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Metal Complexes of an *o,o′*-Dihydroxy Azo Dye. A Spectroscopic Study

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ABSTRACT

Chromium(III) and cobalt(III) complexes of 4-(3′,5′-dinitro-2′-hydroxyphenylazo)-3-hydroxy-2-naphthanilide, known as TRH and Co-TRH respectively, were studied by NMR, IR, Raman and UV–Vis spectroscopy in order to determine the number of, and the structures of their structural isomers. NMR data for Co-TRH clearly indicated one major isomer, which was identified as the N_α *isomer having the phenyl nitrogen chelating with the Co(III) ion. No useful NMR information was obtained for TRH, because it is paramagnetic; however, TLC results suggested a single isomer. IR and Raman spectra of the complexes suggested that the ligand in TRH and Co-TRH displayed both azo and hydrazone characteristics. These could be the resonance forms of the six-membered chelate ring adjacent to the naphthalene moiety. The UV–Vis absorption band for TRH showed a bathochromic shift with respect to that for Co-TRH. This was attributed to the relatively ionic nature of TRH.*

INTRODUCTION

Metal complexes of 4-(3′,5′-dinitro-2′-hydroxyphenylazo)-3-hydroxy-2-naphthanilide (DHHN) are an important class of negative charge control agents (CCAs) used in electrophotographic application.[1] The chromium complex of DHHN, known as Aizen Spilon Black TRH, or TRH in short, is particularly useful.[2] The synthesis of TRH and its derivatives[2,3] and of the

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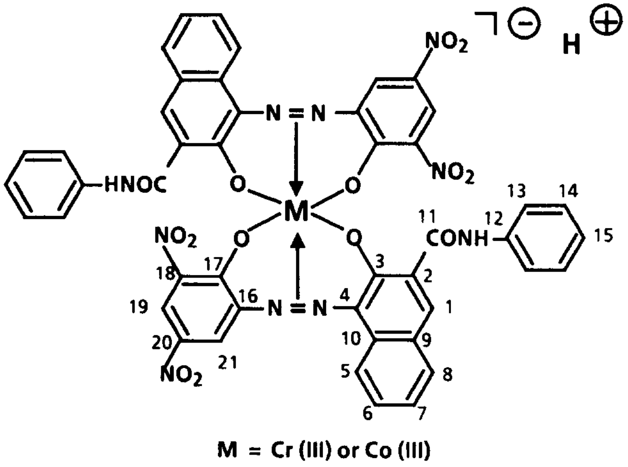

Fig. 1. The possible structural isomers of a TRH-type complex.

azo-hydrazone tautomerism of DHHN[4] have been previously described. In this paper, we investigate the isomerism of TRH and its cobalt counterpart (denoted by Co-TRH) by spectroscopic means. The structure in Fig. 1 is being used in various publications to represent all the possible structural isomers of a TRH-type complex.

The isomerism of the metal complexes of *o,o′*-dihydroxydiaryazo compounds was a subject of intense study in the 1960s and 1970s.[5,6] As summarized in a recent review,[6] four types of isomerism have been reported, viz., (i) stereo or geometrical isomerism, (ii) N_α–N_β isomerism, (iii) azo-hydrazone isomerism and (iv) isomerism due to non-planarity of a hydrazone ligand. Without X-ray data, our study was limited to N_α–N_β and azo-hydrazone isomerism. Nevertheless, one might predict, based upon Schetty's rules, a meridional configuration for TRH-type complexes.[6]

The simplified reaction scheme shown in Fig. 2 illustrates the formation of four possible isomeric structures, **H1**, **A1**, **A2** and **H2**, where **H** and **A** stand for hydrazone and azo respectively, for a metal complex having an 1-(hydroxyphenylazo)-2-naphthol type ligand. **A1** and **H2**, which are the N_α isomers, are more favourable than **H1** and **A2**, the N_β isomers, because these structures suffer from the buttress effect.[6] In addition, azo dyes of DHHN type, which contain a 2-naphthol complexing component, have always yielded the N_α isomer.[7] This could be related to the tautomerism of DHHN type azo compounds.[4,8] With this understanding, one might expect the first three isomers out of the following ten structural isomers **$M(A1)_2$**, **$M(H2)_2$**, **M(A1)(H2)**, **M(A1)(A2)**, **$M(A2)_2$**, **$M(H1)_2$**, **M(A1)(H1)**, **M(A2)(H1)**, **M(A2)(H2)**, and **M(H1)(H2)** for a TRH type 1:2 metal-azo complex. The major purpose of this work was to determine if there is more than one isomer for TRH and Co-TRH and, if possibile, to identify the isomer(s).

