

Fig. 3. Raman spectra of the Sn(IV)-(HCl, Sn(IV)-HBr and Sn(IV)-HCl-HBr solutions in the glassy state.

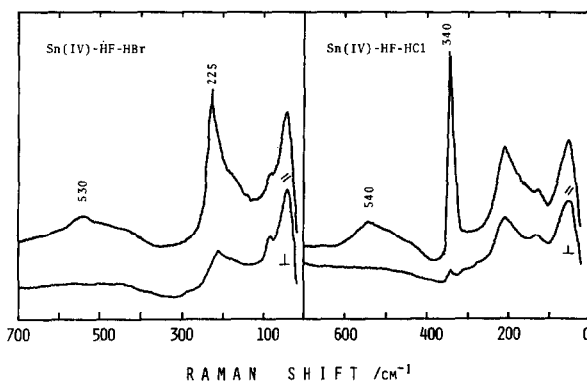


Fig. 4. Raman spectra of the Sn(IV)-HF-HCl and Sn(IV)-HF-HBr solutions in the glassy state.

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### Complexes of bivalent cations with a hydroxamic acid from maize extracts

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Cyclic hydroxamic acids may constitute up to 2% of the dry weight of Gramineae such as wheat, maize and rye.<sup>1</sup> The chelating properties of hydroxamic acids<sup>2</sup> suggest that those present in

Gramineae may play a role in the plant mineral nutrition.<sup>3</sup> We report here the stability constants of complexes between bivalent cations and 2,4-dihydroxy-7-methoxy-1,4-benzoxazin-3-one

(DIMBOA), the main hydroxamic acid isolated from maize extracts.<sup>4</sup>

#### EXPERIMENTAL

Stability constants of the complexes were determined by potentiometric titration of a 3.4 mM solution of the cation (as chloride) in 0.66 mM HClO<sub>4</sub> with a 10 mM solution of the anion of DIMBOA (pH 8.5), under constant ionic strength (0.1 M with NaClO<sub>4</sub>). Titrations were carried out at  $3 \pm 0.5^\circ$ . Under these conditions the decomposition of DIMBOA<sup>5</sup> was negligible (half-life = 32.7 hr) compared with the time needed for titration (20 min). The pK<sub>a</sub> of DIMBOA at this temperature and ionic strength was 6.96. The data obtained was analyzed by the method of Bjerrum.<sup>6</sup> Distribution diagrams were calculated with a modified version of the program COMICS.<sup>7</sup>

#### RESULTS AND DISCUSSION

The formation curves (Fig. 1) allow the estimation of the logarithms of the stability constants of the 1:1 complexes of Cu (5.4), Ni (4.5), Zn (4.2), Mn (3.4) and Ca (3.0) and of the 2:1 complexes of Ni (3.6) and Zn (3.5). The low stability of the Mg complex and the insolubility of the Fe complex precluded the estimation of their stability constants. A precipitate appeared during the titration of the Cu when an  $\bar{n}$  value of 0.5 was reached.

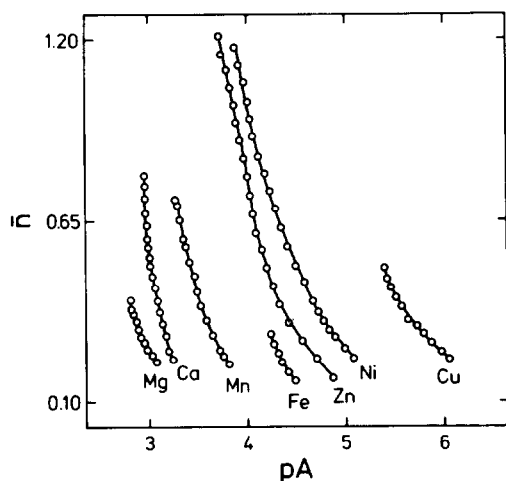


Fig. 1. Formation curves for complexes between DIMBOA and bivalent cations.  $pA = -\log [DIMBOA]$ .

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The formation constant of the 1:1 complex between DIMBOA and Cu has been determined by the method of Irving-Rosotti at 10, 20 and 30°. Extrapolation of these data to 3° gives a value of  $\log K_1 = 5.7$ , comparable to that reported in this paper. The formation constants of the 1:1 complexes follow the Irving-Williams order, i.e. Mn(Ni(Cu)Zn, as shown for other ligands.<sup>9</sup> The complexes of DIMBOA were less stable than those of hydroxamic acids of the type Ar-NOH-CO-Ar,<sup>10</sup> probably a reflection of the greater pK<sub>a</sub> values of these latter acids.

