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Cobalt(II) Complexes with Bidentate Schiff Bases as the Dioxygen Carriers

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The new group of high-spin oxygen carriers, containing the cobalt(II) ion coordinated with the bidentate Schiff base, was investigated. The formation of the pentacoordinated complex Co(Schiff base)$_2$–amine under oxygen-free conditions was proved spectrophotometrically. Stability constants for the pentacoordinated complexes were determined. The monomeric character of the formed dioxygen adduct was proved by the EPR, spectrophotometric and volumetric methods. A new method of determination of the stability constants for the oxygenated complexes, based upon the volumetric measurements, is proposed.

Introduction

Chelate compounds of cobalt(II) with Schiff bases are known as the systems reversibly bonding molecular oxygen. The complexes with tetradentate Schiff bases have been broadly investigated [1–7, 16]. They have the square planar structure and contain the low-spin cobalt(II) ion. In solution, in the presence of additional monodentate ligand (usually nitrogen base) they have the square pyramidal structure. Complexes with the pentadentate Schiff bases are high-spin and have the structure of the trigonal bipyramid [8, 9].

The subject of our studies is the group of high-spin Co(II) complexes, whose ability to the reversible oxygen bonding has not been examined. Cobalt(II) complexes with bidentate Schiff bases have the structure of the distorted tetrahedron, both in the solid and in the non-coordinating solvents [10]. In the solid they are not able to bind the oxygen molecule, while in solution they gain this ability only at very low temperatures (–70 °C), in the absence of the nitrogen base. In the presence of oxygen, in solutions, they undergo slow, irreversible oxidation. The rate of this process depends on the solvent, temperature and type of complex. In the presence of strong σ-donor nitrogen ligands the complexes under study are able to bind the oxygen molecule in a couple of cycles, at temperatures around 0 °C.

Our studies concern the explanation of the phenomena combined with the formation of the complex capable of the dioxygen uptaking and the determination of the structure of the dioxygen adduct.

Experimental

Co(II) complexes with the bidentate Schiff bases were synthesized under inert gas atmosphere (Schlenk apparatus) as described in [10].

Amines were distilled and stored over molecular sieves. Toluene was distilled over sodium. Dimethylformamide was purified by distillation of the DMF–water–benzene heteroazeotrope, followed by distillation under diminished pressure and stored over the molecular sieves.

Electronic spectra were recorded on a Cary 14 spectrophotometer, with a thermostatic device. Temperature measurement error was 0.3 °C. Samples of complexes were weighed before each measurement in a cuvette sealed with a silica rubber stopper. Argon was passed through a cuvette, leaving it through a syringe filled with solvent, placed in a stopper. Argon was passed through for 30 min and the content of a syringe was injected into a cuvette. The cuvette was weighed again to establish precisely the amount of solvent. Amines were dosed with a calibrated microsyringe (Zimmerman). The amount of added amine was also checked by weighing.

Volumetric measurements were carried out by means of a thermostatted gas burette; the reaction vessel was closed with a rubber stopper, so that the amine could be dosed with a microsyringe.

The composition of the O_2/N_2 gas mixture at different partial oxygen pressures was established by gas chromatography.

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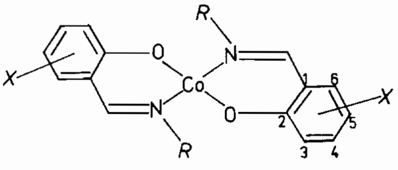
TABLE I. Names and Structures of the $Co(BSB)_2$ Complexes.



Complex	R	X
$Co(salprop)_2$	$n\text{-}C_3H_7$	H
$Co(salbut)_2$	$n\text{-}C_4H_9$	H
$Co(sal\ i\text{-}but)_2$	$i\text{-}C_4H_9$	H
$Co(sal\ s\text{-}but)_2$	$s\text{-}C_4H_9$	H
$Co(sal\ t\text{-}but)_2$	$t\text{-}C_4H_9$	H
$Co(salben)_2$	$C_6H_5CH_2$	H
$Co(bensalbut)_2$	$n\text{-}C_4H_9$	5,6-benzo
$Co(vanbut)_2$	$n\text{-}C_4H_9$	$3\text{-}OCH_3$

The EPR spectra were recorded on a JES-ME ESR 3X spectrometer (band X).

