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POTENTIOMETRIC, IR AND THERMAL CONDUCTIMETRIC STUDIES ON CHELATES OF CHROMOTROPIC ACID WITH SOME TRANSITION METALS

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ABSTRACT

The stepwise stability constants of complexes of chromotropic acid with Cr(III), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) are determined by the Calvin-Bjerrum potentiometric titration method in a medium of 0.1 μ ionic strength and at $27 \pm 0.1°$ C. The solid complexes of the previously mentioned transition metal ions in addition to V(IV) and Mn(II) were prepared and subjected to elemental analysis, IR, thermogravimetric and thermal conducti-metric studies. It was found that for all specimens the activation energies lie in the range of typical semiconductors. The conduction mechanism was explained according to the ligand field theory.

INTRODUCTION

Chromotropic azo dyes find wide applications as chromophoric and metallochromic indicators [1,2]. Chromotropic acid was used for spectrophotometric determination of some rare earth metals [3]. Dichlorochromotropic acid has been used for the determination of titanium in the presence of a considerable excess of uranium [4,5]. Iron, molybdenum and titanium have been determined spectrophotometrically using chromotropic acid [6,7].

This study was undertaken to prove that both of the hydroxyl groups of chromotropic acid are ionizable and also to determine potentiometrically the stepwise formation constants of the chromotropic acid complexes with some transition metal ions. Thermal conductivity and IR absorption spectra of the solid complexes were studied in order to throw some light on the structure

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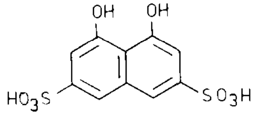
and nature of bonding of the compounds. Chromotropic acid is 4,5-dihydroxynaphthalene-2,7-disulfonic acid.



EXPERIMENTAL

All reagents used were of the purest grade provided by BDH (England). Stock 0.001 M chromotropic acid was prepared in deionized water. The metal salts used were chlorides of Cr(III), Mn(II), Fe(II), Co(II), Ni(II), vanadyl sulfate, copper acetate and zinc nitrate. Metal salt solutions of concentration 0.01 M were prepared in deionized water and standardized by recommended methods [8]; then 0.001 M solutions were prepared by accurate dilution. Solutions of 0.1036 N nitric acid, 0.0994 N NaOH and 1 M potassium nitrate were also prepared.

Three mixtures were prepared and potentiometrically titrated as previously described [9] using a pH meter (Orion Research Model 701A digital Ionalyzer) at 27 ± 0.1° C. The curves were plotted accordingly. Correction blank curves for metal salts were also performed.

The average number of protons $\bar{n}_A$ associated with the ligand at different pH values, average number of ligand molecules $\bar{n}$ attached per metal ion, and free ligand exponents pL were calculated using previously described methods [9,10]. All calculations were done using the Cairo University ICL 2957 VME computing system. The solid complexes were prepared by mixing the 0.01 M metal salts with 0.02 M ligand as sodium salt in 50% ethanol–water, and the mixture was left overnight; the collected complexes were washed with bidistilled water and recrystallized from a 50 : 50 (v/v) alcohol–water mixture. The complexes were dried in air, then stored in a vacuum desiccator for several days and subjected to elemental and thermogravimetric analysis. The IR spectra of the free ligand and metal complexes were recorded as KBr discs using a Pye Unicam SP 1000 infrared spectrophotometer.

For electrical measurements chromotropic acid and its complexes were pressed into pellets at a pressure of about 600 kg cm^{-2}, which was chosen because at this pressure the electrical conductivity was independent of load [11]. The specimen was fixed to the double electrode by silver paste. The sample holder with specimen was placed inside a vertical wire wound tube furnace with the coils running in opposite directions to eliminate fields caused by the heating current. The applied voltage must be within the linear range of the I–V relation to verify the ohmic nature of contacts. Moreover, after the voltage was applied no time dependence of the electrical resistance was observed, indicating that the ionic contribution in conduction is negligible.

The d.c. measurements were made with stabilized d.c. power supply BS 275, and a Leybold model 532-01 current measuring amplifier. The electromotive force (e.m.f.) of the thermocouple (0.1 mm chromel–alumel wires) was monitored by a digital multimeter PM 2421 to record the temperature of the sample. Measurements were made every 3° C in the working range.

