

SYNTHESIS AND CHARACTERIZATION OF SOME FIRST ROW TRANSITION METAL PICRATES

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Transition metal picrates of the empirical compositions $Ti(\text{Picrate})Cl_3$, $Ti(\text{Picrate})_2Cl_2$, $Cr(\text{OH})(\text{H}_2\text{O})_6(\text{Picrate})_2$ and $M(\text{H}_2\text{O})_x(\text{Picrate})_2$ (where $M = \text{Mn}(\text{II}), \text{Fe}(\text{II}), \text{Co}(\text{II}), \text{Ni}(\text{II}), \text{Cu}(\text{II})$ and $\text{Zn}(\text{II})$ and $x = 4$ for $\text{Cu}(\text{II})$, 8 for $\text{Fe}(\text{II})$ & 6 for others) have been prepared and characterized by elemental analysis, molar conductance, magnetic susceptibility measurements, infrared and electronic spectral studies. Molar conductances and molecular weights of the soluble metal picrates show that $TiCl_3(\text{Picrate})_2$ is non-electrolyte whereas others are 1:2 electrolytes. Magnetic susceptibility and electronic spectral studies indicate that $\text{Cu}(\text{II})$ picrate is square planar, whereas those of $\text{Cr}(\text{III})$, $\text{Mn}(\text{II})$, $\text{Fe}(\text{II})$, $\text{Co}(\text{II})$ and $\text{Ni}(\text{II})$ are spin-free octahedral. The infrared spectral studies of the hydrated and anhydrous metal picrates show: (i) that phenolic group of the picric acid is involved in bonding with the metals; (ii) the water molecules in the hydrated metal picrates are coordinated and (iii) the $-\text{NO}_2$ groups do not participate in bonding with the metals.

In spite of much work on the synthesis of the first row transition metal picrates, the compositions of these compounds do not appear to be well established¹. As the compositions of these compounds are controversial and there is no previous work on their structural aspects, it was thought of interest to synthesise the first row transition metal picrates and study their structures employing various physico-chemical methods such as molar conductance, molecular weight determination, magnetic susceptibility measurements, infrared and electronic spectral studies.

EXPERIMENTAL PROCEDURE

All the chemicals used were of BDH or equivalent quality. Solvents were purified and made anhydrous employing the standard literature procedures.

Preparation and analysis of the compounds

$Ti(\text{Picrate})Cl_3$ was prepared by the direct reaction between excess of $TiCl_4$ and picric acid in an inert atmosphere. The reaction mixture was refluxed on an oil bath till evolution of HCl ceased. Excess of titanium tetrachloride was filtered off and the resulting brown solid compound washed with chloroform and dried in vacuo. The compound was purified by dissolving it in THF and subsequent removal of the solvent by distillation and drying in vacuo.

$Ti(\text{Picrate})_2Cl_2$ was prepared by the reaction of $TiCl_4$ and picric acid in $\sim 1:4$ molar ratio in toluene. The reaction mixture was refluxed in an oil bath till evolution of HCl ceased. The resulting yellow coloured solid was filtered, washed with benzene and dried in vacuo; m.p. $\sim 110^\circ\text{C}$.

$Cr(\text{OH})(\text{Picrate})_2 \cdot 6\text{H}_2\text{O}$ was prepared by dissolving freshly prepared chromium hydroxide in hot aqueous solution of picric acid. The solution was evaporated to dryness on a water bath and the green solid obtained was dried in air. It was washed with hot benzene to remove the unreacted picric acid and dried.

$Fe(\text{Picrate})_2 \cdot 8\text{H}_2\text{O}$ was prepared by mixing together hot concentrated aqueous solutions of barium picrate and ferrous sulphate. Before mixing the above solutions, some sulphurous acid was added to ferrous sulphate solution to reduce any contamination of Fe^{3+} to Fe^{2+} and the excess of the acid was removed by heating the solution. The precipitate of the BaSO_4 formed by the metathetic reaction was filtered off and the green coloured solution concentrated on a water bath (any precipitate of BaSO_4 formed during concentration was filtered off) till incipient crystallization. The yellow coloured crystals of ferrous picrate separating from the solution were filtered, washed with cold water, dried in air and finally washed with chloroform and again dried in air.