Results and Discussion

The structure of a complex responsible for the oxygen bonding, formed in the system $Co(BSB)_2$–amine–solvent (BSB = bidentate Schiff base), was determined spectrophotometrically.

Formulae of the initial complexes and abbreviations used in this paper are collected in Table I. All complexes present similar spectra in the range 500–2000 nm, characteristic for the tetragonally distorted Co(II) tetrahedral complexes [13, 14] (Fig. 1). There are some differences in the position of bands (components of the $^4T_2(F) \rightarrow {}^4T_1(F)$ transition [12, 13]), depending on the solvent used: 1320 and 870 nm in CCl_4; 1300 and 875 nm in toluene, xylene and triethylamine; 1280 and 880 nm in chloroform; 1250 and 900 nm in DMF; 1230 and 920 nm in methanol. Molar absorption coefficients ϵ do not depend on the solvent. Since ϵ is a measure of tetrahedral complex concentration, the DMF does not coordinate to metal ions. Differences in band position in DMF and in the other solvents are due to the solvation of the complex by the DMF. Drastic differences were observed in a molar absorption coefficient ϵ for the ~1300 nm component, depending on the kind of complex: from 48 for $Co(salben)_2$ to 82 for $Co(sal\ t\text{-}but)_2$. This is related to the spacial hindrance on the α-carbon of the substituent in the Schiff base and with the degree of distortion of the tetrahedral complex.

Addition of amine to the solution of a complex, under an oxygen-free atmosphere, causes intensity decay of bands characteristic for tetrahedral $Co(BSB)_2$ complex. No new bands appear in the broad concentration range of amine (Fig. 1). However, at certain amine concentrations, depending upon the kind of complex, solvent and temperature, only one band, of low intensity, is observed in the range 1500–700 nm (Fig. 2). This band, characteristic for

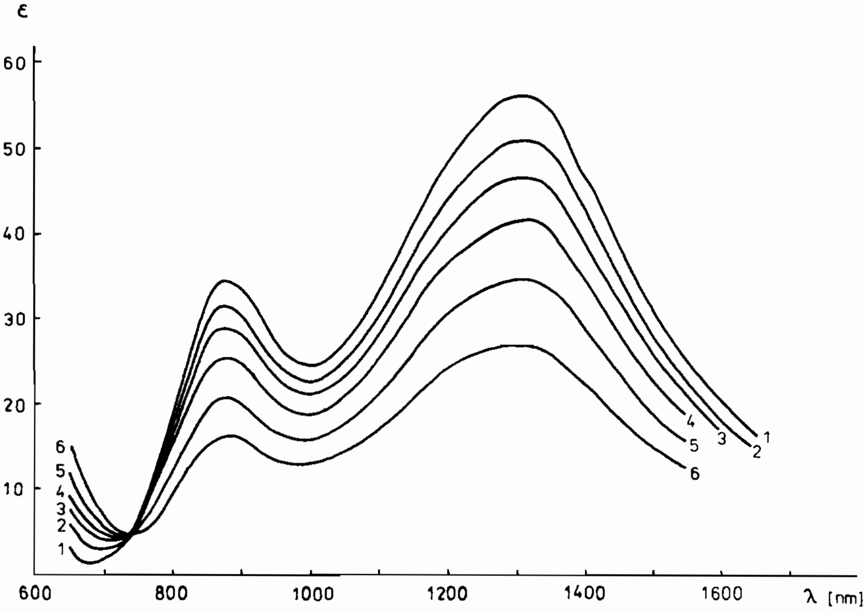


Fig. 1. Electronic spectra in the near IR of the system $Co(salbut)_2$–$n\text{-}BuNH_2$–toluene for various amine concentrations c_B: 1) 0.0 M, 2) 9.87×10^{-3} M, 3) 0.01833 M, 4) 0.02842 M, 5) 0.04563 M, 6) 0.07030 M. c_o = 0.01564 M, t = 2 °C.

