Inorganica Chimica Acta, 98 (1985) 55–58

Influence of the Oxygen on Cobalt(II) Thiosemicarbazide Complexes in Various Solvents

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Received July 20, 1984

Abstract

The influence of bubbling oxygen into solutions containing cobalt(II) and thiosemicarbazide was studied by spectrophotometry. Several solvents were used: ethylacetate, 1-propanol, ethanol, propylencarbonate, dimethylacetamide and water. The results obtained suggest that the main effect is due to the free ligand oxidation, and that cobalt(II) probably coordinates O_2 molecules during complex formation. The oxidation to cobalt(III) seems to occur only in water, probably because of high donicity.

Introduction

A recent paper was published about the formation equilibria of cobalt(II)–thiosemicarbazide complexes in various solvents [1]. The investigation was carried out in a nitrogen atmosphere, as the presence of air influences the reaction time of the chemical system.

In this paper the formation equilibria were studied in an oxygen atmosphere in order to explain the previously observed influence of air. Some spectrophotometric data were collected by varying either the concentration ratio of the reagents or the time from the beginning of the reaction.

The solvents used were the same as those used in previous work *i.e.,* ethylacetate (EtAc), n-propanol (n-PrOH), ethanol (EtOH), propylencarbonate (PC), dimethylacetamide (DMA) and water.

Experimental

Solvents were dried and purified in the usual way [2]. The water content of the products was determined using Karl-Fischer reagent and was found to be less than 0.05% in all cases.

Thiosemicarbazide (Fluka A6) was recrystallized from bidistilled water. Cobalt(II) perchlorate (Fluka A6), previously dried at 90 °C for 48 h, contained six crystallization water molecules. Due to the cobalt concentrations this contribution to the total water content was less than 30 ppm. The samples obtained by mixing cobalt(II) and ligand source solutions, each one pre-treated with nitrogen for 30 minutes, were submitted to nitrogen or oxygen atmosphere (flow = 105 ml/min).

All measurements were done by spectrophotometry in the visible region, which also allowed examination of configurational changes of cobalt(II). Solutions were 2.4×10^{-4} mol L^{-1} in metal and $0.48 \div 7.2 \times 10^{-3}$ mol L^{-1} in ligand.

Absorbance variations in the visible region were recorded as a function of the time from mixing.

By UV spectrophotometry, standard preliminary tests were also performed on ligand solutions in every solvent to check the influence of oxygen and nitrogen on the ligand. Both visible and UV spectra were recorded on a Perkin-Elmer spectrophotometer at 25 ± 0.1 °C, using quartz cells of 0.2 and 5 cm path lengths.

Results

The spectrophotometric behaviour of each reagent solution was checked in all the solvents.

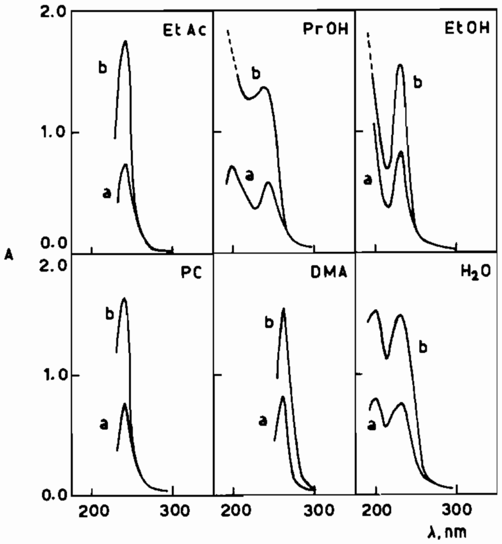


Fig. 1. UV spectra of thiosemicarbazide solutions in various solvents; *a*: without oxygen bubbling; *b*: after two hours of oxygen bubbling. Blank: solvent.

0020-1693/85/$3.30

Cobalt(II) perchlorate and thiosemicarbazide (Ts) solutions were stable for several days in the nitrogen atmosphere, while the ligand solution showed a spectral modification under O_2 (Fig. 1). The spectra of complexes only under nitrogen became stable after 5–120 minutes, depending on the solvent used.

