

## Complexes of Organic Arsonic Acids: Part IX—Complexes of Cr(III) & Co(II) with Arylarsonic Acids

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Complexes of Cr(III) and Co(II) with arylarsonic acids having the general formula  $(X.C_6H_4.AsO_3)_m.M.nH_2O$ , have been isolated [when  $M = Cr(III)$ ,  $m = 1.5$  and  $n = 2, 2.5, 4$  or  $5$ ; when  $M = Co(II)$ ,  $m = 1$  and  $n = 0.5, 1$  or  $1.5$ ;  $X = H, p-CH_3, p-Cl, p-Br, p-OCH_3, o-OCH_3, o-COOH$  or  $o-NO_2$ ]. The complexes have been characterized on the basis of elemental analysis, magnetic moment and IR and reflectance spectral studies. The  $AsO_3$  group of dibasic arylarsonic acids acts as a tridentate ligand in all the complexes and *o*-carboxyphenylarsonic acid behaves as a tetradentate ligand. On the basis of high melting points and insolubility in common organic solvents, a polymeric structure seems probable for these complexes. In most of the Co(II) complexes, the unusual ferromagnetic character is indicated by the magnetic susceptibility measurements at different temperatures. Distorted octahedral structures are proposed for both Cr(III) and Co(II) complexes.

IN continuation of our studies on arylarsonic acids<sup>8-16</sup>, complexes of Cr(III) and Co(II) with phenylarsonic acid (A) and its derivatives; (B) *p*-methyl-, (C) *p*-chloro-, (D) *p*-bromo-, (E) *p*-methoxy-, (F) *o*-methoxy-, (G) *o*-carboxy- and (H) *o*-nitrophenylarsonic acids have been isolated and characterized. Cr(III) forms thermally stable basic polymers with arsenic and phosphinic acids, which are useful as anticorrosive adherents<sup>1</sup>. Co(II) complexes with methylarsonic acid<sup>2</sup>, *o*-amino-phenylarsonic acid<sup>3</sup>, phenylarsonic acid<sup>4</sup> and Schiff bases<sup>5,6</sup> having  $AsO_3H_2$  groups and a mixed ligand complex<sup>7</sup> of Co(II) containing urea and phenylarsonic acid have also been reported.

### Materials and Methods

Arylarsonic acids were prepared by the reported methods<sup>17-19</sup>.

Cr(III) complexes were prepared by refluxing aqueous solution of chromium(III) acetate and ethanolic solution of the required acid for 30 min. Co(II) complexes were obtained by adding cobalt(II) acetate to the boiling solution of the required acid in absolute ethanol and refluxing till the precipitate settled down. The complexes were purified by washing the precipitate repeatedly with hot ethanol and drying *in vacuo*.

Chromium was estimated by treating the complex with conc.  $H_2SO_4$  and igniting it in air to  $Cr_2O_3$ . Cobalt was determined volumetrically by titration with EDTA. The analysis for C, H, N and halogens and magnetic and IR and reflectance spectral studies were carried out as reported earlier<sup>16</sup>.

### Results and Discussion

The results of elemental analyses (Table 1) suggest that the complexes may be represented by

the general formula  $(X.C_6H_4.AsO_3)_m.M.nH_2O$ . When  $M = Cr(III)$ ,  $m = 1.5$  and  $n = 2, 2.5, 4$  or  $5$  for  $M = Co(II)$ ,  $m = 1$  and  $n = 0.5, 1$  or  $1.5$ . For both the series  $X = H, p-CO_3, p-Cl, p-Br, p-OCH_3, o-OCH_3, o-COOH$  or  $o-NO_2$ .

Due to insolubility of the complexes in common organic solvents the measurements of conductivity and determination of molecular weights could not be carried out. Insolubility of the complexes along with their high melting points suggests that the complexes are probably polymeric.

