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Coordination Compounds with Biomimetic N_2S_2 and N_2S_4 Ligands: Synthesis and Spectral Studies on Divalent Transition Metal Complexes of Benzildithiosemicarbazone and Thiocarbohydrazone

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Abstract

Cobalt(II), nickel(II), copper(II) and palladium(II) complexes of benzildithiosemicarbazone (BDTSC), and tetraaza macrocyclic iron(II), cobalt(II), nickel(II) and copper(II) chelates derived from metal–ion catalyzed condensation (template synthesis)** of benzil and thiocarbohydrazide have been prepared and characterized by elemental analysis, conductance, magnetic moment and spectral data. The synthesis and spectral data of a tetraaza macrocyclic complex of Co(II) derived from the condensation of Co–BDTSC with benzil is included. The Co–BDTSC complex is found to react reversibly with molecular oxygen.

Introduction

Although the complexes containing four nitrogen atoms or two nitrogen atoms and two oxygen atoms in an equatorial plane have been studied extensively [1–10], those of chelates containing N_2S_2 in an equatorial plane and serving as model compounds have received little attention [11].

Here, we report the preparation and characterization of divalent transition-metal complexes of benzildithiosemicarbazone, (BDTSC) and tetraaza macrocyclic complexes obtained by template synthesis of benzil and thiocarbohydrazide. Studies on a tetraaza macrocyclic cobalt chelate obtained by the condensation of Co–DBTSC with benzil are also presented.

Experimental

Preparation of Benzildithiosemicarbazone (BDTSC)

To a refluxing solution containing benzil (I) (0.04 mol) dissolved in 50 ml of methanol and thiosemicarbazide (II) (0.08 mol) dissolved in 50 ml of hot water, 3 ml of concentrated hydrochloric acid was added. The reaction mixture was kept on a hot water bath for 30 min. A light yellow-coloured product **III** was separated out which was filtered and dried. The product was recrystallized from ethanol.

Preparation of Complexes

Co(II), Ni(II), Cu(II) and Pd(II) complexes of BDTSC

The metal salt and BDTSC were dissolved in distilled water and methanol, respectively. The reaction mixture containing equimolar (0.01 M) metal salt solution and BDTSC solution was refluxed in a 500-ml round-bottom flask for 2 h and cooled. The solid obtained was washed with hot water and then with methanol. The complexes were recrystallized from ethanol and dried at 80 °C.

Tetraaza macrocyclic cobalt complex

Equimolar (0.01 M) solutions of the Co–BDTSC complex and benzil were taken in a 250-ml round-bottom flask and refluxed for 16 h. On cooling, a deep red precipitate was obtained, washed with methanol, recrystallized from ethanol and dried at 80 °C.

Tetraaza macrocyclic complexes of Fe(II), Co(II), Ni(II) and Cu(II) with benzil and thiocarbohydrazide

Equimolar (0.01 M) solutions of benzil (I) and thiocarbohydrazide (VII) were mixed in a 500-ml round-bottom flask. A sufficient quantity of the metal salt solution was added and the mixture was refluxed for 2 h. On cooling, the precipitate formed was washed first with hot water and then with ethanol. The product was recrystallized from ethanol and dried at 80 °C.

The synthesis of BDTSC and of the metal complexes are represented in Scheme 1.

The metal salts $FeCl_2 \cdot 4H_2O$, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$ and $PdCl_2$ used were AR grade.

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**The term 'template synthesis' is used to describe ligand formation by condensation in the presence of a metal ion.

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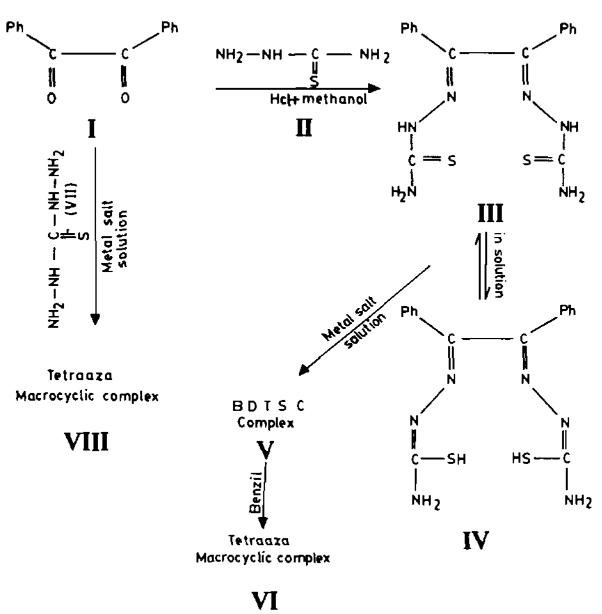


Scheme 1.