Under oxygen, the spectra varied with time from mixing of reagents in several different ways depending on solvents and initial concentration ratios Ts/Co. Two classes of Ts/Co ratios were identified in the solvents to display significant variations. These two classes can be regarded as 'low' ratio and 'high' ratio. The differences between the values used in the various solvents are due to the different stabilities of the complexes. Values used are listed below:

Solvent	'low' ratio Ts/Co	'high' ratio Ts/Co
EtAc	2	10
1-PrOH	2	10
EtOH	2	10
PC	5	10
DMA	5	10
Water	10	30

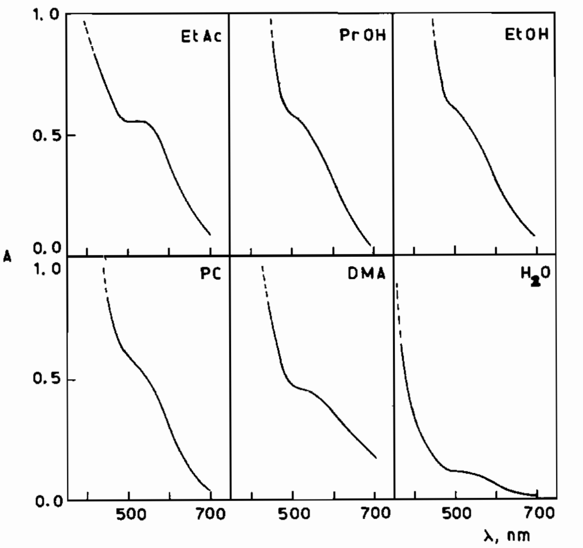


Fig. 2. Visible spectra of cobalt(II)–thiosemicarbazide complex after oxygen bubbling for one hour. $C_M = 2.4 \times 10^{-4}$ M; Ts/Co = 10; d = 5 cm; blank = solvent.

In Fig. 2 the spectra of the formed complexes are reported after one hour under oxygen using 'high' ratios. These spectra generally agree with those obtained under nitrogen.

The trend of the absorbance *vs.* time under oxygen and nitrogen is reported in Fig. 3 at a single wavelength using both 'low' and 'high' ratios. In PC and DMA the spectra obtained at 'low' ratios differ from those obtained both at 'high' ratios and in the other solvents. These spectra accounted for a tetrahedral configuration [3] of cobalt(II) as shown in Fig. 4,

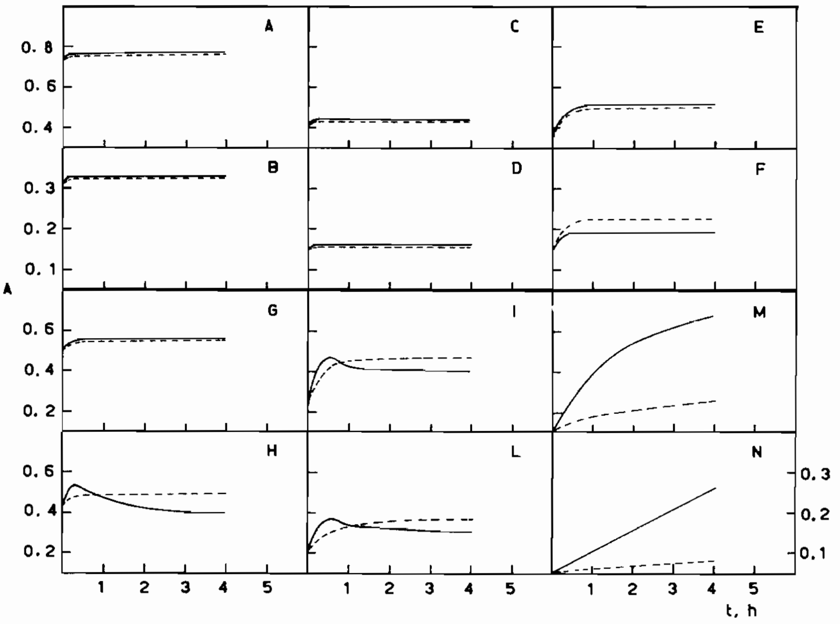


Fig. 3. Absorbance values *vs.* time of the cobalt(II)–thiosemicarbazide complex at different ratios C_L/C_M in oxygen (——) and nitrogen (– – –) atmosphere. $C_M = 2.4 \times 10^{-4}$ M; d = 5 cm; blank = solvent; EtAc = 537 nm; 1-PrOH = 540 nm; EtOH = 540 nm; PC = 530 nm; DMA = 540 nm; Water = 520 nm; A) $C_L/C_M = 10$; B) $C_L/C_M = 2$; C) $C_L/C_M = 10$; D) $C_L/C_M = 2$; E) $C_L/C_M = 10$; F) $C_L/C_M = 2$; G) $C_L/C_M = 10$; H) $C_L/C_M = 5$; I) $C_L/C_M = 10$; L) $C_L/C_M = 5$; M) $C_L/C_M = 30$; N) $C_L/C_M = 10$.

