

Some New *Trans*-Bis(Dimethylglyoximato)cobalt(III) Complexes Containing Coordinated Azide— Synthesis and Spectra

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Some new azidocobaloximes of the general formula *trans*-Co(DH)₂LN₃(DH⁻—ON=C(CH₃)₂—C(CH₃)₂=N—OH; L—NH₂, aniline, pyridine or N₃⁻) have been synthesized and their i.r and u.v spectra obtained. The u.v spectra of the conjugate bases of these complexes have also been obtained. A detailed study of the charge-transfer spectra of the complexes and their conjugate bases has been carried out.

RECENT literature on the chemistry of the cobaloximes indicates that not much attention has been paid to the possibility of studying the azidocobaloximes. Such a study should be interesting, in view of the duality of the behaviour of cobalt as a soft acid with dimethylglyoxime and the Schiff bases and as a hard acid with ethylenediamine and related ligands¹. As part of a study of the equilibria and reactions of nonelectrolytes of the type *trans*-acidoaminebis(dimethylglyoximato)cobalt(III) we have included the cobalt-azide system for investigation^{2,3}. This paper reports the synthesis and spectra of diazidobis(dimethylglyoximato)cobaltate(III), and of some *trans*-azidoaminebis(dimethylglyoximato)cobalt(III) systems, where 'amine' represents typical bases like ammonia, pyridine and aniline.

Experimental

Materials : All the chemicals used for the preparations were analytical reagents (BDH). Pyridine and aniline were distilled once before use.

Synthesis : The starting material was Co(DH)₂(H₂O)Cl prepared by the method of Ablov⁴.

***trans*-Na[Co(DH)₂(N₃)₂].2H₂O(I) :** A solution of sodium azide (5.7 gm, 0.087 mol.) was added to a suspension of [Co(DH)₂(H₂O)Cl] (10 gm, 0.029 mol.) in 30 ml of water with stirring for 20-30 minutes. A red-violet solution of diazidobis(dimethylglyoximato)cobaltate(III) was obtained, from which the solid complex separated on cooling at 0-5°. The complex was then filtered, dried and recrystallized from ethanol (yield 50%). Anal: Found : C, 24.51; H, 3.62; Co, 13.58 per cent. Calcd. for Na[Co(DH)₂(N₃)₂].2H₂O; C, 24.25; H, 3.56; Co, 13.63 per cent.

***trans*-[Co(DH)₂(NH₃)N₃(II) :** Ammonia (25%, 0.7 ml, 0.0092 mol.) was added in drops with

stirring to a saturated solution of I (2 gm, 0.0046 mol.) containing two drops of glacial acetic acid. Red precipitate of II was formed immediately. The mixture was stirred for 30 mts. and the complex was filtered, washed with alcohol and ether and dried. Recrystallization was done from ethanol (yield 70%). Anal: Found : C, 27.4; H, 4.52; Co, 16.82 per cent. Calcd. for Co(DH)₂(NH₃)N₃; C, 27.6, H, 4.92; Co, 16.92 per cent.

***trans*-Co(DH)₂(py)N₃(III) :** Pyridine (0.7 ml, 0.0092 mol.) was added in drops with stirring to a saturated solution of I (2 gm, 0.0046 mol.) containing two drops of glacial acetic acid. Red precipitate of III was formed immediately. The mixture was stirred for 30 mts and the complex filtered, washed with alcohol and ether and dried. Recrystallization was done from ethanol (yield 80%). Anal: Obsd. : C, 38.31; H, 4.51; Co, 14.31 per cent. Calcd. for Co(DH)₂(py)N₃; C, 38.05; H, 4.66; Co, 14.36 per cent.

***trans*-[Co(DH)₂(aniline)N₃(IV) :** An alcoholic solution of aniline (0.80 ml, 0.009 mol) was added in drops with stirring to a saturated solution of I (2 gm, 0.0046 mol) in the presence of two drops of glacial acetic acid. Shiny, pale red precipitate of IV was formed immediately. The mixture was stirred for fifteen minutes, washed with alcohol and ether and dried. Recrystallization was done from ethanol (yield 80%). Anal: Found : C, 39.49; H, 4.89; Co, 13.75 per cent. Calcd. for Co(DH)₂(aniline)N₃; C, 39.62; H, 4.98; Co, 13.88 per cent.

Spectra : The infrared spectra were recorded in KBr disks with Perkin-Elmer 337 IR spectrophotometer. The u.v and visible spectra were recorded in 10 vol. % ethanol with a Beckman DK-2A recording spectrophotometer.