$\text{Mn}(\text{II})$, $\text{Co}(\text{II})$, $\text{Ni}(\text{II})$, $\text{Cu}(\text{II})$ and $\text{Zn}(\text{II})$ picrates were prepared by dissolving the respective metal carbonates in hot aqueous solution of picric acid. The unreacted metal carbonate was removed by filtration and the solution concentrated till crystallization. The crystals of metal picrates were filtered and recrystallized from hot aqueous solution.

TABLE I

ANALYTICAL RESULTS, MOLAR CONDUCTANCE, MOLECULAR WEIGHTS AND MAGNETIC MOMENTS OF TRANSITION METAL PICRATES

Compound	Colour	Metal (%)	Nitrogen (%)	H ₂ O (%)	Molar conductance at 10 ⁻³ M (cm ² mhos/mole)	μ eff (B.M.)	Mol. Wt.
Ti (Picrate)Cl ₃	Brown	12.54 (12.52)	10.30 (10.90)	Diamag.	..
Ti (Picrate) ₂ Cl ₂	Yellow	8.77 (8.33)	14.60 (14.60)	..	1.44(C ₆ H ₅ NO ₂)	..	604 (575)
[Cr (OH) (H ₂ O) ₅] (Picrate) ₂ H ₂ O	Green	8.92 (8.21)	12.54 (13.20)	17.40 (17.06)	..	3.940	..
[Mn (H ₂ O) ₆] (Picrate) ₂	Yellow	8.31 (8.88)	13.70 (13.57)	17.60 (17.44)	288(H ₂ O)	6.154	204 (206.33)
[Fe (H ₂ O) ₆] (Picrate) ₂ ·2H ₂ O	Yellow	9.40 (8.50)	12.60 (12.80)	21.07 (21.96)	310(H ₂ O)	5.430	199* (206.66)
[Co (H ₂ O) ₆] (Picrate) ₂	Yellowish red	9.20 (9.48)	14.37 (13.40)	16.10 (17.30)	267(H ₂ O)	4.916	205 (207.66)
[Ni (H ₂ O) ₆] (Picrate) ₂	Yellowish green	9.40 (9.48)	13.08 (13.40)	16.82 (17.33)	278(H ₂ O)	3.285	208 (207.66)
[Cu (H ₂ O) ₆] (Picrate) ₂	Olive green	11.03 (10.72)	14.50 (14.20)	11.50 (12.16)	266(H ₂ O)	1.880	210* (209.23)
[Zn (H ₂ O) ₆] (Picrate) ₂	Yellow	10.14 (10.33)	13.48 (13.35)	17.03 (17.19)	273(H ₂ O)	Diamag.	208 (209.7)

Calculated values are given in parentheses.

Molecular weights given in parentheses are apparent values except for Ti (Picrate)₂Cl₂, expected for 1:2 electrolyte.

* Agree with the formulation of the complex as [M(H₂O)₆] (Picrate)₂.

Metals were analyzed by standard procedures after destroying the organic part at first with a mixture of nitric and hydrochloric acids and then with concentrated sulphuric acid. Nitrogen was estimated by micro-analysis. The amount of water in the hydrated metal picrates was estimated by heating them to ~ 160°C and finding out the loss in weight. The analytical data are given in Table 1.

PHYSICAL MEASUREMENTS

Electrical conductance was measured on a WTW conductivity meter. Molecular weight determinations were made on Vapor Pressure Osmometer model 301A. Magnetic measurements of the metal picrates were carried out at room temperature on Cahn Faraday Electrobalance using Hg [Co(CNS)₄] as calibrant and diamagnetic corrections were estimated by the procedure of Figgis and Lewis². The magnetic moments, molar conductances and molecular weights of the metal picrates are included in Table 1. Electronic spectra were obtained on Cary-14 recording spectrophotometer using water as solvent. The spectra in nujol mull were recorded using the technique described by Lee et al³. The position of the absorption bands and their assignments are given in Table 2. The various spectral parameters Dq , B' and β were calculated by using the matrix of Tanabe and Sugano⁴ and these results are also included in Table 2.

