

Synthesis and Characterisation of Cobalt(III) Chelates of Symmetrical 3-Nitro-1, 5-diarylformazans

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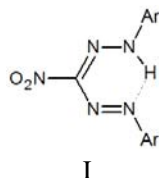
Abstract: The synthesis and characterisation of cobalt(III) chelates of 3-nitroformazans have been described. These chelates have been characterized as tris chelates on the basis of elemental analysis, IR and ^1H NMR studies. These studies reveal that the coordination of the cobalt(III) to the ligands occurs through the nitrogen atoms 1 and 5 of the formazyl group and that the NO_2 group of the ligand does not take part in coordination. The structure of these chelates contains three symmetric six membered CN_4Co rings.

Keywords. Formazans, Chelates, Coordination, Cobalt, Symmetrical

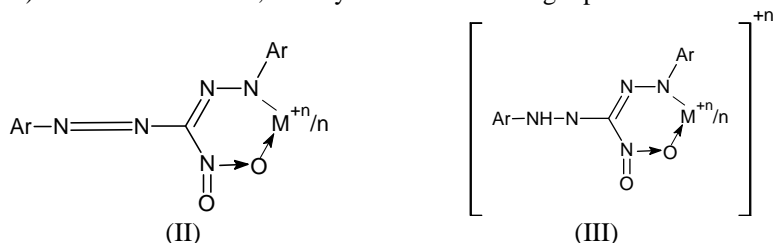
Introduction

Transition metal complexes of polyazo ligands have attracted considerable attention in the last few years. Despite the fact that synthetic route to formazans were well developed over a half century ago¹ and there are now over one thousand reported derivatives², the coordination chemistry of formazans has not received much attention. Publications describing transition metal-formazans complexes have appeared sporadically since the 1940³⁻¹². There have been almost no systematic investigation¹³⁻¹⁶. Also there is little known about the structure of metal complexes of 3-nitroformazans¹⁷⁻²⁰, although the metal-binding properties of these ligands are associated with colour changes, and as a result found applications as dyes or as metal-sensing agents²¹⁻²⁵.

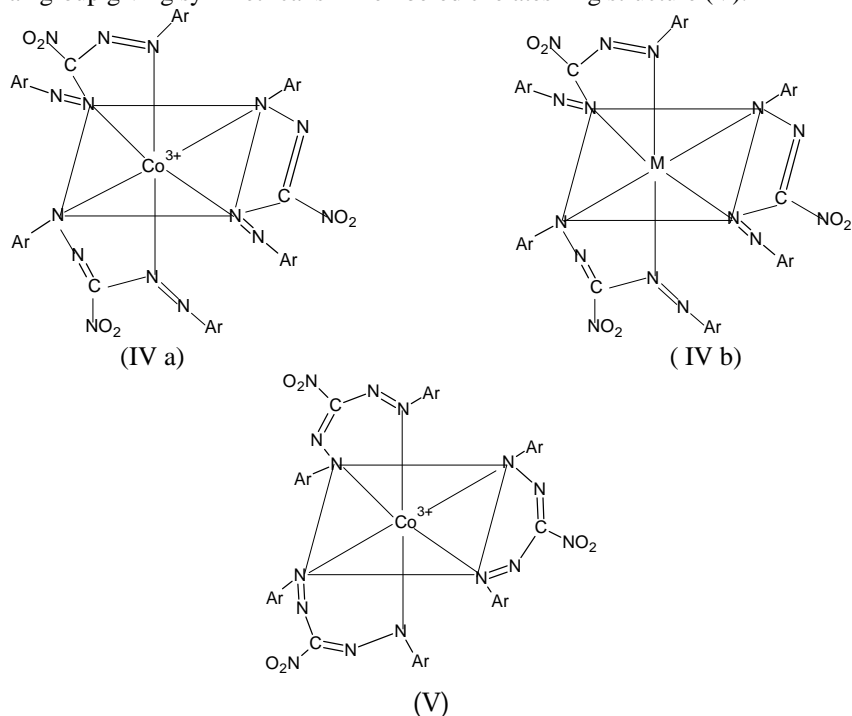
3-Nitroformazans (3NFz)²⁶, prepared by reacting diazotized aromatic amine with nitromethane in cold are known to be intramolecularly hydrogen bonded. Their IR and ^1H NMR spectra indicate that the NH group is strongly chelated and a symmetrical structure (I), out of many geometric isomers has been suggested¹⁷ and confirmed on the basis of x-ray studies^{27,28}.



