

## Synthesis, Characterization, Solvatochromic Behavior and Crystal Structures of Complexes $[\text{Co}^{\text{III}}(\text{salophen})(\text{thioacetamide})_2]\text{ClO}_4$ and $[\text{Co}^{\text{III}}(\text{salophen})(\text{thiobenzamide})_2]\text{ClO}_4$

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Two new cobalt(III) complexes of the Schiff base *N,N'*-disalicylidene-1,2-phenylendiimine dianion (salophen), *trans*- $[\text{Co}^{\text{III}}(\text{salophen})(\text{ta})_2]\text{ClO}_4$ , (ta = thioacetamide) (**1**) and *trans*- $[\text{Co}^{\text{III}}(\text{salophen})(\text{tb})_2]\text{ClO}_4$ , (tb = thiobenzamide) (**2**) were synthesized and characterized using single-crystal X-ray diffraction and spectroscopic techniques. Both complexes show solvatochromism in a variety of solvents. Complex (**1**) crystallized from  $\text{CHCl}_3$  as a solvate of orthorhombic symmetry, space group  $Pca2_1$  with  $a = 17.3480(10)$  Å,  $b = 18.7522(10)$  Å,  $c = 18.8128(11)$  Å,  $\alpha = \beta = \gamma = 90^\circ$ , and  $Z = 8$ . The cobalt(III) center lies in a distorted octahedral environment. The crystal structure of (**1**) consists of two independent  $[\text{Co}^{\text{III}}(\text{salophen})(\text{ta})_2]^+$  cations and  $\text{ClO}_4^-$  anions held together essentially *via* hydrogen bonds and  $\pi$ - $\pi$  stacking interactions. Complex (**2**), forming also a  $\text{CHCl}_3$  solvate, crystallized in the monoclinic space group  $P2_1/n$  with  $a = 14.710(3)$  Å,  $b = 13.506(3)$  Å,  $c = 18.595(4)$  Å,  $\beta = 100.295(4)^\circ$ , and  $Z = 4$ . The geometry around cobalt(III) center is a distorted octahedron. The crystal structure of (**2**) contains a  $[\text{Co}^{\text{III}}(\text{salophen})(\text{tb})_2]^+$  complex with a remarkably twisted salophen ligand. Both complexes, (**1**) and (**2**), contain approximately one disordered  $\text{CHCl}_3$  molecule per Co in the solid state.

**Keywords:** Cobalt(III) complexes, Salophen Schiff base, X-Ray crystal structure, Solvatochromism

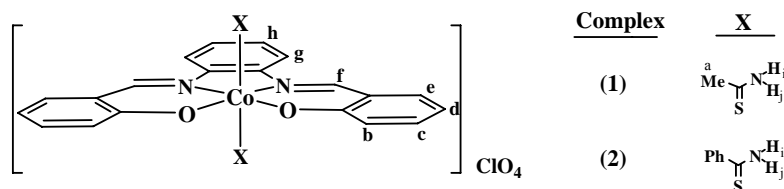
### INTRODUCTION

Quadridentate Schiff base cobalt complexes have been widely studied, particularly as homogeneous catalysts, oxygen carriers, and models of compounds with biological function [1-12]. It is known that variation of the size and nature of the ligand can be responsible for changes in the coordination geometry around central metal ions. The electronic absorption spectrum of a complex is strongly dependent on these structural changes, as well as the interaction of the solvent molecules

with the coordination environment of the complex. We have recently reported the solvatochromic properties of *trans*- $[\text{Co}^{\text{III}}(\text{acacen})(\text{ta})_2]\text{ClO}_4$  and *trans*- $[\text{Co}(\text{BA})_2\text{en}(\text{ta})_2]\text{PF}_6$  complexes with the possible application in chemical sensors [13]. Appropriate tailoring of the geometry around the central metal ions is of key importance in the modification of the spectroscopic and solvatochromic properties of the complexes [14].

In continuation of our studies on the electronic spectra of cobalt(III) complexes in various solvents we decided to synthesize and study the nature of the complexes formed by the tetradentate Schiff base ligand salophen and two thioamide

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Scheme 1

ancillary ligands. The electronic absorption spectra of the complexes show strong dependence on the type of the solvent used and a substitution reaction is envisaged for the complexes in coordinating solvents such as acetonitrile. Herein, we report the result of our spectroscopic studies along with the X-ray crystal structures of *trans*-[Co<sup>III</sup>(salophen)(ta)<sub>2</sub>](ClO<sub>4</sub>) (**1**) and *trans*-[Co<sup>I</sup>(salophen)(tb)<sub>2</sub>](ClO<sub>4</sub>) (**2**), the first [Co<sup>III</sup>(salophen)X<sub>2</sub>]<sup>+</sup> structures containing S-donor axial ligands (Scheme 1).

## EXPERIMENTAL

### Materials and General Methods

All chemicals were purchased from commercial sources and used as received. Elemental analyses were performed by using a Perkin-Elmer 2400II CHNS-O elemental analyzer. Infrared spectra (KBr pellet) were recorded on a FT-IR JASCO 680 instrument. Electronic spectra were obtained on a JASCO V-570 spectrophotometer. <sup>1</sup>H NMR spectra were measured with a Bruker AVANCE DR X500 spectrometer (500 MHz). Proton chemical shifts are reported in ppm relative to internal standard Me<sub>4</sub>Si.

### Preparation of H<sub>2</sub>salophen Ligand

H<sub>2</sub>salophen, *N,N'*-disalicylidene-1,2-phenylenediimine was prepared according to the literature by condensation of 1,2-phenylenediamine with salicylaldehyde (1:2 mol stoichiometric ratio) in methanol (or ethanol) at room temperature (r.t.) and was purified by recrystallization from hot ethyl acetate [15]. Yield 90%. FT-IR (KBr, cm<sup>-1</sup>): ν<sub>max</sub> 3300-3400 (m, br, OH), 1615 (s, C=N). UV-Vis: λ<sub>max</sub> (nm) (ε, M<sup>-1</sup> cm<sup>-1</sup>) (CH<sub>3</sub>CN): 362 (10276), 333 (17750). <sup>1</sup>H NMR (CD<sub>3</sub>COCD<sub>3</sub>, 500 MHz): δ = 7.00-7.04 (m, 4H, H<sub>b</sub>, H<sub>d</sub>), 7.46-7.52 (m, 6H, H<sub>c</sub>, H<sub>g</sub>, H<sub>h</sub>), 7.65 (dd, 2H, H<sub>e</sub>), 8.94 (s, 2H, H<sub>f</sub>), 13.1 (s, 2H, OH).