RESULTS AND DISCUSSION

Potentiometric results

Values of $\bar{n}_A$ were calculated from the titration curve of the first and second mixtures [9]. The formation curve of the proton–ligand system extends over 0.1–2.00, indicating that the two naphthalenic protons dissociate from the ligand molecule. Values of pK_1 and pK_2 were found to be 4.85 and 7.50 respectively. The rapid attainment of equilibrium during titration, and the absence of significant drift in pH meter readings indicate the absence of hydrolysis in the system.

From the titration curves of the three mixtures, $\bar{n}$ values of the metal complexes were determined at various pH values. The $\bar{n}$ values (0.1–1.8, Fig. 1), indicate the formation of 1 : 1 and 1 : 2 complexes. The stability constants were computed by interpolation at half $\bar{n}$ values and are listed in Table 1. From the titration curves of mixtures of metal ions and organic ligand one can make some general remarks:

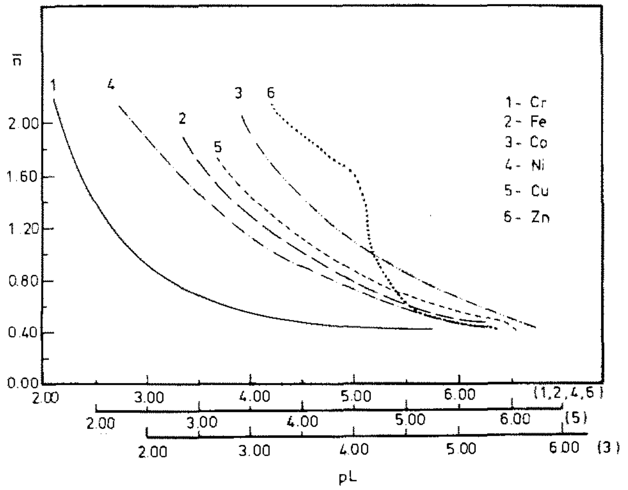


Fig. 1. Formation curves of transition metal complexes with chromotropic acid.

TABLE 1

Metal–ligand stability constants of Cr(III), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) with chromotropic acid (disodium salt)

Cation	Z	$1/r$	I_2	EN	log β_1	log β_2
H	1	–	–	–	4.85	7.50
Cr	24	1.45	–	1.60	4.45	6.85
Fe	26	1.56	–	1.83	6.00	9.45
Co	27	1.39	586	1.88	5.52	9.05
Ni	28	1.45	599	1.91	5.85	9.27
Cu	29	1.39	648.6	1.90	5.93	9.33
Zn	30	1.35	633.5	1.65	5.85	10.90

Z, Atomic number; r, ionic radius; I_2, second ionization potential in eV; EN, electronegativity; β_1, β_2, first and second stepwise formation constants of metal chelates.

(1) Addition of metal ions to the ligand solution lowers its original pH; also the same effect occurs on adding the ligand to the metal solution due to the liberation of H^+ ions in solution through the reaction $M^{++} + H_2A \rightleftharpoons MA + 2H^+$, which was obeyed for all the titrations of di- and trivalent metal ions studied in the present work except with Mn(II) and VO.

(2) No precipitation occurs during the titration with NaOH.

(3) The order of stability constants (log β_2) is found to be Zn > Fe > Cu > Ni > Co > Cr. This order of stability is in agreement with the order reported earlier by other workers [12,13]. The values observed also indicate that log β_2 increases with the increase in ionization potential and reciprocal ionic radius. The observed order, Zn > Ni also supports the results of other workers [14,15]. The reversal of this order is attributed to stearic factors.

In all cases, the values of log β_2 were greater than log β_1; the difference log β_2 − log β_1 for various metal complexes does not indicate a purely statistical addition of the second ligand. The differences observed showed no definite trend and it seems probable that the cation is modified by addition of the first ligand. Forces leading to the interaction of the singly charged 1 : 1 complex with the second molecule of the ligand are of quite different types and orders from those operating between the solvated metal ion and the first ligand molecule [16].

Solid complexes

The solid complexes were prepared by reacting 1 : 1 and 1 : 2 stoichiometric proportions of metal ions and ligand. In all cases 1 : 1 complexes were obtained, as shown by elemental analysis. Thermogravimetric data (Table 2) showed that all complexes contain two types of water molecules. The first one, released within the temperature range 100–120 °C, can be considered as weakly bonded water of hydration molecules in the outer sphere of the

TABLE 2

C, H and thermogravimetric analysis results of solid chelates of transition metals with chromotropic acid (CR)