Infrared spectra of the picric acid and metal picrates were recorded on a Perkin-Elmer Spectrophotometer, Model 621 using nujol technique in the 4,000—200 cm⁻¹ region. More important absorption bands and assignments thereof are given in Table 3.

DISCUSSION

All the metal picrates under present investigation explode when heated at ~ 300°C and are insoluble in organic solvents such as CCl₄, CHCl₃, benzene etc. Ti (Picrate)₂Cl₂ is soluble in nitrobenzene and THF. Other metal picrates except those of Cr³⁺ and Ti (Picrate)Cl₃ are soluble in water, alcohol, acetone, THF etc. Molar conductances of the compounds in nitrobenzene, or water and their molecular weights in THF or water (Table 1) show that Ti (Picrate)₂Cl₂ is non-electrolyte, whereas other metal picrates are 1:2

TABLE 2

ELECTRONIC SPECTRAL BANDS AND THEIR ASSIGNMENTS

Compound	Medium	Bands (cm ⁻¹)	Assignments	10 Dq (cm ⁻¹)	LFSE (k cal/mole)
Picric acid	nujol	28985*, 39200*
[Cr (OH) (H ₂ O) ₅] (Picrate) ₂ · H ₂ O	"	17390, 24400	⁴ A _{2g} (F) → ⁴ T _{2g} (F), ⁴ T _{1g} (F)	17390	56·03
[Mn (H ₂ O) ₆] (Picrate) ₂	water	28010 (22400)*, 25000 (15600)* 41660 (21200)*
[Fe (H ₂ O) ₆] (Picrate) ₂ · 2H ₂ O	"	10990 (3·3), 28010 (29600)*, 25000 (21200)*, 41320(22600)*	⁵ T _{2g} → ⁵ E _g (D)	10990	12·52
[Co (H ₂ O) ₆] (Picrate) ₂	"	8600 (2·5), 28010 (30500)*, 25000 (21500)*, 41320 (23300)*	⁴ T _{1g} → ⁴ T _{2g} (F)
[Ni (H ₂ O) ₆] (Picrate) ₂	"	8500 (2·75), 13800 (3·0), 15380 (2·875), 28010 (30200)*, 25000(21200)*, 41665 (28600)*	³ A _{2g} → ³ T _{2g} (F), ³ T _{1g} (F) → ¹ E _g	8500	29·06
[Cu (H ₂ O) ₄] (Picrate) ₂	"	12300(11·75), 28170 (31875)*, 25000 (22500)*, 41665 (27500)*	² E _g → ² T _{2g}	12300	21·02
	nujol	13500	² E _g → ² T _{2g}		

Molar extinction coefficients are given in parentheses.

*represents intraligand transitions.

electrolytes. The molecular weight of Cu (II) picrate indicates that two water molecules are added to the complex in the axial position giving it an octahedral geometry. This type of behaviour for square planar Copper (II) complexes in donor solvents is quite common and well documented in literature⁵. The insolubility of the chromium compound may be due to its being a monomeric basic salt or a polymeric compound through hydroxo bridging. Since Cr (III) picrate gives a normal magnetic moment as discussed below, no large deviation from monomeric behaviour is expected⁶.

Magnetic Studies

The values of the corrected magnetic moments given in Table 1 show that Ti (IV) and Zn (II) picrates, as expected for d⁰ and d¹⁰ electronic configuration respectively, are diamagnetic. The magnetic moments of Cr (III), Mn (II), Fe (II), Co (II) and Ni (II) picrates are well within the range observed for most of the octahedral complexes of these metal ions². For Cu²⁺, a d⁹ system having only one unpaired electron in 3d orbitals, a magnetic moment of 1.73 B.M. is expected. The values of the magnetic moments for square planar and tetrahedral Cu (II) complexes lie in the ranges 1.83-1.86 and 1.89-1.92 B.M. respectively⁷ (higher orbital contribution to the moment is expected for a tetrahedral arrangement of the ligands than for the planar one). The value of the magnetic moment of Cu(II) picrate is close to those of Cu(II) square planar complexes.