### Preparation of [Co<sup>II</sup>(salophen)] Complex

[Co<sup>II</sup>(salophen)] was prepared according to the literature by the reaction of 1.58 g (5 mmol) of *N,N'*-bis(salicylidene)-1,2-phenylenediimine with 1.25 g (5 mmol) of Co(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O in 400 ml of boiling methanol yielding 1.50 g (80%) of violet-brown needles of Co<sup>II</sup>(salophen) which were washed with methanol and diethyl ether [16].

### Preparation of *trans*-[Co<sup>III</sup>(salophen)(ta)<sub>2</sub>](ClO<sub>4</sub>) (**1**)

To prepare the title compound, (**1**), a homogenized mixture of 1.120 g (3 mmol) of [Co<sup>II</sup>(salophen)], 0.900 g (12 mmol) of thioacetamide, and 1.200 g of silica gel in a porcelain dish was heated at 80 °C for 30 min. The color changed from cherry red to dark brown. The reaction mixture was then cooled to room temperature and treated with 50 ml of chloroform. A solution of 0.368 g (3 mmol) sodium perchlorate in 3 ml methanol was then added and the mixture was stirred for 30 min and finally filtered off. The filtrate was left in the open air and slow evaporation of the solvent at room temperature gave a dark red microcrystalline powder. Recrystallization from chloroform furnished dark red crystals of a CHCl<sub>3</sub> solvate of (**1**) with a solvent content of *ca.* 1 molecule per Co. Yield: 50%. Anal. calcd. for C<sub>24</sub>H<sub>24</sub>ClN<sub>4</sub>O<sub>6</sub>S<sub>2</sub>Co: C 46.27, H 3.88, N 8.99; found: C 45.52, H 3.80, N 8.90. ν<sub>max</sub>/cm<sup>-1</sup> (KBr): 3330 (m, N-H), 1610 (s, C=N), 1323 (m, C-N), 705 (m, C=S), 1083 (s, ClO<sub>4</sub>). <sup>1</sup>H NMR (500 MHz, (CD<sub>3</sub>COCD<sub>3</sub>) δ: 2.22 (s, 6H<sub>a</sub>, CH<sub>3</sub>), 6.76 (m, 2H, H<sub>d</sub>), 7.31 (br d, 2H, J = 8.5 Hz, H<sub>b</sub>), 7.39 (m, 2H, H<sub>c</sub>), 7.55 (AA'XX', 2H, J<sub>m</sub> = 3.2, J<sub>o</sub> = 6.3 Hz, H<sub>h</sub>), 7.65 (dd, 2H, J<sub>m</sub> = 1.47, J<sub>o</sub> = 7.87 Hz, H<sub>e</sub>), 8.39 (AA'XX', 2H, J<sub>m</sub> = 3.2, J<sub>o</sub> = 6.3 Hz, H<sub>g</sub>), 8.88 (s, 2H, H<sub>f</sub>), 9.89 (br s, 2H, NH<sub>i</sub>), 10.99 (br s, 2H, NH<sub>j</sub>).

### Preparation of *trans*-[Co<sup>III</sup>(salophen)(tb)<sub>2</sub>](ClO<sub>4</sub>) (**2**)

This complex was prepared by a procedure similar to

the one used for **(1)** except that thiobenzamide was used instead of thioacetamide. Recrystallization from chloroform furnished dark red crystals of a  $\text{CHCl}_3$  solvate of **(2)** with a solvent content of *ca.* 1 molecule per Co. Yield: 55%. Anal. calcd. for  $\text{C}_{34}\text{H}_{28}\text{ClN}_4\text{O}_6\text{S}_2\text{Co}$ : C, 54.66; H, 3.78; N, 7.50; found: C 53.07, H 3.57, N 7.25.  $\nu_{\text{max}}/\text{cm}^{-1}$  (KBr): 3403 (m, N-H), 1609 (s, C=N), 703 (m, C=S), 1322 (m, C-N), 1095 (s,  $\text{ClO}_4$ ).  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{COCD}_3$ )  $\delta$ : 6.76 (br t, 2H,  $\text{H}_d$ ), 7.37-7.69 (m, 18H,  $\text{H}_{\text{Ph,h,b,c,e}}$ ), 8.50 (m, 2H,  $\text{H}_g$ ), 8.99 (br s, 2H,  $\text{H}_f$ ), 10.20 (br s, 2H,  $\text{NH}_i$ ), 11.48 (br s, 2H,  $\text{NH}_j$ ).

### X-Ray Crystallography for **(1)** and **(2)**

Dark red crystals suitable for X-ray crystallography were obtained by slow evaporation of chloroform solutions of the complexes at room temperature. X-ray data were collected on a Bruker Smart APEX CCD diffractometer with graphite monochromated Mo  $\text{K}\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation and  $0.3^\circ$   $\omega$ -scan frames covering approximately the whole sphere of the reciprocal space. Cell refinement and data reduction were made with the help of the SAINT program [17]. Corrections for absorption were made with the multi-scan method and program SADABS [17]. The structures were solved using direct methods (SHELXS-97) and refined against  $F^2$  using the SHELXL-97. [18]. Both solids were  $\text{CHCl}_3$  solvates with disordered solvent and an approximate solvent content of 1  $\text{CHCl}_3$  per Co. Therefore, the solvent was squeezed with program PLATON [19] prior to the final refinement. A summary of the crystal data along with further details of the structure determinations are given in Table 1.

## RESULTS AND DISCUSSION

### Spectral Studies

Ambidentate ligands can bond to a metal center through more than one kind of atom. The classic examples are the thioamide ligands which can bind in a monodentate fashion through the S or the N atom [13,20]. For example, thioacetamide and thiobenzamide exist as the two resonance structures presented in Scheme 2.

