Inorganica Chimica Acta, *127* (1987) L19–L20

The ^{1}H NMR Spectra of the 8-Quinolinolato Complexes of Aluminium(III), Gallium(III), Indium(III) and Thallium(III)

PHILLIPA ADDY, DENNIS F. EVANS
and RICHARD N. SHEPPARD

*Inorganic Chemistry Laboratories, Imperial College,
London SW7 2AY, U.K.*

(Received September 17, 1986)

8-Quinolinol (8-hydroxyquinoline, oxine) is a useful analytical reagent for a variety of metal ions [1]. Complexes of the type M(oxine)$_3$ can theoretically exist as facial (*fac*) or meridional (*mer*) isomers. X-ray crystallographic studies of Cr(oxine)$_3$ [2] and Mn(oxine)$_3$ [3] have shown that they are the *mer* isomers. In 1968, Baker and Sawyer [4] studied and assigned the ^{1}H NMR spectra of Al(oxine)$_3$, Co(oxine)$_3$ and Rh(oxine)$_3$ in dimethylsulphoxide solution at 100 MHz. Three sets of ligand resonances were observed in each case, showing that the *mer* isomers were also present in solution. For the *fac* isomers all three rings are equivalent. We have measured the ^{1}H NMR spectra at 250 MHz (CDCl$_3$ solutions) of Al(oxine)$_3$, Ga(oxine)$_3$, In(oxine)$_3$ and Tl(oxine)$_3$, which present a variety of magnetic behaviour.

Experimental

Al(oxine)$_3$, Ga(oxine)$_3$, Ir(oxine)$_3$ and Tl(oxine)$_3$ [5] were prepared by standard methods. Partially deuteriated oxine [6] was obtained by heating 0.5 g oxine, 2.4 cm^3 38% DCl and 2.4 cm^3 D$_2$O at *ca.* 95 °C for 2 days. The ^{1}H NMR spectrum of this solution after dilution with an equal volume of D$_2$O showed that [H$_7$]/[H$_5$] was *ca.* 2.3. The other ring hydrogens were unaffected.

^{1}H NMR spectra were recorded on a Bruker WM-250 FT spectrometer. A 2-dimensional correlated shift spectrum [COSY-45] was obtained for Al(oxine)$_3$.

Results and Discussion

Al(oxine)$_3$

The ^{1}H NMR spectrum was quite complex, and was assigned in conjunction with the 2D spectrum (Fig. 1), which enabled the resonances from the same ligand to be picked out. No resonances from the *fac* isomer could be detected. Some discrepancies with the data of Baker and Sawyer [4] may arise from the different solvents used. The considerable upfield shift of one H$_2$ resonance can be explained, as suggested by Baker and Sawyer [4], by the fact that one of the H$_2$ protons lies above the plane of a ligand, and will experience a large ring-current effect.

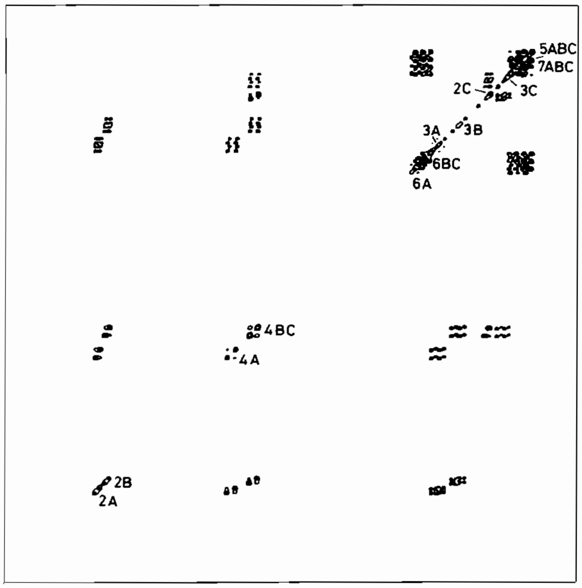

Fig. 1. 2D correlated shift spectrum (COSY-45) for Al(oxine)$_3$. Shift range for each axis is 9.21 ppm to 6.85 ppm.

Ga(oxine)$_3$

At 0 °C, the spectrum was very similar to that of Al(oxine)$_3$. However, at 20 °C, appreciable broadening of the resonances was observed, which became much more marked at 40 °C, indicating the onset of fluxionality. At 20 °C with Ga(2-Me oxine)$_3$, five sets of sharp multiplets were observed and one sharp Me resonance, indicating fast fluxional behaviour. This is not surprising, since a molecular model shows that, in the *mer* isomer, there is considerable steric interference between one Me group and a ligand (*cf.* ref. 7).