There is a considerable number of references available in literature concerning bis chelates of formazans with cobalt(II) but tris chelates of formazans with cobalt(III) are rarely reported²⁹. Thus, the method given here in the experimental section for the synthesis of cobalt(III) chelates of 3-nitro-1, 5-diarylformazans is being reported for the first time.



The symmetrical 3-nitro-1, 5 diarylformazans are the versatile complex forming agents as their coordination to cobalt(III) may occur in number of ways, because of the large number of coordination centres in them. The chelation of (I) with cobalt(III) may occur through, (i) one of the oxygen atoms of the nitro group and one of the four nitrogens of the formazans group giving structures (II) and (III), (ii) nitrogens 1 and 4 of the formazans group giving structures (IVa) or (IVb) having cis or trans geometry respectively or (iii) nitrogen 1 and 5 of the formazan group giving symmetrical six membered chelates ring structure (V).



Ar = phenyl, *o*-tolyl, *p*-tolyl, *o*-anisyl, *p*-anisyl, *p*-bromophenyl, *p*-chlorophenyl, *p*-phenity

In the present investigation, cobalt(III) chelates of some symmetrical 3-nitroformazans have been synthesized and characterized on the basis of elemental analysis and spectral studies. Also an attempt has been made to establish the site of chelation and ring size in these chelates on the basis of IR and 1H NMR spectral studies.

Experimental

The ligands namely 3-nitro-1,5-diphenylformazan, 3-nitro-1,5-*di-o*-tolylformazan, 3-nitro-1,5-*di-p*-tolylformazan, 3-nitro-1,5-*di-o*-anisylformazan, 3-nitro-1,5-*di-p*-anisylformazan, 3-nitro-1,5-*d-p*-phenitylformazan 3-nitro-1,5-*di-p*-chloroformazan and 3-nitro-1,5-*di-p*-bromoformazan were prepared by the reported methods¹⁷.

Preparation of cobalt(III) chelates of 3-nitro-1,5-diarylformazans

A convenient method for the synthesis of pure tris(3-nitro-1,5-diarylformazan) cobalt(III) chelates was the reaction of hexaminecobalt(III) chloride with 3-nitro-1,5-diarylformazans. The details of which are given below:

An aqueous solution of hexaminecobalt(III)chloride (500 mg in minimum quantity of distilled water), silver nitrate (953.27 mg) and sodium nitrate (2.5 g) were heated on a hot plate for 20-25 minutes to precipitate silver chloride completely. The solution was filtered and the filtrate was added to the methanolic solution of ligand (500 mg in 50 mL).

The resulting solution was refluxed for 18-20 h and the reddish brown crystals thus formed were filtered and thoroughly washed with distilled water. The complex thus obtained was again purified by column chromatography using silica column. The dark reddish brown band of the complex, which eluted out first, using benzene as eluent, was concentrated and recrystallized twice from chloroform- hexane. The impurities adhering on the top of the column moved only with methanol. These were of gummy nature and could not be crystallised. However, these unidentified products showed a negative test for cobalt.

Estimation of cobalt

Cobalt in these chelates was estimated spectrophotometrically with phenylazobenzaldoxime³⁰ and was occasionally re-checked by EDTA titration method³¹ using xylenol orange indicator.

Estimation of nitrogen

Nitrogen in these chelates was estimated by Kjeldhal's method³².

Spectral studies

The IR of these chelates were recorded on M-80 IR spectrophotometer. The results are summarized in Table 2. The ¹H NMR spectra of these chelates were recorded on 300 MHz Bruker Avance spectrophotometer and the results are summarized as follows.

Tris(3-nitro-1,5-diphenylformazanato)cobalt(III)

Molecular Formula: C₃₀H₃₀N₁₅O₆Co; Elemental analysis (%) Found (Calcd): N- 23.88 (24.30), Co- 6.72 (6.80); IR (KBr pellets, cm⁻¹): 1560 (NO₂, asym), 1490 (N=C-N, asym), 1410 (N=N, sym), 1370 (N=C-N, sym), 1270 (NO₂, sym), 840 (C-N of C-NO₂); ¹H NMR (CDCl₃): 7.25- 7.45(m, aromatic).

Tris(3-nitro-1,5-di- o-tolylformazanato)cobalt(III)

Molecular Formula: C₄₅H₄₂N₁₅O₆Co; Elemental analysis (%) Found (Calcd): N- 21.73 (22.19), Co- 6.05(6.20); IR (KBr pellets, cm⁻¹): 1565 (NO₂, asym), 1510 (N=C-N, asym), 1410 (N=N, sym), 1375 (N=C-N, sym), 1270 (NO₂, sym), 840 (C-N of C-NO₂); ¹H NMR (CDCl₃): 2.36(s, -CH₃), 7.1-7.6(m, aromatic).