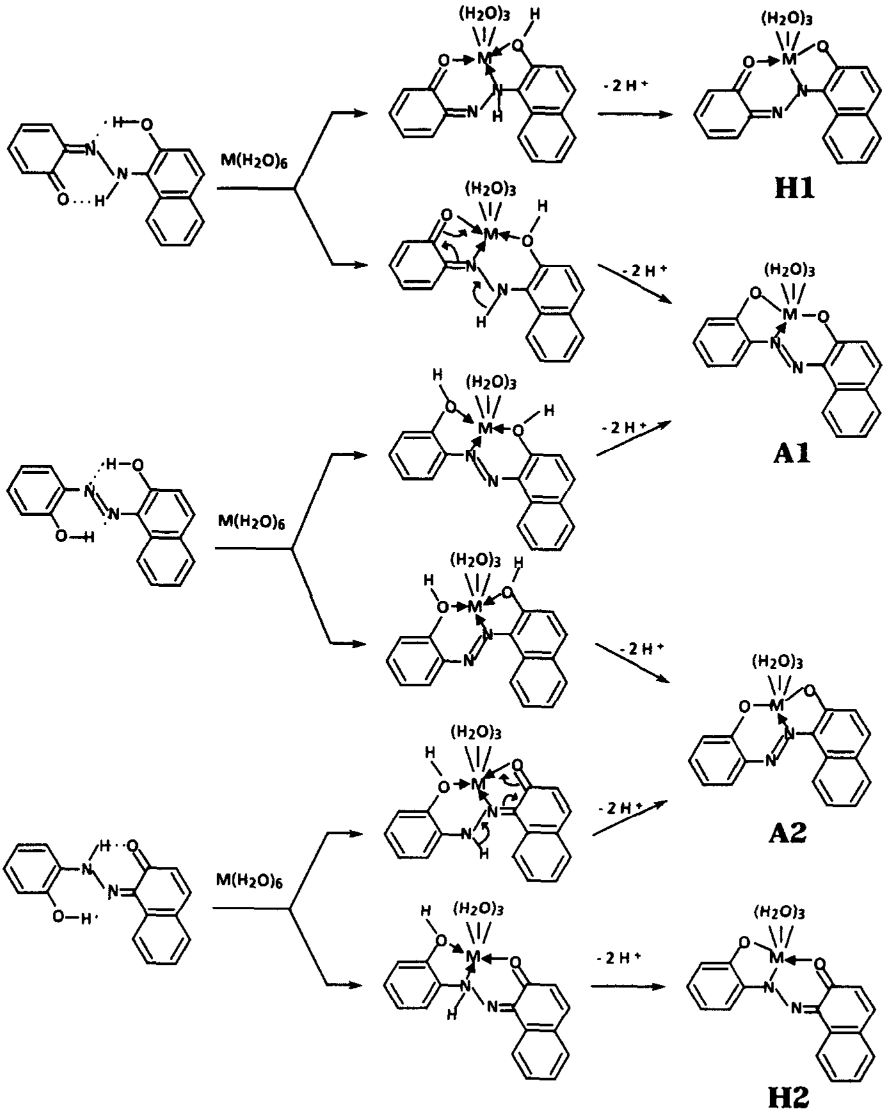

Fig. 2. The formation of four isomeric structures, **H1**, **A1**, **A2** and **H2**.

EXPERIMENTAL

Instrumentation

IR spectra (in potassium bromide) were recorded on a Parkin-Elmer 1750 Fourier transform spectrometer. Raman measurements were performed with the 4880 Å line of an argon-ion laser at power of 30–120 mW. A spex triple-monochromator system was used to reduce the level of scattered light.