In(oxine)$_3$

Six sharp and well-separated multiplets were observed at 20 °C, as expected for a molecule completely fluxional on an NMR time scale. The possibility that the complex actually exists in the *fac* form can be excluded, since in this isomer all three H$_2$ protons lie above ligands [4], and the H$_2$ resonance would appear considerably upfield from its observed position. An ambiguity in the assignment

0020-1693/87/$3.50

TABLE I. NMR Data for Al(oxine)$_3$, Ga(oxine)$_3$, In(oxine)$_3$ and Tl(oxine)$_3$ in $CDCl_3$ Solution

Compound	Proton	δ (ppm)					
		2	3	4	5	6	7
Al(oxine)$_3$	A	8.85	7.42	8.28	[a]	7.51	[a]
	B	8.81	7.36	8.18	[a]	7.49	[a]
	C	7.22	7.15	8.18	[a]	7.49	[a]
Ga(oxine)$_3$[b]	A	8.86	7.44	8.30	[a]	7.52	[a]
	B	8.82	7.35	8.20	[a]	7.50	[a]
	C	7.23	7.16	8.20	[a]	7.50	[a]
In(oxine)$_3$		8.56	7.40	8.28	7.03	7.50	7.18
Tl(oxine)$_3$		8.63	7.46	8.28	6.99	7.51	7.17
$J(^{203/205}Tl-^1H)$ (Hz)		+108.8	+62.2	+34.7	±10.4	±38.9	∓37.4

[a] Complex pattern, not analyzed. [b] At 0 °C, all other data at *ca.* 20 °C.

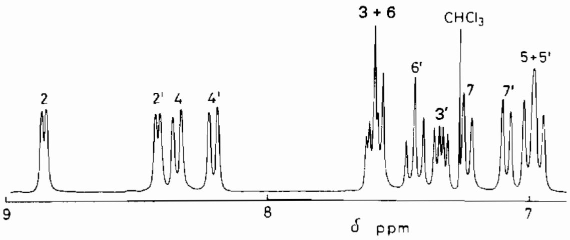

Fig. 2. The ^1H NMR spectrum of Tl(oxine)$_3$.

of H_5 and H_7 was resolved by studying In(oxine)$_3$ prepared from oxine which had been unequally deuteriated in the 5 and 7 positions.

Tl(oxine)$_3$

Like In(oxine)$_3$, this molecule is completely fluxional. However, thallium has two isotopes with spin 1/2, and very similar magnetic moments (^{203}Tl, 29.5% abundant, μ = 1.5960 nuclear magnetons and ^{205}Tl, 70.5% abundant, μ = 1.6116 nuclear magnetons). Appreciable $^{203/205}Tl-H$ splittings are observed for all six ligand resonances (Fig. 2 and Table I). The relative signs of the $^{203/205}Tl-^1H$ coupling constants were obtained by double irradiation [8]. Since there was no detectable inter-ring coupling, the relative signs of the coupling constants to the two different rings could not be determined. In Table I, it is assumed that $J(^{203/205}Tl-^1H_2)$ (a vicinal coupling) has an absolute positive sign. The presence of the $^{203/205}Tl-^1H$ splitting shows that the process which equilibrates the three ligands is, in fact, an intramolecular one, and does not involve complete dissociation of a ligand.

Acknowledgement

We thank Ms. Sue Johnson for assistance with the NMR spectra.

References

1 R. G. W. Hollingshead, 'Oxine and its Derivatives', Part 1, Butterworths, London, 1954.
2 K. Folting, M. M. Cox, J. W. Moore and L. L. Merritt, *J. Chem. Soc., Chem. Commun.*, 1170 (1968).
3 R. Hems, T. J. Cardwell and M. F. Mackay, *Aust. J. Chem., 28*, 443 (1975).
4 B. C. Baker and D. T. Sawyer, *Anal. Chem., 40*, 1945 (1968).
5 F. Feigl and L. Baumfield, *Anal. Chem. Acta, 3*, 83 (1949).
6 P. Addy, D. F. Evans and Q. de Souza, in preparation.
7 H. Irving, F. J. Butler and M. F. Ring, *J. Chem. Soc.*, 1489 (1949).
8 J. P. Maher and D. F. Evans, *Proc. Chem. Soc.*, 208 (1961).