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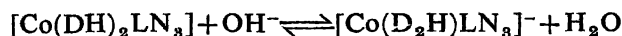
Results and Discussion

The nonelectrolyte complexes of the type *trans*-Co(DH)₂LN₃ were prepared by treatment of the base L(pyridine, ammonia or aniline) with [Co(DH)₂(N₃)₂]⁻. The complexes were assigned a *trans*-configuration on the basis of the δ_{OH} observed at 1740-50 cm⁻¹ in the i.r spectra of these complexes (Table 1)⁵. In alkaline solution the proton involved

TABLE 1—INFRARED ABSORPTION FREQUENCIES OF THE AZIDOCOBALOXIMES(III) IN CM⁻¹

Complex	N ₃		DMG			
	ν _{asym}	ν _{sym}	δ _{OH}	ν _{C=N}	ν _{NO}	
Co(DH) ₂ (N ₃) ₂ ⁻	2015 2036	1296	1742	1581	1086	1223
Co(DH) ₂ (NH ₃)N ₃	2024	1296	1749	1570	1078	1231
Co(DH) ₂ (an)N ₃	2030	1292	1740	1575	1088	1232
Co(DH) ₂ (py)N ₃	2016	1276	1748	1560	1090	1231

in hydrogen-bonding is removed in a rapid reversible reaction²



The infrared absorption spectra (4000-400 cm⁻¹) of the complexes were obtained in KBr disks. Table 1 shows the important i.r frequencies of the coordinated azide and dimethylglyoxime. The frequencies characteristic of coordinated NH₃, pyridine and aniline were observed. The intense absorption at 2010-2040 cm⁻¹ is due to the azide asymmetric stretch⁶ while the weaker absorptions at 1270-1290 cm⁻¹ are due to the symmetric stretching vibrations of the coordinated azide (ν_{sym}).

U. V. and Visible Spectra: Table 2 shows the characteristic u.v. and visible absorption maxima and the corresponding assignments for the azidocobaloximes. The ligand field spectra of the complexes show one band at 470-490 nm for the nonelectrolytes and at 540 nm for [Co(DH)₂(N₃)₂]⁻ which may be assigned to the spin-allowed ¹A_{1g} → ¹T_{1g} transition⁷ with the other spin-allowed ¹A_{1g} → ¹T_{2g} band masked by the intense charge-transfer bands. The positions of the maxima correspond to the following order of the spectrochemical series:

NH₃ > py > An > N₃⁻, consistent with previous results⁸. The weak field of N₃⁻ arises out of the destabilization of the t_{2g} orbitals due to π-interactions from N₃⁻.

The CT spectra (Fig. 1, Table 2) of the *trans*-[Co(DH)₂N₃L] complexes show maxima mainly centred at 245-250 nm and 295-335 nm. [Co(DH)₂(NH₃)N₃] and [Co(DH)₂(py)N₃] show maxima at 298 nm and 305 nm respectively while very broad bands are observed at 330 nm and 332 nm for Co(DH)₂(aniline)N₃ and Co(DH)₂(N₃)₂⁻ respectively, the order roughly paralleling the ligand field

maxima. Studies of the CT spectra of the cobaloximes have also been made by Yamano *et al*⁹ who assign the 245 nm band to intra-ligand π-π* transitions in the coordinated dimethylglyoxime. In their studies with a Co(DH)₂(X-py)₂ series (X-py = substituted pyridines), Yamano *et al*⁹ have observed

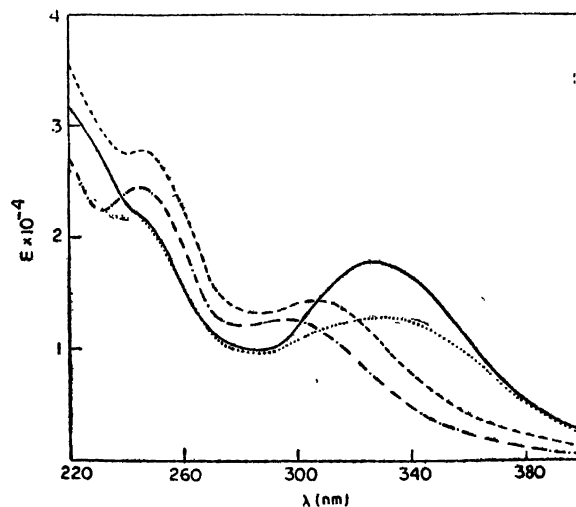


Fig. 1. U.V. Spectra of the azidocobaloximes(III)
 ----- Co(DH)₂(py)N₃, - - - - - Co(DH)₂(NH₃)N₃,
 Co(DH)₂(an)N₃, - · - · - Co(DH)₂(N₃)₂⁻
 Temp: 30°; [HClO₄] = 0.1 M

TABLE 2—ELECTRONIC ABSORPTION MAXIMA (NM) OF THE AZIDOCOBALOXIMES(III)

Complex	¹ A _{1g} → ¹ T _{1g}	σL → e _g [*]	dπ(t _{2g}) → π* π - π*
Co(DH) ₂ (NH ₃)N ₃	483 (2.47) ^a		295 (4.11) 308 (4.39)
Co(DH) ₂ (py)N ₃	485 (2.51)		308 (4.15) 246 (4.45)
Co(DH) ₂ (an)N ₃	495 (2.70)		330 (4.16) 247 (4.27)
Co(DH) ₂ (N ₃) ₂ ⁻	540 (2.58)		381 (4.18) 246 ^b (4.27)
Co(D ₂ H)(NH ₃)N ₃ ⁻		365 ^b (3.60)	285 (4.43) 260 (4.60)
Co(D ₂ H)(py)N ₃ ⁻		370 ^b (3.60)	288 (4.43) 260 (4.56)
Co(D ₂ H)(an)N ₃ ⁻		381 ^b (3.59)	288 (4.36) 258 (4.55)
Co(D ₂ H)(N ₃) ₂ ⁻		380 ^b (3.62)	280 ^b (4.38) 258 (4.53)

