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Studies on Complexes of Arylazooximes. I. Structure of Ligands and Cobalt(III) Chelates

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C-Nitrosation of aldehyde arylhydrazones gives rise to arylazooximes. Infrared and electronic spectra favor this formulation. Arylazooximes which undergo extensive intermolecular hydrogen bonding can apparently exist in geometrically isomeric forms. They form very stable tris complexes with trivalent cobalt; a number of new chelates are reported. Infrared data suggest the existence of five-membered chelate rings in these complexes. The *trans* configuration of the tris chelates is conclusively demonstrated from their proton magnetic resonance spectra. The sterically unfavorable *cis* isomer could not be identified. The phenylhydrazone of ω-nitroacetaldehyde reacts with cobalt(II) or cobalt(III) salts in presence of excess amines to produce tris(phenylazoacetaldoximato)cobalt(III). The tris chelates absorb very strongly in the visible region and no evidence for crystal field bands could be obtained.

Introduction

Nitrosation of arylhydrazones of aldehydes by *n*-amyl nitrite leads to a class of products which has been traditionally described as arylazooximes.[1] This description plus the question of geometric structure of these compounds is briefly examined in the present paper. Cobalt(III) chelates of arylazooximes were first reported by Hunter and Roberts.[2] A few nickel(II) complexes were subsequently isolated by Malatesta, *et al.*[3] We have undertaken systematic magnetic and spectroscopic investigations of the transition metal chelates of arylazooximes. In the present work, several tris chelates of cobalt(III) are described. There are two significant problems in relation to the structure of these chelates. The first one concerns the size of the chelate ring and the second one deals with the stereochemistry around the metal atom. The former problem is examined in the light of infrared data. As possible chemical evidence for chelate-ring size, the reaction of cobalt salts with the phenylhydrazone of ω-nitroacetaldehyde is studied. The stereochemistry of the tris chelates is established utilizing proton magnetic resonance (pmr) data.

Experimental Section

Preparation of Compounds.—The **arylazooximes** were synthesized by allowing the appropriate arylhydrazone to react with excess *n*-butyl nitrite which we found to be as effective as *n*-amyl nitrite (used in the original procedure of Bamberger, *et al.*[1]). For ligands derived from aliphatic aldehydes, best yields are obtained when ether is used as a solvent and no base is employed. For arylazooximes derived form aromatic aldehydes, the nitrosation reaction was carried out in dry methanol in the presence of sodium methoxide. Apart from such variations, experimental details are essentially analogous to those reported elsewhere.[1] Characterization of a few typical arylazooximes in shown in Table I. **Deuteration of arylazooximes** was carried out by precipitating their solutions in dry dioxane with deuterium oxide. **ω-Nitroacetaldehyde phenylhydrazone** was synthesized by coupling nitroethane with benzenediazonium acetate.[4]

Tris(arylazooximato)cobalt(III) usually crystallized out[2] on adding a solution of arylazooxime (0.03 mol) in ethanol to aqueous cobalt(II) acetate (0.01 mol). Recrystallization from ethanol or hexane gave dark violet crystalline solids.

Reaction of Hexaamminecobalt(III) Chloride with Phenylazoacetaldoxime.—A 250-mg sample of the ligand was dissolved in 10 ml of 95% ethanol and to it was added 125 mg of hexaamminecobalt(III) chloride dissolved in 5 ml of water. On heating on a steam bath, ammonia was evolved and the color of the solution gradually turned deep violet. Within 30 min tris(phenylazoacetaldoximato)cobalt(III) separated out in good yield (90%). Identical results were obtained when dichlorobis(ethylenediamine)cobalt(III) chloride was used instead of the hexaammine complex.