Electronic spectral studies

The electronic spectrum of octahedral [Cr (H₂O)₆]³⁺ gives three bands at 17400, 24600 and 38000 cm⁻¹ assigned to ⁴A_{2g} (F) → ⁴T_{2g} (F), ⁴T_{1g} (F) and ⁴T_{1g} (P) transitions respectively⁸. But in some Cr³⁺ complexes the ⁴A_{2g} (F) → ⁴T_{1g} (P) transition is usually submerged under charge transfer and/or intraligand transitions in the U.V. range⁹. The nujol spectrum of Cr (III) picrate gives bands at 17390, 24400, 28670 and 38460 cm⁻¹. The first two bands in the complex may be assigned to ⁴A_{2g} (F) → ⁴T_{2g} (F) and ⁴T_{1g} (F) transitions respectively. The remaining two bands in the complex may be attributed to intraligand

transitions because they correspond to picric acid bands at 28985 and 39200 cm^{-1} . Using the relations :

$$B_{35} = \frac{2\nu_1^2 + \nu_2^2 - 3\nu_1\nu_2}{15\nu_2 - 27\nu_1} \quad \text{and} \quad \beta_{35} = \frac{B_{35} \text{ complex}}{918}$$

the values of B_{35} and β_{35} work out to be 705 cm^{-1} and 0.768 respectively which lie in the range usually accepted for octahedral Cr (III) complexes. The calculated value, 24417 cm^{-1} for the transition ${}^4A_{2g} \rightarrow {}^4T_{1g}$ (F) is in fairly good agreement with the observed value, 24400 cm^{-1} for the above transition. The values of 10 D_q and LFSE are 17390 cm^{-1} and 56.03 k cal/mole respectively.

In Mn (II) complexes no spin-allowed transitions are expected and spin-forbidden transitions of very weak intensities (ϵ_{max} 0.01—0.04 for Oh and 1-4 for T_d) are observed. The Mn (II) picrate is not sufficiently soluble to permit the recording of its spectrum in concentrated solution. The spectrum of the above complex recorded in 0.5 M aqueous solution yields no bands in the visible region. The nujol spectrum of the complex also does not give any band in the above region. The spectrum of the complex in 0.000025 M aqueous solution, however, yields one broad band at 28010 cm^{-1} and two shoulders at 25000 and 41660 cm^{-1} with ϵ_{max} values of 22400, 15600 and 21200 respectively, which are evidently due to intraligand transitions because they are also observed in the aqueous solution of picric acid¹⁰. Just like the spectrum of Mn (II) picrate, the spectra of Fe (II), Co (II), Ni (II) and Cu (II) picrates also yield one broad band and two shoulders in the ranges 28010-28170, 25000 and 41320-41665 cm^{-1} with ϵ_{max} values of 29600-31875, 21200-22500 and 22600-28600 respectively due to the intraligand transition.

The spectrum of octahedral Fe $(\text{H}_2\text{O})_6^{2+}$ shows a broad band at 10300 cm^{-1} assigned to ${}^5T_{2g} \rightarrow {}^5E_g$ (D) transition⁶. The visible region spectrum of the aqueous solution of Fe (II) picrate gives a broad band at 10990 cm^{-1} ($\epsilon_{max} = 3.3$) which may be assigned to ${}^5T_{2g} \rightarrow {}^5E_g$ (D) transition. The values of 10 D_q and LFSE calculated from the above transition come out to be 10990 cm^{-1} and 12.52 k cal/mole respectively.