Complex M/L	C%		H%		Loss% at 100–120 ° C			Loss% at 140–220 ° C		
	Calc.	Found	Calc.	Found	Calc.	Found	No. of H_2O [a]	Calc.	Found	No of H_2O [b]
VO–CR·$6H_2O$	23.02	23.50	3.07	3.00	13.81	14.78	4	6.91	6.44	2
Cr–CR·$6H_2O$	22.97	22.00	3.06	3.20	17.23	17.02	5	3.45	3.24	1
Mn–CR·$6H_2O$	22.84	22.80	3.04	3.10	13.70	14.20	4	6.85	7.00	2
Fe–CR·$6H_2O$	22.80	23.60	3.04	3.50	13.68	15.02	4	6.84	7.22	2
Co–CR·$6H_2O$	22.67	23.1	3.02	3.40	13.60	14.57	4	6.80	6.65	2
Ni–CR·$6H_2O$	22.68	22.9	3.02	3.00	13.61	14.08	4	6.80	6.95	2
Cu–CR·$6H_2O$	22.48	21.90	2.99	3.40	13.48	14.30	4	6.74	7.01	2
Zn–CR·$6H_2O$	22.40	22.80	3.98	3.10	16.80	16.42	5	6.72	6.90	1

[a] Hydrated water molecules. [b] Coordinated water molecules.

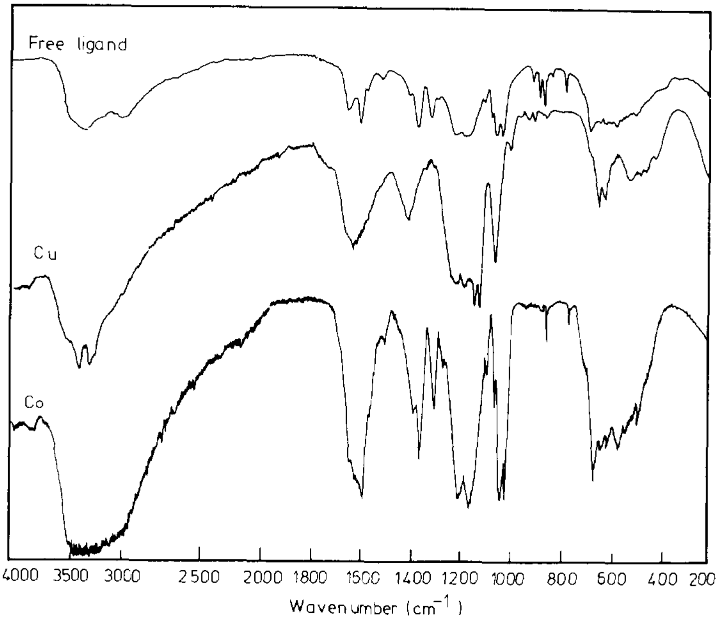


Fig. 2. Infrared spectra of chromotropic acid and its Cu(II) and Co(II) complexes.

complexes. The second type of water molecules, released in the temperature range 140–220 ° C, may be considered as coordinated water molecules in the inner sphere of the complexes. The results indicate that almost two molecules are present coordinated in the inner sphere. The mode of bonding of the ligand molecules to the metal ions was examined by recording the IR spectra of the complexes compared with that of the ligand. Representative spectra are shown in Fig. 2 and the band frequencies are given in Table 3. The IR spectrum of the ligand molecule shows bands at 3400 and 1150 cm^{-1}

TABLE 3

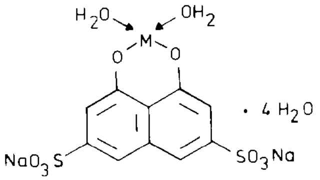
Main IR bands of chromotropic acid (CR) and its solid transition metal chelates

Compound	νOH [a]	δOH [a]	γOH [a]	νC=C	γCH	νSO_3^-	M → O
Free ligand CR	3400	1150	785	1590, 1640	850	1040, 1210	–
V–CR·$4H_2O$	3400 vb	1140 w	–	1620	850 vw	1040, 1200 b	–
Cr–CR·$4H_2O$	3400 vb	1130	–	1600	–	1045, 1200	620 vw
Mn–CR·$4H_2O$	3430 b	1120 w	–	1625	–	1040, 1190	630 w
Fe–CR·$4H_2O$	3450 vb	1150 wb	–	1630	820 vw	1040 w, 1200 b	620 w
Co–CR·$4H_2O$	3400 vb	1160	785	1590 s, 1620 w	850	1040, 1210	665
Ni–CR·$4H_2O$	3440 b	1100 w	–	1600, 1630	840 w	1050, 1200	630
Cu–CR·$4H_2O$	3360, 3440	1120 sp	–	1600, 1620	830	1050, 1200 w	625 sp
Zn–CR·$4H_2O$	3450 b	1120 sh	–	1625	840 w	1040, 1200	640 sp

