COMPLEXES OF DYSPROSIUM, HOLMIUM AND YTTRIUM WITH KOJIC ACID

R. C. AGARWALA AND S. P. GUPTA

Department of Chemistry, D.N. College, Meerut-250002

ABSTRACT

Rare earth complexes of kojic acid of the general composition $[Ln(C_6H_5O_4)_3(H_2O)_2]$ (where Ln represents Dy^{+3}, Ho^{+3} and Y^{+3}) have been studied. These complexes have been isolated and characterised by analyses, conductometric, amperometric, magnetic and I.R. spectral studies. Composition and I.R. spectra of the complexes show that kojic acid is acting as a bidentate ligand and the two water molecules are also present in the coordination sphere.

EXPERIMENTAL

Materials and Methods

THE measurement of conductance and *i.r.*, spectra of the samples were made as reported earlier[1]. Kojic acid was of BDH (AR) quality. Solvents were reagent grade and were purified and dried before use.

A Toshniwal manual polarograph (CLO-2) with Pye scalamp galvanometer in the external circuit, was employed for carrying out amperometric titrations. The polarographic cell was kept immersed in a water thermostat maintained at $30 \pm 0.1°$ C.

susceptibilities were determined by Gouy's method, using copper sulphate pentahydrate as a calibrant. The rare earths (Dy, Ho and Y) were estimated as their oxides by direct combustion of the complexes. To make an actual estimate of water molecules bound per chelate, larger quantities of the compounds (0.4 g) were heated around 120° to constant weight. The percentage loss in weight was assumed to correspond to the number of water molecules. The microanalyses for carbon and hydrogen were carried out at the I.I.T., Kanpur. The analytical data are given in Table I, other physical properties are summarised in Table II.

TABLE I

Analytical data

Complex			Carbon (%)	Hydrogen (%)	Metal (%)	Water (%)
$[Dy(C_6H_5O_4)_3(H_2O)_2]$	..	Calcd.:	34·78	3·05	26·14	5·79
		Found:	34·76	3·01	26·21	5·35
$[Ho(C_6H_5O_4)_3(H_2O)_2]$	..	Calcd.:	34·64	3·04	26·43	5·76
		Found:	34·20	3·05	26·33	5·80
$[Y(C_6H_5O_4)_3(H_2O)_2]$	..	Calcd.:	39·43	3·47	16·22	6·57
		Found:	39·49	3·09	16·19	6·10

TABLE II

Physical properties

| Complex	Colour	Yield (%)	Dec. temp.	Molar Conductance $\Omega - 1$ cm^2 mole^{-1} (10^{-3} M Nitromethane)[5,6]
$[Dy(C_6H_5O_4)_3(H_2O)_2]$	Cream	~50	260–290	23 (non-electrolyte)
$[Ho(C_6H_5O_4)_3(H_2O)_2]$	White	~60	270–295	29 do.
$[Y(C_6H_5O_4)_3(H_2O)_2]$	Yellow	~65	250–295	25 do.

Fischer capillary with a drop time of 3·4 sec was used for the dropping mercury electrode. Purified hydrogen was used for deaeration. Magnetic

Preparation of the Complexes.—A general method employed for the preparation of rare earth complexes of kojic acid is described here.

Aqueous solutions of kojic acid (0·02 M) and lanthanide acetate (0·02 M) in the molar ratio 4 : 1 were mixed. The solutions were kept stirred by scratching the wall of the container; crystalline precipitates began to form in case of Ho^{+3}, whereas in the case of Dy^{+3} and Y^{+3} the precipitates were obtained after the concentration of the reaction mixture on a water-bath. The reaction mixtures, after keeping for about 2 hours at room temperature, were filtered and washed successively with water, ethanol and ether. The compounds were dried in vacuum.

ion has often been observed[2]. The magnetic moments observed for the kojates of dysprosium and holmium are 10·44 B.M. and 10·15 B.M. respectively which are in fair agreement with those reported for typical lanthanide sulphates[3].