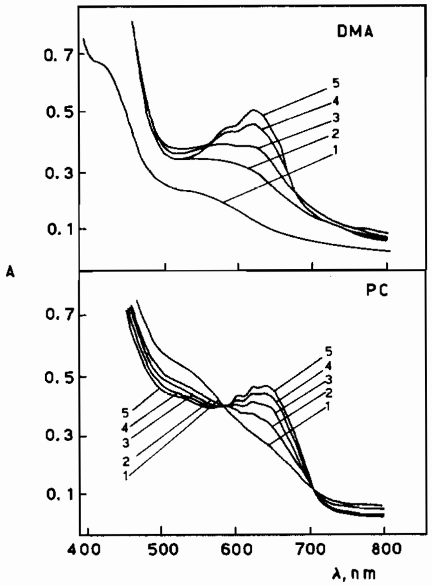


Fig. 4. Visible spectra of the complex in PC and DMA. $C_M = 2.4 \times 10^{-4}$ M; d = 5 cm; blank = solvent. PC: without oxygen (1), after 1 h (2), 3 h (3), 5 h (4), 6 h (5) of oxygen bubbling. DMA: without oxygen (1), after 15 min (2), 1 h (3), 2 h (4), 3 h (5) of oxygen bubbling.

while in the other cases the spectra displayed an octahedral coordinated cobalt(II).

When water is used as solvent the absorbance displayed in oxygen is much greater than in nitrogen, while such a difference is very limited in the other solvents.

All complexes obtained under oxygen atmosphere at 'low' ratios were treated with excess of ligand, to obtain a 'high' ratio. In all the solvents examined the spectra displayed after a few minutes became very similar to those resulting from bubbling oxygen in solutions of reagents with 'high' initial ratio.

Discussion

From the results obtained, some aspects of the behaviour of the examined chemical systems under oxygen atmosphere can be pointed out. Whilst free cobalt was found to be indifferent to oxygen, the free ligand Ts displayed a spectral change when submitted to it (Fig. 1). An absorbance increase is a general rule in all the examined solvents, even if differences cannot be easily estimated. This behaviour appears to account for a Ts oxidation, resulting in the formation of disulphide as reported elsewhere [4–6] and described for thio-group [7, 8], available from tautomeric equilibrium.

In EtAc, PrOH and EtOH the influence of oxygen on the complex formation seems to be very low. Spectra at 'high' Ts/Co ratios do not differ from those obtained under nitrogen. When these ratios become 'low' a lower absorbance is displayed (Fig. 2), but further ligand addition causes the same absorbance values to rise as with 'high' initial ratios. It is in such a way that free Ts oxidation can be assumed, removing the ligand available for complexation.

Due to the high complex stability, this effect becomes important on complex formation only when ligand is not in excess.

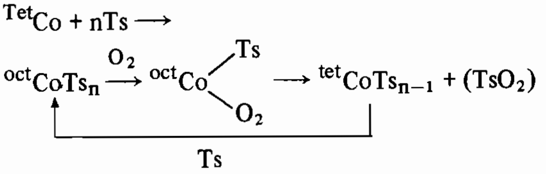
In PC and DMA the complexes formed at 'low' Ts/Co ratios (in this case 'low' means 5 instead of 2 as for the above discussed solvents) are strongly modified by oxygen, accounting for weaker complexes. Moreover with PC and DMA the decrease of available ligand causes the formation of a tetrahedral complex instead of the original octahedral one [1], as shown in Fig. 4.

This appearance of a species with lower absorptivity (at the wavelength of the octahedral maximum) justifies the trend displayed in Fig. 3. However in these solvents further ligand addition, after oxygen bubbling at 'low' ratios, restores the octahedral form displayed using 'high' initial ratios.

From such observations it can be concluded that complexes are less sensitive to oxygen the more stable they are. The stability order found in the previous paper under nitrogen agrees with this assumption: EtAc ≃ PrOH > EtOH > PC > DMA. Furthermore, under nitrogen, tetrahedral complexes were also found in PC and DMA, even if quantitative equilibrium data are assumed to be mainly due to the oxidation of the free ligand.

The absorbance trend *vs.* time, shown in Fig. 3 for complexes in PC and DMA accounts for a reaction taking place through an intermediate, which can explain the absorbance decrease after an initial increase.