The spectrometer slits were set for a resolution of 0·5 or 4 cm^{-1}. The sample (in potassium bromide) was kept at room temperature during measurement with a scanning range of 900–2000 cm^{-1}. ^{13}C NMR spectra (in DMSO or in the solid state) were recorded on a Bruker CXP spectrometer operating at 50·3 MHz in a superconducting magnet system (Cryomegnet Systems, Inc.). Proton-enhanced cross-polarization used 3–6 ms contact times, high power (H1 = 12 G) proton decoupling and recycle times of 1–3 s. Magic angle spinning (4–4·5 kHz) was performed in a Doty Scientific probe with about 100 mg of each sample packed into 6-mm o.d. sapphire rotors. The TOSS technique for sideband suppression was used for all measurements. Typically, 256–10 000 scans were averaged for each spectrum. ^{1}H and ^{1}H–^{13}C 2D NMR spectrometry was performed on a Bruker AM-360 system equipped with 5 mm QNP probe.[4] UV–Vis spectra were recorded on a Hewlett-Packard 8451A diode array spectrophotometer.

Materials

TRH was from Hodogaya Chemical Co. Ltd (Tokyo, Japan) and its preparation has been described previously.[2,3] Co-TRH was prepared by reacting 2·0 equivalents of DHHN monosodium salt[4] with 1·1 equivalents of Co(II) acetate tetrahydrate in ethylene glycol.[2] Elemental analysis of the resulting Co-TRH showed: C 53·20, H 3·72, N 13·12, Co 5·41, corresponding well with the calculated values for a formula of $(C_{46}H_{27}N_{10}O_{14}Co)\cdot(HOCH_2CH_2OH)$, viz., C 54·13, H 3·10, N 13·15, Co 5·55. Co-TRH which was prepared in water instead of ethylene glycol showed C 52·35, H 2·70, N 13·15, Co 5·42. These are close to the expected values for $(C_{46}H_{27}N_{10}O_{14}Co)\cdot(3H_2O)$, viz., C 52·27, H 3·13, N 13·26, Co 5·59.

RESULTS AND DISCUSSION

^{1}H-NMR spectroscopy has been used successfully to distinguish N–N isomers for cobalt complexes of *o,o'*-dihydroxydiphenylazo compounds[9], however, it cannot be used directly for chromium complexes. This is because cobalt(III) is diamagnetic while chromium(III) is paramagnetic, which tends to broaden the NMR signals. This was indeed the case for TRH. Both ^{1}H and ^{13}C NMR spectra were obtained for Co-TRH. The NMR peak assignments given in Table 1 were made based partly on the information extracted from a ^{1}H–^{13}C 2D spectrum of Co-TRH (shown in Fig. 3).

The NMR results clearly indicate a major isomer, if not single, for Co-TRH. The changes in the ^{13}C chemical shifts at C-1p, C-3, C-16 and C-17 carbon atoms, before and after complexation, is significant and revealing.

TABLE 1

^{1}H and ^{13}C NMR Peak Assignments for DHHN[5] and Co-TRH[a]

	^{1}*H NMR*		^{13}*C NMR*	
	DHHN	*Co-TRH*	*DHHN*	*Co-TRH*
1p	8·78 (s, 1H)	8·54 (s, 1H)	144·55	140·17
2			125·96	129·83
3			175·83	167·69
4			134·46	136·94
5p	8·40 (d, 1H) Δ not clear	8·03 (d, 1H) Δ = 8·1 Hz	121·13	122·51
6p	7·74 (t, 1H) Δ = 7·2 Hz	7·97 (t, 1H) Δ = 7·8 Hz	131·42	130·62
7p	7·49 (t, 1H) Δ = 7·2 Hz	7·57 (t, 1H) Δ = 7·1 Hz	126·50	125·37
8p	7·95 (d, 1H) Δ = 7·4 Hz	8·97 (d, 1H) Δ = 8·6 Hz	131·00	129·69
9			128·00	127·24
10			126·58	125·90
11			162·27	162·12
12			138·37	137·72
13p	7·79 (d, 2H) Δ = 7·6 Hz	7·20 (d, 2H) Δ = 8·0 Hz	119·90	118·89
14p	7·41 (t, 2H) Δ = 7·5 Hz	7·14 (t, 2H) Δ = 7·8 Hz	128·98	128·59
15p	7·15 (t, 1H) Δ = 7·4 Hz	6·99 (t, 1H) Δ = 7·3 Hz	123·85	123·64
16			130·24	150·84
17			161·70	151·39
18			135·92	134·31
19p	8·63 (d, 1H) Δ = 3·1 Hz	9·51 (d, 1H) Δ = 2·7 Hz	122·36	115·40
20			135·65	134·39
21p	8·42 (d, 1H) Δ = 3·1 Hz	8·72 (d, 1H) Δ = 2·7 Hz	110·97	122·70
—N—H	11·54 (s, 1H)	9·89 (s, 1H)		
—O—H (naphthyl)	16·30 (s, 1H)			

