

Some New Cobalt(III) Complexes of Triazene 1-Oxides

INDU TUCKER & R. P. SINGH

Department of Chemistry, University of Delhi, Delhi 110007

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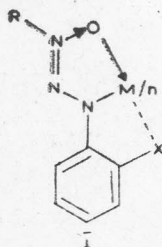
P. S. ZACHARIAS*

School of Chemistry, University of Hyderabad, Hyderabad 500001

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New cobalt(III) complexes of some potentially tridentate ligands, triazene 1-oxides, have been prepared and their stereochemistries and electronic spectra studied. The complexes are found to be *trans*-octahedral. The ligands are found to behave as bidentates forming 1:3 complexes with the metal ion.

THE triazene 1-oxide ligand system in (I) can behave as bidentate¹ or tridentate² depending on the nature of the substituent X. When X is a coordinating group like OCH₃, SCH₃, OC₂H₅ etc., the ligand becomes tridentate forming 1:2 octahedral complexes with bivalent metal ions. When X is H, CH₃ etc., it behaves as a bidentate ligand forming 1:3 complexes with trivalent metal ions. When X is F, Cl, Br or I, the ligand behaves as a tridentate ligand also but the X-M interaction is rather weak³. Since the halogens (X group) are not very strong coordinating groups, it should be rather easy to force them out of the coordination sphere making the ligand bidentate in nature and in such a situation it should form 1:3 complexes with the metal ions. Thus, (I) can form 1:2 complexes with bivalent metal ions and, under different experimental conditions, 1:3 complexes with trivalent metal ions providing a model system for the study of the oxidation-reduction phenomenon in metal chelates. Keeping this in view, we have prepared cobalt(III) complexes of I when X = F, Cl or Br. The corresponding cobalt(II) complexes are already reported². For convenience the ligand system in structure I will be abbreviated as (R-C₆H₄X) and the complex as (R-C₆H₄X)₃Co where X is F, Cl, Br or I.



Materials and Methods

The different ligands used were synthesized by the general method^{1,4} involving diazotization of the corresponding aniline and coupling it with the re-

quired hydroxylamine. Normal oxidation of cobalt(II) in the presence of required amount of ligand always resulted in cobalt(III) chelates already reported while the hexamine cobaltic chloride method gave an impure product which was difficult to purify. The addition of cobalt(III) tricarboxylate solution to an ethanolic solution of appropriate ligand with vigorous stirring produced dark-violet tris chelates which on recrystallization from a mixture of hexane and dichloromethane gave pure products.

Characterization of the complexes was done on the basis of C, H and N analyses. Magnetic susceptibility measurements were carried out on solids using Gouy method. Electronic spectra were recorded on a Cary 14 spectrophotometer in benzene using quartz cells. PMR measurements were done on a Varian A-60 spectrometer in CDCl₃ solution using TMS as the internal standard.

TABLE 1 — CHARACTERIZATION DATA FOR COBALT(III) COMPLEXES

Compound	Found (Calc.), %		
	C	H	N
(CH ₃ -C ₆ H ₄ F) ₃ Co	44.35 (44.52)	4.40 (4.24)	22.52 (22.26)
(CH ₃ -C ₆ H ₄ Cl) ₃ Co	41.03 (40.91)	3.95 (3.90)	21.10 (20.80)
(CH ₃ -C ₆ H ₄ Br) ₃ Co	33.41 (33.64)	3.41 (3.20)	16.95 (16.82)
(CH ₃ - <i>p</i> -CH ₃ C ₆ H ₃ Cl) ₃ Co	43.50 (43.70)	4.60 (4.55)	19.31 (19.12)
(CH ₃ - <i>m'</i> -CH ₃ C ₆ H ₃ Cl) ₃ Co	43.30 (43.70)	4.60 (4.55)	19.22 (19.12)
(CH ₃ - <i>m'</i> -CH ₃ C ₆ H ₃ CH ₃) ₃ Co	54.52 (54.36)	6.71 (6.54)	21.30 (21.14)
(C ₂ H ₅ -C ₆ H ₄ F) ₃ Co	47.21 (47.37)	5.00 (4.93)	19.84 (20.72)
(C ₂ H ₅ -C ₆ H ₄ Cl) ₃ Co	43.65 (43.76)	4.62 (4.56)	19.05 (19.15)
(C ₂ H ₅ -C ₆ H ₄ Br) ₃ Co	36.51 (36.42)	3.85 (3.79)	15.41 (15.93)
(C ₂ H ₅ - <i>m'</i> -CH ₃ C ₆ H ₃ Cl) ₃ Co	46.35 (46.28)	5.25 (5.14)	18.32 (18.00)

