

Synthesis and characterization of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cr(III), Fe(III), Ru(III) and Rh(III) complexes with 1,1-(2,6-pyrimidyl)bisbenzothiazole-2-thione

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Metal complexes with 1,1-(2,6-pyrimidyl)bisbenzothiazole-2-thione (PBT) of the type $M(PBT)_2Cl_2$ $M'_2(PBT)_2Cl_6$ where $Mh = Mn(II), Co(II), Ni(II), Cu(II)$ and $Zn(II)$ and $M' = Cr(III), Fe(III), Ru(III)$ and $Rh(III)$ have been synthesized and characterized by elemental analysis, magnetic susceptibility, IR, ^1H NMR and electronic spectral studies. The results reveal that the ligand is coordinating through pyrimidine N- and thiocarbonyl S-atoms of the mercaptobenzothiazolyl group. The $M(PBT)_2Cl_2$ complexes appear to be octahedral whereas $M'_2(PBT)_2Cl_6$ complexes are proposed to have a chlorine-bridged dimeric octahedral structure.

Pyrimidine and its derivatives are of considerable biological significance. Many pyrimidine derivatives exhibit antithrombotic activity¹. They are also used as antimicrobial, antibacterial and antimalarial drugs². Some pyrimidyl ureas and thioureas are also used as effective herbicides^{3,4}. 2-Mercaptobenzothiazoles are reported to have many industrial and medicinal applications^{5,6}. In continuation of our studies on the synthesis and characterization of biheterocyclic ligands and their metal complexes^{7,8}, we report here the synthesis and characterization of the title ligand (Structure I) derived from sodium mercaptobenzothiazolide and 2,6-dichloropyrimidine and its complexes with the Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Ru(III) and Rh(III) ions.

Experimental

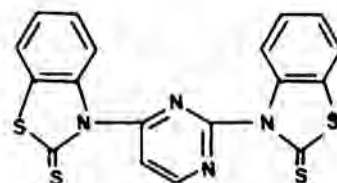
2-Mercaptobenzothiazole, 2,6-dichloropyrimidine (Aldrich), $CrCl_3$, $FeCl_3$ and metal chlorides (all BDH) and other metal trichlorides (Johnson Matthey) were used as received.

Preparation of the ligand

To a solution of 2-mercaptobenzothiazole (8.35 g, 0.05 mol) in anhydrous xylene (100 ml), sodium hydride (4.8 g, 0.2 mol) was added slowly and the reaction mixture was stirred overnight at room temperature. 2,6-Dichloropyrimidine (3.72 g, 0.025 mol) dissolved in anhydrous xylene (50 ml) was added to the above solution. After heating the mixture under reflux for ~32 h, the solution was evaporated *in vacuo*. The resulting solid was purified by column chromatography on silica gel using acetone as eluant. Yield 55%, m.p. 120 °C.

Preparation of the complexes

The ligand solution (1 g, 2.4 mmol) in acetone (50 ml) was mixed with the solutions of the respective metal chlorides in 1:2 (metal:ligand) molar ratio in the same solvent. For the preparation of trivalent metal complexes, the metal chlorides and the ligand (2.4 mmol) were taken in 1:1 stoichiometric ratio. In each case, the solution was refluxed with stirring for ~10-12 h. The coloured product which appeared after keeping the mixture for few days was filtered and washed with acetone and finally dried *in vacuo*. The elemental analysis and physical measurements were performed as described earlier⁷.



(I)

Results and discussion

The analytical and physical data of the compounds under study are presented in Table 1. The analytical results are in good agreement with the proposed compositions of the ligand and the metal complexes. The IR spectrum of the ligand displays an absorption peak at 1630 cm^{-1} which is assigned to the $\text{C}=\text{N}$ stretching frequency and a band observed at 1050 cm^{-1} is attributed to the $\nu\text{C}=\text{S}$ mode⁹. A comparison of the spectra of the uncomplexed ligand and its metal complexes indicate that the $\text{C}=\text{N}$ and $\text{C}=\text{S}$ bands are shifted to lower wavenumbers by $10\text{--}50\text{ cm}^{-1}$ and $30\text{--}45\text{ cm}^{-1}$, respectively.

