

## Synthesis and characterization of chromium(III), manganese(II), iron(III), cobalt(II), nickel(II), copper(II), cadmium(II) and dioxouranium(VI) complexes of 4(2-pyridyl)-1-(2,4-dihydroxybenzaldehyde)-3-thiosemicarbazone

Gaber M Abu El-Reash, Ibrahim M M, Kenawy\*, Usama El-Ayaan & Mohamed A Khattab  
Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt

Received 4 November 1993; revised and accepted 13 June 1994

A few complexes of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and dioxouranium(VI) with 4(2-pyridyl)-1-(2,4-dihydroxybenzaldehyde)-3-thiosemicarbazone have been synthesised and characterized on the basis of elemental analysis, IR, electronic NMR, and magnetic moment data. An octahedral structure is proposed for the Cr(III), Fe(III), Co(II) and Ni(H<sub>3</sub>PBT)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O complexes; a tetrahedral structure for the Mn(II) and Ni<sub>2</sub>(PBT)OAc·H<sub>2</sub>O complexes and a square planar structure for the Cu(II) complexes. The antimicrobial and antifungal activities of H<sub>3</sub>PBT and of its metal(II) complexes are investigated. The results reveal that H<sub>3</sub>PBT exhibits greater antimicrobial activities than its complexes.

The sulphur compounds containing NS and NSO donor atoms<sup>1-3</sup> and their 3*d*-metal complexes have been found to exhibit fungicidal, bactericidal, antiviral and antitubercular activities. Studies on metal complexes of 2-hydroxybenzaldehyde-3-thiosemicarbazone<sup>4,5</sup> or 2-hydroxybenzaldehyde-4-substituted-3-thiosemicarbazone<sup>6</sup> have been reported. In this paper we report the preparation and characterization of some new metal complexes derived from 4(2-pyridyl)-1-(2,4-dihydroxybenzaldehyde)-3-thiosemicarbazone (H<sub>3</sub>PBT) with some transition metal ions.

### Materials and Methods

4(2-pyridyl)-3-thiosemicarbazide was synthesized according to the literature method<sup>7</sup>. The ligand H<sub>3</sub>PBT was prepared by boiling an ethanolic solution of 4(2-pyridyl)-3-thiosemicarbazide with 2,4-dihydroxybenzaldehyde (1:1) under reflux in the presence of a few drops of glacial acetic acid. The yellow crystals of H<sub>3</sub>PBT (m.p. 203°C) formed were removed by filtration, washed with ethanol and recrystallized from hot ethanol.

### Preparation of the complexes

All the complexes were prepared by refluxing equimolar amounts of H<sub>3</sub>PBT and the hydrated metal salts, e.g. chloride and acetate, in ethanol or water for 2 h. The resulting solid complexes were filtered off hot, washed with ethanol followed by diethyl ether and dried *in vacuo* over CaCl<sub>2</sub>.

All the measurements were carried out as reported earlier<sup>8</sup>. The ligand solution for potentiometric titrations was prepared in purified dioxane while metal chlorides were prepared in doubly distilled water.

The following solutions were titrated potentiometrically against carbonate-free KOH solution (0.01 M) in 50% aqueous dioxane:

(a) 2.5 ml of (10<sup>-2</sup> M) HClO<sub>4</sub> + 2.5 ml (2.0 M) NaClO<sub>4</sub> solution, (b) (a) + 5 ml of (10<sup>-2</sup> M) ligand solution, (c) (b) + 0.5 ml of (10<sup>-2</sup> M) metal ion solution.

The total volume was adjusted to 25 cm<sup>3</sup> and the titrations were performed at 25°C and μ = 0.2 mol dm<sup>-3</sup> (NaClO<sub>4</sub>).