A tentative description could be made, taking into account cobalt(II) property of coordinating oxygen [9].



$$
\begin{aligned}
&{}^{\mathrm{Tet}}\mathrm{Co} + n\mathrm{Ts} \longrightarrow \\
&{}^{\mathrm{oct}}\mathrm{CoTs}_n \xrightarrow{\mathrm{O_2}} {}^{\mathrm{oct}}\mathrm{Co}\genfrac{}{}{0pt}{}{\diagup \mathrm{Ts}}{\diagdown \mathrm{O_2}} \longrightarrow {}^{\mathrm{tet}}\mathrm{CoTs}_{n-1} + (\mathrm{TsO_2}) \\
&\uparrow\underline{\qquad\qquad\qquad\qquad\qquad\qquad}\,\big| \\
&\qquad\qquad\qquad \mathrm{Ts}
\end{aligned}
$$

Species involved in the above qualitative scheme are reported without considering charges, solvent coordination, or possible proton dissociation equilibria. In particular, (TsO_2) describes the product and/or products obtained from Ts oxidation, instead of a well-identified compound. The above scheme could be seen as being a more complete description (of a metal catalyzed oxidation) with respect to the generally accepted one [10]: in such a way the (TsO_2) is better represented by Ts· radical, undertaking dimerization, and O_2^-, re-entering the oxidation process until peroxide or water is formed.

We can also suggest similar reactions for EtAc, PrOH, EtOH even if the lack of a configurational change did not provide evidence to support the presence of an intermediate.

With water the situation is less simple. The only possible configuration is octahedral and in addition the complex is so weak that low Ts/Co ratios are not available.

However, the complex formed in water shows a spectrum with large differences between values obtained in oxygen and nitrogen. This behaviour can be caused by the formation of a cobalt(III) complex [11] with higher absorptivity. It can thus be concluded that in water cobalt(II) is oxidized when coordinated by Ts, in addition to the oxidation of Ts itself.

The cobalt oxidation can be assumed to take place only in water, whilst in other solvents used, a decrease in cobalt(II) electronic density could be induced by electron attraction of coordinated ligand and/or oxygen. This effect probably does not lead to the separation of formally oxidized cobalt(III), except for water.

The oxidation in water agrees with the highest donor number [12] displayed by this solvent.

The solvent donicity influences the redox potential of a couple, due to an interaction which increases with the acceptor power of each species [13, 14]. When both oxidized ($CoTs_3^{+3}$) and reduced ($CoTs_3^{+2}$) forms are positively charged (thus mainly acting as acceptors) the former is more stabilized than the latter.

Acknowledgement

This work was carried out with financial support from the Consiglio Nazionale delle Ricerche (C.N.R., Rome), which also awarded a grant to one of us (A.M.G.).

References

1 V. Carunchio, A. Messina, R. Bucci and A. M. Girelli, *Ann. Chim. (Rome), 74,* 231 (1984).

2 J. A. Riddick and W. B. Burger, 'Techniques of Chemistry' Vol. 2, Wiley-Interscience, 1970.

3 C. J. Ballhausen and Chr. Klixbull Jørgensen, *Acta Chem. Scand., 9,* 397 (1955).

4 T. N. Chernova, S. V. Lugovoi and V. D. Chistota, *Sb. Nauch. Tr., Magnitogorsk. Gornomet. Inst., 112,* 138 (1973); *Chem. Abstr., 80,* 127500v (1974).

5 S. V. Lugovoi and T. N. Chernova, *Nov. Polyarogr., Tezisy Dokl. Vses. Soveshch. Polyarogr.,* in Stradins (Ed.), 6th 1975, 132; *Chem. Abstr., 85,* 200064r (1976).

6 U. D. Gomwalk and A. McAuley, *J. Chem. Soc. (A),* 2948 (1968).

7 T. J. Wallace and A. Schriesheim, *J. Org. Chem., 27,* 1514 (1962).

8 T. J. Wallace, A. Schriesheim and W. Bartok, *J. Org. Chem., 26,* 1311 (1963).

9 J. Burgess *et al.*, 'Inorganic Reaction Mechanisms' Vol. 1, part 1, Chap. 3, The Chemical Society, London, 1971.

10 G. Capozzi and G. Modena, 'The Chemistry of the Thiol Group', Vol. II, pg. 806, in S. Patai (Ed.), London, 1974.

11 N. M. Samus' and A. V. Abbov, *Russ. J. Inorg. Chem., 6,* 1042 (1961).

12 V. Gutman and R. Schmid, *Coord. Chem. Rev., 12,* 263 (1974).

13 V. Gutman 'The Donor–Acceptor Approach to Molecular Interactions', Plenum Press, New York, 1978, pag. 121.

14 A. Messina and G. Gritzner, *J. Electroanal. Chem., 101,* 201 (1979).