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COMPLEXATIONS OF METAL CATIONS WITH CYCLOTETRACHROMOTROPYLENE IN WATER AND METHANOL

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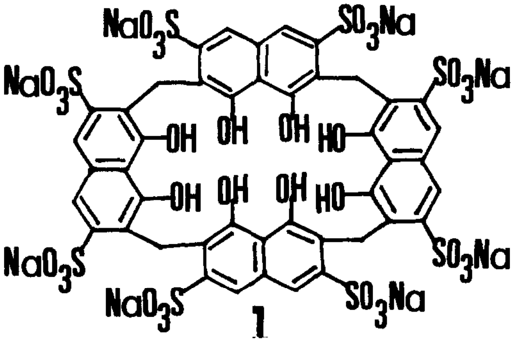
Abstract: Mg^{2+}, Fe^{2+}, Co^{2+}, Cu^{2+} and Zn^{2+} form 1:1 complexes with cyclotetrachromotropylene (1) in water and methanol. Ni^{2+} forms a 1:1 complex with 1 in water, but a 2:1 host to guest complex in methanol. The stability constants are larger in methanol than in water.

Cyclotetrachromotropylene, 1, is conformationally flexible.[1,2] In both the boat (1a) and chair (1b) conformations, there is a plane containing four hydroxyl oxygen atoms (the boat conformation has a second parallel plane containing another four hydroxyl oxygen atoms). The oxygen atoms of the hydroxyl groups are preorganised for complexation, similar to the calixarenes in the cone conformation[3,4] and the spherands.[5] This paper reports our study on the complexation of six divalent metal cations with 1 in water and in methanol using electronic absorption spectroscopy.



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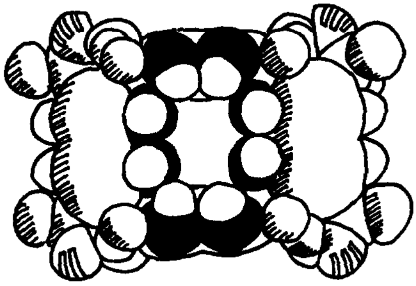
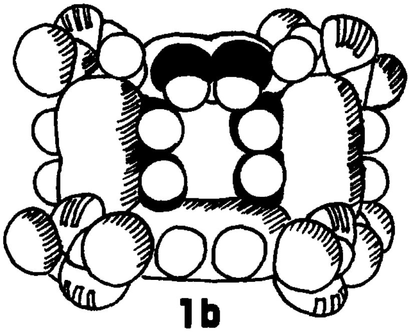


1a



1b

Results and Discussion

That 1 forms complexes, in water and methanol, with the divalent metal cations used in this work (Mg^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}) is indicated by (1) an increase in the absorbance at 450 nm (the visible spectra of 1 in the presence of various concentrations of Ni^{2+} in water (Figure 1) and Mg^{2+} in methanol (Figure 2) are shown) and (2) a change in the colour of 1 (Table I). All the metal cations form complexes of 1:1 stoichiometry with 1 in water. In methanol, all the metal cations except Ni^{2+} also form complexes of 1:1 stoichiometry with 1. Ni^{2+} forms a complex of 2:1 host to guest stoichiometry. The stoichiometry of each of the complexes is supported by the consistency in the calculated stability constant (examples for 1:1 and 2:1 stoichiometries shown in Tables II and III respectively) and the intersection point of the titration curve of absorbance versus metal cation concentration (examples for 1:1 and 2:1 stoichiometries shown in Figures 3 and 4 respectively). The stability constants at 25° are given in Table IV. The enthalpy ΔH^{o} and entropy ΔS^{o} values, obtained from the temperature dependence of the stability constant plots (an example shown in Figure 5), are given in Table V.