[a] H_2O molecules. b, broad; vb, very broad; w, weak; vw, very weak; sp, split; s, strong.

which are assigned to νOH and δOH modes of vibration. The complexes show broad or split bands in the region 3450–3300 cm^{-1}, which can be assigned to water of hydration coordinated to the central metal ions as confirmed by TGA. The splitting and shift of the δOH band in the spectra of the chelates indicate the deprotonation of the naphthalenic OH groups and participation of this group in chelation. This is supported by the disappearance of the γOH of the ligand at 785 cm^{-1} in the spectra of the complexes. All the complexes investigated show a band at 650–600 cm^{-1} characteristic of the $M \rightarrow O$ dative bond [17] which is not obviously present in the spectrum of the ligand. The shift in the C=C stretching vibration bands which appears at 1590 and 1640 cm^{-1} for the chromotropic acid as a result of chelation can be taken as a criterion for formation of complex species which may disturb the skeletal C=C vibrations. Bands due to C–H in plane deformation, ϕ–O stretching of the phenolic system, stretching SO_3^- band and various C–C stretching modes appear in the 1400–1000 cm^{-1} region.

Based on the above results, we propose that the reaction between chromotropic acid disodium salt and metal ions occurs by the displacement of two protons from each ligand molecule, in addition to coordination through two water molecules in the inner sphere, and an extra two or four weakly bonded water molecules in the outer sphere of the complexes. The complexes can generally be represented by



Thermal conductivity

The temperature dependence of conductivity of the solid complexes is shown in Fig. 3. For all samples two activation energies are observed within the temperature range 300–550 K. This behavior is probably due to two different conduction mechanisms. In extrinsic (impure) semiconductor, the impurity levels can lie both in the allowed and in the forbidden bands at various distances from the top of the valence band and the bottom of the conduction band, Such localized levels play a significant role in the conduction mechanisms.

Following the behavior of a typical extrinsic semiconductor, it may be assumed that at moderate temperatures the predominant conduction mechanism is the excitation of carriers from donor localized levels to the conduction band. In such cases we are dealing with extrinsic behavior where the activation energy ΔE_e is relatively low.

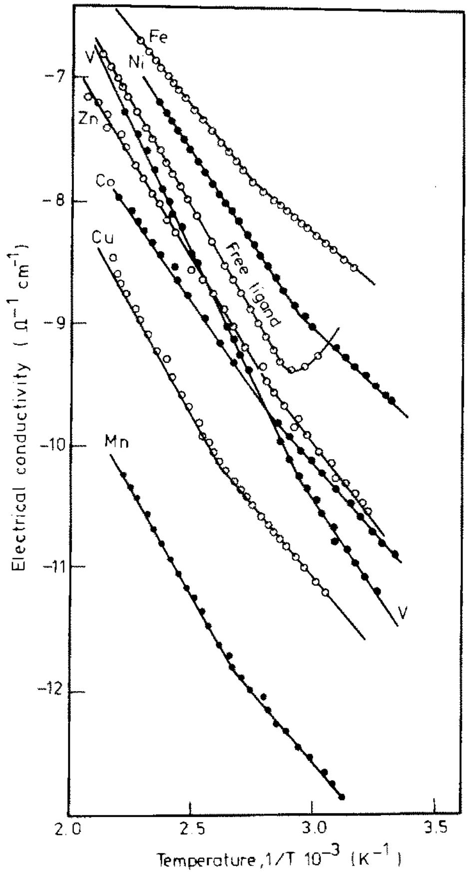


Fig. 3. Variation of electrical conductivity as a function of reciprocal absolute temperature for solid complexes of chromotropic acid with some transition metals.

On increasing the temperature the intrinsic region may be reached, where the carriers are thermally activated from the valence band to the conduction band. In this region the activation energy ΔE_i will be higher (Table 4). The extrinsic–intrinsic transition temperature is almost independent of the transition metal.

The dependence of activation energy ΔE_i on the number of *d* electrons is shown in Fig. 2. This behavior allows us to assume that the *d* electrons might contribute to the conduction process. This agrees with the behavior of *d* electrons in the weak fields, where the d^n and d^{n+5} configurations are identical [18].