### Results and Discussion

The analytical and physical data for the metal complexes are listed in Table 1. The complexes are stable in air and insoluble in common organic solvents but soluble in DMF and dimethyl sulphoxide. The molar conductivities in DMSO solution (Table 1) indicate a nonelectrolytic nature for all the complexes<sup>9</sup>. The high value of NiCl<sub>2</sub> and FeCl<sub>3</sub> complexes suggest partial dissociation in DMSO.

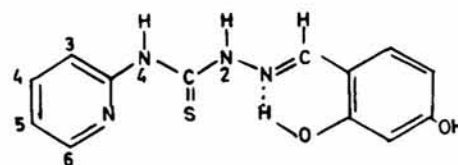
The NMR spectrum of H<sub>3</sub>PBT in *d*<sub>6</sub>-DMSO shows three signals at σ = 11.1, 10.6 and 10.2 ppm relative to TMS which disappear upon deuteration and may be assigned to the *ortho* OH (phenolic) proton, the NH (4) and NH (2) pro-

Table 1—Analytical and physical data of the complexes

Compound (colour)	m.p. °C	Found (Calcd.), %				$\Lambda_M$ (ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )	Dq	B	$\beta$	$\mu_{\text{eff}}$ (BM)
		M	Cl	C	H					
Mn(H <sub>2</sub> PBT)Cl yellow	> 300	14.5 (14.4)	9.5 (9.4)	41.2 (41.3)	2.8 (2.9)	4	—	—	—	6.2
Mn(HPBT).H <sub>2</sub> O yellowish brown	> 300	15.4 (15.2)	—	43.3 (43.5)	3.0 (2.8)	4	—	—	—	6.1
Co(H <sub>3</sub> PBT) <sub>2</sub> Cl <sub>2</sub> .4H <sub>2</sub> O brown	> 300	7.8 (7.6)	9.2 (9.1)	40.3 (40.1)	4.2 (4.1)	17	—	—	—	4.2
Ni(H <sub>3</sub> PBT) <sub>2</sub> Cl <sub>2</sub> .2H <sub>2</sub> O yellowish green	239	8.0 (7.9)	9.8 (9.6)	42.3 (42.1)	3.7 (3.8)	37	1058	856	0.82	3.1
Ni <sub>2</sub> (PBT)OAc.H <sub>2</sub> O pale brown	> 300	24.6 (24.5)	—	37.7 (37.5)	3.0 (2.9)	—	—	—	—	3.3
Cu(H <sub>2</sub> PBT)Cl.2H <sub>2</sub> O green	253	15.1 (15.0)	8.5 (8.4)	37.2 (37.0)	3.7 (3.6)	12	—	—	—	1.66
Cu <sub>2</sub> (HPBT)(OAc) <sub>2</sub> .2H <sub>2</sub> O dark green	> 300	22.7 (22.4)	—	36.1 (36.0)	3.4 (3.5)	2	—	—	—	1.4
Cr(H <sub>2</sub> PBT) <sub>2</sub> Cl.H <sub>2</sub> O red	> 300	7.9 (7.6)	5.4 (5.2)	46.2 (46.0)	3.4 (3.5)	23	1656	714	0.78	3.6
Fe(H <sub>2</sub> PBT)Cl <sub>2</sub> dark brown	> 300	13.5 (13.5)	17.3 (17.1)	37.5 (37.7)	2.8 (2.7)	35	674	613	—	4.8
Zn(H <sub>2</sub> PBT)Cl.H <sub>2</sub> O yellow	245	16.3 (16.1)	9.0 (8.7)	38.1 (38.4)	3.3 (3.2)	—	—	—	—	—
Zn(H <sub>2</sub> PBT).H <sub>2</sub> O yellow	> 300	15.4 (15.2)	—	41.7 (41.9)	3.9 (3.7)	2	—	—	—	—
Cd(H <sub>2</sub> PBT)Cl yellow	234	25.9 (25.8)	8.3 (8.2)	35.7 (35.9)	2.5 (2.6)	9	—	—	—	—
Hg(HPBT).H <sub>2</sub> O pale yellow	> 300	39.7 (39.7)	—	—	—	11	—	—	—	—
UO <sub>2</sub> (HPBT).3H <sub>2</sub> O reddish brown	> 300	39.2 (39.0)	—	25.8 (25.6)	2.6 (2.8)	2	—	—	—	Diam.

