Synthesis, Characterization and Spin-Crossover Behaviors of [Co(hydroxycarboxylato)(triphos)] Complexes

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2,2,2-Tris(diphenylphosphinomethyl)ethane (triphos) coordinates to $Co(BF_4)_2{\cdot}6H_2O$ to synthesis the red-violet cationic complex of $[Co(triphos)(solv)_2]^{2+}$ (solv: solvent) in THF/EtOH at room temperature. Addition of 2-hydroxy-2-D-carboxylic acids (L) into the cationic solution as co-ligands yields the red-brown complexes of [Co(L-2-hydroxy-2-methylacetato)(triphos)] (I), (Co(D-2-hydroxy-2-phenylacetato)(triphos)] (II), (Co(L-2-hydroxy-2-phenylacetato)(triphos)] (III) and [Co(D-2-hydroxy-2-phenyl-2-methylacetato)(triphos)] (IV). The complexes are characterized by elemental analysis, IR-, UV-vis.-, NMR- and Mass-spectroscopy. All complexes are paramagnetic. Variable temperature studies on magnetic susceptibilities (χ_M) measurements show the spin-crossover behaviors of the complexes with $\Delta H_{sc} = -5.3$ to -6.8 kJ mol^{-1} and $\Delta S_{sc} = -31$ to -36 J mol^{-1} K^{-1} in methanol.

The triphos ligands, $R_1C(CH_2PR_2)_3$, lead frequently to unusual coordination properties in triphos-metal templates (triphos-M).[1–2] Such triphos-metal templates have been used extensively for stabilizing the inorganic ligands.[1–3] With suitable co-ligands, these templates form complexes of $[\text{triphos-ML}_n]^{n+}$ that are frequently stable at different oxidation states of metal ions.[4–6] The transition metal complexes with easily replaceable tertiary phosphorus ligands are used in many homogeneous catalytic reactions.[5] To gain understanding the mechanism of catalytic reactions, one must investigate the chemical properties and reactivities of the transition metal-phosphino-unit in detail. In this connection, insertion of a multi dentate phosphino ligand is of significant interest. Through using these ligands one can exercise strong influences on the stereochemistry and hence also on the reactivities of the respective complexes. Synthesis, characterization and crystal structures of some Co^{n+}-complexes with such tridentate ligands as 2,2,2-tris(diphenylphosphinomethyl)ethane (triphos) using different amino acids, *o*-phenyldiamine, *o*-hydroxythiols, *o*-dithiols, *o*-hydroxyphenols, *o*-aminophenols, formats, acetates, etc. as co-ligands, have been reported.[6]

The complexes of transition metal ions exhibiting the spin-crossover behaviors between the low-spin (ls) and high-spin (hs) isomers are well documented.[7–9] In this regard, temperature-induced and solvent-dependent spin-crossover behaviors of Co/Fe-complexes have also been published. The complex of $[CoCl_2(triphos)]$ has been reported to show a spin-crossover equilibrium in THF.[6e]

However, the synthesis of such complexes involves two steps: (i) synthesis of an intermediate species, $[Co(triphos)(solv)_2]^{2+}$, which was first developed by L. Sacconi et al.[1] through the reaction of $Co(BF_4)_2{\cdot}6H_2O$ with triphos and (ii) reaction of this species with different suitable co-ligands such a procedure yields four-/five-coordinated complexes.[6]

The present paper describes the results of investigations along the line of synthesis and characterization of [Co(triphos)(L)] complexes. Variable temperature studies were conducted on magnetic susceptibilities (χ_M) measurements showing spin-crossover behaviors of the complexes in methanol.

