

Scientific paper

Synthesis, Characterization of Tertiaryphosphine Cobalt (III) Complexes with Unsymmetrical NNOS Coordination Spheres and Their Thermodynamic Studies with Aliphatic Amines

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Abstract

Some new cobalt(III) complexes: $[\text{Co}(\text{Chel})(\text{PBU}_3)]\text{ClO}_4 \cdot \text{H}_2\text{O}$ (where Chel: cdsalen, cd5OMesalen, cd5Brsalen, cd5Clsalen, cd5NO₂salen, cdMesalen, cdPhsalen) and cdsalen = {methyl-2-[N-[2-(2-phenolate)methylidynenitrilo]ethyl]aminato(-1)-1-cyclopentenedithiocarboxylate}; cd5OMesalen = {methyl-2-[N-[2-(5-methoxy-2-phenolate)methylidynenitrilo]ethyl]aminato(-1)-1-cyclopentenedithiocarboxylate}; cd5Brsalen = {methyl-2-[N-[2-(5-bromo-2-phenolate)methylidynenitrilo]ethyl]aminato(-1)-1-cyclopentenedithiocarboxylate}; cd5Clsalen = {methyl-2-[N-[2-(5-chloro-2-phenolate)methylidynenitrilo]ethyl]aminato(-1)-1-cyclopentenedithiocarboxylate}; cd5NO₂salen = {methyl-2-[N-[2-(5-nitro-2-phenolate)methylidynenitrilo]ethyl]aminato(-1)-1-cyclopentenedithiocarboxylate}; cdMesalen = methyl-2-{N-[2-(2-hydroxyphenyl)ethylidynenitrilo]ethyl}amino-1-cyclopentenedithiocarboxylate and cdPhsalen = methyl-2-{N-[2-(2-hydroxyphenyl)phenylidynenitrilo]ethyl}amino-1-cyclopentenedithiocarboxylate were synthesized and characterized using elemental analysis, ¹H NMR and IR spectra. The formation constants and the thermodynamic parameters were measured spectrophotometrically for 1:1 adduct formation of $[\text{Co}(\text{Chel})(\text{PBU}_3)]\text{ClO}_4 \cdot \text{H}_2\text{O}$ (where Chel: cdsalen, cd5OMesalen, cd5Brsalen, cd5Clsalen, cd5NO₂salen, cdMesalen, cdPhsalen) as acceptors with some aliphatic amines such as *n*-butylamine, *sec*-butylamine, *tert*-butylamine, benzylamine, dibutylamine and diethylamine as donors, in 98% methanol solvent and in constant ionic strength ($I = 0.1 \text{ M NaClO}_4$) and at various temperatures $T = 283$ to 313 (K) by using Ketelaar and van't Hoff equations. The trend of the reactivity of the donors (amines) toward a given cobalt(III) Schiff base complex is as follow: *n*-butylamine > benzylamine > *sec*-butylamine > *tert*-butylamine > diethylamine > dibutylamine. Also, the comparison of formation constants and the thermodynamic parameters show that the trend of formation constants of five-coordinate cobalt(III) Schiff base complexes toward a given donor is as follows:

cd5OMesalen > cdsalen > cd5Brsalen > cd5Clsalen > cd5NO₂salen and cdMesalen > cdsalen > cdPhsalen.

Keywords: Thermodynamic parameters, cobalt complex, schiff base, formation constants, amine.

1. Introduction

The chemistry of cobalt Schiff base complexes has been fascinating area for research of interest to the chemists all over the world. Co(II) and Co(III) complexes derived from symmetrical and unsymmetrical Schiff bases, have received attention for their important biological applications.^{1–4} These complexes are able to bind in a rever-

sible form to molecular oxygen and in consequence, have been investigated as model compounds in the study of the natural oxygen carriers, dioxygen carriers and oxygen activators, such as hemoglobin, myoglobin and hemocyanin.^{5–8} Cobalt complexes with Schiff base ligands have been studied, not only due to their novel structural features caused by the multidenticity of these ligands but also in view of their antiviral, antibacterial and antitumor acti-

vity and those containing axial ligands exhibit higher activities.^{9–11} Cobalt(III) Schiff base complexes with amines as five and six coordinated axial ligands have been shown to inhibit the replication of the *ocular hepes* virus. It is well known that these complexes have a high affinity for nitrogenous donors such as histidine residues, and it is possible that they bind to an enzyme that is crucial to viral replication.¹²

As a part of our investigation on the synthesis and characterization of unsymmetrical tetradentate Schiff bases and their metallic complexes,^{13,14} Here, we report some novel apparently five-coordinate Co(III) complexes with apical tertiary phosphine as ligand, [Co(cdsalen)(PBU₃)]ClO₄·H₂O, [Co(cd5OMesalen)(PBU₃)]ClO₄·H₂O, [Co(cd5Brsalen)(PBU₃)]ClO₄·H₂O, [Co(cd5Clsalen)(PBU₃)]ClO₄·H₂O, [Co(cd5NO₂salen)(PBU₃)]ClO₄·H₂O, [Co(cdMesalen)(PBU₃)]ClO₄·H₂O, [Co(cdPhsalen)(PBU₃)]ClO₄·H₂O. In earlier studies, were reported the relationships between the steric and the electronic effects on the stability of the different Schiff base five-coordinate cobalt(III) complexes.^{15–19} In continuation, we report the synthesize and the thermodynamic study of some new five-coordinated cobalt(III) complexes in equilibrium with amines as the sixth ligand in methanol as solvent at various temperatures with the goal of evaluating the effect of axial and equatorial substitution (R) on electronic properties.