Reaction of ω-Nitroacetaldehyde Phenylhydrazone (Abbreviated NAP) with Cobalt Salts.—(1) On mixing methanolic solutions of NAP and cobalt(II) acetate with each other, no visible change took place at room temperature. On heating to reflux for a few hours, the color of the solution darkened slightly but only the starting materials could be recovered from the solution. On addition of sodinm or potassium hydroxide (1 mol for each mole of NAP) to the methanolic solution containing NAP and cobalt(II) acetate, a deep brown color developed but no complex could be isolated. The deep brown color is merely that of the conjugate base of NAP. Attempted oxidation (by passing air for a prolonged period or by adding H_2O_2) of solutions containing cobalt(II) acetate and NAP with or without the addition of alkali failed to give any cobalt(III) complex of NAP. There was no reaction when hexaamminecobalt(III) chloride and NAP were mixed in aqueous methanol and the solution was heated to reflux.

(2) A solution of NAP (1 g) in 40 ml of concentrated aqueous ammonia was added to a filtered solution of 0.45 g of cobalt(II) acetate in 10 ml of water. The volume of the mixture was adjusted to 100 ml by addition of water. Nothing happened when the solution was stirred overnight at room temperature. However, on heating it on a steam bath, the color darkened and finally a black solid started separating. After 2 hr, the solution was cooled and then filtered. The black solid, on recrystallization from 95% ethanol, yielded 300 mg of dark violet crystals of tris(phenylazoacetaldoximato)cobalt(III) (Table I). The same results were obtained when the above reaction was carried out under pure nitrogen. Replacement of cobalt(II) acetate with other cobalt(II) salts or with hexaamminecobalt(III) chloride resulted in the same final product. Replacement of ammonia with methylamine or triethylamine also furnished the same complex when the experimental conditions were slightly modified. If the amine is not present in large excess (*e.g.*, if 3 ml instead of 40 ml of ammonia is used in the above experiment), a greenish blue amorphous solid is obtained and the yield of tris(phenylazoacetaldoximato)cobalt(III) is very poor or even nil.

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[1] E. Bamberger and W. Pemsel, *Ber.*, **36**, 85 (1903).

[2] L. Hunter and C. B. Roberts, *J. Chem. Soc.*, 823 (1941).

[3] L. Malatesta and R. Pizzoti, *Gazz. Chim. Ital.*, **76**, 141 (1946).

[4] E. Bamberger, *Ber.*, **31**, 2626 (1898); E. C. S. Jones and J. Kenner, *J. Chem. Soc.*, 919 (1930).

TABLE I

CHARACTERIZATION OF COMPOUNDS

Compound					% C		% H		% N	
R	Ar	L[a] or Co[b]	Formula	Mp, °C	Calcd	Found	Calcd	Found	Calcd	Found
H	C_6H_5	L	$C_7H_7N_3O$	92	56.37	56.57	4.73	4.81	28.16	28.31
H	$C_6H_4CH_3(p)$	L	$C_8H_9N_3O$	133	58.88	59.43	5.56	5.58	25.74	25.90
$C_6H_4CH_3(p)$	$C_6H_4CH_3(p)$	L	$C_{15}H_{15}N_3O$	136	71.14	70.80	5.97	5.66	16.60	16.52
$C_6H_5CH_2$	C_6H_5	L	$C_{14}H_{13}N_3O$	78	70.30	70.51	5.40	5.94	17.60	17.47
H	C_6H_5	Co	$C_{21}H_{18}N_9O_3Co$	204	50.09	49.86	3.60	3.90	25.04	24.92
CH_3	C_6H_5	Co	$C_{24}H_{24}N_9O_3Co$	241[c]	52.84	52.70	4.44	4.31	23.12	22.85
C_2H_5	C_6H_5	Co	$C_{27}H_{30}N_9O_3Co$	183–186	55.20	55.30	5.15	5.30	21.46	20.90
n-C_3H_7	C_6H_5	Co	$C_{30}H_{36}N_9O_3Co$	145–146	57.23	56.91	5.76	5.70	20.03	20.06
$CH_2C_6H_5$	C_6H_5	Co	$C_{42}H_{36}N_9O_3Co$	88	65.18	65.03	4.69	4.45	16.30	16.18
H	$C_6H_4CH_3(p)$	Co	$C_{24}H_{24}N_9O_3Co$	213	52.84	53.07	4.44	4.60	23.12	23.17
CH_3	$C_6H_4CH_3(p)$	Co	$C_{27}H_{30}N_9O_3Co$	226	55.20	54.84	5.15	5.00	21.46	21.53
$C_6H_4CH_3(p)$	C_6H_5	Co	$C_{42}H_{36}N_9O_3Co$	241	65.18	65.36	4.69	4.80	16.30	15.97

