Inorganica Chimica Acta, 113 (1986) 187–191

Yttrium-89 Magnetic Resonance Study of Simple Coordination Complexes

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Received August 12, 1985

Abstract

^{89}Y FT NMR studies of some simple salts and complex ions have been carried out on a Varian FT80A spectrometer at 3.895 MHz. Corresponding gadolinium salts with the matching counterion have been used as relaxation reagents. Shifts dependent on complexation equilibria have been observed for the carboxylate salts.

Introduction

There have been relatively few reports [1–6] of ^{89}Y magnetic resonance studies of yttrium salts and complexes despite the 100% abundance of the isotope and its $I = ½$ value. This is primarily due to its low sensitivity, low resonance frequency, and unfavourable relaxation times. At ambient temperature the non-dipolar relaxation contributions can render the negative nOe a liability in proton decoupled spectra, since a decrease in signal magnitude will occur if these contributions exceed 80% of the net relaxation. Some ^{1}H–^{89}Y and ^{13}C–^{89}Y coupling constants (J) have been reported from ^{1}H and ^{13}C spectra [7–9], and directly from ^{89}Y of some organometallic compounds. A novel use of ^{89}Y zero-field magnetic resonance to investigate the magnetic properties of iron–manganese alloys has also been reported [10].

A general investigation of ion pairing in lanthanide salts led us to prepare and examine some yttrium derivatives, and in this paper we report preliminary studies on these and reexamine some simple salts.

Experimental

The ^{89}Y spectra were obtained at a nominal frequency of 3.895 MHz using a Varian FT80-A spectrometer with variable frequency capability and a 10 mm probe insert. This frequency is below the normal lower limit of the instrumentation (5 MHz), and tuning was characterised by a relatively flat response. However, respectable signals were obtained with no problem from 1 M solutions of $Y(NO_3)_3$ using long pulse delay times to allow for the long relaxation times [5]. Addition of about 1% (mole ratio) of gadolinium nitrate enabled the spectra to be obtained with a repetition time equal to the acquisition times of 0.5 to 1 s. The paramagnetic gadolinium salt acts as a relaxation reagent (PARR) without appreciable alteration of the chemical shifts at these mole ratios. Any line broadening was less than that introduced by the sensitivity enhancement correction to the FID (approx. 1 Hz). For each salt studied, a gadolinium compound of the same type and counterion was added as the appropriate PARR. The number of scans needed to obtain a spectrum with more than 3:1 signal to noise varied from the order of ten for the most concentrated to 10^4 for the least concentrated solutions. The lowest concentrations at which spectra could reasonable obtained was about 0.1 M. Frequency (chemical shift) measurements were reproducible to about 0.1 ppm for the most concentrated to about 0.2 ppm for the least concentrated. Shifts are given in ppm relative to the zero concentration extrapolation for the perchlorate salt (3.8977750 MHz).

All yttrium salts and complexes investigated were made in our laboratory from Y_2O_3. The salts $[(C_4H_9)_4N]_3YCl_6$ [11] and $[(C_4H_9)_4N]_2Y(NO_3)_5$ were prepared as described in the literature [12], and $Y(NCS)_3$ was prepared as the tetra-n-butylammonium salt [13]. After repeated crystallization, the salts were analysed for yttrium content by the EDTA titration method.

Solutions were prepared in water, except for the hexachloro and pentanitrato derivatives which were prepared in nitrobenzene. The external D_2O field frequency lock was used in all cases.

Results and Discussion

It has been previously shown [3, 4] that the chemical shift of the yttrium (3+) ion varies with concentration. Similar variations have been established for a number of metal ions [14]. Some metal ions behave

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like the alkali metal ions, the shifts reflecting primarily electrostatic ion pairing effects, while others behave like aluminum (3+) with a greater tendency to form coordinate covalent interactions. Yttrium is expected to be more like the latter since it is known to form stable complex ions with both the halides and the nitrate ion, which can be isolated in non-aqueous solution. Our observation on the simple salts of yttrium in solution parallel the previous results [2–4], in which the perchlorate and nitrate show low frequency (high field) shifts with increasing concentration, while the halides and other salts show varying low field (high frequency) shifts. For the nitrate, perchlorate and chloride, an essentially linear dependence of shift on concentration occurs as shown in Fig. 1. The shifts for $^{89}YBr_3$ were identical to the chloride, while shifts for the iodide were essentially zero. The pseudo halide $Y(NCS)_3$ was shifted upfield slightly more than the perchlorate.