The distribution of species in a solution containing DIMBOA, citric acid and malic acid, and Cu(II), Zn(II), Ca(II), Mn(II) and Fe(III) cations was calculated at pH 5.5, the pH of the plant extract. Citric and malic acids are two of the most abundant complexing agents found in maize exudates. The concentrations used in the calculations were those determined in whole plants.<sup>4,11,12</sup> Formation constants were obtained from the literature.<sup>3,13</sup> Under these conditions, 57% of the DIMBOA remained uncomplexed, while the complexes CaL, FeL<sub>2</sub> + FeL<sub>3</sub>, CuL, ZnL + ZnL<sub>2</sub> and MnL with L = DIMBOA anion were 35, 7, 0.1, 0.5 and 0.3% of the total DIMBOA, respectively. In all cases, these complexes accounted for a substantial proportion of the total cation (Table 1). More of each cation was complexed by DIMBOA than by citric and malic acids together. Thus, it is possible that DIMBOA and other related hydroxamic acids in Gramineae may participate in the plant mineral nutrition as chelating agents. To further establish the participation of hydroxamic acids in mineral nutrition it would be necessary to determine their concentration as well as that of organic acids, cations and hydrogen ions in the different plant compartments at the tissular and cellular levels.

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Table 1. Complexation of cations by DIMBOA, citric acid and malic acid at pH 5.5

| Cation  | % of total metal complexed by |             |            | % of free ion |
|---------|-------------------------------|-------------|------------|---------------|
|         | DIMBOA                        | Citric acid | Malic acid |               |
| Fe(III) | 74.6                          | 25.3        | 0.1        | 0.0           |
| Zn(II)  | 70.3                          | 4.2         | 2.8        | 22.7          |
| Cu(II)  | 55.1                          | 37.6        | 5.7        | 1.6           |
| Mn(II)  | 22.8                          | 0.8         | 10.1       | 66.3          |
| Ca(II)  | 11.8                          | 0.6         | 1.1        | 86.5          |

Concentrations used (mM): DIMBOA (7), citric acid (1.9), malic acid (1.3), Fe (0.21), Zn (0.04), Cu (0.02), Mn (0.075) and Ca (21).

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## Isolation of dithiocarbamate anions as salts of biscyclopentadienyl titanium(IV) chelates

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**Abstract**—A series of  $[\text{Cp}_2\text{TiL}]^+[\text{RR}'\text{NCS}_2]^-$  complexes, where L is the conjugate base of acetylacetone, benzoylacetone or 8-hydroxyquinoline and  $\text{R} = \text{CH}_3$ ,  $\text{R}' = \text{C}_6\text{H}_5\text{CH}_2$ ;  $\text{R} = \text{C}_2\text{H}_5$ ,  $\text{R}' = \text{C}_6\text{H}_4\text{CH}_3$ ;  $\text{R} = \text{H}$ ,  $\text{R}' = \text{C}_5\text{H}_9$ ;  $\text{RR}' = \text{C}_6\text{H}_{12}$ , have been synthesised in aqueous medium by the reaction of  $[\text{Cp}_2\text{TiL}]^+\text{Cl}^-$  with  $\text{RR}'\text{NCS}_2\text{Na}^+$ . Conductivity measurements in nitrobenzene solution indicate that these complexes are electrolytes. Both the IR and NMR studies demonstrate that the ligand L is chelating in all these complexes. Consequently, tetrahedral coordination about the titanium atom is proposed. In addition to these studies, elemental analyses and magnetic susceptibility have been carried out for these complexes.

### INTRODUCTION

During the course of our recent investigations,<sup>1–3</sup> we elucidated that coordination of four oxygen or two oxygen and two nitrogen atoms by strong covalent bonds to the  $\text{RR}'\text{M}^{2+}(\text{IV})$  moiety ( $\text{R} = \text{R}' = \text{C}_5\text{H}_9$ ;  $\text{R} = \text{C}_5\text{H}_9$ ,  $\text{R}' = \text{C}_4\text{H}_4\text{N}$ ;  $\text{R} = \text{C}_3\text{H}_5$ ,  $\text{R}' = \text{C}_9\text{H}_7$  and  $\text{M} = \text{Ti}$  or  $\text{Zr}$ ) would lead to weakening of the metal-ring bonds. In this communication we report an extension of these studies to the dithiocarbamate derivatives of biscyclopentadienyl titanium(IV) chelates, with the aim that behaviour of free dithiocarbamate anion would provide additional information on the nature of bonding. A number of complexes of the type  $[\text{Cp}_2\text{TiL}]^+[\text{RR}'\text{NCS}_2]^-$ , where L is the conjugate base of acetylacetone, benzoylacetone or 8-hydroxyquinoline and  $\text{R} = \text{CH}_3$ ,  $\text{R}' = \text{C}_6\text{H}_5\text{CH}_2$ ;  $\text{R} = \text{C}_2\text{H}_5$ ,  $\text{R}' = \text{C}_6\text{H}_4\text{CH}_3$ ,  $\text{R} = \text{H}$ ,  $\text{R}' = \text{C}_5\text{H}_9$ ;  $\text{RR}' = \text{C}_6\text{H}_{12}$  have been synthesised. These compounds possess a low solvation energy, as evident from the ease of their preparation.