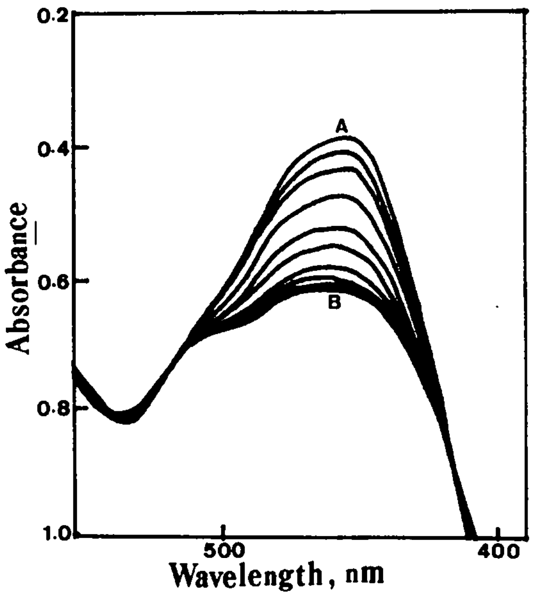


Fig. 1 Visible spectra of 1 in water in the presence of various concentrations of $NiSO_4 \cdot [1]_o = 1.50 \times 10^{-4}$ M; $[NiSO_4]_o$ = 0 (A) to 6.84×10^{-4} M (B).

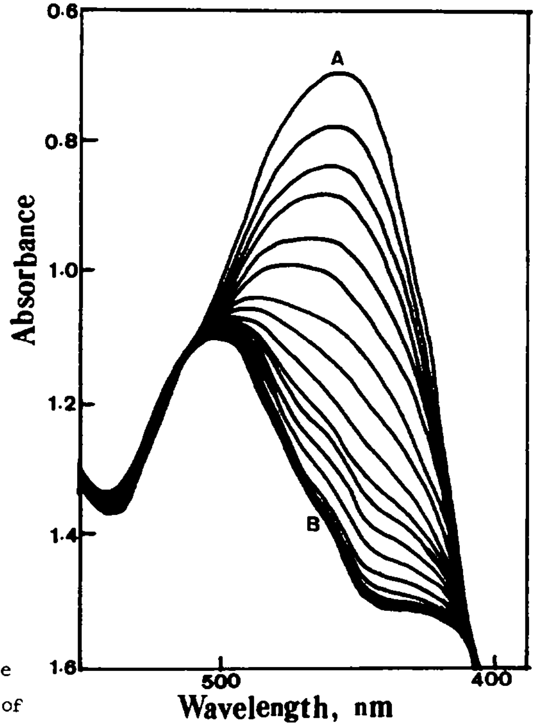


Fig. 2 Visible spectra of 1 in methanol in the presence of various concentrations of $MgSO_4 \cdot [1]_o = 3.00 \times 10^{-4}$ M; $[MgSO_4]_o$ = 0 (A) to 9.68×10^{-4} M (B).

Table I. Colours of 1 on Complexation

cation	colour of complex (H_2O)	colour of complex (MeOH)
Mg^{2+}	red[a]	reddish brown
Fe^{2+}	reddish brown	brown
Co^{2+}	red[a]	reddish brown
Ni^{2+}	orange red	orange brown
Cu^{2+}	brown	green
Zn^{2+}	red[a]	reddish brown

[a] No change in colour since colour of 1 is red in the absence of any added metal cation.

Table II. Complexing of 1 with $ZnSO_4$ in Methanol at 29°; $[1]_o = 3.00 \times 10^{-4}$ M

$[ZnSO_4]_o$ (M)	A_{450}	K_{11}	log K_{11}
0.50×10^{-4}	0.775	2.19×10^4	4.32
1.00×10^{-4}	0.901	1.90×10^4	4.28
1.49×10^{-4}	1.033	2.29×10^4	4.36
1.99×10^{-4}	1.142	2.28×10^4	4.36
2.97×10^{-4}	1.325	2.55×10^4	4.41
3.95×10^{-4}	1.424	2.44×10^4	4.39
4.92×10^{-4}	1.484	2.47×10^4	4.39
5.88×10^{-4}	1.526	2.66×10^4	4.42
$\varepsilon_H = 2113$			
$\varepsilon_{HG} = 5433$	average	2.35×10^4	4.37 ± 0.04

