NMR Spectroscopic Correlations for a Series of Triangular μ-Oxoruthenium Acetate Clusters containing Substituted Pyridine Ligands†

J. Chem. Research (S),
1997, 338–339†

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The ^1H and ^{13}C NMR chemical shifts of the acetate and pyridine ligands (α-position) in a series of $[Ru_3O(CH_3CO_2)_6L_3]^+$ clusters are linearly correlated with the pK_a (L), but exhibit variable trends at the various positions as a consequence of the inductive, paramagnetic anisotropy and ring current effects and the ligand interactions through the Ru_3O core.

NMR spectroscopy has successfully been employed in the characterization[1–11] of μ-oxoruthenium acetate clusters of general formula $[Ru_3O(CH_3CO_2)_6L_3]^+$, and in the investigation of their electron-transfer[12] and substitution kinetics.[13–17] This type of compound exhibits a triangular structure, as shown in Fig. 1, strongly held together by intramolecular μ-oxo, μ-acetate and metal–metal bonds.

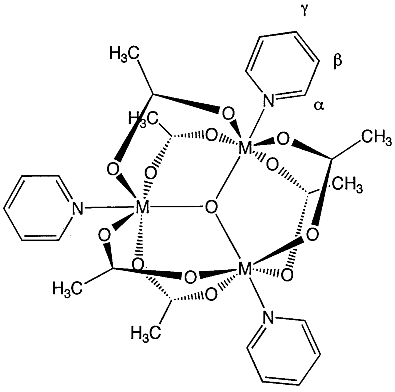

Fig. 1 Structural representation of $[Ru_3O(CH_3CO_2)_6(py)_3]^+$

In spite of the relatively large number of systems reported in the literature,[1–11] the available NMR data are rather scarce and unsuitable for comparison purposes because of the different conditions employed for the measurements. Here we report a correlation study based on the ^1H and ^{13}C NMR chemical shifts measured for a series of $[Ru_3O(CH_3CO_2)_6L_3]^+$ complexes, as a function of the basicity (pK_a), E_L and σ_p parameters for the several substituted pyridine ligands (L) employed.

Experimental

The triangular clusters $[Ru_3O(CH_3CO_2)_6(acpy)_3]BF_4$ (acpy = 4-acetylpyridine), $[Ru_3O(CH_3CO_2)_6L_3]PF_6$ [where L = bipy (4,4′-bipyridine), py (pyridine), tbpy (4-*tert*-butylpyridine), vpy (4-vinylpyridine), ampy (4-aminopyridine)] and $[Ru_3O(CH_3CO_2)_6(py)_2L]PF_6$ (where L = acpy, bipy and vpy) have been synthesized and characterized previously.[18]

^1H and ^{13}C NMR spectra were recorded on a Bruker AC 200 spectrometer, using 10^{-2} mol dm^3 solutions of the clusters in CD_3CN. The reported chemical shifts (δ) are relative to Me_4Si.

Results and Discussion

Symmetric Clusters.—The ^1H NMR spectra of the symmetric $[Ru_3O(CH_3CO_2)_6L_3]^+$ clusters consist of characteristic peaks distributed in three regions: 0.2–0.8 (H_α-L), 5.8–6.6 (H_β-L) and 2.4–5.2 ppm (CH_3). The corresponding ^{13}C NMR spectra exhibit peaks at −2 to −7 (C_α-L), 96–113 (C_β-L) and 141–164 ppm (C_γ-L) and at 96–113 (CH_3) and 197–218 ppm (CO_2^-). The complete data obtained in this work can be seen in Table 1.

In order to rationalize the NMR data for the series of complexes, the possible correlations with ligand (L) parameters such as pK_a, ΣE_L[19] and σ_p[20] were exploited in this work. In general, the best linear correlations were obtained with pK_a, as shown in Table 2. The ΣE_L parameter has been introduced for electrochemical purposes,[19] *e.g.* prediction of E^0 values, while σ_p is a typical substituent parameter, particularly suitable for ligand data correlations.

Table 1 ^1H and ^{13}C NMR chemical shifts for $[Ru_3O(CH_3CO_2)_6L_3]^+$ and $[Ru_3O(CH_3CO_2)_6(py)_2L]^+$ clusters[a]

L[b]	pK_a^d	ΣE_L^e	σ_p^f	H_α-L	H_β-L	H_γ-L	H_3C	C_α-L	C_β-L	C_γ-L	CH_3	CO_2^-
$(acpy)_3$	3.60	0.90	0.50	0.81	5.87		5.20	−7.0	125.5	141.3	113.1	196.8
$(bipy)_3$	4.82	0.81	0.44	0.56	6.04		5.02	−6.4	126.4	143.1	112.6	197.1
$(py)_3$	5.28	0.75	0.00	0.25	5.82	6.57	4.82	−6.4	126.6	138.1	114.5	199.3
$(vpy)_3$	5.62	0.60	−0.04	0.29	6.00		4.70	−6.0	127.1	147.2	111.0	199.6
$(tbpy)_3$	6.14	0.69	−0.20	0.30	6.15		4.55	−6.0	127.0	164.1	111.2	200.6
$(ampy)_3$	9.39	0.36	−0.66	g	6.62		2.39	−2.3	136.5	159.5	96.0	217.8
acpy[c]				0.74	5.97		5.07	−6.1	125.2	141.3	113.0	196.8
$(py)_2$				0.28	5.77	6.60	4.92	−6.1	126.7	138.1	114.6	201.3
bipy[c]				0.54	6.10		5.00	−6.4	126.9	143.1	112.6	197.7
$(py)_2$				0.13	5.75	6.57	4.89	−6.3	126.9	138.1	113.1	199.9
vpy[c]				0.42	6.02		4.83	−6.3	127.1	147.2	111.1	199.5
$(py)_2$				0.17	5.81	6.50	4.79	−6.5	126.4	138.0	114.5	199.4