[a] L refers to the free ligand (**1**). [b] Co refers to the cobalt(III) complex (**5**). [c] This melting point is for the product prepared from ω-nitroacetaldehyde phenylhydrazone; analytical data for the material made from phenylazoacetaldoxime is given by A. Chakravorty and K. C. Kalia, *Inorg. Nucl. Chem. Letters*, **3**, 319 (1967). This and all other melting points reported in this table are uncorrected.

Proton resonance measurements were done on a Varian HR-100 spectrometer. Tetramethylsilane was used as the internal standard and frequencies were measured by the side-band technique. Areas were measured planimetrically.

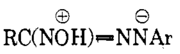
Visible and ultraviolet spectra were measured on a Cary 14 recording spectrophotometer. **Infrared spectra** were taken on a Perkin-Elmer 521 recording spectrophotometer.

Results and Discussion

Structure of the Ligands.—The azooxime structure (**1**) is tautomeric with the nitrosohydrazone structure (**2**). In the nitrosation of arylhydrazones, **2** is probably first formed and immediately tautomerizes to **1**.

$RC({=}NOH)N{=}NAr$ $RC(NO){=}NNHAr$

1 **2**

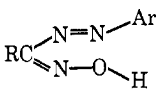


$RC(N\overset{\oplus}{O}H){=}N\overset{\ominus}{N}Ar$

3

R = alkyl

Ar = aryl



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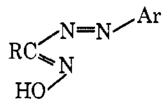

4b

Chemical and spectroscopic evidences[5] show quite conclusively that the usually assumed[1,2] azooxime structure (**1**) is indeed present predominantly, if not exclusively, in the final product.

n–π* and π–π* electronic transitions, characteristic of azo compounds,[6] are observed at ~24,000 and ~33,000 cm^{-1}, respectively, for arylazooximes and their potassium salts (one case is shown in Figure 1 and Table II). Our results agree with those of an earlier report.[7] Infrared spectra of the ligands in solid state and in solution show an intense and somewhat broad (width at half-height, ~50 cm^{-1}) band in the region 1000–1050 cm^{-1}. Deuteration has a very slight effect on the frequency. We assign this band to ν_{N-O} of the azooxime structure. The similarity of the shape and intensity of this band with those of the ν_{N-O} of simple oximes is very striking. In the latter[8] and in N-alkylhydroxylamines,[9] ν_{N-O} is in the range 930–960 cm^{-1}. However, in quinone monooximes, ν_{N-O} shifts to higher frequencies (975–1075 cm^{-1}) owing to

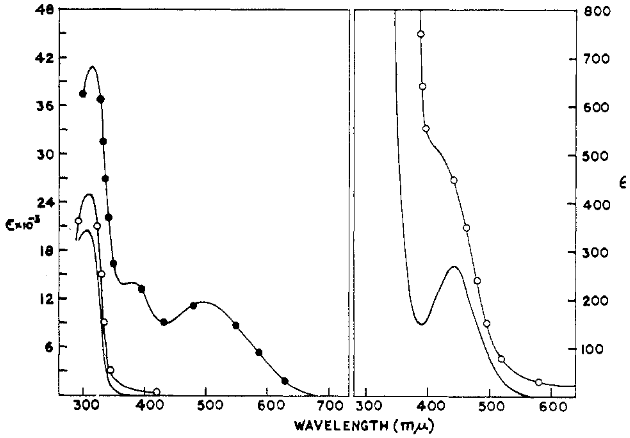

Figure 1.—Electronic spectra: ——, phenylazoacetaldoxime in benzene; —○—○—, phenylazoacetaldoxime (3.48 × 10^{-4} *M*) + KOH (0.05 *M*) in methanol; —●—●—, tris(phenylazoacetaldoximato)cobalt(III) in benzene.