2. Experimental

2.1. Materials

The materials, Salicylaldehyde, 5-methoxysalicylaldehyde, 5-bromosalicylaldehyde, 5-chlorosalicylaldehyde, 5-nitrosalicylaldehyde, 2-hydroxyacetophenon, 2-hydroxybenzophenon, 1,2-ethelenediamine, ammonia solution, carbon disulfide, dimethylsulfate, cyclopentanone, methanol, ethanol, chloroform, hydrochloric acid, cobalt acetate tetrahydrate, tributylphosphine, *n*-butylamine, *sec*-butylamine, *tert*-butylamine, benzylamine, dibutylamine, diethylamine, sodium perchlorate monohydrate were purchased from Merck and Fluka. All reagents were used without further purification. Solvents were purified and dried by conventional methods.²⁰ Amines were purified by drying with KOH and CaH₂ then distilled.

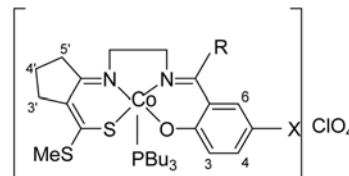
2.2. Physical Measurements

UV-Vis measurements were carried out in a Perkin Elmer (LAMBDA 2) UV-Vis spectrophotometer. The NMR spectra were recorded by Bruker Avance DPX 250 MHz spectrometer. IR spectra were recorded by Shimadzu FTIR 8300 infrared spectrophotometer. Elemental analysis was carried out by Termo Sininngan-Flash 1200.

2.3. Synthesis and Characterization of Complexes

Schiff base ligands H₂cdsalen, H₂cd5OMesalen, H₂cd5Brsalen H₂cd5Clsalen, H₂cd5NO₂salen, H₂cdMesalen and H₂cdPhsalen were prepared in a similar manner according to the literature.^{13,21–23} The complexes shown in Scheme 1 were synthesized as follows. To a refluxing solution of the unsymmetrical ligands (H₂cdXRsalen) (0.1 mmol) in 10 mL of chloroform/methanol (2:1) under N₂ atmosphere, was added a solution of Co(CH₃COO)₂·4H₂O (1 mmol) in methanol (10 mL). The deep brown or red solution Co^(II)(L) complexes was precipitated, then the tributylphosphine (0.1 mmol) was added and the reaction mixture was refluxed for 5–6 hours. The formed Co(II) complex was oxidized by blowing air into the solution for two hours, and the solution was filtered. An appropriate amount of sodium perchlorate (0.1 mmol) was added to the filtered. The resulting green crystals were formed after 48h and the crystals were washed with some water and methanol and were purified by recrystallization in MeOH and H₂O, and were finally dried in vacuum at 30 °C for 48h (See Scheme 1).

Caution: Although no difficulties were experiences, cobalt (III) complexes were isolated as their perchlorates, and therefore, they should be handled as potentially explosive compounds.



Abbreviation of compounds	X	R
[Co(cdsalen)PBU ₃]ClO ₄	H	H
[Co(cd5OMesalen)PBU ₃]ClO ₄	OMe	H
[Co(cd5Brsalen)PBU ₃]ClO ₄	Br	H
[Co(cd5Clsalen)PBU ₃]ClO ₄	Cl	H
[Co(cd5NO ₂ salen)PBU ₃]ClO ₄	NO ₂	H
[Co(cdMesalen)PBU ₃]ClO ₄	H	Me
[Co(cdPhsalen)PBU ₃]ClO ₄	H	Ph

Scheme 1

**{methyl-2-[N-[2-(2-phenolate)methylidynenitrilo]ethyl]aminato(-1)-1-cyclopent-enedithiocarboxylatetri-
butylphosphinecobal(III) perchlorate monohydrate, [Co(cdsalen)(PBU₃)]ClO₄·H₂O.**

Yield: 73%; ¹H NMR (250 MHz, DMSO-d₆, r.t., TMS, δ ppm): 1.17(9H, t, P-CH₃), 1.34–1.76(18H, m, P-(CH₂)₃), 2.57 (2H, m, H^{4'}), 2.80(3H, s, SMe), 3.38–3.59(4H, m, H^{3',5'}), 4.16(4H, m, H^{en}), 6.54(1H, dd, H⁵), 6.79(1H, d, H⁶), 7.16(1H, dd, H⁴), 7.33(1H, d, H³), 8.60(1H, s, CH=N); IR(KBr, cm⁻¹): 754 (ν_{C=S}), 1097(ν_{ClO4}), 1180

($\nu_{C-S} + \nu_{C-N}$), 1275 (ν_{C-O}), 1448 ($\nu_{C=C}$ aromatic), 1600, 1627 ($\nu_{C=N}$), 2947 (ν_{C-H}), 3427 (ν_{O-H}); Elemental Analysis, Found (Calc.): $C_{28}H_{45}N_2ClO_5CoS_2P.H_2O$, C: 48.62 (48.24); H: 6.46 (6.79); N: 4.35 (4.02); S: 8.95 (9.20%).

{methyl-2-[N-[2-(5-methoxy-2-phenolate)methylidynenitrilo]ethyl]aminato(-1)-1-cyclopentenedithiocarboxylatetributylphosphinecobalt(III) perchlorate monohydrate, [Co(cd5OMesalen)(PBu₃)]ClO₄.H₂O.

