H(6′) in complexes **6** and **10** (Table I). From the same reasoning, H(4) signals with a lower absolute CIS value are assigned to those protons attached to thiazole moieties B (*fac*) and F (*mer*) (Figure 1). The observed CIS of H(4) in complex **9** (Table I) supports the above conclusions.

H(6′) signals of A (*fac*) and D (*mer*) rings and H(4) signals of B (*fac*) and F (*mer*) rings have been further assigned by application of the calculated values of ring current contributions for complex **6** (Table III) to complexes **7** and **8**. According to those calculations, the most important effect on the α-protons is the shielding caused by the electron circulation of ring I (Figure 2), and the second in importance is the deshielding contribution corresponding to the current of ring V. In the *mer* isomers (complexes **7** and **8**, Figure 1), the pyridine V (complex **6**, Figure 2) has been substituted by a thiazole ring, which in turn provides a lower deshielding contribution to the H(6′) CIS. H(6′) signals with a CIS of −0.95 ppm (**7**) and −0.98 ppm (**8**) can be assigned to ring A (Figure 1) of *fac* isomers. In the same manner, H(4) signals with CIS values of −0.75 ppm (**7**) and −0.51 ppm (**8**) have to be ascribed to ring B of *fac* isomers. Assignment of H(6′) signals of rings C and E (*mer*) and H(4) of rings G and H (*mer*) (Figure 1) has been performed similarly.

This reasoning is supported by identical results[35] of 360-MHz ^{1}H NMR for tris[2-(2-pyridyl)oxazole]ruthenium(II). In this case, the obtained ratio of *mer* to *fac* isomers is 60:40, which permits unequivocal assignment of H(6′) and H(4) from the intensity of respective signals.

The NMR resonances for the 24 and 20 nonequivalent protons of complexes **7** and **8**, respectively, have been finally assigned from ^{1}H–^{1}H correlation 2D-NMR spectra (COSY)[23] (Figure 3), by using the previously identified probe protons H(6′) and H(4) (Table I). Selbin and co-workers[36] have reported complete assignment of the ^{1}H NMR spectrum of the cyclometalated complex [Ru(bpy)(2-(4-nitrophenyl)pyridine)]$^+$, which apparently is the only NMR study on ruthenium chelates using COSY techniques published to date.

B. ^{13}C NMR. The observed ^{13}C NMR CIS values are positive except those of carbons C(2) and C(4) of complexes **7–9** (Table II). These results are consistent with ligand-to-metal σ-donation as the predominant effect. Metal-to-ligand π-back-donation should be more important for C(2) and C(4).

^{13}C NMR spectral data (at 50 MHz) also demonstrate the presence of *mer* and *fac* isomers, although in this case the smaller difference of CIS values for each signal has not allowed us to assign resonances to individual carbon atoms.

Average observed CIS values have been evaluated by consideration of only σ and π back charge donations. Van der Waals and ring current effects have been generally ignored because their relative contribution to the carbon CIS should be less significant than it is for the smaller proton CIS.

No back-donation effect operates on C(3′) and C(5′) of complexes **6** and **7** (β-carbon atoms of a pyridine moiety), and a slight negative contribution is present in complex **8** (pyrazine ring) as discussed above. These different contributions are apparent from β-carbon CIS values of both types of heterocycles (Table II). The lower CIS of C(3′) of complex **6** can be ascribed to a larger van der Waals effect (deshielding proton and shielding directly attached carbon atom). This contribution was estimated to be −2 ppm from the empirical equation proposed by Cheney.[29] Likewise, no π-back-donation operates on C(5) of complexes **7–9**, as demonstrated by their high similar CIS values.

As discussed for ^{1}H NMR, α-carbons suffer from a lower π-back-donation than γ-carbons. Consequently, σ- and π-effects cancel each other in the latter, yielding almost no CIS. Pyridine C(2′) and C(6′) CIS values are between those of the β- and γ-positions because they have higher σ-donation and lower back-donation effects. Conversely, the negative CIS observed for C(2) and C(4) indicate that back-donation shielding is now predominant, being attributable to the different orbital and electronic features of thiazole vs those of pyridine and pyrazine moieties.

Further work is in progress in order to extend these results to other ruthenium chelates containing five-membered rings with different types (NH, NR, O, Se), numbers, or positions of the heteroatoms included.

Acknowledgment. We thank Prof. M. L. Quiroga of Universidad Complutense for her very helpful comments. G.O. gratefully acknowledges the Ministry of Education for an FPI grant. This work has been supported in part by the Renewable Energies Institute (CIEMAT, Madrid, Spain).

Registry No. **1**, 366-18-7; **2**, 2433-17-2; **3**, 112575-68-5; **4**, 13816-21-2; **6**, 60804-74-2; *fac*-**7**, 112710-04-0; *mer*-**7**, 112708-75-5; *fac*-**8**, 112596-01-7; *mer*-**8**, 112596-03-9; **9**, 112596-05-1.

(35) Unpublished results.

(36) Reveco, P.; Medley, J. H.; Garber, A. R.; Bhacca, N. S.; Selbin, J. *Inorg. Chem.* **1985**, *24*, 1096–1099.