Results and Discussion

From the analytical data of the complexes (Table 1) it is evident that the cobalt(III) complexes have the composition $(R-C_6H_4X)_3Co$. Magnetic susceptibility measurements show that all the present complexes are diamagnetic confirming the tripositive oxidation state of cobalt. In the infrared spectra of the complexes we could not locate any band due to metal-halogen stretching. This means that the halo group is not coordinated and the ligands behave as bidentate and not as tridentate. The analytical data, bidentate nature of the ligands and +3 oxidation state of cobalt indicate that the complexes are six coordinated with an octahedral geometry.

In the tris complex the bidentate ligand is unsymmetrical and hence the complex can exist in the *cis*- and *trans*-octahedral forms. These forms can be distinguished on the basis of their PMR data. The three-fold axis of symmetry in the *cis*-form makes all chelate rings magnetically equivalent and hence one expects only one set of signals for a given set of protons in the PMR spectrum. On the other hand the *trans* isomer is asymmetric and a given group of equivalent protons should show distinct chemical shifts for the three chelate rings. This principle has been used extensively to identify the *cis-trans* isomers of the octahedral species^{5,6}.

The PMR spectral data of the tris chelates of cobalt(III) are reported in Table 2. In all the complexes the NCH_3 and CCH_3 groups show distinct splitting patterns, predominantly overlapping signals with intensity ratio 2:1 and in cases like $(CH_3-m'-CH_3C_6H_3CH_3)_3Co$, well separated signals with intensity ratio 1:1:1 (the ratios were found out by integration). The consistent occurrence of signals of 2:1 or 1:1:1 intensity ratio for NCH_3 (or CCH_3) signals in the above chelates indicates that only one geometrical isomer, the *trans* octahedral form, is present in each case. The *cis* form would have given a single sharp signal only. In the *cis* form all the three aryl groups are crowded on one face of the octahedron. The steric hindrance is probably large enough to preclude the formation of the *cis* form, hence the preference for the *trans* form.

For unambiguous assignment of signals to specific chelate rings it is necessary to determine which two of the three chelate rings are equivalent in the *trans* isomer. This problem is not solved yet. However, it is easy to see that one of the chelate rings is quite different from the other two in the *trans* form and the less intense PMR signal of the NCH_3 or CCH_3 group can be assigned to this ring.

The electronic spectral data of the complexes are presented in Table 3. All of them show a band around 20,000 cm^{-1} and in a few cases a shoulder around 15,000 cm^{-1} . Spin-paired cobalt(III) in an octahedral field shows two spin-allowed transitions, ${}^1T_{1g} \leftarrow {}^1A_{1g}$ (ν_1) and ${}^1T_{2g} \leftarrow {}^1A_{1g}$ (ν_2). In fields of lower symmetry the upper states are split. In the *cis* form (C_{3v}) no splitting of bands is expected and the isomer is essentially cubic^{7,8}. In the *trans* form multiple bands are predicated⁷. However,