Various IR bands (in  $cm^{-1}$ ) due to  $-AsO_3H_2$  group in the spectra of arylarsonic acids are assigned as follows<sup>20-22</sup>:  $\nu OH$ , 2750 and 2250;  $\nu As-C_{(aromatic)}$ , 1125-1077;  $\nu As = O$ ; 935-845 (however, in acids (B), (C) and (D) it splits into a doublet);  $\nu_{as} As \begin{smallmatrix} O \\ \diagdown \\ O \end{smallmatrix}$ , 860-785

and  $\nu_s As \begin{smallmatrix} O \\ \diagdown \\ O \end{smallmatrix}$ , 790-755. The absence of the bands due to  $-OH$  groups in the spectra of the complexes suggests the coordination of metal ions through oxygen of the  $AsO_3$  group. This is further supported by the shift ( $-55$  to  $+70 cm^{-1}$ ) in the positions of symmetric and asymmetric stretching frequencies of  $As \begin{smallmatrix} O \\ \diagdown \\ O \end{smallmatrix}$ -group on complex formation. The  $\nu As = O$  shifts downward by  $35-50 cm^{-1}$  in Cr(III) complexes of acid (E) and the Co(II) complexes of acids (B), (D) and (H). In all the complexes of Cr(III), except that of acid (E) and Co(II) complexes of acids (F) and (G), the downward shifted (by  $10-105 cm^{-1}$ )  $\nu As = O$  band overlaps with the band due to asymmetric stretch of  $As \begin{smallmatrix} O \\ \diagdown \\ O \end{smallmatrix}$ . In Co(II) complexes of acids (C) and (E), the downward shifted (by  $95$  and  $65 cm^{-1}$  respectively)  $\nu As = O$  bands overlap with the band due to phenyl ring. The downward

TABLE 1 — ANALYTICAL AND ROOM TEMPERATURE MAGNETIC MOMENT DATA OF THE COMPLEXES

Complex*	Calc. (%)			Found (%)			$\mu_{\text{eff}}$ (BM)
	C	H	Metal	C	H	Metal	
$(\text{C}_6\text{H}_5\text{AsO}_3)_{1.5}\text{Cr}\cdot 2\text{H}_2\text{O}$	27.84	2.96	13.4	28.06	3.45	13.3	3.62
$(p\text{-CH}_3\cdot\text{C}_6\text{H}_4\text{AsO}_3)_{1.5}\text{Cr}\cdot 2\cdot 5\text{H}_2\text{O}$	30.14	3.70	12.4	30.05	3.87	12.3	3.73
$(p\text{-Br}\cdot\text{C}_6\text{H}_4\text{AsO}_3)_{1.5}\text{Cr}\cdot 2\text{H}_2\text{O}$	21.32	1.97	11.0	20.70	1.96	11.2	3.83
$(p\text{-Cl}\cdot\text{C}_6\text{H}_4\text{AsO}_3)_{1.5}\text{Cr}\cdot 4\text{H}_2\text{O}$	22.70	2.94	10.9	22.43	2.52	11.2	3.57
$(p\text{-OCH}_3\cdot\text{C}_6\text{H}_4\text{AsO}_3)_{1.5}\text{Cr}\cdot 2\cdot 5\text{H}_2\text{O}$	28.50	3.50	11.8	28.44	3.70	11.6	3.83
$(o\text{-OCH}_3\cdot\text{C}_6\text{H}_4\text{AsO}_3)_{1.5}\text{Cr}\cdot 4\text{H}_2\text{O}$	26.86	3.94	11.1	26.94	3.80	11.2	3.83
$(o\text{-COOH}\cdot\text{C}_6\text{H}_4\text{AsO}_3)_{1.5}\text{Cr}\cdot 5\text{H}_2\text{O}$	24.80	3.44	10.2	24.73	3.69	10.3	4.36
$(o\text{-NO}_2\cdot\text{C}_6\text{H}_4\text{AsO}_3)_{1.5}\text{Cr}\cdot 2\text{H}_2\text{O}$	23.71	2.19	—	23.87	2.19	—	3.44
$p\text{-CH}_3\cdot\text{C}_6\text{H}_4\text{AsO}_3\text{Co}\cdot 0\cdot 5\text{H}_2\text{O}$	29.80	2.84	20.9	29.76	2.87	20.6	5.11
$p\text{-Cl}\cdot\text{C}_6\text{H}_4\text{AsO}_3\text{Co}\cdot \text{H}_2\text{O}$	23.11	1.93	18.9	23.59	2.28	19.2	5.19
$p\text{-Br}\cdot\text{C}_6\text{H}_4\text{AsO}_3\text{Co}\cdot 0\cdot 5\text{H}_2\text{O}$	20.75	1.45	17.0	21.02	1.96	17.2	5.46
$p\text{-OCH}_3\cdot\text{C}_6\text{H}_4\text{AsO}_3\text{Co}\cdot 0\cdot 5\text{H}_2\text{O}$	28.19	2.69	19.8	28.00	2.99	19.4	4.94
$o\text{-OCH}_3\cdot\text{C}_6\text{H}_4\text{AsO}_3\text{Co}\cdot \text{H}_2\text{O}$	27.36	2.93	19.2	27.61	3.31	19.5	5.22
$o\text{-COOH}\cdot\text{C}_6\text{H}_4\text{AsO}_3\text{Co}\cdot 1\cdot 5\text{H}_2\text{O}$	25.46	2.43	17.9	25.54	2.56	18.1	4.97
$o\text{-NO}_2\cdot\text{C}_6\text{H}_4\text{AsO}_3\text{Co}\cdot \text{H}_2\text{O}$	22.36	1.86	18.3	22.68	1.75	18.5	5.41