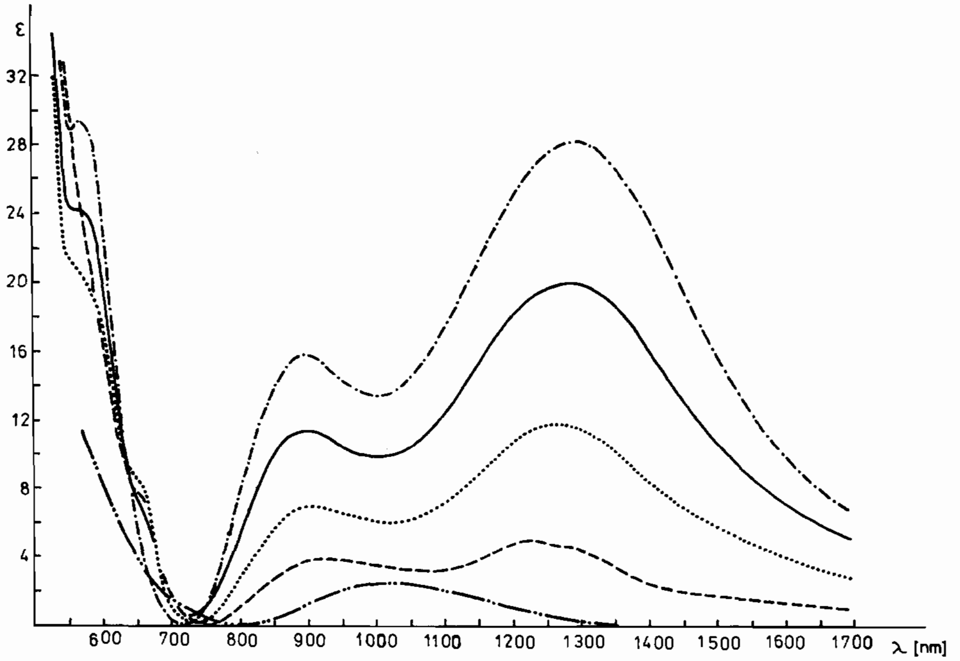


Fig. 2. *Electronic spectra in the near IR of the system Co(salbut)*$_2$*–n-BuNH*$_2$*–toluene at various temperatures:* —·—·— *60 °C,* ——— *40 °C,* ······· *20 °C,* ------- *2 °C,* $c_o = 0.01786$ *M,* $c_B = 0.07144$ *M.* —··—··— *2 °C,* $c_o = 0.01786$ *M,* $c_B = 0.5358$ *M.*

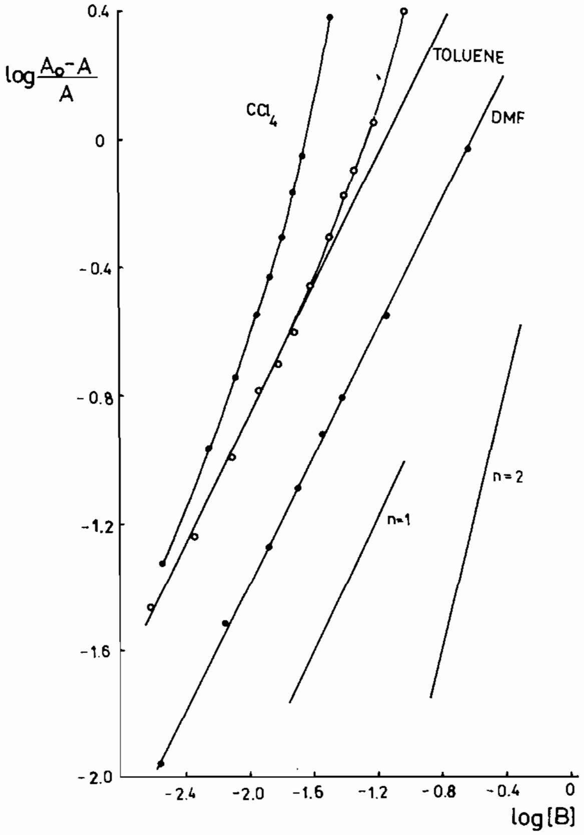


Fig. 3. Dependence of log (A_o – A)/A *vs.* log [B] for Co(salbut)$_2$–n-BuNH$_2$ system in various solvents. $c_o = 0.01564$ *M*, t = 2 °C.