TABLE II

FREQUENCIES (ν, CM^{-1}) AND EXTINCTION COEFFICIENTS (ε, L. MOL^{-1} CM^{-1}) OF ELECTRONIC BANDS IN BENZENE

R	Ar	L[a] or Co[b]	ν (ε)
CH_3	C_6H_5	L[c]	22,700 (260), 32,800 (20,700)
H	C_6H_5	Co	20,800 (10,400), 26,500 (13,400), 31,800 (40,100)
CH_3	C_6H_5	Co	20,400 (11,300), 26,300 (14,100), 31,800 (41,300)
C_2H_5	C_6H_5	Co	20,200 (10,200), 26,300 (13,300), 31,600 (40,300)
$C_6H_4CH_3(p)$	C_6H_5	Co	19,600 (10,200), 25,000 sh (11,400), 30,600 (73,500)

[a] L refers to the ligand (**1**). [b] Co refers to the cobalt(III) complex (**5**). [c] In methanolic solution this ligand has the following absorption data: 23,300 (310), 32,800 (22,500); in methanolic potassium hydroxide (0.05 *M*) solution the spectrum of this ligand (3.48 × 10^{-4} *M*) changes to: 23,800 sh[d] (500), 32,500 (24,900). [d] sh is shoulder.

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(5) K. C. Kalia and A. Chakravorty, to be submitted for publication.

(6) R. Kuhn and F. Bar, *Ann.*, **516**, 143 (1935); A. Burawoy, *J. Chem. Soc.*, 1865 (1937).

(7) P. Grammaticakis, *Compt. Rend.*, **225**, 684 (1947).

(8) A. Palm and H. Werbin, *Can. J. Chem.*, **32**, 858 (1954).

(9) M. Davies and N. A. Spiers, *J. Chem. Soc.*, 3971 (1959).

resonance contribution from a structure having the $-N{=}\overset{+}{O}{-}H$ group.[10] Some contribution from structure **3** can similarly be responsible for the relatively high value of ν_{N-O} of arylazooximes.

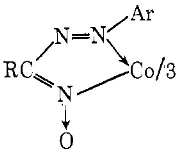
Infrared and pmr data[5] suggest extensive intermolecular hydrogen bonding (in CCl_4 solution, however, appreciable concentration of monomers exist in equilibrium) in arylazooximes. This is also true of simple aldoximes and ketoximes.[11] Intermolecular hydrogen bonding of arylazooximes will be compatible with the geometric structures (assuming *trans* stereochemistry around N=N) **4a** and **4b**. Pmr spectra of some arylazooximes do show two distinct signals for a given group.[5] The results are suggestive of geometrical isomerism (around C=N) as implied by **4a** and **4b**.

Syntheses of Chelates.—Some of the cobalt(III) chelates are reported for the first time. Characterization of complexes is shown in Table I. Arylazooximes have very strong affinity for trivalent cobalt. The tris chelate is obtained immediately on addition of the ligand to a solution containing a cobalt(II) salt. The reaction proceeds even in the solid state.[12] Coordinated ammonia of hexaamminecobalt(III) chloride undergoes facile replacement by arylazooximes.

Qualitative experiments done with phenylazoacetaldoxime and cobalt(II) acetate in methanol show that oxygen is consumed during the chelation reaction. However, even when the reaction is carried out in degassed methanol either under pure nitrogen or under vacuum, only the tris chelate of cobalt(III) crystallizes out. Use of a cobalt to ligand ratio of 1:2 does not make any difference. The exact fate of the electron released under these conditions (oxygen free) is not definitely known. The ligand—a potential nitroso compound—can itself act as the oxidizing agent.