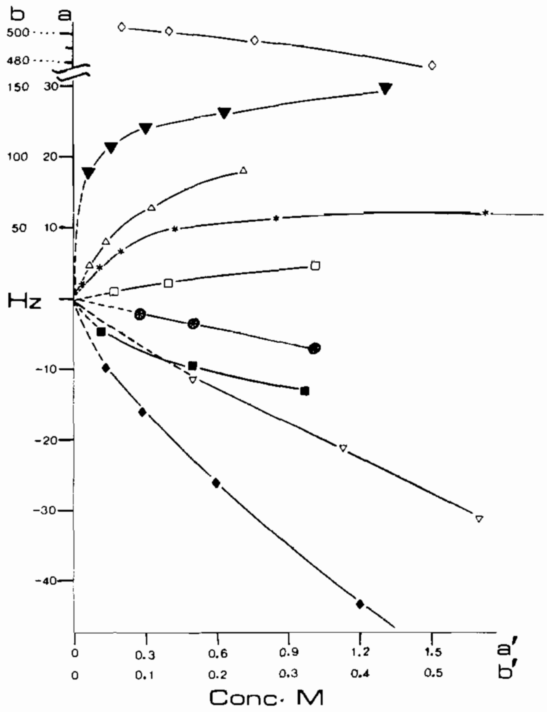

Fig. 1. ^{89}Y Shifts *vs.* Concentration. Scale b, b′: ◇ $Y(EDTA)^-$; ▼ $Y(CH_3COO)_3$. a, a′: △ $Y(ClCH_2COO)_3$; * $Y(HCOO)_3$; □ $Y(Cl)_3$; ⊛ $Y(ClO_4)_3$; ■ $Y(Cl_2CHCOO)_3$; ▽ $Y(CF_3COO)_3$; ◆ $Y(NO_3)_3$.

We were unable to reproduce the turnover to high field shift at the lowest nitrate concentrations as reported previously [3], in fact a slight downfield curve is suggested. The carboxylate derivatives, in general, showed concentration dependence with the typical characteristics of an equilibrium (Fig. 1), the upper limit of which was not reached for the acetate case because of solubility limitations. A similar set of curves have been obtained for lanthanum-139 shifts of acetates and chloroacetates [15], and related to thermodynamic parameters.

An unanticipated concentration dependence for the EDTA derivative, was observed similar to that observed for the nitrate salt. The high K (stability) for the EDTA complex ($\log K = 18$) should preclude any dissociation over the range of concentrations accessible to the NMR study, hence the observed shift must be associated with changes in solvation and ion pairing effects.

Yttrium is often included with the lanthanides in many of its properties, and since the β_n stability constants are available for acetate complexes of the lanthanides [16] these were used as input parameters to generate a best fit for the acetate curve (Fig. 1) and estimate shift parameters for the three species $Y(OOCCH_3)^{2+}$, $Y(OOCCH_3)_2^+$, and $Y(OOCCH_3)_3$. The β_n constants are defined as

$$\beta_n = [MA_n]/[M^{3+}][A^-]^n$$

A non-linear least-squares method was used to converge on a best overall set of values for β_n and chemical shifts to fit the observed data. Some support for using the lanthanide thermodynamic data as a basis for the estimations is afforded by the close similarities reported for the carbonate complexes of yttrium and the early rare earths [17]. The results are shown in Table I, where it can be seen that the adjusted β_n values are not inconsistent with those obtained for the lanthanides [16]. Only a few iterations were required for convergence.