According to the configurational model [19], the transition metal ion tends to lie in one of the stable configurations d^0, d^5 and d^{10}. For the configuration $3 < n < 5$ the tendency to attract electrons is the likely process, i.e. the metal ion will be electron attracting which leads to a decrease of

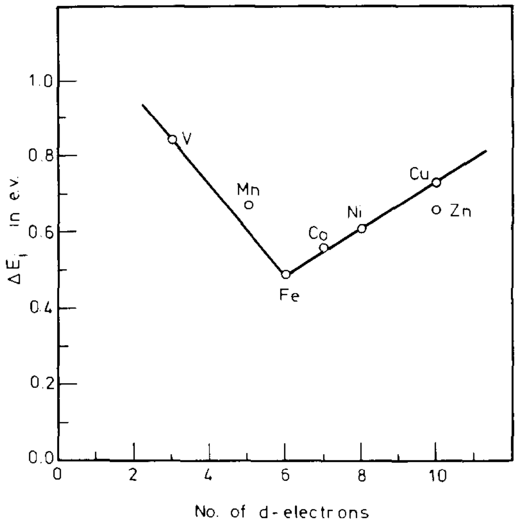


Fig. 4. Dependence of intrinsic activation energy ΔE_i of the solid complexes on the number of *d* electrons of transition metals.

the activation energy. This is the case for V(IV) and Mn(II) ions. This effect will increase the degree of localization giving rise to the observed decrease in the activation energy in going from V to Mn.

On the other hand, for higher electron numbers ($5 < n < 10$) the opposite behavior is expected. As it is well known that the *d* electrons form a very narrow band which gives rise to a strong negative field, then by increasing the number of *d* electrons the repulsion of external electrons is increased. This effect will decrease the degree of localization and consequently increase the activation energy.

TABLE 4

Activation energies of chromotropic acid (CR) and its complexes with transition metals at extrinsic (ΔE_e) and intrinsic (ΔE_i) temperature ranges

Compound	Activation energy (eV)	
	ΔE_i	ΔE_e
Free ligand CR	0.68	–
V–CR	0.85	0.59
Mn–CR	0.67	0.48
Fe–CR	0.49	0.33
Co–CR	0.56	0.44
Ni–CR	0.61	0.39
Cu–CR	0.73	0.49
Zn–CR	0.66	0.50

Note that complexation with Fe, Co and Ni decreases the activation energy of the free ligand, while complexation with Mn and Cu leads to higher activation energy.

REFERENCES

1 L. Sommer and M. Cenek, Chemist Analyst, 56 (1967) 9.
2 T. Katayama, T.H. Miyata and K. Toei, Bull, Chem. Soc. Jpn, 44 (1971) 2712.
3 S. Zelinski and V. Pauch, Zh. Analit. Khim., 25 (1970) 2342.
4 V.I. Kuznetsov, V.I. Basargin and N.T. Kukisheva, Zh. Analit. Khim., 17 (1962) 457.
5 N.V. Tikhonov, Zh. Analit. Khim., 22 (1967) 525.
6 L. Sommer, Chem. Listy, 52 (1958) 1485; Collection Czech. Chem. Commun., 24 (1959) 1649.
7 I.A. Tserkovnitskaya and N.A. Kustova, Zh. Analit. Khim., 23 (1968) 72.
8 F.J. Welcher, The Analytical Uses of Ethylenediaminetetraacetic acid, Van Norstand, Princeton, 1958.
9 R. Sarin and K.N. Munshi, Inorg. Nucl. Chem., 34 (1972) 581.
10 H. Irving and H.S. Rossotti, J. Chem. Soc., (1954) 2904.
11 M. Abou Sekkina and Y.M. Issa, Thermochim. Acta, 83 (1985) 321.
12 D.P. Mellor, and L. Maley, Nature (London), 159 (1947) 370.
13 D.P. Mellor, and L. Maley, Nature (London), 161 (1948) 436.
14 H.M. Irving and R.J.P. Williams, Nature (London), 162 (1948) 746.
15 H.M. Irving and R.J.P. Williams, J. Chem. Soc., (1953) 3192.
16 S. Kakali and B.S. Garg, J. Indian Chem. Soc., 62 (1985) 498.
17 M.A. David, Metal Ligand and Related Vibrations (Ed.), Edward Arnold, 1967, p. 235.
18 B.N. Figgis, Introduction to Ligand Fields, Wiley-Interscience, 1964, p. 75.
19 F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 2nd. edn., Wiley, 1966, p. 660.