the high-spin, hexacoordinated Co(II) complexes [10, 12], has the maximum at 975 nm and 1025 nm for DMF and toluene as solvents, respectively. Nevertheless the analysis of changes in spectra made by the Bent and French method [15] revealed the stoichiometry of the initially-formed complex Co(BSB)$_2$:B = 1:1 (B = amine). The plot of log[(A_o – A)/A] against log [B] (where: A_o = absorbance of the initial solution with [B] = O, A = absorbance of the solution with the amine concentration equal [B]; both absorbances were measured at 1250 and 1300 nm in DMF and toluene respectively) produced in some concentration ranges, depending on the solvent, the line of slope equal to 1, indicative of the formation of the Co(BSB)$_2$B complex (Fig. 3). The above relation allows us to establish the equilibrium constant (1), in the presence of the subsequent equilibrium (1a) for each system under investigation.

$$\mathrm{Co(BSB)_2 + B \overset{K_B}{\rightleftarrows} Co(BSB)_2B} \quad (1)$$

$$\mathrm{Co(BSB)_2B + B \rightleftarrows Co(BSB)_2(B)_2} \quad (1a)$$

The K_B values and the thermodynamic functions calculated from the van't Hoff relation by the least squares method are listed in Table II. The K_B values for toluene solutions at 2 °C exceed those for the DMF solutions. This may be due to the solvation of a complex by the DMF. The second coordination sphere makes the fifth coordination site less acces-

TABLE II. Equilibrium Constants and Thermodynamic Data for the Binding of an Axial Ligand to $Co(BSB)_2$ Complexes:

$$Co(BSB)_2 + B \overset{K_B}{\rightleftharpoons} Co(BSB)_2B$$

Complex	B	Solvent	T [°C]	K_B [M^{-1}]	ΔH [kJ/mol]	ΔS [J/K mol]
$Co(salbut)_2$	$n\text{-}BuNH_2$[a]	toluene	2	13.5 ± 0.6	−24.6 ± 2.1	−67.5 ± 6.7
			23	6.2 ± 0.4		
			43	3.4 ± 0.2		
$Co(salbut)_2$	$n\text{-}BuNH_2$[a]	DMF	−17	7.1 ± 0.5	−19.3 ± 2.1	−58.7 ± 7.9
			−11	5.8 ± 0.4		
			−6	4.9 ± 0.3		
			2	3.8 ± 0.2		
			25	2.0 ± 0.2		
$Co(salben)_2$	$BzNH_2$[b]	toluene	2	37.1 ± 1.8	−30.2 ± 2.5	−76.7 ± 8.4
			20	16.6 ± 1.2		
			32	10.7 ± 0.7		
$Co(salben)_2$	$BzNH_2$[b]	DMF	−14	12.0 ± 0.9	−24.9 ± 1.7	−75.0 ± 5.0
			−7	8.9 ± 0.6		
			2	6.2 ± 0.2		
			10	4.6 ± 0.2		
$Co(salprop)_2$	$PrNH_2$[c]	toluene	2	13.2 ± 0.7	−23.3 ± 2.1	−62.9 ± 7.5
			22	7.2 ± 0.6		
			43	3.5 ± 0.3		
$Co(salprop)_2$	$PrNH_2$[c]	DMF	2	4.7 ± 0.3		
$Co(sal\ i\text{-}but)_2$	$i\text{-}BuNH_2$[d]	toluene	2	8.5 ± 0.6	−18.6 ± 2.5	−49.9 ± 6.6
			20	4.8 ± 0.4		
			32	3.6 ± 0.3		
$Co(sal\ i\text{-}but)_2$	$i\text{-}BuNH_2$[d]	DMF	2	4.0 ± 0.2		
$Co(sal\ s\text{-}but)_2$	$s\text{-}BuNH_2$[e]	DMF	2	<0.1		
$Co(sal\ t\text{-}but)_2$	$t\text{-}BuNH_2$[f]	DMF	2	<0.1		
$Co(vanbut)_2$	$n\text{-}BuNH_2$[a]	DMF	2	5.9 ± 0.3		
$Co(bensalbut)_2$	$n\text{-}BuNH_2$[a]	DMF	2	5.7 ± 0.3		