tons. The strong downfield shift of these protons may be due to intra- or intermolecular hydrogen bonding with the solvent<sup>10</sup>. The signals at 8.66, 8.40, 7.80 and 7.20 ppm may be assigned to H-6, H-3, H-4 and H-5 respectively of pyridyl ring<sup>11</sup>. The signals at 7.28 and 6.4 ppm may be due to *para* OH (phenolic) and the phenyl ring protons. The presence of the -NH proton and the absence of SH proton indicate the thione nature of the ligand (Structure I).

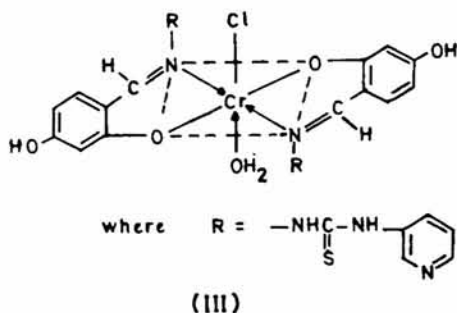
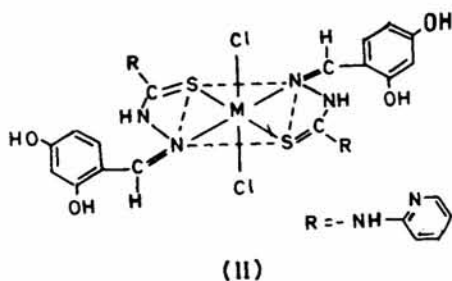
The most characteristic features of the IR spectrum of H<sub>3</sub>PBT have been determined by careful comparison with 4-(2-pyridyl)-3-thiosemicarbazide. The ligand H<sub>3</sub>PBT spectrum (in KBr) shows two bands at 3515 and 3445 cm<sup>-1</sup> assigned to  $\nu(\text{OH})$  in the position 4 and 2, respectively. The bands in the region 3220-3040 cm<sup>-1</sup> are assigned to  $\nu(\text{NH})$  groups. The spectrum shows five bands



(1)

at 1630, 1605, 1600 and 1540 cm<sup>-1</sup> assigned to  $\nu(\text{CN})$  (azomethine),  $\nu(\text{C}=\text{C})$  (phenyl),  $\nu(\text{C}=\text{C})$  and  $\nu(\text{C}=\text{N})$  of pyridine ring and  $\nu(\text{C}-\text{O})$  (phenolic) respectively. The bands located at 1460, 1180, 920 and 730 cm<sup>-1</sup> assigned to thioamide I-IV vibrations<sup>12</sup> have substantial contributions from  $\nu(\text{C}-\text{N})$ ,  $\delta(\text{C}-\text{H})$ ,  $\delta(\text{N}-\text{H})$  and  $\nu(\text{C}-\text{S})$  vibrations.

The average number of proton attached per ligand,  $n_A$  was calculated at different pH values using Irving and Rossotti equation<sup>13</sup>. The values of

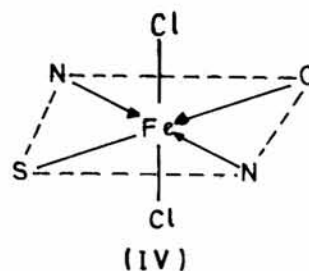


$\log K_1^H$  and  $\log K_2^H$  correspond to 10.3 and 8.5, respectively.