Table III. Complexing of 1 with $NiSO_4$ in Methanol at 29°, $[1]_o = 2.94 \times 10^{-4}$ M

$[NiSO_4]_o$ (M)	A_{465}	K_{21}	log K_{21}
0.50×10^{-4}	0.991	1.36×10^8	8.13
0.75×10^{-4}	1.140	1.12×10^8	8.05
1.00×10^{-4}	1.277	1.21×10^8	8.08
1.24×10^{-4}	1.378	1.23×10^8	8.09
1.48×10^{-4}	1.480	1.49×10^8	8.17
1.95×10^{-4}	1.600	1.73×10^8	8.24
$\varepsilon_H = 1949$			
$\varepsilon_{HG} = 6803$	average	1.36×10^8	8.13 ± 0.06

Table IV. Stability Constants in Water and Methanol at 25°

Cation[a]	log K_{11} (H_2O)	log K_{11} (MeOH)
Mg^{2+}	2.5[b]	3.93 ± 0.05
Fe^{2+}	3.52 ± 0.04	3.49 ± 0.11
Co^{2+}	3.17 ± 0.20	4.21 ± 0.06
Ni^{2+}	3.08 ± 0.06	(8.08 ± 0.06)[c]
Cu^{2+}	3.61 ± 0.10	3.96 ± 0.06
Zn^{2+}	2.94 ± 0.15	4.35 ± 0.04

[a] Anion is SO_4^{2-}; [b] uncertainty is large because of small absorbance changes on complexation; [c] Log K_{21}.

Table V. $-\Delta G^{o}$, ΔH^{o}, and ΔS^{o} Values for Complexations[a]

	H_2O			MeOH		
cation	$-\Delta G^{o}$	ΔH^{o}	ΔS^{o}	$-\Delta G^{o}$	ΔH^{o}	ΔS^{o}
Mg^{2+}				5.4	2.3	25.4
Fe^{2+}	4.8	0	16.1	4.8	4.1	29.7
Co^{2+}	4.3	2.5	22.8	5.7	3.9	32.3
Ni^{2+}	4.2	2.4	22.2	11.0	5.5	55.6
Cu^{2+}	4.9	3.0	26.4	5.4	5.8	37.6
Zn^{2+}	4.0	4.7	29.2	5.9	1.6	25.2

[a] $-\Delta G^{o}$ (at 25°) and ΔH^{o} in Kcal mol^{-1} and ΔS^{o} in cal mol^{-1} deg^{-1}. All complexes are of 1:1 stoichiometry except the Ni^{2+} complex in methanol which is of 2:1 host to guest stoichiometry.

