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A Nuclear Resonance Study of Tris(2-Arylazophenolato)Cobalt(III)

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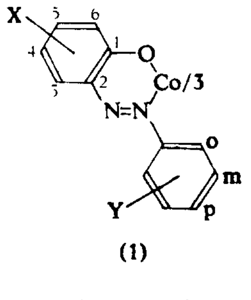
Tris-chelates of cobalt(III) derived from a few 2-arylazophenols are reported. A convenient method of synthesis involves the reaction of hexamminecobalt(III) chloride with the sodium salt of the ligand. No evidence could be obtained for the existence of the sterically unfavourable cis *form. A claim that tris-(2-phenylazo-4-methylphenolato)Co^{III} can exist in* cis *and* trans *forms cannot be reconciled with nuclear resonance and other data. Nor did we succeed in isolating the* cis *form.*

Introduction

It has been known for many years[1] that 2-arylazophenols form well-defined crystalline complexes with transition metal ions. The tris-chelate of cobalt(III) derived from phenylazo-β-napthol was reported by Pfeiffer *et al.*[2] Subsequently a number of analogous chelates having the general structure shown in (1)



(1)

were synthesised by Elkins and Hunter.[3] A proton magnetic resonance (p.m.r.) investigation of the stereochemistry of this class of chelates is reported in this paper.

Experimental Section

Preparation of Compounds. The complexes can be prepared by oxidising an aqueous alcoholic solution containing cobalt(II) acetate and the appropriate ligand with hydrogen peroxide. However, the products obtained by this procedure were often difficult to purify. We found that on heating a solution of hexamminecobalt(III) chloride (.01 mole), 2-arylazophenol (.03 mole) and sodium hydroxide (.03 mole) in aqueous ethanol (70% alcohol) to reflux, ammonia was gradually lost and in about two hours the required tris-chelate separated out in good yield. Two recrystallisations from hexane or ethanol usually gave a pure product. Only in the case of (1) (X = 4–*t*–C_4H_9; Y = *m*–CH_3), chromatography on a small column of silica gel (a 1:20 mixture of benzene and hexane was used as the eluant) was necessary for final purification. Analytical data for complexes are shown in Table I. The ligands used in this study have two common features: (a) a substituent in the 4-position of the phenolic ring; this allowed easy synthesis by exclusive *ortho* azo-coupling, (b) a methyl substituent in at least one of the aromatic rings; this provided sharp and uncomplicated p.m.r. signals required for stereochemical identification of the chelates.

Attempted Separation of cis *and* trans *Forms of (1) (X=4–CH_3; Y=H).* 2.0 g of the crude product made by the hydrogen peroxide method was chromatographed on a column of Fisher (U.S.A.) alumina (80-200 mesh; 100 g) using chloroform as the eluant. From the first band which moved rapidly, 1.6 g of the pure *trans* complex (identified by p.m.r. spectrum) could be isolated. (Careful rechromatography of this product on a column of alumina using benzene-

Table I. Characterization of complexes

Complex				% C		% H		% N	
X	Y	Formula	m.p. °C	Calcd.	Found	Calcd.	Found	Calcd.	Found
4-CH_3	H	$C_{39}H_{33}N_6O_3Co$	212	67.63	67.32	4.80	4.60	12.12	11.85
4-*t*-C_4H_9	*m*-CH_3	$C_{51}H_{57}N_6O_3Co$	155	71.20	70.81	6.68	6.65	9.76	9.53
4-*t*-C_4H_9	*p*-CH_3	$C_{51}H_{57}N_6O_3Co$	213	71.20	71.52	6.68	7.10	9.76	9.68
3,4-benzo	*m*-CH_3	$C_{51}H_{39}N_6O_3Co$	192	72.68	72.63	4.67	4.98	9.97	10.26
3,4-benzo	*p*-CH_3	$C_{51}H_{39}N_6O_3Co$	238	72.68	72.80	4.67	5.07	9.97	9.94

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(1) E. Bamberger, *Ber.*, 33, 1951 (1960).
(2) P. Pfeiffer, Th. Hesse, H. Pfitzinger, W. Scholl, and H. Thielert, *J. Prakt. Chem.*, *149*, 217 (1937).
(3) M. Elkins and L. Hunter, *J. Chem. Soc.*, 1598 (1935).

hexane mixture as the eluant demonstrated its isomeric purity). A second diffuse band yielded 0.2 g of unreacted ligand and some gummy product(s). A third band furnished 0.04 g of a violet crystalline solid which gave a complex p.m.r. spectrum and was not further investigated. No evidence for the *cis* form could be obtained.