Yield: 75%; ¹H NMR (250 MHz, DMSO-d₆, r.t., TMS, δ ppm): 0.94(9H, t, P-CH₃), 1.11–1.30(18H, m, P-(CH₂)₃), 2.19 (2H, m, H^{4'}), 2.33–2.91(4H, m, H^{3',5'}), 3.13(3H, s, SMe), 3.42(3H, s, OMe), 3.86–3.92(4H, m, H^{en}), 6.51(1H, d, H⁴), 6.65(1H, s, H⁶), 6.67(1H, d, H³), 8.33(1H, s, CH=N); IR(KBr, cm⁻¹): 763 ($\nu_{C=S}$), 1099(ν_{ClO_4}), 1120 ($\nu_{C-S} + \nu_{C-N}$), 1272 (ν_{C-O}), 1465 ($\nu_{C=C}$ aromatic), 1610, 1627 ($\nu_{C=N}$), 2931 (ν_{C-H}), 3413 (ν_{O-H}); Elemental Analysis, Found (Calc.): $C_{29}H_{47}N_2ClO_6CoS_2P.H_2O$, C: 47.83 (47.90); H: 6.92 (6.79); N: 4.13 (3.85); S: 8.72 (8.82%).

{methyl-2-[N-[2-(5-bromo-2-phenolate)methylidynenitrilo]ethyl]aminato(-1)-1-cyclopentenedithiocarboxylatetributylphosphinecobalt(III) perchlorate monohydrate, [Co(cd5Brsalen)(PBu₃)]ClO₄.H₂O.

Yield: 78%; ¹H NMR (250 MHz, DMSO-d₆, r.t., TMS, δ ppm): 1.15(9H, t, P-CH₃), 1.34–1.73(18H, m, P-(CH₂)₃), 2.48(2H, m, H^{4'}), 2.80(3H, s, SMe), 3.34–3.43(4H, m, H^{3',5'}), 4.08–4.15(4H, m, H^{en}), 6.72(1H, d, H³), 7.26(1H, d, H⁴), 7.53(1H, s, H⁶), 8.59(1H, s, CH=N); IR(KBr, cm⁻¹): 790 ($\nu_{C=S}$), 1095(ν_{ClO_4}), 1130 ($\nu_{C-S} + \nu_{C-N}$), 1280 (ν_{C-O}), 1450 ($\nu_{C=C}$ aromatic), 1620, 1627 ($\nu_{C=N}$), 2920 (ν_{C-H}), 3433 (ν_{O-H}); Elemental Analysis, Found (Calc.): $C_{28}H_{44}N_2ClO_5CoS_2P.Br.H_2O$, C: 43.62 (43.34); H: 6.31 (5.97); N: 3.86 (3.61); S: 7.97 (8.26%).

{methyl-2-[N-[2-(5-chloro-2-phenolate)methylidynenitrilo]ethyl]aminato(-1)-1-cyclopentenedithiocarboxylatetributylphosphinecobalt(III) perchlorate monohydrate, [Co(cd5Clsalen)(PBu₃)]ClO₄.H₂O.

Yield: 74%; ¹H NMR (250 MHz, DMSO-d₆, r.t., TMS, δ ppm): 1.18(9H, t, P-CH₃), 1.34–1.51(18H, m, P-(CH₂)₃), 2.46(2H, m, H^{4'}), 2.80(3H, s, SMe), 3.26–3.59(4H, m, H^{3',5'}), 4.10–4.16(4H, m, H^{en}), 6.77(1H, d, H³), 7.17(1H, d, H⁴), 7.41(1H, s, H⁶), 8.60(1H, s, CH=N); IR(KBr, cm⁻¹): 749 ($\nu_{C=S}$), 1093(ν_{ClO_4}), 1170 ($\nu_{C-S} + \nu_{C-N}$), 1280 (ν_{C-O}), 1459 ($\nu_{C=C}$ aromatic), 1620, 1633 ($\nu_{C=N}$), 2965 (ν_{C-H}), 3423 (ν_{O-H}); Elemental Analysis, Found (Calc.): $C_{28}H_{44}N_2Cl_2O_5CoS_2P.H_2O$, C: 46.05 (45.97); H: 6.42 (6.34); N: 3.80 (3.83); S: 8.62 (8.76%).

{methyl-2-[N-[2-(5-nitro-2-phenolate)methylidynenitrilo]ethyl]aminato(-1)-1-cyclopentenedithiocarboxylatetributylphosphinecobalt(III) perchlorate monohydrate, [Co(cd5NO₂salen)(PBu₃)]ClO₄.H₂O.

Yield: 85%; ¹H NMR (250 MHz, DMSO-d₆, r.t., TMS, δ ppm): 1.19(9H, t, P-CH₃), 1.36–1.76(18H, m,

P-(CH₂)₃), 2.41(2H, m, H^{4'}), 2.82(3H, s, SMe), 3.14–3.61(4H, m, H^{3',5'}), 4.08–4.19(4H, m, H^{en}), 6.84(1H, d, H³), 7.96(1H, d, H⁴), 8.36(1H, s, H⁶), 8.86(1H, s, CH=N); IR(KBr, cm⁻¹): 760 ($\nu_{C=S}$), 1095(ν_{ClO_4}), 1230 (ν_{C-O}), 1330, 1550 (ν_{NO_2}), 1460 ($\nu_{C=C}$ aromatic), 1640, 1643 ($\nu_{C=N}$), 2949 (ν_{C-H}), 3340 (ν_{O-H}); Elemental Analysis, Found (Calc.): $C_{28}H_{44}N_3ClO_7CoS_2P.H_2O$, C: 45.62 (45.31); H: 6.46 (6.25); N: 5.58 (5.66); S: 8.43 (8.64%).

{Methyl-2-{N-[2-(2-hydroxyphenyl)ethylidynenitrilo]ethyl}amino-1-cyclopent-enedithiocarboxylatetributylphosphinecobalt(III) perchlorate monohydrate, [Co(cdMesalen)(PBu₃)]ClO₄.H₂O.

