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Studies on Some Triazene-1-Oxide Chelates of Trivalent Cobalt

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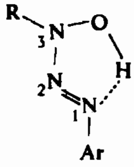
It is shown from infrared and proton magnetic resonance (p.m.r.) data that the product of the reaction of N-methyl or N-ethyl hydroxylamine with an aryldiazonium salt is correctly represented as 1-methyl(or ethyl)-3-aryl-triazene-1-oxide which exists predominantly in the internally hydrogen-bonded form. P.m.r. spectra show that the tris-chelates of Co^{III} *exist exclusively in the* trans *form. The nonexistence of the* cis *isomer is attributed to steric factors. The chelates show electronic transitions at* $\sim 19{,}000$ cm^{-1} *and* $29{,}400$ cm^{-1}. *Probable assignments are briefly discussed.*

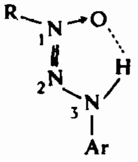
Introduction

Reaction of a diazonium salt (ArN_2X) with a substituted hydroxylamine (RNHOH) results in a triazene derivative which can be formulated as (1a) and/or (1b). Dotted lines indicate hydrogen bonds. Metal chelates of this class of ligands were first prepared by Bamberger *et al.*[1] who assumed hydroxytriazene structure, (1a). A variety of Cu^{II}, Ni^{II}, Co^{II}, Co^{III}, and Fe^{III} complexes were subsequently reported by Elkins and Hunter.[2] The stability constants of a number of chelates and potentiality of these triazene derivatives as analytical reagents have been investigated more recently.[3] We have undertaken a systematic study of the spectral and magnetic properties of transition-metal chelates of these ligands. In the present paper the stereochemistry of the diamagnetic tris-chelates of Co^{III} of a few ligands having $R = CH_3$ or C_2H_5 are examined using proton magnetic resonance (p.m.r.) data. As a prelude to this, the structure of the ligands is investigated. The electronic spectra of the Co^{III}-chelates are also examined.



(1a)

Ar = aryl
R = alkyl or aryl



(1b)

Experimental Section

Preparation of Compounds. N-methylhydroxylamine hydrochloride was made by reducing nitromethane with zinc-dust according to the prescription of Beckmann.[4] The same procedure was used to reduce nitroethane to N-ethylhydroxylamine and nitrobenzene to N-phenylhydroxylamine.[5] The triazene derivatives were synthesized by allowing the appropriately substituted hydroxylamine or its hydrochloride to react with diazotised arylamine in the presence of sodium acetate.[1,6] Deuteration of ligands was carried out by precipitating a solution of the ligand in dry dioxane with deuterium oxide. The Co^{III} chelates were made by oxidising a solution containing the ligand and cobalt acetate with hydrogen peroxide.[2] All chelates studied here, except the one having $R = C_2H_5$, are reported in the literature.[2] Contrary to previous reports,[2] we had no difficulty in getting good C, H and N microanalyses. Characterisation of chelates is shown in Table I.

Proton Resonance Measurements were done on a Varian HR-100 spectrometer. Tetramethylsilane (TMS) was used as the internal standard and frequencies were measured by the side-band technique. Areas were measured planimetrically.

Visible and Ultraviolet Spectra were measured on a Cary 14 recording spectrophotometer using 1-cm. silica cells.

Infrared Spectra were taken on a Perkin-Elmer 521 recording spectrophotometer.

Results and Discussion

Structure of Ligands. Although tautomeric formulation ((1a) and (1b)) is possible for the ligand system under discussion, in no case has the existence of isomer been demonstrated experimentally. From infrared data on N^{15}-labelled compounds it has been convincingly proved[7] that the ligand having $R = Ar = C_6H_5$ exists exclusively as 1,3-diphenyltriazene-1-oxide (type (1b)). In order to establish the structure of the ligands having R = alkyl, we made a comparative study of their infrared spectra with that of 1,3-diphenyltriazene-1-oxide. Some representative results in the

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[1] E. Bamberger, *Ber.*, *29*, 102 (1896); E. Bamberger and E. Renauld, *ibid.*, *30*, 2278 (1897).

[2] M. Elkins and L. Hunter, *J. Chem. Soc.*, 1346 (1938).

[3] N. C. Sogani and S. C. Bhattacharyya, *J. Ind. Chem. Soc.*, *36*, 563 (1959); D. N. Purohit, S. M. Dugar, and N. C. Sogani, *ibid.*, *43*, 703 (1966); D. N. Purohit and N. C. Sogani, *Bull. Chem. Soc. Japan*, *37*, 476 (1964).

[4] E. Beckmann, *Annalen*, *365*, 204 (1909).

[5] "Organic Syntheses, Collected Volume", A. H. Blatt, editor, John Wiley & Sons, Inc., New York, N. Y., p. 445 (1961).