\*Satisfactory analyses for halogens were also obtained.

shift in As = O bands may be ascribed to the bonding of metal ions to the As = O oxygen. This conclusion is corroborated by a small shift in the  $\nu_{\text{As-C}}$  (aromatic) on complex formation. Hence AsO<sub>3</sub> group of the acids acts as a tridentate ligand in all the complexes.

The analytical data coupled with IR studies show that proton of carboxylic acid group remains intact in the complexes of *o*-carboxyphenylarsonic acid. However the doublet at 1650, 1637 cm<sup>-1</sup> assigned to  $\nu_{\text{C=O}}$  in the acid shifts to 1590 and 1580 cm<sup>-1</sup> in Cr(III) and Co(II) complexes respectively indicating the coordination of C = O oxygen to the metal ions<sup>23</sup>. The small change in the position of bands due to substituted groups of the acids in complexes may be due to change in the environment.

The room temperature magnetic moments of all the Cr(III) complexes except that with *o*-carboxyphenyl arsonic acid lie in the range 3.44-3.83 BM which correspond to the spin-only value (3.87 BM) for three unpaired electrons. The reflectance spectral data of all the complexes show the presence of bands in the regions 24,400-22,200 and 16,700-16,400 cm<sup>-1</sup> and also intense broad bands in the regions 44,000-42,000 and 38,000-35,000 cm<sup>-1</sup>. The intensity, shape and energy of the observed bands show that the first two bands may be due to *d-d* transitions while the other two may be attributed to charge-transfer. Assuming an octahedral stereochemistry around Cr(III) the first two bands may be assigned<sup>24</sup> to the transitions  $4T_{1g}(F) \leftarrow 4A_{2g}(F)$  and  $4T_{2g}(F) \leftarrow 4A_{2g}(F)$  respectively. The values of  $D_q$  and  $B$  calculated<sup>25</sup> on the basis of these observed bands are 1640 and 559.7 cm<sup>-1</sup> respectively. On the basis of these values of  $D_q$  and  $B$ , the calculated values for the two-electron transition,  $4T_{1g}(P) \leftarrow 4A_{2g}(F)$ , comes out to be 35,393 cm<sup>-1</sup>. Due to the presence of an intense charge-transfer band in this region, this weak band is not observed. The observed magnetic moment value of 4.30 BM in the case of *o*-carboxyphenylarsonate is a little higher than those reported<sup>26</sup> for octahedral complexes but the presence of bands at 22,700 and 16,400 cm<sup>-1</sup> in