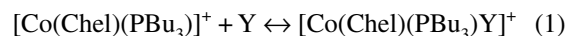
Yield: 70%; ¹H NMR (250 MHz, DMSO-d₆, r.t., TMS, δ ppm): 0.77(9H, t, P-CH₃), 1.18–1.75(18H, m, P-(CH₂)₃), 2.73(2H, m, H^{4'}), 2.77(3H, s, Me), 2.89–2.96(4H, m, H^{3',5'}), 3.16(3H, s, SMe), 3.66–4.11(4H, m, H^{en}), 6.61(1H, dd, H⁵), 6.86(1H, d, H⁶), 7.14(1H, dd, H⁴), 7.64(1H, d, H³); IR(KBr, cm⁻¹): 767 ($\nu_{C=S}$), 1090(ν_{ClO_4}), 1170 ($\nu_{C-S} + \nu_{C-N}$), 1282 (ν_{C-O}), 1438 ($\nu_{C=C}$ aromatic), 1594, 1605 ($\nu_{C=N}$), 2965 (ν_{C-H}), 3320 (ν_{O-H}); Elemental Analysis, Found (Calc.): $C_{29}H_{47}N_2ClO_5CoS_2P.H_2O$, C: 48.73(48.98); H: 6.69 (6.94); N: 4.27 (3.94); S: 8.98 (9.02%).

Methyl-2-{N-[2-(2-hydroxyphenyl)phenylidynenitrilo]ethyl}amino-1-cyclopent-enedithiocarboxylatetributylphosphinecobalt(III) perchlorate monohydrate, [Co(cdPhsalen)(PBu₃)]ClO₄.H₂O.

Yield: 67%; ¹H NMR (250 MHz, DMSO-d₆, r.t., TMS, δ ppm): 0.70(9H, t, P-CH₃), 1.22–1.72(18H, m, P-(CH₂)₃), 2.39(2H, m, H^{4'}), 2.48(3H, s, SMe), 2.75–2.80(4H, m, H^{3',5'}), 3.47–3.65(4H, m, H^{en}), 6.35(1H, dd, H⁵), 6.53(1H, d, H³), 6.87(1H, d, H⁶), 7.16(1H, dd, H⁴), 7.27(2H, m, H^{2'ph}) and 7.70(3H, m, H^{1',3'ph}); IR(KBr, cm⁻¹): 745 ($\nu_{C=S}$), 1096(ν_{ClO_4}), 1140 ($\nu_{C-S} + \nu_{C-N}$), 1235 (ν_{C-O}), 1447($\nu_{C=C}$ aromatic), 1590, 1603 ($\nu_{C=N}$), 2956 (ν_{C-H}), 3310 (ν_{O-H}); Elemental Analysis, Found (Calc.): $C_{32}H_{49}N_2ClO_5CoS_2P.H_2O$, C: 50.93 (51.30); H: 6.64 (6.86); N: 4.02 (3.74); S: 8.73 (8.56%).

2. 4. Equilibrium Measurements

The formation constants, *K*, in all the reactions acceptors with the donors studied were determined by spectrophotometric titration of the mono-phosphine complexes, according to the following equation:



where Chel = cdsalen, cd5OMesalen, cd5Brsalen, cd5NO₂salen and Y = *n*-butylamine, *sec*-butylamine, *tert*-butylamine, benzylamine, diethylamine, dibutylamine.

A solution from each complex (10⁻⁴ M) with a constant ionic strength (*I*) of 0.1 M sodium perchlorate was prepared. Of each solution, 2.5 mL was transferred into

the thermostated cell compartment of the UV-Vis instrument, which was kept at constant temperature 10, 20, 30, and 40 (± 1 °C) by circulating water. Each solution was titrated by adding aliquots of the amine using a Hamilton microlitre syringe. Concentrations of donors were varied in the range of one- to- ten fold in excess.

3. Results and Discussion

3. 1. IR Spectra

In the complexes, the absorption band around 1600 cm^{-1} is assigned to an azomethine (C=N) group.^{24,25} The phenolic (C–O) stretching band is observed at 1230–1290 cm^{-1} .^{24,26,27} The ring skeletal vibrations (C=C) were consistent in the region of 1440–1465 in all complexes.²⁸ Aryl-dithiocarboxylic ligands and some of their sulfur addition products, assigned the bands in the rang 740–800 cm^{-1} to C–S and the bands between 1120–1190 cm^{-1} are probably due to the coupling of $\nu(\text{C-S})$, $\nu(\text{C-N})$.^{29–31} Intense band in 1090–1100 is assigned to perchlorate stretching vibrations, which are typical of non-coordinating perchlorate.³² The weak bands at 2845–2985 cm^{-1} in the ligands are related to C–H modes of vibrations. In cobalt(III) complexes containing PBu_3 these bands were very stronger, assignable to C–H vibrations of PBu_3 . The vibration band in 3000–3400 cm^{-1} is assigned to O–H stretching due to H_2O of the complexes.³³

3. 2. Electronic Spectra

The electronic spectra of all complexes show an intensive absorption band at 370–450 nm region due to π – π^* intraligand transition this band did not really change in all the adduct reaction studied. All the five-coordinated complexes show absorption at 650–750 nm in non coordinating solvents. The absorption band at 650–750 nm vanished to the adduct formation and the six-coordinated product species show a new absorption band at 450–470 nm region that is a shoulder.³⁴