TABLE 2—PMR SIGNALS OF Co(III) COMPLEXES IN $CDCl_3$

Compound	Group	Chemical shifts ^{a,b,c} (ppm)
$(CH_3-C_6H_4F)_3Co$	NCH_3	3.45 (2), 4.15 (1)
$(CH_3-C_6H_4Cl)_3Co$	NCH_3	3.60 ^d
$(CH_3-C_6H_4Br)_3Co$	NCH_3	3.90, 4.10 ^d
$(CH_3-p-CH_3C_6H_3Cl)_3Co$	CCH_3	2.30, 2.40 ^d
	NCH_3	3.48, 3.52
		4.08
$(CH_3-m'-CH_3C_6H_3Cl)_3Co$	CCH_3	2.18 (2), 2.43 (1)
	NCH_3	3.55, 3.70 ^d
$(CH_3-m'-CH_3C_6H_3CH_3)_3Co$	CCH_3	1.28 (1), 2.05 (1), 2.15 (1), 2.30, 2.40 ^d
	NCH_3	3.25 (1), 3.75 (1), 3.93 (1)
$(C_2H_5-C_6H_4F)_3Co$	NCH_2CH_3	1.08, 1.53 ^e
	NCH_2CH_3	3.70, 4.35 ^f
$(C_2H_5-C_6H_4Cl)_3Co$	NCH_2CH_3	1.35 ^{d,e}
	NCH_2CH_3	3.95 ^{d,f}
$(C_2H_5-C_6H_4Br)_3Co$	NCH_2CH_3	1.35 ^{d,e}
	NCH_2CH_3	4.00 ^{d,f}
$(C_2H_5-m'-CH_3C_6H_3Cl)_3Co$	CCH_3	2.15 (2), 2.40 (1)
	NCH_2CH_3	1.30 ^{d,e}
	NCH_2CH_3	4.00 ^{d,f}

a, downfield from TMS; b, figures in parentheses show relative intensities of components for a given group; c, aromatic protons give rise to a complex pattern; d, overlapping protons; e, centre of triplet; f, centre of quartet.

TABLE 3—FREQUENCIES (ν , cm^{-1}) AND EXTINCTION COEFFICIENTS (ϵ , LITRE MOLE⁻¹ cm^{-1}) OF ELECTRONIC BANDS OF COBALT(III) COMPLEXES IN BENZENE

Compound	Band position, cm^{-1} (ϵ)
$(CH_3-C_6H_4F)_3Co$	15,380 (450); 20,620 (895)
$(CH_3-C_6H_4Cl)_3Co$	15,380 (390); 19,230 (910)
$(CH_3-C_6H_4Br)_3Co$	15,620 (360); 20,830 (780)
$(CH_3-p-CH_3C_6H_3Cl)_3Co$	19,080 (890)
$(CH_3-m'-CH_3C_6H_3Cl)_3Co$	15,150 (580); 20,620 (960)
$(CH_3-m'-CH_3C_6H_3CH_3)_3Co$	15,500 (425); 19,460 (1020)
$(C_2H_5-C_6H_4F)_3Co$	15,380 (450); 19,460 (1080)
$(C_2H_5-C_6H_4Cl)_3Co$	15,500 (315); 20,830 (800)
$(C_2H_5-m'-CH_3C_6H_3Cl)_3Co$	15,380 (285); 20,200 (880)

clear cut splittings are rarely observed experimentally.

The energy separation between the bands in the cobalt(III) complexes is ~ 5000 cm^{-1} . The two bands cannot be assigned to ν_1 and ν_2 octahedral transitions because in O_h symmetry transitions are generally separated⁹ by 8,000 cm^{-1} . Also the B value for the triazene 1-oxide complexes is considerably lower than the usual B values observed for a variety of chelates¹⁰. Hence we assign the two bands at $\sim 15,500$ and 20,000 cm^{-1} to split components of the parent 1T_1 state. The relatively high molar extinction coefficients for these bands may be due to the intensity stealing from the nearby lying charge-transfer band.

Thus the results show that the compounds prepared are cobalt(III) complexes of *trans*-octahedral symmetry. This implies that there is no coordination from the X group in the ligand system making it bidentate, thereby substantiating the objective of this project. Further studies on the

oxidation-reduction process of the cobalt(II)-cobalt(III) species involving this ligand system are in progress.

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Table 1 - Electronic spectra of cobalt(II) complexes in various solvents. The table lists absorption maxima (λ_{max}) and molar extinction coefficients (ε) for various complexes in different solvents.