[a] Definitions: A protonated carbon is marked with a p, and s, singlet; d, doublet; t, triplet.

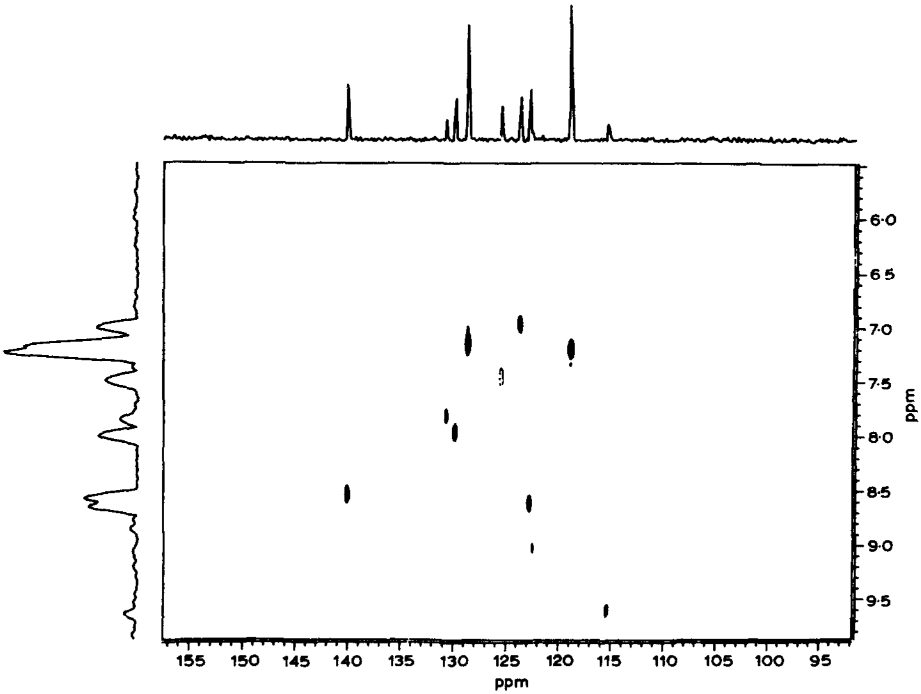

Fig. 3. ^{1}H–^{13}C correlated 2D NMR spectra for Co-TRH in DMSO.

High field shifts for C-1p and C-3, from 145·55 and 140·17 to 175·83 and 167·69 ppm respectively, means that α, β unsaturated carbonyl character or hydrazone contribution of the 2-naphthol component is reduced in Co-TRH as compared with DHHN. But, it is important to note that the hydrazone contribution is not completely eliminated. Down-field shift for C-16 suggests that N_α may complex directly with the cobalt ion, resulting in a reduction in electron density at this carbon atom. The carbonyl character at C-17 carbon, which is present in DHHN, is essentially absent in Co-TRH, as indicated by its chemical shift at 151·39 ppm indicative of a phenol carbon.