Tris(3-nitro-1,5- p-tolylformazanato)cobalt(III)

Molecular Formula: C₄₅H₄₂N₁₅O₆Co; Elemental analysis (%) Found (Calcd): N- 21.98 (22.19), Co- 6.08(6.20); IR (KBr pellets, cm⁻¹): 1565 (NO₂, asym), 1507 (N=C-N, asym), 1405 (N=N, sym), 1365 (N=C-N, sym), 1270 (NO₂, sym), 1130 (N-N-Ar), 830 (C-N of C-NO₂); ¹H NMR (CDCl₃): 2.36(s, -CH₃), 6.8-7.46(m, aromatic).

Tris(3-nitro-1,5-di-o-anisylformazanato)cobalt(III)

Molecular Formula: $C_{45}H_{42}N_{15}O_{12}Co$; Elemental analysis (%) Found (Calcd): N- 19.33 (20.13), Co- 4.32(4.40); IR (KBr pellets, cm^{-1}): 1520 (NO_2 , asym), 1480 ($N=C-N$, asym), 1405 ($N=N$, sym), 1375 ($N=C-N$, sym), 1265 (NO_2 , sym), 1230 ($N-N-Ar$), 830 ($C-N$ of $C-NO_2$); 1H NMR ($CDCl_3$): 4.00(s, $-OCH_3$), 6.82-7.75(m, aromatic).

Tris(3-nitro-1,5-di-p-anisylformazanato)cobalt(III)

Molecular Formula: $C_{45}H_{42}N_{15}O_{12}Co$; Elemental analysis (%) Found (Calcd): N- 19.38 (20.13), Co- 4.29(4.40); IR (KBr pellets, cm^{-1}): 1560 (NO_2 , asym), 1500 ($N=C-N$, asym), 1405 ($N=N$, sym), 1370 ($N=C-N$, sym), 1260 (NO_2 , sym), 1220 ($N-N-Ar$), 840 ($C-N$ of $C-NO_2$); 1H NMR ($CDCl_3$): 3.87(s, $-OCH_3$), 6.82-7.76(m, aromatic).

Tris(3-nitro-1,5-di-p-bromophenylformazanato)cobalt(III)

Molecular Formula: $C_{39}H_{24}N_{15}O_6Br_6Co$; Elemental analysis (%) Found (Calcd): N- 15.12 (15.70), Co- 4.00(4.41); IR (KBr pellets, cm^{-1}): 1550 (NO_2 , asym), 1480 ($N=C-N$, asym), 1400 ($N=N$, sym), 1380 ($N=C-N$, sym), 1285 (NO_2 , sym), 830 ($C-N$ of $C-NO_2$); 1H NMR ($CDCl_3$): 7.25-7.45(m, aromatic).

Tris(3-nitro-1,5-di-p-chlorophenylformazanato)cobalt(III)

Molecular Formula: $C_{39}H_{24}N_{15}O_6Cl_6Co$; Elemental analysis (%) Found (Calcd): N- 18.12 (19.62), Co- 5.28(5.51); IR (KBr pellets, cm^{-1}): 1540 (NO_2 , asym), 1480 ($N=C-N$, asym), 1410 ($N=N$, sym), 1385 ($N=C-N$, sym), 1275 (NO_2 , sym), 820 ($C-N$ of $C-NO_2$); 1H NMR ($CDCl_3$): 7.25-7.75(m, aromatic).

Tris(3-nitro-1,5-di-p-phenitylformazanato)cobalt(III)

Molecular Formula: $C_{51}H_{54}N_{15}O_{12}Co$; Elemental analysis (%) Found (Calcd): N-18.03(18.63), Co-5.08(5.23); IR (KBr pellets, cm^{-1}): 1520 (NO_2 , asym), 1470 ($N=C-N$, asym), 1405 ($N=N$, sym), 1380 ($N=C-N$, sym), 1265 (NO_2 , sym), 1240 ($N-N-Ar$), 845 ($C-N$ of $C-NO_2$); 1H NMR ($CDCl_3$): 1.58-1.66 (t, $-OCH_2CH_3$), 3.74-3.91(q, $-OCH_2CH_3$), 7.28-7.68(m, aromatic).