ω-Nitroacetaldehyde phenylhydrazone,[13] $CH_3C(NO_2){=}NNHC_6H_5$, or its conjugate base failed to give any complex with cobalt(II) or cobalt(III). The formation of a tris complex[14] with properties similar to those of tris(phenylazoacetaldoximato)cobalt(III) would have provided some chemical evidence in favor of six-membered chelate rings (*vide infra*, structure **7**) in the latter. Since the complex is not formed, no conclusion can be drawn. On heating the above phenylhydrazone with cobalt(II) or cobalt(III) salts in the presence of excess amine (ammonia, methylamine, or triethylamine in aqueous or aqueous alcoholic medium), tris(phenylazoacetaldoximato)cobalt(III) is obtained. It is conceivable that the amine acts as an oxygen acceptor in this reduction of the nitro into the nitroso (hence the azooxime) compound. However, the presence of a cobalt(II) or cobalt(III) salt is essential for the reduction. Thus when ω-nitroacetaldehyde phenylhydrazone alone is heated with excess amines, at no stage can phenylazoacetaldoxime be detected in the reaction mixture. The mechanism of the above reduction remains obscure for the present.

Size of the Chelate Ring.—The chelate rings in complexes of arylazooximes can be five (**5** and **6**) or six (**7**) membered. On the basis of analogy with tris(2-arylazophenolato)cobalt(III), the six-membered formulation (**7**) was favored by Hunter, *et al.*[2] On the other hand, analogies with chelates of dimethylglyoxime and related compounds have led other workers[3] to suggest a structure analogous to **5** for the bis chelates of nickel(II). However, these analogies were mere statements and no supporting evidence was presented.[2,3]



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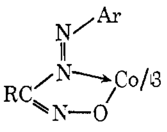

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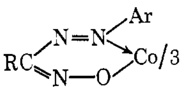

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Infrared data throw some light on the problem. In the tris complexes of cobalt(III), ν_{N-O} appears in the frequency range[15] 1220–1350 cm^{-1}. This large increase of ν_{N-O} over the free-ligand value (1000–1050 cm^{-1}) clearly indicates that in the chelate the ligands do *not* exist in the oxime form. Structures **6** and **7** are unsatisfactory in this regard. It is true that in both cases one can envisage resonance contribution from structures having the $-N{=}\overset{+}{O}-$ grouping. However, recalling that the contribution from this grouping (**3**) is already accounted for in ν_{N-O} of the free ligand, one hardly expects such large shifts of ν_{N-O} to higher frequencies on complex formation.

Structure **5** having the N→O moiety is in harmony with the infrared data. ν_{N-O} of N-oxides and nitrones is generally at a much higher frequency range than that of oximes. A case in hand is dimethylglyoxime (ν_{N-O} ~900, 1000 cm^{-1}) *vs.* its metal chelates (ν_{N-O} 1070–1110, 1190–1260 cm^{-1}).[16] The structures of several chelates of dimethylglyoxime are known[17] and the chelate rings exist in the nitrone form. During chelation, the arylazooximes probably react momentarily in the nitrone form, as some other oximes do.[18] While infrared data are in favor of **5**, the final answer to the question of ring size must await the results of X-ray crystallographic study.[19]

Stereochemistry of Tris Chelates.—The bidentate arylazooximes are unsymmetrical and hence *cis–trans*

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[10] D. Hadzi, *J. Chem. Soc.*, 2725 (1956).

[11] A. Palm and H. Wilson, *Can. J. Chem.*, **31**, 1004 (1953).

[12] When cobalt(II) acetate tetrahydrate and phenylazoacetaldoxime are ground together without the addition of any solvent, a dark violet color, undoubtedly that of the tris complex, quickly develops.

[13] Infrared and pmr data[5] are in accord with this formulation.

[14] This will normally require that the $-NO_2$ and $-N_2HC_6H_5$ groups are *cis* (around C=N) to each other. It was hoped that even if they are *trans*, the conjugate base with a mobile negative charge may have sufficient flexibility leading to proper configuration for a compelling chelation reaction.