Such a negative shift in the $\nu\text{C}=\text{N}$ and $\nu\text{C}=\text{S}$ mode after complexation may be ascribed to the participation of nitrogen atom of the pyrimidine group and the thiono-sulphur atom of the mercaptobenzothiazolyl group in metal-ligand bond formation¹⁰. The IR spectra of the complexes, however, exhibit a weak band at $1620\text{--}1615$ and $1040\text{--}1025\text{ cm}^{-1}$ region which may be ascribed to the uncoordinated $\nu\text{C}=\text{N}$ and $\nu\text{C}=\text{S}$ modes. This observation is in conformity with the bidentate coordination of the ligand.

Coordination through N- and S- atoms is further supported by the appearance of new M-N and M-S absorption bands at $450\text{--}410$ and $380\text{--}350\text{ cm}^{-1}$, respectively in the IR spectra of the complexes. The $\text{M}(\text{PBT})_2\text{Cl}_2$ complexes show a single absorption band in the $340\text{--}300\text{ cm}^{-1}$ region ascribed to the M-Cl stretching frequency¹¹. In the $\text{M}'_2(\text{PBT})_2\text{Cl}_6$ complexes two bands in the regions $340\text{--}300$ and $310\text{--}290\text{ cm}^{-1}$ are observed which may be attributed to the terminal and bridging M-Cl stretching frequencies¹².

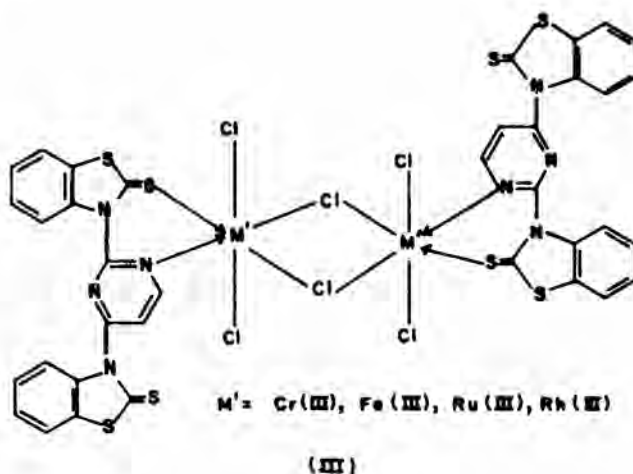
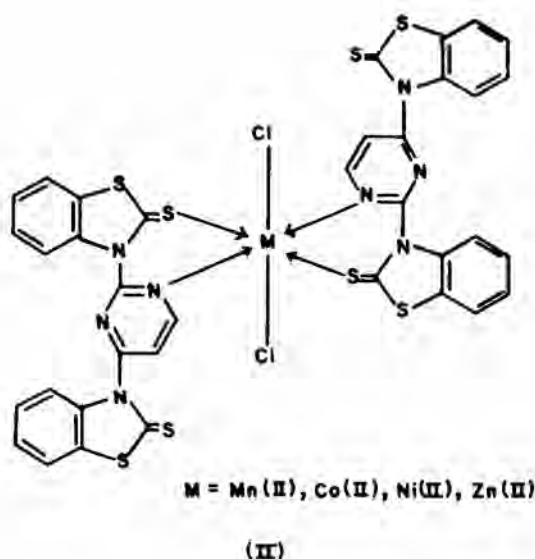
The observed magnetic moments of 3.68, 5.80 and 5.46 BM for Cr(III), Mn(II) and Fe(III) complexes, respectively are within the range required for an octahedral geometry. The electronic spectrum of Cr(III) complex exhibits bands at 20320 and 24680 cm^{-1} which may reasonably be assigned to the ${}^4T_{1g}(F) \leftarrow {}^4A_{2g}(F)$ and ${}^4T_{2g}(F) \leftarrow {}^4A_{2g}(F)$ transitions.

The Mn(II) complex also shows two bands at 15380 and 23800 cm^{-1} assignable to ${}^4T_{1g}(G) \leftarrow {}^4A_{1g}$ and ${}^4E_g(G) \leftarrow {}^6A_{1g}$ transitions, respectively¹³. Two weak bands at 15320 and 18900 cm^{-1} corresponding to the transitions, ${}^4T_{1g} \leftarrow {}^4A_{1g}$ and ${}^4E_g \leftarrow {}^6A_{1g}$, respectively are observed in the Fe(III) complex.