Infrared Studies.—The assignments of various bands of kojic acid and its complexes are presented in Table III. The presence of several absorption peaks in the region 2400–3000 cm^{-1} in all the rare earth complexes show that hydrogen bonding is present in these complexes. Murakami *et al.*[4] have also observed the presence of hydrogen bonding in transi-
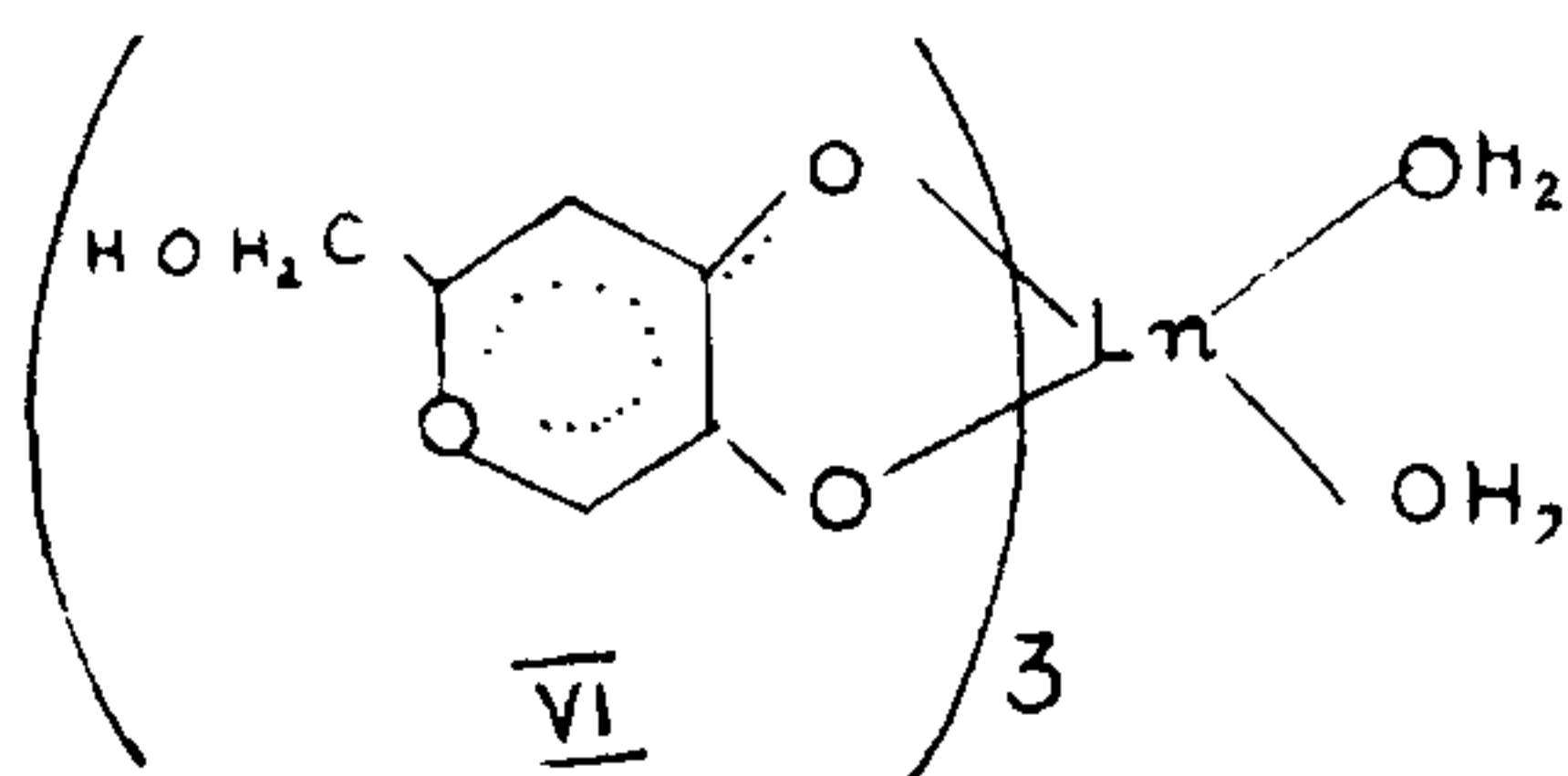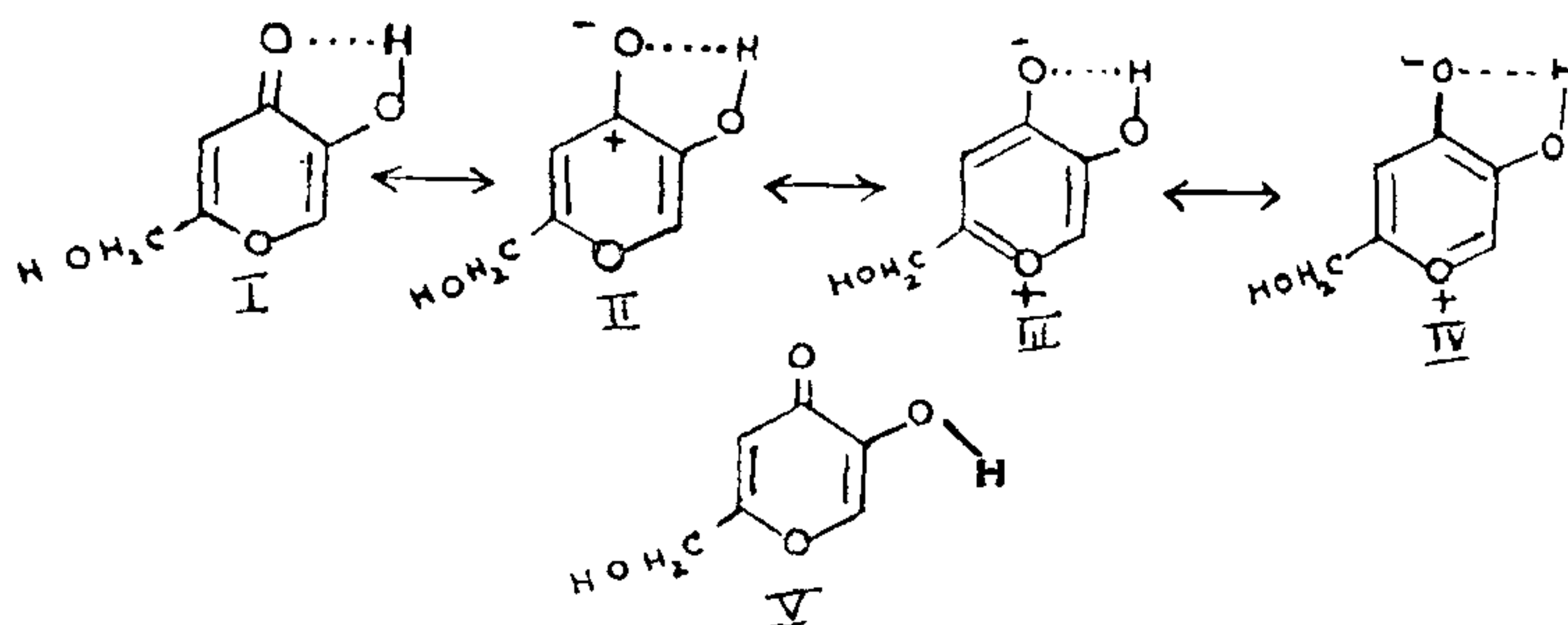
Results and Discussion

