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Reaction of Diaquocobaloxime with Nitrosobenzene

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ABSTRACT The reaction of diaquocobaloxime with nitrosobenzene produces azoxybenzene, azobenzene and a solid, which is a mixture of different cobaloximes. Properties and composition of this solid are described.

Minor amounts of cobaloxime phenylnitroxide and phenylnitroxide radicals are also formed. Their formation is strongly solvent dependent.

In 1971, it has been reported that Co(II) cobaloxime prepared *in situ* from $CoCl_2 \cdot 6H_2O$ and $dmgH_2$, upon reaction with nitrosobenzene gave rise to the phenylnitroxide radical $PhNHO^{\cdot}$ (I), (Swanwick and Waters 1971). It has been suggested that water is a hydrogen source:

$$Co(II) + PhNO + H_2O \xrightarrow{\text{methanol/water}} Co\text{–}OH(III) + \underset{I}{PhNHO^{\cdot}} \qquad (1)$$

No other products of this reaction have been reported. There is also no convincing evidence that the reaction proceeds according to reaction (1). Other possible sources of hydrogen are: organic solvent, OHO bridge of cobaloxime and methyl groups of dmgH ligand. Other radical and organic products could be formed. Also the nature of the cobalt species produced deserves further study. All these possibilities are discussed in this paper.

We have observed (Tyrlik *et al.* 1982) that changing the solvent of reaction (1) changes also the EPR signal of the studied solution. Thus, in aqueous acetone (acetone : water = 1 : 1 vol) diaquocobaloxime (II) reacts with PhNO to produce

cobaloxime phenylnitroxide radical (III) according to reaction (2)

$$\underset{\text{II}}{Co(dmgH)_2 2H_2O} + PhNO \xrightarrow{\text{acetone:water (1:1)}} \underset{\text{III}}{Co(dmgH)_2 N(Ph)O^{\cdot}} \qquad (2)$$

However, upon decrease of water content in the solvent, $PhNHO^{\cdot}$ is formed. These observations contradict the formulation of reaction (1) and indicate strong solvent dependence of this reaction.

Beside the radical compounds formed in the reaction of diaquocobaloxime and PhNO, azoxy- and azobenzene and a solid IV were also isolated. This paper describes the influence of solvents on radical products and the composition of the solid product.

Experimental

Materials and Reactions

Nitrosobenzene was prepared according to established practice from $PhNO_2$ and Zn dust (Vogel 1962). Diaquocobaloxime, $Co(dmgH)_2 2H_2O$, was prepared as previously described (Schrauzer 1968).

Reaction between II and PhNO was carried out under an argon blanket (deoxygenated using BTS catalyst and molecular sieves) but all other materials were handled in air. In a typical reaction 0.66 g (6 mmol dm^{-3}) of PhNO in 60 cm^3 of solvent was added to 1.95 g (6 mmol dm^{-3}) of II using a stainless steel needle and argon overpressure. Upon addition of the blue solution of PhNO to the orange brown $Co(dmgH)_2 2H_2O$ the mixture turned brown-black. A solid of the same colour precipitated as the reaction proceeded. The reaction mixture was stirred at room temperature, and samples were withdrawn for EPR (anaerobic EPR tubes) and GC analyses.

The brown-black solid IV was filtered off and the filtrate was analyzed using GC and TLC. It contained PhNO, azoxybenzene, azobenzene but negligible amounts of $dmgH_2$.

Spectra

The EPR spectra were recorded using a JES-ME-3X type spectrometer in X band and having a field modulation of 100 kHz. Conditions at which the spectra have been recorded are given in the caption of Fig. 1. Routing IR spectra were recorded in KBr or nujol using a Beckmann Acculab apparatus.