3. 3. ^1H NMR Spectra

The ^1H NMR spectra of these complexes are consistent with the suggest formulation and show that the cobalt in these complexes is low spin. In the ligands, the signals observed at 12.84 to 16.10 ppm are attributed to the hydroxyl protons. The second signals observed around 12.00 to 12.52 ppm are assigned to NH or SH protons.¹³ The absences of these protons in the complexes show that the Schiff bases are coordinated. The azomethine proton signals appeared at 8.22 to 8.63 ppm. By comparing the ^1H NMR spectra of all the Schiff bases with those of their corresponding Co(III) complexes, it is noted that there is a down field shift in the frequency of azomethine protons aliphatic bridge confirming coordination of the metal ion

to these groups. The proton chemical shifts for the coordinated PBu_3 appear at 0.70–1.76 ppm. ^1H NMR spectra of substituted phenyl ring of Schiff bases show additional signals. A singlet signal at $\delta = 3.42$ ppm is assigned in the $[\text{Co}(\text{cd5OMesalen})(\text{PBu}_3)]\text{ClO}_4 \cdot \text{H}_2\text{O}$ that have OCH_3 group. The methyl group in azomethene positions ($\text{C}(\text{CH}_3)=\text{N}$) in $[\text{Co}(\text{cdMesalen})(\text{PBu}_3)]\text{ClO}_4 \cdot \text{H}_2\text{O}$ show a singlet signal at $\delta = 2.77$ ppm. These results are in agreement with the observed previous results for metal complexes of phosphine as axial ligand.^{15,16,19}

3. 4. Thermodynamic Studies

The absorption measurements were monitored at various wavelengths in 670–690 nm regions where the difference in absorption between the substrate and the product was the largest after the equilibrium attained. The adduct shows an absorption different from the acceptor, while the donors show no absorption at those wavelengths. As an example, the variation of the electronic spectra for $[\text{Co}(\text{cd5OMesalen})(\text{PBu}_3)]\text{ClO}_4 \cdot \text{H}_2\text{O}$ titrated with *n*-butylamine at $T = 293\text{K}$ in 98% methanol is shown in Figure 1. The isosbestic points for this system show that there are only two species in equilibrium. The same is valid for other systems.

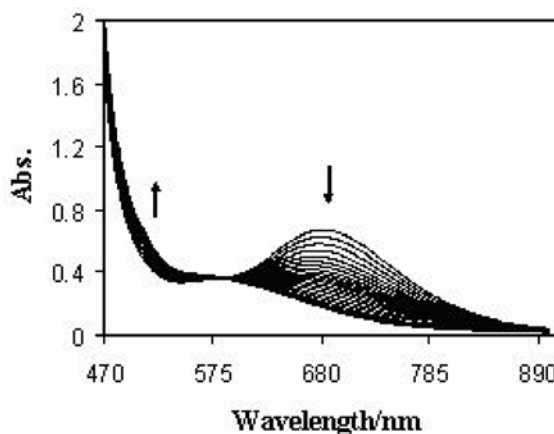


Figure 1. Spectrophotometric titration of $[\text{Co}(\text{cd5OMesalen})(\text{PBu}_3)]\text{ClO}_4 \cdot \text{H}_2\text{O}$ with *n*-butylamine at $T = 293\text{K}$ in 98% methanol.

3. 5. The Formation Constants and the Thermodynamic Parameters

The formation constants of the various cobalt(III) Schiff base complexes studied were calculated by using Ketelaar's equation (2).³⁵

$$P = \frac{1}{(\varepsilon_C - \varepsilon_A - \varepsilon_D)} \cdot \left[\frac{1}{K} + (C_A^\circ + C_D^\circ) \right] \quad (2)$$

where $P = C_A^\circ \times C_D^\circ / (A - A_A^\circ - A_D^\circ)$, C_A° and C_D° are the initial concentrations (mol. dm^{-3}) of the acceptor and the do-

nor, respectively. A is the optical density of the solution including the acceptor and donor, A_A° and A_D° are the optical densities of the pure acceptor and the pure donor in the solution of concentration C_A° and C_D° , ϵ_C , ϵ_A and ϵ_D are the molar extinction coefficients ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) of the complex, the acceptor and the donor, respectively. K is the equilibrium constant of the formed complex and the cell optical path length is 1 cm. The linear plots of P against

($C_A^\circ + C_D^\circ$) should produce a straight line if only a 1:1, and would lead to curve if a 1:2 or a mixture of 1:1 and 1:2 complex are present in a system. The formation constants of the studied cobalt(III) Schiff base complexes were calculated from the ratio of the slope to the intercept by least-square method. The K measurements were repeated at least twice and were reproducible. The linear plots for $[\text{Co}(\text{cd5OMesalen})(\text{PBu}_3)]\text{ClO}_4 \cdot \text{H}_2\text{O}$ titrated with n -

Table 1. The formation constants, $10^{-2} (K)/(\text{dm}^3 \cdot \text{mol}^{-1})$, for the interaction between Co(III) complexes with n -butylamine in 98% methanol at different temperature (K)

Co(III) complexes	283	293	303	313
$[\text{Co}(\text{cd5OMesalen})(\text{PBu}_3)]^+$	14.19±1.31	8.98±0.37	5.55±0.08	4.50±0.09
$[\text{Co}(\text{cdsalen})(\text{PBu}_3)]^+$	12.70±0.33	7.28±0.28	5.03±0.36	4.32±0.15
$[\text{Co}(\text{cd5Brsalen})(\text{PBu}_3)]^+$	10.60±0.86	6.49±0.41	4.61±0.12	3.62±0.09
$[\text{Co}(\text{cd5Clsalen})(\text{PBu}_3)]^+$	7.57±0.27	4.40±0.18	3.62±0.11	2.57±0.06
$[\text{Co}(\text{cd5NO}_2\text{salen})(\text{PBu}_3)]^+$	5.01±0.25	4.15±0.14	3.07±0.15	2.50±0.11
$[\text{Co}(\text{cdMesalen})(\text{PBu}_3)]^+$	17.80±0.01	13.20±0.03	8.15±0.04	5.20±0.08
$[\text{Co}(\text{cdPhsalen})(\text{PBu}_3)]^+$	6.70±0.54	4.25±0.30	3.25±0.39	2.38±0.31