Experimental

All experimental works were carried out under argon in Collecting Flasks. All solvents used were dried and deoxygenated through distillation under argon over Na for ethanol (EtOH), tetrahydrofurane (THF), diethyl ether (DE) and over CaH_2 for dichloromethane (CH_2Cl_2) and petrol ether (PE 40/60). The $Co(BF_4)_2{\cdot}6H_2O$ was prepared following the literature.[10] $Na(BPh_4)$ was used as received from the Aldrich. L-2-hydroxy-2-methyl acetic acid, D-2-hydroxy-2-phenylacetic acid, L-2-hydroxy-2-phenylacetic acid and D-2-hydroxy-2-phenyl-2-methylacetic acid are used as received from the Lancaster. The chelate ligand, 2,2,2-tris(diphenylphosphinomethyl)ethane (triphos) was synthesized as described in the literature.[11] All complexes [Co(triphos)(L)] are strongly hygroscopic and air sensitive.

UV-vis spectra were obtained with a Hitachi U-2000 Spectrophotometer in THF at 25 °C. ^{1}H-NMR and ^{31}P-NMR spectra were run on a Bruker AC 300 FT Spectrometer operating at 300 MHz. High precision NMR sample tubes of type 528-PP (Wilmad Glass

Co., New Jersey) with sealed Wilmad coaxial inserts (WGS-5BL) containing 5% TMS in acetone-d^6 were used as an external standard and instrument lock. The magnetic susceptibilities (χ_M) of the complexes were measured in methanol, based on the Evans ^{1}H-NMR method[12a] using the methanol for temperature calibration.[12b] The magnetic moments (μ/μ_B) were corrected for changes in the solvent's density, changing the concentration of solute with temperature variation.[12c,d] Cyclohexane 0.5% (v/v) was used as an internal reference compound in MeOH. The Mass-Spectrometer was a Finnigan MAT 8400 with integrated Spectro-System (SS) 300, Fast-Atom-Bombardment (FAB), matrix: *p*-Nitrobenzylalcohol, Ionization Temperature: 150 °C (the *m*/*z*-values always shows the most frequent/common isotope). IR spectra were recorded as KBr plates with an FT-IR Spectrometer (Bruker IFS 66) at room temperature.

General Procedure for Synthesis of the Complexes: An equimolar amount of triphos (1.6 mmol) in 20 mL THF was added into the solution of $Co(BF_4)_2{\cdot}6H_2O$ (1.6 mmol) in 20 mL EtOH and the mixture was stirred for 10 min at room temperature. A red-violet cationic complex of $[Co(triphos)(Solv_2)]^{2+}$ (Solv = Solvent) was formed in solution. Addition of an equimolar amount of 2-hydroxy-2-*R*-carboxylic acid (L) as co-ligands into the cationic solution yields the red-brown complexes of [Co(triphos)(L)]. After the solution was stirred for 2–3 h at room temperature, the solvent was removed in vacuo very slowly untill precipitation started. The red-brown precipitate was filtered off and washed with 5 mL EtOH and PE (40/60), 3 times in each. The product in vacuo, dissolved into 10 mL CH_2Cl_2 and passed through a silica column (2.0 × 5 cm). The eluent was dried in vacuo (2–3 10^{-2} mbar) in water bath for 10–12 h; we obtained the red-brown crystals of complexes (I), (II) (III) and (IV). Synthesis of the complex II in the presence of a counter anion ($NaBPh_4$) showed similar results, which indicated the absence of any anion in the complex. Though several attempts were made to grow single crystals for X-ray measurements, unfortunately none succeeded.

[Co(triphos)(L-2-hydroxy-2-methylacetato)] (I): yields 60% (w. r. t. triphos); elemental analysis: for $[C_{44}H_{43}P_3O_3Co{\cdot}1.5H_2O]$ (798.7): found C 66.43, H 5.74%; calcd C 66.17, H 5.81%. MS (FAB) *m*/*z* (%): 771 (5) $[M]^+$, 683 (8) $[Co(triphos)]^+$, 641 (8) $[triphosO]^+$, 625 (10) $[triphos]^+$, 623 (25) $[triphos-H_2]^+$, 563 (15) $[triphosO-Ph]^+$ and 547 (100) $[triphos-Ph]^+$, 439 (20) $[triphos-PPh_2]^+$.