[a]In acetonitrile. [b]See Experimental section. [c]Mixed cluster. [d]Ref. 18. [e]Ref. 19. [f]Ref. 20. [g]Masked.

The H_α-L and C_α-L peaks are shifted upfield with respect to the free ligand, since the corresponding atoms are located very close to the metal centre, and are more susceptible to the local paramagnetic anisotropy. This particular behaviour is very useful for the assignment of the NMR spectra of this

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†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1997, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

Table 2 Linear regression coefficients of ^1H and ^{13}C NMR data for symmetric clusters *versus* the ligand parameters

		^{13}C NMR				^1H NMR		
L-Parameter	Signal	*a*	*b*	r	Signal	*a*	*b*	*r*
pK_a	δ(C=O)	3.9 ± 0.6	179 ± 3	0.96				
ΣE_L		-38 ± 9	228 ± 4	0.91				
σ_p		-16 ± 5	202 ± 4	0.87				
pK_a	$\delta(CH_3)$	-3.2 ± 0.7	128 ± 3	0.92	$\delta(CH_3)$	-0.51 ± 0.06	7.4 ± 0.3	0.97
ΣE_L		32 ± 8	88 ± 3	0.89		5.1 ± 1.0	1.0 ± 0.4	0.93
σ_p		13 ± 5	110 ± 5	0.79		2.1 ± 0.6	4.4 ± 0.5	0.88
	$\delta(C_\alpha$-L)	0.8 ± 0.1	10.6 ± 0.5	0.97	$\delta(H_\alpha$-L)	-0.23 ± 0.06	1.6 ± 0.1	0.92
pK_a		-8 ± 2	0.0 ± 0.7	0.93		0.7 ± 0.2	0.3 ± 0.1	0.91
ΣE_L		-3 ± 1	5.7 ± 1.0	0.86		1.8 ± 0.6	-0.9 ± 0.1	0.85
σ_p								
pK_a	$\delta(C_\beta$-L)	2.0 ± 0.3	117 ± 1	0.95	$\delta(H_\beta$-L)	0.14 ± 0.03	5.3 ± 0.1	0.93
ΣE_L		-20 ± 5	142 ± 2	0.90		-1.3 ± 0.4	7.0 ± 0.2	0.86
σ_p		-8 ± 3	128 ± 3	0.83		-0.5 ± 0.2	6.1 ± 0.2	0.79
pK_a	$\delta(C_\gamma$-L)	3.7 ± 1.9	127 ± 8	0.69				
ΣE_L		-35 ± 22	173 ± 9	0.63				
σ_p		-18 ± 8	149 ± 8	0.72				

type of cluster, since the resonance signals at the α position are greatly discriminated from those at the β and γ positions. The observed chemical shifts seem to follow a linear correlation with the ligand parameters pK_a, E_L and σ_p (Table 2); however, the interpretation is complicated by the involvement of a number of electronic and magnetic contributions, such as (*a*) inductive effects from the metal centre, (*b*) substituent effects on the ligand L and (*c*) paramagnetic anisotropy and ring current effects.

The paramagnetic anisotropy of the cluster seems to be responsible for the upfield shifts, since the inductive effects would lead to downfield shifts at the α position. The variation of the H_α-L chemical shifts along the series of substituted ligands reflects the shielding effects from the increase in the electron density, proportional to the pK_a of L. This trend is reversed in the case of C_α-L, and may be due to the influence of the paramagnetic anisotropy of the metal as well as to the contribution of low-lying excited states.

The influence of paramagnetic anisotropy is expected to decay very rapidly with the distance, and should be negligible at the β position. In fact, the H_β-L, C_β-L and C_γ-L signals occur in the same region as for the free ligands, but are sensitive to the ligand parameters such as pK_a, E_L and σ_p, reflecting the importance of the electronic effects. The chemical shifts for the ^1H and ^{13}C atoms at the β position exhibit a linear correlation with pK_a; however, the downfield shifts observed as a function of pK_a do not reflect the direct influence of the susbtituents on the electron density of the pyridine ring, since in this case a reverse trend would be expected. Presumably, the increase in the ligand basicity is more than compensated for by the stabilization of the triangular ruthenium(III) cluster, thus enhancing its electron-withdrawing power.