In  $\text{Co}(\text{H}_3\text{PBT})_2\text{Cl}_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Ni}(\text{H}_3\text{PBT})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  complexes, the  $\text{H}_3\text{PBT}$  behaves as a neutral bidentate ligand, coordinating through the thione sulphur atom and the nitrogen of the azomethine group (Structure II). This behaviour is revealed by the shift of  $\nu(\text{CN})$  to higher wavenumber and clear change in both the intensity and the position of the thioamide IV bands. The position of the bands assigned to  $\nu(\text{OH})$ ,  $\nu(\text{NH})$  and  $\nu(\text{C}-\text{O})$  remain practically unchanged indicating that  $-\text{NH}$  and  $-\text{OH}$  groups of the ligand are not involved in bonding.

In  $\text{Cr}(\text{H}_2\text{PBT})_2\text{Cl} \cdot \text{H}_2\text{O}$ ,  $\text{Zn}(\text{H}_2\text{PBT})\text{Cl} \cdot \text{H}_2\text{O}$ ,  $\text{Zn}(\text{H}_2\text{PBT})\text{OAc} \cdot \text{H}_2\text{O}$  complexes, the  $\text{H}_3\text{PBT}$  acts as a uninegative bidentate ligand, coordinating via the deprotonated ortho  $\text{OH}$  and  $\text{CN}$  groups (Structure III). This mode of complexation is confirmed by (i) the presence of one band due to  $\nu(\text{OH})$ , (ii) the shift of  $\nu(\text{CN})$  to higher wavenumber and (iii) the existence of  $\nu(\text{NH})$ ,  $\nu(\text{CS})$  and  $\nu(\text{CN})$  (pyridine) around the same position of the ligand suggesting that they are out of coordination sphere. The NMR spectrum of the dilute solution of zinc acetate complex shows new signals in the region  $\delta = 1.9\text{--}2.2$  ppm assigned to the  $\text{CH}_3$ -protons of the acetate group. Also,  $\text{Mn}(\text{H}_2\text{PBT})\text{Cl}$ ,  $\text{Co}(\text{H}_2\text{PBT})\text{OAc} \cdot \text{H}_2\text{O}$  and  $\text{Cd}(\text{H}_2\text{PBT})\text{Cl}$  complexes coordinate with the metal through the same groups in addition to the thione sulphur atom.

In  $\text{Fe}(\text{H}_2\text{PBT})\text{Cl}_2$  complexes,  $\text{H}_3\text{PBT}$  behaves as a tetradentate ligand via deprotonated  $\text{SH}$ ,  $\text{CN}$  of



both azomethine and pyridine ring, and one of the  $\text{OH}$  group without deprotonation. This mode of complexation is confirmed by (i) the presence of two strong bands at  $3480$  and  $3300\text{ cm}^{-1}$  assigned to the uncoordinated and coordinated  $\text{OH}$  groups, respectively; (ii) the splitting of both  $\nu$  and  $\delta(\text{C}-\text{O})$  into two bands confirmed that one of the  $\text{OH}$  groups participate in the coordination, (iii) the shift of both  $\nu(\text{CN})$  (azomethine) and  $\delta(\text{CN})$  (pyridine) to higher wavenumber<sup>14</sup> suggesting coordination with the metal and (iv) the  $\nu(\text{NH})$  and thioamide IV bands are found to be absent and new bands appear due to  $\nu(\text{N}=\text{C}-\text{S})$  and  $\nu(\text{C}-\text{S})$  groups.

The metal to ligand ratio (1:1) yielded  $\text{Co}(\text{II})$  ( $\log K_1 = 10.9$ ) and  $\text{Ni}(\text{II})$  ( $\log K_1 = 11.3$ ) complexes. Iron chloride reacts with the ligand to give 1:1 ( $\log K_1 = 12.3$ ) and 1:2 ( $\log K_2 = 8.8$ ) metal to ligand complexes. The stability constants of the 1:1 complexes decrease in the order of "ionic potential" (or polarizing power), which is defined as formal charge/ionic radius. Thus, corresponding stability constants decrease in the order,  $\text{Fe}(\text{III}) > \text{Ni}(\text{II}) > \text{Co}(\text{II})$ .