[Co(triphos)(D-2-hydroxy-2-phenylacetato)] (**II**): yields 61% (w. r. t. triphos); elemental analysis: for $[C_{49}H_{45}P_3O_3Co{\cdot}3.5H_2O]$ (896.8): found C 65.04, H 5.63%; calcd C 65.63, H 5.81%. MS (FAB) *m*/*z* (%): 834 (10) $[M]^+$, 821 (20) $[M-CH]^+$, 804 (68) $[M-CH_2O]^+$, 683 (100) $[Co(triphos)]^+$, 641 (12) $[triphosO]^+$, 625 (15) $[triphos]^+$ and 563 (28) $[triphosO-Ph]^+$.

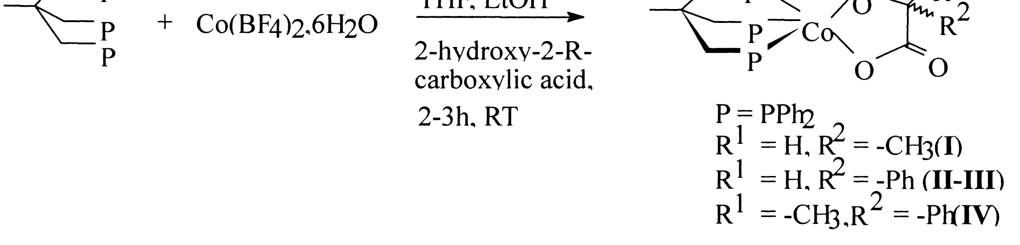
[Co(triphos)-L-2-hydroxy-2-phenylacetato] (**III**): yields 71% (w. r. t. triphos); elemental analysis: for $[C_{49}H_{45}P_3O_3Co{\cdot}1.4H_2O]$ (858.9): found C 68.52, H 5.69%; calcd C 68.52, H 5.61%. MS (FAB) *m*/*z* (%): 834 (25) $[M]^+$, 804 (5) $[M-CH_2O]^+$, 683 (20) $[Co(triphos)]^+$, 641 (10) $[triphosO]^+$, 625 (25) $[triphos]^+$, 563 (17) $[triphosO-Ph]^+$, 547 (100) $[triphos-Ph]^+$ and 439 (22) $[triphos-PPh_2]^+$.

[Co(triphos)(D-2-hydroxy-2-phenyl-2-methyl acetato)] (**IV**): yields 68% (w. r. t. triphos); elemental analysis: for $[C_{50}H_{47}P_3O_3Co{\cdot}1.1H_2O]$ (867.6): found C 69.22, H 5.86%; calcd C 69.22, H 5.72%. MS (FAB) *m*/*z* (%): 848 (25) $[M]^+$, 683 (38) $[Co(triphos)]^+$, 641 (18) $[triphosO]^+$, 625 (25) $[triphos]^+$, 563 (40) $[triphosO-Ph]^+$, 547 (100) $[triphos-Ph]^+$ and 439 (30) $[triphos-PPh_2]^+$.

Results and Discussion

The triphos, 2,2,2-tris(diphenylphosphinomethyl)ethane, coordinates to $Co(BF_4)_2{\cdot}6H_2O$ to form the red-violet cationic complex of $[Co(triphos)(solv)_2]^{2+}$ which in turns reacts with different hydroxy-carboxylic acids as co-ligands, and finally yields the red-brown complexes of [Co(L-2-hydroxy-2-methylacetato)(triphos)] (I), [Co(D-2-hydroxy-2-phenylacetato)-(triphos)] (II), [Co(L-2-hydroxy-2-phenylacetato)(triphos)] (**III**), [Co(D-2-hydroxy-2-phenyl-2-methylacetato)(triphos)] (**IV**). A generalized reaction Scheme 1 is shown below. Synthesis of the complex (II) in the presence of a counter anion ($NaBPh_4$) results in no involvement of the anion in the complex. The ^{1}H- and ^{31}P-NMR spectra of all complexes show their paramagnetic nature in solution. Further, ^{31}P-NMR spectra show a broad peak at 3.0–4.0 ppm which indicates the coordination of the P-atom to the central Co(II) ion. The UV-vis absorption spectra of the complexes in THF are almost identical and show three characteristics bands: (i) a very strong band at < 400 nm associated to the intra-ligand transition band of *triphos*-phenyl ring, (ii) a strong broad band at the range of 435–600 nm (λ_{max} ~ 475 nm), associated to *the metal-to-ligand* charge transfer (ct) band, and (iii) a weak broad band at the range of 625–900 nm, attributed to the ligand field splitting energy (Δ_o).[6e,13,15] All the complexes are very sensitive to the air; a color change from red-brown to light green/green occurs in THF. The complex **IV** shows a broad shoulder at 550–650 nm (red-brown color), which becomes more populated (λ_{max} ~ 575 nm) when exposured to the air (green color).