^a log ε in parenthesis; ^b shoulder

two bands, 315-370 nm (py → Co, LMCT) and 275-305 nm (dπ(Co) → π*(DMG), MLCT). One would also expect to observe maxima due to σ(DMG) → σ*(Co) LMCT which generally appears as a shoulder at 360-380 nm¹⁰ in the Co(DH)₂ systems, with a lower intensity compared to the 300 nm bands and is masked in the spectra of the azidocobaloximes by the intense short wavelength bands. Another absorption masked here is the intra-ligand CT absorption in N₃⁻, expected at 300-350 nm¹¹.

The CT spectra of the conjugate bases, obtained by adding alkali to aqueous solutions of the complexes, are also given in Table 2 (Fig. 2). New

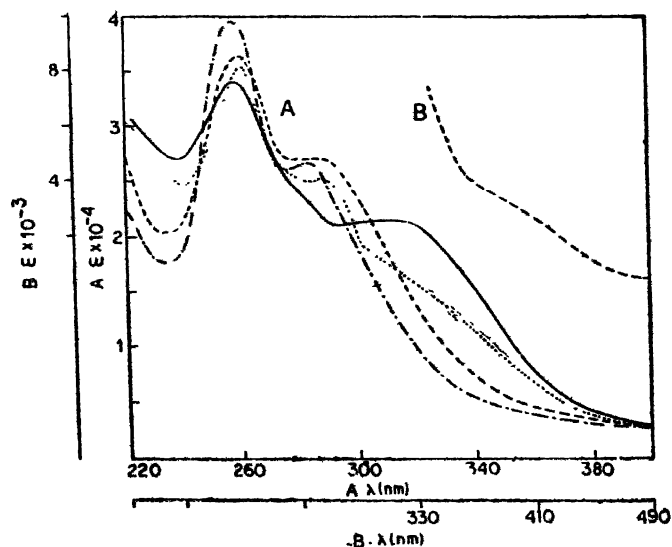
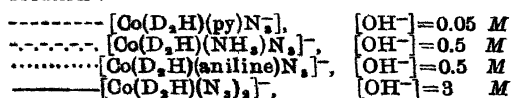


Fig. 2. U.V. Spectra of the azidocobaloximes(III) in alkaline solution :



bands may now be observed at 260 nm, 285 nm and 370-380 nm (shoulders) for all the four complexes and at 320-330 nm (shoulders) for $[\text{Co}(\text{D}_2\text{H})(\text{N}_3)_2]^{2-}$ and $[\text{Co}(\text{D}_2\text{H})(\text{an})\text{N}_3]^-$. The 260 nm bands are due to a red shift of the 245 nm bands of the acid solutions of these complexes. What were apparently single bands in $[\text{Co}(\text{DH})_2(\text{N}_3)_2]^-$ and $[\text{Co}(\text{DH})_2(\text{an})\text{N}_3]^-$ have now been split into two, one at 285 nm and the other at Ca. 320 nm (shoulder). The 285 nm bands appear almost unchanged in all the four complexes and are clearly MLCT bands due to transitions of the type $d\pi(t_{2g}) \rightarrow \pi^*(\text{DMG})$. The π^* -orbital on the donor nitrogen (DMG) atom in the conjugate bases would be at a higher energy level than the respective acid forms and a $d\pi - \pi^*$ MLCT transition would clearly be blue-shifted in the conjugate-base. The shoulders at 370-380 nm could be assigned to $\sigma(\text{DMG}) \rightarrow \sigma^*$ LMCT transitions. These transitions in the spectra of the acid-forms were obviously masked by the more intense bands at shorter wavelengths and are now red-shifted.

The CT spectrum of $\text{Co}(\text{DH})_2(\text{N}_3)_2^-$ in alkaline solution shows an intense absorption at 330 nm and $\text{Co}(\text{D}_2\text{H})(\text{an})\text{N}_3^-$ also shows a shoulder at this wavelength. These bands are obviously much less affected by pH than the MLCT bands mentioned above. In the diazido-complex this band may be assigned to a $(\text{N}_3^-)\sigma \rightarrow \sigma^*(d_z^2)$ LMCT transition while in $\text{Co}(\text{D}_2\text{H})(\text{an})\text{N}_3^-$ a $(\text{an})\sigma \rightarrow \sigma^*(d_z^2)$ LMCT may give this band. On this scale, LMCT bands corresponding to transitions from NH_3 or py to metal would be expected to occur at shorter wavelengths. The occurrence of the aniline \rightarrow metal LMCT band at a longer wavelength is also in accordance with the trend in ionization potentials. Accordingly the highest filled MO in aniline is at a higher energy level than the corresponding MO's in NH_3 and py and this trend should be reflected in the position of the LMCT bands arising from transitions from these MO's.

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