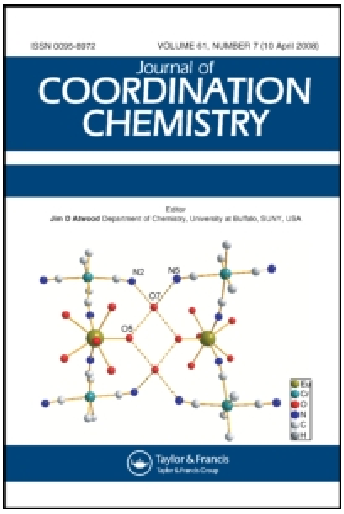

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CHARACTERIZATION OF TRIS-CHELATED ISOMERS USING ^{13}C AND ^{1}H NMR

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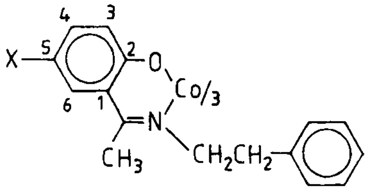
INTRODUCTION

Octahedrally coordinated metal complexes of the type M(A–B)$_3$ where A–B is an unsymmetrical bidentate ligand can exist in two isomeric forms, facial and the meridional. Since the magnetic environments of the ligand atoms in the two forms are different, NMR studies are ideal for distinction between such isomers. This means that each chemical shift found for the free ligand should be reflected by three chemical shifts in the meridional complex but not in the facial complex. In the past, ^{1}H NMR studies have been used to determine the geometry of cobalt (III) chelates of β-diketones,[1] pyrrole-2-aldimine[2], salicyladimine[2], α-aminoacids[3] and other bidentate ligands.[4]–[7]. However, a distinct three line pattern of chemical shifts has been observed for only one or two of the many protons with the rest submerged in crowded proton splitting patterns.

Proton noise-decoupled ^{13}C spectra of such compounds should be elegantly simple and ideal for the identification of these isomers. However, few such studies seem to be reported. Here we report the characterization of the meridional isomers of some new cobalt(III) tris-chelates through ^{13}C and ^{1}H NMR spectral studies. The ligand system



with bulky substituents on nitrogen was chosen so that the metal complexes would adopt an exclusively meridional structure without the admixture of the facial form because of steric factors.

EXPERIMENTAL

The preparation of the cobalt(III) tris-chelate complexes is described in previous work.[8] The p.m.r. measurements were carried out on Perkin Elmer R-32 (90 MHz) or Bruker (200 MHz) spectrometers in CDCl$_3$ with TMS as the internal standard. ^{13}C NMR spectra were recorded on a Bruker instrument at 100.62 MHz. The solvents used were CD$_2$Cl$_2$ or CDCl$_3$.

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TABLE I
^1H NMR data (90 MHz, $CDCl_3$, $SiMe_4$ internal standard) for the methyl signals of the Schiff bases and their cobalt(III) complexes (chemical shifts in ppm).

Compound†	CH_3-C=N	Ar-CH_3
H-HAPPEI	2.15	
Co(HAPPEI)$_3$	2.16	
	2.55	
	2.80	
H-MeHAPPEI	2.15	2.25(s)
Co(MeHAPPEI)$_3$	2.16	2.25
	2.55	2.35
	2.75	2.60
H-ClHAPPEI	2.15	
Co(ClHAPPEI)$_3$	2.16	
	2.55	
	2.75	

†Abbreviations: H-HAPPEI = *N*-(2-phenylethyl)-2-hydroxyacetophenonimine, H-MeHAPPEI = 5-Methyl-*N*-(2-phenylethyl)-2-hydroxyacetophenonimine and H-ClHAPPEI = 5-Chloro-*N*-(2-phenylethyl)-2-hydroxyacetophenonimine.

Thin layer chromatography was performed using silica gel and a solvent mixture of chloroform and acetone (3:1 v/v) or benzene and acetone (7:3 v/v) on the metal complexes. Visual inspection of the plate after exposure to iodine showed the presence of only one isomeric form in both cases.

RESULTS AND DISCUSSION

Analytical and i.r. data for the complexes suggest an octahedral unsymmetrical tris-chelated structure with N and O as the coordinating centres. An examination of the p.m.r. spectra of the complexes (*mer*) reveals that a three line pattern could be observed only for the methyl group resonances and these occur at 2.16, 2.55 and 2.80 ppm while the parent signal in the ligand occurs at 2.15 ppm (Table I). However, the two methylene signals which appear as sharp triplets in the ligand spectra are somewhat broadened in the spectra of the complexes probably as a result of unresolved overlapping signals. The signals could not be further resolved.