The most characteristic IR-bands of the complexes are summarized in Table 1. All complexes show strong carbonyl bands $\nu(C{=}O_{asym})$ at 1655–1634 cm^{-1}, a typical band for η^1-coordi-



Scheme 1.

Table 1. IR Data (cm^{-1}) of the Complexes I–IV

Assignments	I	IIa	IIb	III	IV
H–ar	3053s	3053s	3057s	3052s	3052s
C=**O**(asym)	1655s	1634s	1634s	1634s	1653s
C=**C**–ar	1582s	1586s	1589s	1583sh	1582s
C=**C**–valenc	1481vs	1482	1480m	1480m	1480s
C-**H**-deform	1435vs	1438vs	1437vs	1435vs	1435vs
C=**O**(sym)	1401m	1400sh	1375m	1400w	1400w
P–C–ar	1096–1024sb	1038–1034sb	1094–1030sb	1084–1030sb	1084–1023sb
P–C–Ali.	845s	840w	845m	843m	841m

sb = strong broad, vs = very strong, s = strong, m = medium, w = weak.

nated carboxylate groups.[6a,14] The carbonyl bands for free hydroxycarboxylic acid (observed at 1715–1721 cm^{-1}) shifted to the higher energy values (1655–1634 cm^{-1}) upon coordination to the Co(II) ion. The carbonyl bands for η^2-coordinated carboxylate with Co(III) ion are observed at ~1570 cm^{-1} as ν(C=O$_{asym}$) and at ~1400 cm^{-1} as ν(C=O$_{sym}$).[14e,15a] Further, the ν(C=O$_{asym}$) bands for [*triphos*Co(II)-aminocarboxylato triphos]$^+$ complex (η^1-coordination of carboxylate ion) are observed at 1670–1642 cm^{-1}.[6a] The bands at the range of 1581–1589 cm^{-1} are attributed to the ν(C=C–Ar) stretching frequency.[14–15] Other important bands for ν(H–Ar) observed at the range of 3052–3057 cm^{-1}, confirm the presence of the phenyl ring (*triphos*) in the complexes. However, the absence of any ν(O–H) stretching band (usually observed as a strong broad band at ~3452 cm^{-1} for free hydroxy-carboxylic acid) indicates the dissociation of the H-atom as proton through bond formation between [Co(triphos)]$^{2+}$ and hydroxy-carboxylate. Hence, the [Co(triphos)]$^{2+}$ is bonded to hydroxy-carboxylate via O-atoms (from both O–H groups) in a trigonal bi-pyramidal symmetry[14–15] as suggested in the reaction Scheme 1.

Spin-Crossover Behaviors. The complexes of transition metal ions with d^4-d^7 electronic configuration exhibit spin-crossover behaviors between the low-spin and the high-spin isomers, both in solution and in the solid state.[7–9] The choice of ligands (i.e., ligand field splitting energy, Δ_o) in this regard might play an important role in determining the spin-multiplicity of the complexes. These two isomers differ in their spin-state, which can be followed by measuring the electronic spectra and the magnetic susceptibilities at varying temperatures. In view of this consideration, variable temperature studies on magnetic susceptibilities measurements of the complexes I, III and IV are carried out in MeOH. The magnetic susceptibilities (χ_M) of the complexes I, III and IV are measured over the temperature range of 215 to 320 K. Accordingly, the values of magnetic moments (μ/μ_B) were calculated and are listed in Table 2. The magnetic moments of the complexes are found to be 4.3 μ_B at 315 K, which is quite reasonable for high-spin Co(II)-complex of d^7-configuration. The magnetic moment decreases to 3.7 μ_B at 227 K, which corresponds to the more populated low-spin isomer of the complex. The magnetic moments of the complexes increase with increasing temperature and vice versa (see Table 2 and Fig. 1). The coincidence of the heating curve with the cooling curve (see Fig. 2) reveals no hysteresis effect in the system. Hence, the results show a change in the spin-multiplicity of the complexes with temperature variation. That is, a spin-crossover equilibrium is ob-