In form **(I)** the ligand binds through the lone pair of the nitrogen atom and consequently the C-N stretching frequency is lowered while the C=S stretching frequency is raised relative to the free ligands. In form **(II)**, the ligand binds through the

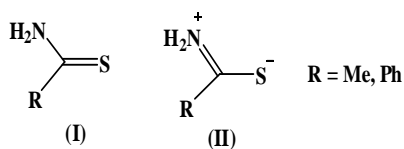
lone pair of the central sulfur atom and as a result, the C-N stretching frequency is raised while the C=S stretching frequency is lowered relative to the free ligands. As we have recently reported [13], the thioacetamide binds to cobalt through the S atom in *trans*- $[\text{Co}^{\text{III}}((\text{BA})_2\text{en})(\text{ta})_2]\text{PF}_6$  and *trans*- $[\text{Co}^{\text{III}}(\text{acacen})(\text{ta})_2]\text{ClO}_4$  complexes. The IR spectrum of the free ligand exhibits the characteristic band of an imine at  $1614 \text{ cm}^{-1}$  [15]. This band is shifted to lower frequencies by 5-6  $\text{cm}^{-1}$  in the corresponding cobalt complexes, due to the coordination of the imine nitrogen [21]. Also, a band at  $3300\text{-}3400 \text{ cm}^{-1}$ , characteristic of the OH group in the free ligand, is absent in the IR spectrum of the complex which indicates that the Schiff base is coordinated in its deprotonated form. The  $\nu(\text{CS})$ , appearing at  $705 \text{ cm}^{-1}$  for the free thiobenzamide, appears at  $703 \text{ cm}^{-1}$  in **(1)** and  $692 \text{ cm}^{-1}$  in **(2)**. The small increase in  $\nu(\text{CN})$  and the small decrease in  $\nu(\text{CS})$  of the coordinated thioacetamide and thiobenzamide, are consistent with the metal sulfur coordination of the thione forms, and conform to the X-ray molecular structures. The stretching vibration of  $\text{ClO}_4^-$  anion is observed at  $1083 \text{ cm}^{-1}$  in **(1)** and at  $1095 \text{ cm}^{-1}$  in **(2)** [22].

The  $^1\text{H}$  NMR spectral data are presented under the heading 'Experimental'. The low field signal, which appears at  $\delta = 13.1$  in the free ligand, due to the extensive hydrogen bond formation, is absent in the NMR spectra of the complexes which clearly indicates that the salophen Schiff base is coordinated as a dianionic ligand. The  $^1\text{H}$  NMR spectrum of **(1)** in  $\text{CD}_3\text{COCD}_3$  is shown in Fig. 1A (assignment as in Scheme 1). The signal appearing as a singlet at  $\sim 2.22$  ppm in the  $^1\text{H}$  NMR spectrum of **(1)** is assigned to the two  $\text{CH}_3$  groups of thioacetamide ligands. The two  $=\text{CH}$  protons,  $\text{H}_f$ , adjacent to the iminic nitrogens appear at 8.88 ppm. The two N-H protons of the coordinated thioacetamide,  $\text{H}_i$  and  $\text{H}_j$ , appear at 9.89 ppm and 10.99 ppm, respectively. The aromatic protons of the phenyl rings in the coordinated Schiff base ligand appear in the appropriate region. The  $^1\text{H}$  NMR spectral data of **(2)** in  $\text{CD}_3\text{COCD}_3$  show features similar to those observed for complex **(1)**, Fig. 1B. The two  $=\text{CH}$  protons,  $\text{H}_f$ , adjacent to the iminic nitrogens appear at the  $\sim 8.99$  ppm. The aromatic protons of the phenyl rings in the coordinated Schiff base ligand and the thiobenzamide appear at 6.8-8.5 ppm range. The two signals at 10.19 ppm and 11.48 ppm, are assigned to the two N-H protons of the coordinated thiobenzamide,  $\text{H}_i$  and  $\text{H}_j$ ,

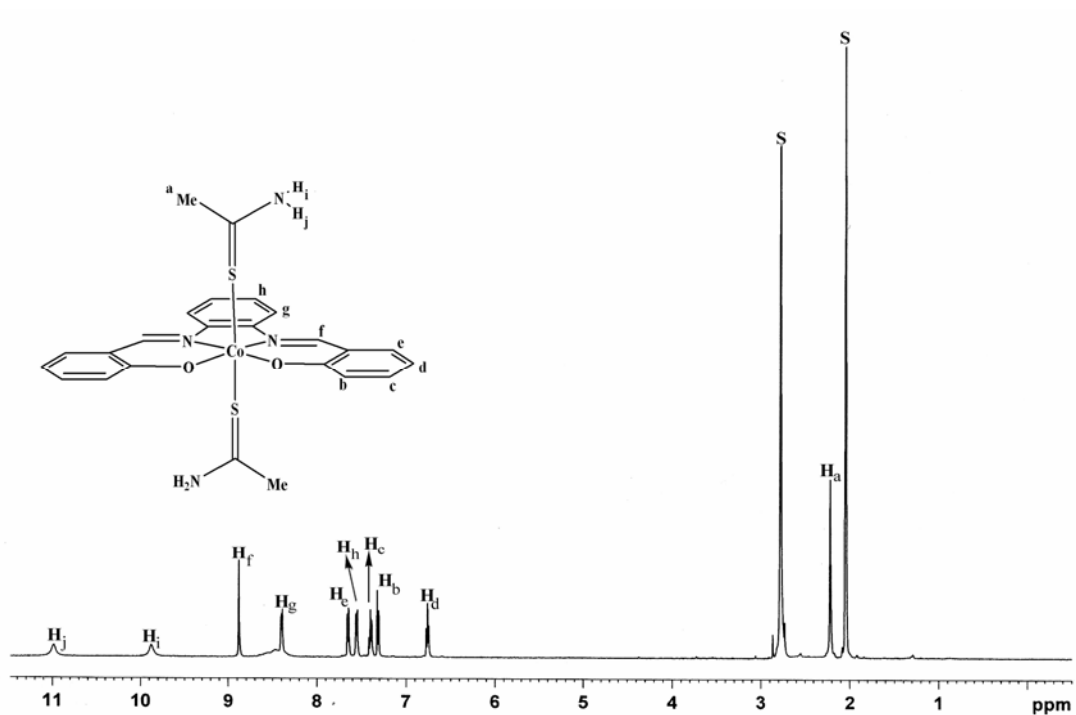
**Table 1.** Crystal Data and Structure Refinement for (1) and (2)