On the assumption that base behaviour towards the proton and the yttrium (3+) ion will be roughly parallel ($pK_a \alpha \log K_{stab}$), a starting set of stability constants for the other carboxylate complexes can be obtained and used to estimate shifts for the analogous complex species. The stability constants and shifts estimated for the formate, chloroacetate and dichloroacetate are also shown in Table I. Within the acetate derivatives, the downfield shifts decrease with decreasing pK_a of the parent acid. A similar trend was reported for the lanthanum-139 shifts [15]. The pooled standard deviation of the fitted curves (Table I) is comparable to the estimated variation in experimental reproducibility.

An attempt to prepare the trichloroacetate derivative resulted in a decarboxylation reaction with the precipitation of yttrium carbonate. The trifluoro derivative is stable and showed a linear concentration dependence of the shift characteristic of the other salts of strong acids.

By analogy with the carboxylate complexes, at low enough concentrations one would expect the shift for the EDTA derivative to curve over to high

TABLE I. Observed and Calculated ^{89}Y Shifts of Carboxylate Salts

Salt	pK_a	Concentration	Shifts^a (ppm)		Estimated shifts^a and constants (ppm)					
			δ(obs.)	δ(calc.)^b	δ(2+)	δ(1+)	δ(0)	β_1	β_2	β_3
CH_3COO^-	4.75	0.430	36.5	36.2	28.2	28.6	47.3	41	369	1328
		0.215	33.9	33.4						
		0.108	30.4	30.2						
		0.054	27.0	26.5						
		0.27	22.6	22.4						
		0	–	0.0						
$HCOO^-$	3.75	3.38	3.4	3.4	−0.5	2.9	4.0	30	142	283
		1.69	3.3	3.2						
		0.84	2.9	2.9						
		0.42	2.5	2.4						
		0.21	1.6	1.8						
		0.11	1.5	1.2						
		0.05	0.5	0.6						
		0	–	0.0						
CH_2ClCOO^-	2.85	0.70	4.4	4.4	2.1	2.0	17.7	3.5	6.0	2.4
		0.35	3.3	3.2						
		0.18	1.8	1.9						
		0.09	1.3	1.2						
		0	–	0.0						
$CHCl_2COO^-$	1.48	1.00	3.3	3.3	−3.4	1.7	−40	2	1	0.1
		0.50	2.1	2.2						
		0.25	1.6	1.6						
		0.13	1.2	1.2						
		0	–	0.0						

[a] Chemical shift relative to $^{89}Y(ClO_4)_3$ (infinite dilution extrapolation). [b] Standard deviation (pooled) = 0.2 ppm.

field. As noted above, this cannot be observed because of the limitations of sensitivity. Conversely, one might anticipate that the carboxylate shifts should curve over to high field at the higher concentrations. This is not observed for the acetate, which might be a solubility limitation, however, neither is it observed for the formate, which appears to reach a steady value at higher concentrations. If the high field shifts are due to changes in ion pairing and solvation, the effects should be more pronounced for the EDTA complex which, typically, has an open side or face for access of solvent or counterion to the metal ion [18].

Both the chloride and nitrate anions form stable complexes with yttrium in non-aqueous environments [11, 12]. For the pentanitrato complex an ^{89}Y signal is easily observed in 1 M solution with the corresponding gadolinium pentanitrato complex added as PARR. The resonance is several Hz wide, and it has been noted [19] from ^{14}N magnetic resonance studies that many of these complexes are moderately labile on the NMR time scale. The resonance occurs close to the 2 M trinitrate shift in aqueous solution (18.5 ppm and 21.1 ppm respectively). Thus complexation in the former, and ion pairing in the latter appear to have a consistent upfield shift (Fig. 1).