Proton Magnetic Resonance Spectra were measured in $CDCl_3$ solution on a Varian HR-100 spectrometer at 100 Mc/sec. Tetramethylsilane was used as internal standard. Chemical shifts were measured by the usual side band technique. Results are shown in Figure 1 and Table II.

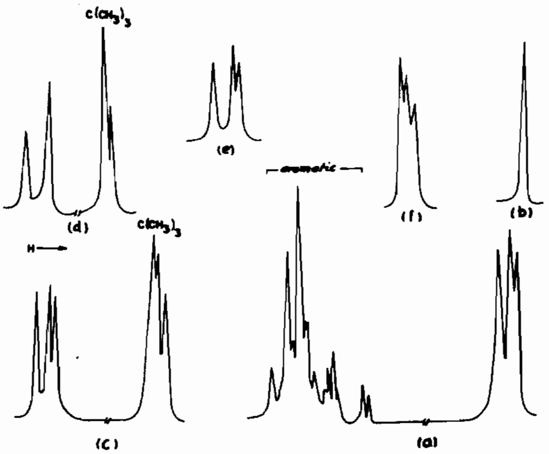


Figure 1. Proton resonance spectra of (a) (1) ($X = 4\text{-}CH_3$; $Y = H$), (b) 2-phenylazo-4-methylphenol, (c) (1) ($X = 4\text{-}t\text{-}C_4H_9$; $Y = m\text{-}CH_3$), (d) (1) ($X = 4\text{-}t\text{-}C_4H_9$; $Y = p\text{-}CH_3$), (e) (1) ($X = 3,4$-benzo; $Y = p\text{-}CH_3$); (f) (1) ($X = 3,4$-benzo; $Y = m\text{-}CH_3$). Unless otherwise labelled the peaks refer to methyl substituents only. Deuterochloroform was used as the solvent in all cases. In (c) and (d) methyl and *t*-butyl resonances were recorded at different amplitudes.

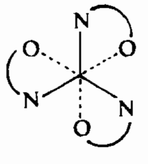
Table II. Methyl proton resonance frequencies

Compound X	Y	Group	Chemical shift[a,b] cps
$4\text{-}CH_3$	H	$4\text{-}CH_3$	215, 219, 227
$4\text{-}t\text{-}C_4H_9$	$m\text{-}CH_3$	$4\text{-}t\text{-}C_4H_9$	126, 130, 133
		$m\text{-}CH_3$	204, 211, 226
$4\text{-}t\text{-}C_4H_9$	$p\text{-}CH_3$	$4\text{-}t\text{-}C_4H_9$	124(1), 129(2)
		$p\text{-}CH_3$	221(2), 239(1)
3,4-benzo	$m\text{-}CH_3$	$m\text{-}CH_3$	193, 200, 208
3,4-benzo	$p\text{-}CH_3$	$p\text{-}CH_3$	220, 226, 246
2-phenylazo-4-methylphenol		$4\text{-}CH_3$	233

[a] From tetramethylsilane. [b] Figures in parenthesis show relative intensity of components for a given group.

Results and Discussion

The bidentate ligand in the chelate (1) is unsymmetrical and hence two geometrical configurations, *cis* (2) and *trans* (3) are permitted. The threefold axis of symmetry in the *cis* form makes all chelate rings magnetically equivalent. On the other hand, in the completely asymmetric *trans* isomer a given group of equivalent nuclei should have distinct chemical shifts for the three chelate rings.