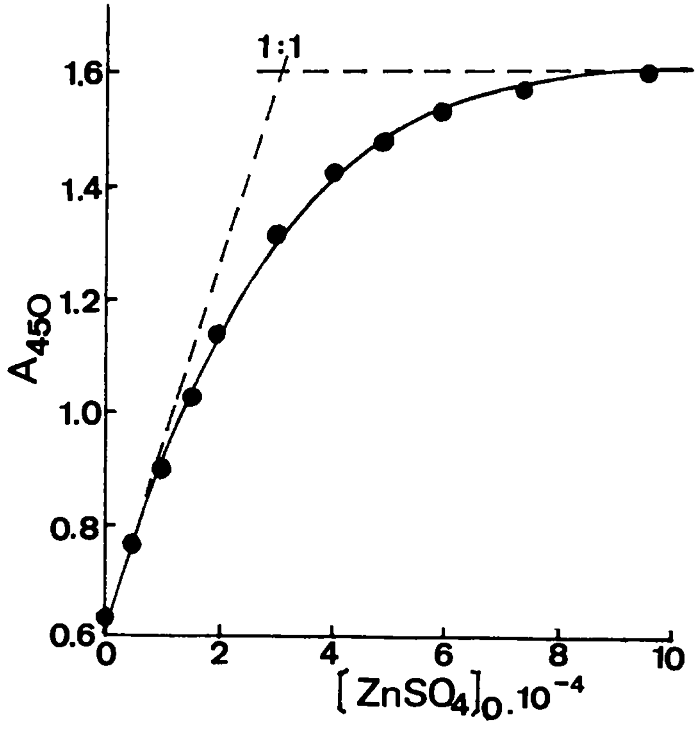


Fig.3 Absorbance at 450 nm versus concentration of $ZnSO_4$ in methanol at 29°C . $[\mathbf{1}]_o = 3.00 \times 10^{-4}$ M .

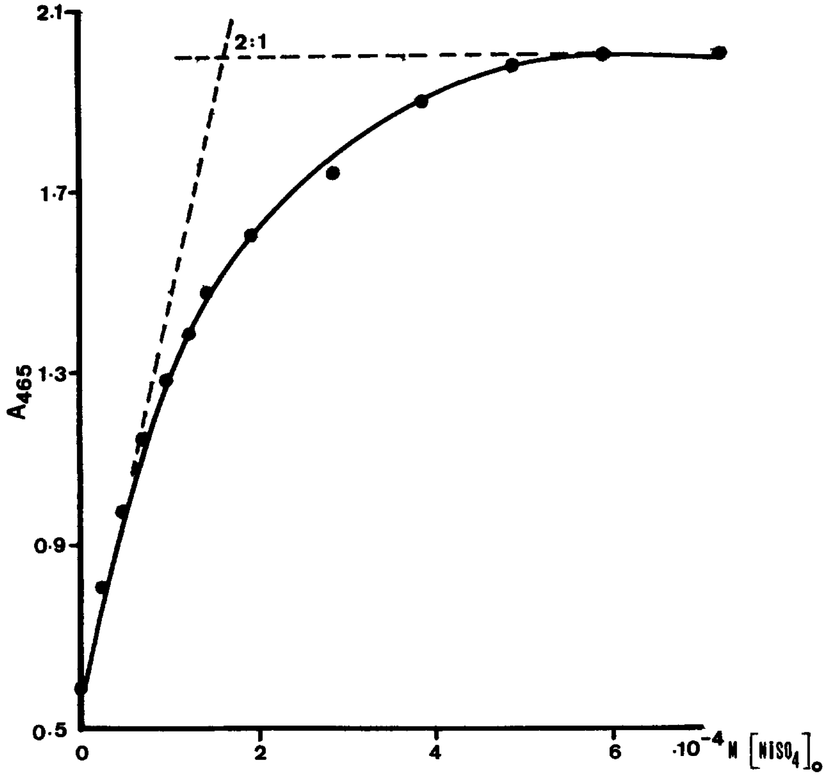


Fig. 4 Absorbance at 465 nm versus concentration of $NiSO_4$ in methanol at 29°. $[\underline{1}]_0 = 3.00 \times 10^{-4}$ M