Based on the above interpretation, one might conclude that $Co(H2)_2$ is the correct structure for Co-TRH. But, Raman spectroscopy detected the presence of azo linkages in both Co-TRH and TRH. The Raman spectra for DHHN, its monosodium salt[4] and TRH are shown in Fig. 4 and those for Co-TRH in Fig. 5. Although the IR spectra of TRH and Co-TRH were almost identical, there are some differences in their Raman spectra. Table 2 summarizes the IR and Raman peak positions and their assignments. The Raman peaks at 1491 and 1177 cm^{-1}, due respectively to *cis* N═N stretching and O—H deformation in DHHN, disappear after complexation. The *trans* N═N peaks are observed in all cases as the strongest peaks at

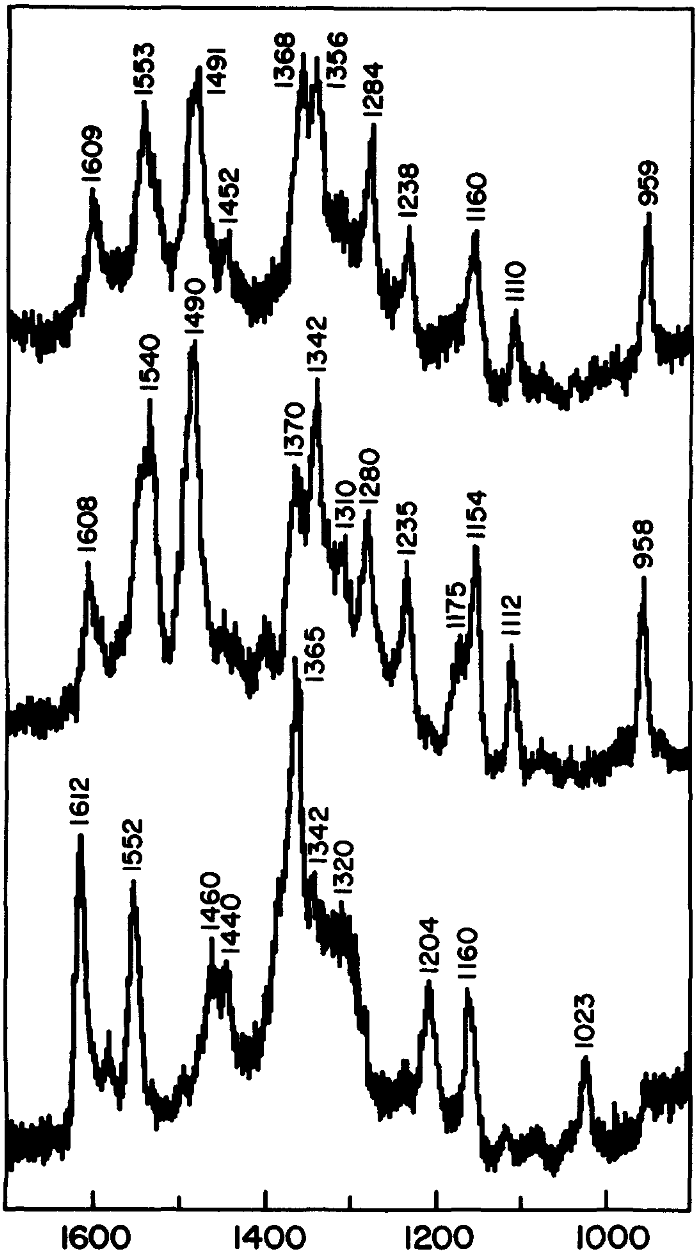

Fig. 4. Raman spectra for DHHN (top), DHHN monosodium salt (middle) and TRH (bottom).

TABLE 2

Peak Assignments for IR and Raman Spectra (Values Given in cm^{-1})[a]