|  |   |   |
|--|---|---|
| Empirical formula <sup>a</sup>   | C <sub>24</sub> H <sub>24</sub> ClCoN <sub>4</sub> O <sub>6</sub> S <sub>2</sub> .CHCl <sub>3</sub> (1) | C <sub>34</sub> H <sub>28</sub> ClCoN <sub>4</sub> O <sub>6</sub> S <sub>2</sub> .CHCl <sub>3</sub> (2) |
| Formula weight   | 742.34  | 866.49  |
| Temperature(K)   | 100(2)  | 100(2)  |
| Radiation, wavelength (Å)  | Mo-Kα, 0.71073  | Mo-Kα, 0.71073  |
| Crystal system, space group  | Orthorhombic, <i>Pca</i> 2 <sub>1</sub>   | Monoclinic, <i>P2</i> <sub>1</sub> / <i>n</i>   |
| <i>a</i> (Å)   | 17.3480(10)   | 14.710(3)   |
| <i>b</i> (Å)   | 18.7522(10)   | 13.506(3)   |
| <i>c</i> (Å)   | 18.8128(11)   | 18.595(4)   |
| $\beta$ (°)  |   | 100.295(4)  |
| <i>V</i> (Å <sup>3</sup> )   | 6120.1(6)   | 3634.9(12)  |
| <i>Z</i>   | 8   | 4   |
| <i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )                                 | 1.611   | 1.583   |
| Crystal color and size (mm <sup>3</sup> )                                      | Dark red, 0.40 × 0.36 × 0.13  | Dark red, 0.55 × 0.27 × 0.16  |
| $\mu$ (mm <sup>-1</sup> )  | 1.093   | 0.933   |
| <i>F</i> (000)   | 3024  | 1536  |
| $\theta$ Range (°)   | 2.42-27.00°   | 2.46-24.99  |
| Index range  | -22 ≤ <i>h</i> ≤ 22<br>-23 ≤ <i>k</i> ≤ 23<br>-18 ≤ <i>l</i> ≤ 23                                       | -17 ≤ <i>h</i> ≤ 17<br>-15 ≤ <i>k</i> ≤ 16<br>-20 ≤ <i>l</i> ≤ 22                                       |
| Reflection collected   | 38388   | 15641   |
| Independent reflections  | 11421 [ <i>R</i> <sub>int</sub> = 0.049]  | 6378 [ <i>R</i> <sub>int</sub> = 0.145]   |
| Reflections with <i>F</i> <sup>2</sup> > 2σ                                    | 9657  | 3386  |
| Absorption correction  | Multi-scan  | Multi-scan  |
| Max. and min transmission  | 0.87 and 0.63   | 0.86 and 0.75   |
| Data/restraints/parameters   | 11421/1/690   | 6378/0/433  |
| Goodness-of-fit on <i>F</i> <sup>2</sup>                                       | 1.033   | 0.963   |
| Final <i>R</i> indices [ <i>F</i> <sup>2</sup> > 2σ ( <i>F</i> <sup>2</sup> )] | <i>R</i> <sub>1</sub> = 0.0470, <i>wR</i> <sub>2</sub> = 0.1089   | <i>R</i> <sub>1</sub> = 0.0769, <i>wR</i> <sub>2</sub> = 0.1913   |
| <i>R</i> indices (all data)  | <i>R</i> <sub>1</sub> = 0.0583, <i>wR</i> <sub>2</sub> = 0.1138   | <i>R</i> <sub>1</sub> = 0.1373, <i>wR</i> <sub>2</sub> = 0.2156   |
| Largest difference peak, hole (e Å <sup>-3</sup> )                             | 0.93 and -0.35  | 0.64 and -0.44  |

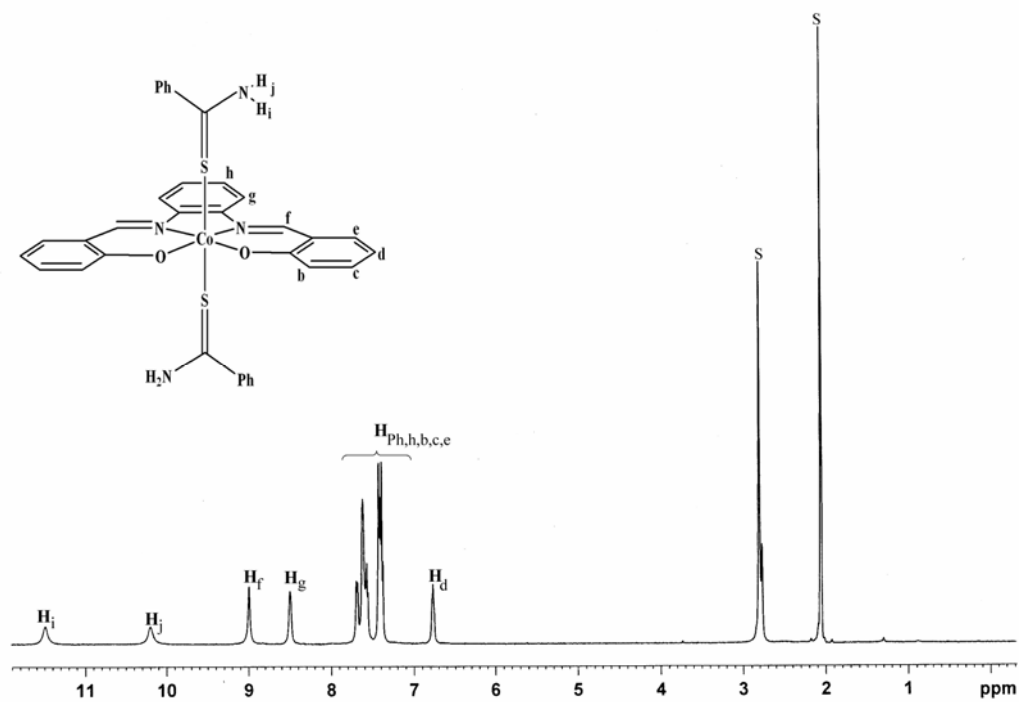
<sup>a</sup>Both compounds were in solid state solvates with disordered and substoichiometric CHCl<sub>3</sub> that was squeezed with program PLATON [19]. The idealized solvent content of both compounds is considered 1 CHCl<sub>3</sub> per formula unit. This idealized solvent content is given here in the empirical formula and quantities derived thereof.

*Scheme 2*

respectively. Since these two hydrogen atoms are involved in different hydrogen bonding patterns in both complexes (*vide infra*, Fig. 3 and 4, Table 3 and 4), the signals due to H<sub>i</sub> and H<sub>j</sub> would presumably appear at considerably different chemical shifts if the hydrogen bonding retains its character in solution. This is most probably the origin of observing a higher chemical shift for the H<sub>j</sub> proton, which is more strongly involved in an



**Fig. 1A.**  $^1\text{H}$  NMR spectrum of  $\text{trans-}[\text{Co}^{\text{III}}(\text{salophen})(\text{ta})_2]\text{ClO}_4$  (1) in  $\text{CDCl}_3$  at 298 K. The spectrum is labeled as to peak assignment discussed in the text.