By contrast, the ^{89}Y resonance for the hexachloro complex, with or without the appropriate PARR, was at first impossible to see. A very long accumulation did eventually yield a very broad line, of more than 1000 Hz width at half height, located some 240 ppm downfield of the aquo-ion shift. The direction of the shift is the same as that observed for the trichloride in water, but of a much larger magnitude. Because of the possibility that certain operating conditions can give rise to artifacts in the baseline which might be mistaken for a broad peak, some confirmation was sought. It has been shown in other transition metal systems [20] that mixed halo-complexes can be obtained and identified by NMR. If such mixtures are undergoing rapid ligand exchange, then only one averaged resonance is expected, which will be very broad if the exchange rate is close to the peak separation in Hz. Thus the broad signal for the hexachloro-complex could be attributed to the coexistence of two or more chloro-anions undergoing chloride ion exchange. Since other evidence [19] suggested that the nitrato complex undergoes less rapid ligand exchange, a mixture of the nitrato and chloro complexes would introduce a less labile species into the system and allow some clearer resolution of the peaks. Two solutions of different chloro:nitrato ratios were examined, and the spectra observed did indicate the appearance of new species considerably downfield of the original nitrato complex. The spectra obtained are shown in Fig. 2, where it can be seen that the species are undergoing exchange at intermediate rates on the NMR time scale. At 1:1 ratio, a very broad resonance is observed at about −260 ppm with a sharper upfield resonance at about −80 ppm. As the nitrato component is increased, the latter sharpens and moves upfield, the former moving downfield.

If the exchange involves loss of ligand as the rate determining step [19], introduction of an excess of the free ligand should decrease the exchange rate. A solution of the hexachloroyttrate anion with excess tetraalkyl ammonium chloride was examined and showed two peaks of about 900 Hz half height width, one to low field (−280 ppm) and the other to high field (−40 ppm) of the original 1000 Hz wide peak (Fig. 2). Thus it seems likely that the hexachloro-complex does undergo some dissociation in solution to give a mixture of species. Because of the high freezing point of nitrobenzene solvent, it was not possible to slow the exchange rates sufficiently to see the separate species, but at least two are anticipated, YCl_6^{3-} and YCl_5^{2-}. Solubility problems in other suitable solvents also presently preclude a low temperature study.

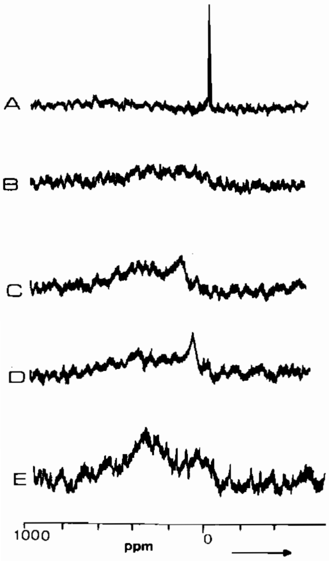

Fig. 2. ^{89}Y Spectra at 3.895 MHz. (A) $Y(NO_3)_5^{2-}$ in nitrobenzene. (B) YCl_6^{3-} in nitrobenzene. (C) 50:50 mixture of A and B. (D) 70:30 mixture of A and B. (E) YCl_6^{3-} *plus* excess Cl^- in nitrobenzene.

Conclusion

Despite the unfavourable sensitivity and relaxation times of the ^{89}Y nucleus, it is readily accessible even on low field multinuclear FT NMR instruments. Because of the similarity of yttrium to the lanthanide elements, it is clearly a useful non-quadrupolar and non-paramagnetic probe for complexes and compounds of these elements, and also other M^{3+} species. Its usefulness as a spin probe [5] may be realized in conjunction with a corresponding PARR, provided the probe situation involves rapid exchange between bound active sites and free ion. Shifts observed on introduction of a PARR with a non-common counterion can introduce shifts which may be due to the counterion rather than the paramagnetic moiety.

The observed chemical shift variations in ^{89}Y complexes suggests that covalent interactions, electrostatic ion pair interactions, and solvent effects all play an important and, as yet, undetermined role. Although the carboxylate complexes exhibit shifts that to some extent reflect anion basicity, there are clearly other factors involved. The observed shift dependencies for these complexes are explicable on the basis of simple equilibria, however, the constants determined must be regarded as speculative at this stage.

A marked difference in lability is demonstrable between the monodentate chloro and potentially bidentate nitrato ligands.

Acknowledgements

We thank the President's NSERC Fund of York University and Canada Manpower and Immigration (SEED Programme) for financial support.

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