Pd and Ni were estimated gravimetrically [12] using dimethylglyoxime. Other metal ions were determined volumetrically by standard procedures [12]. Estimation of carbon, hydrogen and nitrogen was done by CDRI, Lucknow, India.

The molar conductance of the complexes in DMF was determined using a Systronic 303, direct-reading conductivity bridge. Magnetic susceptibility measurements were made using a vibrating sample magnetometer (VSM) operating at field strength of 3 kg to 8 kg at room temperature.

The electronic spectra were recorded on a Carl Zeiss DMR-21 spectrophotometer. Infrared spectra were obtained in the range 4000–180 cm^{-1} on a Perkin-Elmer 983G infrared spectrometer in KBr discs. ^1H NMR spectra were recorded in deuterated DMSO medium on a Varian XL-300 spectrometer at room temperature. An ELICO digital spectrophotometer equipped with 1.0-cm quartz cells was used in the present study.

Results and Discussion

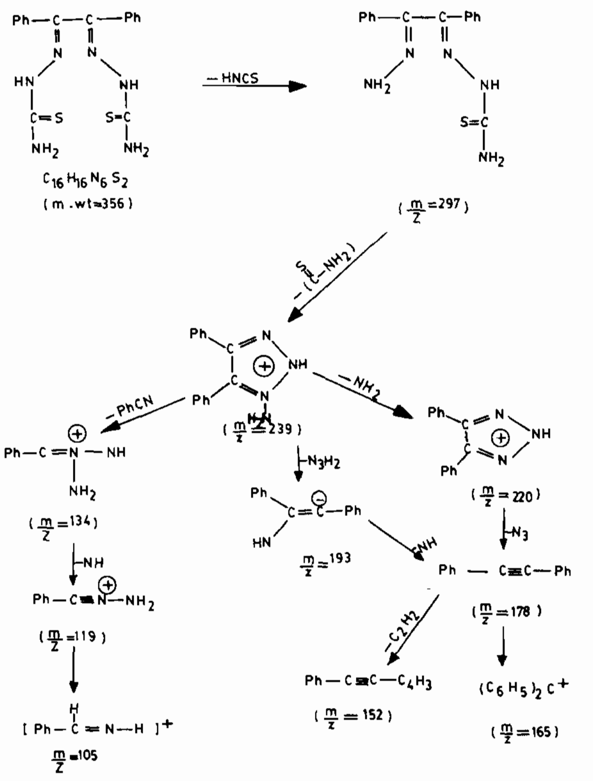
Characterization of BDTSC

BDTSC is characterized on the basis of elemental analysis, infrared, ^1H NMR and mass spectral data. Analytical data for this compound are presented in Table 1 and these are consistent with its molecular formula, $C_{16}H_{16}N_6S_2$.

TABLE 1. Analytical data of BDTSC and complexes

Compound	Colour (melting point (°C))[a]	Analysis: found (calc.) (%)				Molar conductance (ohm^{-1} cm^{-2} mol^{-1})
		C	H	N	M	
BDTSC (LH_2)	light yellow (234–236)	54.63 (53.93)	4.51 (4.49)	21.85 (23.59)		
[CoL]	reddish brown (267–269)	46.42 (46.49)	3.31 (3.39)	21.10 (20.34)	13.70 (14.27)	4.2
[NiL(H_2O)$_2$]	red (329–331)	43.10 (42.79)	3.95 (4.01)	18.50 (18.72)	12.60 (13.08)	4.8
[CuL]	brown (347–348)	45.03 (45.78)	3.41 (3.34)	19.45 (20.02)	16.40 (15.58)	6.7
[PdL]	green (379–381)	42.50 (41.70)	3.07 (3.04)	19.30 (18.25)	23.76 (23.01)	9.0
[Co(mac)] [b]	deep red (327–328)	62.25 (61.12)	3.43 (3.40)	14.75 (14.31)	9.85 (10.04)	6.0
[Fe(mac)] [c]	red (330–332)	57.83 (58.64)	3.68 (3.58)	17.90 (18.24)	8.50 (9.09)	5.5
[Co(mac)] [c]	black (264–266)	58.80 (58.35)	3.60 (3.56)	18.50 (18.15)	9.25 (9.54)	24.3
[Ni(mac)] [c]	reddish brown (364–366)	58.35 (58.37)	3.47 (3.56)	18.91 (18.16)	10.10 (9.52)	23.2
[Cu(mac)] [c]	brown (394–395)	56.90 (57.74)	3.60 (3.52)	18.20 (17.95)	9.85 (10.48)	6.2