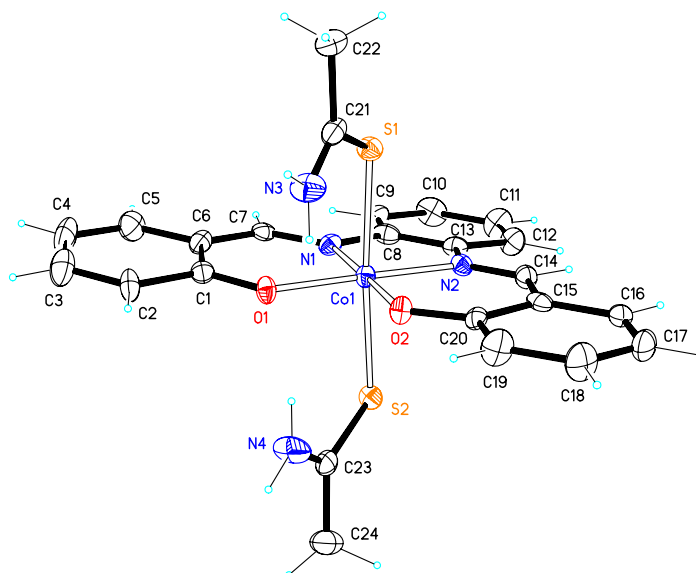
**Fig. 1B.**  $^1\text{H}$  NMR spectrum of  $\text{trans-}[\text{Co}^{\text{III}}(\text{salophen})(\text{tb})_2]\text{ClO}_4$  (2) in  $\text{CDCl}_3$  at 298 K. The spectrum is labeled as to peak assignment discussed in the text.

intramolecular hydrogen bonding relative to H<sub>j</sub> proton.

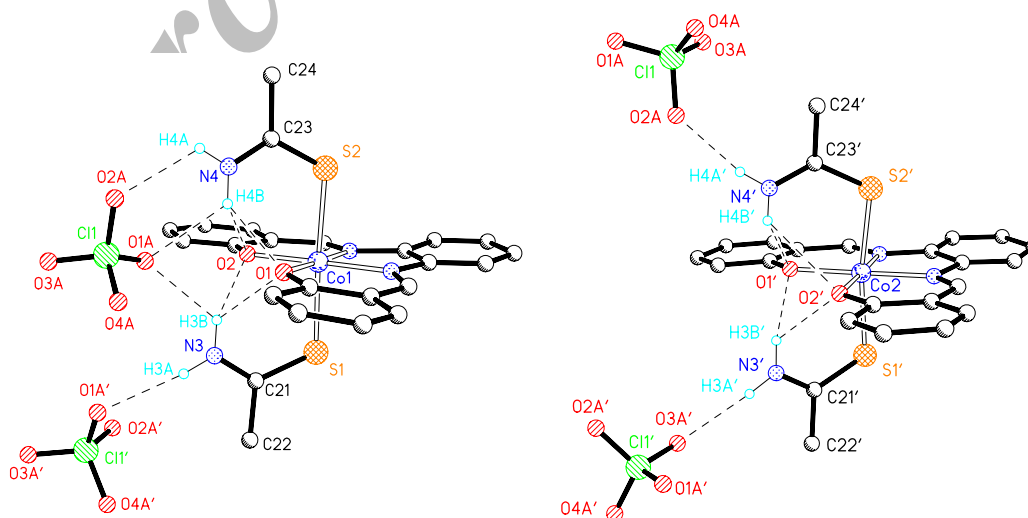
### Description of Structures

**Crystal structure of *trans*-[Co<sup>III</sup>(salophen)(ta)<sub>2</sub>]ClO<sub>4</sub> (1).** The ORTEP drawing of the cation of *trans*-[Co<sup>III</sup>(salophen)(ta)<sub>2</sub>]ClO<sub>4</sub> is presented in Fig. 2. The

asymmetric unit consists of two crystallographically independent, but chemically identical and geometrically very similar complexes that show differences in their environment, particularly with respect to ClO<sub>4</sub> (Fig. 3). The weighted rms positional difference of corresponding non-H atoms of the two complexes is 0.113 Å. In this complex, the Schiff base ligand



**Fig. 2.** ORTEP representation of one of the two independent Co complex cations in (1), showing the atom-numbering and 50% probability displacement ellipsoids.



**Fig. 3.** Hydrogen bonds for the two independent Co complexes in (1) emphasizing the notably different cation-anion interaction of the two. C-bonded hydrogens omitted for clarity.

(ONNO ligand) coordinates the cobalt ion in four equatorial positions, and the two thioacetamide molecules occupy the two axial sites, resulting in a distorted octahedral geometry around the cobalt center. Selected bond distances and bond angles are listed in Table 2. The Co-O and Co-N bond distances of the

salophen ligand in the equatorial plane, Co1-O1 = 1.885(3) Å, Co1-O2 = 1.883(3) Å, Co1-N1 = 1.905(4) Å, Co1-N2 = 1.903(3) Å (values for Co2 are similar), compare well with the Co-O and Co-N distances found in *trans*-[Co<sup>III</sup>(salophen)(morpholine)<sub>2</sub>]ClO<sub>4</sub> (Co-O1 = 1.883(2) Å, Co-O24 = 1.880(2)