DHHN	*TRH*	*Co-TRH*	*Assignment*
3 700–3 200 w, br	3 700–3 200 w, br	3 700–3 200 w, br	Amide v(N—H), v(O—H), H_2O
3 098 w	3 094 w	3 096 w	Aromatic v(C—H)
1 657 m	1 656 m	1 656 m	Amide v(C=O)
1 603 s	1 595 s	1 597 s	Naphthyl ring v(C=C)[14]
1 609 m[b]	**1 612 s**	**1 611 m**	
1 580 m	1 580 s	1 580 s	Hydrazone v(C=O)[10-12]
1 550 s	1 548 s	1 548 s	Asym. v(*o*,*p*-NO_2), hydrazone v(>C=N—N—)[10-12]
1 553 s	**1 552 s**		
	1 528 s	1 529 s	Asym. v(p-NO_2)
1 496 s	1 493 m	1 498 w	Phenyl ring v(C=C)[14]
		1 494 w	
1 491 s			Cis v(N=N)
1 476 s	1 458 s	1 460 s	Phenyl ring v(C=C)[14]
	1 460 m	**1 469 s**	
1 448 s	1 444 m	1 443 m	Aromatic ring v(C=C)[14]
	1 440 m		
		1 405 s	Aromatic ring v(C=C)[14]
	1 361 m	1 368 w	Trans v(N=N)
1 368 s	**1 365 s**	**1 366 s**	
1 325 s	1 329 s	1 329 s	Sym. v(NO_2)
1 350 s	**1 342 s**		
	1 289 s	1 295 s	Sym. v(NO_2)
	1 320 s	**1 298 m**	
1 273 s			Azo v(Ph—O) and hydrazone v(PH—N)
1 284 s			
	1 231 m	1 236 w	hydrazone v(N—N)
1 238 m		**1 235 m**	
1 209 w	1 203 s	1 204 s	Ring C—H in-plane vib.
	1 204 m	**1 206 m**	
1 177 s			O—H def.
1 154 s	1 153 s	1 154 m	v(Ph—N=) and alcohol C—O stretching
1 160 s	**1 160 m**	**1 163 m**	

[a] Definitions: s, strong; m, medium; w, weak; br, broad.

[b] Raman peak positions in bold.

about 1365 cm^{-1}. Absorption bands associated with a hydrazone type structure at 1580 and 1550 cm^{-1} are also detected for DHHN as well as its complexes.[9-11]

The NMR and IR/Raman results for Co-TRH led to a conclusion that **A1** and **H2** are in resonance and the structure of Co-TRH may best be expressed as shown in Fig. 6. This type of structure was proposed for the metal

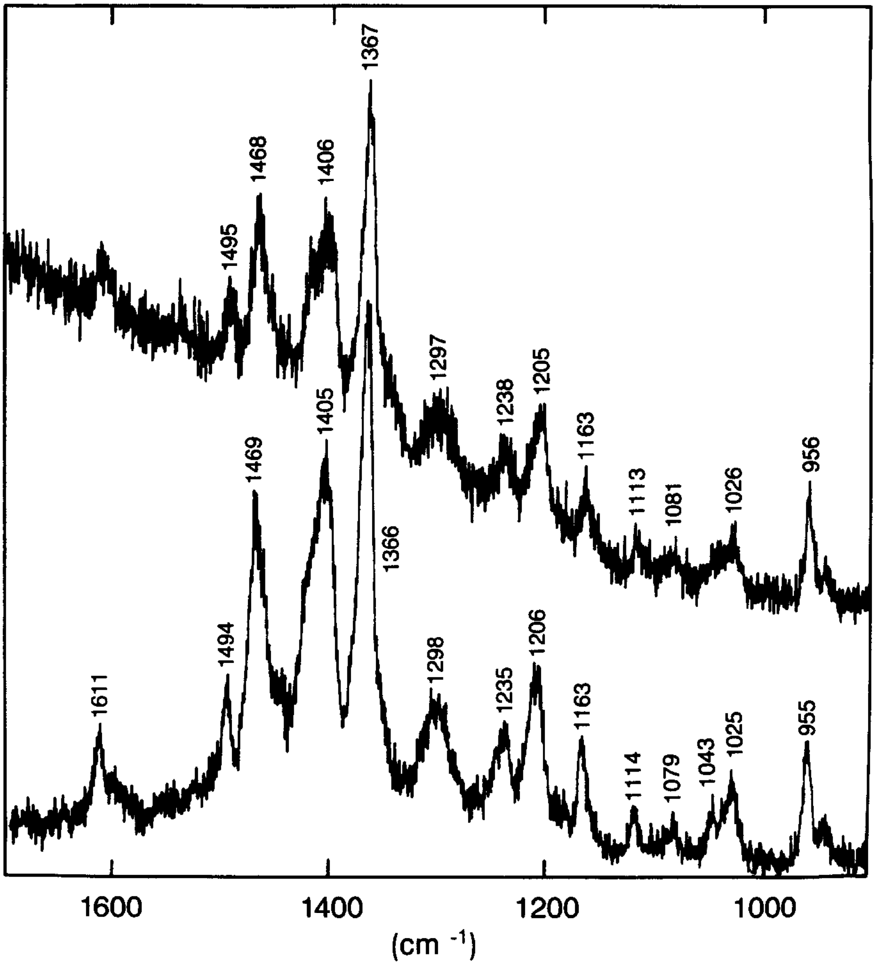

Fig. 5. Raman spectra for Co-TRH prepared in water (top) and in ethylene glycol (bottom).