[a] Decomposition occurs in the range indicated. [b] Tetraaza macrocyclic cobalt complex derived by the condensation of [CoL] and benzil. [c] Tetraaza macrocyclic complexes prepared by template synthesis.


Scheme 2.

The infrared spectrum of BDTSC shows bands at 3422 and 3380 cm^{-1} for N–H; 1605 cm^{-1} for C=N; 1295 and 747 cm^{-1} for C=S and no bands due to C=O, confirming the formation of product **III**.

In the ^{1}H NMR spectrum of BDTSC two peaks are observed at 3.25 and 3.56 ppm with 1:2 ratio, attributable to the imino and amino protons, respectively. The aromatic protons in *ortho* positions to the azomethine group absorb at 7.56 and 7.53 ppm. The remaining protons show signals in the 7.39–7.21 ppm region. The *ortho* protons are deshielded by about 0.25 ppm.

The mass spectrum of BDTSC does not show a molecular ion peak. The fragmentation pattern of this compound is presented in Scheme 2.

The colour, melting point, analytical data and molar conductance of a millimolar solution in DMF at room temperature are given in Table 1.

Magnetic Moments and Electronic Spectra

The tetraaza macrocyclic iron(II) complex shows a lower magneton value of 4.32 BM, which may be attributed to quenching of orbital contribution arising from lower site symmetry [13]. Two bands are observed in the electronic spectrum of this complex at 5300 and 12600 cm^{-1}, assigned to $^5A_{1g} \leftarrow {}^5T_{2g}$ and to $^5B_{1g} \leftarrow {}^5T_{2g}$ transitions, respectively, characteristic of hexacoordinate iron(II) complexes of the type FeL_4X_2 [14]. This complex exhibits an intense metal to ligand charge transfer band at 20380 cm^{-1}, with the iron(II) t_{2g} electrons being transferred to the empty π-type antibonding orbitals in the ligand.

The observed magnetic moment values of 1.8 and 2.3 BM for the Co–BDTSC complex and the tetraaza macrocyclic cobalt chelate product of Co–BDTSC and benzil, suggest a square planar configuration. The magnetic moment of similar cobalt chelate is found to be 3.7 BM in favor of octahedral geometry. The reddish brown color of Co–BDTSC and some weak broad bands present in its electronic spectrum in the region of 10000 to 12000 cm^{-1} are characteristic of square planar stereochemistry [15]. A strong and broad band around 15000 cm^{-1} is also observed, in analogy with other square planar complexes [16, 17]. The condensed product here reported exhibits a narrow band at 8300 cm^{-1} and a broad band at 19230 cm^{-1} as observed in the case of low-spin square planar complexes. The electronic spectra of the tetraaza macrocyclic cobalt complex shows two distinct bands at 16000 and 18520 cm^{-1} attributable to $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)\,(\nu_2)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) transitions, respectively in octahedral field [14]. The interelectronic repulsion (B) and $10Dq$ are found to be 783 and 8550 cm^{-1} respectively. The ratio of observed ν_2 to calculated ν_1 is found to be 1.87, as required for an octahedral cobalt complex [18]. The *LFSE* is calculated and found to be 24.4 kcal/mol.