[15] Generally there are two strong bands in this region. In the case of tris(phenylazoacetaldoximato)cobalt(III) the bands are at 1260 and 1347 cm^{-1}. A comparative study of several spectra leads us to conclude that the 1260-cm^{-1} band corresponds to ν_{N-O}. In the complexes there are no bands below 1200 cm^{-1} that can possibly be assigned to ν_{N-O}.

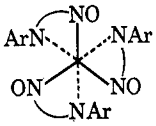
[16] R. Blinck and D. Hadzi, *J. Chem. Soc.*, 4539 (1958); K. Burger, I. Ruff, and F. Ruff, *J. Inorg. Nucl. Chem.*, **27**, 179 (1965).

[17] L. E. Godycki and R. E. Rundle, *Acta Cryst.*, **6**, 487 (1953); E. Frasson, C. Panattoni, and R. Zennetti, *ibid.*, **12**, 1027 (1959); E. Frasson, R. Bardi, and S. Bezzi, *ibid.*, **12**, 201 (1959).

[18] P. Pfeiffer and J. Richarz, *Ber.*, **61**, 103 (1928); P. Pfeiffer, *ibid.*, **63**, 1811 (1930); N. J. Patel and B. C. Halder, *J. Inorg. Nucl. Chem.*, **29**, 1037 (1967).

[19] S. Ramaseshan, work in progress.

(**8**–**9**) isomerism is possible for the tris chelates. It is well known[20–24] that nuclear resonance provides a powerful tool for characterization of these isomers. The *cis* form has a threefold axis of symmetry and all chelate rings are magnetically equivalent. In the *trans* form (no symmetry elements) the three chelate rings may be expected to be magnetically distinct.



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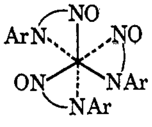

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Some representative pmr data[25] are shown in Figure 2 and Table III. These leave no doubt that the tris chelates of cobalt(III) have *trans* configuration. Thus tris(p-tolylazoformaldoximato)cobalt(III) shows three signals for azomethine protons and three signals for methyl protons (Figure 2a). In each case the three signals are of equal intensity. Similarly tris(phenylazopropionaldoximato)cobalt(III) gives three methyl triplets, two of which seriously overlap (Figure 2b). Particularly interesting is the spectrum of tris(phenylazo-α-phenylacetaldoximato)cobalt(III) (Figure 2c). Two of the three methylene groups are represented by the two singlets (378 and 423 cps). Probably owing to restricted rotation, two protons in the third methylene group become nonequivalent and a four-line AB pattern (363, ~378, 390, and 406 cps) results. It may be noticed (Table III) that, in general, two of the three signals for a given group are closely spaced. Symmetry arguments[21,23] are in line with this observation.

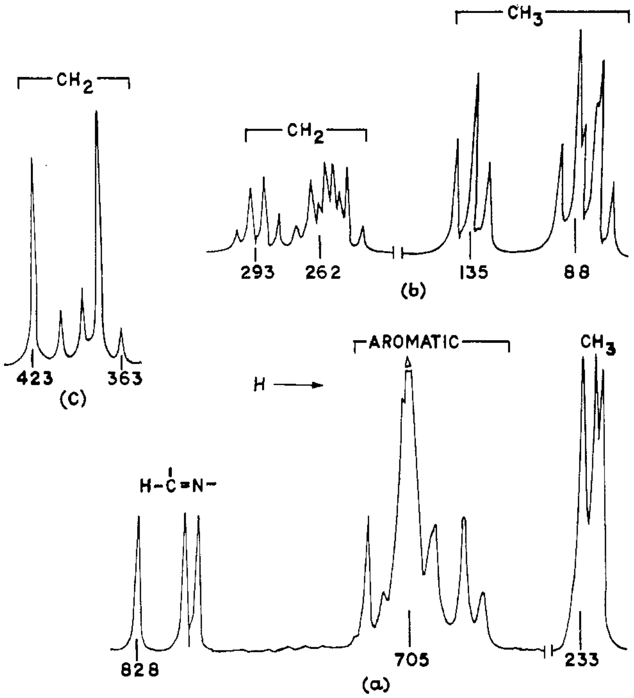

Figure 2.—Pmr spectra of (a) tris(p-tolylazoformaldoximato)-cobalt(III), (b) tris(phenylazopropionaldoximato)coblat(III), and (c) tris(phenylazo-α-phenylacetaldoximato)cobalt(III) in $CDCl_3$. Numerical figures refer to chemical shifts from tetramethylsilane at 100 Mcps.