Table 2. The formation constants, $10^{-2}(K)/(\text{dm}^3 \cdot \text{mol}^{-1})$, for $[\text{Co}(\text{cdsalen})(\text{PBu}_3)]\text{ClO}_4 \cdot \text{H}_2\text{O}$ with various amines in 98% methanol at different temperature (K)

Amine	Cone angle	σ^*	283	293	303	313
n -butylamine	–	+0.85	12.70±0.33	7.28±0.28	5.03±0.36	4.32±0.15
benzylamine	106	+1.20	6.41±0.12	4.34±0.25	3.57±0.18	2.29±0.51
sec -butylamine	113	+0.77	5.71±0.83	4.12±0.39	3.53±0.67	2.11±0.35
$tert$ -butylamine	123	+0.68	3.50±0.13	3.03±0.12	2.10±0.71	1.80±0.06
diethylamine	125	+0.29	3.33±0.35	2.95±0.08	2.02±0.06	1.78±0.10
dibutylamine	~138	+0.23	2.10±0.24	1.80±0.19	1.56±0.10	1.09±0.23

Table 3. The thermodynamic parameter values ΔH° , ΔS° and ΔG° for the compounds with n -butylamine in 98% methanol

Complex	$\Delta H^\circ/(\text{kJ mol}^{-1})$	$\Delta S^\circ/(\text{J K}^{-1}\text{mol}^{-1})$	$\Delta G^\circ/(\text{kJ mol}^{-1})^a$
$[\text{Co}(\text{cd5OMesalen})(\text{PBu}_3)]^+$	-29.03±2.73	-42.47±9.20	-16.16±3.91
$[\text{Co}(\text{cdsalen})(\text{PBu}_3)]^+$	-26.75±4.12	-35.77±13.86	-15.91±5.89
$[\text{Co}(\text{cd5Brsalen})(\text{PBu}_3)]^+$	-26.38±2.34	-35.67±7.90	-15.56±3.35
$[\text{Co}(\text{cd5Clsalen})(\text{PBu}_3)]^+$	-25.37±3.12	-35.00±10.49	-14.76±4.45
$[\text{Co}(\text{cd5NO}_2\text{salen})(\text{PBu}_3)]^+$	-17.57±1.25	-10.19±4.20	-14.48±1.78
$[\text{Co}(\text{cdMesalen})(\text{PBu}_3)]^+$	-30.67±2.66	-45.59±8.94	-16.84±3.79
$[\text{Co}(\text{cdPhsalen})(\text{PBu}_3)]^+$	-24.87±1.66	-34.05±5.60	-14.55±2.38

^a ΔG° values are calculated from $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ at T = 303 K

Table 4. The thermodynamic parameter values ΔH° , ΔS° and ΔG° for $[\text{Co}(\text{cdsalen})(\text{PBu}_3)]\text{ClO}_4 \cdot \text{H}_2\text{O}$ with various amines in 98% methanol

Amine	$\Delta H^\circ/(\text{kJ mol}^{-1})$	$\Delta S^\circ/(\text{J K}^{-1}\text{mol}^{-1})$	$\Delta G^\circ/(\text{kJ mol}^{-1})^a$
n -butylamine	-26.75±4.12	-35.77±13.86	-15.91±5.89
benzylamine	-24.14±2.57	-31.52±8.65	-14.58±3.67
sec -butylamine	-22.99±3.82	-28.18±12.84	-14.44±5.45
$tert$ -butylamine	-17.39±2.34	-12.45±7.88	-13.61±3.35
diethylamine	-16.67±2.70	-10.28±5.09	-13.55±3.86
dibutylamine	-15.34±2.89	-9.37±5.72	-12.50±4.13

^a ΔG° values are calculated from $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ at T = 303 K

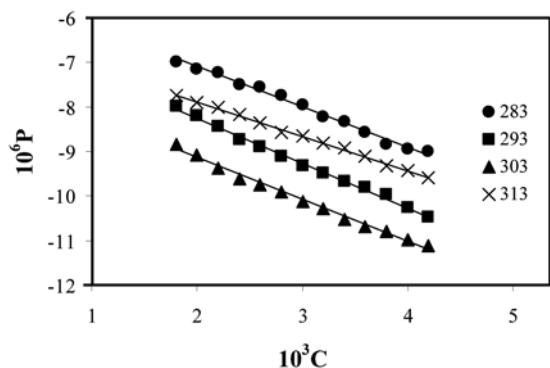


Figure 2. Plots P against C for $[\text{Co}(\text{cd5OMesalen})(\text{PBu}_3)]\text{ClO}_4 \cdot \text{H}_2\text{O}$ with n -butylamine in 98% methanol, where $P = C_A^\circ \times C_B^\circ / (A - A_A^\circ - A_B^\circ)$ and $C = (C_A^\circ + C_B^\circ)$ at 293 K.

buthylamine at various temperatures in 98% methanol are shown in Figure 2 which signify that only a 1:1 adducts is formed. Other systems studied in this work all were lead to linear plots as Figure 2 no curves were observed at all.