[6] N. C. Sogani and S. C. Bhattacharyya, *Anal. Chem.*, *28*, 81 (1956).

[7] T. Mitsuhashi, Y. Osamura and O. Simamura, *Tetrahedron Letters*, 2593 (1965).

Table I. Characterisation of Complexes (2)

Complex			M.p. °C	% C		% H		% N	
R	Ar	Formula		Calcd.	Found	Calcd.	Found	Calcd.	Found
CH_3	C_6H_5	$C_{21}H_{24}N_9O_3Co$	165-66	49.51	49.30	4.71	4.78	24.76	24.48
CH_3	$C_6H_4CH_3(o)$	$C_{24}H_{30}N_9O_3Co$	135	52.28	52.10	5.44	5.40	22.88	22.74
CH_3	$C_6H_4CH_3(m)$	$C_{24}H_{30}N_9O_3Co$	157	52.28	52.03	5.44	5.70	22.88	22.96
CH_3	$C_6H_4CH_3(p)$	$C_{24}H_{30}N_9O_3Co$	157	52.28	52.05	5.44	5.50	22.88	22.75
C_2H_5	C_6H_5	$C_{24}H_{30}N_9O_3Co$	144-45	52.28	52.20	5.44	5.67	22.88	22.76

2000-4000 cm^{-1} region are presented in Table II. An examination of this table leads us to conclude that the compound having R=CH_3 and Ar=C_6H_5 is correctly formulated as 1-methyl-3-phenyltriazene-1-oxide (type (1b)). In CCl_4 solution, the N–H stretch partially overlaps with the ~3200 cm^{-1} band. Deuteration removed this difficulty. The shapes of N–D stretches for the two compounds (Table II) are very similar (width at half-height, ~30 cm^{-1}). ν_{N-H}/ν_{N-D} is 1.34 in both cases. ν_{N-H} and ν_{N-D} for the other ligands used in the present study are essentially identical with those of 1-methyl-3-phenyltriazene-1-oxide. Thus all the ligands are of type (1b).

Table II. Infrared spectra of some ligands in the 2000-4000 cm^{-1} region

Phase	Frequency (cm^{-1})		Assignment
	R=Ar=C_6H_5	R=CH_3; Ar=C_6H_5	
in CCl_4	—	2944	ν_{C-H} (aliphatic) [a]
	3030 sh,[b] 3050	3015 sh, 3040	ν_{C-H} (aromatic) [a]
	3075	3065 sh	
	3205	3205	Overtone[a,c] of aromatic vibration at 1600 cm^{-1}
	3245	3270	ν_{N-H} [d]
	2420	2434	ν_{N-D} [e]
in KBr disc[f]	2305 [g]	2370 [g]	ν_{N-D} [e]

[a] Uneffected by deuteration. [b] sh is shoulder. [c] Also present in metal chelates and in 1,3-diphenyltriazene. [d] Disappears on deuteration. [e] In deuterated compounds. [f] There are bands corresponding to ν_{C-H} and overtone of aromatic vibration at positions close to those in CCl_4. [g] Centre of a broad and asymmetric band having ill-defined structure.

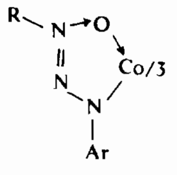
In the crystalline state, ν_{N-D} is quite broad and in the absence of deuteration it was difficult to locate ν_{N-H} which is expected (as calculated from experimental value of ν_{N-D} in conjunction with ν_{N-H}/ν_{N-D} = 1.34) in the range 3100-3200 cm^{-1}. Probably ν_{N-H} is masked by the moderately strong bands (overtone of aromatic vibration at ~3200 cm^{-1}; ν_{C-H} at ~3100 cm^{-1}) that are present in this region.

The low values of ν_{N-H} in solution and in the crystalline state are indicative of hydrogen bonding. P.m.r. spectrum of 1-methyl-3-phenyltriazene-1-oxide in carbon tetrachloride has a low field signal which is of the correct intensity to represent the N–H proton. In the concentration range 1.3 *M* to 0.3 *M* the chemical shift (from TMS) of the signal decreased from 10.40 to 10.30 ppm. This relative insensitivity of the frequency to dilution (together with the infrared data) indicates that at least the majority of the molecules are internally hydrogen-bonded as shown in (1b).[8]

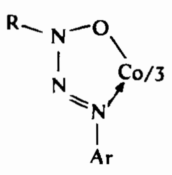
in the infrared spectra of the tri-chelates of Co^{III} (same is true of the bis-chelates of Cu^{II} and Ni^{II}) are very much the same as those of the corresponding ligands (700-3200 cm^{-1}). On this basis the chelates are represented as (2) (*i.e.* derived from (1b)). These results do not, of course, exclude some *resonance* contribution from structure (3) (*i.e.* derived from (1a)). A detailed study of the infrared spectra of the metal chelates of triazene-1-oxide will be presented elsewhere.