### EXPERIMENTAL

#### Reagents and general techniques

All the chemicals and reagents used were of analytical grade. Biscyclopentadienyl titanium(IV) dichloride was obtained from Fluka AG Switzerland and used as such without further purification. Nitrobenzene for conductance measurements was purified by the method described by Fay *et al.*<sup>4</sup> Sodium dithiocarbamates were prepared by the method of Gilman and Blatt.<sup>5</sup>

Microanalyses of carbon and hydrogen contents were carried out in our Departmental Microanalytical laboratory. Titanium, nitrogen and sulphur were estimated by the standard methods as described by Vogel.<sup>6</sup>

Conductance measurements were made in nitrobenzene at  $30.00 \pm 0.05^\circ\text{C}$  using an Elico Conductivity Bridge Model CM82. Solid state IR spectra were recorded in "KBr pellets" in the region  $4000\text{--}200\text{ cm}^{-1}$  with a Perkin-Elmer 621 grating spectrophotometer. Magnetic measurements were carried out by Gouy's method using mercury tetrathiocyanatocobaltate(II) as calibrant. Proton NMR spectra were recorded in  $\text{CDCl}_3$  on a Perkin-Elmer R-32 spectrophotometer at a sweep width of

900 Hz. The magnetic field was calibrated with a standard sample of  $\text{CHCl}_3$  and TMS (1% by volume).

#### Preparation of complexes

An aqueous solution of  $[\text{Cp}_2\text{TiL}]^+\text{Cl}^-$  where L is the conjugate base of acetylacetone, benzoylacetone or 8-hydroxyquinoline was obtained by stirring an aqueous solution of  $\text{Cp}_2\text{TiCl}_2$  with slight excess of acetylacetone, benzoylacetone or 8-hydroxyquinoline for 2 hr. Any resulting precipitate was removed by filtration. The filtrate was then added slowly with shaking, to a concentrated hot aqueous solution of appropriate sodium dithiocarbamate. The precipitate so obtained was digested on water bath at  $60\text{--}70^\circ$  for 1 hr. It was then filtered, washed with hot water, diethyl ether ( $40\text{--}60^\circ$ ) and finally dried under vacuum. In order to remove any acetylacetone impurity, the precipitates were dissolved in dichloromethane and reprecipitated by adding petroleum ether ( $60\text{--}80^\circ$ ).

### RESULTS AND DISCUSSION

Table 1 lists the analytical data and physical characteristics of the complexes. The complexes are quite stable in the solid state and in solution. They are moderately soluble in dichloromethane, chloroform, carbon tetrachloride and nitrobenzene. All the complexes are thermally stable but decompose slowly at higher temperatures without melting. Conductivity measurements reveal that the chelates are 1:1 electrolytes in nitrobenzene. Magnetic susceptibility values at room temperature indicate that all these complexes are diamagnetic in nature.

The assignments of IR bands have been made on the basis of published work. The IR spectra of the compounds show usual peaks for  $\text{C}_5\text{H}_9$  group,<sup>7</sup> viz., the C–H stretching frequency at  $\sim 3000\text{ cm}^{-1}$ , the perpendicular hydrogen wagging mode at  $\sim 860\text{ cm}^{-1}$ , the parallel hydrogen wagging vibration at  $\sim 1030\text{ cm}^{-1}$ . The band owing to C–C stretching mode and ring breathing mode of  $\pi$ -bond occur at  $\sim 1430$  and  $\sim 1170\text{ cm}^{-1}$  respectively. Apart from this, an additional band near  $440\text{ cm}^{-1}$  can be assigned to Ti– $\text{C}_5\text{H}_9$  vibrations.<sup>8</sup>