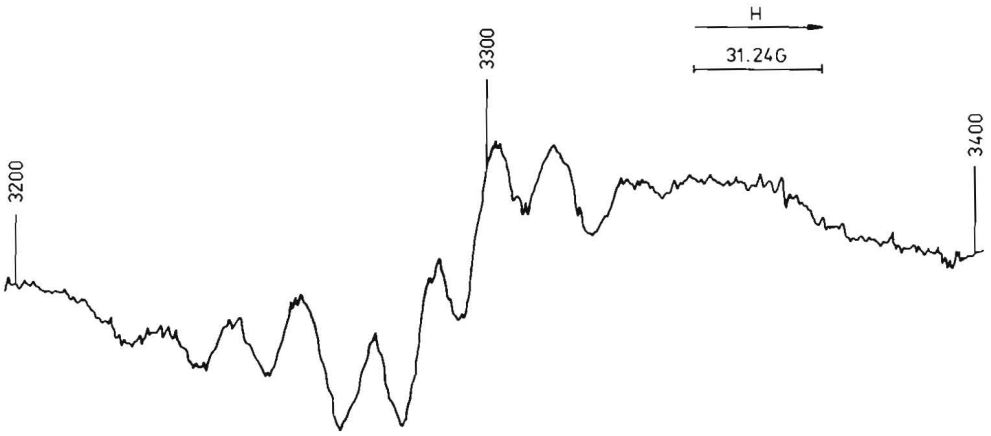

Fig. 1. EPR room temperature signal of cobaloximephenylnitroxide radical as a reaction product of II with C_6H_5NO in CH_3CN (molar ratio = 1).

Thermogravimetric Analysis

Thermograms were obtained with the MOM Derivatograph type OD-102 equipment adjusted to give a linear temperature rise between 20 and 400°C and a heating rate of 3°C/min. The samples were introduced using standard ceramic crucibles. Thermograms were recorded in an argon stream. The sensitivity of the balance was 0.5 mg.

Reactions of IV

Alkaline Hydrolysis

In a typical reaction, 0.1 g of IV was stirred at room temperature with 5 cm^3 of 1.25 dm^{-3} methanolic solution of NaOH. Ethylbenzene ($\sim$ 0.5 mmol dm^{-3}) was added as the internal standard for gas chromatography. The aniline content was determined by GC.

The Reaction with Acetyl Chloride

IV (0.3 g) suspended in 5 cm^3 of Et_2O was treated with 0.5 cm^3 of acetyl chloride for 15 hr in an attempt to capture aniline precursor, Co-NHPh. Trace amounts of acetanilide were observed.

Results and Discussion

Stoichiometry of the Reaction

If diaquocobaloxime is allowed to react with nitrosobenzene for a prolonged time (20-40 hr), a brown-black solid IV precipitates in the reaction mixture. The precipitate contains nearly all cobalt taken for the reaction. Starting from the molar ratio cobaloxime : PhNO = 1 : 1, one can detect, even after a very prolonged reaction time, free nitrosobenzene in the solution together with azoxy- and azobenzene. Other possible reaction products: phenylhydroxylamine, azoxy- and azobenzene are soluble reaction products. Unreacted nitrosobenzene can also be detected in the solution even after a very prolonged reaction time, even for cobaloxime: PhNO molar ratio = 1. Other possible reaction products: phenylhydroxylamine and *p*-aminophenol are absent. Thus, for the molar ratio of II : PhNO = 1 and prolonged reaction times the stoichiometry material balance is as follows:

$$\underset{}{Co(dmgH)_2 2H_2O} + PhNO \rightarrow \underset{}{IV} + \underset{(25\%)}{PhN(O)NPh} + \underset{(10\%)}{PhN{=}NPh} + \underset{(40\text{-}45\%)}{PhNO} \qquad (3)$$

For shorter reaction times (15-60 min), radicals I and III can be detected by EPR. In this case, only traces of azoxy- and azobenzene are observed. Concentration of I and III is probably very low.

Solvent Dependence of Radical Formation

From preliminary experiments, we learned that the reaction of cobaloxime with PhNO is strongly solvent dependent. The EPR spectra of the reaction products in several solvents have been measured. Either the spectrum of $PhHNO^{\cdot}$ (Swanwick and Waters 1971) or the spectrum ascribed to cobaloxime phenyl nitroxide (Fig. 1) could be observed. Radical products dependence on the solvents are classified in Table 1.