[a] $n\text{-}BuNH_2$ = n-butylamine. [b] $BzNH_2$ = benzylamine. [c] $PrNH_2$ = n-propylamine. [d] $i\text{-}BuNH_2$ = iso-butylamine. [e] $s\text{-}BuNH_2$ = sec-butylamine. [f] $t\text{-}BuNH_2$ = tert-butylamine.

sible, and practically prevents the coordination of the sixth ligand. For this reason the pentacoordinated complex in DMF exists in a much broader amine concentration range than in non-polar solvents such as toluene and CCl_4 (Fig. 3).

Passage of oxygen through the $Co(BSB)_2$ solution with amine added is accompanied by the characteristic reversible change of colour from orange-red to red-brown. The electronic spectrum of the oxygenated system is different in comparison to that of the initial complex, mainly in the VIS and UV region (Fig. 4). Intensity of bands deriving from tetrahedral complex declines in the near infrared. Those changes are reversible for DMF solutions, when the oxygenation and deoxygenation procedures are performed at low temperature (0 °C or lower). At room temperature the reversibility is not complete. In the less polar solvents (toluene, xylene) our attempts to achieve the complete reversibility of oxygen uptake failed even at very low temperatures. This is because the initial tetrahedral complexes in such solvents are less resistible to the irreversible oxidation. For this reason the interaction of a system with oxygen was studied mainly for DMF solutions.

Intensity decay of the absorption bands in the range of 1800–700 nm, caused by the passage of oxygen through a solution, gets larger with the increase of the added amine concentration at constant partial oxygen pressure (1 atm, t = 2 °C). The amount of oxygen consumed increases with the amine concentration, to a certain limit. Depending on the system, this limit is 50–80% of the molar content of the cobalt present in solution. At the same

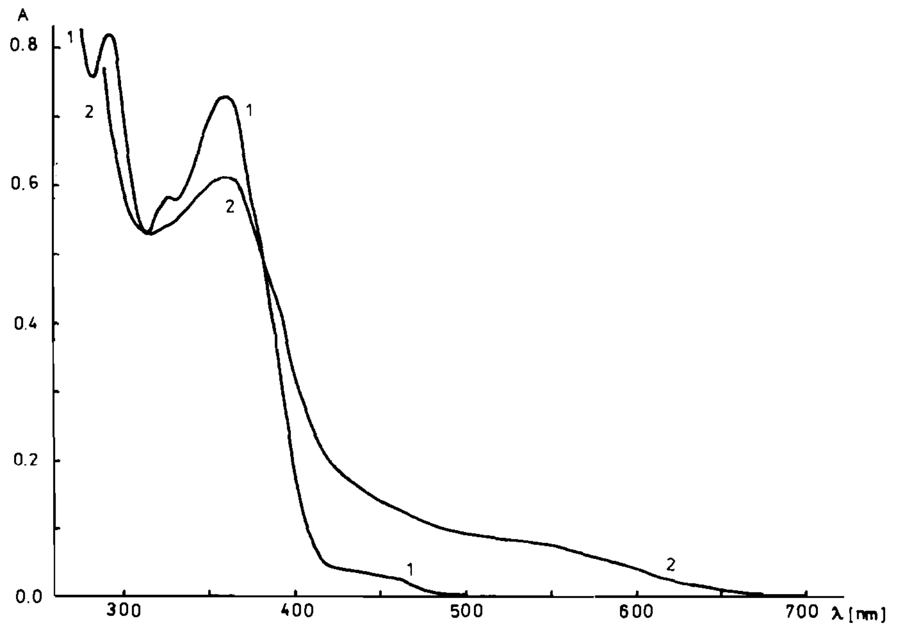


Fig. 4. UV and Vis spectra for $Co(salbut)_2$–n-$BuNH_2$–DMF system. 1) Oxygen-free atmosphere, 2) p_{O_2} = 1 atm. $c_0 = 6.36 \times 10^{-3}$ *M*, $c_B = 0.01910$ *M*, l = 0.1 mm, t = 2 °C.