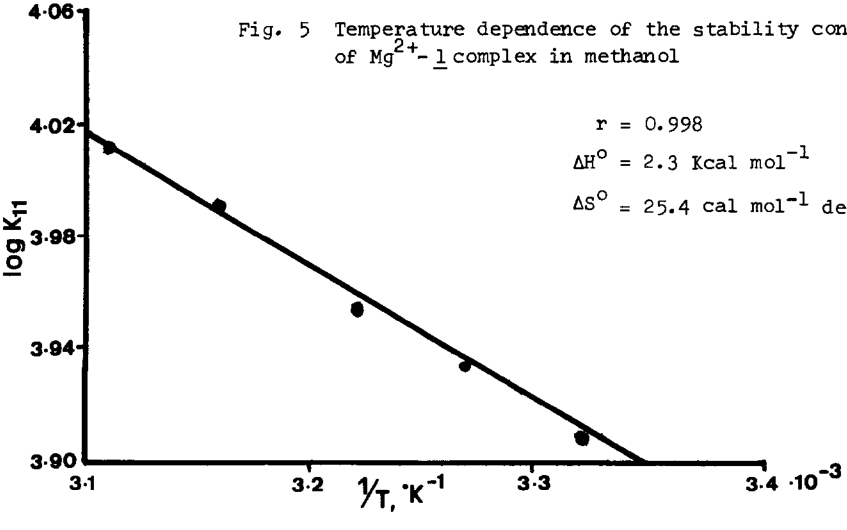


Fig. 5 Temperature dependence of the stability constant of Mg^{2+}-$\underline{1}$ complex in methanol

$r = 0.998$

$\Delta H^\circ = 2.3$ Kcal mol^{-1}

$\Delta S^\circ = 25.4$ cal mol^{-1} deg^{-1}

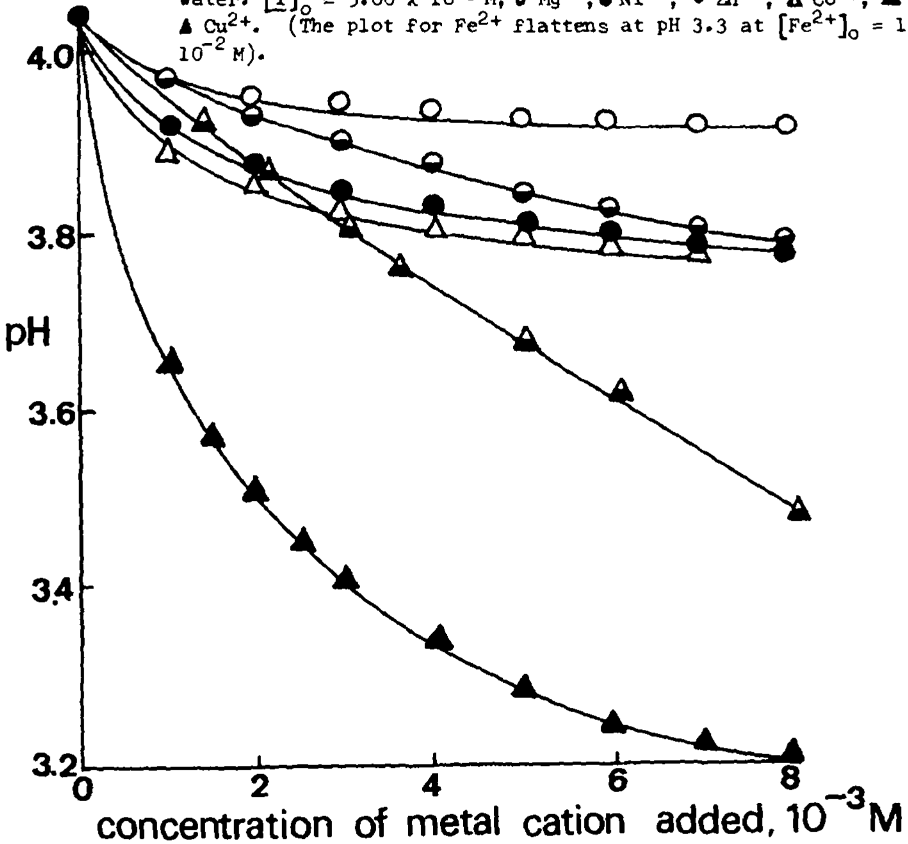


Fig. 6 Variations of pH of 1 with concentrations of added metal cations in water. $[1]_o$ = 5.00 x 10^{-3} M; ○ Mg^{2+}; ◐ Ni^{2+}; ● Zn^{2+}; △ Co^{2+}; ▲ Fe^{2+}; ▲ Cu^{2+}. (The plot for Fe^{2+} flattens at pH 3.3 at $[Fe^{2+}]_o$ = 1.60 x 10^{-2} M).