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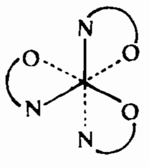

(3)

Examination of Figure 1 and Table II conclusively demonstrates the *trans* structure of the present chelates. Thus while 2-phenylazo-4-methylphenol shows a single methyl signal at 233 cps (Figure 1b), the corresponding cobalt complex shows three equally intense[4] signals at 215, 219, and 227 cps (Figure 1a). The aromatic protons give a complex pattern around 710 cps (Figure 1a). No attempts were made to analyse this region of the spectrum. It may be noticed that for all the chelates, two of the three methyl (or *t*-butyl) signals are closely spaced. An extreme case is that of (1) ($X = 4\text{-}t\text{-}C_4H_9$; $Y = p\text{-}CH_3$) where two of the three signals have completely coalesced (Figure 1d). A similar situation exists in a few other chelate systems and a probable reason for this is discussed elsewhere.[5,6]

No evidence could be obtained for the existence of the *cis* form for the 2-arylazophenol chelates. Considerable data have now accumulated which show that tris-chelates of Co^{III} having an alkyl or aryl substituent on one of the coordinating atoms, exist only in the *trans* form. Examples are chelates of salicylaldimine,[7] pyrrole-2-aldimine,[7] 2-hydroxyacetophenimine,[5] 2-hydroxypropiophenimine,[8] triazene-1-oxide,[6] and arylazooxime.[9] The non-existence of the *cis* form in these cases has been attributed to overcrowding of substituents on one face of the octahedron. The tris-chelates of 2-arylazophenols fit smoothly into this general pattern.

Some time ago it was claimed[10] that (1) ($X = 4\text{–}CH_3$; $Y = H$) made by the hydrogen peroxide method (see Experimental Section) is a mixture that can be separated into two forms by chromatography on a column of silica gel. The two forms have slightly different absorption spectra.[10] However no data that were diagnostic of the nature of the two forms were presented. The authors speculated[10] that these are *cis* and *trans* isomers. Two things make this highly unlikely. (1) Our chromatographic experiment shows that 80% of the crude product obtained by the peroxide method consists of the *trans* form. The remaining 20% consists of other products none of which is the *cis* complex. (2) Statistically, the equilibrium concentration of the *trans* form should be three times that of the *cis* form. In Co^{III} chelates of β-diketones,[11] even though the *trans* form enjoys no special steric

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(4) Two (215 and 219 cps) of the three signals seriously overlap. Visual estimation suggests that these two signals are of comparable intensity. Further, their total intensity, measured planimetrically, is twice that of the third signal (227 cps). Thus there are three signals of equal intensity.

(5) A. Chakravorty and K. C. Kalia, *Inorg. Chem.*, *6*, 690 (1967).

(6) A. Chakravorty, B. Behera, and P. S. Zacharias, *Inorg. Chim. Acta*, *2*, 85 (1968).

(7) A. Chakravorty and R. H. Holm, *Inorg. Chem.*, *3*, 1521 (1964).

(8) A. Chakravorty and B. Behera, *ibid.*, *6*, 1812 (1967).

(9) A. Chakravorty and K. C. Kalia, *Inorg. Nucl. Chem. Letters*, *3*, 319 (1967); K. C. Kalia and A. Chakravorty, *Inorg. Chem.*, in press.

(10) G. Hafelinger and E. Bayer, *Naturwissenschaften*, *51*, 136 (1964).

(11) R. C. Fay and T. S. Piper, *J. Am. Chem. Soc.*, *84*, 2303 (1962); *85*, 500 (1963).

preference over the *cis* form, the former is thermodynamically more favoured and the equilibrium constant, K(*cis*/*trans*), is less than 1/3. The yields of the two forms of (1) ($X=4\text{–}CH_3$; $Y=H$) are reported[10] to be equal, even though whole of the chelate was not recovored from the column. Labelling of the two forms as *cis* and *trans*, will lead to the highly improbable result that the stability of the sterically very unfavourable *cis* form is far in excess[12] of that of the *trans* form.

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[12] 570 mg. of each of the two forms were isolated[10] starting from 2 g. of the chelate. The «*cis* form» is expected to be more polar than the «*trans* form» and should thus be more difficulty eluted from the chromatographic column. Thus the above data on yield leads to: K(*cis*/*trans*) $\geqslant 1$.