temperature and partial oxygen pressure, the maximal intensity decay of Co(II) bands in the electronic spectra would be 50–80% of the absorption of the initial complex. In the neat amine solution the intensity decay of the band deriving from the *octahedral* complex $Co(BSB)_2(B)_2$ was 20–50%. This allows us to state that the pentacoordinated complex is mainly responsible for oxygen uptaking in this system.

The appearance of the subsequent hexacoordinated complex of lower affinity to the oxygen, and the impossibility of the 'almost complete' equilibrium shift (1) towards the pentacoordinated complex, require the consideration of the equilibrium (1) in quantitative measurements. For the same reason the determination of the stoichiometry of the formed oxygenated system is also difficult. For a given amine concentration the amount of oxygen consumed is approximately equal to the decrease of Co(II). This indicates the 1:1 oxygen to complex stoichiometry of the oxygenated system, confirmed by the EPR spectra characteristic for the monomeric oxygenated complexes (Fig. 5). All systems under study show identical EPR spectra, with $A_{\parallel}$ = 18.6 Gs, $A_{\perp}$ = 11.8 Gs, $g_{\parallel}$ = 2.077, $g_{\perp}$ = 2.002 for the frozen solutions and A_0 = 11.4 Gs, g_0 = 2.026 for the liquid one (–10 °C).

The equilibrium of the oxygenation process should be as follows:

$$Co(BSB)_2B + O_2 \overset{K_{O_2}}{\rightleftarrows} O_2Co(BSB)_2B \qquad (2)$$

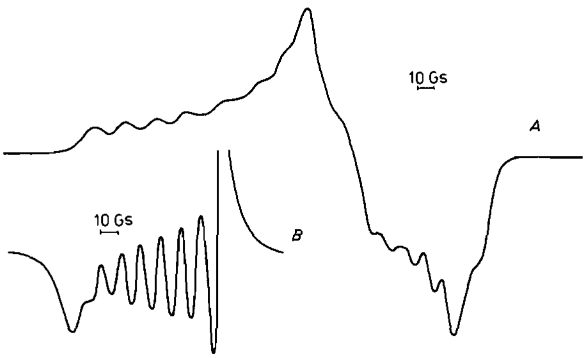


Fig. 5. EPR spectra of $Co(salbut)_2$–n-$BuNH_2$–DMF system, after oxygenation. A) frozen solution, T = 77 K, B) liquid solution, T = 263 K.

It should be noted that after oxygenation the main part of the remaining Co(II) exists as the inactive tetracoordinated complex $Co(BSB)_2$.

This is because of the relatively low K_B constant values. The proper quantitative determination of the complex ability for oxygen uptake requires the consideration of the total equilibrium (3):

$$Co(BSB)_2 + B + O_2 \overset{K_BK_{O_2}}{\rightleftarrows} O_2Co(BSB)_2B \qquad (3)$$

Application of the law of mass action for the equilibrium (3) gives:

TABLE III. Equilibrium Constants and Thermodynamic Data for the Binding of Dioxygen to $Co(BSB)_2B$ Complexes:

$$Co(BSB)_2B + O_2 \overset{K_{O_2}}{\rightleftarrows} O_2Co(BSB)_2B$$

Complex[a]	B	T [°C]	K_{O_2} [atm^{-1}]	ΔH[b] [kJ/mol]	ΔS[b] [J/K mol]
$Co(salbut)_2$	$n\text{-}BuNH_2$	2 −6 −11 −17	31.6 ± 1.0 70.8 ± 5.0 117.5 ± 10.2 245.5 ± 20.0	−63.3 ± 4.0	−201.1 ± 10.5
$Co(salben)_2$	$BzNH_2$	10 2 −12 −14	4.6 ± 0.2 7.4 ± 0.4 12.9 ± 1.0 23.4 ± 2.0	−41.3 ± 3.4	−133.6 ± 7.0
$Co(salprop)_2$	$PrNH_2$	2	18.0 ± 0.8		
$Co(sal\ i\text{-}but)_2$	$i\text{-}BuNH_2$	2	10.0 ± 0.6		
$Co(vanbut)_2$	$n\text{-}BuNH_2$	2	28.8 ± 1.9		

[a] Solvent is DMF. [b] Standard state of 1 atm.

$$K_BK_{O_2} = \frac{[O_2CoL_2B]}{[CoL_2][B]\cdot p_{O_2}} \qquad (4)$$

where: p_{O_2} = partial oxygen pressure.

From the mass balance:

$$[CoL_2] = c_o - [O_2CoL_2B] - [BCoL_2]$$

$$[B] = c_B - [O_2CoL_2B] - [BCoL_2]$$

where: c_o = total concentration of cobalt, c_B = total concentration of amine.

Hence: $K_BK_{O_2}p_{O_2} = ([O_2CoL_2B]/\{c_oc_B - (c_o + c_B)([BCoL_2] + [O_2CoL_2B]) + ([BCoL_2] + [O_2CoL_2B])^2\}$.

Dividing numerator and denominator by $[O_2CoL_2B]$ and assuming

$$K_{O_2}p_{O_2} = \frac{[O_2CoL_2B]}{[BCoL_2]}$$

according to equilibrium (2), will produce after simple algebraic transformations:

$$nc_B^{-1} + K_p^{-1} = Y^{-1} - 1 + \frac{[O_2CoL_2B]}{c_B} \cdot (1 + 2K_p^{-1} + K_p^{-2}) \qquad (5)$$

where

$$K_p = K_{O_2}p_{O_2},\ Y = \frac{[O_2CoL_2B]}{c_o},$$

$$n = (K_BK_p)^{-1} + c_oK_p^{-1} + c_o.$$

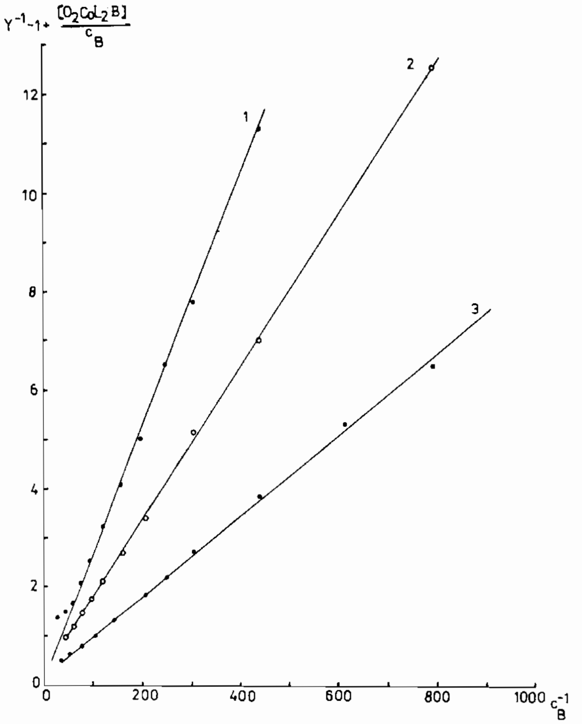


Fig. 6. Dependence of $Y^{-1} - 1 + ([O_2Co(BSB)_2B]/c_B)$ *vs.* c_B^{-1} for $Co(salbut)_2$–$n\text{-}BuNH_2$–DMF system (t = −11 °C): 1) p_{O_2} = 0.14 atm, c_o = 0.01460 *M*, 2) p_{O_2} = 0.60 atm, c_o = 0.01200 *M*, 3) p_{O_2} = 1.00 atm, c_o = 6.29 × 10^{-3} *M*.