**Table 2.** Selected Bond Lengths (Å) and Angles (°) for (1) and (2)

|              | (1)        | (2)       |            |
|--------------|------------|-----------|------------|
| Bond lengths |            |           |            |
| Co1-O2       | 1.883(3)   | Co1-O2    | 1.875(4)   |
| Co1-O1       | 1.885(3)   | Co1-O1    | 1.883(4)   |
| Co1-N2       | 1.903(3)   | Co1-N2    | 1.872(5)   |
| Co1-N1       | 1.905(4)   | Co1-N1    | 1.883(5)   |
| Co1-S1       | 2.2884(13) | Co1-S1    | 2.300(19)  |
| Co1-S2       | 2.3035(13) | Co1-S2    | 2.306(2)   |
| Co2-O2'      | 1.888(3)   |           |            |
| Co2-O1'      | 1.892(3)   |           |            |
| Co2-N2'      | 1.898(3)   |           |            |
| Co2-N1'      | 1.901(4)   |           |            |
| Co2-S2'      | 2.2949(12) |           |            |
| Co2-S1'      | 2.2975(12) |           |            |
| Bond angles  |            |           |            |
| O2-Co1-N1    | 178.50(14) | O2-Co1-N1 | 178.48(19) |
| O1-Co1-N2    | 178.80(15) | N2-Co1-O1 | 179.4(2)   |
| S1-Co1-S2    | 174.68(5)  | S1-Co1-S2 | 171.62(7)  |
| O2-Co1-O1    | 83.63(13)  | O2-Co1-O1 | 84.47(18)  |
| N2-Co1-N1    | 85.36(15)  | N2-Co1-N1 | 85.0(2)    |
| O1-Co1-N1    | 94.90(14)  | N1-Co1-O1 | 94.4(2)    |
| N2-Co1-S1    | 89.03(11)  | N2-Co1-S1 | 87.42(16)  |
| O2-Co1-S1    | 91.40(10)  | O2-Co1-S1 | 90.91(14)  |
| O1-Co1-S1    | 92.15(10)  | O1-Co1-S1 | 92.42(16)  |
| N1-Co1-S1    | 88.33(11)  | N1-Co1-S1 | 88.17(16)  |
| N2-Co1-S2    | 85.76(11)  | N2-Co1-S2 | 84.86(16)  |
| O2-Co1-S2    | 90.20(10)  | O2-Co1-S2 | 93.17(14)  |
| N1-Co1-S2    | 90.20(11)  | N1-Co1-S2 | 87.90(16)  |
| O1-Co1-S2    | 93.07(10)  | O1-Co1-S2 | 95.26(16)  |
| O2-Co1-N2    | 96.11(14)  | N2-Co1-O2 | 96.1(2)    |
| O1'-Co2-N2'  | 179.24(14) |           |            |
| O2'-Co2-N1'  | 178.49(14) |           |            |
| S1'-Co2-S2'  | 171.59(4)  |           |            |
| O2'-Co2-O1'  | 83.49(12)  |           |            |
| O2'-Co2-N2'  | 96.30(14)  |           |            |
| O1'-Co2-N1'  | 95.03(14)  |           |            |
| N2'-Co2-N1'  | 85.19(15)  |           |            |

Å, Co-N16 = 1.891(2) Å, Co-N9 = 1.894(2) Å) [15]. The axial Co-S bond distances (Co1-S1 = 2.2884(13) Å, Co1-S2 = 2.3035(13) Å) are in good agreement with the Co-S distances in the related complexes [13,23] (e.g. [Co(NioxH)<sub>2</sub>(Thio)<sub>2</sub>]<sub>2</sub>SiF<sub>6</sub>, Co-S = 2.300-2.318 Å; *trans*-[Co<sup>III</sup>((BA)<sub>2</sub>en)(ta)<sub>2</sub>]PF<sub>6</sub>, Co-S = 2.317 Å; *trans*-[Co<sup>III</sup>(acacen)(ta)<sub>2</sub>]ClO<sub>4</sub>, Co-S = 2.302 Å). The C-S and C-N bond distances for the axial thioacetamide ligands (C21-S1 = 1.707(5) Å, C23-S2 = 1.701(4) Å, C21-N3 = 1.288(6) Å, C23-N4 = 1.290(6) Å) are close to the C=S double bond (1.6854(10) Å) and the C-N single bond (1.3126(12) Å) in free thioacetamide [24]. These values are in good agreement with the corresponding data in *trans*-[Co<sup>III</sup>(acacen)(ta)<sub>2</sub>]ClO<sub>4</sub> [13]. The ligand-cobalt-ligand bond angles are found to be in the range of 83 to 96, deviating somewhat from the ideal, and correlate well with the corresponding values in the related complexes [13]. The (N-H) atoms of the axial thioacetamide ligands are involved in hydrogen bonding with the oxygen atoms of ClO<sub>4</sub><sup>-</sup> and the equatorial Schiff base ligand, as shown in Fig. 3. The geometry of the hydrogen bonds is given in Table 3.

**Crystal structure of *trans*-[Co<sup>III</sup>(salophen)(tb)<sub>2</sub>]ClO<sub>4</sub> (2).** The molecular structure of *trans*-[Co<sup>III</sup>(salophen)(tb)<sub>2</sub>]ClO<sub>4</sub> in

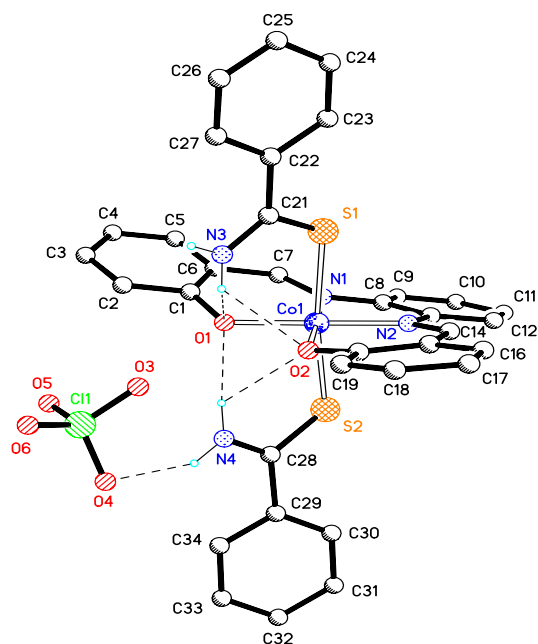
solid state with the atom numbering scheme is presented in Fig. 4 and selected bond angles and distances are listed in Table 2. Similar to the crystal structure of compound (1), the cobalt in compound (2) adopts a modestly distorted octahedral coordination by the four equatorial O and N atoms of the salophen ligand and the two axial atoms of the two thiobenzamides (ligand-cobalt-ligand bond angles 84 to 96° and 172 to 179°). The Co-O and Co-N bond distances of the salophen ligand (Co(1)-O(1) = 1.883(4) Å, Co(1)-O(2) = 1.875(4) Å, Co(1)-N(1) = 1.883(5) Å, Co(1)-N(2) = 1.872(5) Å) and the two axial Co-S bond distances (Co(1)-S(1) = 2.300(19) Å, Co(1)-S(2) = 2.306(2) Å) are in reasonable agreement with the crystal structure of compound (1) and the related complexes discussed above. Unlike solid (1), where the salophen ligands of the two independent complexes are essentially planar (rms aplanarities 0.079 and 0.047 Å, respectively), the salophen ligand in solid (2) is remarkably twisted by showing an rms aplanarity of 0.293 Å and an interplanar angle of 28.2(3)° between the two phenolate rings. The non-planarity of the two thiobenzamide moieties in solid (2) is more usual, which shows thioamide-benzene interplanar angles of 12° and 21°. Both outlined features of solid (2), *i.e.*