Complex	Solvent	λ _{max} (nm)	ε (l·mol ⁻¹ ·cm ⁻¹)
CoCl ₂ ·6H ₂ O	H ₂ O	480	1.5 × 10 ⁴
	Me ₂ SO	480	1.5 × 10 ⁴
CoCl ₂ ·2H ₂ O	H ₂ O	480	1.5 × 10 ⁴
	Me ₂ SO	480	1.5 × 10 ⁴
CoCl ₂ ·4H ₂ O	H ₂ O	480	1.5 × 10 ⁴
	Me ₂ SO	480	1.5 × 10 ⁴

The energy separation between the bands in the cobalt(II) complexes is ~3000 cm⁻¹. The two bands cannot be assigned to ν_1 and ν_2 octahedral transitions because in O_h symmetry transitions are generally separated by 8000 cm⁻¹. Also the B values for the transition I-oxide complexes is considerably lower than the usual B values observed for a variety of cobalt(II) complexes. Hence we assign the two bands at ~1500 and 3000 cm⁻¹ to spin components of the parent T_{2g} state. The relatively high molar extinction coefficients for these bands may be due to the intensity stealing from the nearby charge-transfer band.

Table 2 - Electronic spectra of cobalt(II) complexes in various solvents. The table lists absorption maxima (λ_{max}) and molar extinction coefficients (ε) for various complexes in different solvents.

Complex	Solvent	λ _{max} (nm)	ε (l·mol ⁻¹ ·cm ⁻¹)
CoCl ₂ ·6H ₂ O	H ₂ O	480	1.5 × 10 ⁴
	Me ₂ SO	480	1.5 × 10 ⁴
CoCl ₂ ·2H ₂ O	H ₂ O	480	1.5 × 10 ⁴
	Me ₂ SO	480	1.5 × 10 ⁴
CoCl ₂ ·4H ₂ O	H ₂ O	480	1.5 × 10 ⁴
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Thus the results show that the compounds prepared are cobalt(III) complexes of trans-octahedral symmetry. This implies that there is no coordination from the X group in the ligand system making it bidentate thereby substantiating the objective of this project. Further studies on the

and ν_2 oxidation state of cobalt indicate that the complexes are six coordinated with an octahedral geometry. In the first complex the bidentate bands is unambiguously and hence the complex can exist in the cis and trans octahedral forms. These forms can be distinguished on the basis of their EPR data. The three-fold axis of symmetry in the ν_1 form makes all chloride ions magnetically equivalent and hence one expects only one set of signals for a given set of protons in the EPR spectrum. On the other hand the trans isomer is asymmetric and a given group of equivalent protons should show distinct chemical shifts for the three chloride rings. This principle has been used extensively to identify the cis-trans isomers of the octahedral species.

The EPR spectral data of the cobalt(II) cobalt(III) are reported in Table 2. In all the complexes the ν_1 and ν_2 groups show distinct splitting patterns predominantly overlapping signals with intensity ratio 2:1 and in cases like CoCl₂·2H₂O, CoCl₂·4H₂O well separated signals with intensity ratio 1:1. The ratios were lower in some instances. The consistent occurrence of signals in the above chloride ratios for ν_1 and ν_2 of 2:1 or 1:1 intensity ratio for ν_1 and ν_2 groups in the above chlorides indicates that only one geometrical form, the trans octahedral form, is present in each case. The cis form would have given a single sharp signal only. In the cis form all the three ring groups are crowded on one face of the octahedron. The steric hindrance is probably large enough to preclude the formation of the cis form, hence the preference for the trans form.

For unambiguous assignment of signals to specific chloride rings it is necessary to determine which two of the three chloride rings are equivalent in the trans isomer. This problem is not solved yet. However, it is easy to see that one of the chloride rings is quite different from the other two in the trans form and the less intense EPR signal of the ν_1 or ν_2 group can be assigned to this ring. The electronic spectral data of the complexes are presented in Table 3. All of them show a band around 30000 cm⁻¹ and in a few cases a shoulder around 15000 cm⁻¹. Spin-paired cobalt(III) in an octahedral field shows two spin-allowed transitions $T_{1g} \rightarrow E_g$ (ν_1) and $T_{1g} \rightarrow T_{2g}$ (ν_2). In fields of lower symmetry the upper states are split. In the cis form (C_{2v}) no splitting of bands is expected and the former is essentially cubic. In the trans form multiple bands are predicted. However,