The eqn. (5) could be transformed into the Hill equation [11] for $c_B \to \infty$. Numerical analysis of the equation (5) allowed us to neglect the $(2K_p^{-1} + K_p^{-2})$ term, except where $K_p \leqslant K_B$.

The plot of the relation $Y^{-1} - 1 + ([O_2CoL_2B]/c_B = f(c_B^{-1})$ for data obtained from the oxygen absorption measurements at various amine concentrations should produce a straight line. Its slope (n) allows the calculation of K_{O_2}, at the known K_B:

$$K_{O_2} = \frac{K_B^{-1} + c_o}{(n - c_o)\cdot p_{O_2}} \qquad (6)$$

The typical experimental straight lines for the volumetric measurements are shown in Fig.6. Their slopes were calculated by the least squares method. The amount of mol of the $O_2Co(BSB)_2B$ complex was assumed to be equal to that of the uptaken oxygen, calculated for the normal conditions. The K_{O_2} values for the systems under study (Table III) were determined by use of K_B constants, determined spectrophotometrically (Table II). The ΔH and ΔS values were determined from the van't Hoff equation by the least squares method for two systems, which show the most different affinity to the oxygen. They are also shown in Table III.

Theoretically, the K_p^{-1} values could also be obtained directly by extrapolation of the experimental line to $c_B^{-1} = 0$, but the K_{O_2} values obtained in this way have too great an error and no reproducible results could be obtained. Undoubtedly, the formation of the hexacoordinated complex $Co(BSB)_2(B)_2$ at the higher amine concentration could be responsible for this error. Formation of the hexacoordinated complex of lower affinity to the oxygen in comparison to the pentacoordinated complex causes the deviation from the linear dependence $Y^{-1} - 1 + [O_2CoL_2B]/c_B = f(c_B^{-1})$ at higher amine concentrations. For that reason the n slope value should be calculated using only the points which show no systematic deviation from the straight line.

Analysis of eqn. (5) revealed the increase of the method error with increase of the $p_{O_2}K_{O_2}$ value. However, the error could be diminished by using measurements made under low partial oxygen pressure (see Appendix).

Conclusions

The behaviour of our system is similar to that of the known dioxygen carriers. The complex of a square pyramid symmetry is capable of oxygen uptaking and the formed oxygen adduct has the monomeric character.

It seems that the ΔH and ΔS values for the oxygen uptaking reactions are not drastically different in comparison with those for the low-spin Co(II) complexes with tetradentate Schiff bases [1, 4, 16], although such a comparison seems to be rather doubtful because of the great error in determination of these data.

Our present paper should be treated as an introduction to the broader studies of this group of compounds, in the aspect of their ability to the reversible dioxygen uptaking and the tendencies observed in this group of oxygen carriers.

Appendix

The statistical uncertainties in n (see eqn. 5) may be approximated using eqn. 7 [17]:

$$\sigma(n) = \frac{\sqrt{\dfrac{\Sigma y_i^2 - A\Sigma y_i - n\Sigma x_i y_i}{N - 2}}}{\sqrt{\Sigma x_i^2 - \dfrac{1}{N}(\Sigma x_i)^2}} \qquad (7)$$

where:

$$x_i = (c_B^{-1})_i$$

$$y_i = \left(Y^{-1} - 1 + \frac{[O_2CoL_2B]}{c_B}\right)_i$$

A = intercept of the line $Y^{-1} + \dfrac{[O_2CoL_2B]}{c_B} - 1 = f(c_B^{-1})$

N = amount of data points

An estimate for the variance of K_{O_2} is obtained from σ(n) (eqn. 7) by

$$\sigma(K_{O_2}) = \frac{1}{n - c_o}\left(\frac{\sigma(K_B)}{p_{O_2}K_B^2} + K_{O_2}p_{O_2}\sigma(n)\right) + K_{O_2}p_{O_2}^{-1}\sigma(p_{O_2}) \qquad (8)$$

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