Table 1. EPR signals of the product of the reaction of $Co(dmgH)_2 \cdot 2H_2O$ and PhNO in different solvents (room temperature).

Insolubility of reactants	**No detectable signal**	**Signal of $PhNHO^{\cdot}$**	**Ten lines signal (Fig. 1)**
hexane	CH_3OH	EtOH	CH_3CN
benzene	CH_3NO_2	BuOH	DMF
toluene	$PhNO_2$	acetone	acetone:water = 1:1
carbon tetrachloride	acetylacetone	$EtCOCH_3$	acetone:D_2O = 1:1
		THF	$CHCl_3$

Table 2. Composition of different cobaloxime structures – possible components of IV.

Cobaloxime	Symbol	C %	H %	N %
$Co^{II}(dmgH)_2\,2H_2O$	II	29.60	5.50	17.20
$Co^{III}(dmgH)_2(PhNO)$	V	42.42	4.82	17.68
$Co^{III}(dmgH)_2(PhNO)(H_2O)$	VI	42.00	5.20	14.00
$Co^{III}(dmgH)_2N(Ph)OCo^{III}(dmgH)_2$	VII	38.00	4.80	18.40
$Co^{III}(dmgH)_2N(H)OCo^{III}(dmgH)_2$	VIII	31.60	4.60	20.70
$Co^{III}(dmgH)_2OCo^{III}(dmgH)_2$	IX	32.32	4.71	18.83
$H_2OCo^{III}(dmgH)_2OCo^{III}(dmgH)_2$	X	31.36	4.90	18.30
$H_2OCo^{III}(dmgH)_2OCo^{III}(dmgH)_2H_2O$	XI	30.47	5.08	17.75
$Co^{III}(dmgH)_2OCo^{III}(OH)N(C_6H_5)O$	XII	36.40	4.33	13.00

The $PhNHO^{\cdot}$ is formed upon the hydrogen transfer reaction. The radical is formed in alcohols as well as in ketones, formamide and THF. On the other hand, $PhNHO^{\cdot}$ is neither formed in acetone/water nor in acetone/D_2O mixtures. This suggests that the hydrogen in $PhNHO^{\cdot}$ does not stem from the protic solvent. It is likely that it is transferred from the OHO bridge of coordinated dimethylglyoximates.

General Description of IV

The IV is a brown-black solid soluble in chloroform, methanol, ethanol and water, It is moderately soluble in hexane, benzene, carbon tetrachloride, ethyl ether and ethyl acetate. The IV is not a homogeneous substance, but the attempts to get pure individual compounds out of it failed. Thin layer chromatography indicates unstable nature of IV which basically precludes purification by chromatography. Soxhlet extraction of IV with ethyl ether gives rise to small amounts of PhNO and azoxybenzene.

Elemental Analysis of IV

Calculated compositions of different cobaloxime complexes which may be formed in the reaction (Schrauzer 1968) are given in Table 2. Observed composition of IV is 33.3% C, 4.35% H and 16.26% N. Binuclear compounds VII-XII have composition close to IV. The major component of IV could be oxygen bridged binuclear cobaloxime IX contaminated by compounds possessing lower nitrogen content, *e.g.* XII. Simple structures like IV and VI can be excluded.

EPR Spectra of IV

Solutions of IV in $CHCl_3$, methanol and water do not give rise to EPR signal. However, IV is paramagnetic and its EPR signal in the solid is shown in Fig. 2