In  $\text{Cu}(\text{H}_2\text{PBT})\text{Cl} \cdot 2\text{H}_2\text{O}$  complex,  $\text{H}_3\text{PBT}$  behaves as a mononegative bidentate ligand in the thiol form, coordinating via deprotonated  $\text{SH}$  and  $\text{CN}$  (azomethine) groups. The absence of  $\nu(\text{NH})$  and thioamide IV bands and the shift of  $\nu(\text{CN})$  to higher wavenumber confirmed this mode of complexation.

In the  $\text{Mn}(\text{HPBT}) \cdot \text{H}_2\text{O}$ ,  $\text{Hg}(\text{HPBT}) \cdot \text{H}_2\text{O}$  and  $\text{UO}_2(\text{HPBT}) \cdot 3\text{H}_2\text{O}$  complexes,  $\text{H}_3\text{PBT}$  behaves as a binegative tridentate ligand via deprotonated  $\text{OH}$  group, the  $\text{CN}$  (azomethine) and the deprotonated  $\text{CS}$  group in the thiol form. This behaviour is revealed from (i) the disappearance of  $\nu(\text{NH})$ , thioamide I-IV bands and one band of  $\text{OH}$  group, (ii) the appearance of new bands assigned to  $\nu(\text{N}=\text{C}-\text{S})$  and  $\nu(\text{C}-\text{S})$  groups, and (iii) the splitting of  $\nu(\text{C}-\text{O})$  into two bands and the shift of  $\nu(\text{CN})$  to lower wavenumber. Also, in  $\text{Cu}_2(\text{HPBT})(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  complex,  $\text{H}_3\text{PBT}$  acts as a binegative but a tetradentate ligand via the deprotonation of both  $\text{OH}$  and thiol  $\text{C}-\text{S}$  groups, and the  $\text{CN}$  of both azomethine and pyridine ring.

The shift of  $\nu(\text{CO})$  ( $\sim 15 \text{ cm}^{-1}$ ) suggests the absence of a bridging phenolic C–O group. The lowering in  $\mu_{\text{eff}}$  (1.4 B.M.), the insolubility in most of the polar and non polar organic solvents and the high melting point suggests its polymeric nature. The absence of signals assigned to the acetate protons in the NMR spectrum of uranyl complex confirmed that  $\text{H}_3\text{PBT}$  acts as a binegative ligand.

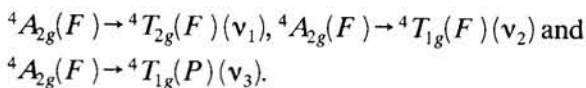
The reaction of  $\text{H}_3\text{PBT}$  with nickel(II) acetate produces a pale brown compound. The analytical data support its formulation as  $\text{Ni}_2(\text{PBT})\text{OAc}\cdot\text{H}_2\text{O}$ . The insolubility of the compound in most of the polar and non-polar organic solvents suggests its polymeric nature. The IR spectrum of the complex shows the phenolic  $\nu\text{C}-\text{O}$  at  $1570 \text{ cm}^{-1}$  indicating the presence of a bridging phenolic C–O group<sup>15</sup>. The bands assigned to  $\nu(\text{OH})$  and thioamide I-IV vibrations are absent and  $\nu\text{CN}$  (azomethine) is shifted to a lower wavenumber. These complexes show new bands assigned to  $\nu(\text{S}-\text{C}=\text{N})$  and  $\nu(\text{C}-\text{S})$  vibrations. The bands assigned to  $\nu(\text{C}=\text{C})$  and  $\nu(\text{CN})$  of pyridine ring remaining around the same position suggests that they do not take part in complexation.