The spectrum of octahedral $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ gives bands at 8500, 19500 and 22000 cm^{-1} assigned to ${}^4T_{1g} \rightarrow {}^4T_{2g}$ (F), ${}^4A_{2g}$ (F) and ${}^4T_{1g}$ (P) transitions respectively¹¹. The spectrum of aqueous solution of Co (II) picrate in visible region shows a band at 8600 cm^{-1} ($\epsilon_{max} = 2.5$). Since the energy and ϵ_{max} value of this band is close to the reported values for ${}^4T_{1g}$ (F) \rightarrow ${}^4T_{2g}$ (F) transition in number of Co (II) octahedral complexes, this band may be assigned to ${}^4T_{1g}$ (F) \rightarrow ${}^4T_{2g}$ (F) transition. The band due to ${}^4T_{1g}$ (F) \rightarrow ${}^4A_{2g}$ (F) and ${}^4T_{1g}$ (P) transitions appear to have submerged with intraligand bands and because of the absence of the bands due to the above transitions, it has not been possible to calculate 10 D_q value and other ligand-field parameters.

The electronic spectrum of octahedral $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ gives four bands at 8500, 13500, 15400 and 25300 cm^{-1} with ϵ_{max} values of 2.0, 1.8, 1.5 and 5.2 respectively. These bands have been assigned to ${}^3A_{2g} \rightarrow {}^3T_{2g}$ (F), 1E_g , ${}^3T_{1g}$ (F) and ${}^3T_{1g}$ (P) transitions respectively⁵. The aqueous solution spectrum of Ni (II) picrate in the visible region gives bands at 8500, 13800 and 15380 cm^{-1} with ϵ_{max} values of 2.75, 3.00 and 2.875 respectively. If the bands at 8500, 13800 and 15380 cm^{-1} in Ni (II) picrate are likewise assigned to ${}^3A_{2g}$ (F) \rightarrow ${}^3T_{2g}$ (F), 1E_g and ${}^3T_{1g}$ (F) transitions respectively, the value of B' comes out to be 1480 cm^{-1} , which is improbable since B' cannot exceed the free nickel ion value (1056 cm^{-1}). Hence the more plausible assignments are : ${}^3A_{2g} \rightarrow {}^3T_{2g}$ (F) : 8500 cm^{-1} ; ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (F) : 13800 cm^{-1} ; and ${}^3A_{2g} \rightarrow {}^1E_g$: 15380 cm^{-1} . Using Tanabe and Sugano diagram, the values of 10 D_q and B' for the complex come out to be 8500 and 850 cm^{-1} respectively which yield a value of 29.06 k cal/mole for LFSE. The calculated values for the transitions ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (F) and 1E_g are 14050 and 15365 cm^{-1} respectively which are in good agreement with the observed values. In view of the foregoing discussion, an octahedral geometry may be proposed for Ni (II) picrate. The spectrum of octahedral $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ shows a broad band at 12600 cm^{-1} ($\epsilon_{max} \sim 12$) assigned to ${}^2E_g \rightarrow {}^2T_{2g}$ transition⁹. Since 2E_g state is highly susceptible to Jahn-Teller distortion which in Cu (II) complexes leads in extreme cases to square planar structure and consequently the 12600 cm^{-1} band is considerably blue shifted⁹. Square planar Cu (II)—DEHPA (di-(2-ethylhexyl)—phosphoric acid) shows a broad band¹² at 13000 cm^{-1} . The visible spectra Cu (II) picrate in nujol and aqueous solution show a broad band at 13500 and 12300 cm^{-1} ($\epsilon_{max} = 11.75$) respectively. These bands may be assigned to ${}^2E_g \rightarrow {}^2T_{2g}$ transition. The position and the intensity of the bands in the above two phases indicate that Cu (II) picrate in the solid state is square planar and it