**Table 3.** The Hydrogen Bonds for (1)

| D-H...A                      | <i>d</i> (D-H) (Å) | <i>d</i> (H...A) (Å) | <i>d</i> (D...A) (Å) | <(DHA) (°) |
|------------------------------|--------------------|----------------------|----------------------|------------|
| N3-H3A...O1A'                | 0.88               | 2.30                 | 3.174(6)             | 173.2      |
| N3-H3B...O2                  | 0.88               | 2.16                 | 2.826(5)             | 132.5      |
| N3-H3B...O1                  | 0.88               | 2.26                 | 2.896(5)             | 128.5      |
| N3-H3B...O1A                 | 0.88               | 2.29                 | 2.907(5)             | 127.0      |
| N4-H4A...O2A                 | 0.88               | 2.46                 | 3.034(5)             | 123.4      |
| N4-H4B...O1                  | 0.88               | 2.12                 | 2.811(5)             | 135.4      |
| N4-H4B...O2                  | 0.88               | 2.38                 | 3.007(5)             | 128.0      |
| N4-H4B...O1A                 | 0.88               | 2.41                 | 3.018(6)             | 126.3      |
| N3'-H3A'...O3A <sup>#1</sup> | 0.88               | 2.22                 | 3.094(5)             | 175.2      |
| N3'-H3B'...O1'               | 0.88               | 2.192                | 2.854(5)             | 132.1      |
| N3'-H3B'...O2'               | 0.88               | 2.22                 | 2.869(5)             | 130.5      |
| N4'-H4A'...O2A <sup>#2</sup> | 0.88               | 2.13                 | 2.987(5)             | 165.8      |
| N4'-H4B'...O1'               | 0.88               | 1.97                 | 2.748(5)             | 146.5      |
| N4-H4B...O1                  | 0.88               | 2.12                 | 2.811(5)             | 135.4      |
| N4-H4B...O2                  | 0.88               | 2.38                 | 3.007(5)             | 128.0      |

Symmetry transformation used to generate equivalent atoms: #1: -x+1/2, y-1, z-1/2; #2: x, y-1, z





**Fig. 4.** The Co complex in (2) and its hydrogen bonds. C-bonded hydrogens omitted for clarity.

the pronounced twist of the salophen ligand and the conformation and orientation of the thiobenzamide ligands, appear to be caused by  $\pi$ - $\pi$  stacking contacts (e.g. between pairs of diaminobenzene rings or pairs of thiobenzamide benzene rings) and other crystal packing effects. The hydrogen bonding and interaction tendencies between the *trans*-[Co<sup>III</sup>(salophen)(tb)<sub>2</sub>] cation and the ClO<sub>4</sub> anion in solid (2) show similar trends as in solid (1), as may be seen from a comparison of Figs. 3 and 4. The geometry of hydrogen bonds in (2) is given in Table 4.

### Solvatochromic Studies

The electronic absorption spectra of *trans*-[Co<sup>III</sup>(salophen)(ta)<sub>2</sub>]ClO<sub>4</sub> (1) and *trans*-[Co<sup>III</sup>(salophen)(tb)<sub>2</sub>]ClO<sub>4</sub> (2) were measured in solution in various organic solvents (Table 5). The electronic absorption spectrum of complex (1) shows a distinct shoulder at 600 ( $\epsilon = 2025$ ) and a true maximum at 497 nm ( $\epsilon = 8107$ ), while that of complex (2) shows two true maxima at 614 ( $\epsilon = 2652$ ) and 500 nm ( $\epsilon = 7190$ ) in chloroform. It is interesting to note that the two similar absorption bands appear at 518 and 378 nm in the spectrum of *trans*-[Co<sup>III</sup>(acacen)(ta)<sub>2</sub>]ClO<sub>4</sub> [13]. The transitions have been assigned as a combination of thioamide  $\rightarrow$  acacen LLCT (metal mediated ligand to ligand charge transfer) and thioamide  $\rightarrow$  Co LMCT (ligand to metal charge transfer) [13]; some Co-centered d-d transition is also possible. The red shift of about 100 nm in the position of these bands on going from acacen complex to the salophen complexes may be ascribed to the reduction in energy of the salophen  $\pi$ -level relative to acacen due to the fused phenyl ring in salophen which facilitates the  $\pi$ -electron delocalization [25]. The positions of these bands are solvent-dependent and show negative solvatochromic shift. The solvents with dielectric constants below 20.7 (No. 1 to 4), exhibit small solvatochromic shifts of the band (12 nm). It is reasonable to assume that the first coordination sphere of the bis-(thioacetamide) and bis-(thiobenzamide) complexes remain intact in these solvents, and the observed solvatochromic shifts presumably are due to the direct interaction of the solvent molecules with thioacetamide and thiobenzamide. The structural integrity of these complexes in solution is confirmed by their <sup>1</sup>H NMR spectra in (CD<sub>3</sub>)<sub>2</sub>CO (Figs. 1A and 1B).

In the coordinating solvents, the color changes are brought

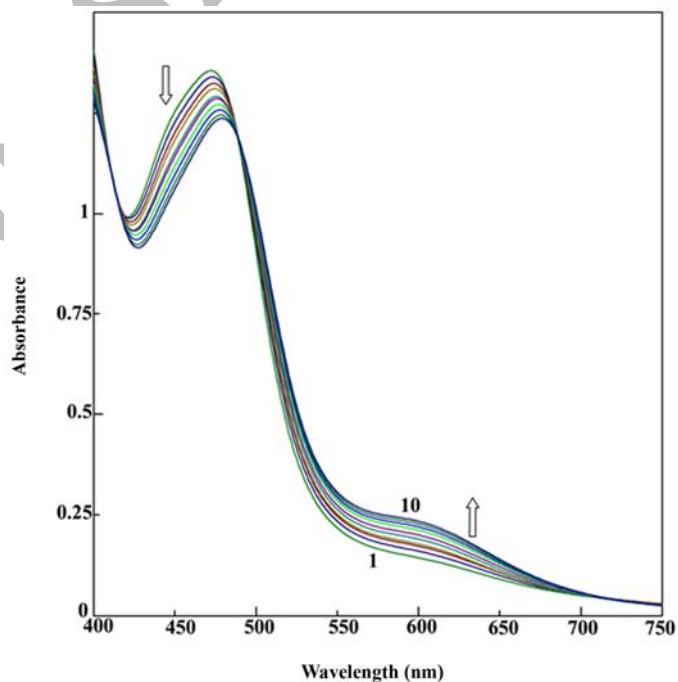
**Table 4.** The Hydrogen Bonds for (2)

| D-H...A     | <i>d</i> (D-H) (Å) | <i>d</i> (H...A) (Å) | <i>d</i> (D...A) (Å) | $\angle$ (DHA) (°) |
|-------------|--------------------|----------------------|----------------------|--------------------|
| N3-H3B...O1 | 0.88               | 2.10                 | 2.829(8)             | 139.7              |
| N3-H3B...O2 | 0.88               | 2.21                 | 2.818(7)             | 125.6              |
| N4-H4A...O4 | 0.88               | 2.19                 | 2.967(9)             | 147.5              |
| N4-H4B...O1 | 0.88               | 2.07                 | 2.832(8)             | 144.3              |
| N4-H4B...O2 | 0.88               | 2.35                 | 2.944(8)             | 125.4              |
| N4-H4B...O3 | 0.88               | 2.51                 | 2.957(9)             | 112.1              |