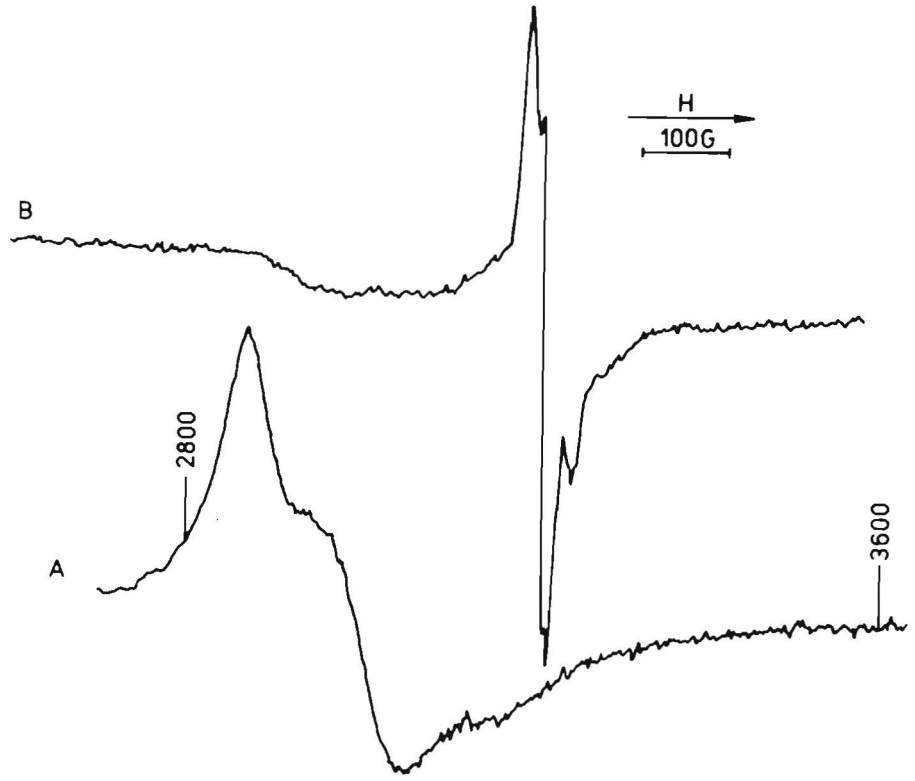

Fig. 2. EPR signals of: **A**. solid diaquocobaloxime; **B**. solid IV. Spectra recorded in 135 K.

together with the signal of the solid starting material – diaquocobaloxime. The IV does not absorb at all in the region characteristic for absorption of diaquocobaloxime, which indicates that diaquocobaloxime has reacted completely. Soxhlet extraction of IV with ethyl ether does not change the EPR signal. It is also not changed upon the prolonged storage in the air. Observed signal closely resembles that which (Chatgilialoglu and Ingold 1981) appears in the solid PhNO upon irradiation. Paramagnetic component could therefore be PhNO complexed with a cobalt diamagnetic species.

Another possibility is the presence of a mixture of paramagnetic substance V or XII and a diamagnetic compound IX or the alike.

Thermogravimetry of IV

Up to 130°C, there is practically no loss of mass (Fig. 3). First significant mass loss occurs between 130-155°C. Several cobaloximes which were studied by ther-