Table 2. Values of Magnetic Moments (μ/μ_B), Equilibria Constants (K_{sc}) and Free Energy Change (ΔG/kJ mol^{-1}) at Different Temperatures (T/K) for Complexes I, III and IV in Methanol

Complex I (8.568 × 10^{-3}M):				Complex III (5.754 × 10^{-3}M):				Complex IV (5.486 × 10^{-3} M):			
T/K	μ/μ_B	K_{sc}	ΔG/kJ mol^{-1}	T/K	μ/μ_B	K_{sc}	ΔG/kJ mol^{-1}	T/K	μ/μ_B	K_{sc}	ΔG/kJ mol^{-1}
227.47	3.731	0.614	0.923	215.14	4.023	0.323	2.021	228.99	3.973	0.366	1.912
238.57	3.885	0.449	1.589	237.59	4.115	0.249	2.743	239.46	4.027	0.320	2.267
248.80	3.953	0.385	1.975	247.92	4.142	0.228	3.044	250.02	4.059	0.294	2.543
259.42	4.014	0.331	2.383	258.83	4.159	0.215	3.307	260.80	4.084	0.273	2.813
270.22	4.031	0.314	2.603	270.01	4.179	0.201	3.606	271.11	4.101	0.259	3.040
278.97	4.041	0.304	2.759	280.83	4.191	0.192	3.851	281.31	4.117	0.247	3.268
288.77	4.075	0.280	3.055	291.88	4.225	0.168	4.325	291.63	4.146	0.225	3.612
302.56	4.131	0.237	3.626	303.54	4.271	0.136	5.021	303.83	4.196	0.189	4.202
315.70	4.193	0.191	4.343	315.25	4.318	0.106	5.867	315.79	4.241	0.158	4.851
300.33	4.126	0.241	3.552	301.45	4.274	0.134	5.019	303.25	4.187	0.195	4.119
293.75	4.101	0.259	3.291	290.46	4.230	0.164	4.352	289.53	4.147	0.225	3.595
285.34	4.072	0.283	2.993	281.81	4.202	0.184	3.962	279.81	4.122	0.244	3.286
276.56	4.044	0.305	2.727	271.51	4.183	0.198	3.654	269.83	4.099	0.261	3.015
				262.02	4.157	0.217	3.326				
ΔH_{sc}/kJ mol^{-1}			−6.82	ΔH_{sc}/kJ mol^{-1}			−5.83	ΔH_{sc}/kJ mol^{-1}			−5.36
ΔS_{sc}/J mol^{-1} K^{-1}			−34.8	ΔS_{sc}/J mol^{-1} K^{-}1			−35.6	ΔS_{sc}/J mol^{-1} K^{-}1			−31.4

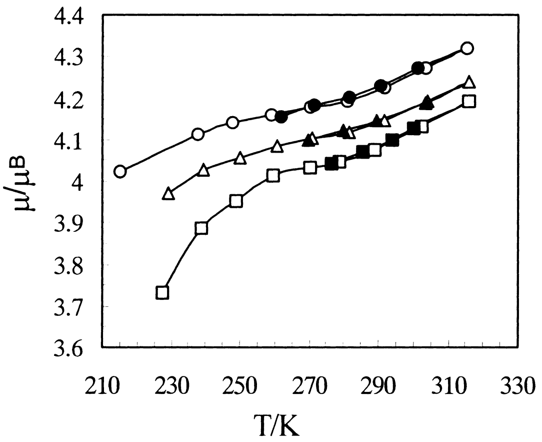


Fig. 1. Change of magnetic moments (μ/μ_B) with temperatures (T/K) for spin-crossover equilibria in methanol (white points: heating, dark point: cooling): complexes **I** (8.568×10^{-3} M, -□-), **III** (5.754×10^{-3} M, -○-) and **IV** (5.486×10^{-3} M, -△-)