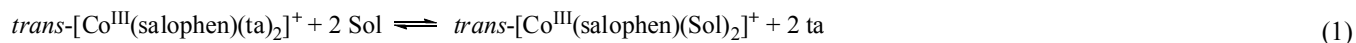
**Table 5.** Electronic Absorption Data for *trans*-[Co<sup>III</sup>(salophen)(ta)<sub>2</sub>]ClO<sub>4</sub> (**1**) and *trans*-[Co<sup>III</sup>(salophen)(tb)<sub>2</sub>]ClO<sub>4</sub> (**2**) in Solvents of Various Polarities

| Sample | Solvent         | Dielectric constant | <b>(1)</b>            |  | <b>(2)</b>            |  |
|--------|-----------------|---------------------|-----------------------|--|-----------------------|--|
|        |                 |                     | $\lambda_{\max}$ (nm) | $\epsilon$ (M <sup>-1</sup> cm <sup>-1</sup> ) | $\lambda_{\max}$ (nm) | $\epsilon$ (M <sup>-1</sup> cm <sup>-1</sup> ) |
| 1      | Dichloromethane | 4.8                 | 600(sh)               | 2246   | 614                   | 2726   |
| 2      | Chloroform      | 8.9                 | 600(sh)               | 2025   | 614                   | 2652   |
| 3      | Ethylacetate    | 6.0                 | 589(sh)               | 1843   | 600                   | 2435   |
| 4      | Acetone         | 20.7                | 588(sh)               | 2085   | 599                   | 2174   |
| 5      | Acetonitrile    | 37.5                | 583(sh)               | 1542(sh)                                       | 588                   | 1633   |

about by the direct attachment of the solvent molecules to the metal center. For example, methanol, acetonitrile, and DMF, are solvents in which large changes are expected both in the positions and  $\epsilon$  of the absorption bands. This is actually the case for *trans*-[Co<sup>III</sup>(acacen)(ta)<sub>2</sub>]ClO<sub>4</sub> complex showing the red shift of about 60 nm on going from chloroform to methanol [13]. In the case of **1** and **2** the shift is not as large and the bands are red shifted by just about 15 nm. It seems that the solvent effect now has been augmented by the role played by the additional phenyl ring in salophen. It seems reasonable to assume that the two axial thioamide ligands are replaced by solvent molecules. Further clues to these points are supplied by the electronic absorption spectral changes of the acetonitrile solutions of the complexes in the presence of excess thioacetamide and thiobenzamide. This is achieved, for example, by adding increasing amounts of thioacetamide to a solution of *trans*-[Co<sup>III</sup>((salophen)(ta)<sub>2</sub>] ClO<sub>4</sub> (**1**) in acetonitrile and monitoring the absorption spectral changes, Fig. 5. The absorption maximum moves from 472 nm in pure acetonitrile to 487 nm (a red shift of about 15 nm) after adding excess (60 times molar ratio) thioacetamide. Similar changes are observed for the first shoulder moving from 574 to 590 nm. Two well-defined isosbestic points are observed during the first 9 additions at 490 nm and 415. These results are indicative of the existence of a reversible equilibrium in acetonitrile solution involving association/dissociation of the thioacetamide ligand as presented in Eq. (1).

**Fig. 5.** The absorption spectral traces of *trans*-[Co<sup>III</sup>(salophen)(ta)<sub>2</sub>]ClO<sub>4</sub>·CHCl<sub>3</sub> (**1**) in acetonitrile upon addition of thioacetamide at 298K.

The  $\lambda_{\max}$ (590 nm) in the final solution is close to that measured in chloroform (600 nm). Considering the microscopic reversibility principle, the dissociation of the axial



thioacetamide ligands in acetonitrile and other coordinating solvents is evident. These observations may be rationalized based on the assumption that the CT bands are mainly of LLCT character and the electronic transitions occur from the  $\pi\pi(\text{C}=\text{S})$  of the coordinated thioacetamide and thiobenzamide to the  $\pi^*$  of salophen chelate, mediated by the central Co atom. This is analogous to certain low spin  $d^6$  complexes such as *trans*-[Co<sup>III</sup>(acacen)(ta)<sub>2</sub>]ClO<sub>4</sub>, *trans*-[Co<sup>III</sup>((BA)<sub>2</sub>en)(ta)<sub>2</sub>]PF<sub>6</sub> [13], Mo(diphos)(CO)(NO)(dtc) [26] and several  $d^8$  Ni(diimine)(dithiolate) [27] and  $d^{10}$ , Zn(phen)(C<sub>6</sub>H<sub>5</sub>S)<sub>2</sub> [28], Zn(SC<sub>6</sub>H<sub>4</sub>-CH<sub>3</sub>-p)<sub>2</sub>(dic) complexes [29].

## CONCLUSIONS

The structural, spectroscopic, and solvatochromic properties of *trans*-[Co<sup>III</sup>(salophen)(ta)<sub>2</sub>]ClO<sub>4</sub> (**1**) and *trans*-[Co<sup>III</sup>(salophen)(tb)<sub>2</sub>]ClO<sub>4</sub> (**2**) complexes have been investigated. The molecular structures of these complexes show that the thioacetamide and thiobenzamide ligands are S-bonded and occupy the axial positions. The coordination geometry around the Co(III) center in complexes is a distorted octahedron. The donating ability of thioacetamide and thiobenzamide fall below that of common solvents: MeOH, CH<sub>3</sub>CN, and DMF. The compounds exhibit a long wavelength LLCT, mediated by the metal center. The observed solvatochromism is explained by the effect that solvents of low dielectric constant have on the LLCT and a facile replacement of the thioacetamide and thiobenzamide ligands by the coordinating solvents.

## Supplementary Material

CCDC 683871 and 715148 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

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