A remarkable behaviour is observed for the ^1H signals of the acetate ligands, as a function of the ligand L parameters. It should be noted that the influence of the substituents at L can only be transmitted to the acetate protons via the Ru_3O centre. Therefore, the chemical shifts for the CH_3 groups can be used to probe the changes in the electronic structure of the metal cluster, induced by the substituted pyridine ligands. In fact, the ^1H chemical shifts for the CH_3 groups decrease as the pK_a of L increases. The observed shielding effect is consistent with an increase in the electron density of the cluster.

The ^{13}C chemical shifts for the carboxylate group seem to be influenced by the paramagnetic anisotropy of the cluster, as well as by the basicity of the ligand L. The increase in the electron density of the cluster reduces the net spin, thus decreasing the paramagnetic effect. This would explain the inverse trend in the linear variation of the ^{13}C chemical shifts for the carboxylate group *versus* pK_a(L).

Less Symmetric Clusters.—The discussion on the NMR data for the symmetric clusters can also be extended to the less symmetric ones, of the type $[Ru_3O(CH_3CO_2)_6(py)_2L]^+$, exhibiting C_{2v} symmetry. Typical results are shown in Table 1.

In the less symmetric clusters, the mutual influences of the various ligands are readily apparent in the NMR spectra. In general, if a resonance peak for the ligand L in the $[Ru_3O(CH_3CO_2)_6(py)_2L]^+$ cluster is shifted upfield with respect to the symmetric $[Ru_3O(CH_3CO_2)_6L_3]^+$ cluster, the corresponding peak for the pyridine ligand is shifted downfield with respect to $[Ru_3O(CH_3CO_2)_6(py)_3]^+$, and vice versa. This type of compensation phenomena results from the high degree of electronic coupling within the cluster. Because of the mutual interactions, the NMR data for the less symmetric clusters seem to be less sensitive to the ligand parameters, departing from the linear correlations reported for the symmetric species. Another interesting aspect is that the resonance signals for the acetate ligands opposite to L are much closer to those observed in the symmetric species $[Ru_3O(CH_3CO_2)_6L_3]^+$, while the resonance signals for the vicinal acetates are comparable to those for $[Ru_3O(CH_3CO_2)_6(py)_3]^+$. This fact indicates the existence of *trans*-influence in the triangular clusters.

We are grateful to FAPESP, CNPq and PADCT for financial support and a fellowship (to A. D. P. A.).

Received, 14th February 1997; Accepted, 2nd June 1997
Paper E/7/01058C

References

1 F. A. Cotton and J. G. Norman, Jr., *Inorg. Chim. Acta*, 1972, **6**, 411.
2 A. Spencer and G. Wilkinson, *J. Chem. Soc. Dalton*, 1972, 1570.
3 A. Spencer and G. Wilkinson, *J. Chem. Soc. Dalton*, 1974, 786.
4 J. A. Baumann, D. J. Salmon, S. T. Wilson, T. J. Meyer and W. E. Hatfield, *Inorg. Chem*., 1978, **17**, 3342.
5 C. Bilgrien, S. Davis and R. S. Drago, *J. Am. Chem. Soc*., 1987, **109**, 3786.
6 S. Davis and R. S. Drago, *Inorg. Chem*., 1988, **27**, 4759.
7 T. Dong, H. Lee, T. Lee and C. Hsieh, *J. Chin. Chem. Soc*., 1992, **39**, 393.
8 S. A. Simanova, A. N. Belyaev, V. I. Bashmarkov, O. N. Troshina, A. V. Shchukarev and F. I. Danilova, *Russ. J. Gen. Chem*., 1993, **63**, 1378.
9 H. E. Toma and A. D. P. Alexiou, *J. Chem. Res. (S)*, 1995, 134.
10 H. E. Toma and A. D. P. Alexiou, *J. Braz. Chem. Soc*., 1995, **6**, 267.
11 M. Abe, Y. Sasaki, Y. Yamada, K. Tsukahara, S. Yano and T. Ito, *Inorg. Chem*., 1995, **34**, 4490.
12 J. L. Walsh, J. A. Baumann and T. J. Meyer, *Inorg. Chem*., 1980, **19**, 2145.
13 Y. Sasaki, A. Tokiwa and T. Ito, *J. Am. Chem. Soc*., 1987, **109**, 6341.
14 M. Abe, Y. Sasaki, A. Nagasawa and T. Ito, *Bull. Chem. Soc. Jpn*., 1992, **65**, 1411.
15 M. Abe, Y. Sasaki, T. Yamaguchi and T. Ito, *Bull. Chem. Soc. Jpn*., 1992, **65**, 1585.
16 Y. Sasaki, A. Nagasawa, A. Tokiwa-Yamamoto and T. Ito, *Inorg. Chim. Acta*, 1993, **212**, 175.
17 G. Powell, D. T. Richens and A. K. Powell, *Inorg. Chim. Acta*, 1993, **213**, 147.
18 H. E. Toma, C. J. Cunha and C. Cipriano, *Inorg. Chim. Acta*, 1988, **154**, 63.
19 A. B. P. Lever, *Inorg. Chem*., 1990, **29**, 1271.
20 C. Hansch, A. Leo and R. W. Taft, *Chem. Rev*., 1991, **91**, 165.