Results and Discussion

The chemical analysis of these chelates show that they have 1:3 stoichiometry with the composition $Co(L)_3$ (where L -formazanato anion) and thus are tris chelates. The disappearance of ν_{NH} in their IR spectra which was found to be present in the corresponding ligands in the range $3200-2900\text{ cm}^{-1}$, absence of NH signal in their 1H NMR spectra which was present in the corresponding ligands between 14-15 ppm from TMS in $CDCl_3$, non appearance of new bands characteristic of metal-nitrito type of linkage $\left(\begin{array}{c} -N-O \rightarrow M \\ | \\ O \end{array} \right)$ at 1360 cm^{-1} and $1110-1050\text{ cm}^{-1}$ and

no appreciable³³⁻³⁶ change in the frequencies of vibrations of nitro groups as compared to those of corresponding ligands indicate that these chelates are formed by the substitution of imine hydrogen atom of formazan ring by cobalt(III), there by ruling out the possibility of structure (II) and (III).

The $\nu_{N=C-N}(\text{asym})$, $\nu_{N=N}(\text{sym})$, $\nu_{N=C-N}(\text{sym})$ and ν_{N-N-Ar} stretching frequencies of tris(3NFz) $Co(III)$ chelates appear in the range $1480-1450\text{ cm}^{-1}$, $1430-1380\text{ cm}^{-1}$, $1350-1330\text{ cm}^{-1}$ and 1180 cm^{-1} respectively. The corresponding group frequencies of free ligands also appear in the same ranges. The distinction between two structure IV and V could be made only by 1H NMR studies.

In case of trans form IVb is the geometry of these chelates all the three unsymmetrical chelate rings will be magnetically non-equivalent and therefore we should expect six such signals for the six chemically indential magnetically non-equivalent substituents on the aryl groups.

In the case, the tris (3NFz)Co(III) chelates have five membered ring having cis geometry (Iva), then there should be separate ^1H NMR signals for the two chemically identical but magnetically non-equivalent substituents on the two aryl groups of a chelate ring.

The tris (3-nitroformazanato) cobalt(III) chelates exists only in one isomeric form as only a single spot is observed on TLC plate for each complex. The ^1H NMR of these tris chelates also show a single signal for the chemically equivalent substituents on the aryl groups.

The ^1H NMR spectrum of tris (3-nitro-1,5-*di-p*-anisylformazanato)Co(III) showed only a single $-\text{OCH}_3$ signal at 3.87 ppm from TMS in CDCl_3 . Also a single $-\text{OCH}_3$ signal at 4.00 ppm from TMS in CDCl_3 was observed in ^1H NMR spectrum of tris (3-nitro-1,5-*di-o*-anisylformazanato)Co(III). Similarly the ^1H NMR of tris (3-nitro-1,5-*di-p*-tolylformazanato)Co(III) showed a single $-\text{CH}_3$ signal at 2.36 ppm from TMS and only a single $-\text{CH}_3$ signal was observed at 2.36 ppm from TMS in the ^1H NMR spectrum of tris(3-nitro-1,5-*di-o*-tolylformazanato) cobalt(III). The ^1H NMR signal due to aromatic protons in all the tris (3-NFz)Cobalt(III) chelates appear as a multiplet in the range 6.00-8.00 ppm from TMS in CDCl_3 .

Thus, the ^1H NMR data of tris(3NFz)cobalt(III) chelates suggest that these chelates contain three magnetically equivalent symmetric six membered chelate rings. The above results establishing the presence of symmetric six membered chelates rings in tris(3NFz) cobalt(III) chelates is further supported by the fact that in the ^1H NMR spectrum of tris(3-nitro-1,5-*di-p*-phenitylformazanato)Co(III) only one triplet (1:2:1) due to $-\text{CH}_3$ centered at 3.84 and only one quartet (1:3:3:1) due to $-\text{OCH}_2$ centered at 1.62 ppm from TMS in CDCl_3 due to *p*- OCH_2CH_3 substituent was observed.

The ^1H NMR of tris(3-nitro-1,5-*p*-phenitylformazanato)cobalt(III) chelate showing only one triplet due to $-\text{CH}_3$ and one quartet due to $-\text{OCH}_2$ of *p*- OCH_2CH_3 substituent confirms that these chelates have a symmetrical six membered chelate ring structure (V).

Conclusion

From the above results and discussion, it is inferred that:

- i) The cobalt(III) chelates of 3-nitro-1,5-diarylformazans have stoichiometry of 1:3 and are neutral and thus characterized as tris chelates formed cobalt(III).
- ii) The nitro group of 3-nitro-1,5-diarylformazans do not participate in coordination.
- iii) All the tris(3-nitro-1,5-diarylformazanato)cobalt(III) chelates, synthesized and reported here have symmetrical six membered chelate ring structure, V.

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