The thermodynamic parameters of the studied complexes were calculated by using of the well-known van't Hoff equation (3).

$$\ln K = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (3)$$

where K is the equilibrium constant, R is the gas constant and T is the temperature in Kelvin. Thermodynamic parameters of the studied complexes were obtained from the linear plots of $\ln K$ against $1/T$. The values of ΔH° and ΔS° were obtained from the slope and the intercept, respectively. The ΔG° of complex formation was obtained according to equation 4. The formation constants and the thermodynamic parameters data are collected in Tables 1 to 4.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (4)$$

The linear plots of $\ln K$ against $1/T$ for $[\text{Co}(\text{cd5OMesalen})(\text{PBu}_3)]\text{ClO}_4 \cdot \text{H}_2\text{O}$ with the n -butylamine at various temperatures in methanol 98% is shown in Figure 3. Similar plots are obtained for other systems.

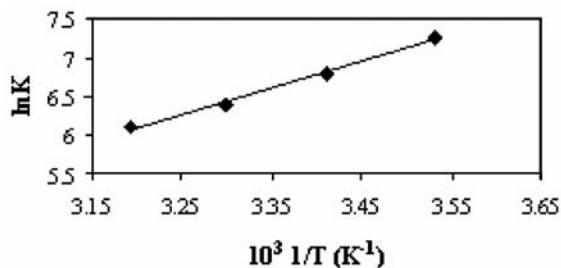
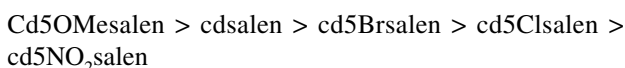


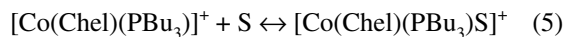
Figure 3. Plot of $\ln K$ against $1/T$ for $[\text{Co}(\text{cd5OMesalen})(\text{PBu}_3)]\text{ClO}_4 \cdot \text{H}_2\text{O}$ with n -butylamine, in 98% methanol.

3. 6. The Electronic Effect of Para Substituted Schiff Base Ligands

The electronic effect of substitutional groups bonded to Schiff base ligands coordinated to Co(III) ion was studied. The studies on $[\text{Co}(\text{Chel})(\text{PBu}_3)]^+$ where Chel = cdsalen, cd5OMesalen, cd5Brsalen, cd5Clsalen and cd5NO₂salen with n -butylamine as donor in methanol 98% were carried out. On the bases of the results (Tables 1, 3), the formation of the adducts follow the sequence below:



This is in according to the electronic effect that the charge donation from Co(III) ion to Schiff base's π^* molecular orbital is increased by electron withdrawing groups on the Schiff base ligands.¹⁹ In the *para* substituted Schiff base ligands, the formation constants varies as can be expected from the electronic effects of the substitutes at position 5. Thus, the formation constants decreases according to the sequence OMe > H > Br > Cl > NO₂, i.e. in order of an increase in both electron-withdrawing and π -acceptor qualities of the substitutes and the donor ability of the ligand groups (mainly the phenoxy groups). Similar results have been reported previously for electrochemical properties of the analogous Cu(II), Ni(II) and Co(III) systems.^{36–38} In fact, for the selected Schiff bases, Hammett type relationships were found between the $\log K$ values and σ_p , the *para*-substitute constant.³⁹ However, since the substitutes at position 5 are indeed *para* to the respective phenolic hydroxyl groups, the occurrence of these Hammett type correlations would indicate that the $\log K$ for the Schiff bases actually varies as a function of the acidity of the hydroxyl group through the ligand series. On the other hand, the NO₂ group makes the Schiff base a poor donor ligand (and a good acceptor ligand), so it is needed by the sixth ligand for stabilize the five-coordinated complexes. The $[\text{Co}(\text{cd5NO}_2\text{salen})(\text{PBu}_3)]^+$ has the least formation constant toward n -butylamine, while the $[\text{Co}(\text{cd5OMesalen})(\text{PBu}_3)]^+$ has the highest because OMe is a donating group. According to the literature if in the six-coordinated complexes, a water molecule or a solvent molecule occupies the sixth position, the interaction with the donor base is very weak.^{15,19,34} Therefore it seems that, for this type of five-coordinated complexes, there is a tendency for the interaction with a solvent molecule to form six-coordinate complex according to the following equation (5):



where S = water or solvent molecule.

The reaction is shifted to the right by decreasing the electron donating power of Schiff base. Therefore, the cobalt atom in $[\text{Co}(\text{cd5NO}_2\text{salen})(\text{PBu}_3)]^+$ complex has a greater acceptor property than $[\text{Co}(\text{cdsalen})(\text{PBu}_3)]^+$, $[\text{Co}(\text{cd5Brsalen})(\text{PBu}_3)]^+$, $[\text{Co}(\text{cd5Clsalen})(\text{PBu}_3)]^+$ and $[\text{Co}(\text{cd5OMesalen})(\text{PBu}_3)]^+$ and forms more stable com-

plexes with H₂O or solvent molecule (equation 5). Therefore, their tendency for the reaction with donor bases decrease, hence their formation constants, *K*, with donors are lower.¹⁸

3. 7. The Effect of the Donors

In this work, we have examined eight donors, *n*-butylamine, *sec*-butylamine, *tert*-butylamine, benzylamine (as primary amines), diethylamine, dibutylamine (as secondary amine), triethylamine, tri-*n*-butylamine (as tertiary amines). Tertiary amines do not have any interaction with the synthesized complexes. The amines have an important steric factor that is shown by Troglor's cone angle.³⁹ Cone angle for *sec*-butylamine, *tert*-butylamine, benzylamine, diethylamine, dibutylamine is 113°, 123°, 106°, 125° and ~138°, respectively. The cone angle for *n*-butylamine is unpublished. The steric effect is increased with increase in cone angle, and formation constants were decreased by increasing cone angles (see Table 1 and 2). The other factor for amines is the electronic effect. This effect is shown by σ^* values of Taft, which are +0.85, +0.77, +0.68, +1.20, +0.29 and +0.23 for *n*-butylamine, *sec*-butylamine, *tert*-butylamine, benzylamine, diethylamine and dibutylamine, respectively.⁴⁰ It was found that the formation constants are in the following sequence:

n-butylamine > benzylamine > *sec*-butylamine > *tert*-butylamine > diethylamine > dibutylamine.