The magnetic moments of $[NiBDTSC(H_2O)_2]$ and the corresponding tetraaza macrocyclic Ni(II) complex are found to be 2.89 and 2.65 BM, respectively, in favor of octahedral geometry with a $^3A_{2g}$ ground state term symbol [14]. In the electronic spectra of $[NiBDTSC(H_2O)_2]$ and the nickel macrocycle bands at 8900, 8850 (ν_1); 15500, 15870 (ν_2) and 24390, 25000 (ν_3) cm^{-1} are attributable to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$; $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transitions, respectively. The spectral data are utilized to compute important ligand field parameters using the LF theory of spin-allowed transitions in d^8 configuration [19]. The value of B_{35} and $10Dq$ are used to calculate ν_2 and/or ν_3 and results are given in Table 2. The electronic and spectral data together with reported magnetic moment values of nickel complexes suggest an octahedral geometry for our complexes [14, 20].

The magnetic moments of Cu–BDTSC and the corresponding tetraaza macrocyclic copper complex are found to be 1.72 and 2.04 BM, respectively, which is in the range normally observed for copper complexes. The magnetic moment values of the copper complexes indicate no metal–metal interaction. The electronic spectrum of Cu–BDTSC shows a strong and broad band at 20200 cm^{-1}, which may be interpreted in terms of square planar geometry. The absence of any bands below 10000 cm^{-1} eliminates the possibility of a tetrahedral or pseudotetra-

TABLE 2. Electronic spectral data and ligand field parameters of nickel complexes

Complex (L = BDTSC)	Method of evaluation	ν_1	ν_2	ν_3	B_{35}	$\delta\nu$ [a]	B_{35} [b]	10*Dq*	$\nu_2 - \nu_1$	ν_2/ν_1	*LFSE* (kcal/mol)
[$NiL(H_2O)_2$]	observed values	8900	15500	24390				8900	6600	1.74	25.42
	A	10*Dq*	14481	25249	802	−140	0.77	8900	5581	1.62	
	B	10*Dq*	14645	25239	879	±860	0.84	8900	5745	1.64	
	C	10*Dq*	14429	23960	779	−1076	0.75	8900	5524	1.62	
[Ni(mac)]	observed values	8850	15870	25000				8850	7020	1.79	25.28
	A	10*Dq*	14636	25204	866	±1234	0.83	8850	5786	1.65	
	B	10*Dq*	14705	26145	954	±1165	0.92	8850	5855	1.66	
	C	10*Dq*	14247	23373	738	−1627	0.71	8850	5397	1.61	

[a] Difference in the observed value and calculated value of frequencies. [b] Ratio of the free ion and of complex.

hedral environment in this complex [21, 22]. A band at 15 870 cm^{-1} in the electronic spectrum of the tetraazamacrocyclic copper complex has been assigned to a $^2E_g \rightarrow {}^2T_{2g}$ transition suggesting that the complex has an octahedral arrangement around the metal ion.

The corresponding BDTSC complex with palladium is diamagnetic. In the electronic spectrum, it shows four absorption bands at 16 400, 25 640, 34 250 and 38 300 cm^{-1}. The first low-energy, spin allowed band has been assigned to a $^1A_{1g} \rightarrow {}^1A_{2g}$ transition similar to the one assigned by Jørgensen in $PdCl_4^{2-}$ [23]; the bathochromic shift is expected because of the spectrochemical difference between the BDTSC ligand and Cl^-. The second and third bands are spin allowed transitions which may be due to $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1E_g$ transitions, respectively. The highest energy band is assigned to a charge-transfer from ligand to metal. The values of the delta parameters have been evaluated from our data using the equations suggested by Lever [18]. These are 24 260, 17 430 and 6567 cm^{-1}, for Δ_1, Δ_2 and Δ_3, respectively. The first delta value is much larger than the other two for this complex, consistent with the idea that it is of square planar geometry.

Infrared Spectral Data

Complexes of BDTSC

A band at 3422 cm^{-1} in the IR spectrum of BDTSC remains in all complexes, indicating non-participation of the terminal nitrogen atoms in coordination. The secondary NH vibration occurs at 3380 cm^{-1} in the BDTSC spectrum and is absent in the spectra of all complexes. A strong and sharp band at 1605 cm^{-1} is assignable to the amide (>C=N–) and to the NH_2 bend [24]. In all complexes a new band is observed at 1572 ± 2 cm^{-1} due to participation of the azomethine nitrogen atom in chelation. In the spectra of all complexes, new bands are observed at 1615 ± 5 cm^{-1} attributable to the contribution of terminal NH_2 or >C=N– groups that are formed in thiol form.