The uranyl complex exhibits three bands at 910, 810 and  $260 \text{ cm}^{-1}$ , assigned to  $\nu_3$ ,  $\nu_1$  and  $\nu_4$ , respectively, of the dioxouranium ion<sup>16</sup>. The force constant ( $F$ ) for bonding sites of the  $\text{U}=\text{O}$  vibration was calculated by the method of Mc Glynn *et al.*<sup>17</sup> as  $6.84 \text{ mdyne } \text{Å}^{-1}$ .

New bands observed in the complexes at 580-520, 480-450, 390-350 and  $340-310 \text{ cm}^{-1}$  are tentatively assigned to the  $\nu(\text{M}-\text{O})$ <sup>18</sup>,  $\nu(\text{M}-\text{N})$ <sup>19</sup>,  $\nu(\text{M}-\text{S})$ <sup>18</sup> and  $\nu(\text{M}-\text{Cl})$ <sup>20</sup> vibrations.

The band positions, magnetic moments and the calculated ligand field parameters are given in Table 1.

The electronic spectrum (DMSO) of  $\text{Cr}(\text{H}_2\text{PBT})_2\text{Cl}\cdot\text{H}_2\text{O}$  shows three strong absorption bands at 16560 ( $\nu_1$ ), 21000-23580 ( $\nu_2$ ), and  $30860 \text{ cm}^{-1}$  ( $\nu_3$ ) (ref. 21). The three spin allowed transitions for chromium (III) in octahedral field are:



The magnetic moment value and the ligand field parameters (ref. 22) confirmed the octahedral configuration.

The  $\mu_{\text{eff}}$  values for the manganese(II) compounds are as expected for high spin  $3d^5$  systems. The electronic spectra provide evidence for te-

trahedral structures in two ways. Firstly, the fact that the spectra in the  $23400-24600 \text{ cm}^{-1}$  region is clearly observed indicates tetrahedrally coordinated manganese (ref. 15), and secondly tetrahedral complexes where the Laporte restriction is not so rigid generally exhibit spectra with molar extinction coefficient in the  $1-10 \text{ l cm}^{-1} \text{ mol}^{-1}$  range<sup>23</sup>.

The electronic spectrum (DMSO) of  $\text{Fe}(\text{H}_2\text{PBT})\text{Cl}_2$  complex shows several bands at 14700, 20000, 25250 and  $27600 \text{ cm}^{-1}$  assigned to  ${}^4T_{1g} \rightarrow {}^6T_{1g}(G)$  and  ${}^4T_{1g} \rightarrow {}^4E_g(G)$  transitions. Although  $d-d$  transitions are forbidden in high spin iron (III) complexes, the high intensity bands at  $25250-27600 \text{ cm}^{-1}$  may be ascribed to borrowing of intensity from a low lying charge transfer ligand band<sup>24</sup>. The magnetic moment and the ligand field parameters indicate that it is of the spin-free octahedral type.

The electronic spectrum (DMSO) of  $\text{Ni}(\text{H}_3\text{PBT})_2\text{Cl}_2\cdot 2\text{H}_2\text{O}$  is consistent with octahedral geometry showing two  $d-d$  transition bands at 16950, 24040 and  $27600 \text{ cm}^{-1}$  assignable to transitions  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F) (\nu_2)$  and  ${}^3A_{2g}(P) (\nu_3)$ , respectively. The  $Dq$ ,  $B$  and  $\beta$  values have been obtained<sup>25</sup>. The  $\beta$  value show a trend of covalent bonding. The electronic spectrum (DMSO) of  $\text{Ni}_2(\text{PBT})\text{OAc}\cdot(\text{H}_2\text{O})$  is consistent with the tetrahedral geometry showing one  $d-d$  transition band, at 14080 assignable to  ${}^3T_1(F) \rightarrow {}^3A_2(F) (\nu_3)$  and a band at  $23900 \text{ cm}^{-1}$  corresponding to an excited state derived from the  ${}^1G$  term<sup>26</sup>. The  $\nu_3$  appears as two peaks and a shoulder. This splitting may be attributed either to a ground state geometrical distribution<sup>27</sup> or to Jahn-Teller splitting to the excited state<sup>28</sup>.