In the complex, the metal cation is coordinated to the oxygen atoms of the hydroxyl groups of 1, as indicated by the decrease in the pH of a given concentration of 1 upon the addition of a metal cation (Figure 6). However, the hydroxyl groups remain largely unionised in the complexes since the decrease in the pH are relatively small (the largest monodeprotonation observed in the Cu^{2+} complex is only 14.5%, as calculated from the equilibrium pH of 3.2). The metal cation is probably coordinated to all the six hydroxyl oxygen atoms of 1 in the chair conformation in the 1:1 complexes (the predominant conformation in non-alkaline medium[2]), since all the reported crystal structures of 1:1 metal cation — calixarene complexes show that the central metal cation is coordinated to all the phenolic oxygen atoms.[3,4]

The large positive ΔS^o values (Table V) show that the driving force for complexations is the gain in entropy. This gain in entropy comes from the changes in solvations of the metal cation and 1 on complexation. The planar oxygen ligands are already "preorganised" for complexation,[3,5] and no significant unfavourable entropy contribution is expected from them. Our case differs from that reported[6] for dicyclohexyl-18-crown-6 where the flexible oxygen ligands are not "preorganised" for complexations. As a result, the ΔS^o values for complexations in the latter are relatively small.[6]

The stability constants are larger in methanol than in water (Table IV), although the differences are relatively smaller than those observed in crown ethers[7] and cryptands[8,9] (an exception is Zn^{2+} which complexes with cryptand 211 with about the same stability constants in water and methanol[8]). The structural similarity between the ligands (OH) and the solvents could be a reason for the smaller solvent effects on the stability constants.

Experimental

1 was prepared as reported earlier.[1,2] All metal salts were commercial samples.

Visible spectra were recorded with a Hitachi 300 spectrophotometer.

pH measurements were taken with a Beckman 3500 pH meter.

Calculations of stability constants. The absorbance in the 450 nm region was used for the calculations of stability constants. For each set of experiment, the concentration of 1 was kept constant ($\sim 3 \times 10^{-4}$ M) and the metal cation concentration varied until complete complexation was observed.

For a 1:1 stoichiometry complex, the stability constant, K_{11}, is defined by

$$K_{11} = \frac{[H \cdot G]}{[H][G]} \qquad (1)$$

where H.G, H, and G denote the complex, host 1, and the metal cation guest respectively.

The stability constant, K_{21}, for a 2:1 stoichiometry complex (host to guest) is

$$K_{21} = \frac{[H_2 \cdot G]}{[H]^2[G]} \qquad (2)$$

Since the extinction coefficients of 1 and the complex could be determined (the former from the absorbance in the absence of any metal cation and the latter from the absorbance at complete complexation), the concentrations of the host, metal cation, and complex before complete complexation was reached could be calculated using Beer-Lambert Law. For example, in the case of 1:1 complex

$$[H \cdot G] = \frac{A - \varepsilon_H [H]_o}{\varepsilon_{HG} - \varepsilon_H} \qquad (3)$$

$$[H] = [H]_o - [H \cdot G] \qquad (4)$$

$$[G] = [G]_o - [H \cdot G] \qquad (5)$$

where A is the absorbance, ε_H and ε_{HG} the extinction coefficients of 1 and the complex respectively, $[H]_o$ and $[G]_o$ the initial concentrations of 1 and the metal cation respectively.

The average of six or more calculated values was taken as the stability constant (see Tables II and III).

Thermodynamic data. The stability constants were determined at four to five different temperatures (29° - 50°) and each experiment was done in duplicate. A plot of log K versus $\frac{1}{T}$ (equation 6)[10] yields the ΔH^o (slope of the plot) and ΔS^o values (intercept). The free energy ΔG^o was then calculated[10] from equation 10 for 25°.

$$\log K = \frac{-\Delta H^o}{4.576} \times \frac{1}{T} + \frac{\Delta S^o}{4.576} \qquad (6)$$

$$-\Delta G^o = RT \ln K \qquad (7)$$

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