Strong and sharp bands are observed at 1295 and 747 cm^{-1}, due to the C=S vibrations in the ligand spectrum. These bands disappear in all metal chelates and instead new bands arise around 640 cm^{-1}, characteristic of C–S vibrations formed after complexation [25]. The absence of bands in the ligand spectrum in the 2800–2650 cm^{-1} region indicates that BDTSC remains in the thione form at least in the solid state [26]. These facts are compatible with enolization of the $-NH-CS-NH_2$ group in the ligand to form $-N{=}CSH-NH_2$, which then loses the thiol proton and forms a covalent bond between the sulfur and the metal ion. In the far infrared, the M–S and M–N vibrations are observed at 335–322 and 440–435 cm^{-1}, respectively. A band at 3495 in the spectrum of the nickel complex is assigned to the OH vibration of coordinated water [27].

Tetraaza macrocyclic cobalt complex

The infrared spectrum of the tetraaza macrocyclic cobalt complex is almost identical to the spectrum of Co–BDTSC, except for the disappearance of the terminal $-NH_2$ bands.

Tetraaza macrocyclic complexes

A medium intensity band at 3300 cm^{-1} in the infrared spectrum of thiocarbohydrazide (TCH) is assigned to the N–H stretching of the $-NH_2$ (terminal) group. A broad band in the region between 3200 and 3100 cm^{-1} is attributable to the imino N–H vibration, which is probably involved in intramolecular hydrogen bonding.

In the infrared spectra of the complexes, bands due to carbonyl and NH_2 groups are absent, indicating condensation of benzil with thiocarbohydrazide. In all complexes a strong band at 1590 cm^{-1} is assigned to azomethine nitrogen atoms participating in coordination. Bands are also observed around 1615 cm^{-1}, due to >C=N– formed upon complexation. In the TCH spectrum, strong bands at 1275 and 750 cm^{-1} are due to C=S vibrations. These bands disappear in all complexes which show bands around

625 cm^{-1} instead, characteristic of C–S vibrations [25]. This sulfur–metal covalent bond shows in the far-IR spectra of all complexes in the 330–320 cm^{-1} region. The corresponding M–N bands appear in the 400–415 cm^{-1} region [27].

^{1}*H NMR Spectra*

In the nuclear magnetic resonance spectrum of BDTSC, two signals are observed at 3.25 and 3.56 ppm, assigned to NH and NH_2 protons, respectively. In all the complexes obtained with this ligand, the signal due to NH disappears. The absorption peaks corresponding to NH_2 and to aromatic protons for the complexes occur in the ranges of 3.35–3.36 and 7.83–7.05 ppm respectively. In the case of the nickel complex, a broad signal is observed around 7.66 ppm, due to coordinated water.

In the NMR spectra of the tetraaza macrocyclic cobalt complex, the absorptions due to NH and to NH_2 are not present. The NMR spectrum of this cobalt complex is presented in Fig. 1, where only the aromatic protons are observed.

Based on the results that we have presented so far, the structures V and VIII are tentatively assigned for the M–BDTSC complexes and their corresponding macrocycles.

An attempt was made to determine whether Co–BDTSC reacts reversibly with molecular oxygen. The electronic absorption spectra of a solution of this complex after bubbling with an inert gas (A), after bubbling with oxygen gas at 0 °C (B), and after deoxygenating by bubbling again with an inert gas (D), are given in Fig. 2. Pyridine was used as the axial