Identification of the N-CH_2 proton signal which was almost submerged by background noise was made possible by spin decoupling at 3.05 δ. A singlet signal emerged with enhanced intensity at 3.80 δ confirming its identity. The complex multiplet of aromatic protons in the ligands also increases in signal number in the spectra (90 MHz) of the chelated complexes but it is difficult to pick out all 27 signals of the unsubstituted ligand at 200 MHz. It is only possible to clearly distinguish 21 signals. Thus in the p.m.r. spectra of these meridional complexes the three line pattern expected

TABLE II

^{13}C NMR Chemical shift data for selected resonances (ppm).

Line	Co(MeHAPPEI)$_3$	Assignment†	Co(HAPPEI)$_3$	H-HAPPEI
1	173.23		174.66	
2	171.62	-*C*=N	172.84	176.94
3	170.94		171.79	
4	165.76		167.97	
5	165.64	(Ar)-*C*(2)	167.78	169.83
6	163.99		166.46	
7	140.68			
8	140.43			
9	139.32			
10	133.92			
11	133.09			
12	130.02			
13	129.77			
14	129.12			
15	128.68			
16	128.31			
17	128.03			
18	127.72			
19	127.23			
20	126.79			
21	126.30			
22	125.89			
23	125.62			
24	125.06			
25	124.96			
26	124.53			
27	124.31			
28	123.94			
29	123.72			
30	123.233			
31	122.89			
32	122.48			
33	122.33			
34	121.46			
35	78.99			
36	78.74			
37	77.56			
38	77.28	solvent		
39	77.10	solvent		
40	76.63	solvent		
41	76.14			
42	75.86			
43	75.67	solvent impurity		
44	75.18	solvent impurity		
45	57.04		57.58	
46	56.27	N-*C*H$_2$	56.98	53.52
47	54.06		56.73	
48	38.16		38.37	
49	37.17	Ph-*C*H$_2$	36.96	39.78
50	36.89		36.71	
51	36.80			
52	20.77			
53	20.46	-*C*H$_3$-C$_5$		
54	19.19		19.77	
55	18.97	*C*H$_3$-C=N	19.37	16.83
56	17.67		18.15	

†The signals for which no assignments are given are due to aromatic carbons. Chemical shifts are given relative to TMS as internal standard.

for each of the parent lignad signals could be only observed clearly for the methyl resonances.

As expected the proton noise-decoupled ^{13}C NMR spectra of the pure meridional complexes are elegantly simple and most of the parent signals of the ligand can be seen to be resolved into three line patterns. For example, the ligand 5-methyl-*N*-(2-phenylethyl)-2-hydroxyacetophenonimine has 17 carbons; the ^{13}C NMR spectrum of the corresponding cobalt(III) meridional complex shows 51 signals (excluding solvent and reference peaks, Table II). The signals from the aromatic carbons cluster in the full spectrum of tris[*N*-(2-phenylethyl)-2-hydroxyacetophenoniminato]cobalt(III) but on expansion shows nearly three times the number of signals expected for the ligand.

We assign the sharp signal at 176.94 ppm in the unsubstituted ligand spectrum, at 171.79, 172.84, 174.66 ppm in the unsubstituted complex and at 170.94, 171.62 and 173.23 ppm in the 5-methyl substituted complex to the azomethine carbon resonances. For organic molcules possessing the >C=N- and -N=C- groups, the carbon-13 resonance occurs in the regions 142.5–163 and 152.5–162.5 ppm respectively.[9] It is observed that the peaks at 176.94 169.83 and 146.50 ppm in the unsubstituted ligand have considerable lower signal intensities than all others in the spectrum. The spectrum being a pulsed one, these three signals can be assigned to the three of the quaternary carbons (slowly relaxing) in the molecule, *viz* the azomethine carbon, the aromatic carbon attached to the phenolic oxygen and the aromatic carbon adjacent to the -CH_2 group, respectively.

Of these three quaternary carbons, the azomethine carbon and the aromatic carbon adjacent to the phenolic oxygen appear in considerably deshielded regions (away from the usual aromatic region) due probably to their attachment to electronegative atoms. In methylsalicylate the signal of the aromatic carbon to which the phenolic OH is attached occurs at 162.38 ppm with low signal intensity.[10] The signal at 146.50 ppm might therefore be assigned to the aromatic carbon adjacent to the methylene group. Each of these three signals of the ligand shows a three line pattern in the spectrum of the complexes. It may be noted that in the NMR spectrum of the complexes, of the three signals attributable to a given aliphatic carbon or proton two are significantly deshielded while the third shows only a slight downward shift with respect to the parent signal in the ligand.

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