Analytical results show 1 : 3 metal to ligand stoichiometry in all cases. All the rare earth complexes behave as non-electrolytes as revealed by their molar conductance measurements in nitromethane (Table II).

Amperometric Titrations.—Amperometric titrations, both direct and reverse, were carried out using 2 M potassium nitrate as supporting electrolyte and 0·2% gelatine as the maximum suppressor, at an applied potential of 1·2 V (metal) and 0·95 V (ligand) respectively. The results of these titrations also prove the existence of 1 : 3 complex in all these systems.

Magnetic Measurements.—The *f* electrons of the lanthanide ions are shielded from the perturbing effect of ligand by the outerlying *s* and *p* electrons. Therefore, a behaviour similar to the free gaseous

tion metal complexes and have proposed the following four resonating structures (I–IV) for kojic acid. The absorption bands at 1680 cm^{-1} and 1620 cm^{-1} in the spectra of the kojic acid have been assigned to the non-hydrogen bonded (structure V) and hydrogen-bonded (structure IV) carbonyl hydrogen modes, respectively. When kojic acid forms a complex with a rare earth ion (as is illustrated by structure VI), the former mode disappears and the latter shifts to lower frequencies.

The other significant bands, appearing at 1585 cm^{-1} and 1575 cm^{-1} in the free kojic acid which are due to stretching modes of $C = C$ vibrations, also shift to lower frequencies through the formation of metal coordinate bonds. Thus, the shifts of both $C=O$ and $C=C$ bands to lower frequencies in the spectra of all the rare earth complexes seem to indicate that the contribution of resonance structures II, III and IV. in which a hydrogen atom is replaced by a metal ion, becomes greater as metal coordinate bonds are formed. The resonance interaction involving structures II, III and IV tends to delocalize olefinic and carbonyl π electrons over both γ-pyrone and chelate rings, thereby decreasing the double bond character of olefinic and carbonyl bonds.

Further evidence for the presence of a metal-oxygen bond in the complexes may be considered due to the disappearance of stretching and deforma-

TABLE III

Significant peaks in the infrared spectra of lanthanide kojates (cm^{-1})

Kojic Acid	Dy (III)–Kojate	Ho (III)- Kojate	Y (III)–Kojate	Assignment
3715–3725 (sb)	..	..	..	ν (OH) of Phenol.
..	3300–3400 (sb)	3300–3360 (sb)	3245–3445 (sb)	ν (OH) of H_2O.
..	3,100 (m sh) 2,930 (w) 2,470 (w)	3,100 (m sh) 2,940 (w) 2,480 (w)	3,150 (m sh) 3,080 (w sh) 2,490 (w)	ν (OH) H–bonded.
1,680 (s) 1,620 (s)	1,600–1,620 (s) 1570–1590 (sb)[a]	1615–1630 (s) 1570–1595 (sb)[a]	1,620–1635 (s) 1580–1600 (sb)[a]	ν (C=O) of Ketone.
1,585 (s) 1,575 (m sh)	1,530 (w) 1,520 (w) 1,510 (w)	1,515–1,540 (w) 1,480 (s)	1,525–1,550 (b) 1,475 (w)	ν (C=C)
1,381 (m) 1,340 (s)	..	..	..	δ (OH) of Phenol.
..	1,025 (m) 980 (m)	1,000 (w) 970 (m)	970 (m) 945 (m)	δr (H_2O) Coordinated water.
860 (s) 770 (s)	860 (s) 800 (s)	885 (s) 825 (s)	885 (s) 820 (s)	ν (C−H) out of plane.
..	750 (w)	775 (w)	775 (w sh)	δw (H_2O) Coordinated water.
..	390 (m)	390 (m)	400 (m)	ν (M–O)

s, strong; w, weak; Sh, shoulder; b, broad; δr, rocking; δw, wagging.

[a] broadness of the band may be due to overlapping of δ (H_2O) of coordinated water.

tion OH of phenolic group on complexation. A weak absorption band around $400\ cm^{-1}$ has also been observed in the spectra of all complexes which may be due to M–(o) stretching vibrations.

1. Agarwala, R. C., Gupta, S. P. and Rastogi, D. K., *J. Inorg. Nucl. Chem.*, 1974, 36, 208.

2. Cotton, F. A. and Wilkinson, G., *Advanced Inorganic Chemistry*, 2nd Edn., Interscience, N.Y., 1957, p. 1056.

3. Figgs, B. N. and Lewis, J., *Techniques of Inorganic Chemistry*, Interscience, N.Y., 1965, 4, 137.

4. Murakami, Y. and Mera, K., *Bull. Chem. Soc. Japan*, 1966, 39, 396.

5. Gill, N. S. and Nyholm. R. S., *J. Chem. Soc.*, 1959, p. 3997.

6. Donoghue, J. T. and Drago. R. S., *Inorg. Chem.*, 1963, 2, 1158,