TABLE III

PROTON RESONANCE FREQUENCIES[a] OF TRIS(ARYLAZOOXIMATO)COBALT(III)

Compound			
R	Ar	Group	Chem shift,[b,c] cps
H	C_6H_5	H	796, 806, 824
H	$C_6H_4CH_3(p)$	H	801, 808, 828
		$C_6H_4\mathit{CH_3}(p)$	224, 227, 233
CH_3	C_6H_5	CH_3	202, 215, 253
CH_3	$C_6H_4CH_3(p)$	CH_3	206, 217, 251
		$C_6H_4\mathit{CH_3}(p)$	224, 227, 231
C_2H_5	C_6H_5	$\mathit{CH_3}CH_2$	78,[d] 88,[d] 135[d]
		$CH_3\mathit{CH_2}$	251,[e] 262,[e] 293[e]
n-C_3H_7	C_6H_5	$\mathit{CH_3}CH_2CH_2$	61,[d] 70,[d] 103[d]
		$CH_3\mathit{CH_2}CH_2$	130,[f,g] 183[f]
		$CH_3CH_2\mathit{CH_2}$	250,[d] 257,[d] 291[d]
$C_6H_4CH_3(p)$	C_6H_5	$C_6H_4\mathit{CH_3}(p)$	229, 233, 236
$CH_2C_6H_5$	C_6H_5	$\mathit{CH_2}C_6H_5$	378, 384,[h] 423

[a] Aromatic protons give signals in the region 680–825 cps and are not tabulated. [b] From tetramethylsilane at 100 Mcps in $CDCl_3$. [c] Unless otherwise indicated, the tabulated frequencies of each group represent bands (or multiplets) of equal intensity. [d] Center of a triplet ($J \approx 7.5$ cps). [e] Center of a quartet ($J \approx 7.5$ cps). [f] Center of a sextet ($J \approx 7.5$ cps). [g] Intensity of this sextet is twice that of the sextet at 183 cps. [h] Center of a four-line AB pattern ($J \approx 16$ cps) with one line masked by the 378-cps signal.

We did not get any evidence for the *cis* form in any of our preparations.[26] It is quite generally observed that tris chelates of cobalt(III) having an alkyl or aryl substituent on one of the coordinating atoms exist exclusively in the *trans* form. Examples are provided by complexes of salicylaldimine and its derivatives,[21] triazene 1-oxide[23] and 2-arylazophenol.[24] It is believed that in these cases overcrowding of substituents on one face of the octahedron makes the *cis* form so much less stable than the *trans* form that only the latter is obtained under normal synthetic conditions. On the basis of formulation **5** for tris chelates of arylazooximes, both *cis* and *trans* forms have three substituents projecting from corners of each face of the octahedron. In the *cis* form, three aryl groups project from one of the faces while in the *trans* isomer at least one of the substituents on each face is an oxygen atom. The latter arrangement may be expected to be sterically more favorable and in practice only the *trans* form obtains.[27]

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[27] However, we have conclusive evidence that tris(arylazooximato)-rhodium(III) can be isolated in *both cis* and *trans* forms. This is largely, if not wholly, related to the larger size of Rh(III) (compared to Co(III)). This demonstrates the critical balance of steric factors in tris complexes derived from arylazooximes. The Rh(III) chelates and halogen-bridged dinuclear Pd(II) chelates of arylazooximes will be described in part II of this series: K. C. Kalia and A. Chakravorty, to be submitted for publication.