Therefore, the major factor in reactivity of these bases for the replacement reaction of the solvent molecule in the sixth position is governed by the steric factor (equation 5), i.e. by increasing the cone angle, the formation constants decrease.

3. 8. The Electronic Effect of the Equatorial Schiff Base Ligands

The substitutional effects on imine bond were studied by determining the formation constants for [Co(cdMesalen)(PBu₃)]⁺ and [Co(cdPhsalen)(PBu₃)]⁺ with *n*-butylamine. These values for electron releasing methyl Schiff bases were more than those for electron withdrawing phenyl Schiff bases (Table 5). As for the stabilization of the five-coordinate complex, the donation power of Schiff base is important, therefore the cobalt atom in [Co(cdPhsalen)(PBu₃)]⁺ complex has more acceptor properties than cobalt atom in [Co(cdMesalen)(PBu₃)]⁺. The

refore, it forms a more stable complex with the solvent molecule (equation 5), so its tendency to react with the *n*-butylamine donor decrease. Therefore, the replacement of the solvent molecule in sixth position by the amine donor is more difficult in the phenyl complex compared to the methyl one, so its adduct formation constants, *K*, are lower (See Table 5).⁴¹

3. 9. Thermodynamic Parameters

3. 9. 1. The Heat of Formation

The ΔH° value and its sign, is dependent on two factors, one of these factors, is the solvation effect, the other one is the heat of formation of the complex.⁴² In these studies, the heat of formation is negative because of bond formation in all reactions. The solvation effect for five and six coordinate complexes is not different due to the same charge, although it seems likely that the five coordinate complex is better solvated because it is smaller and more polar than six-coordinate complex. The solvation effect for the donors is related to the interaction of solvent with the amines and this contribution to ΔH° may be positive once equilibrium is reached. In all cases we found that the ΔH° values are negative and this results shows that the complex formation contribution to ΔH° values is more important. The enthalpy changes of amines toward these complexes are related to the formation constants for these systems and with enhancing the tendency of adduct formation, the enthalpy changes becomes more negative (Tables 3, 4).

3. 9. 2. The Entropy Values

The ΔS° value and its sign are also dependent on two factors: one of these factors in the difference in the number of the particles (*n*) of the initial substances and the product complexes. The *n* for all systems studied is -1. Concerning the first factor, the entropy change is decreased. The second factor is the liberation of the solvent molecules from the solvation shells.⁴² Among the factors, which affects ΔS° is the solvation of the amines. According to the electronic factor of the amines, as the solvent molecules released during the adduct formation is higher, the ΔS° becomes more positive (See Tables 3, 4). With reference to the second factor, the entropy change is increased, but the entropy change for all reactions is negative, and it shows that the first factor is more important. This results shows that two factors are important and determi-

Table 5. The formation constants, $10^{-2}(K)/(\text{dm}^3 \cdot \text{mol}^{-1})$, for the interaction between Co(III) complexes with *n*-butylamine in 98% methanol at different temperature (K).

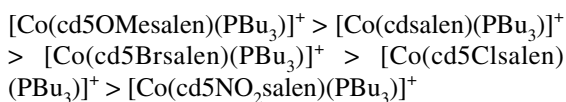
Co(III) complexes	283	293	303	313
[Co(cdMesalen)(PBu ₃)ClO ₄ · H ₂ O	17.80±0.01	13.20±0.03	8.15±0.04	5.20±0.08
[Co(cdsalen)(PBu ₃)ClO ₄ · H ₂ O	12.70±0.33	7.28±0.28	5.03±0.36	4.12±0.15
[Co(cdPhsalen)(PBu ₃)ClO ₄ · H ₂ O	6.70±0.54	4.25±0.30	3.25±0.39	2.38±0.31

nes the sign of the outcome ΔS° during the adduct formation.

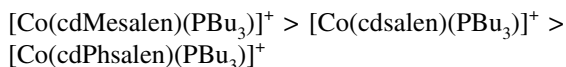
4. Conclusions

By considering the formation constants and the ΔG° of formation for five-coordinated Co(III) Schiff base complexes as acceptors and amines as donors, the following conclusions have been drawn:

1. Reactions are exothermic, $\Delta H^\circ < 0$
2. The formation constants for a given acceptor changes according to the following trend for donors: *n*-butylamine > benzylamine > *sec*-butylamine > *tert*-butylamine > diethylamine > dibutylamine.
3. The formation constants for a given donor and acceptor change according to the following trend for different Schiff base complex due to the steric and the electronic factors:



and



5. Acknowledgements

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Povzetek

Sintetizirali smo vrsto Co(III) kompleksov ter jim določili strukturo z ^1H NMR, IR spektroskopijo ter elementno analizo. Z uporabo Ketelaarjeve in van't Hoffove enačbe smo spektrofotometrično določili tvorbeno konstante kompleksov ter termodinamike parametre reakcij v 98 % metanolu pri konstantni ionski moči (0.1 M NaClO_4) ter različnih temperaturah ($T = 283\text{--}313\text{ K}$), kjer kot donorji nastopajo različni alifatski amini.