TABLE 3

IMPORTANT INFRARED SPECTRAL BANDS AND THEIR ASSIGNMENTS

Compound	ν (OH)	ν as (NO ₂)	δ (HOH)	ρ_r (H ₂ O)	ρ_w (H ₂ O)	ν (M-O)/ ν (Ti-Cl)
Picric acid (CHCl ₃)	3675 (m)	1550(s)	1635(s)
Picric acid (nujol)	3380(s)	1550(s)	1640(m)
Ti (Picrate)Cl ₃	..	1530(s)	525 ^a , 440 ^b
Ti (Picrate) ₂ Cl ₂	..	1545(s)	535 ^a , 445 ^b
[Cr (OH) (H ₂ O) ₅] (Picrate) ₂ · H ₂ O	3605(s), 3540(s), 3465(s)	1560(s)	1625(m)	810	544	440
[Mn (H ₂ O) ₆] (Picrate) ₂	3615(s), 3550(s), 3400(s)	1555(s)	1632(s)	665	542	390
[Fe (H ₂ O) ₆] (Picrate) ₂ · 2H ₂ O	3565(m), 3490(s), 3350(s)	1550(s)	1632(s)	385
[Co (H ₂ O) ₆] (Picrate) ₂	3565 (m), 3500(s)	1550(s)	1636(s)	770	560	342
[Ni (H ₂ O) ₆] (Picrate) ₂	3560(s), 3490(s), 3340(s)	1545(s)	1635(m)	745	425	375
[Cu (H ₂ O) ₄] (Picrate) ₂	3620(m), 3480(s), 3440(s)	1550(s)	1650(w)	820	540	445
[Zn (H ₂ O) ₆] (Picrate) ₂	3620(s), 3510(s), 3450(s)	1550(s)	1630(m)	675	545	365

s=strong, m=medium, w=weak, a and b represent ν (Ti-O), ν (Ti-Cl) respectively.

changes to octahedral geometry in the aqueous solution. This is supported by molecular weight determination of the Cu (II) picrate in aqueous solution. The fact that the solid compound bears a colour similarity to some olive green square planar Cu (II) complexes⁶ confirms the square planar geometry proposed for it.

Infrared spectral studies

The spectra of the picric acid in solid and solution phases (CHCl₃) given in Table 3, show a marked difference in the position of ν (OH) clearly indicating the presence of intramolecular hydrogen bonding between hydrogen of the —OH group and oxygen of the —NO₂ group. To avoid the effect of hydrogen bonding, the nujol spectra of the metal picrates have been compared with the solution spectrum of picric acid. A comparison of the nujol spectra of Ti (IV) picrates with the solution spectrum of picric acid shows the disappearance of ν (OH) at 3675 cm⁻¹ and appearance of two new bands in the ranges 535-525 cm⁻¹ and 445-440 cm⁻¹. ν (Ti-O) in titanium alkoxides and ν (Ti-Cl) in titanium tetrachloride have been reported at 625-500 cm⁻¹ and 485 cm⁻¹ respectively¹³. Hence the bands in 535-525 and 445-440 cm⁻¹ range in Ti (IV) picrates may be attributed to ν (Ti-O) and ν (Ti-Cl) modes respectively. The ν as NO₂ bands should shift to higher frequencies upon coordination¹², since there is no appreciable increase in these modes in Ti (IV) picrates, the possibility of coordination taking place through —NO₂ group is ruled out. The spectra of the hydrated metal picrates give bands in the ranges 3620-3315 and 1650-1630 cm⁻¹, which disappear in the anhydrous compounds. Hence the above bands may be attributed to ν (OH) and δ (HOH) respectively of the water molecules present in the hydrated metal picrates. The ν as NO₂ vibrations remain practically unchanged in the above compounds as compared to the location of these bands in picric acid. Coordinated water is reported to give a band in the range 880-650 cm⁻¹ due to ρ_r (H₂O) mode¹⁴. The bands occurring in the range 820-665 cm⁻¹ in hydrated metal picrates which are absent in the anhydrous compounds may therefore be assigned to coordinated water. The wagging and metal-oxygen stretching vibrations due to coordinated water occurring in the lower region have also been assigned by comparing the spectra of respective hydrated and anhydrous metal picrates. The ρ_w (H₂O) and ν (M-O) have been observed in the ranges 560-425 and 445-365 cm⁻¹ respectively which are very close to the values reported for the corresponding aquated metal complexes¹³.

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