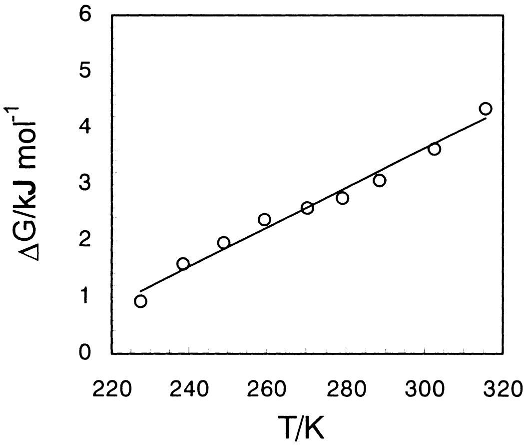


Fig. 2. Typical plot of ΔG/kJ mol^{-1} vs T/K for the spin-crossover equilibrium of the complex I in methanol.

served between the ls- and hs-isomers of the complexes in solution.

The values of spin-equilibrium constants, K_{sc} [$X_{ls}/X_{hs} = (\mu^2-\mu_{hs}^2)/(\mu_{ls}^2-\mu^2)$] and the associated thermodynamic parameters are calculated following the literature.[6e,7] The value of $\mu_{ls} = 1.9\ \mu_B$ is used for ls-isomer of Co(II)-complex of d^7-configuration,[6e] while, the value for hs-isomer ($\mu_{hs} = 4.5\ \mu_B$) is taken from experimental data at the limiting end of high temperature. Therefore, there might be some limitations to the results due to the inability to obtain the limit values of μ_{ls} and μ_{hs} under the present restricted temperature range. The values of spin-equilibria (K_{sc}) constants decrease with increasing temperatures (see Table 2) as the hs-isomers are increasingly populated and vice versa. The values of thermodynamic parameters, ΔH_{sc}/kJ mol^{-1} and ΔS_{sc}/J mol^{-1} K^{-1}, are calculated following the heating data from the linear plot of ΔG/kJ mol^{-1} vs T/K (see Fig. 2 and Table 2). The entropy change is usually interpreted as originating from the change of spin-multiplicity and the change of vibrational freedom. The spin-only term (ΔS_{spin}) for Co(II)-complex ($S = 3/2 \rightarrow S = 1/2$) is reported as 5.8 J mol^{-1} K^{-1}.[8] The entropy and enthalpy changes for spin-crossover Co(II)-systems without ligand dissociation lies between the range of -6 to -30 J mol^{-1} K^{-1} and < 1 to -7 kJ mol^{-1},[9] respectively. The entropy and enthalpy changes for the present system are found to be in the ranges of -31 to -36 J mol^{-1} K^{-1} and -5.3 to -6.8 kJ mol^{-1}, respectively. The entropy and enthalpy changes for the spin-crossover [Co(triphos)Cl_2] complex, accompanying ligand dissociation, are found to be -85 ± 6 J mol^{-1} K^{-1} and -21 ± 3 kJ mol^{-1} in THF,[6e] respectively.

In conclusion, it could be said that the triphos co-ordinates to the Co(II) ion to yield the cationic complex of [Co(triphos)(solv)$_2$]$^{2+}$ which in turns reacts with 2-hydroxy-2-*R*-carboxylic acids as co-ligands to synthesize the red-brown [Co(2-hydroxy-2-*R*-carboxylato(triphos)] complexes. The complexes are found to be paramagnetic and to show the spin-crossover behaviors with $\Delta H_{sc} = -5.3$ to -6.8 kJ mol^{-1} and $\Delta S_{sc} = -31$ to -36 J mol^{-1} K^{-1} in methanol.

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