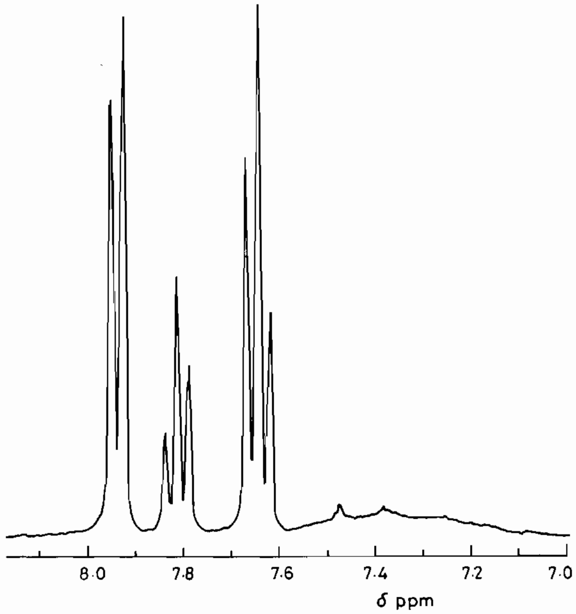
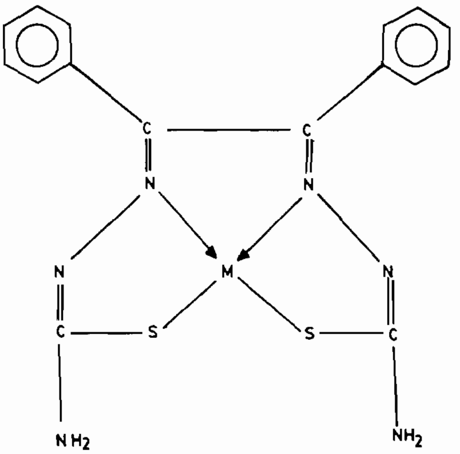
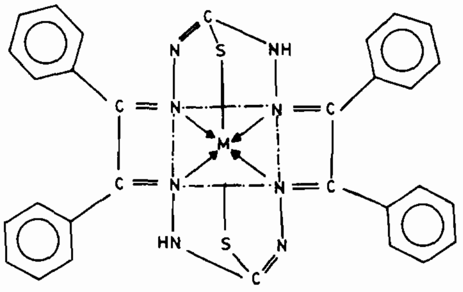


Fig. 1. ^{1}H NMR spectrum of tetraazamacrocyclic cobalt complex derived by condensation of Co–BDTSC and benzil in d_6-DMSO medium (δ in ppm) at room temperature.



V. Structure of metal complexes where M = Co(II), Ni(II), Cu(II), Pd(II).



VIII. Structure of macrocyclic metal complexes where M = Co(II), Fe(II), Ni(II) and Cu(II).

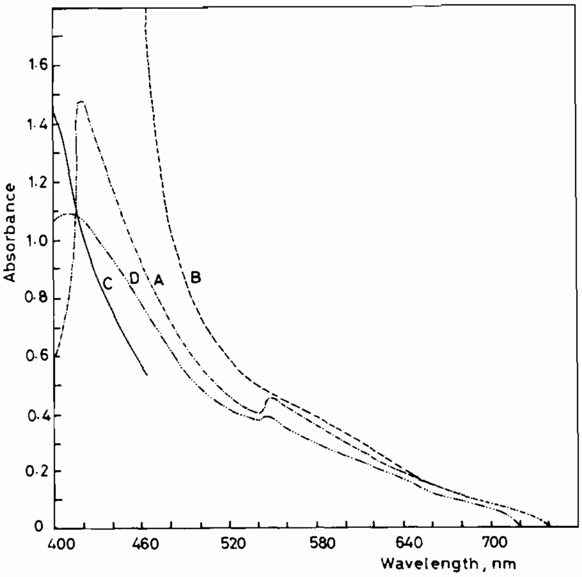


Fig. 2. Absorption spectra of Co–BDTSC complex in DMF medium containing 0.5% pyridine: A, after bubbling with an inert gas; B, after passing oxygen gas at ~0 °C; C, on dilution of solution under the conditions of B; D, after bubbling with an inert gas. [Co–BDTSC] = 5.0 × 10^{-4} M.

ligand. The difference in the spectra, curves (A) and (B) of Co–BDTSC in solution in the presence and in the absence of O_2, is attributed to the formation of an oxygenated form of the complex or to formation of a Co(III)–BDTSC complex. However, on bubbling with an inert gas, d–d bands appear (curve D) at 410 and 550 nm, indicating the presence of the original species, that is the deoxygenated form. Hence, the electronic absorption spectra suggest at least in the qualitative sense, the possibility of reversible oxygen binding by Co–BDTSC.

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