The magnetic moment values for cobalt(II) complexes are near the spin only value for high spin octahedral complexes<sup>29</sup>. The electronic spectrum shows a strong peak in the  $23260-24600 \text{ cm}^{-1}$  region which is due to the  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P) (\nu_3)$  transitions. The other characteristic bands for  $d-d$  transitions are difficult to recognize in these complexes and the ligand field parameters could not be calculated.

The magnetic moments of  $\text{Cu}(\text{H}_2\text{PBT})\text{Cl}_2\cdot 2\text{H}_2\text{O}$  and  $\text{Cu}_2(\text{HPBT})(\text{OAc})_2\cdot 2\text{H}_2\text{O}$  complexes are 1.66 and 1.4 BM at room temperature. The value observed for copper chloride complex is in the range for high spin copper(II) complexes having monomeric structures<sup>30</sup>. The lowering in  $\mu_{\text{eff}}$  of copper acetate complex may be attributed to the covalent nature of the metal sulphur bond or the polymeric structure. The electronic spectra of these complexes show bands  $\sim 15870-17250$  and



Table 2—Antimicrobial activity of H<sub>3</sub>PBT and its complexes

Compound	Actual inhibition zone diameter (mm)						
	<i>Esche- richia coli</i> - ve	<i>Staphylococcus aureus</i>	<i>Althrobacter simplex</i>	<i>Bacillus megaterium</i>	<i>Alternaria citri</i>	<i>Aspergillus niger</i>	<i>Eusarium odum</i>
H <sub>3</sub> PBT	15	24	15	13	18	20	21
Cu(H <sub>2</sub> PBT)Cl <sub>2</sub> ·2H <sub>2</sub> O	15	20	18	12	14	16	20
Ni(H <sub>3</sub> PBT) <sub>2</sub> Cl <sub>2</sub>	23	25	25	17	18	19	18
Co(H <sub>3</sub> PBT) <sub>2</sub> Cl <sub>2</sub> ·4H <sub>2</sub> O	10	18	16	17	19	23	22

25100-27000 cm<sup>-1</sup>. The position of the bands indicates that these complexes have a square planar stereochemistry<sup>24</sup>. In the present complexes, the bands appear to have its origin in *d-d* transitions, which can be assigned to <sup>2</sup>B<sub>1g</sub> → <sup>2</sup>A<sub>1g</sub> and <sup>2</sup>B<sub>1g</sub> → <sup>2</sup>E<sub>g</sub> in increasing order of energy. The appearance of a high energy band at ~25000 cm<sup>-1</sup> has been a subject of lively discussion in recent years. Some authors have attributed the presence of this band to polymeric structures of the copper complexes<sup>31-33</sup>.

Finally, the UV spectrum of the uranyl complex shows a band at 25316 cm<sup>-1</sup> assigned to <sup>1</sup>E<sub>g</sub> → π<sub>u</sub><sup>3</sup>. This band is similar to the O-U-O symmetric stretching frequency for the first excited state<sup>34</sup>.

The antimicrobial activity data for H<sub>3</sub>PBT and its copper(II), nickel(II) and cobalt(II) complexes are presented in Table 2. The results clearly illustrate that the compounds have both antibacterial and antifungal potency against all the organisms tested. The moiety [4(2-pyridyl)3-thiosemicarbazide] seemed to have no effect on the growth of gram-negative bacteria and *A. niger*, whereas the same moiety highly suppressed the growth of *Staph. aureus* and to a lesser degree for *B. megaterium*, *Alternaria citri* or *Furarium odum*. The ligand (H<sub>3</sub>PBT), did not affect the growth of *E. coli*, but remarkably inhibited the growth of *Ar. simplex*. The antimicrobial activity against *Staph. aureus* of the metal complexes were much lower as compared to the organic ligand and to a higher degree as compared to [4(2-pyridyl)3-thiosemicarbazide]. This was also the case with the anti-*E. coli* activity of the metal complexes, except with Ni(II) complex in which the phenomenon was reversed.