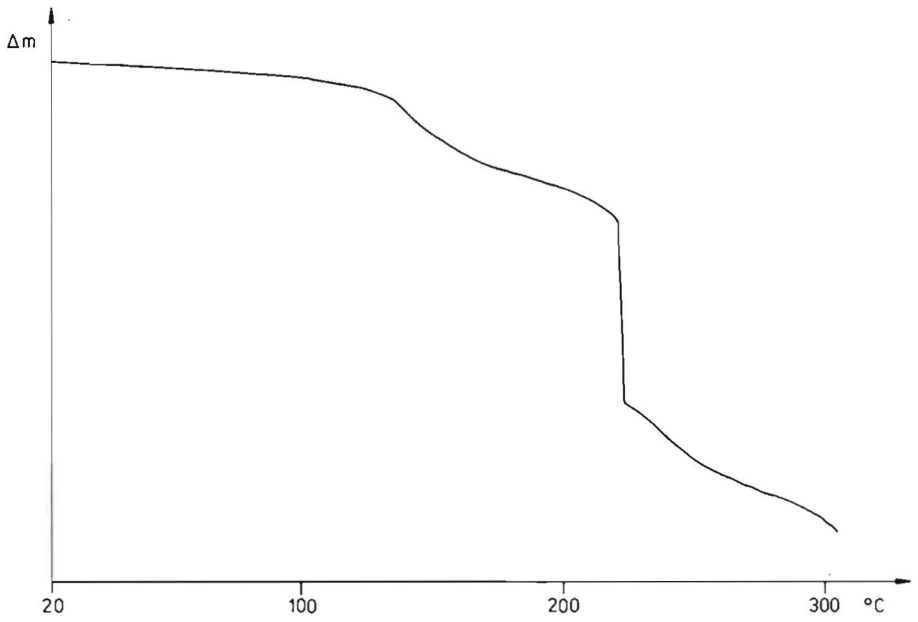

Fig. 3. Mass loss curve of IV; Δm – sample weight.

mogravimetry (Malinowski *et al.* 1980) possessed axial ligands like H_2O, CH_3OH, CH_3COCH_3. All these ligands dissociate in temperatures up to 110°C showing distinctive loss of mass. It may, therefore, be concluded that there is no easily dissociating ligand in IV. Violent decomposition at 215°C is similar to explosion of other cobaloximes occurring at ~ 215°C.

IR Spectra of IV

In the infrared spectrum of IV, the numerous additional bands in comparison with starting material have been observed (Fig. 4, Table 3). The formation of new Co—N and Co—O bonds may have been expected. The literature reports the

Table 3. Far infrared band positions for diaquocobaloxime and IV.

$Co(dmgH)_2 2H_2O$										**values in cm^{-1}**					
370								510		665				750	760
Product IV										**values in cm^{-1}**					
253	272	340	408	420	440	460	485	510	520	565	620	690	740	750	

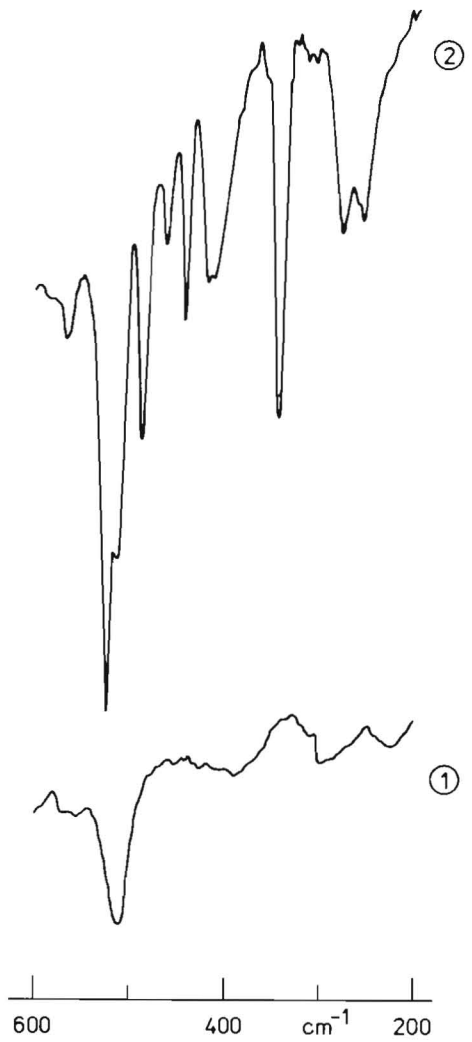

Fig. 4. IR spectra of: **1**. diaquocobaloxime; **2**. IV.

existence of the bands in the region 500-300 cm^{-1} (Table 4) without any attempts to assign them (Cleare and Griffith 1967, Wieghardt and Siebert 1970).

A rather useful case for comparison is $Co(CO)_3NO$ where Co—N stretching vibration is observed at 565 cm^{-1} (Dowell *et al.* 1961). The stretching vibration of Co—O in different compounds was noted between 250 and 450 cm^{-1} (Table 3). The IR spectrum of IV supports the possibility of the existence of newly formed Co—O—Co and Co—N—O—Co (or Co—NH—O—Co) structural units. Also

Table 4. Literature IR data for Co—N and Co—O compounds.