complexes of *o*-hydroxyazobenzene.[11] TRH is likely to have a similar situation, because it was shown to have a single isomer by TLC. (As was reported by Hodogaya Chemical Co., Ltd, TRH was analyzed by TLC as follows: 2 μl 0·25% TRH in DMF was spotted on a silica gel TLC plate (Merk, Art 5735), the plate was developed with a mixed solvent of *n*-butanol/pyridine/water at a volume ratio of 6/3/4; the length of

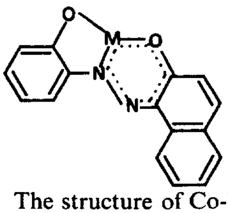

Fig. 6. The structure of Co-TRH.

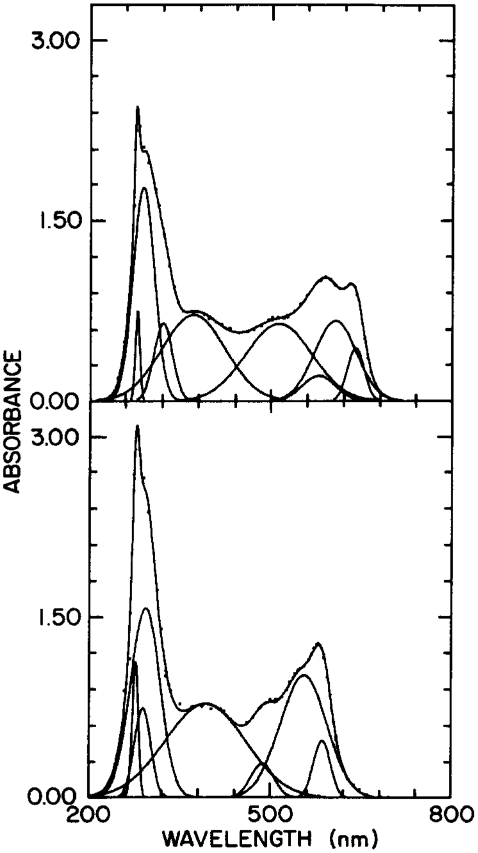

Fig. 7. The deconvoluted absorption profile for the spectra of TRH (top) and Co-TRH (bottom).

development was 7·5 cm after 1 h, and a single spot was detected at a R_f value of 0·63).

The UV-Vis spectra of TRH and Co-TRH are very dissimilar, as shown in Fig. 7, where the absorption profiles have been deconvoluted into individual Gaussian peaks. The peak positions are summarized in Table 3, which includes the data for DHHN[4] for comparison. In contrast to several known examples where significant bathochromic shifts were found due to complexation,[13] the absorption maxima for DHHN, TRH and Co-TRH remained relatively unchanged (at 574, 582 and 578 nm correspondingly). However, the long wavelength absorption peaks for DHHN and TRH at 622 and 630 nm are not present for Co-TRH. This type of phenomenon has been reported for 2:1 azo metal complexes and has been attributed to a lack of ionic character for Co-TRH.[13] It has been established that the extent of

TABLE 3
Deconvoluted UV-Vis Absorption Peak Positions

Peak no.	*DHHN*		*TRH*		*Co-TRH*	
	λ_{max} (*nm*)	*Area* (%)	λ_{max} (*nm*)	*Area* (%)	λ_{max} (*nm*)	*Area* (%)
1	438	33	502	50	483	11
2	553	40	569	8	551	77
3	581	7	596	33	582	13
4	622	20	630	9	—	—

the bathochromic shift is directly proportional to the ionic strength in the metal–oxygen bonds in a metal complex.[13]

In conclusion, there is only one (major) structural isomer for TRH and Co-TRH, their structures obeying Schetty's rules, with N_α chelating with the metal ion. The chelated ligand showed both azo and hydrazone resonance forms. UV–Vis results suggested that TRH was as ionic as DHHN while Co-TRH is much more covalent.

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