In the tris-complex (2), the bidentate ligand is unsymmetrical. This means that the complex can have two possible geometrical configurations, *cis* (4) and *trans* (5). Like donor atoms are arranged facially in

Stereochemistry of Co^{III} chelates. Except for some changes in the position and intensity, the main features the *cis* form which, therefore has a threefold axis of symmetry. As a result of this all chelate rings are magnetically equivalent in this form. On the other hand, the *trans* isomer has no elements of symmetry and a given group of equivalent



(2)



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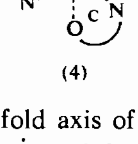

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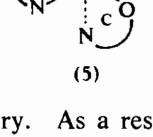

(5)

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[8] Cryoscopy in benzene[1] suggested essentially monomeric species (molecular weight 151) in ~0.1*M* solution. In ~0.4*M* solution the observed molecular weight is 187, presumably due to association.

nuclei should have different chemical shifts for the three rings. In recent years this principle has been used to establish the configuration of several tris-chelates of trivalent elements.[9-15]

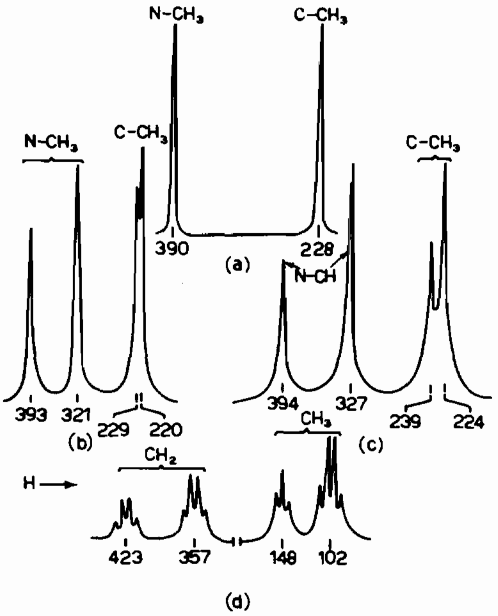

Figure 1. Nuclear magnetic resonance spectra of (a) 1-methyl-3-*p*-tolyltriazene-1-oxide, (b) Co^{III} chelate of 1-methyl-3-*p*-tolyltriazene-1-oxide, (c) Co^{III} chelate of 1-methyl-3-*m*-tolyltriazene-1-oxide, (d) Co^{III} chelate of 1-ethyl-3-phenyltriazene-1-oxide. Solvent was CDCl$_3$. Numerical figures refer to chemical shift in cps (at 100 Mc/sec) from TMS.

Some representative p.m.r. data for complexes are illustrated in Figure 1. To be specific we shall abbreviate the chelates as (2) (R, Ar). 1-Methyl-3-*p*-tolyltriazene-1-oxide gives rise to two singlets representing the two methyl groups. In the corresponding Co^{III} chelate, (2) (CH$_3$, *p*-tolyl), there are two widely separated signals (321 and 393 cps) having the intensity ratio 2:1, the signal at higher field being more intense. Both these signals are assigned to N–CH$_3$ on the basis of their chemical shifts. The C–CH$_3$ group of the *p*-tolyl fragment also produces two (overlapping) signals of unequal intensity. (2) (CH$_3$, *m*-tolyl) exhibits a very similar pattern. However, in this case the two C–CH$_3$ signals are better separated and the ratio of their intensities is found to be 2:1. The parent chelate, (2) (CH$_3$, C$_6$H$_5$), (not shown in the Figure 1) shows two N–CH$_3$ signals (321 and 394 cps in CDCl$_3$) again having the intensity ratio 2:1. The corresponding ligand, 1-methyl-3-phenyltriazene-1-oxide has one sharp N–CH$_3$ signal at 393 cps. All chelates show a complex pattern around 700 cps arising from aromatic protons. No attempts were made to analyse this region of the spectrum.