Table 1 — Analytical and physical data of PBT and its complexes

Compound (colour, mp °C)	Found/(Calcd), %						Yield %	μ_{eff} (BM)
	C	H	N	S	Cl	M		
PBT (Yellow, 120)	52.92 (52.68)	2.50 (2.44)	13.23 (13.66)	30.98 (31.22)	-	-	55	-
$\text{Cr}_2(\text{PBT})_2\text{Cl}_6$ (Green, >300)	37.62 (37.99)	1.89 (1.76)	9.86 (9.85)	22.35 (22.52)	19.00 (18.73)	9.50 (9.15)	60	3.68
$\text{Mn}(\text{PBT})_2\text{Cl}_2$ (White, 230)	45.70 (45.67)	2.00 (2.11)	11.55 (11.84)	27.00 (27.06)	7.90 (7.51)	5.63 (5.81)	62	5.80
$\text{Fe}_2(\text{PBT})_2\text{Cl}_6$ (Red, >300)	37.50 (37.73)	1.81 (1.75)	9.92 (9.78)	22.50 (22.36)	18.80 (18.60)	9.50 (9.78)	56	5.46
$\text{Co}(\text{PBT})_2\text{Cl}_2$ (Green, 300)	45.39 (45.47)	2.00 (2.11)	11.50 (11.79)	27.09 (26.95)	7.89 (7.47)	6.10 (6.21)	60	4.72
$\text{Ni}(\text{PBT})_2\text{Cl}_2$ (Green, 300)	45.60 (45.47)	2.15 (2.11)	11.95 (11.79)	26.60 (26.95)	7.50 (7.47)	6.50 (6.21)	56	3.09
$\text{Cu}(\text{PBT})_2\text{Cl}_2$ (Darkgreen, 290)	45.30 (45.24)	2.10 (2.09)	11.82 (11.73)	26.60 (26.81)	7.70 (7.43)	6.50 (6.70)	60	1.85
$\text{Zn}(\text{PBT})_2\text{Cl}_2$ (White, 310)	45.32 (45.19)	2.20 (2.09)	11.90 (11.72)	26.90 (26.78)	7.32 (7.43)	6.92 (6.80)	55	-
$\text{Ru}_2(\text{PBT})_2\text{Cl}_6$ (Black, > 300)	34.70 (34.92)	1.83 (1.62)	9.00 (9.05)	20.50 (20.70)	17.11 (17.22)	-	50	2.02
$\text{Rh}_2(\text{PBT})_2\text{Cl}_6$ (Orange, >300)	34.62 (34.87)	1.73 (1.61)	9.39 (9.04)	20.70 (20.66)	19.00 (19.01)	-	50	0.06

PBT = 1,1-(2,6-pyrimidyl)bisbenzothiazole-2-thione = $\text{C}_{18}\text{H}_{10}\text{N}_4\text{S}_4$



The room temperature magnetic moment (4.72 BM) of the Co(II) complex is slightly lower than the normal value for an octahedral Co(II) complex. In its electronic spectrum two bands at 16320 and 26630 cm^{-1} assignable to ${}^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$ and ${}^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$ transitions, respectively are observed which are suggestive of an octahedral environment around the metal ion¹⁴.

The Ni(II) complex has been assigned an octahedral geometry on the basis of its electronic spectrum which shows two bands at 18550 and 26320 cm^{-1} assigned to the ${}^3T_{1g}(F) \leftarrow {}^3A_{2g}$ and ${}^3T_{2g}(F) \leftarrow {}^3A_{2g}$ transitions, respectively which are characteristic of an octahedral structure. The magnetic moment (3.09 BM) is also consistent with the proposed octahedral structure. The Cu(II) complex shows a strong band at 13330 cm^{-1} attributable to ${}^2T_{2g} \leftarrow {}^2E_g$ transition in an octahedral stereochemistry around the Cu(II). The magnetic moment value of 1.85 BM also supports an octahedral structure for this complex. The magnetic moment values of 2.02 and 0.06 BM, respectively for the Ru(III) and Rh(III) complexes are indicative of an octahedral structure of these metal ions. The Ru(III) complex exhibits only one band at 19350 cm^{-1} corresponding to ${}^2A_{2g} \leftarrow {}^1A_{1g}$ transition whereas Rh(III) complex shows two bands at 16550 and 21300 cm^{-1} assigned to ${}^1A_{2g} \leftarrow {}^1A_{1g}$ and ${}^1B_{1g} \leftarrow {}^1A_{1g}$ transitions. The Zn(II) complex is diamagnetic, as expected. The stoichiometry (1:2) and bidentate na-

ture of the ligand, however, suggests an octahedral geometry for the Zn(II) complex.

On the basis of above discussions, an octahedral structure for the bivalent metal complexes (Structure II) and a chlorine-bridged dimeric structure for the trivalent metal complexes (Structure III) may be proposed.

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