Compounds	ν(Co—N) cm^{-1}	ν(Co—O) cm^{-1}	other νcm^{-1}	Literature
$Co(dmgH)_2CN \cdot py$	$514(\nu Co\text{–}N\ dmgH)_2$	$370_{(Co\text{–}OH_2O)}$	$1730_{(OHO)}$	Yamanaki and Honokabe (1971)
$CH_3Co(dmgH)_2H_2O$	512			Yamanaki and Honokabe (1971)
$K[Co(dmgH)_2OH]NCO$	514 $435_{Co\text{–}N(py)}$			Szafrański and Popova (1975)
	513 $464_{Co\text{–}N(py)}$			
$Co(dmgH)_2py \cdot NCS$	$377_{Co\text{–}N(NCS)}$			Rutherford and Thorton (1980)
$[Co(dmgH)_2(NO)H_2O][Co(dmgH)_2NO_2] \cdot 2H_2O$			$1628_{(NO)}$	Chatgilialoglu and Ingold (1981)
		$429_{\nu s(Co\text{–}O)}$		
$[(NH_3)_4Co(NH_2)O_2Co(NH_3)_4]Cl_4 3H_2O$		$374_{\nu as(Co\text{–}O)}$		Shibahara and Mori (1978)
		$620_{\nu s(Co\text{–}O)}$		
$[(NH_3)_5CoO_2Co(NH_3)] \cdot Cl_5$		$440_{\nu as(Co\text{–}O)}$		Shibahara and Mori (1978)
$Co(CO)_3NO$	$565_{Co\text{–}N(NO)}$		$1822_{(NO)}$	Dowell *et al.* (1961)
$[Co_2(py)_4(OHO)_2]py_2$		360–340		Cleare and Griffith (1967)
$[CoClpyNO_3]_2$	$230_{Co\text{–}N(py)}$	$260_{\nu(Co\text{–}O)(NO_2)}$		Pherson and Losario (1975)
$Co(py)_2(NO_3)_2$	$250_{Co\text{–}N(py)}$	$285_{\nu Co\text{–}O(NO_2)}$		Pherson and Losario (1975)
$\{Co_2[NO_2(OH)_2](NO_2)_6\}^{3-}$	318, 350, 401, 437, 512 (without individual assignment)			

compounds possessing Co—N—Ph structural unit are possible. The IR spectrum of IV after ether extraction does not change.

The formation of considerable amounts of azoxy- and azobenzene in the reaction (3) must be due to deoxygenation of PhNO . The probable acceptor of oxygen is Co(II) cobaloxime forming Co(III) cobaloxime. Diamagnetic Co(III) cobaloxime should, therefore, be formed at the expense of paramagnetic Co (II) cobaloxime. This is indeed confirmed by the EPR study as there is no signal of Co(II) cobaloxime in IV. EPR spectrum of solid IV consists of asymmetric triplet which is very similar to the spectrum of solid PhNO . It seems that Co(III) cobaloximes form a matrix for $PhNO^{\cdot}$ radicals. Their coordination seems to be rather strong as soxhleting of IV with diethyl ether leaves EPR signal intact. Another possibility is $PhNH^{\cdot}$ radical complexed with cobaloxime. In fact, alkaline hydrolysis of IV gives minor amounts of aniline and acetanilide which supports this suggestion.

Thermogravimetry confirms the conclusions that, in IV, there is no volatile axial ligands connected to the cobaloxime, as there is no mass loss in the temperature range 95-115°C.

It may be due to the fact that axial positions are used for formation of Co(III)—O—Co(III) frame-work and for the Co(III)—N bonds, both of which were observed by IR.

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تفاعل ثنائى اكوكوبالوكسيم مع نتروبنزين

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ان تفاعل ثنائى اكوكوبالوكسيم مع النتروبنزين ينتج آزوكسى بنزين وآزوبنزين وجزءا صلبا هوخليط من كوبالوكسيمات مختلفة وقد وصفت خواص وتركيب هذا الجزء الصلب.

وكذلك تتكون كميات قليلة من الكوبالوكسيم فنايل نتر و أوكسيد، وفنايل نتر و اوكسيد وان تكوينها ليعتمد اعتمادا كبيرا على نوع المذيب.