TABLE 2 — MAGNETIC SUSCEPTIBILITIES OF Co(II) COMPLEXES AT DIFFERENT TEMPERATURES

Temp. (K)	$\mu_{\text{eff}}$ (BM)	$\theta$ values	Temp. (K)	$\mu_{\text{eff}}$ (BM)	$\theta$ values
$p\text{-CH}_3\cdot\text{C}_6\text{H}_4\text{AsO}_3\text{Co}\cdot 0\cdot 5\text{H}_2\text{O}$			$p\text{-OCH}_3\cdot\text{C}_6\text{H}_4\text{AsO}_3\text{Co}\cdot 0\cdot 5\text{H}_2\text{O}$		
83	5.58		80	5.38	
105	5.30		108	5.25	
131	5.35		131	5.18	
165	5.33	+15	163	5.10	+16
220	5.25		215	5.01	
293	5.11		295	4.94	
$p\text{-Cl}\cdot\text{C}_6\text{H}_4\text{AsO}_3\text{Co}\cdot \text{H}_2\text{O}$			$o\text{-OCH}_3\cdot\text{C}_6\text{H}_4\text{AsO}_3\text{Co}\cdot \text{H}_2\text{O}$		
82	5.34		82	5.31	
106	5.33		97	5.31	
129	5.30		107	5.34	
163	5.26	+9	130	5.34	0
213	5.18		162	5.34	
293	5.19		213	5.27	
			296	5.22	
$p\text{-Br}\cdot\text{C}_6\text{H}_4\text{AsO}_3\text{Co}\cdot 0\cdot 5\text{H}_2\text{O}$			$o\text{-COOH}\cdot\text{C}_6\text{H}_4\text{AsO}_3\text{Co}\cdot 1\cdot 5\text{H}_2\text{O}$		
87	5.57		80	4.58	
103	5.52		97	4.60	
126	5.47		116	4.68	
161	5.53	+3	161	4.82	-21
216	5.44		212	4.88	
294	5.46		292	4.97	

its reflectance spectrum indicates distorted octahedral structure for the Cr(III) complex with *o*-carboxyphenylarsonate.

The room temperature magnetic moment values of the Co(II) complexes show the presence of orbital contribution, expected for octahedral species. The study of magnetic susceptibilities of Co(II) complexes at different temperatures (80-293°K) is quite interesting (Table 2). Contrary to the usual behaviour of octahedral Co(II) complexes, the magnetic moments of the present cobalt(II) complexes with acids (B) to (G) decrease with increase in temperature<sup>27</sup>. This behaviour may be attributed to the presence of

ferromagnetic interaction in the complexes. In Co(II) complex of *o*-carboxyphenylarsonic acid the -COOH group is coordinated to the central metal ion and thus ferromagnetic interaction may not be possible in this complex. The reflectance spectra of the Co(II) complexes show the presence of two strong bands in the regions 7700-7550 and 18500-18200  $\text{cm}^{-1}$  and a weak band in the region 16450-16150  $\text{cm}^{-1}$ . Thus on the basis of magnetic and reflectance studies<sup>24</sup>, a distorted octahedral structure is proposed for Co(II) complexes. The values of  $D_q$  and  $B$ , have been calculated<sup>25</sup> and are in the ranges 875-860 and 802-769  $\text{cm}^{-1}$  respectively. These values almost correspond to the values ( $D_q = 830 \text{ cm}^{-1}$  and  $B = 845 \text{ cm}^{-1}$ ) for the octahedral phenylphosphonate-cobalt(II) found by Grinonbeau<sup>28</sup> and coworkers. Thus phenylphosphonic acid and arylarsonic acids have almost equal ligand field strengths and nephelauxetic effects.

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