Electronic Spectra of Chelates.—The cobalt(III) complexes give intensely purple solutions in alcohol, chloroform, and benzene. Some spectral data in benzene are shown in Figure 1 and Table II. Low-spin d^6 ions in an octahedral crystal field show two spin-allowed transitions which may get split in fields of lower symmetry.[28] In no case could crystal field bands be confidently located for the tris chelates of arylazo-oximes. Intense allowed transitions in the visible region probably mask them completely.

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Proton Nuclear Magnetic Resonance Studies of the Ethylenediaminetetraacetic Acid Complexes of Rhodium(III)

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The proton nmr spectra of several complexes of ethylenediaminetetraacetic acid (EDTA) with rhodium(III) have been studied in aqueous solutions from pH 0 to 10. For the monoaquo and monochloro EDTA complexes the spectra indicate that EDTA acts as a pentadentate ligand at low pH values (~1), with one uncoordinated carboxylate group. At higher pH values (~4–8) the spectra for the monoaquo complex indicate that ionization of the unbound carboxylic acid proton is accompanied by coordination to form the sexadentate complex. The spectra of the dichloro and dibromo EDTA complexes confirm that EDTA functions as a tetradentate ligand and indicate that the complexes have the *trans* configuration (with respect to the carboxylate oxygen atoms).

The structures of metal–ethylenediaminetetraacetic acid (EDTA)[1] complexes in aqueous solutions have been studied extensively by a variety of physicochemical techniques.[2] These studies have established that EDTA can occupy five or six positions in the coordination sphere of a metal ion (coordination number of 6). However, in many cases the number of donor atoms bound to the metal ion in a given complex has not been established definitely, although it is of considerable interest.[2] The work of Hoard and his colleagues[3] has established the X-ray crystal structures of several of the complexes in the solid phase, but extrapolation to the solution phase is questionable.

Rhodium(III) has been shown to form complexes with EDTA and some of these have been isolated.[4–8] The monoaquo complex[5–7] ($Rh(HEDTA)(OH_2)$) and its ammonium,[5] potassium,[5] and sodium[6,7] salts have been prepared, resolved, and studied by chemical and X-ray analyses and by infrared, spectrophotometric, polarographic, and potentiometric techniques.[5–9] These studies have led to the conclusion that EDTA functions as a pentadentate ligand. The acid and sodium salts of the monohalo complexes $Rh(HEDTA)X^-$ (X = Cl, Br, I) have been isolated and studied by similar methods;[6–8] the data indicate that the complexes contain pentadentate EDTA. The acid,[5] potassium,[5] and sodium[8] salts of the dichloro and dibromo complexes ($Rh(H_2EDTA)Cl_2^-$ and $Rh(H_2EDTA)Br_2^-$) have been isolated, resolved, and studied by the same methods. On the basis of these measurements EDTA has been shown to be tetradentate; however, conclusions have not been made about the stereochemistry of the complexes (four geometrical isomers are possible, as indicated in Figure 4C). Gillard and Wilkinson[9] have studied the infrared spectra of several of the complexes in D_2O solutions and have concluded that the structures are the same in both the solid and solution phases. No Rh(III)–EDTA complex in which EDTA acts as a sexadentate ligand appears to have been prepared, and, to date, no evidence has been presented which demonstrates that a sexadentate Rh(III)–EDTA complex is formed in solution. The present work is believed to include the first evidence for the formation of this species in solution in a limited pH range.

The current investigation has been undertaken to study the proton nmr spectra of several Rh(III)–EDTA complexes as a function of pH (pH 0–10) and to determine the structures and stereochemistry of the complexes in aqueous solution. Such studies of Rh(III)–EDTA complexes have not been reported previously and are of interest for comparison with the data obtained by other methods.[5–9] Proton nmr spectroscopy

(1) EDTA denotes the tetraanion $(OOCCH_2)_2NCH_2CH_2N(CH_2COO)_2^{4-}$, HEDTA the trianion $(OOCCH_2)_2NCH_2CH_2N(CH_2COO)(CH_2COOH)^{3-}$, and H_2EDTA the dianion $(HOOCCH_2)(OOCCH_2)NCH_2CH_2N(CH_2COOH)(CH_2COO)^{2-}$.

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