## References

- 1 Ali M A & Livingstone S E, *Coord chem Rev*, 13 (1974) 101.
- 2 Cleare M J, *Coord chem Rev*, 12 (1974) 349.
- 3 Williams D R, *Chem Rev*, 72 (1972) 203.

- 4 Albov A V & Gerbelev N V, *Russ J Inorg Chem*, 9 (1964) 1260.
- 5 Albov A V & Gerbelev N V, *Russ J Inorg Chem*, 10 (1964) 624.
- 6 Shah K J & Shah K M, *J Indian chem Soc*, LXII (1985) 729.
- 7 Bazavora I M, Dubenko R G & Pel'kis P S, *J organi Khimii*, 14 (1976) 195.
- 8 Bekheit M M, Ibrahim K M & Abu El-Reash G M, *Bull Soc Chem Fr*, 4 (1988) 631.
- 9 Geary W J, *Coord chem Rev*, 7 (1971) 81.
- 10 La Planche L A & Rogers M T, *J Am chem Soc*, 86 (1964) 337.
- 11 Sudha L V & Sathyanarayana D N, *J coord Chem*, 13 (1984) 207.
- 12 Rao C N R, *Chemical application of infrared spectroscopy* (Academic Press, NY) 1963, 300.
- 13 Irving H M & Rossotti H S, *J chem Soc*, (1953) 3397.
- 14 Bannerjea D & Singh I P, *Indian J Chem*, 6 (1968) 34.
- 15 Jorgensen C K, *Inorg chem Acta Rev*, 2 (1962) 65.
- 16 Hsieh A T T, Sheahan R M & Water B O, *Aust J Chem*, 28 (1975) 885.
- 17 Mc Glynn S P, Smith J K & Neely W C, *J chem Phys*, 35 (1961) 105.
- 18 Ferraro J R, *Low frequency vibrations of inorganic and coordination compounds* (Plenum Press, New York) 1971.
- 19 Ferro J R & Walkers W R, *Inorg Chem*, 4 (1965) 1382.
- 20 Clark R J H, *J chem Soc* (1963) 1377.
- 21 Preti C & Tosi, *Can J Chem*, 52 (1975) 2845.
- 22 Rostogi D K, Sharma K C, Dua S K & Teotia M F, *J inorg nucl Chem*, 37 (1975) 685.
- 23 Lever A B P, *Inorganic electronic spectroscopy* (Elsevier, Amsterdam) 1968.
- 24 Bertrand J A & Eller P G, *Inorg Chem*, 13 (1974) 927.
- 25 Konig E, *Structure Bonding* (Berlin), 9 (1971) 175.
- 26 Goodgame D M L, Goodgame M & Cotton F A, *J Am chem Soc*, 83 (1961) 4161.
- 27 Furlani C & Morpurgo G, *Z physik Chem (Frankfurt)*, 18 (1961) 93.
- 28 Weakliem H A & Mc Clure D S, *J Appl Phys Suppl*, 33 (1962) 347.
- 29 Jorgensen C K, *J inorg nucl Chem*, 24 (1962) 1521.
- 30 Kato H, Fanning J C & Jonassen H B, *Rev*, 64 (1969) 99.
- 31 Procter I M, Hathaway B J & Hodgson P G, *J inorg nucl Chem*, 34 (1972) 3698.
- 32 Billing D E, Hathaway B J & Nicholis P, *J chem Soc*, A (1969) 3161.
- 33 Hathaway B J, Billing D E & Budley R J, *J chem Soc*, A (1970) 1420.
- 34 Mc Glynn S P, Smith J K & Neely W C, *J Molec Spectrosc*, 6 (1961) 164.