The persistent 2:1 intensity ratio of N–CH$_3$ (or C–CH$_3$) signals in the above chelates leads us to believe that we are dealing with only one geometrical isomer in each case. Repeated recrystallization of the chelates did not affect their physical properties or their p.m.r. spectra. The p.m.r. data are in fact compatible with *trans* structures of the chelates. In this isomer, as already pointed out, each chelate ring is, in principle, symmetrically distinct. However, it can be seen that to convert *cis* (all chelate rings are equivalent) to the *trans* form, it is only necessary to interchange the positions of O and N in any one of the three chelate rings (*e.g.* ring C in converting (4) to (5)). The rings A and B in the *trans* form (5) may thus be expected to be more akin to each other than to ring C. In several cases it has been previously observed that out of the three signals expected of a *trans* tris-chelate two are closely grouped together[10-14] or even merge completely.[11,12] The triazene-1-oxide chelates, (2), belong to the latter class. We tentatively assign the less intense signal to ring C and the more intense signal to rings A and B. In the p.m.r. spectrum of (2) (C$_2$H$_5$, C$_6$H$_5$) (Figure 1), the two quartets ($J = 7.0$ cps) corresponding to methylene groups again have the intensity ratio 2:1. The methyl groups show a triplet at 148 cps and a "quartet" (1:3:3:1) at 102 cps, the latter being twice as intense as the former. The methyl "quartet" can be resolved into two overlapping triplets (1:2:1) having a chemical shift of ~7 cps. Thus in this case the three expected methyl triplets are experimentally observable.

We failed to detect the existence of *cis* form in any of our preparations. This can be understood as follows. In the *cis* form all three aryl groups are crowded on one face of the octahedron. The steric hindrance is large enough to preclude the existence of the *cis* form. The complex, (2) (CH$_3$ *o*-tolyl) was found to be quite unstable in solutions of organic solvents, *e.g.* chloroform, carbon tetrachloride and benzene and reproducible spectral work could not be done. In this case it is probable that even the *trans* configuration is sterically unfavourable. Several other examples of the exclusive population of the *trans* form due to steric reasons are known.[10-14] It may however, be noted that even in the absence of steric factors, the *trans* form is found to be thermodynamically more favored than *cis* form, *e.g.* in Co^{III} chelates of β-diketones[9] and particularly in tris(salicylaldehydo)V^{III} complexes.[15]

Electronic Spectra of Co^{III} chelates. All the chelates reported here are dark-violet in the crystalline state and give stable (except for (2) (CH$_3$, *o*-tolyl)) violet solutions in organic solvents. Spectral data in benzene solution are shown in Table III. Spectra in chloroform are essentially identical with those in benzene except for small differences in intensity. The co-ordination sphere of these chelates is of the type CoN$_3$O$_3$. Spin-paired Co^{III} in octahedral (O$_h$) crystal fields shows two spin-allowed transitions: $^1A_{1g} \rightarrow {}^1T_{1g}$ (ν_1) and $^1A_{1g} \rightarrow {}^1T_{2g}$ (ν_2). In fields of lower symmetry ν_1 shows splitting[10,12,13,16,17] presumably due to removal of degeneracy of the excited state.

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[9] R. C. Fay and T. S. Piper, *J. Am. Chem. Soc.*, *84*, 2303 (1962); *85*, 500 (1963).
[10] R. G. Denning and T. S. Piper, *Inorg. Chem.*, *5*, 1056 (1966).
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[12] A. Chakravorty and K. C. Kalia, *ibid.*, *6*, 690 (1967).
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Table III. Frequencies (cm^{-1}) and extinction coefficients (lit. $mole^{-1}$ cm^{-1}) of electronic bands in benzene at 28°C

Compound	Frequency (extinction coefficient)
(2) (CH_3, C_6H_5)	19,200 (1400); 29,400 (24,000)
(2) (CH_3, *m*-tolyl)	19,000 (1430); 29,400 (21,000)
(2) (CH_3, *p*-tolyl)	19,000 (1450); 29,400 (21,000)
(2) (C_2H_5, phenyl)	19,200 (1520); 29,400 (24,000)

It is tempting to assign the ~19,000 cm^{-1} band of the triazene-1-oxide chelates to ν_1. The frequency is of the right magnitude. Values of ν_1 for a few other chelates of the CoN_3O_3-type are as follows: ~16,000 cm^{-1} in salicylaldimines[16] and some related chelates;[12,13] ~19,000 cm^{-1} in chelates of α-amino acids.[10,17] The observed extinction coefficient (ϵ) at ν_1 in these cases is never higher than 400; generally it is much less.

The relatively high intensity (ϵ, ~1400, Table III) of the ~19,000 cm^{-1} band of (2) militates against its assignment to ν_1 unless borrowing of intensity[18] from some allowed transition[19] is invoked. An alternative assignment is that the ~19,000 cm^{-1} band actually represents a metal-ligand charge-transfer transition which has completely masked the genuine ν_1 band occurring at some frequency nearby.

Acknowledgments. Thanks are due to Mr. K. C. Kalia for assistance. The grant of Junior Research Fellowship to P.S.Z. by Council of Scientific and Industrial Research is gratefully acknowledged.

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(18) R. F. Fenske, *J. Am. Chem. Soc.*, *89*, 252 (1967).

(19) The very intense transition at 29,400 cm^{-1} (Table III) clearly represents an allowed transition.